SAND2020-6056R

GLOBAL PERSPECTIVE
OF ENERGY STORAGE

2020

2019 Annual Peer Review Report

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

TABLE OF CONTENTS

POSTERS

PEER REVIEW 2019 AGENDA AT A GLANCE

Monday	**September 23, 2019**
2:00-3:00pm	Early Registration
3:00-4:00pm	Postdoctoral Poster Set-up
4:00-5:00pm	Peer Review Orientation
5:00-6:00	Postdoctoral Poster Sessions
6:00-8:00	Meet & Greet Reception

Tuesday	**September 24, 2019**
7:00-8:00am	Breakfast
8:00-9:00am	DOE Welcome and Overivew
9:00-10:00am	Partnerships
10:00-10:15am	Break
10:15-11:30am	Equitable Regulatory Environment
11:30-12:45pm	Industry Acceptance
12:45-1:45pm	Lunch
1:45-3:00pm	Materials I
3:00-3:15pm	Break
3:15-4:15pm	Safety Performance
4:30-6:00pm	Poster Session I

Wednesday	**September 25, 2019**
7:00-8:00am	Breakfast
8:00-8:15am	Plenary Review & Overview
8:15-9:30am	Reliability
9:30-9:45am	Break
9:45-11:00am	Analytics
11:00-12:15pm	Materials II
12:30-1:30pm	Lunch
1:30-3:15pm	Materials II [Continued]
3:15-3:30pm	Break
3:30-4:45pm	Power Electronics
4:45-6:15pm	Poster Session II

PARTNERS

The Office of Electricity leads the Department of Energy's efforts to ensure a resilient, reliable, and flexible electricity system. OE accomplishes this mission through research, partnerships, facilitation, modeling and analytics, and emergency preparedness. The DOE OE has partners in academia, industry, state and federal government, professional organizations and standards bodies. Our participating institutions offer enhanced opportunities for networking and visibility within the energy storage research and development space.

ACADEMIA

University of Alaska – Many Traditions One Alaska
University of Arkansas
NM State University
New Mexico Tech
Northeastern University
Stony Brook University
Texas Arlington
Texas – The University of Texas at Austin
The University of California Irvine – Let There Be Light
The University of Tennessee Knoxville
Davidson
Clemson University
University of Houston
The City University of New York
SFCC – Santa Fe Community College
South Dakota State University
SMU
The Ohio State University
Michigan State University
UNC Charlotte
Washington University in St. Louis
The University of Utah
University of Washington

INDUSTRY

- Celebrating 65 years, 1951–2016, Anza Electric Cooperative, Inc
- CEC
- Burlington Electric Department
- East Penn / ecoult — Energy Storage Excellence
- EWEB
- GeneSiC Semiconductor
- Green Mountain Power
- NAATBatt International
- PNM
- NRECA — America's Electric Cooperatives
- 55th Anniversary Creare
- EPRI — Electric Power Research Institute
- epb
- ESA — Energy Storage Association
- Hawai'i Electric Light
- Los Alamos — where discoveries are made
- Helix Power
- Mustang Prairie Energy
- Strategen
- Urban Electric Power
- WattJoule
- UET UniEnergy Technologies

STATE

- NELHA
- DOER — Massachusetts Department of Energy Resources
- New Mexico EMNRD — Energy, Minerals and Natural Resources Department
- Connecticut Energy Environment
- California Energy Commission

FEDERAL

- Bonneville Power Administration
- Department of Energy, United States of America
- NHTSA

STANDARDS

- NFPA
- IEEE — Advancing Technology for Humanity
- IEC

INTERNATIONAL

- nite — National Institute of Technology and Evaluation
- Energy Market Authority — Smart Energy, Sustainable Future

BY THE NUMBERS

30 Journal Articles
- 22 Published
- 8 Under Peer Review

10 Conference Proceedings
- 5 Technical Reports

12 Patents
- 6 Granted
- 6 Applications Filed

50 Technical Presentations

23 Invited Talks

12 Seminars and Webinars

CESA, IEEE, and prominent universities

Pacific Northwest NATIONAL LABORATORY

OAK RIDGE National Laboratory

12

Peer reviewed journal articles published

Including ACS Applied Energy Materials, Advanced Materials, Nanoscale, ChemSusChem

10

PNNL Technical Reports issued

WA CEF installation, Nantucket, Hawaiian Electric

100+

presentations

MRS, ECS, ACS, IEEE, Beyond Li-ion, ESA, State Energy and Utility Commissions, World Bank, US-Korea Clean Energy Policy Summit

11

Journals

4

Conferences

25

Talks

5

Intellectual Property

Professional Societies

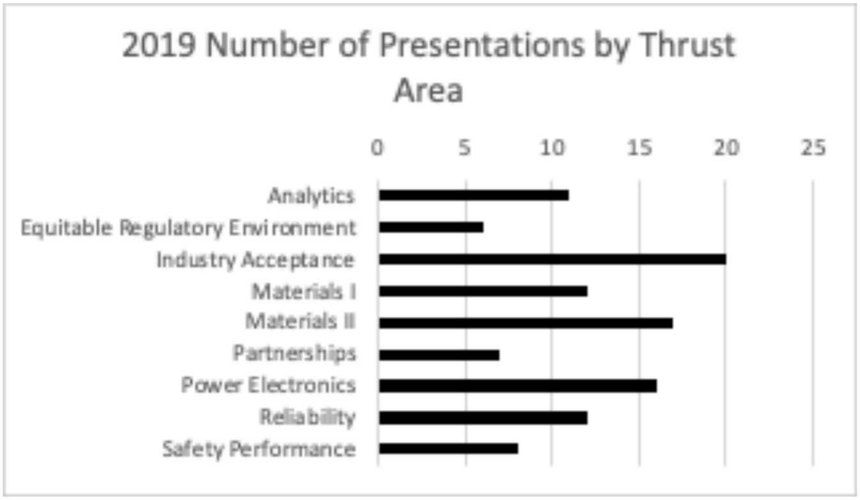
Organized (2) 2018 MRS Fall symposium on ES Technologies

Organized ECS Symposium on Flow Batteries

Organized International Collation Energy Storage

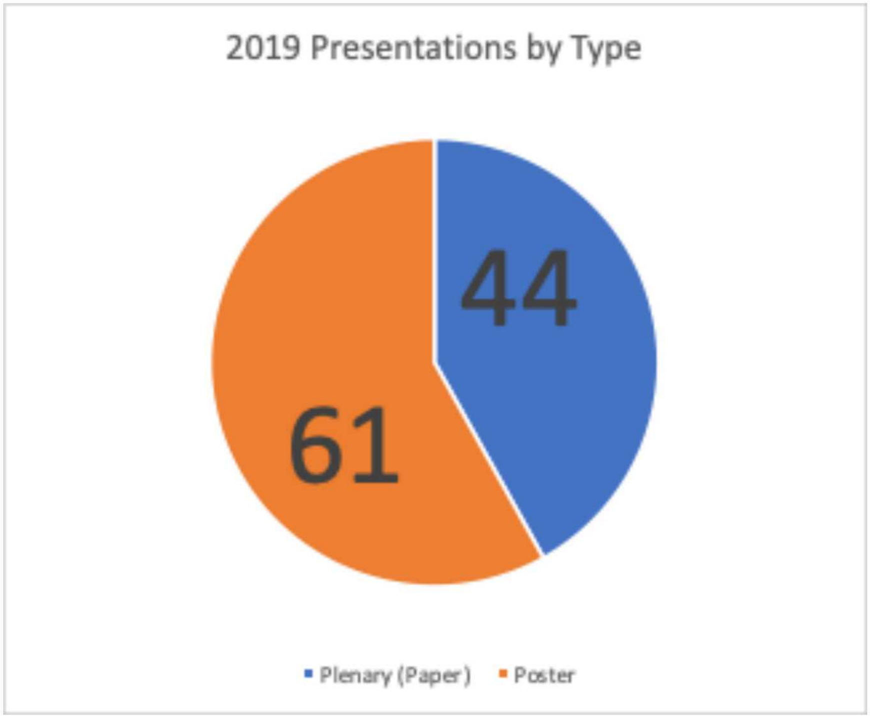
Co-chair IEEE Energy Storage Collaboration Team (ESCT)

STATICS

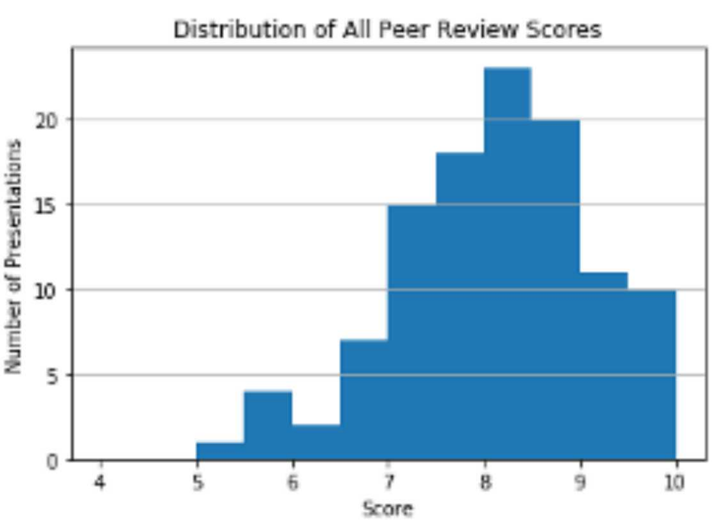


The number of presentations for each thrust area are reflected in the chart and table.

Analytics	Equitable Regulatory Environment	Industry Acceptance	Materials I	Materials II	Partnerships	Power Electronics	Reliability	Safety Performance
11	6	20	12	17	7	16	12	8



There were 61 poster presentations and 44 plenary presentations at the 2019 Peer Review.



The average score for all presentations and posters was 8.08/10.

ELECTRICITY ADVISORY COMMITTEE MEMBERS

The mission of the Electricity Advisory Committee is to provide advice to the U.S. Department of Energy in implementing the Energy Policy Act of 2005, executing the Energy Independence and Security Act of 2007, and modernizing the nation's electricity delivery infrastructure.

John Adams
Electric Reliability Council of Texas

Christopher Ayers
NC Utilities Commission Public Staff

Tom Bialek
San Diego Gas & Electric Company

Laney Brown
AVANGRID

Paul Cicio
Industrial Energy Consumers of America

Armond Cohen
Clean Air Task Force

Robert Cummings
North American Electric Reliability Corporation

Ann Delenela
Ameren

Kimberly Denbow
American Gas Association

Andrew (Drew) Fellon
Trane Energy Supply Services

Flora Flygt
American Transmission Company (Ret.)

Sheri Givens
Givens Consulting

Lisa Grow
Idaho Power

Michael Heyeck
The Grid Group LLC
Committee Chair

Paul Hudson
General Infrastructure, LLC

Lola Infante
Edison Electric Institute

Mladen Kezunovic
Texas A&M University

Clay Koplin
Cordova Electric Cooperative

Arthur Kressner
Grid Connections, LLC

Charlotte Lane
West Virginia House of Delegates

Shaun Mann
Tri-State Generation and Transmission

Jeff Morris
WA State House of Representatives

Richard S. Mroz
Resolute Strategies

Bryan Olnick
Florida Power and Light

Delia Patterson
American Public Power Association

Darlene Phillips
PJM Interconnection

Anda Ray
Electric Power Research Institute

Wanda Reder
Grid-X Partners, LLC
Committee Vice Chair

Pam Silberstein
National Rural Electric Cooperative Association

Ramteen Sioshansi
The Ohio State University

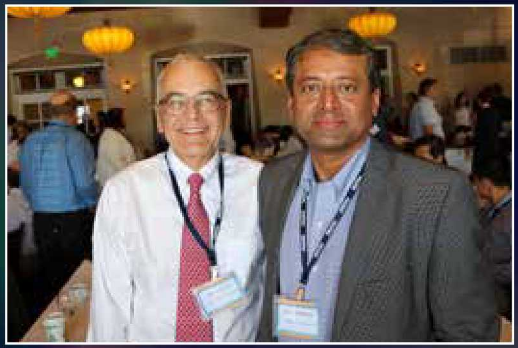
Marcos Valenzuela Ortíz
National Control Center for Energy in Mexico (CENACE)

David Wade
Electric Power Board of Chattanooga

Tom Weaver
American Electric Power

REVIEWERS

Venkat Banunarayanan, PMP
Dr. Stephen Bayne
Flora Flygt
Mark Gaiser
Jim Greenberger, J.D.*
Jonathan Hawkins
C. Michael Hoff
Pramod Kulkarni
Dr. Bor Yann Liaw
Dr. Nian Liu
Dr. Madhav Manjrekar
Dr. Steve Martin
Josh Mauzey
Dr. Michael Mazzola
Dr. Neville Moody
Michael Perry
Dr. Vittal S. Rao
Uzma Siddiqi
Dr. Ramteen Sioshansi
Dr. Grigorii Soloveichik
Dr. Tony Van Buuren



Name	Organization
Roghieh Abdollahi	Clemson University
Abbas Akhil	New Mexico Legislature
Jan Alam	Pacific Northwest National Laboratory
Birendra Ale Magar	New Mexico State University
Travis Anderson	Sandia National Laboratories
Mitchell Anstey	Davidson College
Anant Argawal	The Ohio State University
Stan Atcitty	Sandia National Laboratories
Sijo Augustine	New Mexico State University
Michael Aziz	Harvard University
William Bachmann	
Ross Baldick	University of Texas at Austin
Patrick Balducci	Pacific Northwest National Laboratory
Sanjoy Banerjee	City College of New York
Venkat Banunarayanan *	NRECA
Richard Baxter	Mustang Prarie
Stephen Bayne *	Texas Tech University
Christopher Bejger	The University of North Carolina at Charlotte
Donald Bender	Sandia National Laboratories
Atri Bera	Michigan State University
Dhruv Bhatnagar	Pacific Northwest National Laboratory
Andrew Binder	Sandia National Laboratories
Kevin Blackman	Helix Power Corporation
Jonathan Bock	Sandia National Laboratories
Daniel Borneo	Sandia National Laboratories
Randy Brost	Sandia National Laboratories
Andrea Bruck	Northeastern University
Raymond Byrne	Sandia National Laboratories
Allison Campbell	Pacific Northwest National Laboratory
Babu Chalamala	Sandia National Laboratories
Hee Jung Chang	Pacific Northwest National Laboratory
Zhong Chen	University of Arkansas
Yang-Tse Cheng	University of Kentucky
Madhu Chinthavali	Oak Ridge National Laboratory
Daiwon Choi	Pacific Northwest National Laboratory
Kathy Cleavall	Sandia National Laboratories
Ricky Concepcion	Sandia National Laboratories
Alasdair Crawford	Pacific Northwest National Laboratory
Frank Currie	Sandia National Laboratories

PEER REVIEW AT-A-GLANCE

213 ATTENDEES

67 ORGANIZATIONS

Name	Organization
Valerio De Angelis	Urban Electric Power
Eric Deichmann	Sandia National Laboratories
Peter Dickens	Sandia National Laboratories
Jonathan Duay	Sandia National Laboratories
Hai Duong	Advanced Research Projects Agency -Energy (ARPA-E)
Matthew Fayette	Pacific Northwest National Laboratory
Ruozhu Feng	Pacific Northwest National Laboratory
Kyle Fenton	Sandia National Laboratories
Medhi Ferdowsi	Innocit
Flora Flygt	DOE Energy Advisory Board
Vanshika Fotedar	Pacific Northwest National Laboratory
Ondine Frauenglass	Santa Fe Community College (SFCC)
Amalie Frischknecht	Sandia National Laboratories
Cy Fujimoto	Sandia National Laboratories
Mark Gaiser	New Mexico State Energy Office
Bruce Gnade	Southern Methodist University
Stephen Gomez	Santa Fe Community College (SFCC)
Mike Gravely	California Energy Copmmission
James Greenberger	NAATBatt International
Martha Gross	Sandia National Laboratories
Vipin Gupta	Sandia National Laboratories
Gabriel Gurule	Albuquerque Institute of Math and Science (AIMS)
Imre Gyuk	Department of Energy
Cynthia Hall	NM Public Regulation Commission
Charles Hanley	Sandia National Laboratories
Brian Harris	Advisor to PRC Commissioner Steve Fischmann
Brendan Hawkins	City College of New York
Alexander Headley	Sandia National Laboratories
Jacquelynne Hernandez	Sandia National Laboratories
John Hewson	Sandia National Laboratories
C. Michael Hoff *	NEC Enery Solutions, Inc.
Aaron Hollas	Pacific Northwest National Laboratory
Eric Hsieh	Department of Energy
Qin Huang	University of Texas at Austin
Jinchao Huang	Urban Electric Power
Alex Huang	University of Texas Austin

Name	Organization
Robert Jeffers	Sandia National Laboratories
Hee Jung Chang	Pacific Northwest National Laboratory
Carina Kaainoa	California State University Los Angeles
Mark Kaiser	
Gail Kaplan	Sandia National Laboratories
Robert Kaplar	Sandia National Laboratories
Donald Karner	Electric Applications, Inc.
Saiid Kassaee	Oak Ridge National Laboratory
Matthew Kim	Northeastern University
William Kipnis	Siemens Smart Infrastructure
Igor Kolesnichenko	Sandia National Laboratories
Snehal Kolhekar	City College of New York
Patrick Kopfle	
Clay Koplin	Cordova Electric Cooperative (CEC)
Radha Sree Krishna Moorthy	Oak Ridge National Laboratory
Harish Krishnamoorthy	Department of Energy EERE
Pramod Kulkarni *	Customized Energy Solutions
Andrew Kurzawski	Sandia National Laboratories
Joshua Lamb	Sandia National Laboratories
Timothy Lambert	Sandia National Laboratories
Matthew Lazarewicz	Helix Power Corporation
Jeremy Lewis	New Mexico State Land Office
Bosong Li	Pacific Northwest National Laboratory
Guosheng Li	Pacific Northwest National Laboratory
Xiaolin Li	Pacific Northwest National Laboratory
Boryann Liaw *	Idaho National Laboratory
Matthew Lim	Sandia National Laboratories
Nian Liu	Georgia Tech University
Xingbo Liu	Pacific Northwest National Laboratory
Xi Liu	Pacific Northwest National Laboratory West Virginia University
Jeremy Long	Rio Rancho High School 2019 TARC Team Captain
Xiaochuan Lu	Pacific Northwest National Laboratory
Xu Ma	Pacific Northwest National Laboratory
Syam Madhusoodhanan	University of Arkansas

** denotes Peer Reviewer*

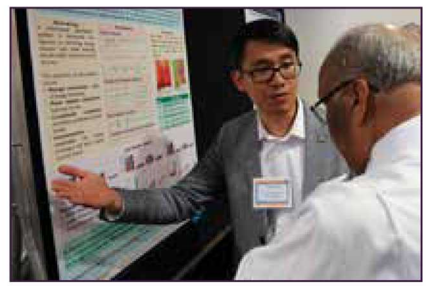
Name	Organization
Madhav Manjrekar *	University of North Carolina Charlotte
Amy Marschilok	Stony Brook University
Michael Marshak	University of Colorado
Steven Martin *	Iowa State University of Science and Technology
Fernando Martinez	NM Renewable Energy Transmission Authority
Joshua Mauzey	Southern California Edison
Michael Mazzola *	University of North Carolina Charlotte
Will McNamara	Sandia National Laboratories
Austin Mier	New Mexico Tech
Henry Mignardot	Santa Fe Community College (SFCC)
Ayyoub Momen	Oak Ridge National Laboratory
Kendall Mongird	Pacific Northwest National Laboratory
Todd Monson	Sandia National Laboratories
Neville Moody *	Sandia National Laboratories (Retired)
M A Moonem	University of Alaska Fairbanks
Alejandro Moreno	Department of Energy
Jacob Mueller	Sandia National Laboratories
Rangachary Mukundan	Los Alamos National Laboratory
Vijay Murugesan	Pacific Northwest National Laboratory
Nadeesha Nambukara Wellala	Pacific Northwest National Laboratory
Jagjit Nanda	Oak Ridge National Laboratory
Sri Narayan	University of Southern California
Tu Nguyen	Sandia National Laboratories
Samuel Ojetola	Sandia National Laboratories
Todd Olinsky-Paul	Clean Energy States Alliance (CESA)
Rebecca O'Neil	Pacific Northwest National Laboratory
Matthew Paiss	Pacific Northwest National Laboratory
Howard Passell	Sandia National Laboratories
Rajankumar Patel	Pacific Northwest National Laboratory
Stephen Percival	Sandia National Laboratories
Andre Pereira	Department of Energy
Amanda Peretti	Sandia National Laboratories
Michael Perry *	United Technologies Research Center (UTRC)

Name	Organization
Misc PNNL GS	Pacific Northwest National Laboratory
Nataraj Pragallapati	New Mexico State University
Harry Pratt	Sandia National Laboratories
Yuliya Preger	Sandia National Laboratories
Heather Prudhomme	Sandia National Laboratories
Satish Ranade	New Mexico State University
Vittal Rao *	Texas Tech University
David Reed	Pacific Northwest National Laboratory
Sam Roberts	Sandia National Laboratories
Ismael Rodriguez Perez	Pacific Northwest National Laboratory
David Rosewater	Sandia National Laboratories
Sharon Ruiz	Sandia National Laboratories
Surya Santoso	University of Texas at Austin
Laura Sapienza-Grabski	Helix Power Corporation
Ben Schenkman	Sandia National Laboratories
Susan Schoenung	Longitude 122 West
David Schoenwald	Sandia National Laboratories
Noah Schorr	Sandia National Laboratories
Ethan Self	Oak Ridge National Laboratory
Nimat Shamim	Pacific Northwest National Laboratory
Mariko Shirazi	University of Alaska Fairbanks
Randy Shurtz	Sandia National Laboratories
Uzma Siddiqi *	Seattle City Light
Nicholas Sinclair	Case Western Reserve University
Ranbir Singh	GeneSiC Semiconductor
Ramteen Sioshansi *	The Ohio State University
Tyler Siska	Albuquerque Public Schools
Oleksiy Slobodyan	Sandia National Laboratories
Leo Small	Sandia National Laboratories
Trevor Smith	Sandia National Laboratories
David Sokoloff	Sandia National Laboratories
Grigorii Soloveichik *	Advanced Research Projects Agency/Energy (ARPA-E)
Laurence Sombardier	Natural Energy Laboratory of Hawaii Authority (NELHA)
Luke Spangenburg	Santa Fe Community College (SFCC)
Tony Sparks	Albuquerque Public Schools
Erik Spoerke	Sandia National Laboratories
Vincent Sprenkle	Pacific Northwest National Laboratory
June Stanley	Sandia National Laboratories

ATTENDEES

Name	Organization
Michael Starke	Oak Ridge National Laboratory
Tyler Stevens	Sandia National Laboratories
Paula Szyper	NAATBatt International
Esther Takeuchi	Stony Brook University
Kenneth Takeuchi	Stony Brook University
Reinaldo Tonkoski	South Dakota State University
Preston Torres	Sandia National Laboratories
Loraine Torres-Castro	Sandia National Laboratories
Rodrigo Trevizan	Sandia National Laboratories
Jeremy Twitchell	Pacific Northwest National Laboratory
Tony van Buuren *	Lawrence Livermore National Laboratory (LLNL)
Charlie Vartanian	Pacific Northwest National Laboratory
Igor Vasiliev	New Mexico State University
Vish Viswanathan	Pacific Northwest National Laboratory
Jesse Wainright	Case Western Reserve University
Wei Wang	Pacific Northwest National Laboratory
Hsin Wang	Oak Ridge National Laboratory
Donghai Wang	Pacific Northwest National Laboratory
Felipe Wilches-Bernal	Sandia National Laboratories
Steve Willard	Electric Power Research Institute
Reed Wittman	Sandia National Laboratories
Marissa Wood	Lawrence Livermore National Laboratory (LLNL)
David Wood	Oak Ridge National Laboratory
Di Wu	Pacific Northwest National Laboratory
Biwei Xiao	Pacific Northwest National Laboratory
Gautam Yadav	Urban Electric Power
Litao Yan	Pacific Northwest National Laboratory
Hengzhao Yang	
Xiaoqin Zang	Pacific Northwest National Laboratory
Tom Zawodzinski	Oak Ridge National Laboratory
Xiaowen Zhan	Pacific Northwest National Laboratory
Xin Zhang	Boston University
Cheng Zhu	Lawrence Livermore National Laboratory (LLNL)

** denotes Peer Reviewer*



POSTDOCTORAL POSTER SESSIONS

Postdoctoral work is inclusive of all the thrust areas.

Operando Investigations of Bismuth Additives on the Rechargeability of MnO_2 in Alkaline Batteries

Northeastern University

Andrea M. Bruck, Matthew Kim, Joshua Gallaway

Northeastern University

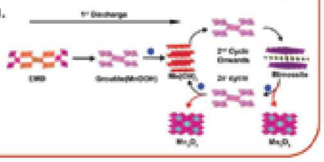
Department of Chemical Engineering, Northeastern University

Background

Zn/MnO_2 alkaline batteries have been identified as a viable option for the modernization of grid scale energy storage due to their projected cost (~$50/kWh), scalability, and safer components when compared to non-aqueous alternatives. For this system to reach its maximum capacity, the full $Mn^{4+/2+}$ redox couple must be reversible over thousands of cycles with high mass loading. The following reaction has been proposed to occur in alkaline systems:

$$MnO_2 + xH_2O + xe^- \leftrightarrow MnO_{2-x}(OH)_x + xOH^- \quad \text{where } x = 2$$

Recently, success in rechargeability > 3000 cycles has been demonstrated with the incorporation of various electrode constituents which alter the fundamental discharge and charge process and form the δ-MnO2 (birnessite) on the first cycle which is identified as the reversible reaction.



Gallaway et al.; *Journal of The Electrochemical Society*, (2018) 165, 13, A2935-A2947

Yadav et al.; *Materials Today Energy*, (2017) 6, 198-210

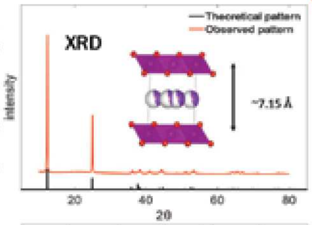
K_xMnO_2 as model material

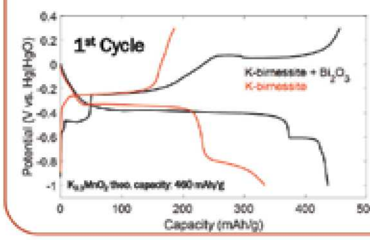
Potassium birnessite was synthesized in our lab. Considering birnessite as the reversible phase we want to understand:

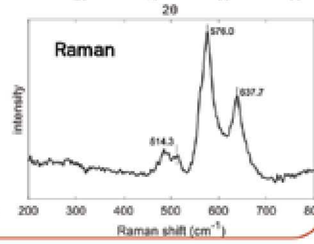
(1) What is the role of Bi_2O_3 in the electrode

(2) What is the mechanism for MnO_2 reversibility

(3) What is the optimal way to incorporate Bi into the electrode*



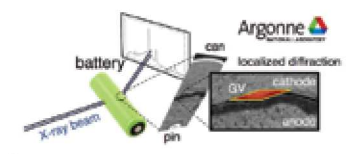




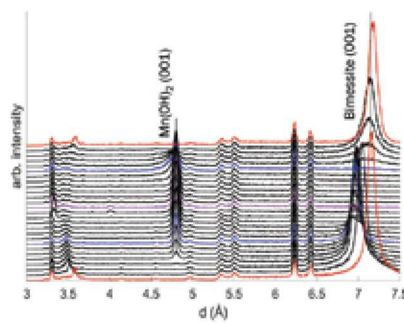
Operando studies of K_xMnO_2

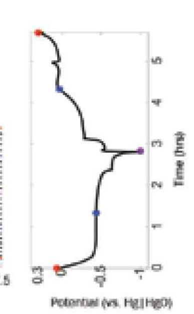
Synchrotron Energy Dispersive X-ray Diffraction

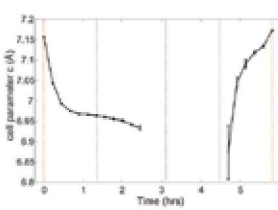
- Fully intact batteries are cycled at Argonne National Lab's Advanced Photon Source
- The white beam (~50-200 keV) penetrates the cell casing and subsequent diffraction on the internal material changes are detected
- Non-destructive technique identifies intermediates and kinetically driven reactions that may be unstable for ex situ characterization

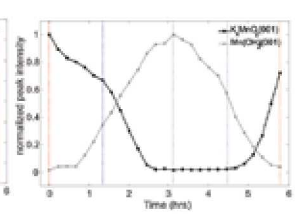


Galloway et al.; Journal of Power Sources, (2016) 321, 135-142







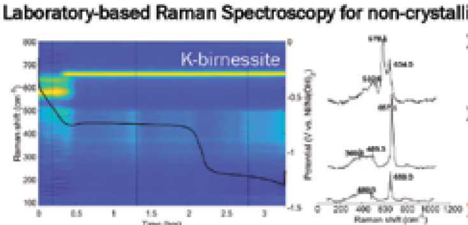


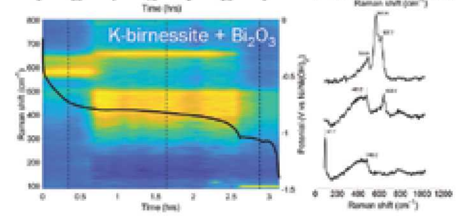
- Most notably, no intermediate phases such as MnOOH or Mn_3O_4 were detected by diffraction experiments indicating a two-phase reaction

EDXRD Collaboration:
Matthew Kim (Northeastern) and David Arnot (Sandia) testing batteries at beamline 6BM-A of APS. Our institutions are working together for the operando characterization of battery reactions.

Sandia National Laboratories

Laboratory-based Raman Spectroscopy for non-crystalline intermediates

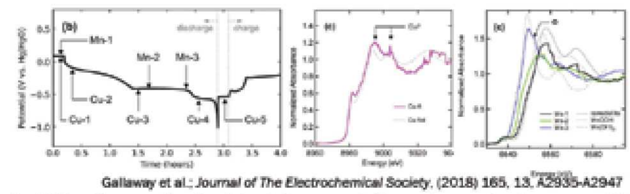




- Birnessite, Mn_3O_4, and $Mn(OH)_2$, and Bi metal could be identified
- In the presence of Bi_2O_3 small quantities of Mn_3O_4 form but disappear during the second plateau
- Bi_2O_3 suppresses the formation of the irreversible phase and allows for the full conversion to $Mn(OH)_2$

Gosztola et al.; *Journal of Electroanalytical Chemistry*, (1989), 271, 141-154

Summary and Next Steps



Gallaway et al.; *Journal of The Electrochemical Society*, (2018) 165, 13, A2935-A2947

1. Diffraction methods detect two crystalline phases in the reversible reaction, birnessite (MnO_2) and $Mn(OH)_2$
2. However, Raman spectroscopy revealed the formation of Mn_3O_4 during discharge which is suppressed in the presence of Bi_2O_3
3. We are specifically interested in the final plateau of the discharge where Bi_2O_3 redox activity is possible with the disappearance of Mn_3O_4

Our next beamline run is scheduled at NSLS-II for XAS to better probe the redox activity of Bi and Mn with improved temporal resolution.

Acknowledgements

This work was supported by the U.S. Department of Energy (DOE) Office of Electricity, Dr. Imre Gyuk, Energy Storage Program Manager. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02- 06CH11357.

U.S. DEPARTMENT OF ENERGY

Interfacial Engineering in Sodium Batteries

Martha M. Gross, Amanda Peretti, Stephen Percival, Leo Small, Babu Chalamala, and Erik D. Spoerke (PI)*
Sandia National Laboratories, Albuquerque, NM, USA
margros@sandia.gov *edspoer@sandia.gov

Motivation & Objective: High temperature operation of traditional molten sodium batteries has restricted their deployment due to issues with high material costs, longevity, parasitic energy losses, and safety. We are developing low temperature (< 150°C) molten sodium batteries that promise safe, cost-effective, and reliable energy storage for the electric grid.

Overview: Molten Sodium (Na) Batteries

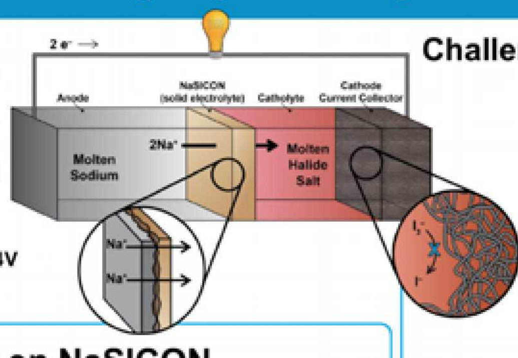
- Molten Na anode
- NaSICON separator
- 25 mol% NaI in $AlBr_3$ catholyte

Redox Chemistry:

$Na \rightarrow Na^+ + e^-$

$I_3^- + 2e^- \rightarrow 3I^-$ $E^0_{cell} \sim 3.24V$

$2Na + I_3^- \rightarrow 2Na^+ + 3I^-$



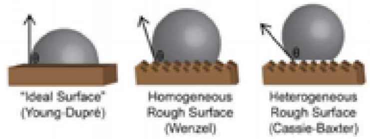
Challenges in Low Temperature Molten Batteries

- Temperature > 100°C to maintain Na in molten state
- **Poor Na wetting on ceramic separator**
- Low ceramic ionic conductivity
- Unknown interactions between ceramic & catholyte
- Catholyte materials selection – molten at low temperatures
- Materials compatibility with molten salt catholyte
- **Poor charge transfer at cathode current collector**

Na Wetting on NaSICON

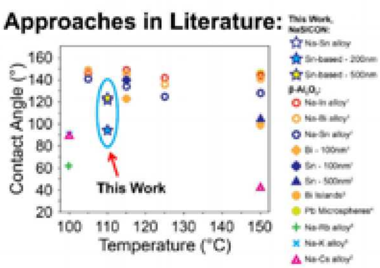
Contact Angle Measurements

Surface Roughness:



- Surface roughness has strong effect on Na wetting
- **Polishing not enough**, not always practical

Approaches in Literature:

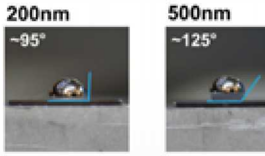


- All coatings and alloys researched at < 150°C studied on β"-Al_2O_3
- Contact angles achieved in literature still too high
- Standard PbO showed no improvement on NaSICON
- Sn investigated as alloying metal with good Na^+ conductivity

Na-Sn alloy:

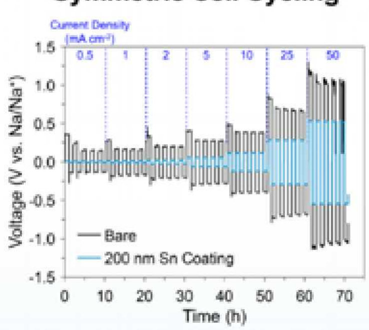
- No improvement in contact angle by alloying Na with Sn

Sn-based Coating:



- **Critical Thickness**: Thickness of Sn-based coating below which complete alloying occurs
- Incomplete alloying (excess coating) results in poor contact angle

Symmetric Cell Cycling



Drastic reductions in overpotentials make functional battery testing feasible

Catholyte-Current Collector Interface

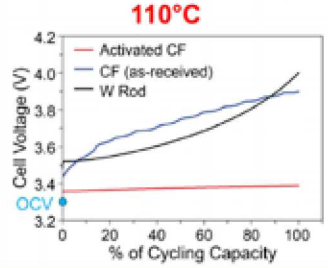
Full Cell Assembly:

- Molten Na anode
- NaSICON separator
  - Anode side: Sn-based coating
- 25mol% NaI in $AlBr_3$ catholyte
- **Different cathode current collectors tested**

Important Properties of the Current Collector

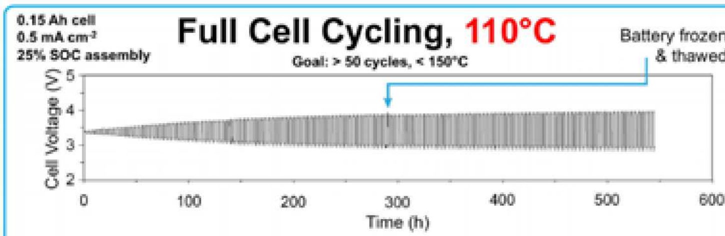
- Fast Charge Transfer
- High Surface Area
- Chemically & Electrochemically Inert

Full Cell, Single Charge: 110°C



- Tungsten (W) rod: high stability, low surface area
- Carbon Felt (CF) – 1000x surface area of W rod, but no improvement in overpotential
  - poor charge transfer
- Activation of CF: thermal treatment by heating 400°C in air, or acid treatment by cleaning with 0.1M HCl
- **Activated CF dramatically lowers overpotential**

Full Cell Cycling, 110°C



- Integration of Sn-based coating and activated CF enables long-term battery cycling: **Battery achieves > 150 cycles!**
- Even after freeze/thaw, interfaces remain intact

Conclusions & Future Work

- **First demonstration of long term cycling of a fully molten sodium battery at 110°C**
  - made possible by integration of Sn-based coating on NaSICON and activated carbon felt cathode current collector
- Technical Advance of Sn-based coating filed: "Surface Treatments of NaSICON Ceramics for Improved Molten Interfaces." SD: 15128, September, 2019.
- Future work: Further reduction in cell operating temperature and increased scaling of battery system operation and performance

Careful tailoring of material interfaces is critical to high battery performance at low operating temperatures

Acknowledgements
This work was supported by the U.S. Department of Energy Office of Electricity Energy Storage Program, managed **by Dr. Imre Gyuk**.

Energy Storage Analysis for Regional Demonstration Projects

Alexander Headley, Tu Nguyen, Ray Byrne - Sandia National Laboratories

Overview

In FY19, we performed analyses to assist with planning, project development, and valuation for: the Eugene Water & Electric Board in OR, Atrisco Heritage High School in Albuquerque, NM, Minnesota Power, BQ Energy in NY, and the NELHA research campus in HI. In these analyses, we optimize the benefits from energy storage for the customers for different grid applications such as peak demand charge reduction, PV utilization, and time-of-use rate structures. Below is analysis from two particularly interesting cases.

Community Distributed Generation in NY

Background

Recent changes to pricing in NY include updates to increase the value of energy storage. BQ Energy, a community distributed generation developer in NY, requested analysis of three different solar projects for energy storage integration.

Unique Considerations

Value Stacking in NY

- Six value streams
- Time-of-generation windows
- Generation requests

Proposed Solar Projects

	A	B	C
MW DC	7.5	3.0	0.75
MW AC	5	2	0.577
Fixed Values (2018)			
E - $/kWh	0.02741	0.02741	0.02741
DRV - $/kWh	0.01765	0.00417	N/A
LSRV - $/kW	2.56	N/A	14.08
CC - $/kWh	0.0225	N/A	0.12

System Configurations

- DC vs. AC coupling

Analysis

- PV modeled with PVLib
- AC-tied, DC-tied, DC excess charging

Optimization Framework

$$\max_{P_c, P_D} \sum_{t=1}^{T} P_{out,t} \cdot (ICap_t + DRV_t + LSRV_t + E + CC + LBMP_t)$$

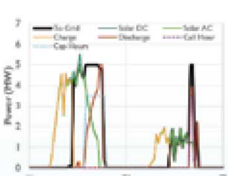
$$\text{subject to} \quad SOC_t = SOC_{t-1}\eta_s + \Delta t\left(P_{C,t-1}\eta_C - P_{D,t-1}\right)$$

$$P_{out,t} = \eta_{inv}\left(P_{DC,t} + P_{D,t} - P_{C,t} - P_{curtail,t}\right)$$

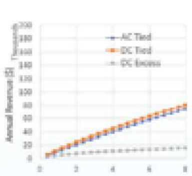
$$P_{C,t} \le P_{DC,t} - P_{dC,t}$$

Results

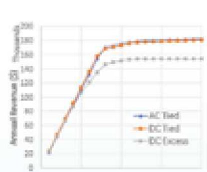
- Value from coincident peak discharge (38%), scheduled calls (30%), and LBMP arbitrage (24%)
- AC / DC tied similar value in low energy applications



Project A optimal ESS dispatch schedule



Project B 2-7PM Capacity Option



Project B Coincident Peak Capacity Option

Project Status

- BQ Energy soliciting energy storage proposals for Projects A & B

Energy Storage and Large Scale Hydrogen Production – NELHA Research Campus

Background

The NELHA campus will soon support a large water electrolysis facility generating hydrogen for three fuel cell buses. Early tests of the facility more than doubled the peak demand for the campus.

Unique Considerations

Hydrogen Production

- 250kW electrolyzer
- Flexible operation from 10-100%

Analysis

- Time-of-use and flat rate options
- With and without hydrogen facility

Research Campus

Demand and Energy Charges

$$\min_{P_C, P_D, P_{H_2}} \; P_{peak} \cdot C_{Dem} + \sum_{t=1}^{T} P_{PG,t} \cdot \frac{\Delta t}{60} \cdot \left(C_{E,t} + C_{fuel,10\%}\right) + \frac{\sum_{t=1}^{T} S_{+} + S_{-}}{K}$$

$$\text{subject to} \quad SOC_t = SOC_{t-1} + \frac{\Delta t}{60}\left(P_{C,t-1}\eta_{RT} - P_{D,t-1}\right) \quad \text{Battery SOC Model}$$

$$P_{PG,t} = P_{Dem,t} + P_{H_2,t} + P_{C,t} - P_{D,t} - P_{sol,t} + P_{curt,t}$$

Hydrogen Facility

$$SOE_{H_2,t} = SOE_{H_2,t-1} + \frac{\Delta t}{60} P_{H_2,t} - D_{H_2,t} \quad \text{Hydrogen Storage Model}$$

$$0 \le SOE_{H_2,t} \le SOE_{H_2,max}$$

$$P_{H_2,t} - \alpha_{H_2,t} \cdot P_{H_2,max} \le 0 \quad \text{Operation Limits}$$

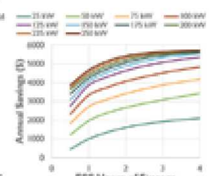
$$P_{H_2,t} - 0.1 \cdot \alpha_{H_2,t} \cdot P_{H_2,max} \ge 0$$

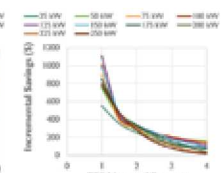
$$S_{+} - S_{-} = P_{PG,t} - P_{PG,t-1}$$

Results

No Hydrogen Production

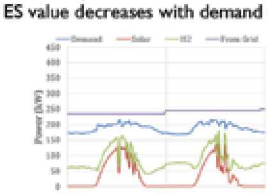
- Savings up to ~$5500/year

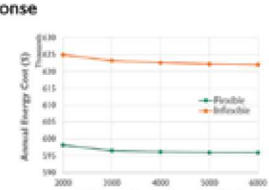




With Hydrogen Production

- Flexible operation would save ~$25000/year
- ES value decreases with demand response





Project Status

- NELHA / HNEI investigating hydrogen facility interface and control to lower demand increases
- Continued work on microgrid development which may incorporate more energy storage

Acknowledgements

This work was supported through the Energy Storage Program managed by **Dr. Imre Gyuk** within the US Department of Energy's Office of Electricity. Also, a special thanks to collaborators Laurence Sombardier and Keith Olson from NELHA as well as Mitch Ewan at HNEI.

Zincate-Blocking Polymeric Separators for Zn/MnO_2 Batteries

Igor Kolesnichenko,[1] David Arnot,[1] Matthew Lim,[2] Timothy N. Lambert,[1]* Gautam Yadav,[3] Jungsang Cho,[3] Michael Nyce,[3] Sanjoy Banerjee[3]

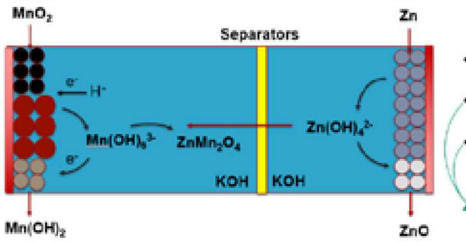
[1]*Department of Photovoltaics & Materials Technologies, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

[2]*Department of Energy Storage Technology & Systems, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

[3]*Department of Chemical Engineering, The CUNY Energy Institute at the City College of New York, Steinman Hall Room 316, 160 Convent Avenue, New York, New York 10031, USA*

***Email:** tnlambe@sandia.gov

Background and Objectives



Cathode Failure Mechanisms:

- Formation of irreversible Mn_3O_4.
- Formation of irreversible $ZnMn_2O_4$.
- Passivation from an insulating ZnO layer.

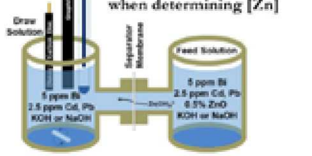
Caused by $Zn(OH)_4^{2-}$ crossover

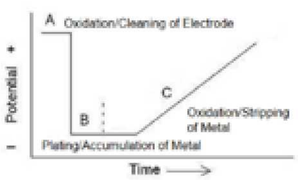
Objectives:

- Synthesize separators selective for blocking zincate, while allowing for crossover of hydroxide
- Cast membranes with thicknesses similar to those of commercial separators and establish the aforementioned selectivity outside of cells
- Implement into prototype cells and demonstrate an improvement in battery performance

Zinc Diffusion Analysis

Presence of Bi, Cd, and Pb allows for consistent results when determining [Zn]





A. J. Bard, L. R. Faulkner, Electrochemical Methods, (2001) 438–466.

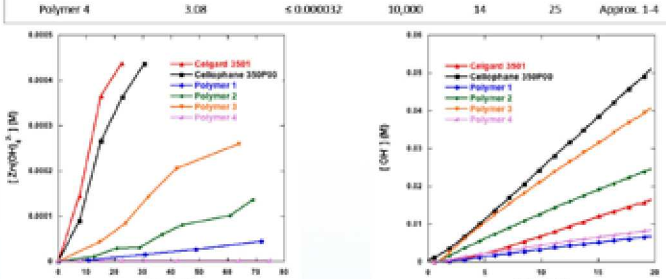
Anodic stripping voltammetry (ASV) allows for much faster screening of separators compared to ICP-MS, with similar limits of detection.

ASV Analysis of Zn performed for the first time in alkaline conditions.

J. Duay, T.N. Lambert, R. Aidun, *Electroanalysis*, 29 (2017) 1-8.

Polymeric Separators

Separator	Hydroxide Diffusion Coefficient (cm^2/min) *10[illegible]	Zincate Diffusion Coefficient (cm^2/min) *10[illegible]	Selectivity	Water Uptake (%)	Thickness (μm)	Conductivity (mS/cm)
Celgard 3501	6.74	5.7	1.18	68	25	12.2
Cellophane 350P00	17.4	2.0	8.70	96	25	13.8
Polymer 1	2.48	0.049	50.6	11	30	5.83
Polymer 2	9.43	0.17	55.5	17	30	7.19
Polymer 3	15.4	0.42	36.7	47	30	8.79
Polymer 4	3.08	≤ 0.000032	10,000	14	25	Approx. 1-4

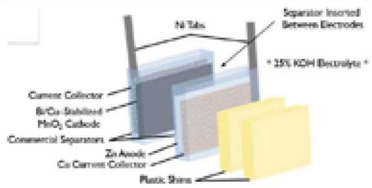


Polymers 1-3 show a greatly improved selectivity ratio over commercial separators for screening out zincate, while allowing for hydroxide crossover. Polymer 4 has an even higher selectivity ratio, but is also far less conductive, resulting in lower practical cycling rates.

Future Goal:

Attain a selectivity ratio on par with Polymer 4, while retaining a conductivity similar to those of commercial separators

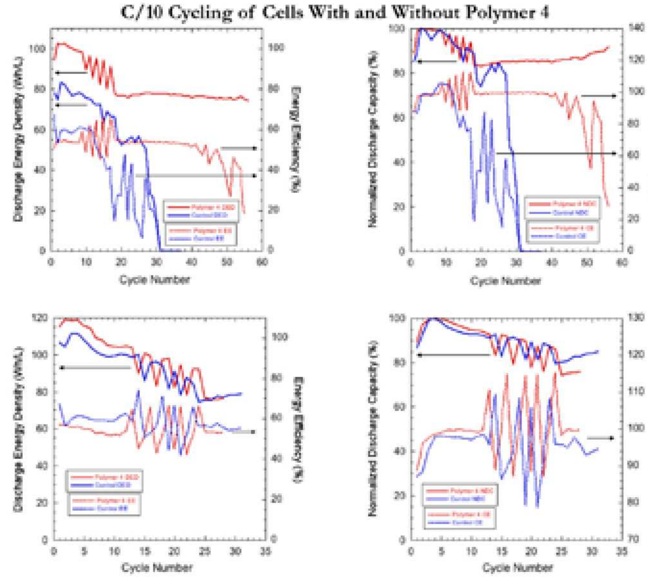
Battery Assembly and Cycling



Journal of Power Sources, 395 (**2018**) 430-438

Control cells are assembled by wrapping both the anode and cathode in 3 layers of Cellophane, while the cells containing Polymer 4 are assembled by wrapping only the anode in 3 layers of Cellophane, inserting Polymer 4 between the electrodes (as shown to the left) and using the cathode as received from CUNY, with no additional wrapping.

C/10 Cycling of Cells With and Without Polymer 4



Conclusions and Research Output

- Prepared flexible polymeric membranes that are resistant to zincate, while maintaining hydroxide permeability on par with commercial separators
- Conductivity constraints limit the rates at which functional batteries containing the fabricated separators can be cycled → **Need to improve upon conductivity**
- Preliminary data from Zn–MnO_2 cells shows cycling at C/10 rates that is on par with cells using commercial separators

Publications

- Kolesnichenko, I. V.; Arnot, D. A.; Lim, M. B.; Lambert, T. N. "Zincate–Blocking Functionalized Separators for Secondary Zn/MnO_2 Batteries" *in final preparation*
- Arnot, D. A.; Lim, M. B.; Kolesnichenko, I. V.; Lambert, T. N. "Development of Zincate–Blocking Separators and Their Application in Zinc–Manganese Oxide Batteries" *in preparation*

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. Department of Energy or the United States Government. Dr. Imre Gyuk, Director of Energy Storage Research, Office of Electricity is thanked for his financial support. The views expressed herein do not necessarily represent the views of the U.S.

Sandia National Laboratories

Exceptional service in the national interest

Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge

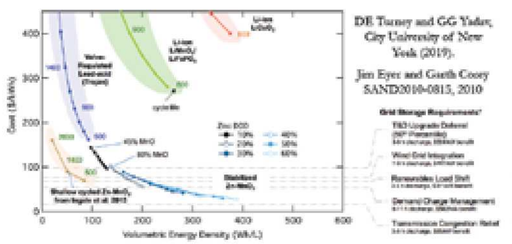
Matthew B. Lim[1], Elijah I. Ruiz[2], Timothy N. Lambert[2,*], Gautam G. Yadav[3], Damon E. Turney[3], Sanjoy Banerjee[3]

[1]*Energy Storage Technology & Systems Department, Sandia National Laboratories, Albuquerque, NM 87185, USA*
[2]*Photovoltaics & Materials Technologies Department, Sandia National Laboratories, Albuquerque, NM 87185, USA*
[3]*The CUNY Energy Institute at the City College of New York, Department of Chemical Engineering, New York, NY 10031, USA*

*Email: tnlambe@sandia.gov

Background and Objectives

Zn/MnO_2 batteries for the grid: Energy-dense, safe, abundant, low-cost materials



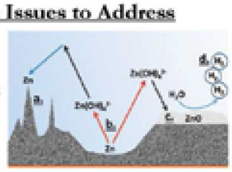
DE Turney and GG Yadav, City University of New York (2019).

Jim Eyer and Garth Corey SAND2010-0815, 2010

- Up to 400 Wh/L, 150 Wh/kg and ~$18/kWh as primary cell
- Commercialized by Urban Electric Power, ***but only under limited depth-of-discharge (DOD) conditions***
  - ~100 Wh/L, $200/kWh

Anode Issues to Address

- Shape change
- Dendrite formation
- Passivation
- H_2 evolution



J. Fu et al., *Adv. Mater.* 29, 1604685 (2017)

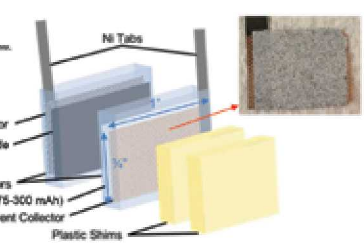
Objectives

- **Increase achievable cycle life and energy density by pre-saturating electrolyte with ZnO to inhibit dissolution and migration of zinc from the anode.**
- **Study effect of ZnO saturation at different depths of discharge, *relative to total zinc species in the system*, and at different KOH concentrations in a more commercially relevant limited-electrolyte system.**

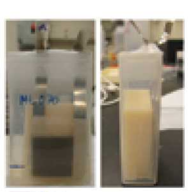
Experimental Plan

Due to the sensitivity of MnO_2 to $Zn(OH)_4^{2-}$, use NiOOH as the cathode material instead to examine the effect of ZnO saturation at different Zn DOD.

M. Kelly et al., *J. Electrochem. Soc.* 2017, 164, A3684.



- 3 mL 25%, 32%, or 45% KOH electrolyte with/without saturated ZnO
- Cycled between 1 and 1.93 V vs. Zn at C/10 relative to full anode capacity ≈ **75 mA/g_{anode}**
- Zn DOD limits of 14%, 21%, 35% **relative to all Zn+ZnO in system**
- Cells considered failed when discharge capacity fell below 80% of DOD limit

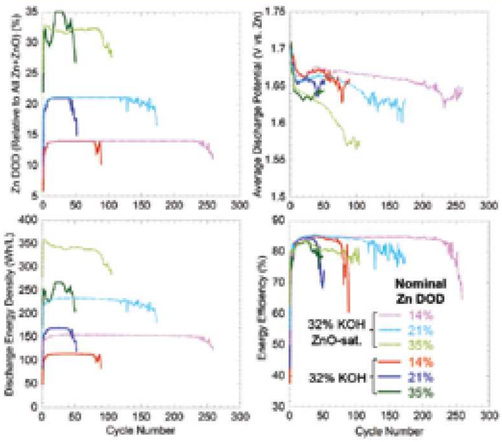


Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government. Dr. Imre Gyuk, Director of Energy Storage Research, Office of Electricity is thanked for his financial support. The authors also thank Bonnie McKenzie at Sandia National Laboratories for SEM characterization, and Michael Nyce at the CUNY Energy Institute for providing sintered NiOOH electrodes.

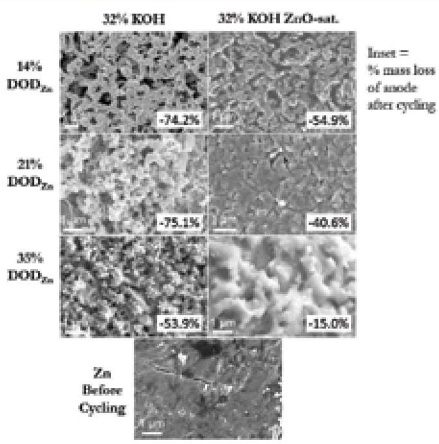
SAND No. SAND2019-11032 C

Cycling Results

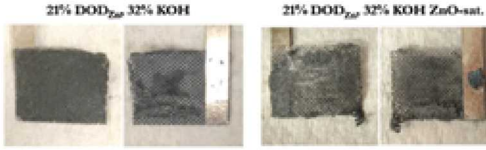


Cells with saturated electrolyte last significantly longer with no energy losses due to voltage and similar energy efficiency compared to cells with regular electrolyte cycled at same DOD, ***even when including dissolved ZnO in capacity***

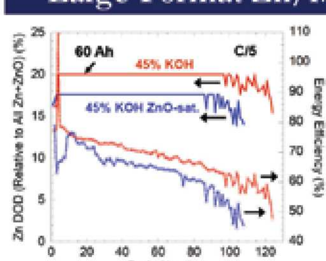
Post-Cycling Characterization



- Anodes in ZnO-saturated electrolyte yield more compact Zn deposits indicating more homogeneous current density
- They also lose less mass during cycling despite significant Zn deposition on the bottom and through separator.



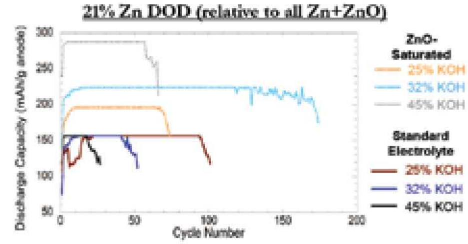
Large-Format Zn/MnO_2 Cell



- Cells with saturated electrolyte last >100 cycles, though slightly less than cells with 45% KOH only, and lower energy efficiency
  - Zinc clogs separator, creating soft short-circuit

Effect of KOH Concentration

21% Zn DOD (relative to all Zn+ZnO)

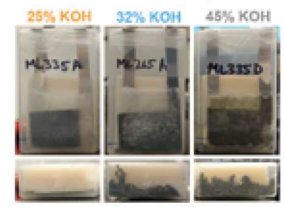


- Cells with 45% KOH fail more quickly with more zinc growth outside electrode than cells with less concentrated electrolyte
- ZnO saturation *reduces* cycle life in 25% KOH at 21% Zn DOD

Initial wt% KOH	mol/L Zn(II) at Saturation	mAh in Dissolved ZnO
25	0.45	72.4
32	0.74	119
45	1.50	241

J. Electrochem. Soc. 1967, **114**, 1045.
J. Chem. Soc. Faraday Trans. 2, 1974, 70, 1978.

Cycled Cells with ZnO-Saturated Electrolyte



Bottom view (front of cell facing down)

Conclusions and Future Work

- Pre-saturating electrolyte with ZnO increases lifetime of Zn/Ni cells at high Zn utilization (≥14% DOD) without energy losses, but only at higher KOH concentrations
  - 32% KOH appears to be optimal concentration
- ZnO saturation has no benefit on Zn/MnO_2 cells with commercial separators → **Need to develop zincate-blocking separators** to isolate zincate in anode and suppress deposition away from anode
  - Should be **flexible and conductive**
  - Potential for >250 Wh/L and <$100/kWh
  - Ongoing collaboration with City College of New York
- Further reduce electrolyte usage to reduce material cost
  - Want **~2 mL/mL anode** (ours ~ 40 mL/mL anode)
  - Electrolyte is effectively saturated with zincate in operando

Research Output

Publications

- MB Lim, TN Lambert, EI Ruiz. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge", *to be submitted Sep-Oct 2019.*

Talks

- MB Lim, M Kelly, J Duay, IV Kolesnichenko, TN Lambert. "Improving Cycle Life and Active Materials Utilization for Rechargeable Alkaline Zn–MnO2 Batteries". 235th Electrochemical Society Meeting, Dallas, TX (May 28, 2019).
- MB Lim, TN Lambert. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge". 31st Rio Grande Symposium on Advanced Materials, Albuquerque, NM (Sep 16, 2019).
- MB Lim, IV Kolesnichenko, DJ Arnot, TN Lambert. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zn–Ni and Zn–MnO2 Batteries at High Zinc Depth-of-Discharge". 236th Electrochemical Society Meeting, Atlanta, GA. (Oct 15, 2019).

Poster

- MB Lim, IV Kolesnichenko, DJ Arnot, TN Lambert. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge". Los Alamos National Laboratory Postdoc Research Symposium, Los Alamos, NM (Aug 27, 2019).

Reliability Testing of Lead Acid Battery Module for grid services

Nimat Shamim, Vilayanur V. Viswanathan, Daiwon Choi, Alasdair J. Crawford, Ed Thomsen, Mark Gross, David M. Reed, Vincent L. Sprenkle

Battery Materials & Systems Group, Pacific Northwest National Laboratory, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Introduction:

The advanced or carbon-enhanced negative electrode lead acid battery modules are used for renewable Energy Storage Applications due to their high cycle life, low cost and sustainability, However, there is still a lot to understand in terms of reliability for grid services. A lead acid battery modules has been tested for grid services such as frequency regulation. Test procedure and results are shown below.

Figure 1: Carbon Battery (Ref: C&D technologies)

Measurements :

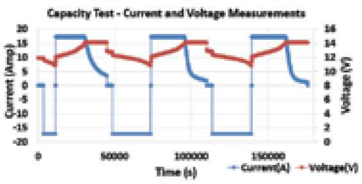
- Voltage
- Current
- Charge and Discharge Capacity
- Charge and Discharge Energy
- Cumulative Discharge Energy
- Round-trip efficiency (RTE),
- Internal Resistance

Objectives of the Project

- Develop a reliable testing protocol for lead acid battery module for grid services.
- Gain fundamental understanding of degradation mechanism of Lead Acid Battery module while used for grid services.
- Compare results with other battery chemistries to determine a reliable application specific battery technology for grid services.

Testing Procedure

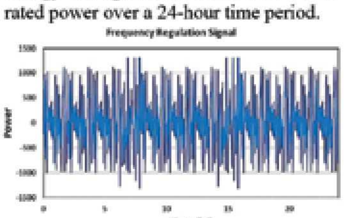
a) Capacity Test: It measures the battery capacity per cycling conditions described. Capacity test has been performed periodically to determine the capacity degradation of battery.



1. CC/CV charge to 100% SOC at C/10 rate to 14.1 V, hold till I < C/40 , Rest 1 hour
2. Discharge at 10-hour rate (17.24 amperes) to 10.8V, Rest 1 hour
3. Charge to 100% SOC , Rest 1 hour

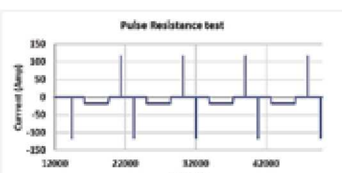
Repeat steps 2-3 thrice.

b) Frequency Regulation Test: The frequency regulation(FR) signal from the US DOE-OE Energy Storage Performance Protocol is applied. Power is normalized with respect to the rated power over a 24-hour time period.



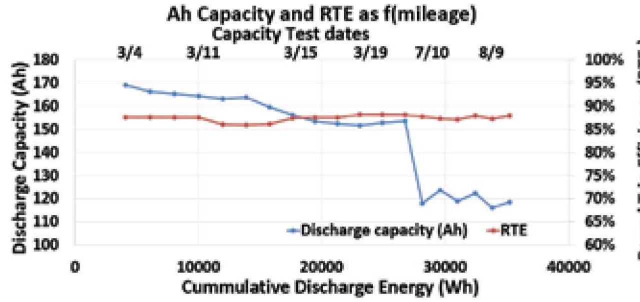
- Rated Power 1240 Watt
- Initial SOC 80%
- The SOC is reduced by 23% in one FR cycle
- The Battery module is charged back to initial SOC after one FR cycle.

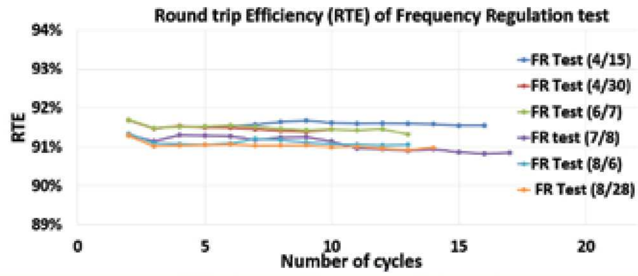
c) Pulse Resistance Test: A charge pulse and discharge pulse is applied. The internal resistance is calculated as the ratio of the change in voltage and current at the end of pulse.



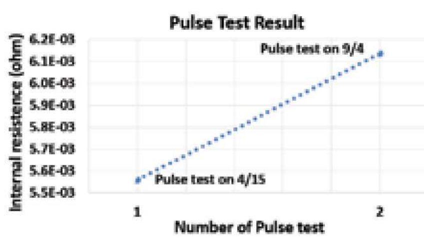
- Resistance is measured in every 10% ΔSOC decrementing from 100% SOC
- 6 second pulse width
- During pulse ΔSOC = 0.1%
- *Internal resistance* $= \Delta V/\Delta A$

Results and Discussion:





- Rated Capacity is 172 Ah while measured initial capacity was 169 Ah
- Round Trip Efficiency (RTE) is constant for all capacity tests. The FR RTE changed only 1% over the entire test duration.
- 30% decrease in Ah capacity. Capacity loss due to loss of active material; resistance increase of 10% does not play a major role (RTE unchanged).



- Internal Resistance increased 10% with time.
- Further pulse test will be done to determine the degradation profile of lead acid battery module.

Future Work:

- Peak shaving grid service testing will be performed.
- Degradation will be compared with that for volatile FR signal
- The results will be analyzed to characterize the performance reliability of lead acid battery module for grid services.
- The same tests will be conducted for other battery chemistry modules and the results will compared.

Acknowledgements

This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is a operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830.

U.S. DEPARTMENT OF ENERGY

Contact: **Dr. Nimat Shamim**
Post Doctoral Researcher
Battery Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: nimat.shamim@pnnl.gov

Synthesis of Advanced Magnetic Materials for Inductors and Transformers

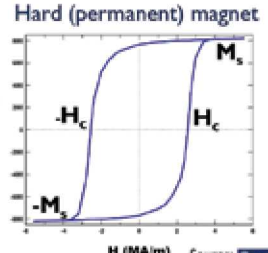
Tyler E. Stevens, Todd C. Monson, Charles J. Pearce, Riley E. Lewis, Jessica N. Dyer, Mark A. Rodriguez, Bonnie McKenzie, Sara Dickens & Stan Atcitty

Sandia National Laboratories, Albuquerque, NM 87185

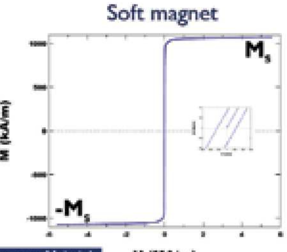
Project Objective

The size requirements of power electronics are determined by the necessary components. Magnetic materials contribute to this significantly, and to maximize efficiency and size, new magnetic materials are required. One of the main challenges has been developing materials that work in conjunction with high frequency semiconductor switches. This year, we sought to fabricate iron nitride/Ni-P layered composite transformer cores and demonstrate decreased losses in comparison to neat iron nitride at frequencies up to 100 kHz and temperatures of 150 °C. To achieve this, we have focused on identifying and optimizing synthetic routes to yield phase pure iron nitrides and then incorporating them into composites. This has resulted in materials with good performance up to 1 MHz.

Hard (permanent) magnet



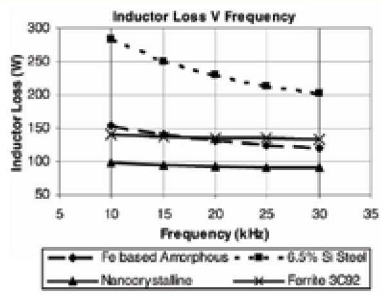
Soft magnet



Source: Spontaneous Materials

M_s = saturation magnetization
H_c = coercivity

- Hysteresis and Eddy current losses
- **Develop new soft magnetic materials that work in conjunction with high frequency semiconductor switches**



B.J. Lyons, J.G. Hayes, M.G. Egan, Magnetic Material Comparisons for High-Current Inductors in Low-Medium Frequency DC-DC Converters, IEEE, 2007, 71. Specifications: V_i = 200V, V_o = 400V, P_o = 40kW.

- Current magnetic materials experience significant loss as frequency is increased

Magnetic Material	J_s (T)	ρ ($\mu\Omega\cdot$m)	Cost
VITROPERM (Vacuumschmelze)	1.20	1.15	High
Metglas 2605SC	1.60	1.37	High
Ferrite (Ferroxcube)	0.52	5x10^6	Low
Si steel	1.87	0.05	Low
γ'-Fe_4N	1.89	> 200	Low

($J = \mu_0 \cdot M$)

- γ'-Fe_4N has a higher saturation polarization (J_s) and electrical resistivity than Si steel
- Use of abundant elements (Fe and N) will keep costs low

Synthesis and purification of iron nitride

Metathesis- effective for early transition metals

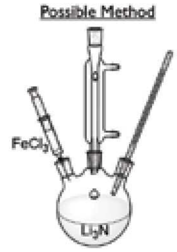
$MX_n + Li_3N \longrightarrow M_yN + LiX$

Group	MX_n	Product
4	$TiCl_4$	TiN
	$ZrCl_4$	ZrN
	$HfCl_4$	HfN
5	VCl_3	VN, V_2N
6	$CrCl_3$	Cr, Cr_2N
7	MnI_2	Mn_4N, Mn
8	$FeCl_3$	Fe
10	$NiCl_2$	Ni

- Effective for group 4-7 metals
- Reactions with group 8 – 10 metals generate too much heat
- Decomposition to elemental metal

- Current methods don't work for Fe and Ni
- Need new method

Possible Method

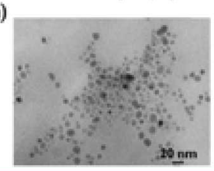


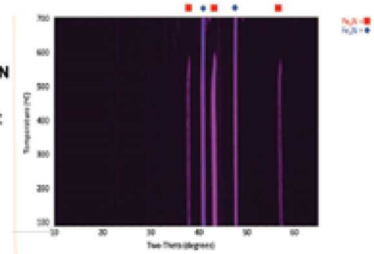
Excess solvent should act as heat sink and allow for isolation of desired product

Results

$$FeCl_3 + Li_3N \xrightarrow[\text{oleylamine, -LiCl}]{350\ °C} \text{mixture of } Fe_2N/\ Fe_3N$$

- Mixed product if all materials are combined at beginning
- Fe_2N is only product if $FeCl_3$ is added at 80 μL/min
- Fe(II) precursor results in Fe_3N (higher Fe concentration)



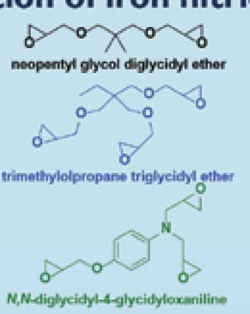


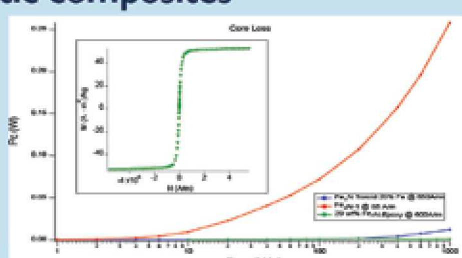
- Using a heat treatment, commercial $Fe_{(2-4)}N$ can be converted to 95 % phase pure Fe_4N

Incorporation of iron nitride into soft magnetic composites

Iron nitride + $H_2N(CH_2)_6NH_2$

- Ball milling was used to generate a fine mixture of iron nitride and hexamethylenediamine
- Composites have successfully been formed using a 1:1and 1:0.75 molar ration of Iron nitride/ hexamethylenediamine and combining the mixture with an epoxy
- Several systems are being evaluated based on molecular weight and T_g





- Preliminary data indicate low core loss at high frequency

Output

- "Soft magnetic materials for a sustainable and electrified world" J. M. Silveyra, E. Ferrara, D. L. Huber, and T. C. Monson Science **2018**, *362*, 0195.
- "Soft Magnetic Multilayered FeSiCrB-Fe_xN Metallic Glass Composites Fabricated by Spark Plasma Sintering" T. C. Monson, B. Zheng, R. E. Delany, C. J. Pearce, E. D. Langlois, S. M. Lepkowski, T. E. Stevens, Y. Zhou, S. Atcitty, and E. J. Lavernia *IEEE Magnetics Letters* **2019**, *10*, 7102505.
- "Synthesis and Magnetic Properties of Iron Nitrides," T. E. Stevens, R. E. Lewis, C. J. Pearce, M. A. Rodriguez, S. Dickens, B. B. McKenzie, S. Atcitty, T. C. Monson, American Chemical Society National Meeting 2019, Orlando, FL, March 31 – April 4, 2019.
- "Synthesis of Nanostructured Ferroic Materials for Energy Conversion," T. C. Monson, T. E. Stevens, D. A. Vargas, R. M. Van Ginhoven, B. Zheng, Y. Zhou, M. Fraga, E. Lavernia, Materials Science & Technology 2018, Invited Presentation, Columbus, OH, Oct. 14 -19, 2018.

Acknowledgements

This work was supported by DOE Office of Electricity Energy Storage Program, Dr. Imre Gyuk, Program Manager.
We thank Kerry-Ann Stirrup for assistance with XRD.

Novel Phenazine Derivatives as Anolytes for Aqueous Redox Flow Batteries

Nadeesha P. Nambukara Wellala, Aaron Hollas, Ruozhu Feng, Vijayakumar Murugesan, Xin Zhang, Zimin Nie, Yuyan Shao, David Reed and Wei Wang

Battery Materials & Systems Group, Pacific Northwest National Laboratory, Richland, WA 99354

Pacific Northwest NATIONAL LABORATORY

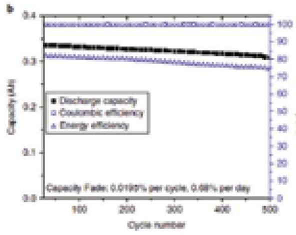
Proudly Operated by Battelle *Since 1965*

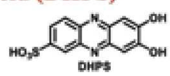
Introduction: The redox flow batteries (RFB) are promising candidate in grid energy storage due to high safety, independent tuning of energy and power and scalability.

➤**All Vanadium RFB**
- ✧High energy capacity
- ✧Long term stability
- ✧High cost

➤**Organic RFB**
- ✧Easy functionalization
- ✧Low cost

➤**7,8-Dihydroxyphenazine-2-sulfonic acid (DHPS)**





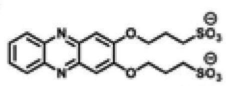
- ✧High solubility (1.4 M in 1 M NaOH and 1.8 M in 1M KOH)
- ✧High reversible anolyte capacity 65 Ahl^{-1}
- ✧Energy efficiency >75%
- ✧Capacity retention 90% after 500 cycles

➤**Decomposition of DHPS**

Objective: Discover how various substitution groups in phenazine derivatives affect solubility and stability

Results and Discussion:

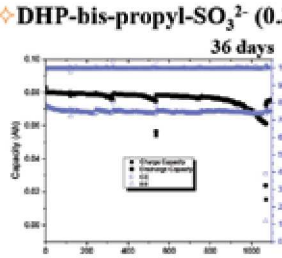
➤ **Phenazine Derivative I**



2,3-Dihydroxyphenazine-bis(propylsulfonate) (DHP-bis-propyl-SO_3^{2-})

➤ **Redox Flow Battery Performance**

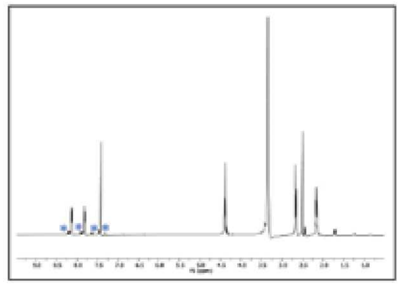
✧**DHP-bis-propyl-SO_3^{2-} (0.30 M)**



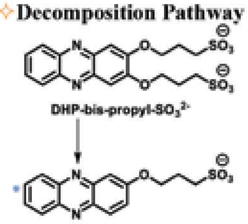
- ✧Significant capacity loss is due to precipitation of decomposed anolyte
- ✧DHP-bis-propyl-SO_3^{2-} decomposes to its mono-substituted derivative

Condition: Anolyte; DHP-bis-propyl-SO_3^{2-} in 0.8 M KH_2PO_4/0.2 M K_2HPO_4
Catholyte; excess $K_4Fe(CN)_6$/$K_3Fe(CN)_6$ in same buffer solution.

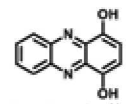
➤ **NMR Study on Capacity Loss (^{1}H NMR in DMSO-d_6)**



✧**Decomposition Pathway**



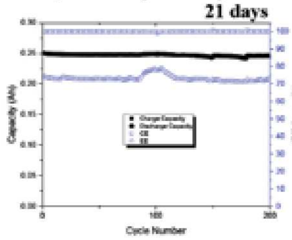
➤ **Phenazine Derivative II**



1,4-Dihydroxyphenazine (1,4-DHP)

➤ **Redox Flow Battery Performance**

✧**1,4-DHP (0.42 M)**



- ✧Solubility of deprotonated 1,4-DHP is 0.36 M in 1 M NaOH and 0.53 M in 2 M KOH
- ✧1.6% capacity decay after 200 cycles (0.008% per cycle, 0.076% per day)

Condition; Anolyte; 1,4-DHP in 2 M KOH
Catholyte; excess $K_4Fe(CN)_6$/$K_3Fe(CN)_6$ in 2 M KOH.

Summary:

- ✧Capping of phenoxy groups of 2,3-DHP with propyl sulfonate groups does not protect from self reduction
- ✧1,4-DHP has low solubility but higher cycling stability compare to DHPS

Future Work:

- ✧Develop new phenazine derivatives to further study effect of substitution pattern on solubility and stability
- ✧Study the decomposition pathways of the new phenazine derivatives
- ✧ Modify the stable phenazine derivatives to improve their solubility

Acknowledgements:

This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558.
PNNL is operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830

U.S. DEPARTMENT OF ENERGY

Contact: Aaron Hollas
Battery Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: aaron.hollas@pnnl.gov
Tel: (509) 375 4449

References:
Hollas et al. *Nature Energy* **2018**, *3*, 508-514.

Advanced Cathodes for Intermediate-Temperature Na-Metal Halide Batteries

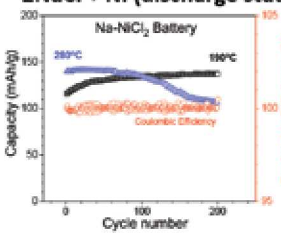
Xiaowen Zhan, Xiaochuan Lu, Jeff F. Bonnett, Nathan L. Canfield, David M. Reed, Vincent L. Sprenkle, and Guosheng Li*

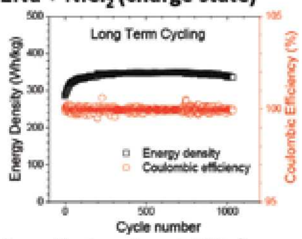
Battery Materials & Systems Group, Pacific Northwest National Laboratory, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY

Background: IT Na-MH Battery Technology

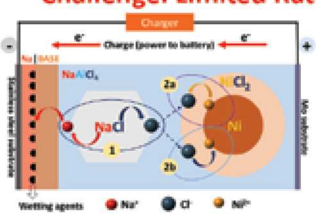
2NaCl + Ni (discharge state) ↔ 2Na + $NiCl_2$ (charge state)





- Slow cell degradation (particle growth) and excellent cycling stability[1]
- Low-cost polymer sealing[2]

Challenge: Limited Rate Capability @ Lower T



PNNL solutions

- Anode Interface engineering
  - ➢ Bilayer BASE design[3]
  - ➢ Na/BASE wetting agents[4]

Objective: Determine the cathode reaction kinetics and further improve the rate performance.

From Ni/NaCl to Ni/NaX (Br and I) Cathodes[5]

Theoretical Reactions:

2NaCl + Ni ⇔ 2Na + $NiCl_2$

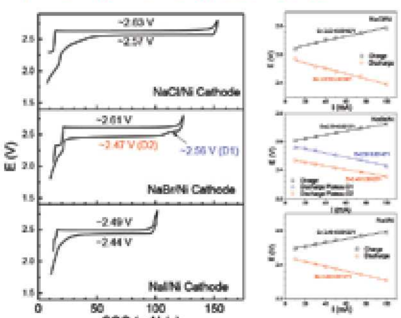
E_o = 2.60 V at 190°C

2NaBr + Ni ⇔ 2Na + $NiBr_2$??

E_o = 2.57 V at 190°C

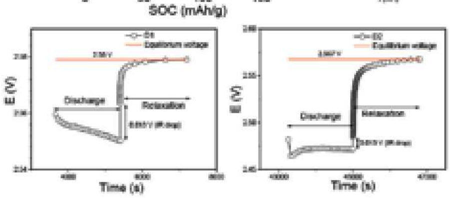
2NaI + Ni ⇔ 2Na + NiI_2

E_o = 2.46 V at 190°C



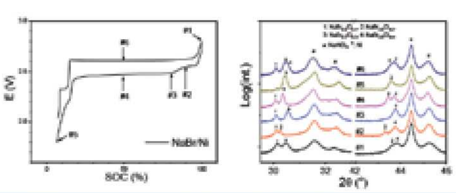
GITT:

- Same IR drop of 0.013 V (1.3 Ohm) for D1 and D2
- Extra overpotential for D2 possibly from mass diffusion

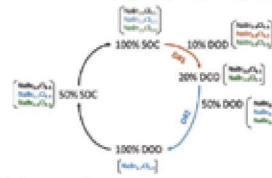


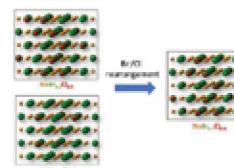
XRD & Synchrotron HR-XRD:

- Different $NaBr_xCl_{1-x}$ mixed phases identified
- $NiBr_{2x}Cl_{2-2x}$ rather than $NiBr_2$ forms during charge



Origin of Extra Discharge Plateau





Br^-/Cl^- ion exchange:

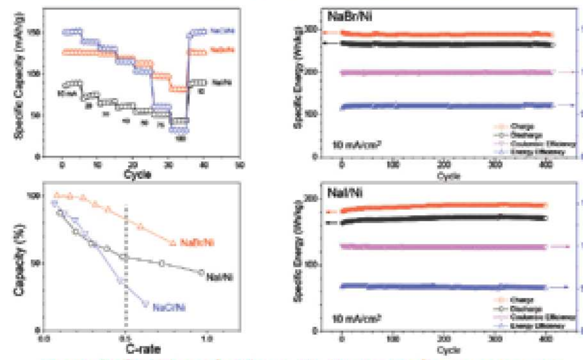
$$xNaBr + NaAlCl_4 \Leftrightarrow xNaCl + NaAlBr_xCl_{4-x}$$

- Confirmed by LC-Mass result: x=0.24

Overall cell reaction:

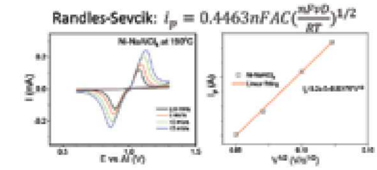
$$2NaBr_xCl_{1-x} + Ni \Leftrightarrow 2Na + NiBr_{2x}Cl_{2-2x}\ (E_o = 2.58\ V)$$

Superior Rate Performance of NaBr/Ni



Fast Salt Dissolution → Rate Enhancement

Randles-Sevcik: $i_p = 0.4463nFAC(\frac{nFvD}{RT})^{1/2}$



Diffusivity from CV

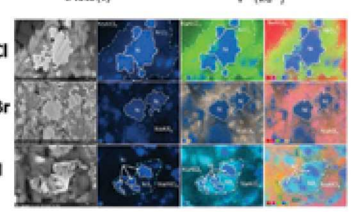
Cathode	D (cm²/s)
$NiCl_2$	1.9×10^{-8}
$NiBr_2$	1.0×10^{-8}
NiI_2	3.0×10^{-8}

Slower diffusion: thin $NiBr_2$ layer

Ni/NaCl

Ni/NaBr

Ni/NaI



Solubility from ICP

Sample	Solubility
NaCl	2.2 mol%
NaBr	6.6 mol%
NaI	2.4 mol%

Faster salt dissolution (rate-determining step): high rate capability

Conclusions:

- **The NaBr/Ni cathode delivered 174 Wh/kg at 100 mA (~0.8C), which is 2.5 times of conventional NaCl/Ni cells.**
- **The superior rate capability of NaBr/Ni is ultimately attributed to the faster sodium bromide salt dissolution, which enables easier Br^- anion transfer.**

Acknowledgments

This work is supported by U.S. Department of Energy (DOE) Office of Electricity (Contract No. 70247) and partially by the International Collaborative Energy Technology R&D Program of the Korea Institute of Energy Technology Evaluation and Planning, the Republic of Korea Ministry of Trade, Industry & Energy (No. 20158510050010) and POSCO. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. PNNL is operated by Battelle for the DOE under Contract DE-AC05-76RL01830.

U.S. DEPARTMENT OF ENERGY

Contact: Guosheng Li, Ph.D.
Battery Materials & Systems Group
Pacific Northwest National Laboratory
Email: guosheng.li@pnnl.gov

[1] Li et al., *Nat. Commun.* 7, 10683 (2016).
[2] Change et al., *J. Power Sources*, 348, 150 (2017).
[3] Jung et al., *J. Power Sources*, 396, 297 (2018).
[4] Chang et al., *J. Mater. Chem. A*, 6, 19703 (2018).
[5] For more details of this work please refer to: *Zhan et al.*, **Elucidating the role of anionic chemistry towards high-rate intermediate-temperature Na-metal halide batteries**, *Energy Storage Maters.*, https://doi.org/10.1016/j.ensm.2019.08.021.

VALIDATED RELIABILITY AND SAFETY PERFORMANCE

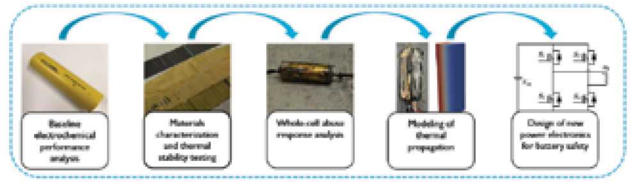
Each of the collaborative laboratories has a significant focus on safety and reliability of grid energy storage systems. This effort includes coordinating DOE Energy Storage Systems (ESS) Safety Collaborative which bring together stakeholders from industries that range from national laboratories, electric utilities, standards organizations, and manufacturing companies. Sandia also provides workshops and organizes technical conferences, including the Energy Storage Safety Forum, an annual technical meeting for the worldwide research community.

Multi-scale Thermal Stability of Lithium-Ion Batteries as a Function of Chemistry and State of Charge

Heather Barkholtz, Yuliya Preger, Sergei Ivanov, Jill Langendorf, Loraine Torres-Castro, Joshua Lamb, Babu Chalamala, and Summer Ferreira

Motivation & Objectives

Experimentally quantify Li-ion battery failure at the materials level during abusive and non-abusive conditions to enable:
…informed decision making about preferred operating conditions for different batteries
…modeling of battery degradation and thermal propagation
…translation of failure understanding to technologies for intervention
…safe and reliable energy storage for a resilient grid



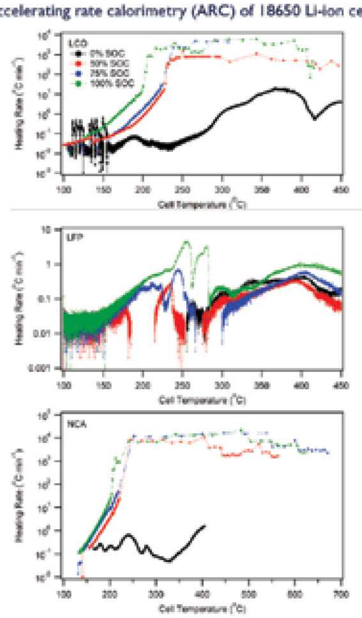
- Relate component to whole cell failure for popular commercial Li-ion chemistries
- Compare failure response from fully charged to fully discharged state

Milestones

•Whole cell calorimetry for LCO, LFP, NCA at 0, 50, 75, and 100% SOC
•Calorimetry of separator, anode, and cathode components at 0, 50, 75, and 100% SOC

Whole Cell Failure

Accelerating rate calorimetry (ARC) of 18650 Li-ion cells

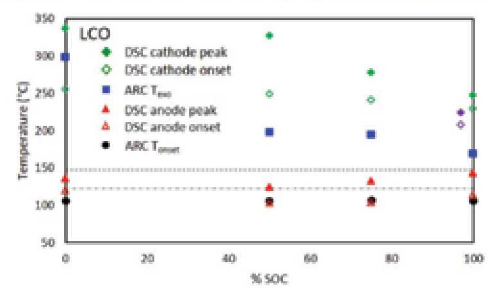


Cell	SOC (%)	T_{onset} (°C)	T_{exo} (°C)	HR_{max} (°C min^{-1})	$HR_{max,norm}$ (°C min^{-1} Ah^{-1})
LCO	0	105.8	298.1	18.4	7.4
	50	96.6	202.5	1116.9	447
	75	106.5	193.3	4822.3	1930
	100	106.4	168.4	6053.5	2420
LFP	0	105.9	---	0.4	0.4
	50	100.8	---	0.3	0.3
	75	100.7	---	0.7	0.6
	100	100.9	240.5	4.5	4.1
NCA	0	164.9	391.8	1.5	0.5
	50	140.7	182.2	10810.3	3730
	75	131.7	169.4	16107.4	5550
	100	132.5	165.9	21480.4	7410

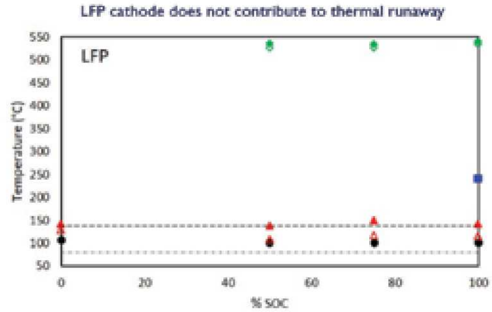
T_{onset}: self-heating (> 0.02 °C min^{-1}); T_{exo}: thermal runaway (> 1 °C min^{-1})

Multi-scale Comparison

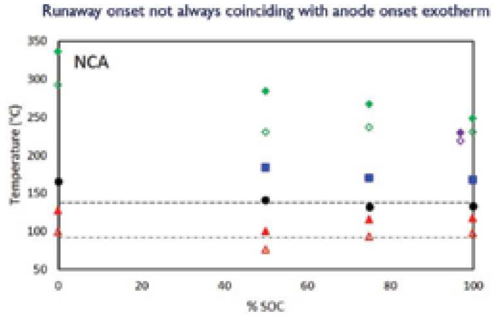
Metal oxide cathodes contribute to runaway only in combination with solvent



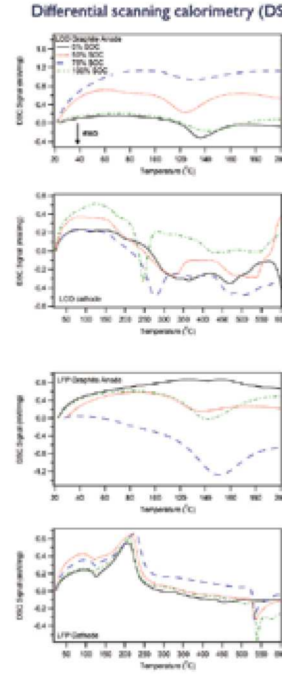
LFP cathode does not contribute to thermal runaway

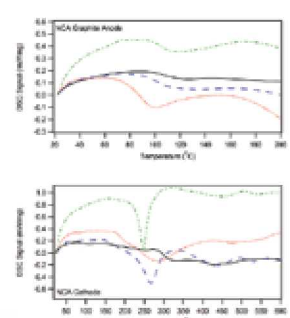


Runaway onset not always coinciding with anode onset exotherm



Differential scanning calorimetry (DSC)





Conclusions

- Variability in key ARC temperatures can be traced back to cell component chemistry and SOC
- SEI decomposition is typically the onset of thermal runaway and does not vary with SOC
- LFP cathode does not contribute to runaway; metal oxides contribute only in combination with solvent
- Importance of standard calorimetry protocols to get 'true' onset temperatures

Publications: Barkholtz et al. *J. Power Sources* **2019**, *435*, 226777
Shurtz et al. *J. Electrochem. Soc.* **2019**, *166*, 12, A2498-A2502.

Presentations: 2019 Electrochemical Society Spring Meeting

Other: Development of nation-wide calorimetry collaborative

Funded by the U.S. Department of Energy, Office of Electricity, Energy Storage program. Dr. Imre Gyuk, Program Director

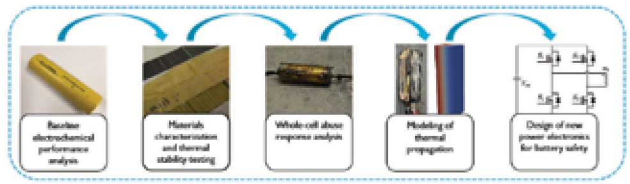
Durability and Reliability of Commercial Lithium-Ion Cells as a Function of Chemistry and Cycling Conditions

Yuliya Preger, Heather Barkholtz, Armando Fresquez, Summer Ferreira, and Babu Chalamala

Motivation & Objectives

Experimentally quantify Li-ion battery failure at the materials level during abusive and non-abusive conditions to enable:
…informed decision making about preferred operating conditions for different batteries
…modeling of battery degradation and thermal propagation
…translation of failure understanding to technologies for intervention
…safe and reliable energy storage for a resilient grid

- Understand difference in aging behavior as a function of chemistry, environment, and use case for popular commercial Li-ion chemistries
- Relate fading performance to changes in core electrochemical and materials properties



Milestones

- Complete cycling of LFP, NCA, NMC cells to 80% capacity
- Complete calendar aging of LFP, NCA, NMC to 80% capacity

Study Design

Design of experiment approach with two cells at each set of conditions, all within manufacturer specifications

Commercial cell specifications

Battery	LFP (A123)	NCA (Panasonic)	NMC (LG Chem)
Capacity	1.1 Ah	3.2 Ah	3.0 Ah
Voltage	3.3 V	3.6 V	3.6 V
Max Discharge Current	30 A	6 A	20 A
Operating T	-30 to 60°C	0 to 45°C	0 to 50°C

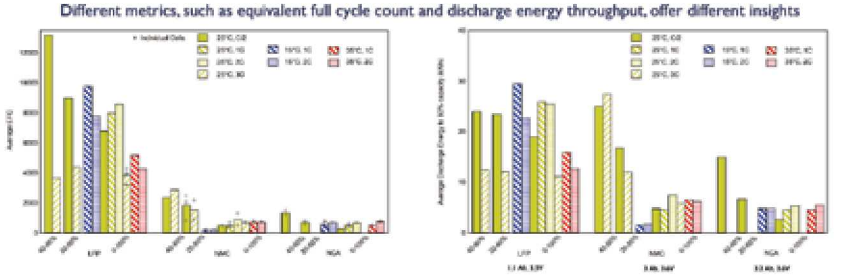
Cycling conditions for all cells

DOD, Temperature, Discharge Rate*			
40-60%, 25°C, 0.5C	0-100%, 15°C, 1C	0-100%, 15°C, 2C	40-60%, 25°C, 3C
20-80%, 25°C, 0.5C	0-100%, 25°C, 1C	0-100%, 25°C, 2C	20-80%, 25°C, 3C
0-100%, 25°C, 0.5C	0-100%, 35°C, 1C	0-100%, 35°C, 2C	0-100%, 25°C, 3C

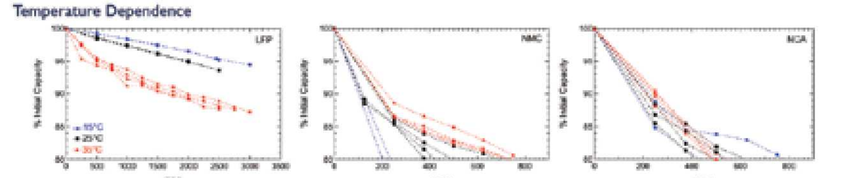
*Charge rate always C/2

Performance

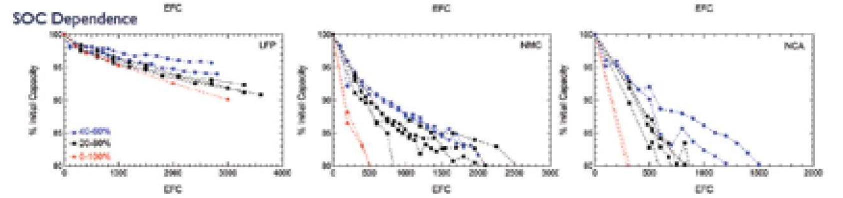
Different metrics, such as equivalent full cycle count and discharge energy throughput, offer different insights



Temperature Dependence



SOC Dependence

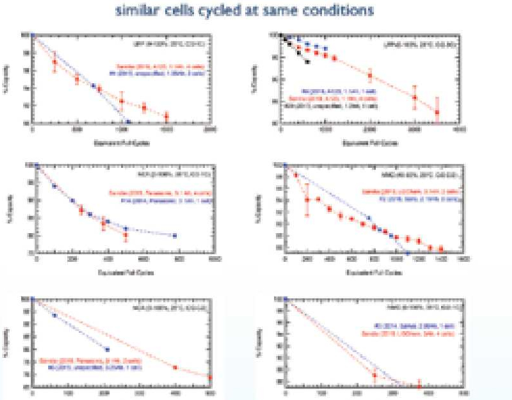


Broader Trends

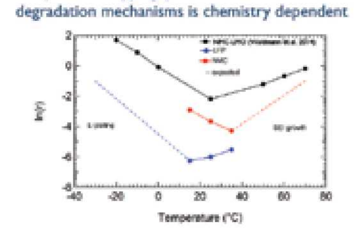
Summary of Variable Dependence for Commercial Cells

Chemistry	Other Conditions	Performance
Temperature (°C)		
LFP	0-100%, 1C/1C	25 > 40 > 50 > 60
LFP	0-100%, 1C/1C	35 > 55
LFP	0-100%, 1C/1C	5 > -5 > 13 > -20 > 30
LFP	0-100%, 0.5C/1C	15 > 25 > 35
NCA	0-100%, 0.5C/0.5C	25 ~ 30 ~ 40 ~ 50 ~ 60 > 20 > 15 > 5 > 0
NCA	0-100%, 0.5C/1C	15 ~ 25 ~ 35
NMC	0-100%, 1C/1C	25 > 50 > 60 > 70 ~ 0 > -10 > -20
NMC	3.0-4.2V, 0.5C/1C	35 > 50 > 25
NMC	3.75-4.2V, 1C/1C	45 > 20
NMC	various	45 > 20
NMC	0-100%, 0.5C/1C	35 > 25 > 15
Depth of Discharge (% or V)		
LFP	60°C, 0.5C/0.5C	45-55 ~ 40-60 ~ 25-75 ~ 10-90 ~ 5-95
LFP	30°C, 1C/1C	47.5-52.5 > 20-80 ~ 0-100 > 45-55 > 35-65 ~ 25-75
LFP	40°C, 1C/1C	45-55 ~ 25-75 ~ 0-100
LFP	25°C, 0.5C/1C	40-60 > 20-80 ~ 0-100
NCA	25°C, 1C/1C	0-60 ~ 10-70 ~ 40-100 > 0-100
NCA	40°C, 0.5C/0.5C	3.4-4.0 > 3.0-4.0 > 3.0-4.1 > 3.6-4.2 > 3.4-4.2 > 3.0-4.2 > 3.0-4.3
NCA	25°C, 0.5C/1C	40-60 > 20-80 > 0-100
NMC	20°C, 1C/1C	37.5-62.5 > 0-100 > 25-75 > 10-90 > 20-80 ~ 5-95
NMC	35°C, 1C/1C	47.5-52.5 > 45-55 > 40-60 > 25-75 > 10-90 ~ 0-100
NMC	25/35/45°C, 0.33C/1C	40-60 ~ 32.5 - 67.5 ~ 25-75 > 17.5-82.5 > 10-90 > 0-100
NMC	25°C, 6C/6C	0-20 > 20-40 ~ 40-60 ~ 60-80 > 80-100 > 0-100
NMC	25°C, 0.5C/1C	40-60 > 20-80 > 0-100
Discharge Rate (C-rate)		
LFP	25°C, 0-100%, 0.5C	0.04C > 0.2C ~ 0.5C > C > 2C
LFP	25°C, 2.5-3.7V, 0.5C	0.2C > 1C > 2C > 3C > 4C > 5C
LFP	15/25/35°C, 0-100%, 0.5C	0.5C ~ 1C ~2C > 3C
NCA	25°C, 3-4.2V, 0.5C	2C > 1.5C
NCA	15/25/35°C, 0-100%, 0.5C	2C > 1C > 0.5C
NMC	0-100%, 1C	1C > 2C at 20°C; 1C ~ 2C at 45°C
NMC	35°C, 10-90%, 0.33C	0.33C ~ 1C ~ 2C
NMC	15/25/35°C, 0-100%, 0.5C	no systematic dependence

Comparison to previous examples of similar cells cycled at same conditions



Temperature tipping point for transition between degradation mechanisms is chemistry dependent



Broad Trends
LFP consistently best at < 10°C and NMC at > 35 °C
NCA and NMC particularly sensitive to full discharge

Consistent Lifetimes
Reasonable agreement across different studies for cells cycled at similar conditions

Conclusions

- Equivalent full cycle count is the most common literature metric, but other metrics such as discharge energy are more useful for application
- Dependence on different variables is broadly consistent across the literature, and highly chemistry-specific (especially temperature)

Presentations: 2018 Battery Safety Conference, 2019 Energy Storage Safety & Reliability Forum, 2019 Electrochemical Society Spring Meeting
Other: Development of publicly accessible battery data repository + analytics tool

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
SAND No.

Funded by the U.S. Department of Energy, Office of Electricity, Energy Storage program. Dr. Imre Gyuk, Program Director.

Heat Release from Thermal Decomposition of Layered Metal Oxide Cathodes in Lithium-Ion Batteries

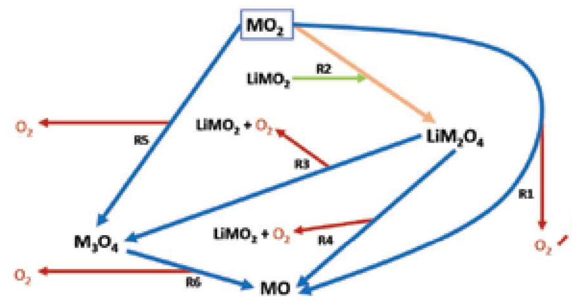
Randy C. Shurtz, John C. Hewson
Fire Science and Technology, Sandia National Laboratories, Albuquerque, NM

Introduction

- Stationary energy storage systems (ESS) are increasingly deployed to maintain a robust and resilient grid.
- As system size increases, financial and safety issues become important topics.
- Holistic approach: electrochemistry, materials, and whole-cell abuse will fill knowledge gaps.
- Models enable knowledge to be applied different scenarios and larger scales.
- Existing thermal runaway models successful for initial single-cell thermal runaway.
- Model features needed to evaluate safety for large Li-Ion systems include:
  - Applicability to batteries with different form factors, chemistries, SOC.
  - Predictions dependent on material properties.
  - High-temperature chemistry to predict cascading failure.
- Thermodynamics provide a foundation for modeling chemical heat release

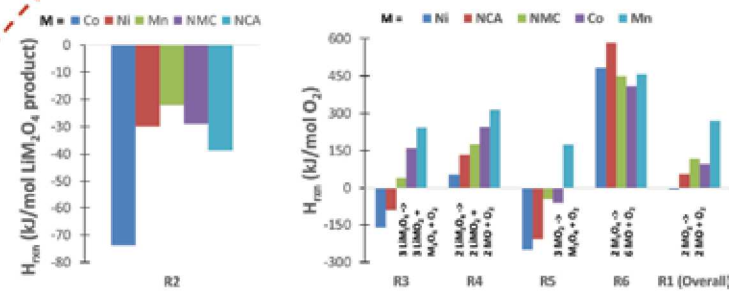
Decomposition of Layered Metal Oxides

- De-lithiated (high SOC) MO_2 cathodes experience multi-step decomposition
- Most steps produce oxygen except for exothermic formation of LiM_2O_4 spinel



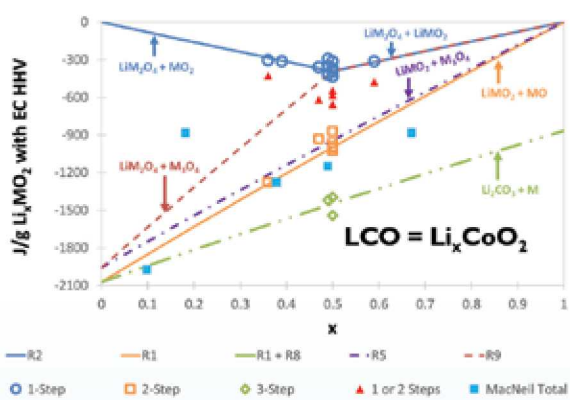
Predicting Cathode Heat Production

- Heats of reaction can now be calculated for decomposition of any Li_xMO_2 with
  - Arbitrary M (single metals or mixtures of Ni, Co, Mn, and Al)
  - Arbitrary x (low x = high SOC)
- Required assembling a new compilation of 32 formation enthalpies from 42 sources
- Electrolyte solvent combustion adds more heat (-472 kJ/mol O_2 for EC)

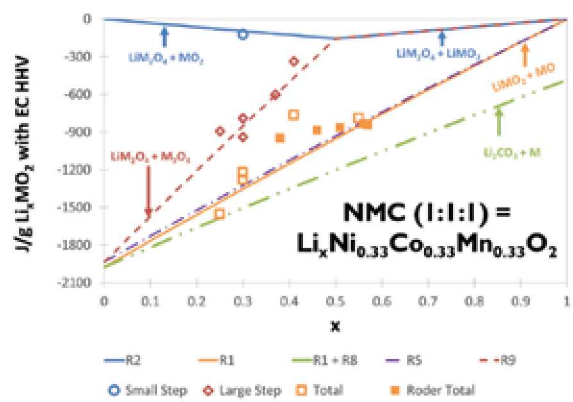


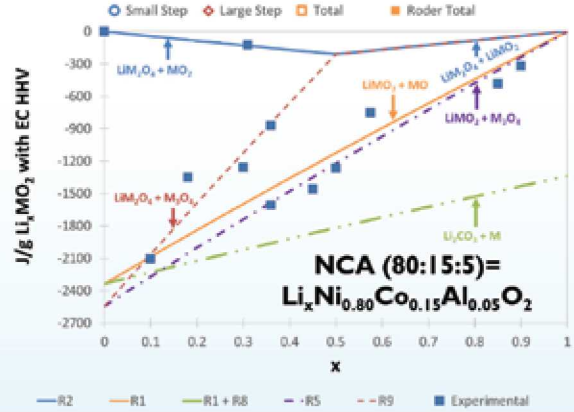
Calorimetry Data Demonstrate Effectiveness of Predictions for Pure and Mixed Metal Oxides

- Calculated heat generation with full combustion of solvent compared to calorimetry data
- Explains trends observed for different states of charge (x) and pure or mixed metal oxides (M)
- 60 calorimetry measurements extracted from 24 sources, scrutinized and processed for comparisons



Predicted and Measured Heat Release Agree for 3 Commercial Cathodes with Varying SOC





Conclusions and Next Steps

- First demonstration of heat release predictions from arbitrary metal oxides with varying SOC
- Allows rapid, *a priori* safety assessments for candidate Li-ion cathode materials
- Facilitates identification of chemical events from thermal data
- Distribution to occur through publication and development of a web-based heat-release calculator
- Cathode thermal runaway models to be developed will utilize these predictions as a sub-model

Acknowledgements:
- Funded by Dr. Imre Gyuk through the U.S. Department of Energy; Office of Electricity
- Special thanks to the following people for providing experimental data, thoughtful discussions, and advice
- Summer Ferreira • Loraine Torres-Castro • Joshua Lamb • Andrew Kurzawski • Yuliya Preger

Energy Storage Models for Risk-Averse Optimization

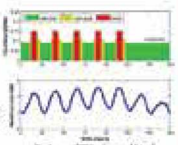
David Rosewater (Sandia), Ross Baldick (UT Austin), and Surya Santoso (UT Austin)

Self-guided-summary

Abstract—When batteries supply behind-the-meter services such as arbitrage or peak load management, an optimal controller can be designed to minimize the total electric bill. The limitations of the batteries, such as on voltage or state-of-charge, are represented in the model used to forecast the system's state dynamics. Control model inaccuracy can lead to an optimistic shortfall, where the achievable schedule will be costlier than the schedule derived using the model. To improve control performance and avoid optimistic shortfall, we develop a novel methodology for high performance, risk-averse battery energy storage controller design. Our method is based on two contributions. First, the application of a more accurate, but non-convex, battery system model is enabled by calculating upper and lower bounds on the globally optimal control solution. Second, the battery model is then modified to consistently underestimate capacity by a statistically selected margin, thereby hedging its control decisions against normal variations in battery system performance. The proposed model predictive controller, developed using this methodology, performs better and is more robust than the state-of-the-art approach, achieving lower bills for energy customers and being less susceptible to optimistic shortfall.

Problem Statement

Consider a hypothetical commercial electrical customer billed for power under both time-of-use (TOU) and a $50/kW demand charge.



Customer TOU price and load

Electric Bill without BESS

$$f_{bill} = \Delta t\, \mathbf{c}^T \mathbf{l} + \max(\mathbf{l})\, d$$

Electric Bill with BESS

$$f_{bill} = \Delta t\, \mathbf{c}^T (\mathbf{l} + \mathbf{p}) + \max(\mathbf{l} + \mathbf{p})\, d$$

where p is the battery system power that element wise subtracts from l when the battery system is discharging. The problem is thus formulated: design a control algorithm to optimally calculate a vector of battery system power p that minimizes the customer's bill f_{bill} without exceeding the battery's limits

Methods

We compare three controller models: the state-of-the-art energy reservoir model (ERM), a more accurate charge reservoir model (CRM), and a modified *risk-averse* CRM. To perform a **pseudo-empirical analysis** of the optimal schedules calculated from each model we simulate how the battery system would respond to each control signal using an extended CRM that incorporates additional constraints and parameters to improve its accuracy. The simulation model uses slightly different functions and parameters, enabling an analysis of the effects of model and parameter uncertainty on controller performance.

Simulation Results

The results of all three models, with open-loop and closed-loop implementation, are compared using a simulation model with either mean capacity, or extreme capacity. Total bill reduction is used to measure performance and optimistic short-fall is used to measure robustness.

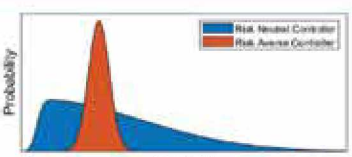
TABLE VI
SUMMARY OF RESULTS FROM SIMULATED CONTROL SCENARIOS

Controller Scenario	Sim-Model*	Total Bill	% Savings	Optimistic Short-fall**
Baseline	–	$340.88	–	
ERM OL Cal	–	$274.91	18.0%	–
ERM OL Ach	mean	$273.95	18.9%	-$0.96
ERM CL Ach	mean	$273.56	12.0%	-$1.35
ERM CL Ach	extreme	$273.69	12.0%	-$1.22
–upper bound	–	$292.52✓		
CRM OL Cal	–	$269.55	13.1%	–
–lower bound	–	$228.84✓		
CRM OL Ach	mean	$274.98	18.5%	$5.43
CRM CL Ach	mean	$269.55	14.3%	$0.00
CRM CL Ach	extreme	$292.53	5.9%	$22.98
–upper bound	–	$274.21✓		
RA CRM OL Cal	–	$271.22	12.5%	–
–lower bound	–	$235.35✓		
RA CRM OL Ach	mean	$271.17	12.8%	-$0.05
RA CRM CL Ach	mean	$271.08	12.4%	-$0.14
RA CRM CL Ach	extreme	$271.21	12.4%	-$0.01

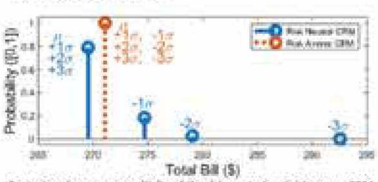
✓ denotes that the solution to the non-convex problem satisfies the bound.
* The extended CRM is used to simulate the BESS being controlled. It's parameters are selected to represent average behavior 'mean', or 'extreme case' lower than nominal available energy as described in Section VI.
** Optimistic Shortfall compares the bill achieved by applying control action to the simulated BESS to the open-loop calculated bill from each controller. Cal - calculated, Ach - achieved, OL - open-loop, CL - closed-loop, RA - risk averse

Main idea

The proposed BESS controller **performs better** and/or is **more robust** to fluctuating capacity than state-of-the-art controllers.



Notional examples of risk-neutral and risk-averse control bill savings probability density functions



Control performance sensitivity of the risk-neutral and risk-averse CRM based model predictive controllers.

Models

Energy Reservoir Model (ERM)

[illegible] (3a)

subject to: [illegible] (3b)–(3g)

where [illegible] is the ac electrical power provided to charge battery system, [illegible] is the ac electrical power discharged from the battery system, [illegible] is the battery SoC, [illegible] is the peak demand power and the differential matrix D is shown in (4).

$$\mathbf{D} = \frac{1}{\Delta t}\begin{bmatrix} -1 & 1 & 0 & \cdots & \cdots & 0 \\ 0 & -1 & 1 & 0 & \cdots & \vdots \\ \vdots & & & \ddots & \ddots & \vdots \\ 0 & \cdots & & 0 & -1 & 1 \end{bmatrix} \quad (4)$$

Charge Reservoir Model (CRM)

[illegible] (5a)

subject to: [illegible] (5b)–(5n)

where [illegible] is the dc electrical power provided to battery, [illegible] is the battery terminal voltage, [illegible] is the slack voltage used in calculation of an upper bound, [illegible] is the battery open-circuit voltage, and [illegible] is the peak power demand.

Risk-Averse Capacity (value at risk)

[illegible] (9)

where [illegible] is the random component of the battery's capacity, assumed to be a zero-mean, normal distribution.

[illegible] (10)

Bounding the Global Minimum

The CRM is a non-convex, non-pseudoconvex problem, hence we cannot grantee that a gradient based solver will find the globally optimal solution. An upper bound to a minimization problem can be found by restricting the feasible set (adding additional constraints) while a lower bound can be calculated by expanding the feasible set (relaxing or removing constraints).

Lower Bound (convex relaxation)

[illegible]

subject to: (5d) and (5f) through (5n) unchanged

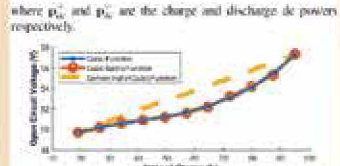
relaxing (5b) [illegible] (7a)

relaxing (5c) [illegible] (7b)

[illegible] (7c)

relaxing (5e) [illegible] (7d)

where [illegible] and [illegible] are the charge and discharge dc powers respectively.



Upper Bound (convex restriction/approximation)

[illegible]

subject to: (5b) and (5f) through (5n) unchanged

restricting (5c) [illegible] (8a)

restricting (5d) [illegible] (8b)

approx. (5e) [illegible] (8c)

[illegible] (8d)

[illegible] (8e)

[illegible] (8f)–(8j)

Conclusions

- In this paper we develop and demonstrate an advanced methodology for designing BESS controllers under ToU price arbitrage and peak demand charge management applications.
- The proposed CRM based model predictive controller outperforms the ERM, but is sensitive to BESS capacity.
- The risk-averse CRM still outperforms the ERM, but is more robust to variations in BESS performance
- This methodology for can be applied wherever the risk profile of a scheduled service is asymmetric.
- Incremental improvements in controller performance can reduce the cost of deploying storage to make the grid more efficient and resilient.

This work was funded in part by the U.S. Department of Energy Office of Electricity Energy Storage Program.

Sandia National Laboratories

Battery Management System Standards

David Rosewater
(working group chair)

Working Scope / Purpose

Scope:

This recommended practice includes information on the design, installation, and configuration of battery management systems in stationary applications, including both grid-interactive, standalone cycling and standby modes. This document covers battery management hardware, software, and configuration. Hardware capabilities in large systems include: grounding and isolation; passive and active balancing; and wired or wireless sensors. Software capabilities include: algorithms for optimal operation with reduced risk; best practices for verification and validation; alarms; and communication with external systems. Common settings are discussed along with setting selection methods. Battery types that this document covers include lithium-ion, sodium-beta, advanced lead-acid, and flow batteries. General factors for other types are provided.

This document does not cover battery management systems for mobile applications such as electric vehicles; nor does it include operation in vehicle-to-grid applications. Energy management systems, which control the dispatch of power and energy to and from the grid, are not covered.

Purpose

Well-designed battery management is critical for the safety and longevity of batteries in stationary applications. This document is intended to inform battery system designers and integrators in the challenges to battery management design. This document assists in the selection between design options by supplying the pros and cons of a range of technical solutions.

Many aspects of battery management design require integration with other systems such as energy management or charge control systems. System integration can be made difficult or impossible without a minimal level of communication interface and control interface standardization. To address this issue, this document offers recommendations and best practices for interface design to streamline system integration.

Four study groups were formed at the kickoff meeting in January and presented their initial findings in June.

- Requirements
- Architecture
- Modeling
- Failure Modes

Expected Timeline

2018 – PAR submitted to IEEE

2019 – WG Kickoff Meeting

2020 – Drafting Sections

2021 – Review/Editing

2022 – Balloting

IEEE P2686 Recommended Practice for Battery Management Systems in Stationary Energy Storage Applications

A new working group has formed within the IEEE energy storage and stationary battery (ESSB) committee to develop a recommended practice for battery management systems (BMS).

Well-designed battery management is critical for the safety and longevity of batteries in stationary applications. This document is intended to inform battery system designers and integrators in the challenges of BMS design and will assists in the selection between design options by supplying the pros and cons of a range of technical solutions.

Many aspects of battery management design require integration with other systems such as energy management or charge control systems. System integration can be made difficult or impossible without a minimal level of communication interface and control interface standardization. To address this issue, this document will offer recommendations and best practices for interface design to streamline system integration.

The scope of the working group's efforts includes collating and communicating information on the design, installation, and configuration of battery management systems in stationary applications, including both grid-interactive, standalone cycling and standby modes. The document we are working on covers BMS hardware, software, and configuration. Hardware capabilities in large systems include: grounding and isolation; passive and active balancing; and wired or wireless sensors. Software capabilities include: algorithms for optimal operation with reduced risk; best practices for verification and validation; alarms; and communication with external systems. Common settings are discussed along with setting selection methods. Battery types that this document covers include lithium-ion, sodium-beta, advanced lead-acid, and flow batteries. General factors for other types are provided.

Study Groups

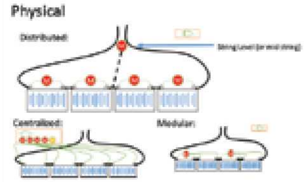
Requirements

Primary Functions

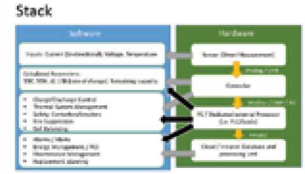
- **Safety:** Protection, Prevention and mitigate of catastrophic thermal events (fire, cell overheating, cell venting)
- **System Protection:** Prevent damage to cells, pack, string, or system from abuse, faults, or failure conditions
- **Ensure Proper System Function:** Maintain the system within proper operational parameters to meet system design requirements.

Architecture

Physical



Stack



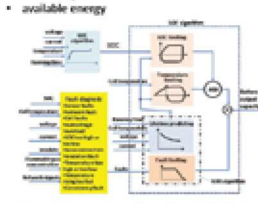
Modeling

Role:

- Predicting performance
- Estimate the battery internal states
- Control battery operation

States:

- State of charge
- State of health
- State of life
- Available power
- available energy



L. Lu et al. / Journal of Power Sources 226 (2013) 272–288

Failure Modes

Categories From IEEE 1679:

- General
- Short circuits
- Overdischarge
- Overcharge
- Thermal runaway
- Electronic failures

If you have knowledge of BMS design and would like to participate in the development of a new IEEE recommended practice, then please contact the working group chair, David Rosewater dmrose@sandia.gov, and join us for the next working group meeting at the IEEE ESSB 2020 Winter General Meeting in Orlando FL, February 10-14. https://cmte.ieee.org/pes-essb/event/essb-2020-meeting-orlando-fl/

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
SAND No. [illegible]

This work was funded by the U.S. Department of Energy, Office of Electricity, Energy Storage Program.

Sandia National Laboratories

Reliability Testing of Li-ion Batteries for Stationary Applications

Daiwon Choi, Alasdair J. Crawford, Nimat Shamim, Vilayanur V. Viswanathan, Ed Thomsen, Mark Gross, David M. Reed, Vincent L. Sprenkle

Pacific Northwest National Laboratory, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Introduction

To increase the utilization of intermittent renewable energy resources, cost effective, safe and long cycle life electrochemical energy storage is required[1]. Therefore, various types of lithium-ion batteries are currently deployed for stationary energy storage applications due to high voltage, energy density, and long cycle life. However, state-of-the-art lithium-ion battery performance as a stationary energy storage is not well explored and understood compared to vehicle application in terms of reliability[2]. In this work, four different Li-ion battery chemistries including NCA and LFP type cells are subjected to grid duty cycles specified to frequency regulation and peak shaving services. Our test setup, protocol and updated results will be compared and discussed.

Objectives and Methodology

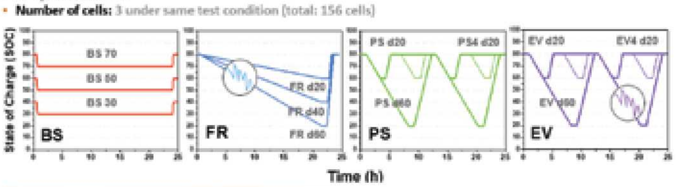
- Develop standardized testing protocols for industry specific reliability.
- Understand degradation of DC components and AC modules under grid duty cycles
- In parallel with field deployed system, enable testing under controlled and accelerated conditions – develop State of Health Model

Variables

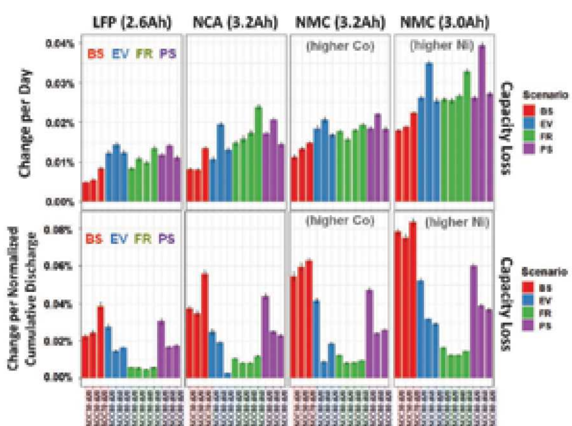
- **Time :** 24h grid cycle (1day)
- **State-of-Charge (SOC) :** 20~80%
- **Depth of Discharge (DOD or ΔSOC) :** 20, 40, 60%
- **Power (C-rate):** within cell specifications (voltage window)
- **Temperature :** 25°C
- **Number of cells:** 3 under same test condition (total: 156 cells)

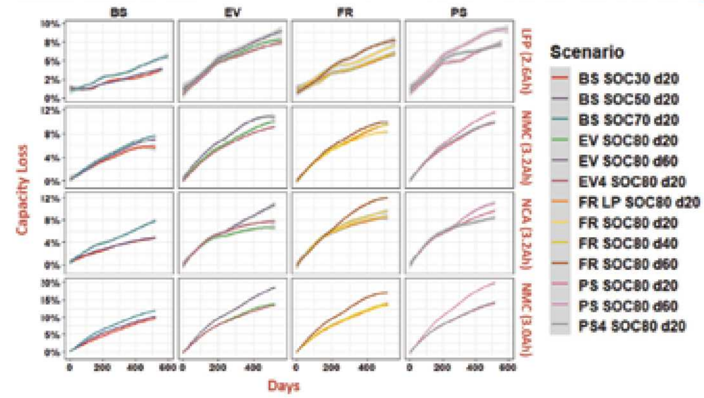
Schedules (# of conditions)

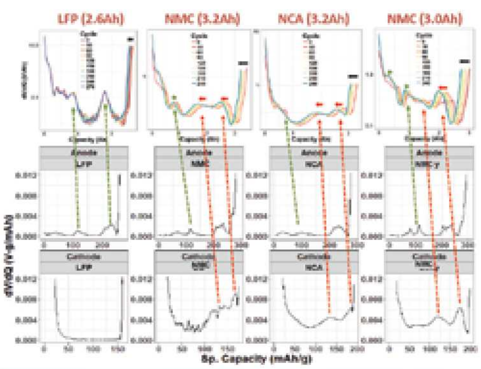
- **BS : Baseline (3)** – aging at different SOC levels
- **FR : Frequency Regulation (4)**
- **PS : Peak Shaving (3)**
- **EV : Electric Vehicle (3)**



Results and Discussion







Summary and Perspective

- LFP cells have better aging, capacity, and energy retention.
- Frequency regulation service degrades the least per energy utilized.
- Even with same battery chemistry, cycling stability varies with cell engineering.
- dV/dQ analyses and be applied for *in-situ* battery health monitoring
- Higher SOC level degrades the battery the most.
- Cathode dissolution occurs for NCA and NMC cells

Future Work

- Test methods developed here will be applied to larger energy storage modules and systems including Li-ion, lead acid, high temperature sodium and flow batteries.
- Additional 192 test channels will be installed for better resolution and response time including temperature, OCV, DC resistance, AC impedance, cyclic voltammetry monitoring.
- Testing more battery chemistries from different vendors
- In-operando/post-mortem cell characterization using advanced techniques.

Acknowledgements

This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is a operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830

U.S. DEPARTMENT OF ENERGY

Contact: Daiwon Choi, Ph.D.
Battery Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: daiwon.choi@pnnl.gov
Tel: (509) 375-4341

References

1. Z. Yang, J. Zhang, M.C.W. Kintner-Meyer, X. Lu, D. Choi, J.P. Lemmon, J. Liu, "Electrochemical Energy Storage for Green Grid", *Chemical Reviews*, 111(5), p. 3577-3613 (2011)
2. A. Crawford, Q. Huang, M.CW Kintner-Meyer, J.-G. Zhang, D. Reed, V.L. Sprenkle, V.V. Viswanathan*, D. Choi*, "Lifecycle Comparison of Selected Li-ion Battery Chemistries under Grid Duty Cycle Combinations", *Journal of Power Sources*, 380, p.185-193 (2018).

Battery Reliability Laboratory at PNNL

David Reed, Daiwon Choi, Vilayanur Viswanathan, Alasdair Crawford
Ed Thomsen, Nimat Shamim, Mark Gross, Vince Sprenkle

Battery Materials & Systems Group,
Pacific Northwest National Laboratory, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY

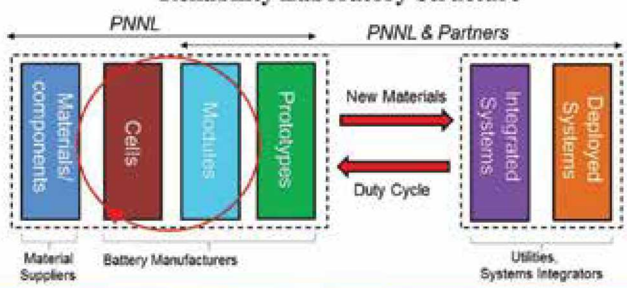
Proudly Operated by Battelle Since 1965

Introduction: To accelerate the development and deployment of energy storage into the electric infrastructure, it is critical to test the reliability of batteries and battery components for increased acceptance of the technology. The performance and lifetime of storage systems under grid duty cycles should be quantified and disseminated throughout the industry. In addition, findings from technologies tested under grid duty cycles should be used to direct research related to degradation and aging of the technology.

Objectives

- Establish a world class battery testing laboratory to predict the lifetime of battery components
- Utilize strong on-site characterization facilities (i.e. NMR, XPS, TEM, APT, etc.) to understand degradation mechanisms on batteries tested under grid duty cycles.
- Create innovative material solutions to existing technologies to increase reliability by understanding Materials-Performance relations for various battery technologies
- Provide battery operation guidelines and independent validation of performance to end users to maximize battery lifetime

Reliability Laboratory Structure



Energy Storage Technologies (3-5 kW)

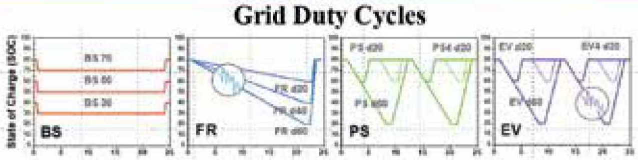
Phase I (FY 2019)

Li-ion
K2 Energy
AllCell Technologies
Na Metal Halide
Fiamm Na $NiCl_2$
Pb Acid
C&D Technologies
V Flow Battery
ITN Energy Systems, Inc[2]
Ni-Fe
Iron Edison

Phase II (FY 2020)

Li-ion
LG Chem
King County (2nd life)
Pb Acid
RSR Technologies
Flow Battery
UniEnergy (V)
ESS, Inc. (Fe)
Ni- Zn
NGK
Salt water (Na-ion)
Bluesky Energy

Grid Duty Cycles



Li ion cells and Module Testing

ITN V Flow Battery

NHR Module Testers/Cyclers

Pb Acid Module Testing

Na Metal Halide Testing

Future Work

- Phase II will provide additional capacity, technologies, and testers/cyclers in FY20.
- Testing linked to field deployed systems to validate component performance.

Acknowledgements
This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is a operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830

U.S. DEPARTMENT OF ENERGY

Contact: David Reed
Battery Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: david.reed@pnnl.gov
Tel: (509) 375-4534

References*

1. US Patents 9,819,039, 9,123,931, 9,077,011, 8,628,880
2. US Patent Application 0099480

* These patents were developed under DOE-OE Contract

In-situ Reliability Studies of Vanadium Redox Flow Batteries: High Voltage Stressor

Rajankumar Patel [a], David Reed [a], Allison Platt [b], Elizabeth Fisher [b], Chaojie Song [b]

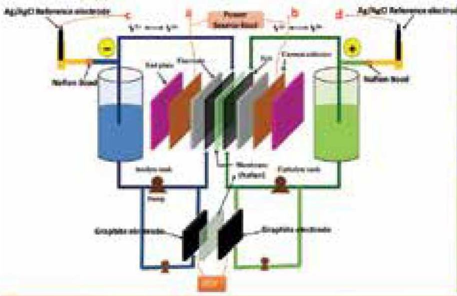
[a] Battery Materials & Systems Group, Pacific Northwest National Laboratory, Richland, WA 99352

[b] Energy, Mining & Environment, National Research Council Canada, Vancouver, BC V6T1W5

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

Introduction: Vanadium redox flow batteries (VFRB) suffers from performance fading over long cycling. To fundamentally understand the reliability and degradation mechanism, and to eventually develop models for aging prediction that can help reduce the duration and cost associated with real lifetime tests, is imperative for their in real applications. This is the first installment of this stress tests: High Voltage. Stressors aid in aging prediction which is essential to estimate the overall lifetime and the cost of a battery system



***In-situ* measurements:**

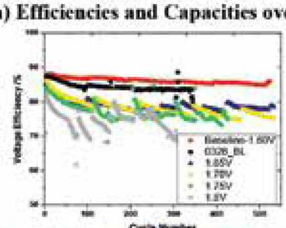
- $V_{Full\ cell}$ (b vs. a)
- $V_{cathode\ vs.\ Ref(+)}$ (b vs. d)
- $V_{anode\ vs.\ Ref(-)}$ (a vs. c)
- $V_{cathode\ vs.\ Ref(-)}$ (b vs. c)
- OCV
- Polarization curves (such as full cell (b vs. a), cathode (b vs. d) and anode (a vs. c))
- Ac impedances

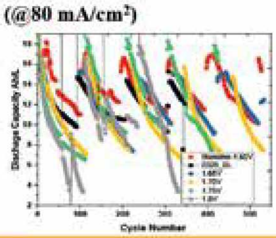
Objectives and Approaches:

- High cutoff voltage considered as a stressor to accelerate the VRFB cell and component degradation and gain fundamental understanding of degradation mechanism.
- VRFB usually operates with voltage limits to 1.55-1.65 V due to the electrode corrosion and oxygen evolution in the catholyte. For Stressor tests, voltage ranged 1.6 V - 1.8 V (depending on the cutoff voltage reaches 80% SOC at constant current charge using 80 mA/cm²) tested for 500 cycles with electrolyte remixing at every 100 cycles.

Results and Discussion:

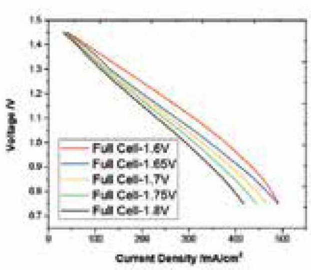
a) Efficiencies and Capacities over cycling (@80 mA/cm²)



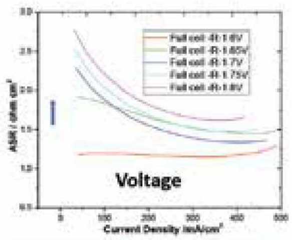


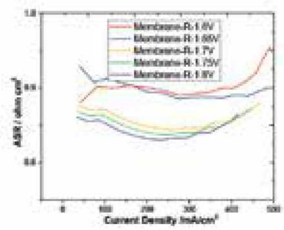
- Higher voltage leads to decay more significantly

b) Polarization curves after remixing



Stressor (V)	Polarization (mV)
1.6 (baseline)	50
1.65	100
1.7	170
1.75	150
1.8	185



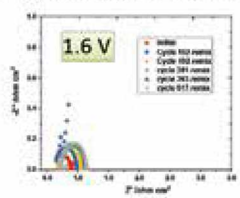


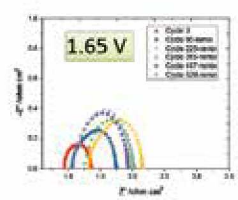
Full Cell R= $(OCV-V_{output})/I$

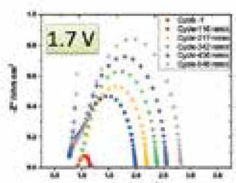
Membrane R= $(V_{cathode\ vs.\ Ref(+)}-V_{cathode\ vs.\ Ref(-)})/I$

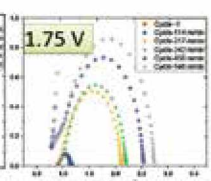
- The resistances of full cell gradually increased over cycling.
- The resistances of membranes after cycling is larger than that of original one and then keep constant over cycling.
- Higher upper voltage can lead to enhanced full cell resistances.
- 1.8V upper voltage caused increase in polarization, resistance, and capacity fade.

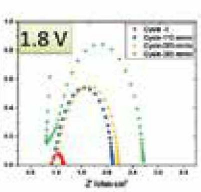
c) AC impedances after remixing











Stressor	1.60 V	1.65 V	1.70 V	1.75V	1.8V
ΔR-charge transfer resistances/ohm cm²	0.15	0.6	1.5	1.4	TBA

- Slightly decay was observed for full cell polarization mainly due to cathode.
- The enhancement of resistances over cycling mainly results from the increasing charge transfer resistances.
- Higher voltage can lead to greatly improved charge transfer resistances.
- For every 100 cycles, cathode performance decays with increasing cycles. However, there is no significant influence on anode performances. Higher upper voltage could result in more significant cathode decay.

Future Work:

- Single or multi- stressors including anolyte and catholyte starvation will be studied to accelerate the VRB decay;
- Establish correlation between cell performances and electrolyte composition or electrode or bipolar plates properties over cycling. .

U.S. DEPARTMENT OF ENERGY

Acknowledgements

This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is a operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830.

Contact: **Dr. Rajankumar Patel**
Post-doctorate Research Associate
Battery Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: rajankumar.patel@pnnl.gov ; Tel: (509) 375-6906

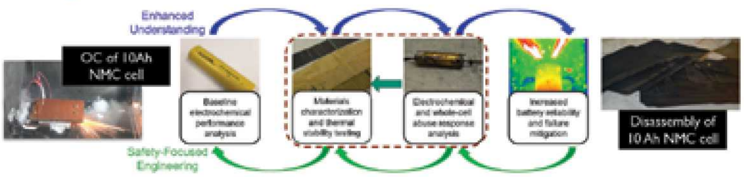
Sandia National Laboratories
SNL Energy Storage Technology and Systems – Energy Storage Safety
Funded by Dr. Imre Gyuk
U.S. Department of Energy; Office of Electricity; Energy Storage Systems Program

Mechanisms and Materials Impact of Abused Li-ion Batteries

Loraine Torres-Castro, Josh Lamb, Eric Deichmann, June Stanley, Chris Grosso, Jill Langendorf, and Lucas Gray

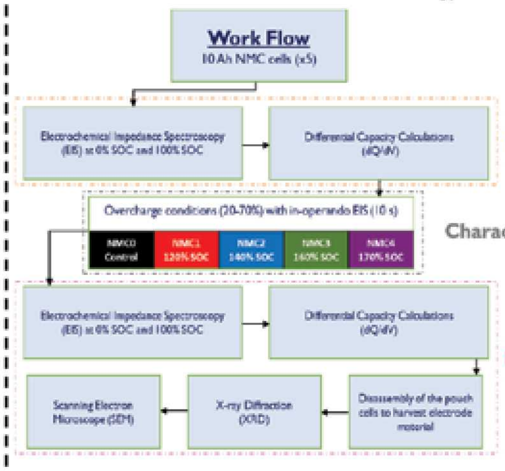
Introduction

- Stationary energy storage systems (ESS) are increasingly deployed to maintain a robust and resilient grid.
- As system size increases, financial and safety issues become important topics.
- Holistic approach: electrochemistry, materials, and whole-cell abuse will fill knowledge gaps.
- Simple passive monitoring of a cell or battery is often unable to identify the onset of failure until it is too late to intervene.
- The prevention of catastrophic failure requires detection of internal faults well before they have developed to the point of no return.
- Understanding the degradation mechanisms of the battery components during abusive conditions is essential to influence the development of new component designs that are more resilient to abusive conditions.



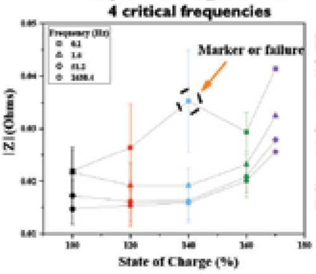
Methodology

*SOC – State of Charge
*OC – Overcharge
*SOH – State of Health



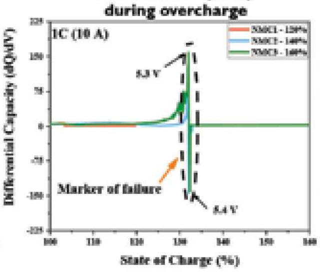
Failure Mechanisms of Overcharged NMC Pouch Cells

Impedance magnitude at 4 critical frequencies



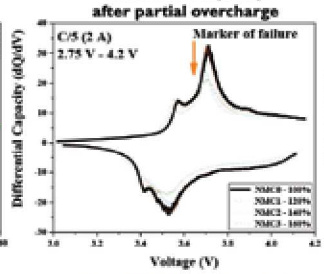
- Several overcharge procedures were applied to 10 Ah NMC single cells.

Differential capacity during overcharge



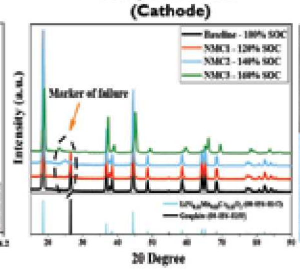
- The dQ/dV calculated during the OC procedure exhibited a redox reaction between 130-135% SOC.

Differential capacity after partial overcharge



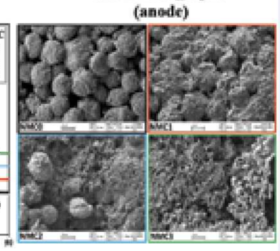
- The dQ/dV calculated after mild OC demonstrated loss of lithium inventory and active material.

X-ray Diffraction (Cathode)



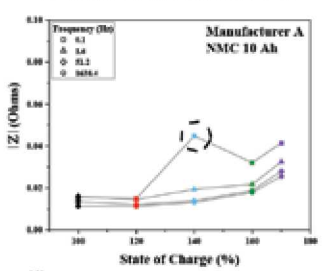
- The analysis of the XRD diffractograms depicted the decomposition of the cathode.

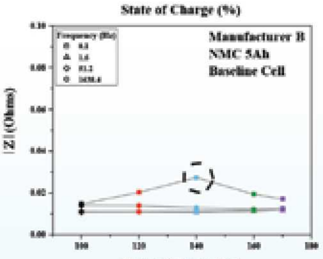
SEM micrographs (anode)



- The SEM images revealed the presence of dendrites and the deformation of the mesocarbon microbeads.

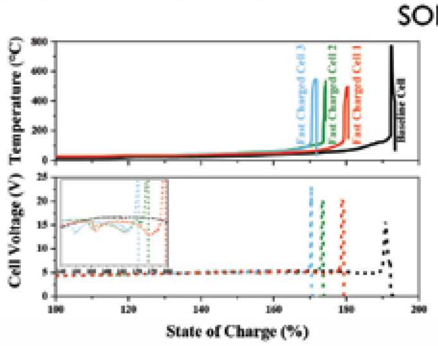
Is the failure marker consistent across manufacturers?





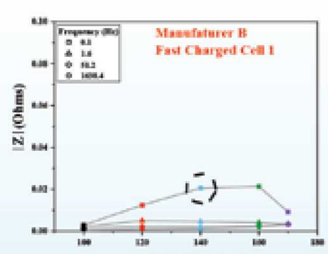
- Degradation marker identified for the NMC chemistry during strenuous conditions is independent of manufacturer and capacity.

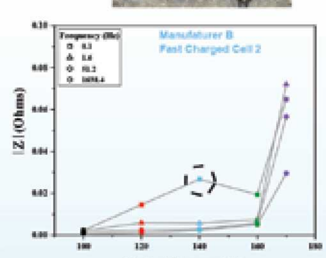
What happens if the initial SOH is compromised?

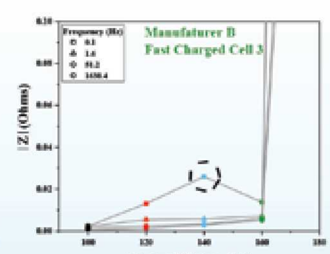


- The initial SOH of three cells was manipulated, and the abuse response was characterized.
- The onset SOC to thermal runaway decreased as the initial SOH was aggravated.
- The overall resistance in the form of magnitude as a function of the state of charge presented the failure marker at 140% SOC, independent of initial SOH.

$$|Z| = \sqrt{Z_{REAL}^2 + Z_{IMG}^2}$$







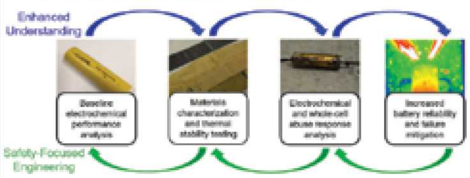
Funded by Dr. Imre Gyuk through the U.S. Department of Energy; Office of Electricity. A special thanks to the following people for thoughtful discussions, advice, and experiment design: C. Orendorff, S. Ferreira, Y. Preger, R. Shurtz and J. Hewson.

Mitigation of Failure Propagation in Multi-Cell Lithium-ion Batteries

Loraine Torres-Castro, Joshua Lamb, June Stanley, Chris Grosso and Lucas Gray

Introduction

- Stationary energy storage systems (ESS) are increasingly deployed to maintain a robust and resilient grid.
- As system size increases, financial and safety issues become important topics.
- Holistic approach: electrochemistry, materials, and whole-cell abuse will fill knowledge gaps.
- Safety of LIB has long focused on the impact and aftermath of a single cell failure.
- Failure of a single cell (inside a pack) may solely have little impact on the safety of the system; however, the thermal and electrical impact on other cells in the pack may be sufficient to cause a cascading runaway effect.
- Work presented here examines the failure propagation behavior of small battery modules and multi-modules constructed with pouch cells, and the development of propagation mitigation strategies.



Methodology

Part I: No Thermal Management

5 pouch cells packed together → Cells in pack charged to 100% SOC → Failure initiated by mechanical nail penetration

Part II: Passive Thermal Management Between Cells

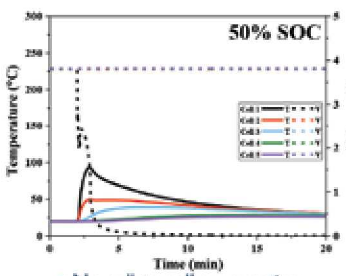
5 pouch cells pack together with Al or Cu plate separators → Cells in pack charged to 100% SOC → Failure initiated by a mechanical nail penetration

Part III: Passive Thermal Management Between Modules

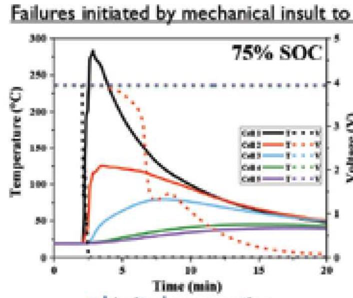
Packs electrically connected in a 3S3P configuration with Al or Cu spacers between modules → Modules charged to 100% SOC → Failure initiated by a mechanical nail penetration

Part I. No Thermal Management

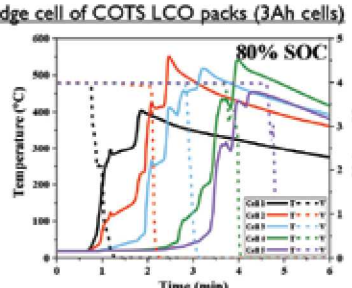
Failures initiated by mechanical insult to edge cell of COTS LCO packs (3Ah cells)



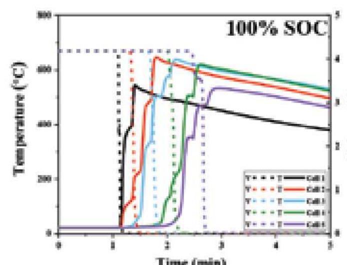
- No cell to cell propagation.
- Thermal runaway of initial cell failure was minimal.



- Limited propagation.
- Damage was observed for Cell 2, but no thermal runaway events seen for Cell 3 to Cell 5.

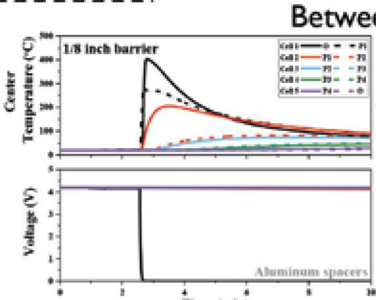


- Full failure propagation.
- Cascading failure to the entire battery over ~240 s.

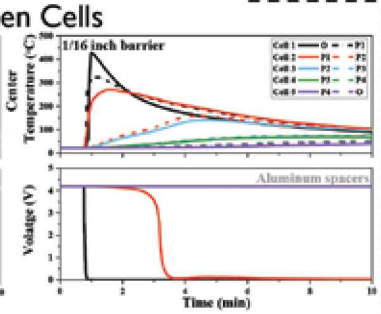


- Full propagation to adjacent cells.
- Cascading failure to entire battery over ~82 s.

Part II. Thermal Management Between Cells

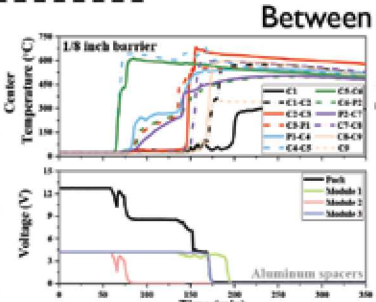


- Peak temperatures reached ~400 °C.
- Energetic thermal runaway was not observed beyond the initial failed cell.

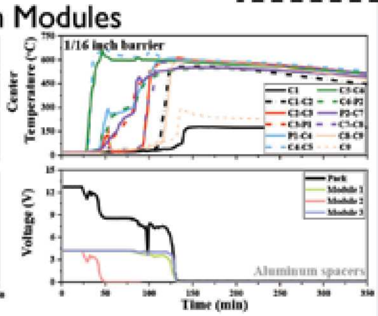


- Limited propagation (from cell 1 to 2).
- The second cell was able to reach ~300 °C and eventually lost voltage.

Part III. Thermal Management Between Modules



- Cells within the target 1S3P module were rapidly consumed.
- Outer modules did not initiate thermal runaway until ~120 seconds after initial failure.



- Initial failure immediately consumes cells within the central 1S3P module.
- Outer modules show signs of failure ~20 seconds after initial initiation.

Summary

- As the size and complexity of battery packs increases, single cell failures within a pack become significantly more likely – this work looked at the mechanisms of how a single-cell failure might impact a larger battery, as well as how it might be mitigated.
- Limiting the SOC exhibited a meaningful impact on propagating failure; however, this comes at a high cost to total energy storage.
- Unmitigated fully charged pouch cells saw a complete consumption of the packs.
- Al barriers were used as a means of passive thermal management to slow or halt thermal runaway propagation between cells.
- 1/16" plates limited propagation to a single cell, while 1/8" plates arrested it altogether for single module battery packs.
- The same plates between modules of a 3S3P pack configuration were not sufficient to mitigate the failure propagation.

Funded by Dr. Imre Gyuk through the U.S. Department of Energy, Office of Electricity. A special thanks to the following people for thoughtful discussions, advice, and experiment design: C. Orendorff, Y. Preger, S. Ferreira, R. Shurtz and J. Hewson.

Sandia National Laboratories
SNL Energy Storage Technology and Systems – Energy Storage Safety
Funded by Dr. Imre Gyuk
U.S. Department of Energy: Office of Electricity; Energy Storage Systems Program

Predicting Limits of Cascading Thermal Runaway in Li-Ion Pouch Cells

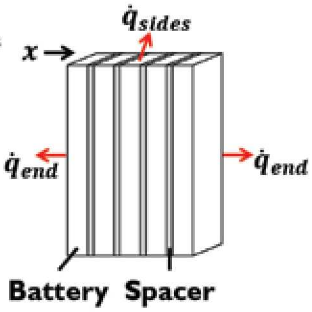
Andrew J. Kurzawski, John C. Hewson
Fire Science and Technology, Sandia National Laboratories, Albuquerque, NM

Introduction

- Stationary energy storage systems (ESS) are increasingly deployed to maintain a robust and resilient grid.
- As system size increases, financial and safety issues become important topics.
- Holistic approach: electrochemistry, materials, and whole-cell abuse will fill knowledge gaps.
- Models enable knowledge to be applied different scenarios and larger scales.
- Cascading failure in Li-Ion systems depends on thermal and chemical processes:
  - Heat generation from chemical reactions.
  - Conductive heat transfer through and between cells.
  - Convective heat transfer to surrounding gases.
- Comparison between experiments and models provides a measure of model performance and elucidates data beyond what is measured.

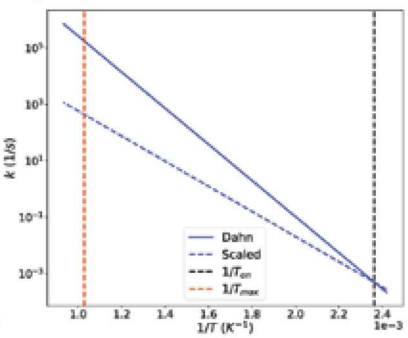
Finite Element Model of Pouch Cells

- Discretization in one direction (*x*)
- Multi-layered system of batteries and spacers
- System of 5 LiCoO2 3 Ah pouch cells
- Empirical chemical reactions
  - SEI decomposition
  - Anode-electrolyte (Shurtz)
  - Cathode-electrolyte
  - Short circuit
- Experimental data
  - Nail penetration in first cell
  - State of charge (SOC) 50-100%
  - Copper and aluminum spacers
  - Measured skin temperature with thermocouples between cells



Limiting High-Temperature Rates

- Initial investigations with empirical reactions found propagation velocity at peak temperatures to be over-predicted by ~2 orders of magnitude.
- Velocity scales with the reaction rate and thermal diffusivity as $v \approx \sqrt{\dot{\omega}\alpha}$.
- We limit high temperature rates while fixing the onset rate by adjusting the Arrhenius pre-exponential and activation energy together.



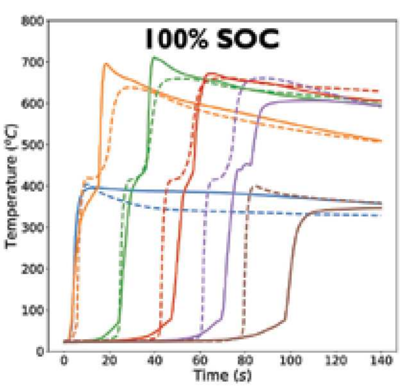
Model and Experimental Comparisons

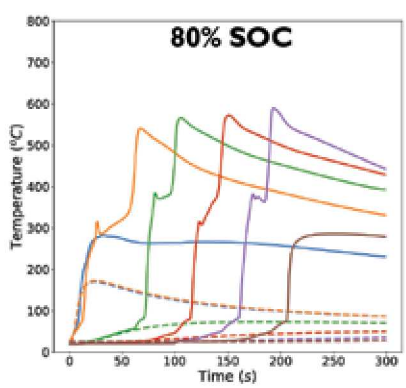
100% SOC

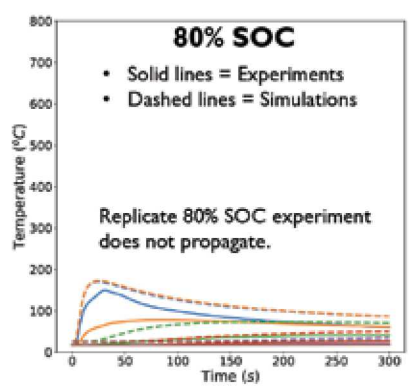
- Predicted heat release over heat capacity: Q/c_p = 207
- Heat release per mass is 519 J/g

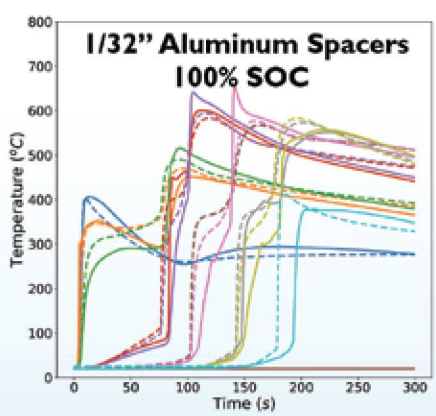
80% SOC

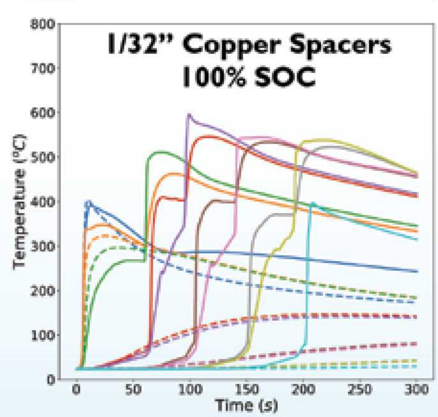
- Two of four experiments propagated, but simulations do not propagate.
- Q/c_p decreased by 6.7%
- Heat release per mass is 483 J/g
- Need to improve short circuit model for the nail.











1/32" Al Spacers

- Net heat capacity increase of 15%
- Q/c_p decreased by 13%
- Predicted and observed propagation still occurs but slower.

1/32" Cu Spacers

- Net heat capacity increase of 21%
- Q/c_p decreased by 17%
- Observed propagation occurs but predictions fail to propagate.

Summary

- Both models and experiments show homogeneous distribution of heat capacity is more effective at mitigating propagation than heterogeneous distribution of heat capacity.
- Initial short circuit model contributes to differences.
- Predictions more sensitive to heat capacity changes than reality.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
SAND No. SAND2019-1045-C

Acknowledgements:

- Funded by Dr. Imre Gyuk through the U.S. Department of Energy: Office of Electricity
- Special thanks to the following people for providing experimental data, thoughtful discussions, and advice
- Loraine Torres-Castro, Joshua Lamb, Randy Shurtz, Summer Ferreira, Yuliya Preger, Jacob Mueller, and Alex Headley

Sandia National Laboratories
SNL Energy Storage Technology and Systems – Energy Storage Safety
Funded by Dr. Imre Gyuk
U.S. Department of Energy; Office of Electricity; Energy Storage Systems Program

Thermal Runaway Testing and Database Development of Large-format Li-ion Cells at ORNL and SNL

J. Stanley, H. Wang, L. Torres-Castro, E. Deichmann, X. Zhu, S. Allu, J. Lamb, C. Grosso, and L. Gray

Introduction

- Safety Roadmap from 2017 Safety Forum identified an important area for future expansion of stationary energy storage applications
- Industry lacks a database of 'battery thermal runaway risk' data for Li-ion cells
- Safety risks become important topics as system sizes increase
- Safety is not a priority in the battery development stage, but is one of the most important concerns for applications
- Common solutions:
  - Conservative in engineering the system with armor-like protection
  - Implementing isolation solutions to prevent fire propagation
- Assist first responders to make proper decisions in case of a battery fire
- Results will be collected in a usable database for the Li-ion battery development community

Methodology

A)

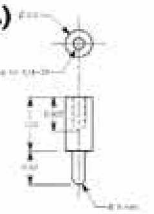
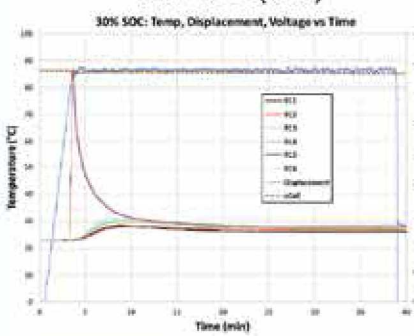


Image 1:
A) The 6 mm indenter – modified attachment to work with existing hydraulic equipment
B) Single cell prepped for testing with thermocouples and voltage sense leads

B)

- Protocol was developed with specific test parameters to initiate failure in large format Li-ion cells
  - 6 mm diameter blunt indenter
  - Indentation speed of 0.05" per minute
  - Indent until ≥ 100 mV voltage drop or full penetration
- Single cells were extracted from modules obtained from an EV application at ORNL then shipped to SNL (two different EV applications will eventually be tested)
- Tests will be repeated (in duplicate) for the following 4 states of charge (SOC): 30%, 50%, 75% and 100%, at both ORNL and SNL

30% SOC (SNL)



- Two cells tested at 30% SOC
- SOC based on the nominal capacity of the cell after cycling
- Displacement of ~4.0 mm
- Force reached was just under 2,200 N
- No significant voltage drop (3.88 V to 3.75 V)
- No thermal runaway event, max temp = 86.8°C

A)

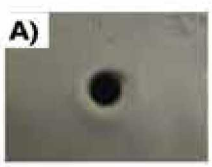
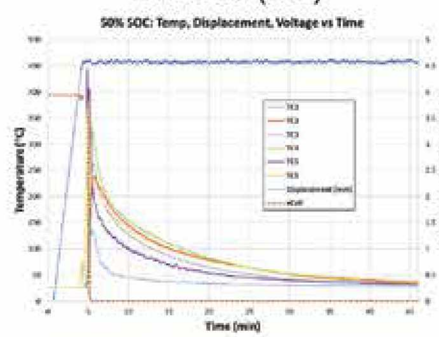


Image 2:
A) Post-test Indenter hole of the 30% SOC cell
B) Side view of cell swelling (indenter can be seen at the top of the image)

B)

50% SOC (SNL)



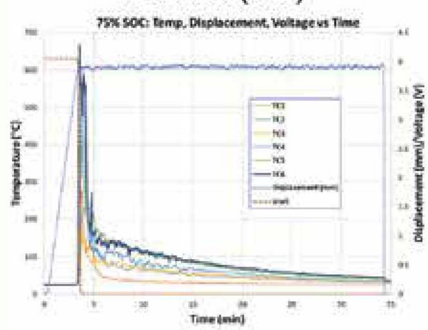
- Two cells tested at 50% SOC
- SOC based on the nominal capacity of the cell after cycling
- Displacement of ~4.7 mm
- Force reached was ~ 2,120 N
- Voltage drop to 0V (beginning voltage of 3.95 V)
- Thermal runaway event, max temp = 444.6°C

A)

Image 3:
A) Post-test Indenter hole of the 50% SOC cell
B) Side view of cell swelling and seam separation, showing interior contents

B)

75% SOC (SNL)



- One cell tested at 75% SOC (thus far)
- SOC based on the nominal capacity of the cell after cycling
- Displacement of ~4.1 mm
- Force reached was just ~ 2,050 N
- Complete loss of voltage (beginning voltage of 4.07 V)
- Significant thermal runaway event, max temp = 668.3°C

A)

Image 4:
A) Post-test Indenter hole of the 75% SOC cell
B) Side view of cell swelling, charring and seam separation showing interior contents

B)

Future Work

- Complete our abuse testing of the single cells already received at 75% SOC (1 cell) and 100% SOC (2 cells)
- Acquire individual cells from battery modules from another EV application
- Perform indenter abuse tests on these cells at same SOCs
- Acquire single cells from large-format Li-ion batteries that are acquired from stationary energy storage applications
- Perform indenter abuse tests on large-format cells at same SOCs
- Deliver data to ORNL for entry into database

Funded by Dr. Imre Gyuk through the U.S. Department of Energy; Office of Electricity. A special thanks to the following people for thoughtful discussions, advice, and experiment design: C. Orendorff, B. Hanks, and K. Fenton.

NEW MEXICO TECH
SCIENCE • ENGINEERING • RESEARCH UNIVERSITY

Internal pressure measurements during the thermal runaway of cylindrical lithium ion batteries

Frank Austin Mier, Simone M. M. Hill, Michael J. Hargather
Mechanical Engineering Dept., New Mexico Tech

Sandia National Laboratories

Abstract

Under abuse conditions, batteries exhibit a build up of pressure during thermal runaway until the vent mechanism bursts (or "ruptures"). The ability to measure this pressure rise is important to understand thermal runaway and onset of venting failures. Delicate components within cylindrical cells make directly accessing the inside of the battery impractical, so measurement of the cylindrical case's mechanical response to the pressure build up avoids this limitation. Here, experiments are performed to demonstrate how strain gauges may be used to perform noninvasive pressure measurement of batteries under thermal abuse conditions. A laboratory scale test apparatus has been constructed for these experiments, and analytical expressions have been established to describe internal pressure as a function of strain.

Figure 1: Strain gauges mounted to an empty 18650 size battery case

Pressure as a function of case strain

Pressure contained within an enclosed cylinder will cause mechanical stress along its length (longitudinal, *L*) and circumference (hoop, *H*). To measure stress components, strain gauges are adhesively bonded to the outside of the cylinder wall as shown in Figure 1. Analytical expressions relate hoop and longitudinal stresses to the contained pressure [1]:

$$\sigma_H = \frac{PD}{2b} \quad \text{and} \quad \sigma_L = \frac{PD}{4b}$$

The strain on the cylinder can be expressed in both directions as functions of the stress components and thermal expansion [2]:

$$\epsilon_H = \frac{\sigma_H}{E} - \frac{\nu\sigma_L}{E} + \alpha dT \quad \text{and} \quad \epsilon_L = \frac{\sigma_L}{E} - \frac{\nu\sigma_H}{E} + \alpha dT$$

The above expressions may be combined and simplified into a single expression for internal pressure as a function of case strain measurements independent of thermal effects:

$$P = \frac{4Eb}{D(1+\nu)}(\epsilon_H - \epsilon_L)$$

Strain measurement test fixture

A test apparatus was constructed to measure case strain under thermal abuse as shown in Figure 2. The central chamber was built from a 4-NPT size steel pipe with an 87 mm diameter by 305 mm long interior. Electrical heaters rated at 2,880 W are wrapped around the pipe and are capable of heating the chamber's interior at 9.57˚C/min. A double-pane insulation structure is used along with helium inside the chamber to increase the heating rate. A remote data acquisition system measures case strain, chamber pressure, and the temperatures of the battery, interior gas, and chamber wall. This system also switches heater relays and operates purge valves. A battery holder was fabricated to minimize heat conduction from chamber walls while securely holding the battery and multiple thermocouples.

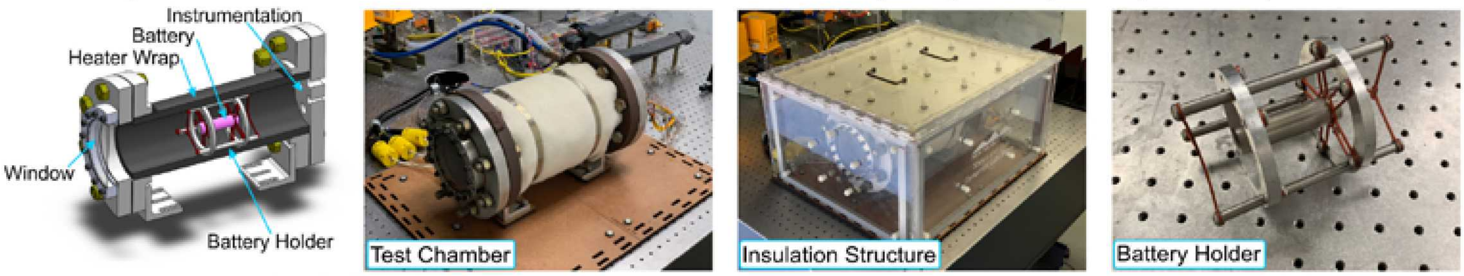


Figure 2: Annotated SolidWorks model and photographs of various aspects of the test apparatus for the case strain measurement experiment

Thermal response of 18650 format battery case

An open, cylindrical 18650 battery case was heated from ambient to 180˚C at approximately 4˚C/min to evaluate systematic errors. Shown in Figure 3, raw strain measurements were collected then corrections for gauge thermal output, gauge rotation, gauge transverse sensitivity, and cylinder curvature were made. The maximum deviation from zero strain corresponds to an apparent pressure of 160 kPa. Since there is no possible build up of pressure in the open cylinder, this may be used as an upper bound for measurement uncertainty due to the thermal response for this specific gauge and cylinder combination.

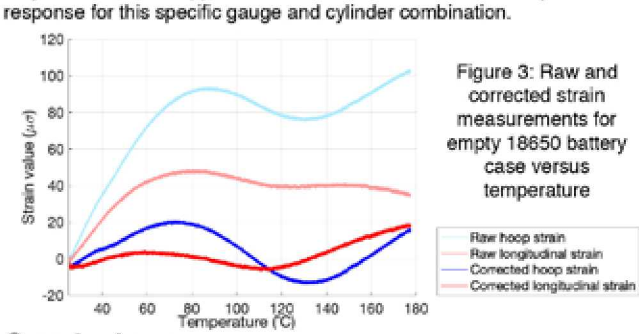


Figure 3: Raw and corrected strain measurements for empty 18650 battery case versus temperature

Carbon dioxide (CO_2) gas cylinder internal pressure

A closed (pressurized) steel cylinder filled with 12 g of CO_2 was heated until the point of burst, and a second trial with an open (unpressurized) cartridge was performed as a baseline. Pressure, calculated from strain, is shown against temperature in Figure 4. Closed cartridge pressure build up is compared to an isochoric heating of CO_2 with the same specific volume as the cartridge [3]. The cartridge yielded prior to burst causing an upward trend in apparent pressure.

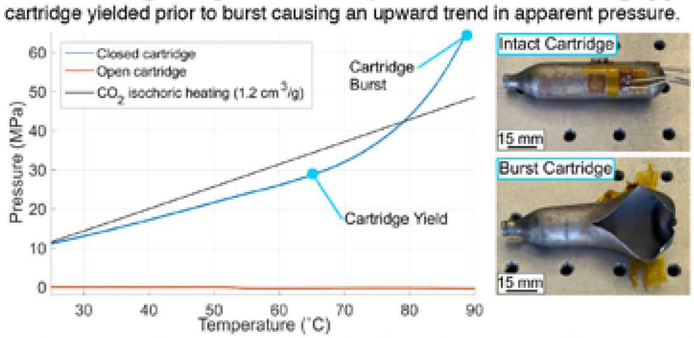


Figure 4: Cartridge pressure during heating (left) and images if an intact and burst cartridge (right)

Conclusions

A method for measuring the build up of pressure during thermal runaway was developed from the measurement of case strain. An analytical expression was formulated for pressure as a function of case strain values. A test fixture was designed and fabricated to measure strain under thermal abuse conditions. An initial trial quantified uncertainty due to gauge thermal response. Another trial demonstrated the ability to measure pressure build up via the isochoric heating of a CO_2 cartridge.

Ongoing research

Live battery abuse tests will focus on determining the accuracy of the internal pressure measurement methodology's accuracy and quantitatively describing the trends of the internal pressure build up prior to venting onset. LG brand, model HE2 batteries will be tested because the lithium cobalt oxide cathode chemistry is known to demonstrate venting failures under thermal abuse [4]. These vent caps burst around 1.906 MPa which will be used to evaluate the measurement accuracy [5].

References and Acknowledgements

[1] W. C. Young and R. G. Budynas. Roark's Formulas for Stress and Strain. McGraw Hill, 7th edition, 2002.
[2] J. R. Barber. Intermediate Mechanics of Materials. Springer, 2011.
[3] E. Lemmon. Reference fluid thermodynamic and transport properties database (refprop). Technical report, NIST.
[4] E. P. Roth et al. Advanced technology development program for lithium-ion batteries: Thermal abuse performance of 18650 li-ion cells. Technical Report SAND2004-0584, Sandia National Laboratories, 2004.
[5] Mier, F. A., 2018. "Measurement of 18650 format lithium ion battery vent mechanism flow parameters". Master's thesis, New Mexico Institute of Mining and Technology.

- This work is supported by Sandia National Laboratories and funding comes from the U. S. Department of Energy Office of Electricity Energy Storage Program under Dr. Imre Gyuk, Program Director, with contracts PO 1739875 and PO 1859922.
- Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Dr. Michael J. Hargather ♦ Associate Professor of Mechanical Engineering ♦ EMRTC Research Scientist ♦ michael.hargather@nmt.edu ♦ www.nmt.edu/mjh

EQUITABLE REGULATORY ENVIRONMENT & ANALYTICS

The equitable regulatory environment thrust area supports research to enhance the energy storage regulatory environment through: estimating the value of energy storage for different applications and scenarios; developing control strategies that maximize revenue or benefit to the grid; identifying new control strategies and applications for energy storage; assessing public policy to identify and mitigate barriers for energy storage; developing standards; and evaluating projects.

Planning Considerations for Energy Storage in Resilience Applications

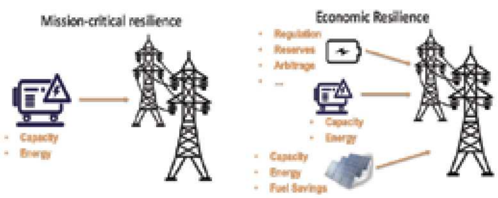
JB Twitchell, SF Newman, RS O'Neil, MT McDonnell

Pacific Northwest NATIONAL LABORATORY

Abstract

This work presents the proceedings and lessons learned at a conference workshop that discussed the role of energy storage in supporting electric system resilience, which took place at the Natural Energy Laboratory of Hawaii Authority's (NELHA) Conference on Energy Storage Trends and Opportunities in December 2018. A location-based framework for resilience planning is presented, as is a microgrid planning tool capable of identifying resource mixes that will meet site-specific resilience needs. Case studies of successfully deployed resilience projects from around the U.S. demonstrate the proposed planning principles in practice, and takeaways from a workshop discussion identify additional research needs.

Energy Storage and Resilience



From a site-based perspective, resilience is about acquiring a backup source of generation to meet energy needs when the grid is down. Traditionally, the only option for this was a backup generator. But with high upfront costs and limited operation for revenue generation, this was an expensive proposition that effectively limited resilience to entities that have a mission-critical need for it, such as hospitals and military bases.

Due to its operational flexibility, energy storage devices can be paired with generation resources to provide a range of monetizable grid services when not being used for resilience. That revenue can offset the system's cost and enable a broader range of facilities to invest in resilience on a cost-effective basis.

Problem Statement

Reliability is an objective concept defined by mandatory standards and reporting metrics. These standards and metrics facilitate the development of tangible planning objectives and make reliability a monetizable service. Reliability standards are firm requirements that a utility must meet.

Resilience is a subjective concept, lacking specific standards and metrics, or even an agreed-upon definition. Lacking those, tangible planning objectives cannot be readily developed, and resilience is not a monetizable service. Absent standards, resilience is a goal that is pursued subject to cost effectiveness.

Defining Resilience in Terms of Reliability Metrics

System Average Interruption Duration (SAIDI) is a commonly used reliability metric that measures how long, in minutes, the average customer is without service during the year. To ensure that uncontrollable external events do not mask reliability issues, SAIDI scores are "normalized" by removing major events. While these events are filtered out of reliability reporting, they provide a starting point for identifying resilience needs, as demonstrated in these SAIDI scores from Hawaiian Electric Companies subsidiaries:

Utility	Average Non-Normalized SAIDI Score, 2008-2017	Average Normalized SAIDI Score, 2008-2017	Difference
Hawaiian Electric	201.8	121.7	39.7%
Maui Electric	272.5	120.3	55.9%
Hawai'i Electric Light	280.8	142.8	49.1%

If we want to improve resilience, these major events are where we start

ABOUT

Pacific Northwest National Laboratory

The Pacific Northwest National Laboratory, located in southeastern Washington State, is a U.S. Department of Energy Office of Science laboratory that solves complex problems in energy, national security, and the environment, and advances scientific frontiers in the chemical, biological, materials, environmental, and computational sciences. The Laboratory employs nearly 5,000 staff members, has an annual budget in excess of $1 billion, and has been managed by Ohio-based Battelle since 1965.

For more information on the science you see here, please contact:

Jeremy Twitchell
Pacific Northwest National Laboratory
620 SW 5th Ave. Suite 810
Portland, OR 97204
(971) 940-7104
jeremy.twitchell@pnnl.gov

A Locational Approach to Resilience Planning

1. **Define critical loads.** Identifying specific loads that must be maintained in a grid outage breaks resilience into achievable, incremental objectives.
2. **Identify major events of concern.** Understanding the shape of the resilience need is necessary to establish tangible planning objectives.
3. **Establish planning objectives.** Defining success first – what the resilient assets will be expected to do – will translate into clear objectives.
4. **Engage in iterative site and local grid planning.** Local grid needs will define values for the project to pursue, and projects may drive needs for communication and control upgrades on the local grid to enable their value.
5. **Throughout the process, consider questions of ownership, cost allocation, and rate design.** These policy decisions have significant ramifications on the value of resilience assets and how they will be used.

U.S. DEPARTMENT OF ENERGY

This work was funded by the Energy Storage Program within the Department of Energy's Office of Electricity, under the direction of Dr. Imre Gyuk.

www.pnnl.gov

Model Predictive Frequency Control of Low Inertia Microgrids with Energy Storage Systems

Ujjwol Tamrakar, [1] David A. Copp, [2] Tu Nguyen, [2] and Reinaldo Tonkoski [1]
[1] South Dakota State University, [2] Sandia National Laboratories
Contact Information: tonkoski@ieee.org

South Dakota State University

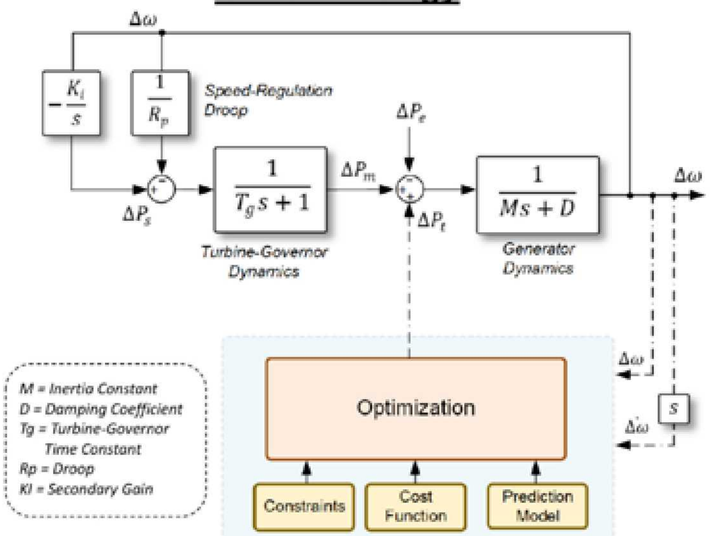
Sandia National Laboratories

1. Motivation and Objectives

- Fast-frequency control strategies are required in low inertia microgrids to maintain frequency.
- Energy storage systems (ESSs) can provide energy buffer required for fast-frequency services.
- However, ESSs need to be dispatched optimally from a technical as well as economical point-of-view.
- Model Predictive Control (MPC) approach proposed.

• Allows system operator to dispatch ESS optimally as per system requirements and conditions
• Incorporate ESS constraints
  • Ramp-rate limits
  • Converter size limits

2. Methodology



1 . Frequency Dynamics Model:

$$\begin{bmatrix}\dot{\Delta\omega}\\ \ddot{\Delta\omega}\end{bmatrix} = \begin{bmatrix}0 & 1\\ -\left(\frac{D}{MT_g}+\frac{1}{R_p M T_g}\right) & -\left(\frac{D}{M}+\frac{1}{T_g}\right)\end{bmatrix}\begin{bmatrix}\Delta\omega\\ \dot{\Delta\omega}\end{bmatrix} + \begin{bmatrix}0\\ \frac{-1}{MT_g}\end{bmatrix}(\Delta P_e)$$

2. Formulation of the Model Predictive Control:

$$\text{minimize } J = \sum_{k=t}^{t+T-\tau}\left(x_k^{\top} Q x_k + \Delta p_k^{\top} R \Delta p_k\right) \longleftarrow \textit{Cost Function}$$

subject to

$$x_{k+\tau} = A x_k + B\Delta p_k \quad \forall k \in \mathcal{T}, \longleftarrow \textit{System Dynamics}$$

$$|\Delta p_k| \le P_{max} \quad \forall k \in \mathcal{T}, \longleftarrow \textit{Peak Power Limit}$$

$$\|\Delta p_{k+\tau} - \Delta p_k\|_\infty \le S \quad \forall k \in \mathcal{T}, \longleftarrow \textit{Ramp-Rate Limit}$$

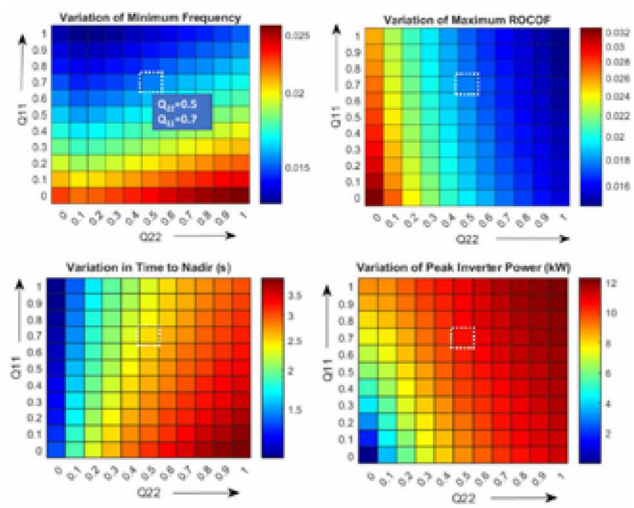
3. Optimal Control Action:

$$\Delta p^* := [\Delta p_t^*, \Delta p_{t+\tau}^*, \ldots, \Delta p_{t+T-\tau}^*] \longrightarrow \Delta p_t = \Delta p_t^*$$

3. Results and Analysis

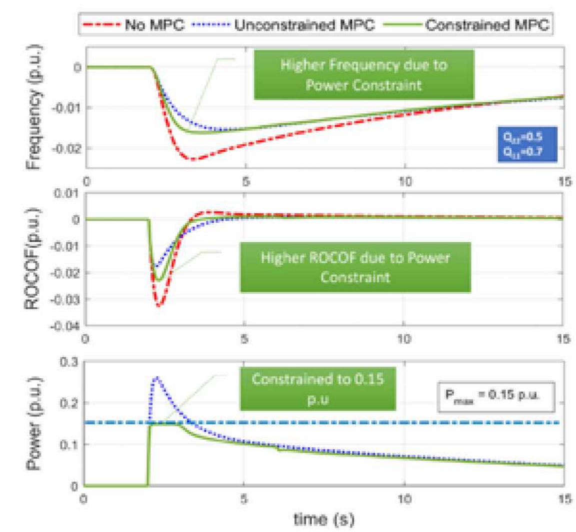
3A. Effect of Varying Weighting Parameters

- System Parameters: M = 4 s, D =1.5%, R_p = 5%, T_g = 0.2s
- MPC Settings: τ = 0.02s, T = 1 s (Prediction Horizon)



- Varying parameters allows system operator to play between frequency/ROCOF reduction vs. energy usage from ESS.
- Intuitively control system dynamics.

3B. Constrained Vs. Unconstrainted Operation



4. Conclusions and Future Work

- Fast acting ESS based on MPC able to reduce frequency deviation and ROCOF.
- Weighting parameters allows system operator to control behavior as desired.
- Verify controller performance with Power-Hardware-in-the-Loop Simulations at SDSU's Microgrid Lab.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

SAND 1031601

Distributed Controls Using Energy Storage for Improved Grid Stability and Resilience

Roghieh Biroon, Pierluigi Pisu (Clemson University) and David Schoenwald (Sandia National Laboratories)
Email: rabdoll@Clemson.edu, pisup@Clemson.edu, and daschoe@sandia.gov

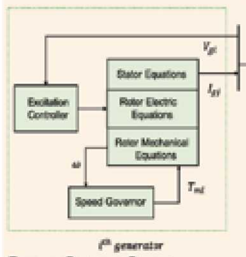
Abstract

This poster illustrates modeling, simulation, and control design approaches to develop and ultimately deploy a distributed control strategy using energy storage to improve power grid stability and resilience.

Motivation

A **distributed approach** to wide-area control design has the potential to **improve grid stability** over a wider area while increasing the **robustness to failure** of any one actuator than is possible in a centralized approach. **Energy storage systems** are excellent candidates to implement this strategy. Energy storage can **absorb/discharge both active and reactive power** to the grid with **very fast** response times.

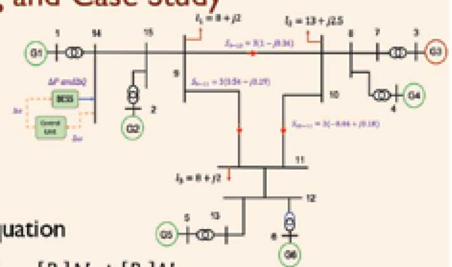
System Modeling and Case Study



Power System Structure

System Equation

$$[Y_{bus\_DQ}]\Delta V_{QD} = [P_G]\Delta I_G - [P_L]\Delta I_L + [P_B]\Delta I_B$$

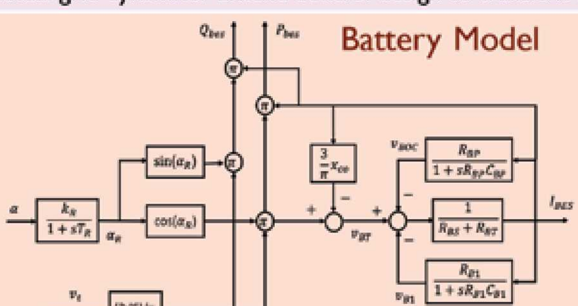


Case study model

Project Objectives

- Goal: Develop control algorithms for wide-area power grids using distributed energy storage for power injection to improve grid stability.
- Schedule: Project is currently 6 months into a planned 3 year duration.
- Year 1 Tasks: Develop battery model incorporating inverter dynamics to enable use of the firing angle as a control input. Simulate and analyze oscillation dynamics of case study model. Design decentralized control algorithm to damp inter-area oscillations in case study system.
- Year 2 Tasks: Conduct sensitivity analysis on control performance to storage size and locations. Design a hierarchical control strategy allowing remote measurement feedback at selected storage sites.
- Year 3 Tasks: Develop case studies for larger grid models reflecting actual grid dynamics. Extend control design to transient stability.

Battery Model



Δα is the inverter firing angle to control the power factor

$$P_{BES} = \frac{3\sqrt{6}}{\pi} v_t I_{BES} \cos(\alpha_R)$$

$$Q_{BES} = \frac{3\sqrt{6}}{\pi} v_t I_{BES} \sin(\alpha_R)$$

$$I_{BES_d} = \frac{v_{td}P_{BES} - v_{tq}Q_{BES}}{v_t^2}$$

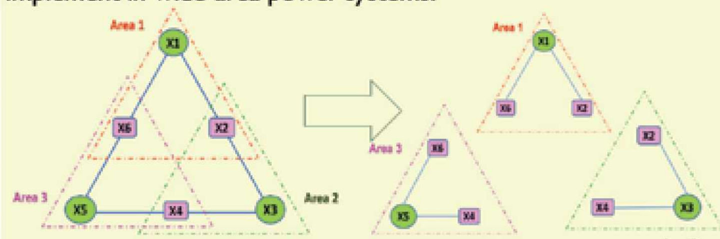
$$I_{BES_q} = \frac{v_{tq}P_{BES} + v_{td}Q_{BES}}{v_t^2}$$

$$\begin{bmatrix}\Delta\dot{V}_{BOC}\\ \Delta\dot{V}_{B1}\\ \Delta\dot{\alpha}_R\end{bmatrix} = A_b\begin{bmatrix}\Delta V_{BOC}\\ \Delta V_{B1}\\ \Delta\alpha_R\end{bmatrix} + B_b\begin{bmatrix}\Delta v_q\\ \Delta v_d\end{bmatrix} + E_b\Delta\alpha$$

$$\begin{bmatrix}\Delta I_{bd}\\ \Delta I_{bq}\end{bmatrix} = C_b\begin{bmatrix}\Delta V_{BOC}\\ \Delta V_{B1}\\ \Delta\alpha_R\end{bmatrix} + D_b\begin{bmatrix}\Delta v_q\\ \Delta v_d\end{bmatrix}$$

Control Design Approach

Decentralized control using overlapping decompositions[1] will be designed for the system. This approaches is more practical in large-scale systems since no exchange of information among different areas is necessary which makes the control design easier to implement in wide-area power systems.



[1]Siljak, D. D. (1991). Decentralized control of complex systems. New York: Academic Press.

$$X = [X_1, X_2, X_3, X_4, X_5, X_6]^T$$

Conclusions

- Battery model has been developed incorporating inverter dynamics to enable use of the firing angle as a control input.
- Simulations and eigensystem analysis has been conducted on a three area power system for case study.
- Control design approach will initially focus on a decentralized strategy using the overlapping decompositions method.
- Future work will include sensitivity analysis of control performance to location and size of energy storage in grid.
- Performance comparisons of decentralized control strategies vs. hierarchical control approaches will also be studied.
- Initial control design objective will be on small signal stability with investigations into transient stability planned for Year 3.
- Future work will also address larger case study models reflecting dynamics from actual power grids.

Acknowledgements

Funding provided by US DOE Energy Storage Program managed by **Dr. Imre Gyuk** of the DOE Office of Electricity.

Clemson University Electric Power Research Association

Energy Storage Planning for Clean Energy Target

David A. Copp[1], Tu A. Nguyen[2], Robb Thomson[3], Raymond H. Byrne[2], Babu R. Chalamala[2]
[1] University of California at Irvine, CA [2] Sandia National Laboratories, NM [3] Retired Fellow at NIST, MD
Email: dcopp@uci.edu, tunguy@sandia.gov, robbm@toast.net, rhbyrne@sandia.gov, bchalam@sandia.gov

Abstract

In this work, we developed an optimization approach to analyze the amount of energy storage and renewable generation required for 100% clean energy target. Given locations of renewable generation, we solve an optimization problem to find the amount of solar PV and wind resources at each site and to size energy storage to balance a utility's demand. Case studies are conducted using historical weather and demand data from a medium-sized utility in New Mexico, USA.

Methodology

A mathematical optimization problem is formulated the objective of minimizing energy resource sizes while ensuring that the utility's demand is met at all times.

The constraints of this problem include:

- **Storage constraints:** state of charge constraints.
- **Power balance constraint:** load must be met.
- **Curtailment constraint:** renewable curtailment must be limited.
- **Interconnection constraint:** the energy exchanged with other regions must be limited.

Formulation

Objective function:

$$\underset{\substack{\bar{s},\bar{p}^{s},\bar{p}^{w},\bar{p}^{pv},\\ p^{c},p^{d},p^{curt},p^{trade}}}{\text{minimize}} \quad J(\bar{s},\bar{p}^{s},\bar{p}^{w},\bar{p}^{pv},p^{curt},p^{trade})$$

$$J(\bar{s},\bar{p}^{s},\bar{p}^{w},\bar{p}^{pv},\mathbf{p}^{trade}) := w^{e}\bar{s} + w^{p}\bar{p}^{s} + w^{w}\sum_{i=1}^{n_w}\bar{p}_i^{w} + w^{pv}\sum_{i=1}^{n_{pv}}\bar{p}_i^{pv} + \sum_{k=0}^{K-1} w_k^{curt}p_k^{curt} + \sum_{k=0}^{K-1} w_k^{trade}p_k^{trade}$$

Storage and renewable constraints:

$$\underline{\delta}\bar{s} \le s_k \le (1-\bar{\delta})\bar{s}$$
$$s_{k+1} = \eta^{s}s_k + \eta^{c}p_k^{c}\tau - p_k^{d}\tau$$
$$s_0 = \gamma\bar{s}$$
$$s_K = \gamma\bar{s}$$

$$0 \le p_{k,i}^{w} \le \bar{p}_i^{w}$$
$$0 \le p_{k,i}^{pv} \le \bar{p}_i^{pv}$$
$$0 \le p_k^{c} \le \bar{p}^{s}$$
$$0 \le p_k^{d} \le \bar{p}^{s}$$

Power balance constraint:

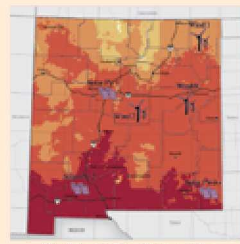
$$p_k^{\ell} = \sum_{i=1}^{n_w} p_{k,i}^{w} + \sum_{i=1}^{n_{pv}} p_{k,i}^{pv} + p_k^{d} - p_k^{c} - p_k^{curt} + p_k^{trade}$$

Curtailment and interconnection constraints:

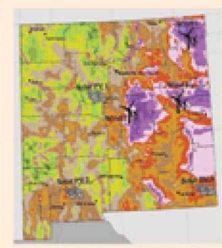
$$0 \le p_k^{curt} \le \bar{p}_k^{curt} \qquad \underline{p}_k^{trade} \le p_k^{trade} \le \bar{p}_k^{trade}$$

Case Studies

- Case studies are conducted using different historical demand profiles and weather data from 2016 to 2018. In each case, we analyze different trade scenarios.



New Mexico Solar Resource Map

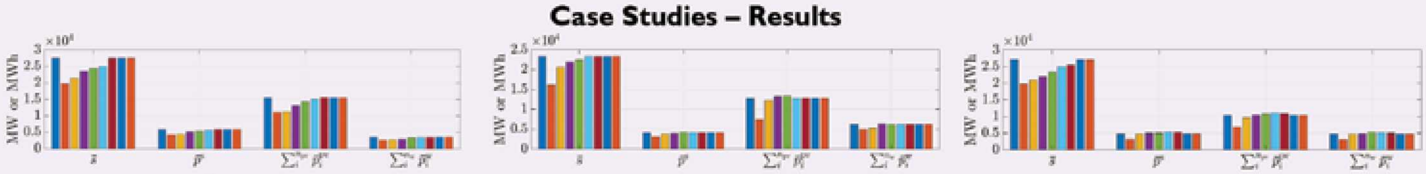


New Mexico Wind Resource Map

Image Credit: NREL

Case	Description
1	2018 demand and TMY data
2	2017 demand and weather data
3	2016 demand and weather data
4	Case 1 with only solar resources
5	Case 1 with only wind resources

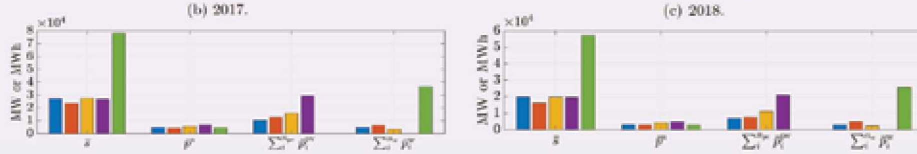
Case Studies – Results



(a) 2016. (b) 2017. (c) 2018.

Key takeaways:

- PV+ES need is dominating against wind.
- Larger ES to accommodate wind vs PV.
- Energy exchange leads to less resources



(a) No trade. (b) Trade allowed all hours.

Conclusions

In this work, energy storage and renewable resources planning for clean energy target have been studied. Specifically, the contributions include: 1. An optimization approach for sizing required renewable resources and energy storage to balance the demand of a utility with 100% renewable generation, 2. Results from case studies for a utility in New Mexico.

Acknowledgements

Funding provided by US DOE Energy Storage Program managed by **Dr. Imre Gyuk** of the DOE Office of Electricity.

Utilization of Existing Generation Fleet Using Large Scale Energy Storage Systems

Tu A. Nguyen and Raymond H. Byrne

Email: tunguy@sandia.gov, rhbyrne@sandia.gov

Abstract

In this work we developed an optimization framework to evaluate the benefit of large-scale energy storage system (ESS) for utilizing an existing generation fleet that often operates at suboptimal working conditions due to peaky nature of the load. The objective is to find the optimal schedule for thermal units and the ESS that minimizes the daily system operating cost. Case studies are conducted to evaluate the operating cost savings by using ESSs for a utility company in Alaska.

Methodology

An MILP problem is formulated to find the optimal schedule for thermal units and the energy storage system (ESS) that minimizes the daily operating cost of a generation fleet. The constraints of this problem include:

- **Energy storage constraints:** state of charge constraints.
- **Power balance constraint:** load must be met.
- **Reserve constraint:** minimum spinning reserve must be met.

The assumptions include:

- ESS operation does not impact hydro scheduling.
- Maximum capacities of transmission lines have not been reached (i.e., congestions do not occur.)

Formulation

Objective function:

$$\min C = \sum_{i=1}^{24} \sum_{g=1}^{N} (f_g^i(P_g^i) cf_g + s_g^i cs_g + \alpha_g^i om_g)$$

- $f_g(P_g^i)$ is the fuel consumption of thermal unit g after time period i based on its power output P_g^i. cf_g is the fuel price for unit g
- s_g^i is a binary variable that indicates unit g starts at time i or not. cs_g is the start-up cost of unit g.
- α_g^i is a binary variable that indicates the status of unit g at time i. om_g is the variable O&M cost of unit g.

Storage constraints:

$$S_i = \eta_s S_{i-1} + \tau(\eta_c P_i^c - P_i^d)$$

$$S_{24} = S_0$$

$$S_{\min} \leq S_i \leq S_{\max}$$

Power balance constraint:

$$\alpha_g^i P_g^{min} \leq P_g^i \leq \alpha_g^i P_g^{max}$$

$$P_i^d - P_i^c + \sum_{g=1}^{N} P_g^i = P_i^{ld}$$

Reserve constraint:

$$\sum_{g=1}^{N} P_g^{max} - P_g^i \geq P_{reserve}^{min}$$

Case Studies

Case studies are conducted to evaluate the operating cost savings by using ESSs for a utility company in Alaska:

- 1 combined cycle, 4 gas units
- Minimum spinning reserve: 10MW if not islanded, 40MW if islanded.
- Natural gas price: 7.92/Mcf.
- Variable O&M cost and start-up cost for each unit are given in the following table.

	Unit 1 Combined Cycle	Unit 2 Natural Gas	Unit 3,4,5 Natural Gas
Variable O&M	$130/hour	$258/hour	$300/hour
Start-up Cost	$1535/start	$2350/start	$1075/start

Case Studies – Annual Savings

	Fuel Cost ($)	O&M Cost ($)	Start-up Cost ($)	Annual Total ($)	Annual Saving ($)
Case 1 – No ESS	31,015,209	1,238,940	154,150	32,408,299	
Case 2 – 40MW/10MWh	30,700,007	1,218,237	59,810	31,978,055	430,244
Case 3 – 40MW/20MWh	30,681,801	1,227,761	24,845	31,934,407	473,891
Case 4 – 40MW/40MWh	30,723,217	1,178,834	15,445	31,917,496	490,802

Case Studies – Thermal Units Schedule

Conclusions

In this study, the benefits of large-scale energy storage system (ESS) for utilizing an existing generation fleet have been studied. Specifically, the contributions include: 1. An optimization framework for scheduling ESS and thermal units to minimize operation cost; 2. Results from case studies for a utility in Alaska.

Acknowledgements

Funding provided by US DOE Energy Storage Program managed by **Dr. Imre Gyuk** of the DOE Office of Electricity.

Siting Energy Storage for Resilient Distribution Systems

Randy C. Brost, rcbrost@sandia.gov

Project Goals:

- Algorithm to design storage and other distribution system components to assure societal benefit during long-term outage.
- Explore semantic graphs for resilient distribution system design.

Why Semantic Graphs?

- Highly flexible representation for data spanning mixed topic areas.
- Graph analysis is a strong tool for managing large problem combinatorics.
- Explicit analysis of both data and relationships.
- Avoids weighting function problems.

FY19 Progress:

- Grid semantic graph:
  - Electrical model
  - Geospatial data
  - Societal benefit data
  - Existing + potential
  - Threat models (flood, fire, landslide,…)
- Resilient distribution configuration design
- Storage / PV / diesel temporal analysis
- Python code in progress, open source planned

FY20 Future Work:

- Improved power/energy analysis
- Multi-temporal
- Multi-threat
- Life-cycle cost analysis
- Geospatial equity
- Real data

Algorithm Summary:

Input: Grid model, Service priorities, Threat, Duration, Control flags.
Output: Set of designs, with selected nodes, edges, switches, capacities.

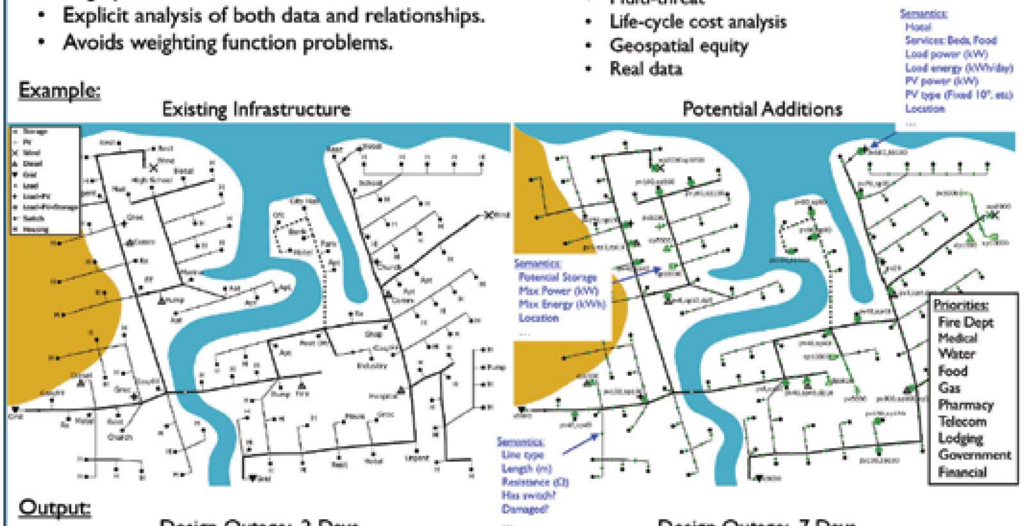
Algorithm:

1. First attempt a solution with only existing primary generation. If this fails, attempt again allowing existing + new generation.
2. Add all nodes which can operate stand-alone for the given duration.
3. Determine services still unfulfilled after stand-alone nodes.
4. Find all nodes which contribute a required service.
5. Select node set covering all required services.*
   - Near existing generation, if capable of covering duration.
   - If none exist, near each other.
6. Add centralized generation:
   a. Select primary, based on design duration:
      - Very short-term: Diesel.
      - Short-term: Diesel backed by storage (for efficiency).
      - Long-term: Storage backed by PV, then diesel (for endurance).
   b. Place primary:
      i. Find primary closest to each load (minimum line resistance). *[For fast analysis, use distance maps, not crossing damage.]*
      ii. Select edges connecting load and primary.
   c. Place secondary:
      i. Find secondary closest to each primary. (Attempt existing first, then new)
      ii. Select edges connecting primary and secondary.
   d. Capacity analysis:
      i. Find connected components.
      ii. Estimate storage, PV, diesel power and energy requirements.**
      iii. Set new generation capacity parameters.
7. If critical nodes remain without power, add collocated generation.
8. If capacity permits, include additional nodes.

* Single solution, or enumeration (future branch-and-bound pruning).
** Calculations are currently a simplified approximation.
Blue indicates implementation not complete.

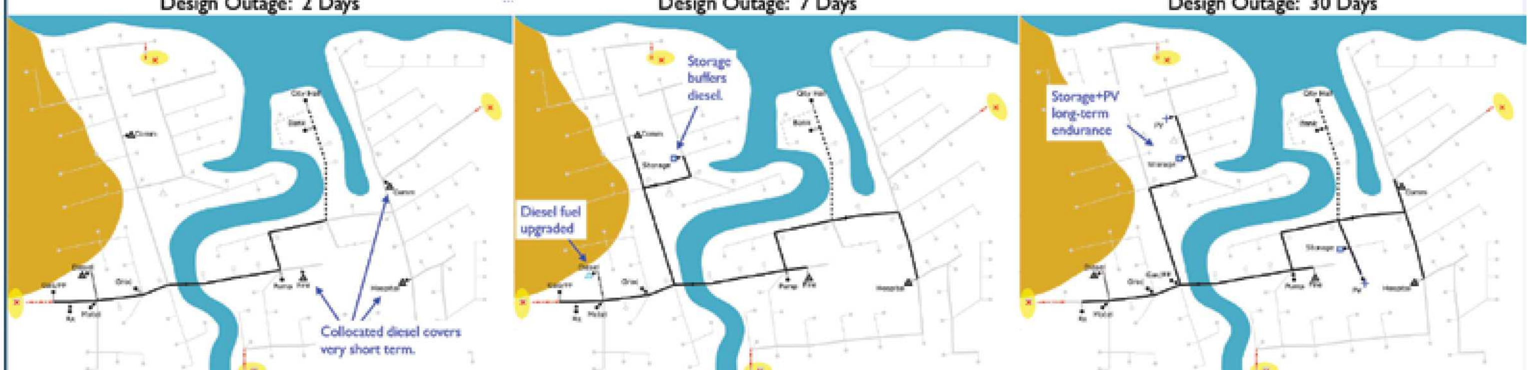
Example:

Existing Infrastructure — Potential Additions

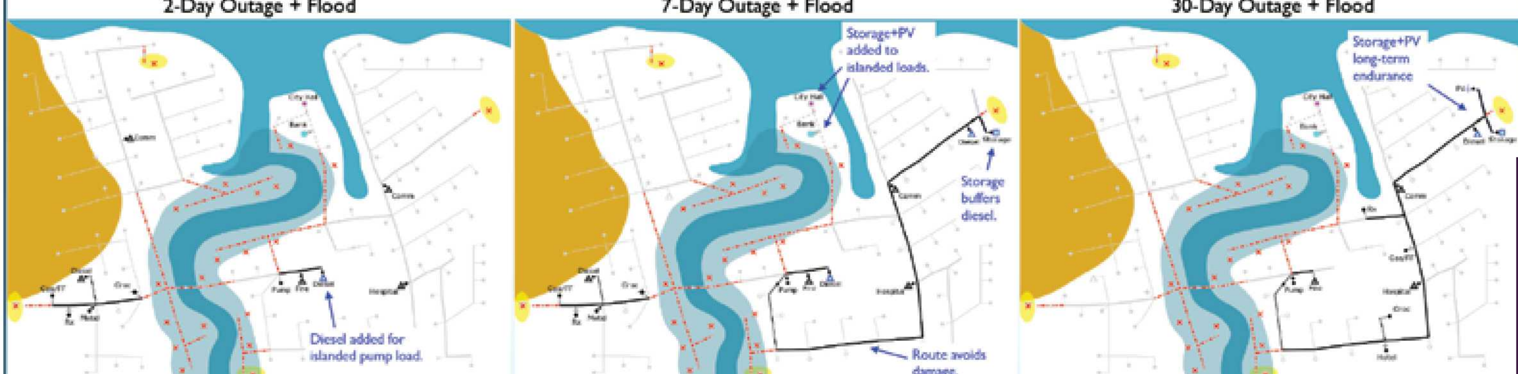


Output:

Design Outage: 2 Days — Design Outage: 7 Days — Design Outage: 30 Days



2-Day Outage + Flood — 7-Day Outage + Flood — 30-Day Outage + Flood



The author would like to thank Dr. Imre Gyuk and his colleagues at the Energy Storage Program at the U.S. Department of Energy Office of Electricity for funding this research.

Continuous-time Look-Ahead Scheduling of Energy Storage in Real-time Markets

Bosong Li, Masood Parvania, Emails: {bosong.li,masood.parvania}@utah.edu

Motivation & Formulation

- With the release of FERC Order. 841, energy storage integration is allowed to participate in the power market from anywhere on the grid.
- Energy storage devices are fast-ramping resources that can provide various ancillary services to maintain the economic and reliable operation of the power system, especially in real-time market.
- Conventional discrete-time modeling fails to capture the time-derivative relationships between the energy, power, and ramping of energy storage devices.

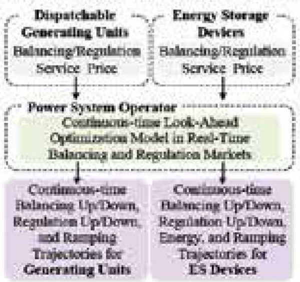


Figure 1: Continuous-time look-ahead scheduling model

- **Objective:** Minimizing the total real-time operation cost

$$\min \int_{T_r}\Big(\rho^{u,G}g^u(t)+\rho^{d,G}g^d(t)+\rho^{G^S}G^S(t)+\rho^{D^S}D^S(t) + \mu^{u,G}R^{u,G}(t)+\mu^{u,S}R^{u,G^S}(t)+\mu^{d,S}R^{d,G^S}(t) + \mu^{d,G}R^{d,G}(t)+R^{u,D^S}(t)+R^{d,D^S}(t)\Big)dt$$

- **Timeline:** The optimization problem is carried out based on the rolling-time horizons.

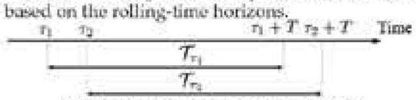


Figure 2: Timeline of the proposed model

- **Gaussian process:** In each look-ahead horizon, the forecast real-time load data are updated using Gaussian process.

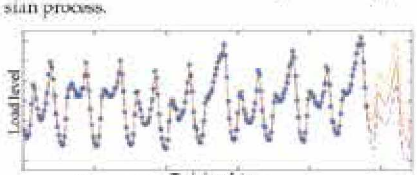


Figure 3: Scheme of Gaussian process

Solving Methodology

- The proposed continuous-time model captures the time-derivative relationships between energy, power, and ramping trajectories of energy storage as follows.
  - Energy and power.

$$\frac{dE^S(t)}{dt} = \eta^c D^S(t) - \eta^{d^{-1}} G^S(t)$$

  - Power and ramping.

$$\frac{dD^S(t)}{dt} = \dot{D}^S(t), \quad \frac{dG^S(t)}{dt} = \dot{G}^S(t)$$

- The proposed continuous-time optimization problem is infinite-dimensional and computationally intractable, and is projected to a finite-dimensional function space using Bernstein polynomials.

Figure 4: Scheme of Gaussian process

$$b_{q,Q}(t) = \binom{Q}{q} t^q (1-t)^{(Q-q)}, \; t \in [0,1]$$

$$e^{(Q)}_{n(Q+1)+q}(t) = b_{q,Q}\left(\frac{t-t_n}{T_n}\right), \; t \in [t_n, t_{n+1}]$$

- The continuous-time trajectories can be expressed using Bernstein polynomials, and the proposed optimization problem can be solved as a MILP problem.
  - Power trajectories.

$$G^S(t) = G^S e^{(Q)}(t), \; D^S(t) = D^S e^{(Q)}(t)$$
$$R^{u,G^S}(t) = R^{u,G^S} e^{(Q)}(t), \; R^{d,G^S}(t) = R^{d,G^S} e^{(Q)}(t)$$
$$R^{u,D^S}(t) = R^{u,D^S} e^{(Q)}(t), \; R^{d,D^S}(t) = R^{d,D^S} e^{(Q)}(t)$$

  - Energy trajectory.

$$e^{(Q+1)}(t) = \mathcal{N} e^{(Q)}(t)$$
$$E^S = E^S_r 1^T_{P+N} + (\eta^c D^S - \eta^{d^{-1}} G^S)\mathcal{W}$$

  - Rmaping trajectories.

$$e^{(Q)}(t) = \mathcal{M} e^{(Q-1)}(t)$$
$$\dot{G}^S = G^S \mathcal{M}, \; \dot{D}^S = D^S \mathcal{M}$$
$$\dot{R}^{u,G^S}(t) = R^{u,G^S}\mathcal{M}, \; \dot{R}^{d,G^S}(t) = R^{d,G^S}\mathcal{M}$$
$$\dot{R}^{u,D^S}(t) = R^{u,D^S}\mathcal{M}, \; \dot{R}^{d,D^S}(t) = R^{d,D^S}\mathcal{M}$$

Case Studies

Energy storage devices are co-optimized with generating units to tackle the deviation between day-ahead and real-time load under the following two cases:

- Case 1. System with no energy storage
- Case 2. System with energy storage

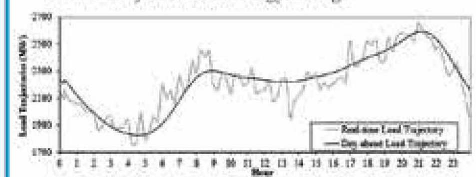


Figure 5: Day-ahead and real-time load trajectories

Table 1: Cost analysis of systems with/without energy storage

	Case 1	Case 2	Reduction Percentage
Balancing service Cost ($)	20,226	18,163	10.20%
Regulation Service Cost ($)	4,670	4,003	14.28%
Total Operation Cost ($)	24,896	22,166	10.97%

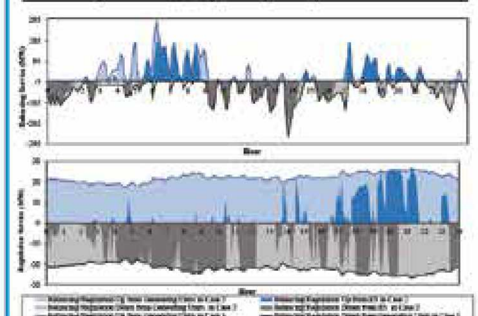


Figure 6: Balancing and regulation service trajectories

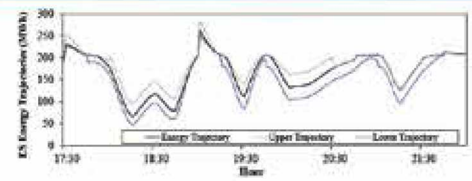


Figure 7: Energy trajectories of energy storage

The corresponding ramping trajectories of energy storage can show the ramping capability it brings to the system.

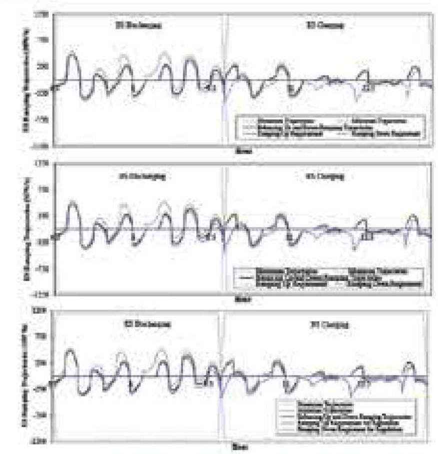


Figure 8: Ramping trajectories of energy storage

Summary and Future Work

- A continuous-time look-ahead optimal scheduling model for the energy storage to provide balancing and regulation services in real-time market is built.
- The infinite-dimensional problem is projected into a finite-dimensional function space using Bernstein polynomials and solved as a MILP problem.
- Further works concern the ancillary services energy storage can provide in different market stages (day-ahead, real-time, etc.) to find the best way to integrate energy storage in power system.

Acknowledgement

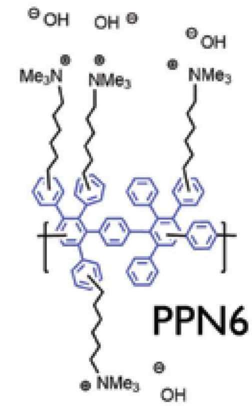
U.S. Department of Energy
Sandia National Laboratories

MATERIALS II

Sandia's energy storage materials science program focuses on technologies that can be grouped in three main categories. Electro-chemical technologies include lead-acid, lithium, sodium, and zinc; and flow batteries. Mechanical technologies include flywheels, compressed air, and pumped hydroelectric storage. Electrical, chemical, and thermal technologies include capacitors, hydrogen, and thermal storage, respectively.

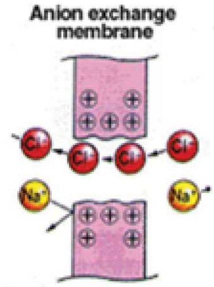
Advanced Membranes for Flow Batteries

Cy Fujimoto



Anion Exchange Membrane (AEM):

1. Polymer that contains bound positive charges.
2. ***Alkaline stable*** AEM allows for new electrochemical applications.
3. There is no accepted ***alkaline stable*** "state of the art" AEM.



Handful of small AEM companies

ecoLECTRO

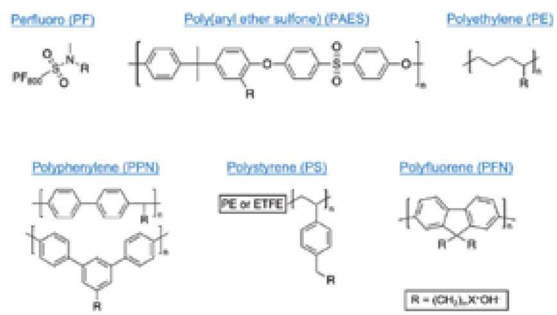
Dioxide Materials

IONOMR

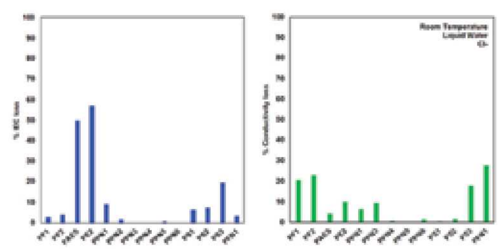
ORION POLYMERS

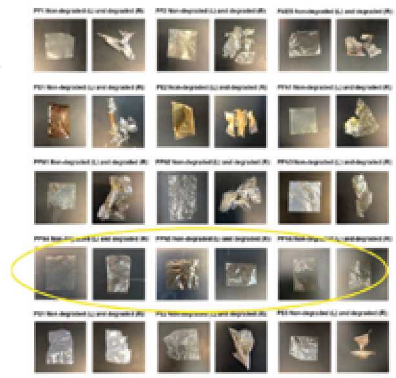
Third Party Durability Study:

Investigate IEC/Conductivity Loss and Mechanical Loss in 1M KOH at 80 °C for 1000 hrs.



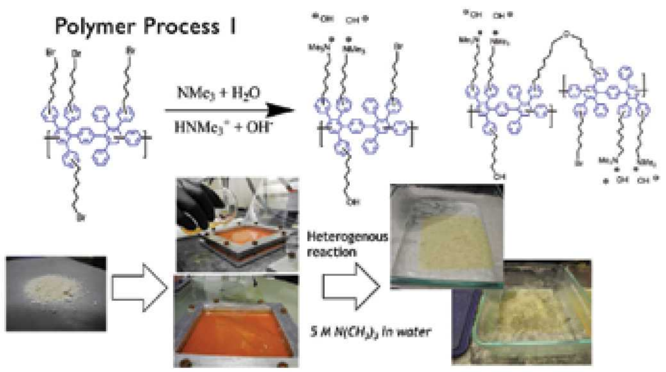
Test Credit: Kelly Meeks and Bryan Pivovar

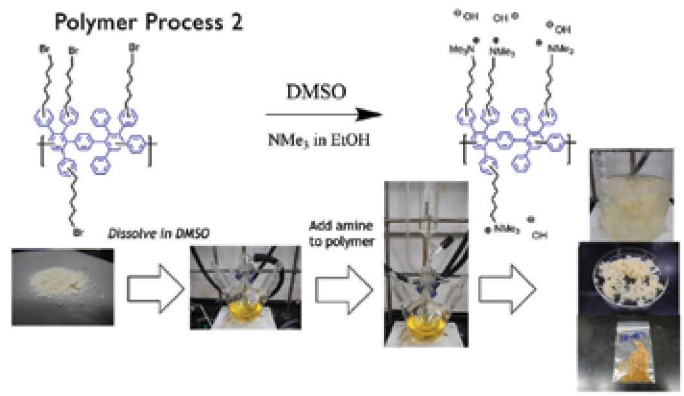




Process of AEM Synthesis:

IEC control important for flow battery membranes, however membrane process (Process 1) that was originally used lacked IEC control. To improve control, a new process was developed (Process 2) and provisional patent is being pursued.





Conclusions/Future:

1. High interest in alkaline stable anion exchange membranes.
2. Various polymers are being investigated, but the SNL polymer has shown promising durability.
3. Issues in controlling polymer IEC was due to processing condition used (Process 1).
4. Developed Process 2 that has shown full conversion of alkyl bromide to ammonium; better IEC control.
5. Membrane commercialization
6. Flow battery testing of new polymer architectures (Travis/Harry), send to collaborators.

Acknowledgements: ***This work was supported through the Energy Storage Program, managed by Dr. Imre Gyuk, within the U.S. Department of Energy's Office of Electricity.***

Electrochemical Energy Storage through Ligand-Based Charge Manipulation

Prof. Mitchell R. Anstey,*[a] Ellen Warner,[a] David Choi,[a] Claudia Hernandez,[a] Nicholas Kennedy,[a] Alexa M. Greenwood,[a] Jonathan Nicoleau,[a] Prof. David N. Blauch,[a] Prof. Neil C. Tomson[b]

[a]Davidson College, Davidson, North Carolina
[b]University of Pennsylvania, Philadelphia, Pennsylvania

The authors are grateful for support from Dr. Imre Gyuk, Babu Chalamala, Travis Anderson and the following institutions:

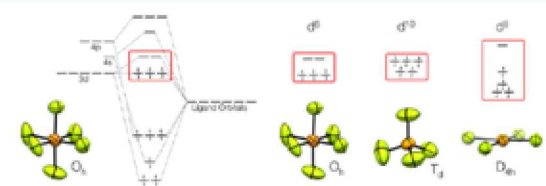
OFFICE OF ELECTRICITY DELIVERY & ENERGY RELIABILITY

Sandia National Laboratories

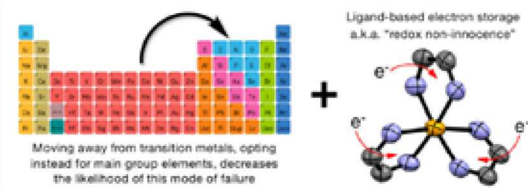
The role of redox-active small molecules in battery systems vary considerably as the system, and its needs, change. Redox flow batteries predominantly rely on molecular electrolytes for charge storage. Lithium-based batteries employ overcharge protectors in the form of aromatic hydrocarbons. Redox shuttles are currently being investigated to assist in the development of lithium-air batteries. In all cases, the redox-active component must be vetted in both of its oxidation states (charged and discharged) to ensure the system will function over its lifetime.

Our group has been investigating methods of charge storage in molecular species and the ensuing structural changes that accompany each new oxidation state. Molecular-scale structural changes are not necessarily detrimental to performance, but without knowledge of their existence, the tools to predict their presence, and the ability to control them, the mechanisms of function (and possible decomposition) can be a black box.

Understanding Electrolyte Failure

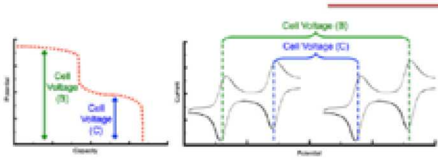


Classical coordination complexes are susceptible to decomposition during redox cycling due to the energy of the electrons involved in the processes.

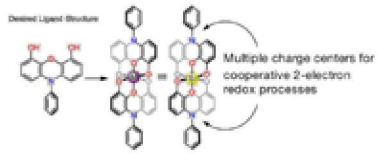


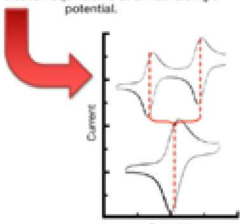
Our Guiding Principles for RFB Development

New Electrolyte Development

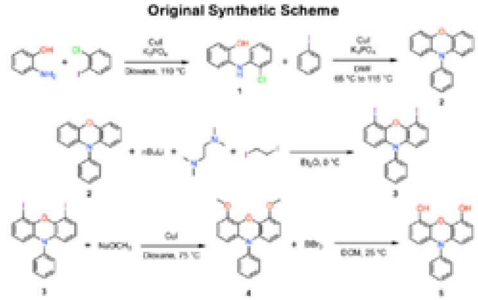


Single potential is critical for battery utility, as a single voltage must be maintained for optimum integration into a device or grid. A complex with many separate redox events leads to voltage step-downs during discharge. To prevent this, we must deliver election equivalents at or near a single potential.

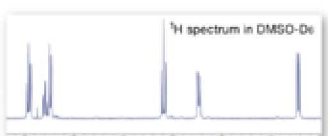




Original Synthetic Scheme



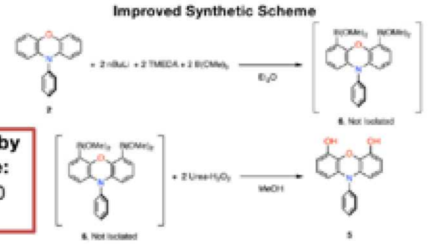
Metallation with Alkali Metals (sodium, potassium)



Both metals show the loss of the OH peak as well as a pronounced upfield shift of remaining ^{1}H NMR signals

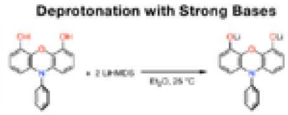
Ethereal solvents were explored with diethyl ether giving the fewest byproducts and easiest isolation

Improved Synthetic Scheme



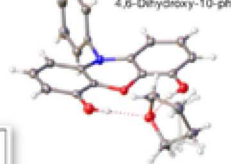
Overall Yield Improved by an Order of Magnitude: ligand synthesized in 20 gram batches

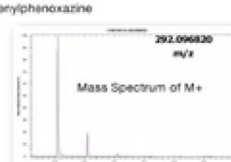
Deprotonation with Strong Bases



Only LiHMDS gave what appears to be product: loss of the hydroxyl, upfield shift of remaining ^{1}H signals

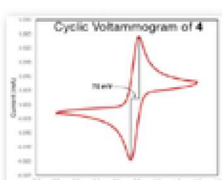
SC-XRD Structure of 4,6-Dihydroxy-10-phenylphenoxazine

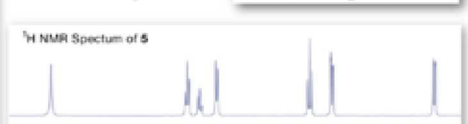




Future Work

Our next goal is to structurally characterize the lithium and sodium salts of the phenoxazine product. In tandem with this effort, the synthesis of main group complexes will begin starting with Group III and Group IV elements to show proof of principle and examine electrochemistry.





U.S. DEPARTMENT OF ENERGY
NNSA

Next Generation Cell design and Material Optimization for Sodium Batteries

Stephen J. Percival, Martha Gross, Leo J. Small, Babu Chalamala, Erik D. Spoerke*
Sandia National Laboratories, Albuquerque, NM, USA
sperciv@sandia.gov *edspoer@sandia.gov (PI)

Motivation

- *Molten sodium batteries offer great promise as a safe, low cost and scalable solution to grid scale energy storage, but high operating temperatures (>275 °C) and solid precipitation at lower temperatures limit their performance and lifetime.*
- *Recent progress has demonstrated lower operating temperatures but new engineering is necessary to enable high throughput testing to determine key parameters, such as interfacial wetting and compatible materials.*
- *Objective: How can fast and reliable testing be achieved through new cell engineering and what materials and interfaces are key to successful battery operation?*
- *We aimed to engineer new test cells to be interchangeable, re-usable and facilitate catholyte and anolyte interaction with charge transfer interfaces.*

Schematic of a NaI Battery

Reversible battery reactions:
Anode: $Na^+ + e^- \rightarrow Na$
Cathode: $3I^- \rightarrow I_3^- + 2e^-$

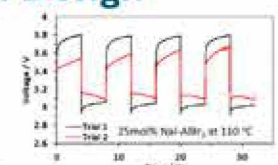
Small, et al. J. Power Sources, 2017, 360, 569-574. Percival, et al. J. Electrochem. Soc., 2018, 165, A3531-A3536.

Low Temp Molten Salt

- $AlBr_3$ compositions identified are **fully molten at 90 °C.**
- $AlCl_3$ compositions still frozen or have large amounts of solids at 90 °C

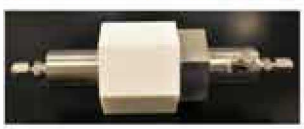
Previous Battery Cell Design

- Demonstrated feasibility of new NaI-$AlBr_3$ chemistry
- Cell made with available glass cell parts not designed for molten salt battery testing
- **Optimization needed for reliable battery testing!**



Large efficiency difference seen during cycling from simply increasing available surface area for salt wetting.

Re-Engineered Cell Variants



- Many new cell designs and geometries built and tested (7 different types!)
- Some designs were time consuming, laborious and could be **used only once!**
- Key lessons learned about cell geometry, interfacial interactions and materials compatibility informed new prototype designs.

New Cell Designs

Enable easy assembly, high throughput and functional geometry

Includes 3 designs that are fully interchangeable and reusable

Importance of Seals

Many times failure was due to materials incompatibilities of the seals and the constituents.

Sodium Compatible Seal Material

Polyethylene seals from molten polyethylene to seal the sodium side
Not re-useable and hard to apply properly
Identified new EPDM o-rings that will not react with sodium metal

Molten Salt Compatible Seal Material

Vapors from molten salt aggressively attacking the epoxy seals

Glass to metal seals eliminate unwanted side reactions from salt vapors

Interfacial Engineering

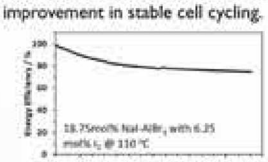
Improper wetting of the sodium or salt with the NaSICON results in:

1. High overpotentials (low energy efficiency)
2. Eventual shorting through the NaSICON

Improper wetting leads to current constriction through small active areas of NaSICON eventually forming shorts

Heating NaSICON to >380 °C with Na induces a chemical change at the interface that improves wetting, leading to stable performance.

Carbon and tin-based thin films also used to enhance wetting. Along with thermally activated carbon felt current collectors, new cells show drastic improvement in stable cell cycling.



New cells cycling >150 cycles (>550 hours)!!!

Impact Summary

- **Engineered cell geometry and materials to enable reliable high throughput testing of new sodium battery chemistries**
- **Careful design has produced a re-usable, interchangeable cell test platform that is safe and easy to use.**
- **This design has facilitated first ever demonstration of high cycle life testing of a molten sodium battery at 110 °C.**

Acknowledgments:
This work was supported through the Energy Storage Program, managed by Dr. Imre Gyuk, within the U.S. Department of Energy's Office of Electricity.

Sandia National Laboratories

Sandia National Laboratories

Solid State Separator Development for Sodium-Based Batteries

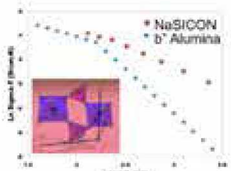
Amanda Peretti, Eric Coker, Mark Rodriguez, Martha M. Gross, and Erik D. Spoerke (PI)*
Sandia National Laboratories, Albuquerque, NM, USA
asperet@sandia.gov *edspoer@sandia.gov

Motivation: We aim to develop zero-crossover solid state separators to enable safe, low cost, long cycle-life, low temperature (<150°C) grid-scale sodium-based batteries.

Key Separator Properties:

- Selective, high ionic conductivity at reduced temperature (<150°C)
- Chemical compatibility (molten Na, molten halide salts, strong base)
- Mechanical robustness
- Low cost, scalable production

Based on its high Na-ionic conductivity (>10^{-3} S/cm at 25°C) and established chemical compatibility, NaSICON ceramics ($Na_3Zr_2PSi_2O_{12}$) are good candidates for development.

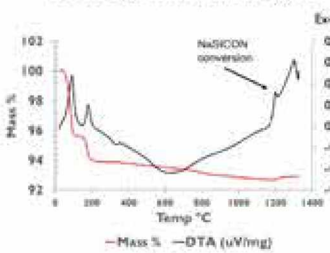


Additional candidate battery chemistries include Zn-MnO_2 or aqueous Na-ion batteries.

Thermal Analyses of Solid State Reaction

$$2ZrSiO_4 + Na_3PO_4 \rightarrow Na_3Zr_2PSi_2O_{12}$$

Differential Thermal Analysis and Thermogravimetric Analysis



Sintered NaSICON

NaSICON Sintered at 1250°C

- DTA/TGA show water removed from precursor powder by ~250°C.
- NaSICON conversion reaction evident between 1170-1230 °C.
- Sintering above 1230°C → poor ceramic integrity (melting?)

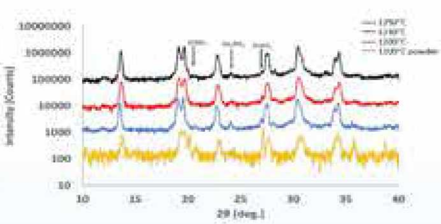
Why is this important?

Complete Conversion of Precursors

*Sintered at 1200°C	Conductivity Average (S/cm)	Standard Deviation
Calcined 600°C	1.72E-04	4.26E-05
No Calcine	5.04E-05	2.81E-05

- XRD confirms presence of Calcining precursor powder to at least 250°C eliminates sodium phosphate hydrates in "as-made" precursor powders.
- Density measurements, though, show that higher calcining temperature (600°C) leads to still better sintered ceramic density.
- Calcining also results in improved ionic conductivity, likely due to improved density.

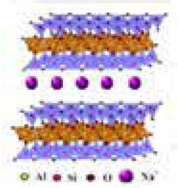
Molten Na Battery Cell Set Up

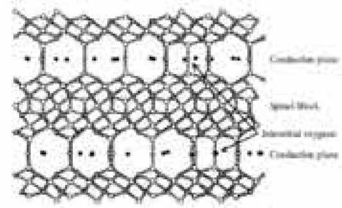


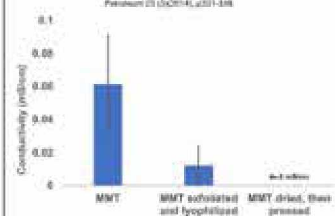
- NaSICON calcined at 600°C, sintered at 1230°C yields >94% density and > 0.4 mS/cm at 25°C.
- These ceramics are suitable for lab-scale testing of molten sodium batteries

Alternative Separator Materials

- The key goal is to make battery separators out of low cost, 2D materials
- Montmorillonite (MMT) i.e., clay is a promising material







- MMT platelet orientation plays a role in the ability of the Na+ ions to move through the composite.
- Increased H_2O content increases conductivity of composite
- Want channels, have to have water in there

Composite Conductivity

	mS/cm	Qualitative Analysis
MMT	9.90E-02	fragile, breaks with minimum effort
MMT:PE-block-PEG	8.76E-05	crumbles at ratios < 1:1, soft and crumbly
MMT:PEG	5.00E-05	pliable and crumbly
MMT:PEG:NaTFSI	4.11E-03	pliable and crumbly
MMT:HDPE	5.95E-02	rigid and snaps

MMT

Symmetric cell with MMT separator (Sn-coated) before and after cycling

- MMT alone is not robust and falls apart upon contact with fluids
- Adding polymers to the composite improves mechanical stability
- Polymers are insulators → addition to a composite decreases overall conductivity
- Adding Sodium trifluoromethanesulfonimide (NaTFSI) to the composite can recover some of the conductivity

Conclusions and Future Directions

- Thermal analyses inform significant details about NaSICON solid state synthesis from $ZrSiO_4$ and Na_3PO_4 precursors.
- Calcining precursor to at least 250°C and sintering to 1230°C allows for reasonable precursor conversion and ceramic densification, leading to functional NaSICON separators.
- MMT composite conductivity is dependent on H2O content and MMT platelet orientation
- Polymer additions to MMT increase robustness but decrease conductivity, which can be mitigated by the addition of Na-ion containing salts.
- Future work will focus on improving NaSICON ceramic conductivity through doping and synthesis of composites with high conductivity and robust mechanical properties.

Understanding thermal analyses and phase behavior can lead to improved ion conductor synthesis.

This work was supported through the Energy Storage Program, managed by Dr. Imre Gyuk, within the U.S. Department of Energy's Office of Electricity.

SAND No.

Sandia National Laboratories

Radialene Radicals for Aqueous Redox Flow Batteries

Christopher M. Bejger, Nicholas Turner, Matthew B. Freeman, & Daniel Jones

Department of Chemistry, University of North Carolina at Charlotte, Charlotte, NC, 28223

UNC CHARLOTTE

NANOSCALE SCIENCE Ph.D. PROGRAM at UNC CHARLOTTE

Abstract

Negatively substituted trimethylenecyclopropane dianions, a class of as hexasubstituted [3]radialenes, are good candidates for active species in redox flow batteries (RFBs) due to their stability in water, reversible electrochemistry, and ability to be tuned synthetically. Hexacyano[3]radialene disodium is investigated as a pH 7 aqueous organic catholyte. The dianion and radical anion are stable in air and aqueous solutions at neutral pH. Systematic introduction of asymmetry via step-wise synthesis leads to enhanced solubility and higher capacity retention during galvanostatic cycling. An aqueous flow cell comprising a disester-tetracyano[3]radialene catholyte, sulfonated-methyl viologen as the anolyte, and a cation exchange membrane provides an operating Vcell = 0.9 V, 99 % coulombic efficiency, and 73 % electrochemical yield over 50 cycles.

Background

Radialenes

- alicyclic compounds in which all ring atoms are sp2-hybridized
- exocyclic carbon-carbon double bonds
- π-systems of radialenes are considered cross-conjugated
- parent, unsubstituted [n]radialenes are unstable
- can support multielectron transfer
- can be isolated in various oxidation states

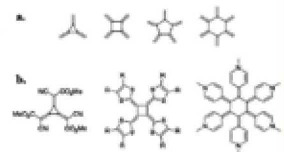
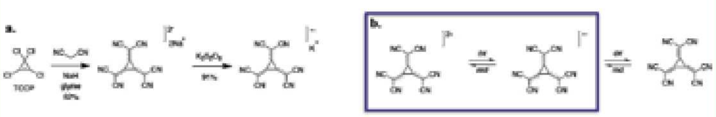


Figure 1. (a) Parent [n]radialenes (n= 3-6) and (b) examples of radialene derivatives.[1,2]

Hexacyano[3]radialene



- ✓ One Step Prep
- ✓ Synthetically Tunable
- ✓ Air Stable
- ✓ Thermally Stable
- ✓ Reversible Redox
- ✓ Low MW
- ✓ Water Soluble
- ✓ Water Stable

Figure 2. (a) Synthesis and (b) redox chemistry of hexacyano[3]radialene.

Aqueous Electrochemical Analysis

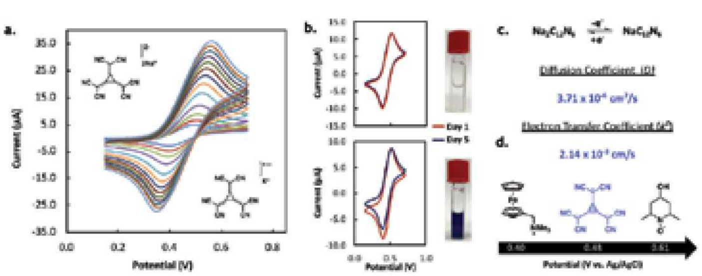


Figure 3. (a) CVs of $Na_2C_6(CN)_6$ (1 mmol) using a GC working electrode, Pt auxiliary electrode, and Ag/AgCl reference electrode measured at various scan rates (0-700 mV/s in water. (b) Stability study of $Na_2C_6(CN)_6$ and $KC_6(CN)_6$ (1 mmol) in water. (c) Diffusion coefficient and electron transfer rate constants. (d) Redox potentials of recently developed aqueous catholytes in comparison to $Na_2C_6(CN)_6$

Galvanostatic Cycling

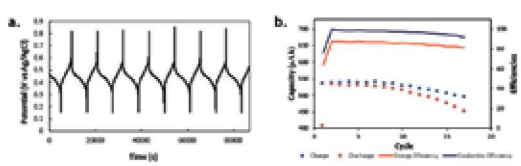
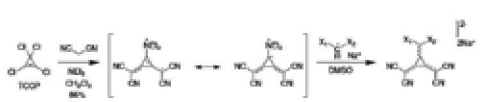


Figure 4 (a) Plot of charging voltage (vs Ag/AgCl) as a function of time for the 1e− cycling experiment of aqueous KC12N6 (10 mM) in an H cell. (b) Plot of capacity, coulombic efficiency, and energy efficiency for 18 cycles.

Stepwise Synthesis: Molecular Engineering

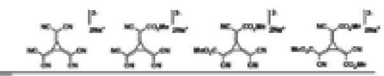


X_a	X_b	E^0_{ox}
CN	CN	0.34
CN	CO_2CH_3	0.26
CO_2CH_3	CO_2CH_3	0.11

Figure 5. Fukunaga's reported synthetic strategy for preparing assorted asymmetric radialene derivatives and the redox potentials of the first oxidation for three example compounds (Measured as TBA salts in MeCN vs SCE).

Solubility Enhancement Via Desymmetrization

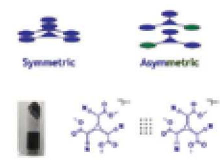
Table 1



Solubility[a]	25 mM	0.19 M	0.5 M	0.85 M
Radical Anion Solubility[b]	< 25 mM	0.08	0.2 M	< 0.1M
$E^{o'}{}_{1/2}$[c]	0.48 V	0.4 V	0.35 V	0.27 V
i_{pa}/i_{pc}	1.03	0.97	1.06	1.15

[a]Calculated from saturated aqueous solutions using UV/Vis spectroscopy.
[b]Measured as a Potassium (K^+) salt
[c]Recorded at 100 mV/s using a glassy carbon electrode & Ag/AgCl reference electrode in water.

Dimerization Mitigation



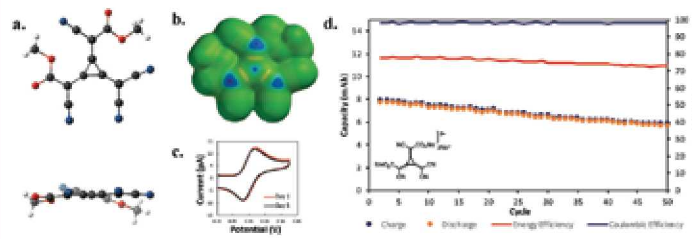
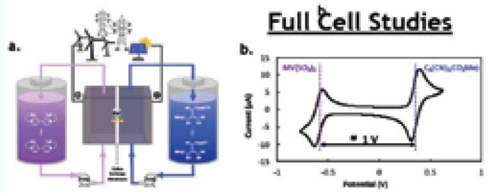


Figure 6. (a) Top and side views of single crystal structure of $2TBA{\cdot}C_6(CN)_4(CO_2Me)_2$. (b) DFT spin density map of $C_6(CN)_4(CO_2Me)_2^{\bullet-}$. (c) Cyclic voltammetry stability study of 1 mmol aqueous solution of $C_6(CN)_4(CO_2Me)_2$ in water over five days. (d) 1e− cycling experiment of aqueous $C_6(CN)_4(CO_2Me)_2$ (0.1 M) in an H cell. Plot of capacity, coulombic efficiency, and energy efficiency for 50 cycles.

Full Cell Studies



- 0.1 M electroactive species
- 25 mA charge/discharge rate
- 5 cm² active area
- 2.5 mL/min flow rate
- Serpentine flow field
- SGL GFD carbon felt electrode

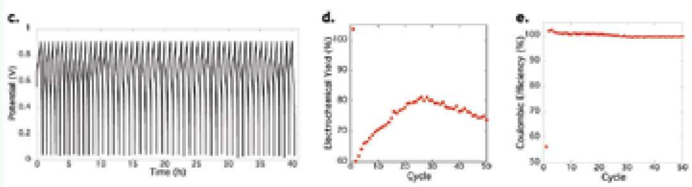


Fig. 7 (a) Schematic of all organic RFB. (b) Cyclic voltammogram of a mixture of $MV(SO_3)_2$ and $Na_2C_6(CN)_4(CO_2Me)_2$. (c) Charge-discharge profile of flow cell. (d) Electrochemical yield over 50 cycles. (e) Coulombic efficiency of the flow cell over 50 cycles.

Solubility Enhancement: Hydrophilic Glycol Derivatives

Fig. 7 Proposed synthesis of PEG-tethered hexasubstituted [3]radialenes.

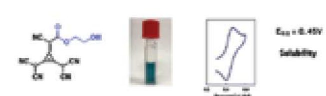


Fig. 8 Solution and CV of oxidized glycol derivative (n=1) in water.

Future Work

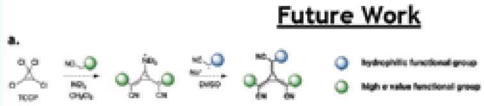


Fig. 9 (a) proposed hierarchical synthesis of [3]radialene derivatives for energy storage. (b) Hypothetical "all-in-one" [3]radialene for aqueous RFBs.

References

(1) Hopf, H.; Maas, G. *Angew. Chemie Int. Ed.* 1992, *31*, 931–954.
(2) Maas, G. [n]Radialenes. In Cross Conjugation; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2016; 79–116.
(3) Fukunaga, T. *J. Am. Chem. Soc.* 1976, *98*, 610–611.
(4) Fukunaga, T.; Gordon, M. D.; Krusic, P. J. *J. Am. Chem. Soc.* 1976, *98*, 611–613.

Acknowledgements

- DOE Office of Electricity
- Imre Gyuk
- Travis Anderson
- Harry Pratt III
- Mitch Anstey

Charlotte Research Scholars

Thomas D. Walsh Graduate Fellowship (M.F.)

NANOSCALE SCIENCE

Instagram @bejgerlab

Materials and Membranes for Megawatt Scale Energy Storage

Oak Ridge National Laboratory

PIs: Jagjit Nanda and Frank M. Delnick

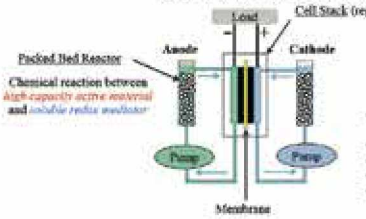
Contributors: Ethan C. Self, Guang Yang, Michelle L. Lehmann, Landon Tyler, Tomonori Saito, Thomas A. Zawodzinski

U.S. Department of Energy

OE Thrust Area : Cost Competitive Energy Storage

(i) Development and demonstration of innovative battery and non-battery energy storage components
(ii) Research on novel materials and system components to resolve key cost and performance challenges for electrochemical energy storage systems based on earth abundant advanced chemistries.

Mediated Na-Ion Redox Flow Battery



Advantages of Mediated Flow Battery

- ✓ Extremely high energy density can be achieved (200 Wh/kg vs. 25 Wh/kg)
- ✓ Accommodate active materials with large volume changes
- ✓ Only ohmic losses in system are through the membrane
- ✓ Improved safety in event of short circuit
- ✓ Low cost (scales with physical size)

Project Objectives

(i) Develop high energy density redox flow batteries (RFBs) using earth abundant materials for megawatt scale energy storage

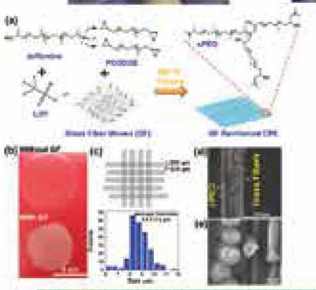
(ii) Develop low cost and scalable approaches to fabricate membranes for nonaqueous RFBs

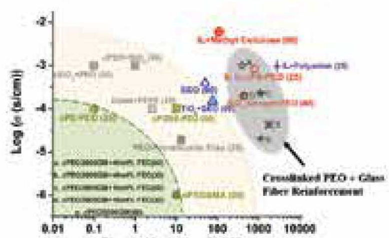
Project Milestones

- Benchmark the performance of a mediated phosphorus/Na-polysulfide nonaqueous RFB
- Synthesize and optimize various Na-based membranes (e.g., crosslinked PEO and PEO/polystyrene (PS) block copolymers) suitable for nonaqueous flow batteries.
  - Targeted metrics: Na^+ conductivity > 10^{-4} S/cm; transference number t_+ > 0.7, Area-Specific Resistance < 20 Ω cm²
- Evaluate mechanical durability of membranes in redox flow cells.
  - Targeted metric: Young's modulus > 10 MPa
- Evaluate chemical/electrochemical stability of membranes *in situ* using NMR, Raman spectroscopy, and AC impedance.
- Quantify crossover rates of redox species through sodium-based polymer membranes

Low Cost Membrane Development for Na-based Nonaqueous RFBs

Stretchable Ionomer | Crosslinked PEO | PEO-Glass Fiber Composite



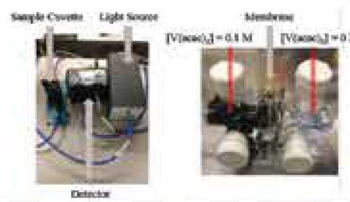


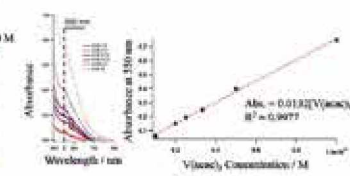
Composite membranes containing crosslinked PEO and glass fiber reinforcement exhibit among the highest Na^+ conductivity and elastic modulus reported to date for polymeric membranes.

In-Situ Crossover Measurements using UV-Vis Spectroscopy

Calibration using Standard Materials

Redox Species: tetraethylammonium vanadium(III) acetylacetonate (TEA-V(acac)$_3$)
Solvent: Acetonitrile
Membrane: TEA-substituted membrane (3M Company)



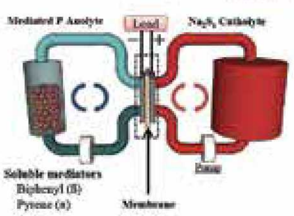


[V(acac)$_3$] in right compartment increases with time

- A UV-vis spectroscopy setup was established to measure crossover of redox species.
- In FY2020, this setup will be used to quantify biphenyl and Na_2S_x crossover through our team's membranes.

Nonaqueous Catholytes and Anolytes for Na-Based RFBs

Targeted Full Cell Chemistry



Cell Stack Reactions (Charge)

Cathode: $2\,Na_2S_4 \rightarrow Na_2S_8 + 2\,Na^+ + 2\,e^-$ E^0 = 2.3 V vs. Na/Na$^+$
Anode: $B^0 + Na^+ + e^- \rightarrow Na^+B^-$ E^0 = 0.2 V vs. Na/Na$^+$
Full Cell: $2\,Na_2S_4 + 2\,B^0 \rightarrow Na_2S_8 + 2\,Na^+B^-$ E_{cell} = 2.1 V

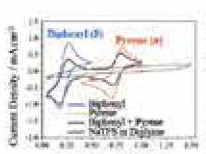
Cell Stack Reactions (Discharge)

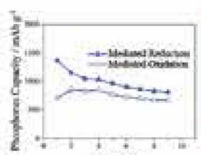
Cathode: $Na_2S_8 + 2\,Na^+ + 2\,e^- \rightarrow 2\,Na_2S_4$ E^0 = 2.3 V vs. Na/Na$^+$
Anode: $Na^+\pi^- \rightarrow \pi^0 + Na^+ + e^-$ E^0 = 0.75 V vs. Na/Na$^+$
Full Cell: $Na_2S_8 + 2\,Na^+\pi^- \rightarrow 2\,Na_2S_4 + 2\,\pi^0$ E_{cell} = 1.55 V

Anolyte: Mediated Red Phosphorus

Charge: $P + 3\,(Na^+B^-) \rightarrow Na_3P + 3\,B^0$
Discharge: $Na_3P + x\,\pi^0 \rightarrow Na_{3-x}P + x\,(Na^+\pi^-)$

Mediated P Anolyte (Half-Cell Configuration)



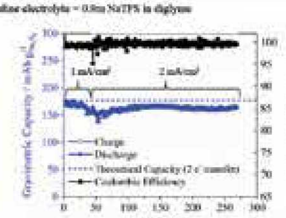


- Anion radical species were used to mediate reversible Na storage in a red P anode (mediated capacities ca. 900 mAh/g$_P$)
- Capacity degradation is mainly due to pyrene decomposition at potentials < 0.5 V vs. Na/Na$^+$
- Alternative mediators to replace pyrene will be identified in FY2020.

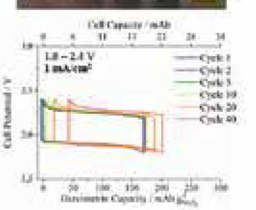
Non-Mediated RFB: Na_2S_x Catholyte/Biphenyl Anolyte

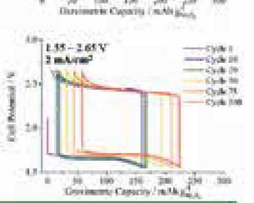
Compartment	Redox Species*	Capacity (mAh)	Concentration (molal)
Catholyte	Na_2S_8	20 (for 2 e⁻ process)	0.006
Anolyte	Biphenyl (B)	100 (5-fold excess)	0.28

*Baseline electrolyte = 0.8m NaTFS in diglyme



Polysulfide solutions (0.5 molal in diglyme)





- A Na_2S_8/biphenyl full cell exhibits excellent cycling stability.
- Future work will quantify kinetic and concentration polarization losses using AC impedance spectroscopy.
- Effect of higher concentrations on cell performance will be evaluated in FY2020.

Future Work

1. Identify alternative mediators to replace pyrene for mediated P anode
2. Evaluate RFB performance at higher Na_2S_8 concentrations (>1 M) and current densities
3. Quantify overpotential losses (activation, ohmic, concentration) using AC impedance
4. Develop a fully mediated RFB (Red P/Na_2S)
5. Quantify crossover of Na_2S_8 and biphenyl through various polymer membranes

Publications and Patents

1. M. L. Lehmann, G. Yang, D. Gilmer, K. S. Han, E. C. Self, R. E. Ruther, S. Ge, B. Li, V. Murugesan, A. P. Sokolov, F. M. Delnick, J. Nanda, T. Saito, Crosslinking of Poly(Ethylene Oxide) Membranes Enables Mechanical Robustness and Improved Sodium-Ion Conductivity with Plasticization *Energy Storage Materials* 2019, *21*, 85-96.
2. E. C. Self, F. M. Delnick, R. E. Ruther, J. Nanda, High Capacity Organic Radical Mediated Phosphorus Anode for Sodium Based Redox Flow Batteries *ACS Energy Lett.* 2019 (Under Review)
3. F. M. Delnick, J. Nanda, E. C. Self, *High Capacity Organic Radical Mediated Phosphorous Anode for Redox Flow Batteries*, United States Patent Application No. 62/701,859. Filed on July 23, 2019.
4. F. M. Delnick, D. Ingersoll, C. Liang, *Polyarene mediators for mediated redox flow battery*, *US Patent No. 9,859,583 B2*, 2018.

Acknowledgements

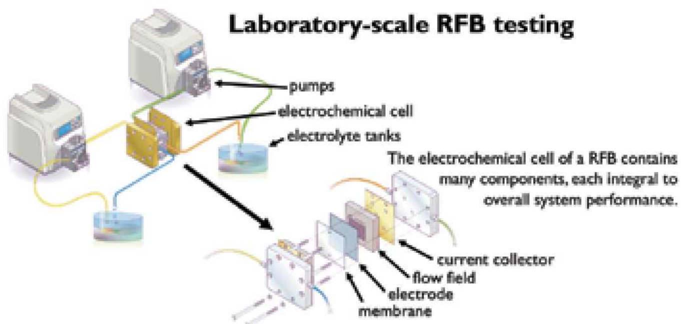
This research is sponsored by the US DOE Office of Electricity Delivery and Energy Reliability through the Energy Storage Program, managed by **Dr. Imre Gyuk**.

Elucidating Molecular Transport through Membranes in Flow Batteries

Leo J. Small, Harry D. Pratt III, Travis M. Anderson
Sandia National Laboratories, Albuquerque, NM, USA
ljsmall@sandia.gov, tmander@sandia.gov

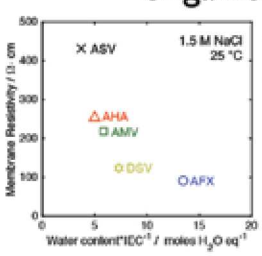
Redox flow batteries (RFBs) offer a readily scalable solution to grid scale energy storage. Understanding ion transport through RFBs enables design of more efficient, longer-lasting RFBs. Here we leveraged previously explored concepts of ion crossover in RFBs to identify key membrane properties in aqueous systems and use this knowledge to improve a higher voltage nonaqueous system.

Laboratory-scale RFB testing



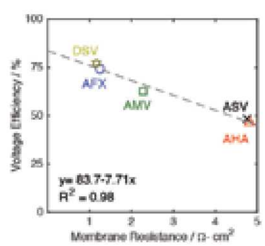
The electrochemical cell of a RFB contains many components, each integral to overall system performance.

Membranes for Aqueous Soluble Organic Flow Batteries



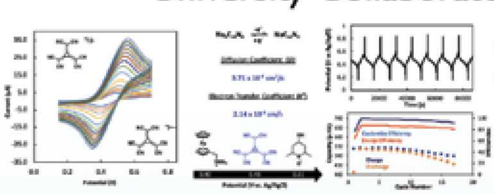
Across several commercial membrane chemistries we observe a systematic trend that membrane resistivity is controlled by the ratio of membrane water content to ion exchange content (IEC).

In turn, the membrane resistance is linearly related to the flow battery voltage efficiency, even after 100 cycles



L.J. Small, H.D. Pratt, T.M. Anderson, J. Electrochem. Soc. 166 A2536-A2542 (2019).

University Collaborators

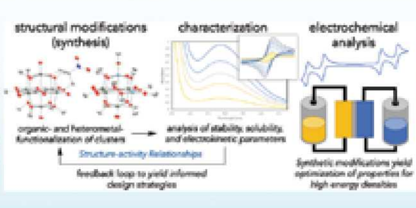


Radialene Radicals for Active Species in RFBs

Prof. Christopher Bejger
UNC Charlotte

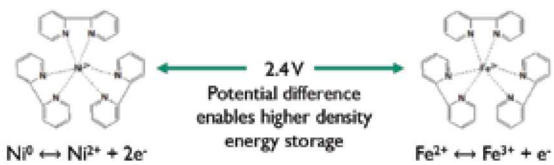
Metal-oxide Clusters as Charge Carriers for RFBs

Prof. Ellen M. Matson
Univ. Rochester

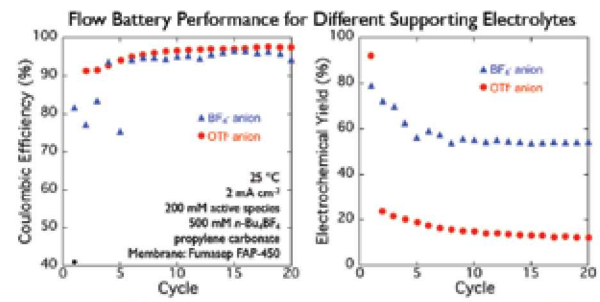


Nonaqueous Metal-Bipyridine Complexes

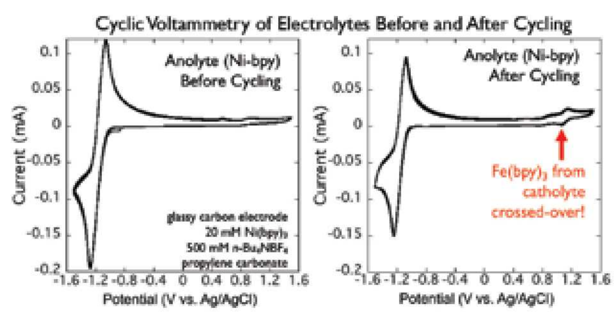
RFBs in nonaqueous solvents offer the advantage of higher operating potentials than aqueous systems, but are often hindered by electrolyte-membrane interactions. We investigated the effects of different solvents and salts on RFB performance, using a metal-bipyridine redox pair and a Fumasep anion exchange membrane.



Junyoung Mun et al. J. Electrochem. Soc. 165 A215-A219 (2018).
Hudak et al. J. Electrochem. Soc. 162 A2188-A2194 (2015).



Use of triflate (OTf$^-$) anion resulted in significant capacity loss vs. BF_4^- anion. Similarly, propylene carbonate performed better than acetonitrile.



Future Work

- How does cation vs. anion size influence bipyridine RFB performance?
  - Measure diffusion coefficients of bipyridine complex in different supporting salts
  - Membrane resistance / RFB voltage efficiency
  - Supporting salt solubility effects
- Identify, understand, and minimize capacity decay mechanisms in nonaqueous RFB
- Test new membranes from Cy Fujimoto (SNL) in aqueous and nonaqueous environments.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
SAND No. SAND2019-10948 C

This work was supported through the Energy Storage Program, managed by Dr. Imre Gyuk, within the U.S. Department of Energy's Office of Electricity.

OFFICE OF ELECTRICITY

Lithium-Pretreated Hard Carbon as High Performance Sodium-ion Battery Anodes

Biwei Xiao, David Reed, Vince Sprenkle and Xiaolin Li

Pacific Northwest National Laboratory, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY

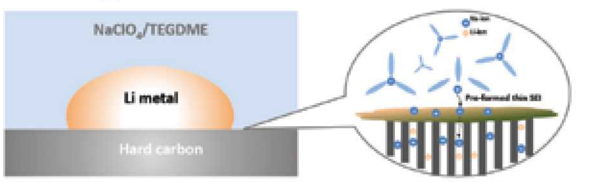
Proudly Operated by Battelle *Since 1965*

Introduction Hard carbon (HC) has been found to be an important anode material for sodium-ion batteries (SIBs). While competitive capacity has been achieved using HC, the performance is still plagued by the low initial Coulombic efficiency (ICE) due to the carbonate electrolyte decomposition that forms a thick solid electrolyte interphase (SEI) and irreversibly trapped Na ions within the nano-pores. It is vital to develop an electrolyte solvent as an alternative to conventional carbonate electrolyte and an approach to offset the low ICE.

Objectives

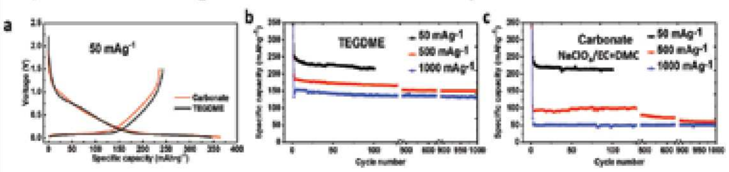
- ❑ Develop an advanced electrolyte that does not intensively decompose, or co-intercalate into the layers of HC.
- ❑ Achieve >90% initial Coulombic efficiency.

Methodology



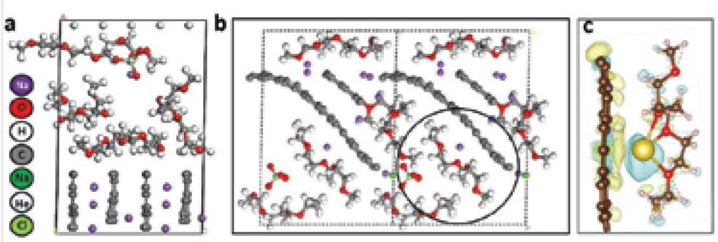
Results and Discussion:

a) TEGDME compared to carbonate electrolyte



➢ TEGDME shows improved performance compared to carbonate electrolyte.

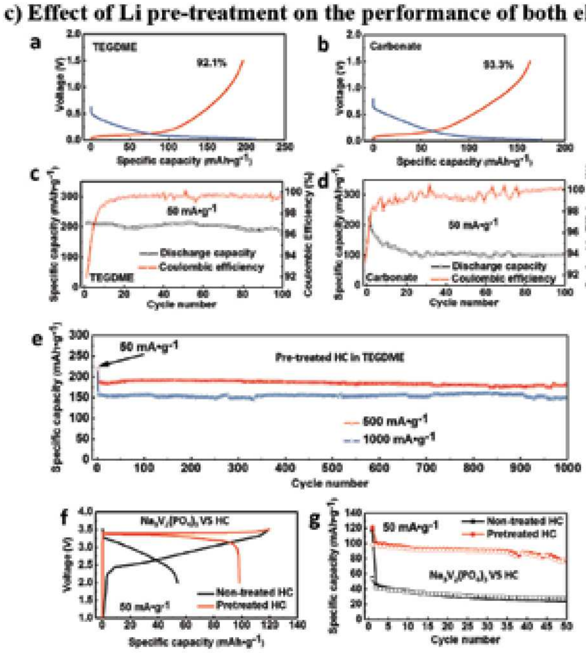
b) AIMD simulation of TEGDME electrolyte



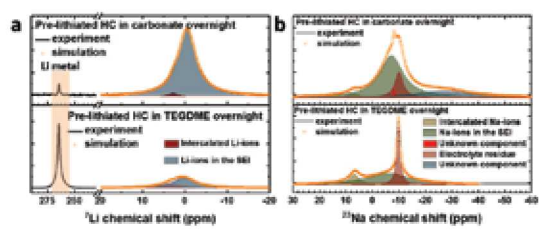
➢ The binding of Na^+ with O in the TEGDME-Na^+ complex is responsible for the stability of TEGDME.

➢ TEGDME does not intercalate into the HC layers.

c) Effect of Li pre-treatment on the performance of both electrolytes



➢ Li-metal treatment increases the ICE in both electrolytes, but the stability is only retained in TEGDME, this approach is able to achieve significantly improved full cell performance.



➢ HC forms thick SEI with large amount of Li-ions and Na-ions.

➢ HC forms thin SEI with little amount of Li-ions and Na-ions.

➢ Both Li-ions and Na-ions pre-intercalate into the HC during pre-treatment.

Future work

❑ Integrate the pre-treatment approach to a large scale cell and verify the feasibility.

Acknowledgements

This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is a operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830

U.S. DEPARTMENT OF ENERGY

Contact: Biwei Xiao, Ph.D.
Battery Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: biwei.xiao@pnnl.gov
Tel: (509)372-4747

References

1. B. Xiao and X. Li *et al.*, *Adv. Energy Mater.*, 2018,**8**,1801441.
2. B. Xiao and X. Li *et al.*, *ChemSusChem.*, 2019,12,133
3. F.A.Soto and X. Li *et al.*, *Adv. Mater.*, 2017, 29, 1606860

Development of sulfide based solid state electrolyte for Na-ion batteries

Atif AlZahrani [a], Daiwei Wang [b], Xiaolin Li [c], David Reed [c], Donghai Wang [b]
[a] Department of Material Science and Engineering, Penn State University, University Park, PA 16802
[b] Department of Mechanical Engineering, Penn State University, University Park, PA 16802
[c] Energy and Environmental Directory, Pacific Northwest National Laboratory, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

Introduction:

Na-ion battery is a promising low cost and high performance battery for grid-scale energy storage and the solid state design are inflammable and hence has great potential to further improve the battery safety. Sulfide-based Na-ion solid electrolytes made of low cost earth abundant elements have high ionic conductivities, which makes them a desirable choice for low-cost solid-state Na-ion batteries. Despite these advantages, the low conductivity and potential release of hazardous H_2S when contacting moisture environment poses a great challenge for using the sulfide-based Na-ion solid-state electrolyte for large scale manufacturing.

Objective:

- Development of low-cost, moisture stable sulfide-based Na-ion solid-state electrolyte without compromising the high ionic conductivity at room temperature.

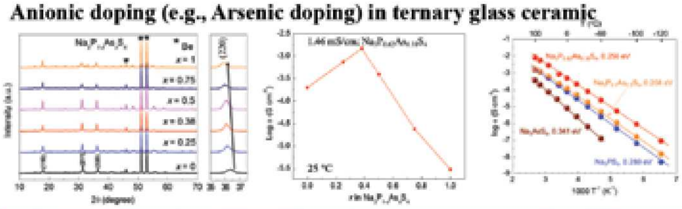
Approach:

- The general approach is to develop highly conductive sulfide-based solid state electrolyte and improve the moisture stability.
  - Improving the ionic conductivity
  - ✓ Appropriate elemental doping to lower the activation energy, expand the crystal lattice and reduce the Na-S binding energy
  - ✓ Introduce Na ion vacancy structure by aliovalent cation substitution.
  - Improving the moisture stability
  - ✓ Anion-substitution with more stable anion (i.e., nitrogen) in Na_3PS_4
- Understanding the structural-thermal-ionic conductivity-moisture sensitivity correlation as fundamental guidance for new electrolyte development

Results and Discussion:

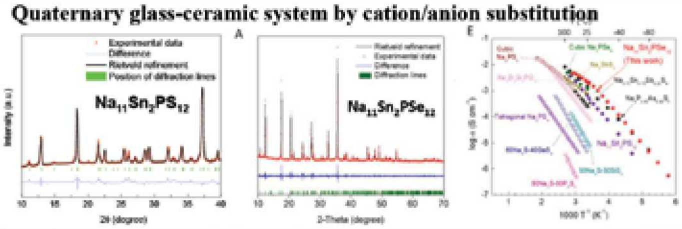
a) Highly conductive sulfide electrolyte

Anionic doping (e.g., Arsenic doping) in ternary glass ceramic



❖ Arsenic doping leads a a low activation energy of 0.256 eV and hence high conductivity of 1.46 mS/cm at room temperature.

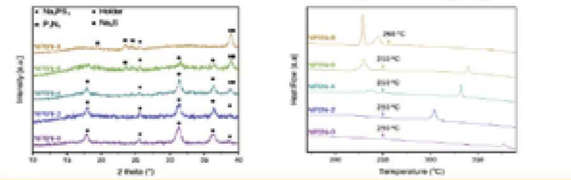
Quaternary glass-ceramic system by cation/anion substitution



❖ Electrolyte doped with Sn and Se can achieve ~2.15 ms/cm conductivity at room temperature.

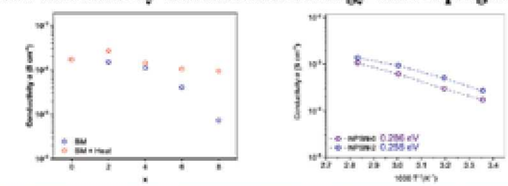
b) Highly conductive moisture stable electrolyte

Structure evolution and thermal stability with doping level



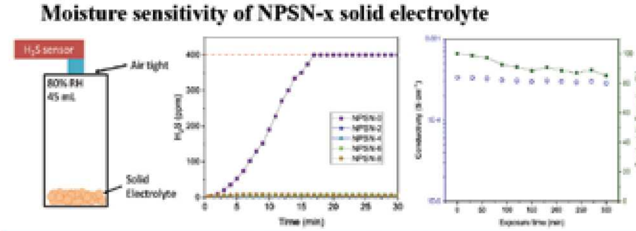
❖ Glass-ceramic material and increasing the doping level leads to more amorphous structure and precipitation of Na_2S.

Ionic conductivity and activation energy with doping level



❖ Ion conductivity decreases with the large increase of the doping level.
❖ The glass-ceramic material obtained after thermal treatment shows higher conductivity than that without heating.
❖ NPSN-2 with appropriate doping level showed higher conductivity and lower activation energy than undoped sample.

Moisture sensitivity of NPSN-x solid electrolyte



❖ N-doping results in a significant reduction of released H_2S (< 10 ppm) while the undoped electrolyte (NPSN-0) released H_2S reaching maximum within 16 min.
❖ N-doped electrolyte only has minor conductivity decrease (from 3.4×10^{-4} to 2.9×10^{-4} S cm^{-1}) after 5 hours exposure (55% RH).

Future Work:

- Investigate the mechanism of H_2S suppression in NPSN-x solid state electrolyte.
- Develop solid-state Na-ion battery utilizing the moisture stable NPSN-x solid-state electrolyte.

Acknowledgements

This work was supported by the U.S. Department of Energy (DOE) Office of Electricity (OE) under contract DE-AC06-76LO1830 through Pacific Northwest National Laboratory.

U.S. DEPARTMENT OF ENERGY

Contact: **Prof. Donghai Wang**
(presented by Dr. Xiaolin Li from PNNL)
Department of Mechanical Engineering
The Pennsylvania State University
Email: dwang@psu.edu; Tel: (814)-863-1287

References
1. Z. Yu, et al. Advanced Materials, 2017, 29, 1605561.
2. Z. Yu, et al. Nano Energy, 2018, 47, 325-330.
3. D.H. Wang et al, under preparation.

Monitoring the State-of-Charge of a Vanadium Redox Flow Battery with the Acoustic Attenuation Coefficient: An In Operando Noninvasive Method

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

Xiaoqin Zang, Litao Yan, Yang Yang, Huilin Pan, Zimin Nie, Zhiqun Daniel Deng, Wei Wang

Energy and Environment Directorate, Pacific Northwest National Laboratory, Richland, WA 99354

Background

Redox flow batteries are increasingly recognized as a promising technology for integrating electricity produced by renewable resources into the total energy mix. As more and more flow battery systems deployed for field testing, their operational efficiency, safety, and reliability become major challenges.

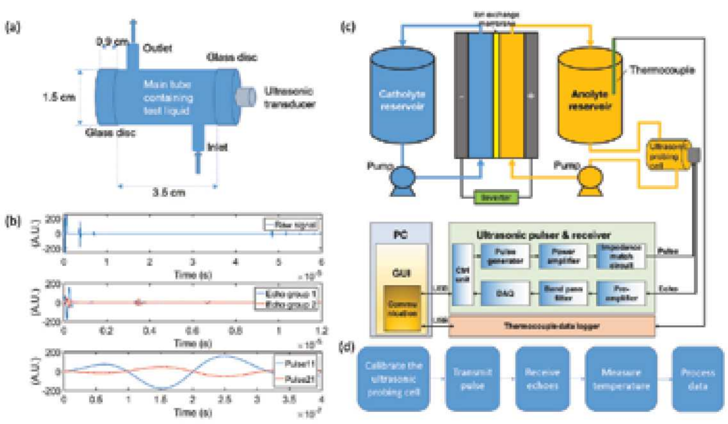
- Maximizing efficiency while maintaining reliable and safe charge-discharge cycling requires close monitoring of the battery state-of-charge (SOC).
- Existing methods for SOC monitoring, including the open-circuit cell voltage method and optical spectroscopic approaches, are either off-line or expensive or unreliable. Thus, the low-cost, real-time and reliable SOC monitoring technology is urgently needed.
- Sound speed is sensitive to temperature, which makes the SOC measurement unreliable in fluctuating temperature conditions.

Objectives

- To design an ultrasonic probing device to monitor the SOC with the acoustic properties of electrolytes of vanadium flow batteries on-line and non-invasively;
- To find a reliable measurement of SOC that can work in the fluctuating temperature conditions.

Experimental Approaches

- **Benchmark test**: measure the sound speed and acoustic attenuation coefficient of the electrolyte solutions at three concentrations and four temperatures to establish the benchmark curves between SOC and acoustic properties;
- ***In operando* validation test**: measure the sound speed and attenuation coefficient of the electrolyte solution in the seventh charge-discharge cycle; compare the SOCs estimated by the acoustic method with the ICP titration results.

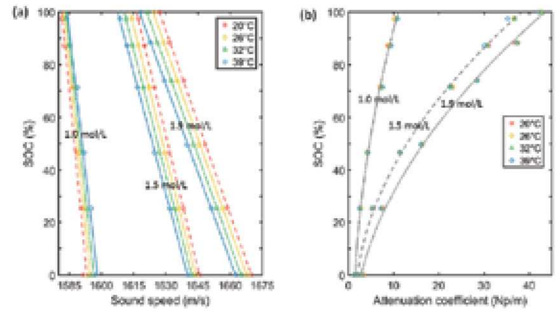


Schematics of the developed in operando flow battery monitoring system.

a) The designed ultrasonic measurement cell;
b) An example of received echoes when the measurement cell is filled with water;
c) System architecture; d) Flow chart of the measurement scheme.

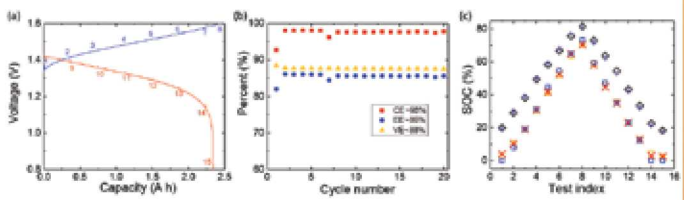
Results and Discussion

1) Benchmark curves



a) SOC measured with sound speed. At all tested concentrations, sound speed varies significantly with temperature;
b) SOC measured with the acoustic attenuation coefficient at 5 MHz. The sensitivity of attenuation coefficient at 5 MHz to temperature in the range of 20 to 39°C is negligibly small.

2) *In operando* validation test



a) The charge curve (in blue) and the discharge curve (in red) of an *in operando* SOC measurement in the seventh cycle;
b) Energy efficiency, columbic efficiency, and voltage efficiency for the first 20 cycles;
c) The SOC measured by the on-line acoustic method in the seventh cycle compared with titration results. The measurement of SOC with the attenuation coefficient has errors of less than 4.8%, more accurate than the sound speed.

Conclusion and Future Work

- The designed ultrasonic probing approach can accurately monitor the SOC of vanadium redox flow batteries *in operando,* in real time and at low cost, regardless of fluctuating temperatures.
- In the future, a battery health and reliability monitoring system will be developed for flow batteries with the ultrasonic probing approach and machine learning methods.

Acknowledgements

This work is supported by the U.S. Department of Energy's (DOE's) Office of Electricity Energy Storage Program and the Office of Technology Transitions. PNNL is operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830.

U.S. DEPARTMENT OF ENERGY

Contact: **Dr. Wei Wang**
Material Scientist
Electrochemical Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: wei.wang@pnnl.gov ; Tel: (509) 372-4097

Regenerated hydrogen-iron flow cell for low-cost distributed long-duration energy storage

Litao Yan, Yuyan Shao and Wei Wang

Contact: Litao.Yan@pnnl.gov

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

Background and motivation

- Redox flow batteries (RFBs) can provide some critical services in many grid energy application;
- Hydrogen metal (e.g. iron and vanadium) flow cells take the advantages of fast reversible kinetics, excellent performance and low-cost reactant materials;
- Water management plays a vital role in achieving a highly reversible hydrogen metal flow battery;
- Hydrogen based flow cell has great potential for long-duration energy storage (LDS, 10-200 hours) due to the compressibility of the hydrogen and the low-cost and earth abundance active materials.

Objective

- Develop a high reversible capacity hydrogen iron flow battery with the assistance of water management;
- Develop a cost effective, flexible, and compact regenerative flow cell system for long term energy storage.

Hydrogen metal (e.g. Fe and V) flow cells

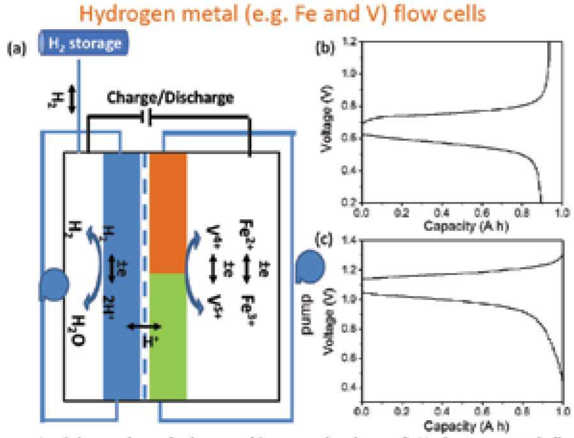


Figure 1. Schematics of the working mechanism of Hydrogen-metal flow cell (a);Charge/discharge profiles for hydrogen iron (b) and hydrogen vanadium flow cell (c). (current density: 300 mA/cm^2)

Challenges of hydrogen metal flow cells

- The acid concentration gradient between two electrodes provides the drive force to drag water molecular to iron electrode, leading to dried membrane;
- Dried membrane results in low capacity utilization, and low electrochemical performance. (e.g. low coulombic efficiency and poor cycling performance.)

Water management on hydrogen iron flow cell:

- Cycling water vapor in the hydrogen electrode during charge process;
- and the water evaporation process after 50th cycle in the iron electrode.

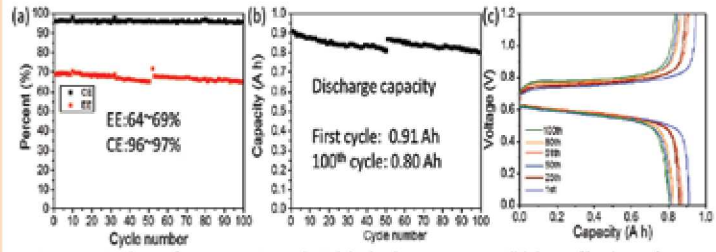


Figure 2. Cycle performance: CE and EE (a); discharge capacity (b) (cut off voltage from 0 to 1.2 V); Voltage profile at different cycles, (1st, 25th, 50th, 51th, 80th and 100th) (cut off voltage window range from 0 to 1.2 V; current density: 300 mA/cm^2)

Future work: LDS system builds on hydrogen iron flow cell

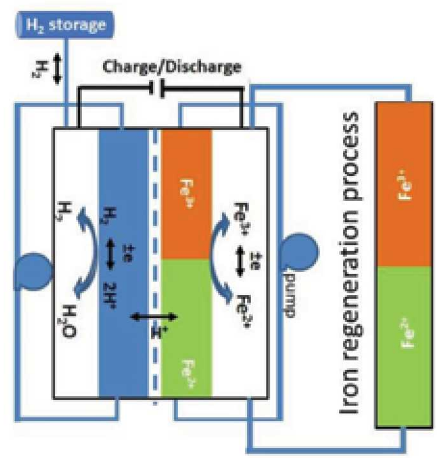


Figure 3. Schematics of the working mechanism of LDS system

Advantages:

- The regeneration of the iron redox couple can reduce energy bearing materials cost and volume in flow battery system;
- higher electrochemical compression of the hydrogen side of the cell can significantly reduce system footprint ;
- higher round-trip efficiency >75% for LDS of 8~200 hours.
- lower system cost.

U.S. DEPARTMENT OF ENERGY

This work on hydrogen iron flow cell is supported by the U.S. Department of Energy's (DOE) Office of Advanced Research Projects Agency-Energy (ARPA-E) through Award DE-AR0000686. PNNL is a multiprogram national laboratory operated by Battelle for DOE under Contract DE-AC05-76RL01830

POWER ELECTRONICS

The DOE OE Energy Storage power electronics thrust area advances power conversion systems (PCS) for grid-tied and off-grid applications. This is driven by the development of new semiconductor switching circuits, as they determine the overall cost, reliability, and performance of the converter. Next generation PCS use advanced semiconductor materials known as wide band gap semiconductors (i.e. Silicon Carbide and Gallium Nitride) that allow for faster switching frequencies, improved voltage breakdown characteristics, and higher operating temperatures.

Extreme Solar: Towards 24-7 Renewable Energy

Jose Tabarez, Nataraj Pragallapati, Olga Lavrova, Satish Ranade
Klipsch School of Electrical Computer Engineering
New Mexico State University,
Las Cruces, NM

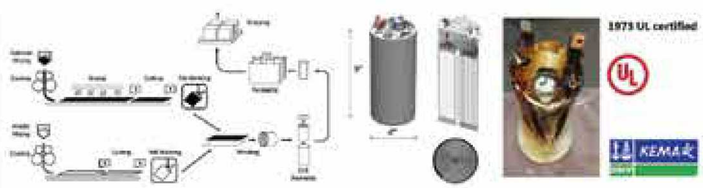
Sullivan Fleming, Irving Derin, Valerio De Angelis
Urban Electric Power
Pearl River, NY

Stan Atcitty Jacob Mueller
Sandia National Laboratories
Albuquerque, NM

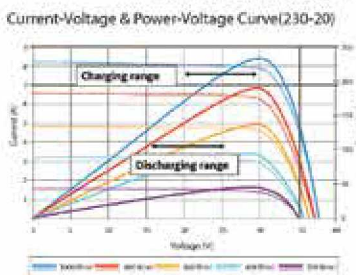
What	Why	Metrics
Take distributed solar to the next level by integrating the UEP's Zn-MnO_2 batteries with solar panels and microinverters.	Increase grid resilience and reliability by deploying distributed energy generation and storage.	Energy in, Energy out Energy efficiency Cost Durability

Tasks
Year 1 (FY19): Proof of concept, installation, monitoring, and operation (completed)
Year 2 (FY20): Dedicated DC/DC converter and batteries mounted directly under the panels
Year 3 (FY21): Cost reduction and commercial production

Safe, Low-cost, wide window of power charging conditions, safe to operate up to 60°C



Installation in New Mexico State University
16 UEP cells connected to solar panels and Enphase inverters

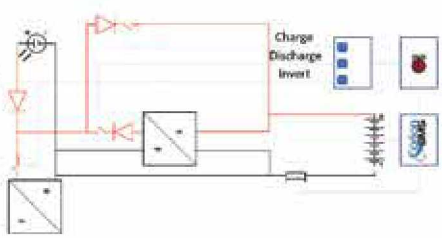


Charging characteristics
Solar MPPT voltage 30V
Cell charging range 1.25V to 1.81V
Battery charging range: 20V to 29V

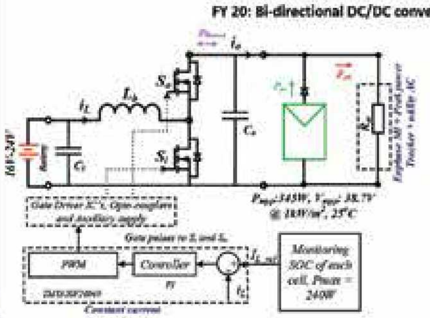
Discharging characteristics
Inverter operation range: 16V to 60V
Cell discharge range 1.5V to 1V
Battery discharge range: 24V to 16V

FY 19: Electrochemical charge solution: direct connection between the solar panels and the battery

Mode of operations
0 to 12 PM: Invert relay closed
12 PM to 3 PM: Charge relay closed
3 PM to 12 AM: Inverter relay closed
7 PM to 8:30 PM: Discharge relay closed



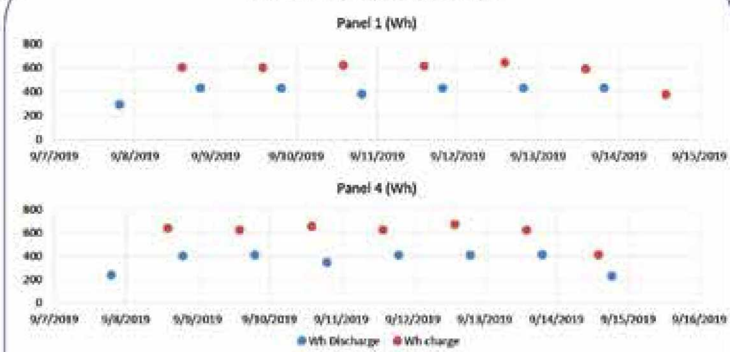
FY 20: Bi-directional DC/DC converter



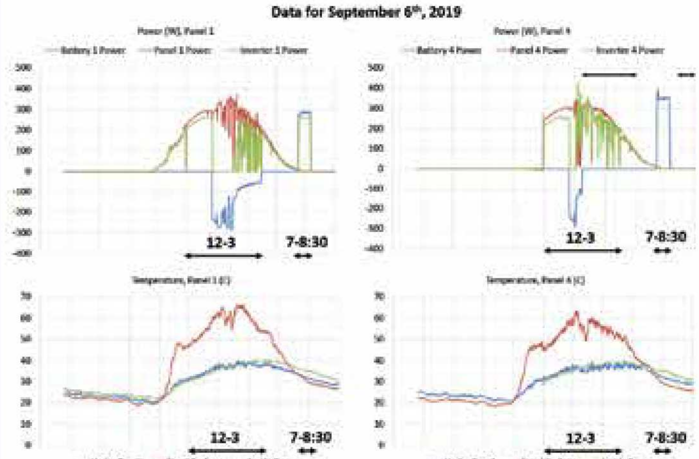
System: Bi-directional dc/dc converter interfaced between battery (16V-30V) and solar PV (P_{mpp}:345W, V_{mpp}: 38.7V@1kW/m², 25°C) terminals, and then Enphase Micro-Inverter is connected between the solar PV terminals to the utility ac grid.

Control system: Enphase Micro-Inverter operates in peak power tracker mode, i.e., to operate the Solar PV at maximum power point. Battery converter is operated in bidirectional power mode (and constant current control mode), i.e., charging the battery from solar PV and discharging the battery to ac utility through inverter.

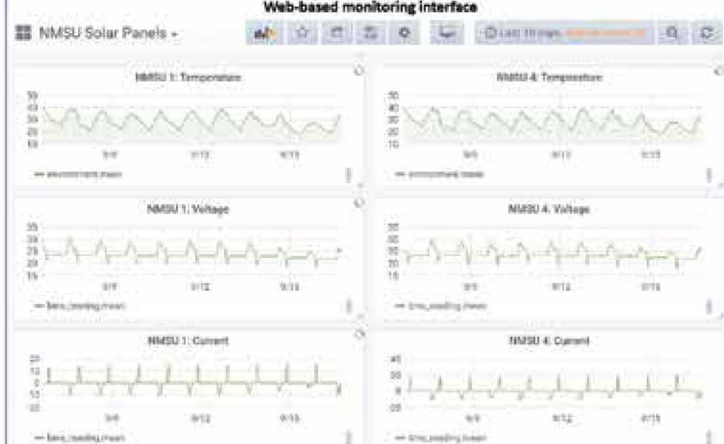
Battery Charge and Discharge Energy



Data for September 6th, 2019



Web-based monitoring interface



This work is supported by the Department of Energy, Energy Storage Program, Dr. Imre Gyuk.
SAND2019-10994 PE

Medium Voltage Direct Current Power Electronics for Alaska Remote Community Interties

M. Shirazi, M. A. Moonem, L Cassel Alaska Center for Energy and Power
W. Thomson, Alaska Village Electric Cooperative
S. Atcitty, Sandia National Laboratories

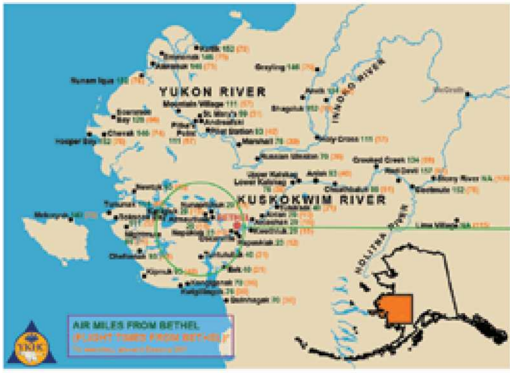


Fig. 1b. The Yukon-Kuskokwim Delta. Villages within green circle considered for MVDC network
Source: https://i0.wp.com/www.ykhc.org/wp-content/uploads/2018/06/YK-Service-Area-Map-no-logo-18-2.png?ssl=1
Accessed: 18-SEP-2018

Fig. 1c. Googlemap overlay by Bill Stamm of AVEC

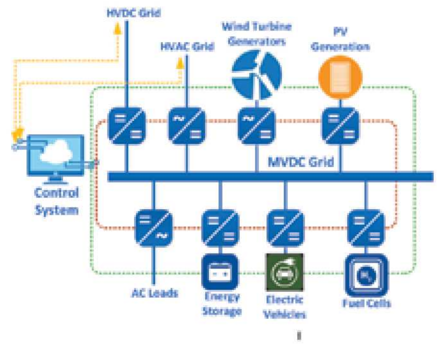


Fig. 2. MVDC Network, image by V. Gevorgian

Background:

- High cost of energy in remote Alaska communities: 2018 average cost in 200 remote Alaska communities (combined 50 MW load) was $0.36/kWh
- Overhead MVAC interties reduce operating costs, but expensive to install and limited in distance: Cost of $350K-$700K/mile and limited to ~20 mi.
- Cable based distribution offers lower installation costs across remote and permafrost terrain but charging current limits distance for AC distribution

MVDC interties:

- MVDC cable interties offer longer distance coverage, reduced voltage drop, and reduced conduction losses.
- MVDC networks also facilitate integration of large-scale **battery energy storage systems**, PV and wind power plants.
- MVDC networks offer enhanced **flexibility and scalability** than their AC counterparts due to simplified synchronization and controllable power flows
- Availability of sub-MW MVDC power electronics is currently the most significant factor limiting exploration of MVDC interties in Alaska.

Objectives and approach:

- Identify region and **utility partner** to perform techno-economic feasibility and for potential future deployment opportunities
- Explore techno-economic feasibility of MVDC interties to connect villages in remote Alaska, comparing cost of MVDC intertie vs. MVAC intertie vs. continued islanded operation (in progress)
- Identify state-of-the-art in MVDC power converters and most promising architectures for lower power applications
- Validate dynamic performance of the MVDC network using switching-level controller hardware-in-the-loop simulations (future)

Partners:

- Alaska Center for Energy and Power, University of Alaska Fairbanks
- Sandia National Laboratories
- Alaska Village Electric Cooperative

Period of Performance:

- August 22, 2018 – August 21, 2021

Activities to date:

- Identified utility partner and target region for techno-economic analysis;
- Studied state-of-the-art and trends in HVDC and MVDC converter topologies, cable, and manufacturers. Identified dual-active bridge (DAB) in conjunction with low voltage AC-DC as most promising topology for lower voltages and power levels.
- Compared costs of AC vs. DC and overhead vs. underground transmission.

LINE #	CONNECTION	LENGTH (MILES)	UP STREAM PEAK LOAD (KW)	RATED VOLTAGE (KV)	MAX RESISTANCE (Ω)	CONDUCTOR DIAMETER (INCH)	CONDUCTOR SIZE (AWG)
1	Oscarville to Napaskiak	1.89	213.68	25	146.244	0.048	<#2
2	Bethel to Atmautluak	18	826.93	25	37.791	0.292	1/0
3	Atmautluak to Nunapitchuk	6.5	671.58	25	46.532	0.158	<#2
4	Bethel to Akiachak	16	1169.40	25	26.723	0.327	2/0
5	Akiachak to Akiak	7	744.93	25	41.950	0.173	<#2
6	Akiak to Tuluksak	17	180.00	25	173.611	0.132	<#2
7	Akiachak to Kwethluk	7	313.68	25	99.622	0.112	<#2

Fig. 3. Preliminary conductor sizing for Bethel area MVDC distribution

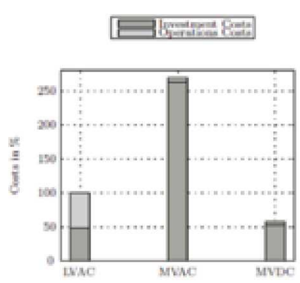


Fig. 3. A 2016 case-study in Germany [3] shows the cost comparison among LVAC (400V), MVAC(6.6kV) and MVDC(± 5kV) systems based on 5 MW (1,300 households) power level. Dual-active bridge (DAB) based DC-DC converters replace the 50/60 Hz transformer at ±5 kV MVDC.

References:
[1] E. Csanyi, "Analysing the costs of HVDC transmission," Electrical Engineering Portal, Online Aug 2014, Available: https://electrical-engineering-portal.com/analysing-the-costs-of-high-voltage-direct-current-hvdc-transmission

SAND. No. SAND2019-10983 PE

We sincerely thank Dr. Imre Gyuk for his continued support of this project.
Dr. Gyuk is the program manager at the DOE Office of Electricity Energy Storage Program.

Sandia National Laboratories

X7R Ceramic Capacitor Lifetime For Pesudo-DC-Link Topologies

Jonathan Bock[1], Lauren Garten[1*], Harlan Brown-Shaklee[1], Derek Wilke[1], and Carl Fitzgerald[1]
1) Sandia National Laboratories, *Now at Naval Research Laboratory

Background

Power electronics require capacitive energy storage devices to smooth switching transients and provide input and output filtering. Thermal losses in the switch, ripple currents imposed on the capacitor, and dielectric losses all can increase the temperature of the capacitor. Elevated temperature operation accelerates dielectric degradation and circuit failure.

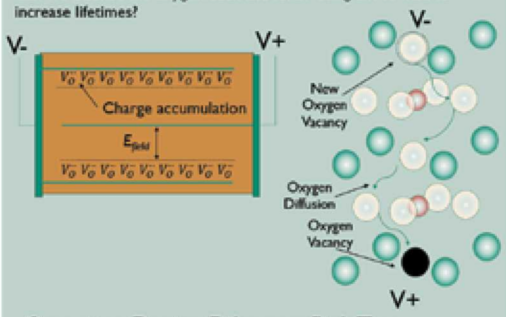
Until new high-temperature dielectrics increase in TRL* other strategies are needed to extend capacitor lifetime. Since degradation is due to electromigration of charged species, a 'healing' can occur if a opposite polarity is applied. Here we investigate this phenomenon by doing accelerated testing under AC conditions. Very slow bipolar switching of DC link (e.g. every other day, 'Pesudo-DC Link') may allow for increased lifetime of MLCC caps.

*Sandia has ongoing work in this area, Please ask if interested!

Capacitor DC Degradation

DC Degradation in ceramic capacitors is caused by the diffusion of oxygen anions toward the anode, thereby leaving the cathode region oxygen deficient. This process decreases the resistance of the dielectric and thereby increases the risk of thermal runaway failure (often to short).

Can we 'bounce the oxygen back and forth' using an AC field to increase lifetimes?



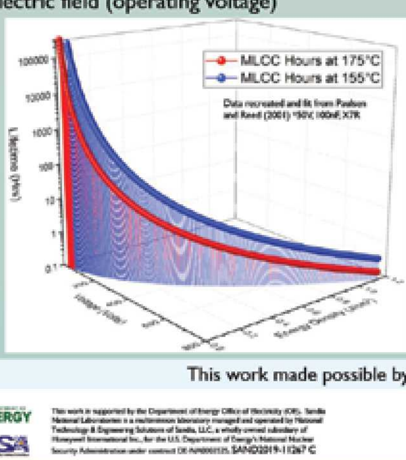
Capacitor Design Dilemma: Pick Two

1. Capacitor Energy Density,
2. Operating Temperature, or
3. Lifetime

Temperature and E_{field} accelerate dielectric degradation and reduce mean time to failure

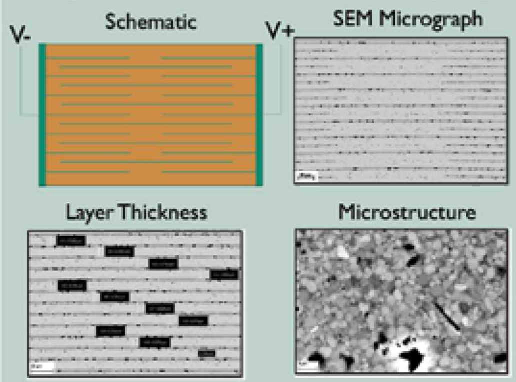
$$U/vol. = \frac{CV^2}{2 * vol.} = \frac{1}{2}\varepsilon_r\varepsilon_0 E_{field}^2$$

Energy density is proportional to the square of electric field (operating voltage)

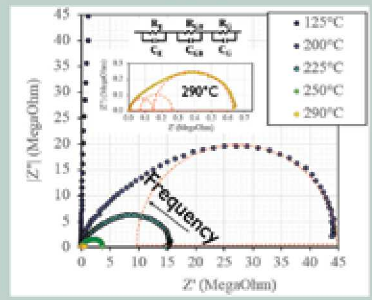


Multilayer Ceramic Capacitor Characterization

Floating electrode design reduces mechanical degradation associated with thermal cycling



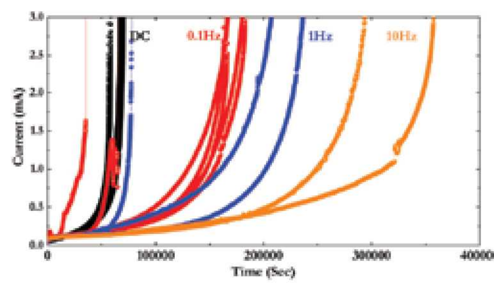
Initial Impedance Shows Normal Behavior



High temperature impedance fit well by widely-accepted 3RC model

AC Aging at 10Vr, 255°C

Extension of lifetime in AC conditions Occurs



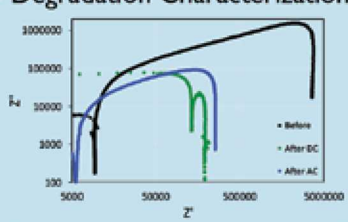
DC and AC HALT performed at ~10x the rated voltage and 125°C above the rated temperature.

- Very large acceleration needed for timely experiments
- Low voltage capacitor used for experiential ease. Less margin exists on HiPot caps for Power Electronic applications

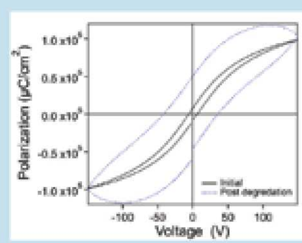
Preliminary studies suggest bipolar switching can increase the time to failure.

- Commercial-series BME ceramic caps have notoriously long pre-wear out Weibull tails. Statistics are needed to confirm findings (Note two 'infant mortal' 0.1Hz samples).

Post- Degradation Characterization



Clear differences in post-degradation impedance exist between AC and DC conditions. Current reason unknown. TEM Studies of Ti^{3+} locations may help pinpoint final $Vo^{\bullet\bullet}$ locations



- AC Degraded samples show similar behavior to DC degradation in PE loops (PE Loop shown above).

Future Work

- 40-sample AC HALT System being built (continuation funding through DOE Vehicle Technology Office)
  - Allows for longer tests/lower accelerations while maintaining timely data collection
- HALT Testing system will be used for mapping of Temperature-Frequency-Voltage Space under AC conditions
- Life extension at 10Hz for 10x overvoltage and 125C overtemperature has been shown….
  - Can life extension be obtained for lower frequencies at less accelerated conditions?
  - Can, e.g., capacitors be 'healed' when a system is not under use (Day-night cycle…'20uHz' frequency) or reverse of polarity each day.

Conclusions

1) AC conditions extend lifetime of ceramic capacitors
2) AC degradation likely tied to oxygen vacancy migration and proceeds via oxygen diffusion
3) Further HALT and Statistics are required to determine the impact to MLCC lifetimes

This work made possible by Dr. Imre Gyuk and the Department of Energy Office of Electricity Delivery and Energy Reliability (DOE-OE).

This work is supported by the Department of Energy Office of Electricity (OE). Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. SAND2019-11267 C

Sandia National Laboratories

Sandia National Laboratories

Advanced Gate Dielectrics for Wide-Bandgap Devices: Structural and electrical properties of epitaxial MgO on 4H-SiC

Peter T. Dickens[1], Michael T. Brumbach[1], Paul Kotula[1], Rebecca Chow[1], Kevin Ferri[2], Stan Atcitty[1], Jon-Paul Maria[2], Jon F. Ihlefeld[3], and Elizabeth A. Paisley[1]

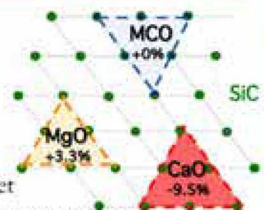
[1] Sandia National Laboratories, [2] Pennsylvania State University, [3] University of Virginia

Motivation

- Power conversion systems are the enabling technology for modern power electronics and energy storage.
- The metal-oxide-semiconductor field effect transistor (MOSFET) is the heart of power conversion systems.
- Wide bandgap semiconductor devices provide the opportunity to improve the performance through access to higher voltages, temperatures, and switching speeds.
- However, high temperature and high voltage SiC MOSFETs are currently unavailable due to issues with oxide layer reliability.

Objective: Develop new oxide layers, $Mg_xCa_{1-x}O$, which are designed to be chemically, structurally, and electrically compatible with SiC for a more reliable and resilient transistor.

Background



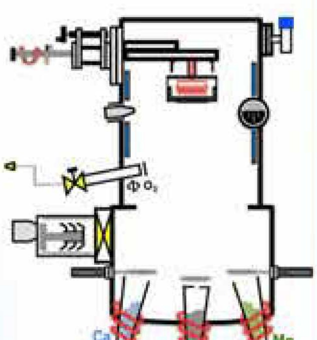
- A good gate insulator must:
  - have sufficiently large band gap
  - have > 1 eV conduction band offset
  - be chemically compatible with the semiconductor
- $Mg_xCa_{1-x}O$ (MCO) is an alloy of MgO and CaO, which have lattice constants that can match directly to SiC.
- To develop gate oxides with reliable performance, it is essential to understand the role of interface chemistry and band offsets.

Technical Approach

- We will investigate the structural, spectroscopic, and electrical properties of epitaxial MgO on 4H-SiC grown by molecular beam epitaxy (MBE) at various temperatures.
  - Our goal will be to optimize MgO growth for a more resilient and reliable gate dielectric.

Metrics

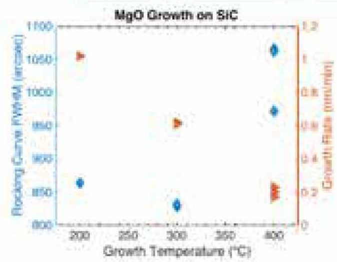
I. Structural properties
  → Abrupt epitaxial interface
  → High dielectric crystallinity
II. Spectroscopic properties
  → Large band offset
III. Electrical properties
  → Low dielectric leakage current

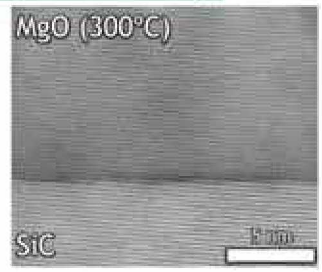


Device design:

I. Structural Properties

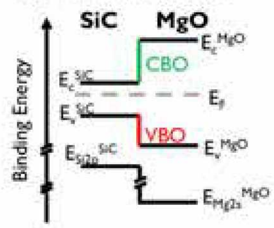
- Crystallinity measured using x-ray diffraction.
  → 300°C shows best crystallinity
- SiC|MgO interface imaged using transmission electron microscopy
  → Abrupt interface, no evidence of intermixing





II. Spectroscopic Properties

- Conduction band offset (CBO) measured using x-ray photoelectron spectroscopy (XPS).

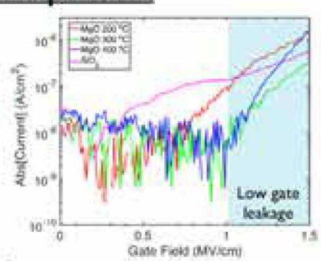


MgO Growth Temperature	CBO (eV)
200 °C	3.0 ± 0.05
300 °C	2.9 ± 0.13
400 °C	2.9 ± 0.04

→ > 1 eV CBO for all growth temperatures

III. Electrical Properties

- Current-voltage measurements performed on MOS capacitors.
  → Low leakage current in films.
- 300 °C demonstrates better leakage characteristics than SiO_2 up to 1.5 MV/cm.



Conclusions

- MgO demonstrates all properties needed to be a good gate insulator on SiC:
  I. Structural compatibility
  II. Large CBO
  III. Low gate leakage
- Growth by MBE is optimized at a growth temperature of 300°C.

Future Work

- Strategic partnership initiated with Auburn University, Prof. Sarit Dahr.
- Characterize the interface using C-V analysis on low doped SiC (10^{16} cm^{-3}).
- Fabricate MOSFET devices to test performance and reliability of transistors using the advanced gate dielectric.

We gratefully acknowledge Dr. Imre Gyuk and the DOE Office of Electricity Energy Storage Program for funding this work

Sandia National Laboratories

Advanced Gate Dielectrics for Wide-Bandgap Devices: Structural and electrical properties of epitaxial MgO on 4H-SiC

Peter T. Dickens[1], Michael T. Brumbach[1], Paul Kotula[1], Rebecca Chow[1], Kevin Ferri[2], Stan Atcitty[1], Jon-Paul Maria[2], Jon F. Ihlefeld[3], and Elizabeth A. Paisley[1]

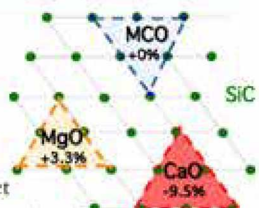
[1] Sandia National Laboratories, [2] Pennsylvania State University, [3] University of Virginia

Motivation

- Power conversion systems are the enabling technology for modern power electronics and energy storage.
- The metal-oxide-semiconductor field effect transistor (MOSFET) is the heart of power conversion systems.
- Wide bandgap semiconductor devices provide the opportunity to improve the performance through access to higher voltages, temperatures, and switching speeds.
- However, high temperature and high voltage SiC MOSFETs are currently unavailable due to issues with oxide layer reliability.

Objective: Develop new oxide layers, $Mg_xCa_{1-x}O$, which are designed to be chemically, structurally, and electrically compatible with SiC for a more reliable and resilient transistor.

Background



- A good gate insulator must:
  - have sufficiently large band gap
  - have > 1 eV conduction band offset
  - be chemically compatible with the semiconductor
- $Mg_xCa_{1-x}O$ (MCO) is an alloy of MgO and CaO, which have lattice constants that can match directly to SiC.
- To develop gate oxides with reliable performance, it is essential to understand the role of interface chemistry and band offsets.

Technical Approach

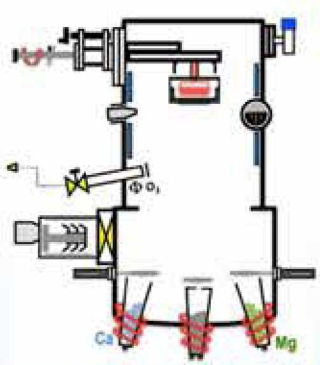
- We will investigate the structural, spectroscopic, and electrical properties of epitaxial MgO on 4H-SiC grown by molecular beam epitaxy (MBE) at various temperatures.
  - Our goal will be to optimize MgO growth for a more resilient and reliable gate dielectric.

Metrics

I. Structural properties
  → Abrupt epitaxial interface
  → High dielectric crystallinity

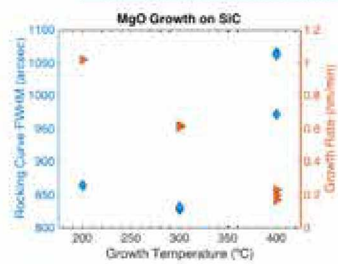
II. Spectroscopic properties
  → Large band offset

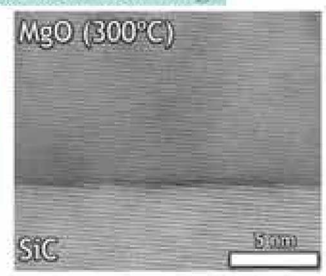
III. Electrical properties
  → Low dielectric leakage current



I. Structural Properties

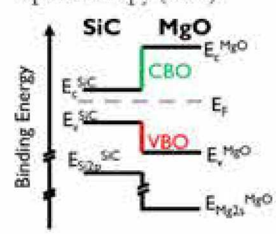
- Crystallinity measured using x-ray diffraction.
  → 300°C shows best crystallinity
- SiC|MgO interface imaged using transmission electron microscopy
  → Abrupt interface, no evidence of intermixing





II. Spectroscopic Properties

- Conduction band offset (CBO) measured using x-ray photoelectron spectroscopy (XPS).

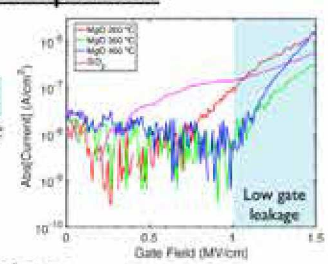


MgO Growth Temperature	CBO (eV)
200 °C	3.0 ± 0.05
300 °C	2.9 ± 0.13
400 °C	2.9 ± 0.04

→ > 1 eV CBO for all growth temperatures

III. Electrical Properties

- Current-voltage measurements performed on MOS capacitors.
  → Low leakage current in films.
- 300 °C demonstrates better leakage characteristics than SiO_2 up to 1.5 MV/cm.



Conclusions

- MgO demonstrates all properties needed to be a good gate insulator on SiC:
  I. Structural compatibility
  II. Large CBO
  III. Low gate leakage
- Growth by MBE is optimized at a growth temperature of 300°C.

Future Work

- Strategic partnership initiated with Auburn University, Prof. Sarit Dahr.
- Characterize the interface using C-V analysis on low doped SiC (10^{16} cm^{-3}).
- Fabricate MOSFET devices to test performance and reliability of transistors using the advanced gate dielectric.

We gratefully acknowledge Dr. Imre Gyuk and the DOE Office of Electricity Energy Storage Program for funding this work

Wide Bandgap Power Electronics Reliability

O. Slobodyan, T. Smith, J. Flicker, A. Binder, R. Kaplar, S. Atcitty
Sandia National Laboratories, Albuquerque, NM 87185 USA

Novel gallium nitride (GaN) devices have potential to help modernize the power grid by making energy storage more flexible and resilient.

GaN


vs.

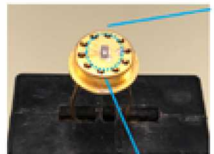

Vertical Gallium Nitride Power Diodes

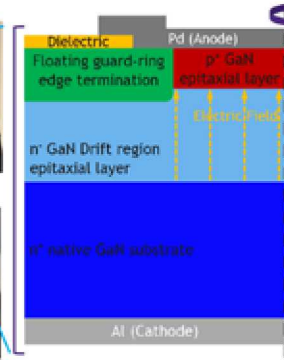
Vertical gallium nitride (v-GaN) diodes take full advantage of GaN to **reduce size, decrease weight & increase efficiency** for power systems.

– But work remains in establishing reliability under realistic conditions for v-GaN diodes.

Double-pulse test circuit (DPTC) can be used to operate and stress a device by continuously switching it between ON & OFF states.

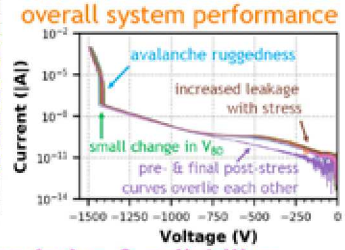
– Allows reliability testing of v-GaN devices under realistic operating conditions.





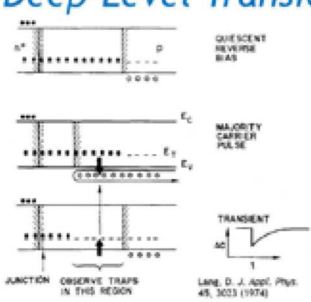
v-GaN Diode Pre- & Post-Stress Current-Voltage Characteristics

-Observed changes relate to material defects and affect overall system performance



➤ **Objective: Understand defects of v-GaN devices and correlate them to device degradation & reliability.**

Deep-Level Transient Spectroscopy Theory



Deep-Level Transient Spectroscopy (DLTS) probes defects in devices by performing transient capacitance measurements at different temperatures.

– Enables measurement of defect trap energies.

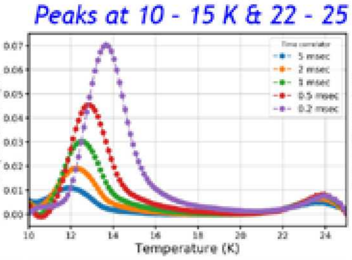
Performed DLTS measurements of an unstressed packaged bare 1200 V-rated v-GaN diode die fabricated by Avogy.

– Applied voltage samples defects in device drift region near p-n junction.

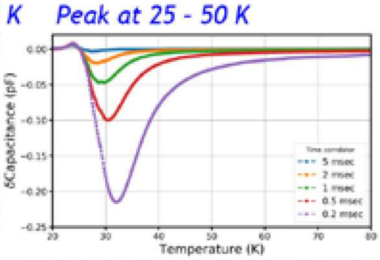

➤ **Yearly Milestone: Verify utility of DLTS for defect analysis of v-GaN devices.**

DLTS Results

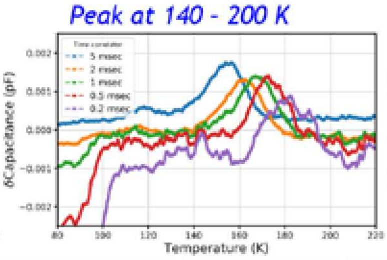
Peaks at 10 - 15 K & 22 - 25 K



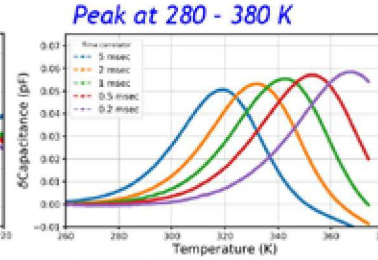
Peak at 25 - 50 K



Peak at 140 - 200 K



Peak at 280 - 380 K



➤ **Obtained several valid DLTS peaks - further data analysis is needed to determine defect parameters.**

Conclusion & Future Work:

- ✓ Successfully probed defects near p-n junction of an unstressed v-GaN high-voltage diode using DLTS.
- ➢ Next step is to determine defect energies & correlate defects to degradation of stressed v-GaN diode.
- ➢ Begin stress-testing of v-GaN diodes beyond the DPTC in true power converter.
- ➢ Recent Publications: O. Slobodyan, T. Smith, J. Flicker, S. Sandoval, C. Matthews, M. van Heukelom, R. Kaplar, and S. Atcitty, "Hard-Switching Reliability Studies of 1200 V Vertical GaN PiN Diodes," *MRS Communications*, vol. 8, no. 4, p. 1413 (December 2018) & V. Veliadis, R. Kaplar, J. Zhang, S. Khalil, J. Flicker, J. Neely, A. Binder, S. Atcitty, P. Moens, M. Bakowski, M. Hollis, "ITRW 2019: Chapter 6: Formulating a Roadmap for WBG and UWBG Materials and Devices", *IEEE Power Electronics Society* (September 2019)

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Acknowledgement - The authors thank Dr. Isik Kizilyalli & Dr. Ozgur Aktas, both formerly of Avogy Inc., for supplying the diodes for this work. The characterization work was supported by the Energy Storage Program managed by Dr. Imre Gyuk of the DOE Office of Electricity, and the fabrication work at Avogy was supported by the SWITCHES program managed by Dr. Tim Heidel of ARPA-E. The views expressed in this poster do not necessarily represent the views of the U.S. Department of Energy or the U.S. Government.

Development of a Battery Chemistry Agnostic Secondary Use Energy Storage System

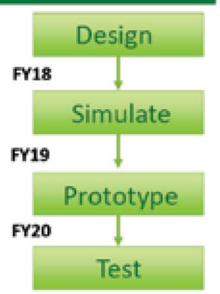
Madhu Chinthavali, Michael Starke, Steven Campbell, Shilpa Marti, Radha Krishnamoorthy, Mitch Smith, Ben Dean
Oak Ridge National Laboratory

Objective

- Develop a secondary use system solution to multiple battery systems with different chemistries and ages.
- The system should be plug-and-play and demonstrate multiple utility-based use cases as defined by PNNL/SANDIA testing protocols.

Approach

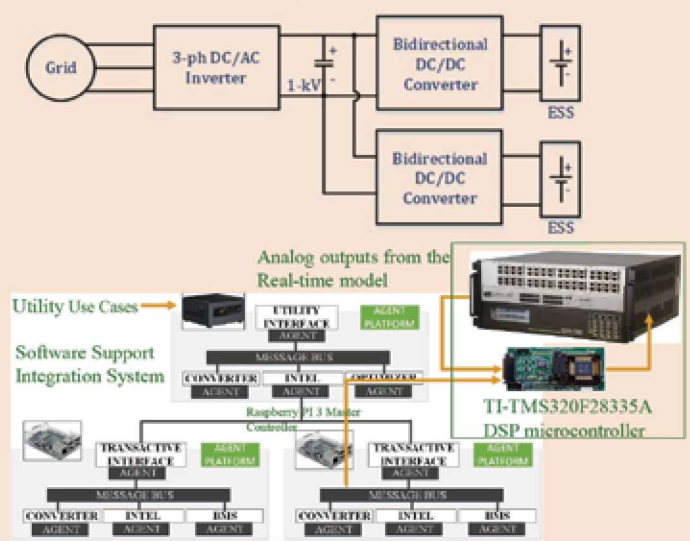
- Overall approach is to develop a system design, simulate the system, develop hardware, and demonstrate technology.
- The system is to be designed such that:
  - compatible to multiple different voltages and power levels to meet secondary use design considerations,
  - be low cost and modular,
  - utilize intelligence to provide means of safety and integration.
  - Utility scale (100kW)

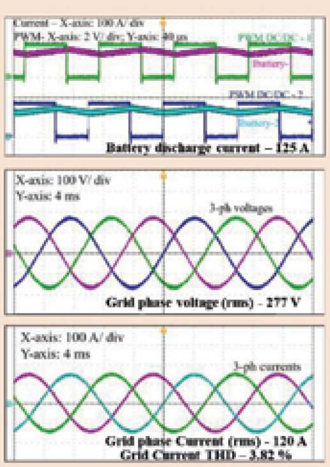


Overall Approach

Results

CHIL





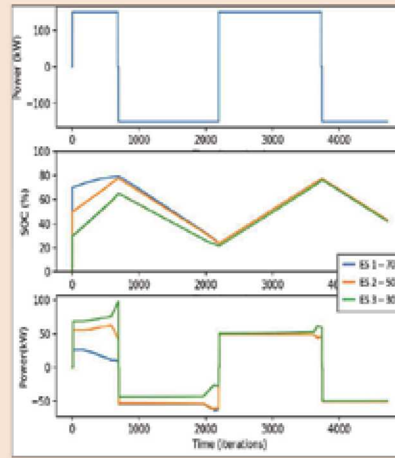
CHIL Results:

- Preliminary validation of the system controls and the power-stage design using real-time platform has been completed.
- The batteries discharging (Boost mode) into the grid at 125 A rated current is shown in the figure to the left.
- The corresponding grid phase voltages and the phase currents at 60 Hz, unity pf are shown in the figure to the left.
- The distortion in the phase currents was approximately 3.82 %.

CHIL results highlighting the discharge of the batteries (Discharge current: 125 A) and the corresponding 3-ph voltages and currents

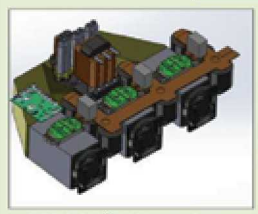
Distributed Optimization

- Developed agent-based framework for flexible system integration with wide-range of hardware (BMS, converters, etc.)
- Implemented distributed optimization for intra-system dispatch using ES net present value
- Demonstrated agent system across multiple network devices running energy storage models
- Demonstrated energy arbitrage use case.

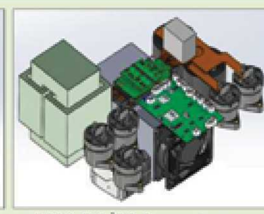


Distributed optimization results

Hardware Prototype



ORNL AC/DC Converter



ORNL DC/DC Converter

Spiers New Technologies Watt Tour

- Designed the dc-dc power stage and inverter power stages.
- The semiconductor losses were evaluated, and the thermal analysis was performed on the power stages.
- The overall layout for the integrated 50-kW prototype was completed.

Conclusions, Challenges, and Future Work

Conclusions:

- Developed distributed hardware, control, and optimizing system to support multiple chemistries and ages for secondary use.
- Completed the hardware-in-the loop platform with the system models and control hardware in a real-time platform and validated the control architecture.

Future Work:

- Development of hardware prototypes.
- Integration of the ESS software interface with the HIL platform
- Run Sandia/PNNL use cases to demonstrate optimization and controls in systems is functional.

Acknowledgements

This work was funded by the Department of Energy, Office of Electricity, Energy Storage Program.

Publications

- M. T. Smith, M. R. Starke, M. Chinthavali, L. M. Tolbert, "Architecture for Utility-Scale Multi-Chemistry Battery Energy Storage," in *IEEE Energy Conversion Congress and Exposition*, Baltimore, MD, 2019.

Residential deployment of a secondary use energy storage system

Michael Starke, Madhu Chinthavali, Zeng Rong, Zheng Sheng, Steven Campbell, Mitch Smith, Ben Dean
Oak Ridge National Laboratory

Objective

- Develop and deploy a secondary use energy storage system in collaboration with Habitat for Humanity.
- Examine use cases and evaluate potential economic savings.

Approach

- Secondary-Use Battery System
- ORNL provided power electronic conversion system and supporting integration software to run use cases and integrate energy storage technology.
- Spiers New Technologies provided battery
- Habitat for Humanity provided site location and site preparation.

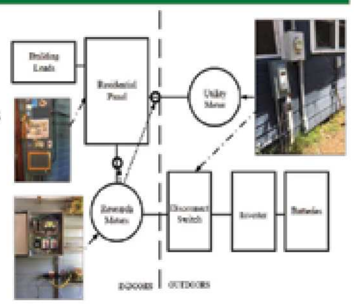


Figure 1. Installation Configuration at Site

- Behind the Meter use case: Behind the meter use cases were evaluated. Utility meters are limited to single directional service to reduce surge of photovoltaic installations behind the meter.

TABLE I. Utility rate structure use case [12]

Rate Name	Rates
SINGLE-PHASE TIME-OF-USE SERVICE	$0.4641 per kWh on-peak $0.0546 per kWh off-peak
• For the period April 16 through October 15, the on-peak hours shall be the hours between 3:00 p.m. and 6:00 p.m., Monday through Friday, excluding holidays are considered off-peak • For the period October 16 through April 15, the on-peak hours shall be the hours between 6:00 a.m. to 8:00 a.m., Monday through Friday, excluding holidays considered off-peak.	

TABLE II. Utility traditional tiered flat energy rate structure [12]

Rate Name	Rates
SINGLE-PHASE	Summer Months First 3,000 kWh @ 11.61 ¢ per kWh Over 3,000 kWh @ 11.03 ¢ per kWh Winter Months First 1,000 kWh @ 11.15 ¢ per kWh Next 2,000 kWh @ 10.51 ¢ per kWh Over 3,000 kWh @ 9.25 ¢ per kWh

Figure 2. Rate structures available

- Communication Setup: The communication infrastructure was setup to support closed loop control and elimination of load during critical peak hours.

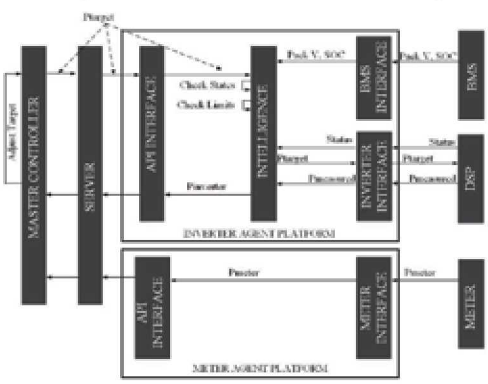


Figure 3. Software – Agent System Architecture

Figure 4. Energy Storage System

Results

- Preliminary Laboratory testing and evaluation on hardware for economic evaluation. Utilized load developed baseline curves to examine load changes and optimal potential.
- Communication delays lead to small transient signatures in energy pushed back. Most of the energy is negated to a zero-net flow.

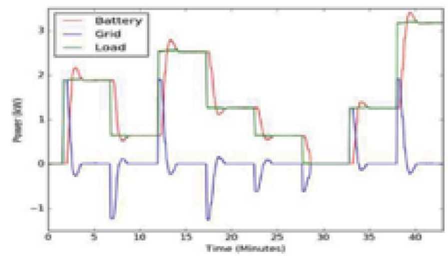


Figure 5. Closed loop control example to cancel load

- Economic comparison of total energy consumption between rate structures shows that the energy storage will not induce significant losses due to overall 90% efficiency.
- Energy storage can save money through 2 factors:
  - Eliminate load during critical peak
  - Electricity price is half of traditional during non-peak.

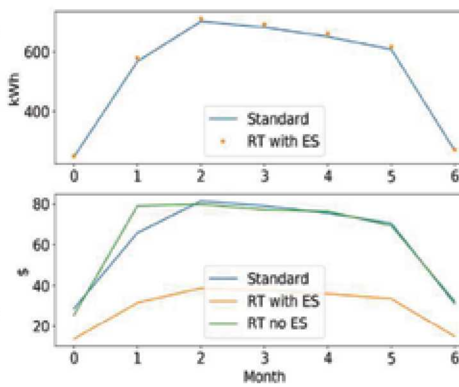


Figure 6. Economic Comparison

Conclusions, Challenges, and Future Work

- Conclusions:
  - A secondary use energy storage system has been deployed and is still undergoing evaluation.
  - The utilization of a secondary use energy storage system for behind the meter applications has significant economic potential however challenges exist.
- Challenges:
  - Utilities are not providing opportunities to do bi-directional metering. This is to spur off large investments on behind the meter resources.
  - Use cases require additional infrastructure to support cost reduction.
- Future Work:
  - Discuss possibility of licensing of Spiers New Technologies with ORNL.
  - Data review at site.

Acknowledgements

This work was funded by the Department of Energy, Office of Electricity, Energy Storage Program.

Publications

- Michael Starke, Madhu Chinthavali, Zeng Rong, Zheng Sheng, Steven Campbell, Mitch Smith, Ben Dean, Residential (secondary use batteries based) energy storage system with modular software and hardware power electronic interfaces, Energy Conversion Congress and Expo, 2019
- M. Starke, M. Chinthavali, B. Taube, D. Spiers, B. Schultz, "Secondary Use Energy Storage System Design Considerations, TechConnect 2019.
- M. Starke, R. Zeng, S. Zheng, M. Smith, M. Chinthavali, Z. Wang, B. Dean, L.M. Tolbert, "A Multi-Agent System Concept for Rapid Energy Storage Development," IEEE Innovative Smart Grid Technologies, 2019.

Engineering Routes Towards Synthesis and Performance of Layered Oxide Cathode Materials for Sodium-ion Batteries

Mengya Li, Yaocai Bai, Rachid Essehli, Ruhul Amin, Ilias Belharouak, Jianlin Li, David L. Wood III

Energy and Transportation Science Division, Oak Ridge National Laboratory, Knoxville, TN 37932

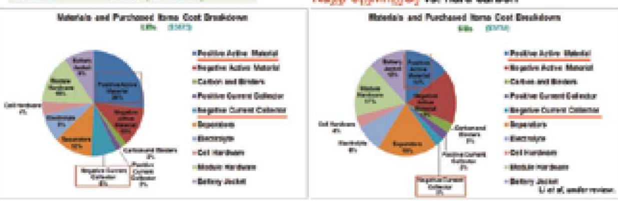
Office of Electricity

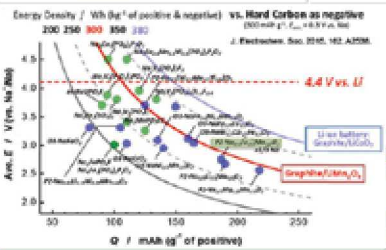
Background

- Li-ion vs. Na-ion batteries

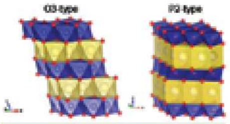
	Abundance in earth crust (ppm)
Lithium	20 (ranked 32nd)
Sodium	27500 (ranked 6th)

For cost analysis (53 kWh battery pack)
- Li-ion Batteries (LIBs): NMC622 vs. graphite
- Na-ion Batteries (SIBs): $Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ vs. hard carbon





Atomic structure matters



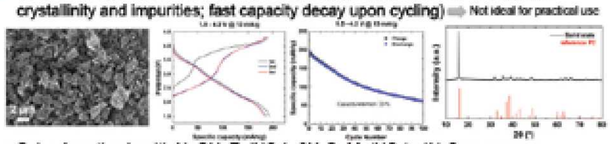
	O3	P2
C-spacing	large	small
Stability upon charge/discharge	low	high
Voltage	high	low
Cell capacity	low	high

Project Goals

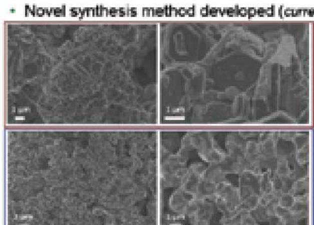
- Develop novel synthesis of low-cost, high-performance cathode material for SIBs.
- Reduce material and electrode processing cost and achieve ≤\$100/kWh for battery grid storage.
- Validate a practical, reliable and safe SIB system.

P2-type $Na_xFe_{1/2}Mn_{1/2}O_2$ cathode

- Solid-state synthesis with two-step annealing (Energy-intensive mixing; Low crystallinity and impurities; fast capacity decay upon cycling) ⇒ Not ideal for practical use



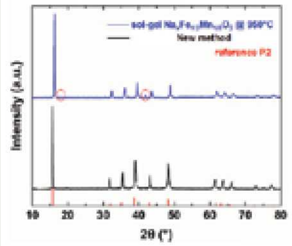
- Sol-gel synthesis with NaOH, $Fe(NO_3)_3\cdot 9H_2O$, $Mn(NO_3)_2\cdot 4H_2O$ precursors
- Novel synthesis method developed (*currently under invention disclosure submission*)



Materials synthesized by sol-gel vs. novel method:
- Sol-gel method: aggregated particles with inhomogeneous size distribution.
- New method: small particles with improved homogeneity.
- With the new method, scalable production can be achieved to ~100 g per batch synthesis.

Crystallinity and impurity level

- X-ray diffraction (XRD) results



- Inductively coupled plasma optical emission spectrometry (ICP-OES) results

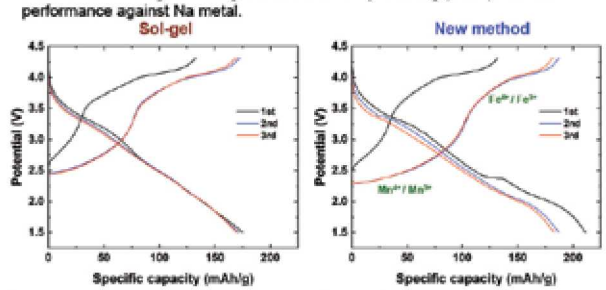
Composition table of P2-$Na_xFe_yMn_{1-y}O_2$

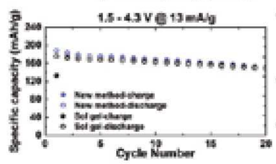
Synthesis method	Na (x)	Fe (y)	Mn (1-y)
Sol-gel	0.71	0.48	0.52
New method	0.56	0.50	0.50

- From XRD:
  - Better crystallinity and less impurities in the final product synthesized by new method
- From ICP:
  - Slightly low Na content for product synthesized by new method

Electrochemical performance

- Galvanostatic charge/discharge at current density 13 mA/g (0.1 C) for half cell performance against Na metal.

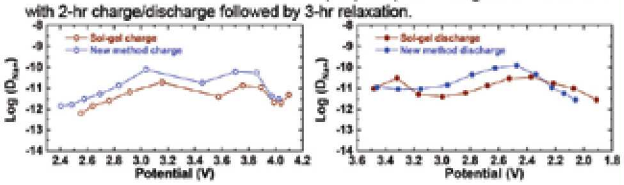




- Initial reversible capacities for P2-$Na_xFe_{1/2}Mn_{1/2}O_2$ synthesized by these two methods are 172 and 187 mAh/g.
- Improved Mn^{4+}/Mn^{3+} redox was observed by switching to new synthesis method.
- Despite the higher initial reversible capacity, cycling performances did not show much difference (capacity retention: 75%).

Kinetic studies of Na-ion diffusion

- Galvanostatic Intermittent Titration Technique (GITT) at 13 mA/g between 1.5-4.3 V with 2-hr charge/discharge followed by 3-hr relaxation.

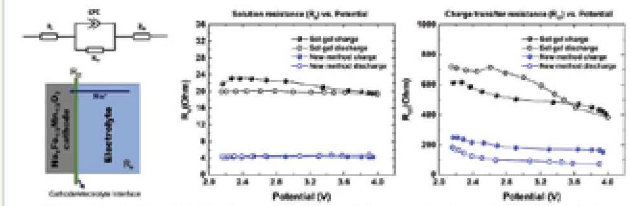


- Higher Na^+ diffusion coefficient observed in P2-cathode synthesized by new method based on Fick's 2nd law of diffusion:

$$D = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2\left(\frac{\Delta E_s}{\Delta E_t}\right)^2$$

m_B: mass of the cathode; V_M: molar volume; M_B: molar mass of the cathode; S: surface area of electrode disk.

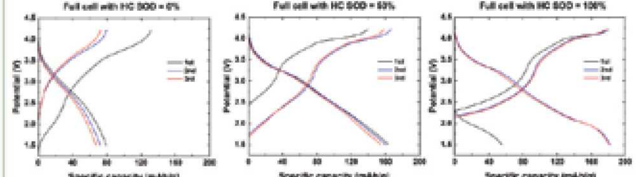
Electrochemical Impedance Spectroscopy



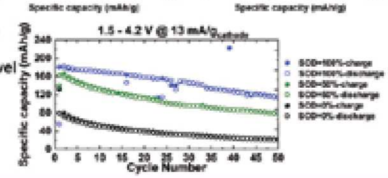
- Higher electrolyte stability, lower solution resistance and charge-transfer resistance observed for P2-cathode synthesized by new method upon charge/discharge.

Routes to improve cycling performance

- Full cells assembled with P2-$Na_xFe_{1/2}Mn_{1/2}O_2$ cathode synthesized by new method and a hard carbon anode (250 mAh/g capacity delivered in half cell @ 0.1 C).



- Full cells against hard carbon anode pre-sodiated with different state of discharge level (SOD) are tested.
- For HC with SOC=100%, full cell capacity retention was improved with achieved 203 Wh/kg based on chemistry.



Summary

Milestone achievement
- Milestone 1: Develop novel synthesis method for low-cost P2-type $Na_xFe_{1/2}Mn_{1/2}O_2$ cathode with capability of scaling up to 50g per batch. ✓
- Milestone 2: Optimize capacity and cycling performance of P2-type cathode in sodium full-cells. ✓
- Milestone 3: Assemble 1.5-Ah pouch cell and obtain 500 cycles at 2C/-2C. Ongoing

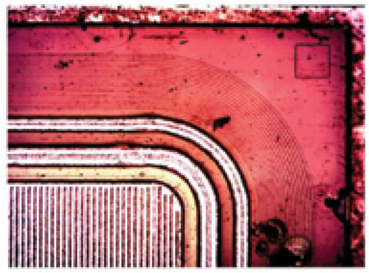
Information dissemination
- Presented at Oak Ridge Postdoctoral Association 7th Annual Research Symposium and won judges' choice best poster award.
- Presented at DOE Na-ion Workshop at PNNL on Aug 27th, 2019.
- Invention disclosure submitted on the novel synthesis method of P2-cathode.

Acknowledgement

- This work is supported by DOE Office of Electricity (Dr. Imre Gyuk, Director of Energy Storage Research).
- The authors would also like to thank Michael Starke and Tom King of ORNL for their technical and programmatic support.

U.S. DEPARTMENT OF ENERGY | Sandia National Laboratories | THE OHIO STATE UNIVERSITY | HPPE | GeneSiC SEMICONDUCTOR






Medium-voltage Power Electronics for Grid-tied Energy Storage Applications

Diang Xing, Boxue Hu, Dr. Kristen Booth, Dr. Jin Wang, Dr. Anant Agarwal, and Dr. Stanley Atcitty

PROJECT OBJECTIVES

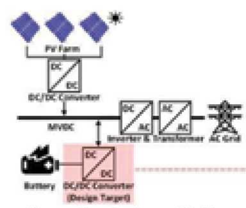
Storage integration with the grid is increasingly important due to an upward trend in use of renewable sources of energy. Compared with the traditional silicon-based power system designs, the designs based on wide bandgap (WBG) devices have shown improved performance for high-voltage, high-power density, and high-switching frequency applications due to material properties.

This project aims to build a power electronic converter with medium-voltage SiC devices for energy storage systems in a medium-voltage distribution grid.

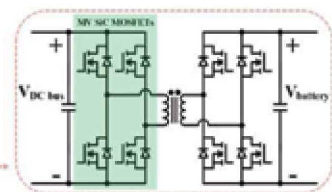
Key Milestones:

- Year 1: Gate drive and auxiliary power supply design for medium-voltage SiC devices. [Finished]
- Year 2: Medium-voltage discrete SiC device evaluation and modeling.
- Year 3: Power module fabrication and DC/DC converter development.

PROPOSED SOLUTION



PV Energy Harvesting System with Storage

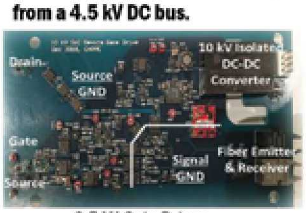


Proposed DC-DC Converter Design

- Implementation with medium-voltage DC bus simplifies the system structure and increases the efficiency of the energy storage system,
- Application of medium-voltage SiC devices increases power density and reduces power loss of the DC/DC converter, and
- High switching frequency of SiC devices leads to fast dynamic response and low current ripple which improves the stability and power quality of the power grid and increases the lifespan of the battery.

MV GATE DRIVER & AUXILARY POWER SUPPLY

A 6.5 kV-rated gate driver with a 10 W self-sustaining auxiliary power supply was developed. This driver can provide high performance power conversion from a 4.5 kV DC bus.



6.5 kV Gate Driver

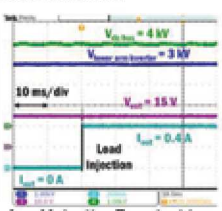
Output Voltage	+18 V / -4 V
Source/Sink Currents	9 A / 9 A
Insulation Voltage	6.5 kV
CMTI	200 kV / µs
Functions	Overvoltage Protection Overcurrent Protection Soft-off During Fault Optical Diagnostics

Gate Driver Profile

4.5 kV Auxiliary Power Supply

Input Voltage	3 to 4.5 kV
Output Voltage	15 V
Max Output Power	10 W
Board Size	152 x 188 (mm)

Auxiliary Power Supply Profile

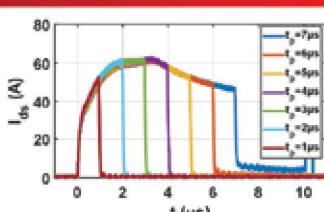


Load Injection Transient in Auxiliary Power Supply

GENESIC 3.3 KV SIC MOSFET EVALUATIONS

Short-circuit Test:

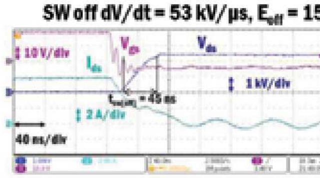
- Test condition: V_{dc} = 2.2 kV, V_{gs} = 18 V, room temperature.
- Maximum short circuit sustaining time = 7 µs.
- Gate driver desaturation protection time <= 1 µs.



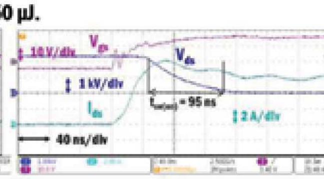
Device Short Circuit Current

Double-pulse Test:

- Test condition: V_{dc} = 2.4 kV, V_{gs} = -4 V (off) & 18 V (on), room temperature.
- SW on dV/dt = 25 kV/µs, E_{on} = 850 µJ;
  SW off dV/dt = 53 kV/µs, E_{off} = 150 µJ.



Device Switches On (2.4 kV 6 A)



Device Switches Off (2.4 kV 6 A)

Funding support from Office of Electricity Energy Storage Program and Dr. Imre Gyuk is gratefully acknowledged.

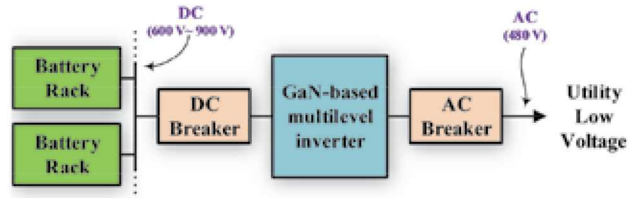
SAND2019-11070 PE Sept. 2019

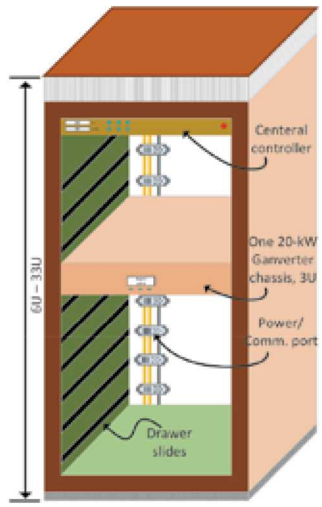
SAND Number: SAND2019-10982 PE

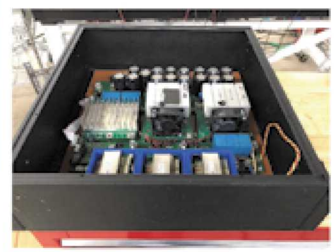
Smart GaN-Based Inverters for Grid-Tied Energy Storage Systems

InnoCit
Innovation City, Power and Energy Solutions

DOE/OE Energy Storage Peer Review 2019







Introduction

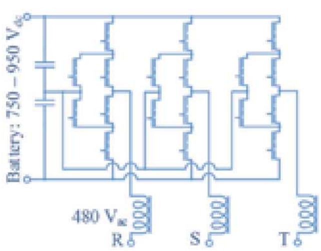
- Energy storage systems and high-power bidirectional converters are the backbone of the future grid.
- Si technology has relatively high conduction losses compared to wide bandgap switches.
- GaN switches can operate at higher switching frequencies.
- By 2022, over 40 GW of energy storage systems will be installed in grid-connected applications.

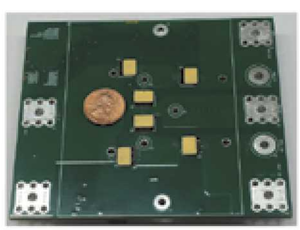
In this project, a GaN-based multilevel inverter is proposed for energy storage applications. This converter interfaces standard battery storage packs. These storage packs have a nominal voltage of 850V to 900V and can reach a low level of 600V under depleted conditions. Hence, a multilevel inverter is proposed to convert this range of input voltage to a 480V grid-tied output. The proposed converter is modular and can ragne from 20 kW to 200 kW.

Technical Approach

A neutral-point clamped multilevel inverter is selected to realize a 20-kW bidirectional inverter module. Then overall inverter is comprised of 1 to 10 modules working in parallel.

- The converter will emulate the natural dampening behavior of droop controllers.
- By adding virtual rotating mass dynamics to the control algorithm, overall inverter will appear as a synchronous generator and can participate in stabilization of the local grid.
- Stacked printed circuit boards (PCB) which include surface mount GaN switches will be used to maximize modularity and reduce the manufacturing cost.





Specific Objectives

- Designing 3U rack-chassis-based enclosures for inverter modules
- Conduct thermal analysis on the enclosures
- Controls and hardware for hot-swap capabilities
- Validate final metrics: efficiency of at least 98.6%, weight < 2.2 lb./kW, volume <0.1 ft^3/kW, noise <45 dBa
- Reliability testing including active bypass and hot-swap features
- IEEE 1547 and UL 1741 and 1741-SA testing for islanding, fault ride-through, …
- UL certification testing
- Remote control and monitoring backbone structure development

Contact Information

- Mehdi Ferdowsi, CEO
  14790 State Route B
  St. James, MO 65559
  ferdowsi@innocit.com
  312-399-7160

Pourya Shamsi, CTO
14790 State Route B
St. James, MO 65559
shamsi@innocit.com
817-832-3128

Acknowledgement

- InnoCit greatly appreciates support of Dr. Imre Gyuk and Dr. Stan Atcitty through DOE SBIR grant DE-SC0013818.

SAND Number: SAND2019-10982 PE

Predicting Reliability, Improving Safety and Resiliency in Grid Connected Battery Energy Storage Systems

University of Houston

Kaushik Rajashekara, Harish Krishnamoorthy, Stanley Atcitty

(Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. SAND2019-11071 PE.)

Sandia National Laboratories

I. Background and Objectives

- Energy storage deployments will grow 10-fold over the next 5 years.
- High string voltage affects both the potential for shock and the potential for arc-flash/blast [Sandia, 2015] – major concern at high penetration.
- Hence, objectives of this project are:
  - Investigate modular, transformer-less multilevel inverter topologies for grid connected battery energy storage systems (BESS).
  - Explore self – battery management system (BMS) and state of charge (SoC) balancing methods for battery/inverter modules interfaced to the grid to improve BESS flexibility as well as reliability.
  - Implement hardware test set-up to analyze device behavior (SiC MOSFET, battery, etc.) under different operating conditions.
  - Study Li-ion battery characteristics and fault tolerant operation through the interfacing converters and assess BESS resiliency.
  - Evaluate the component-level remaining useful life (RUL) index for SiC-FET and Li-ion batteries; then predict the system-level RUL for grid connected modular BES converter system through analytics.

Year	Milestones	Deliverables	Target
Year 1 (Done)	Develop a self – BMS and improved SoC balancing schemes for split battery architecture using Cascaded H-Bridge and Modular Multilevel Converters	A single phase 1 kW laboratory scale hardware prototype using cascaded H-bridge converter to verify the proposed SoC balancing scheme	More than 50 % improvement in rate of SoC balancing using rated current operation compared to UPF operation
Year II (Ongoing)	Evaluate characteristics of Li-ion batteries for changes in internal impedance, capacity degradation, etc., due to effect of variations in depth of discharge, temperature, etc.	Characterization data of Li-ion batteries for BESS applications, with experimental profile	Identify key model parameters to implement component level reliability algorithm for Li-ion batteries
Year III (Upcoming)	Propose component -level reliability prediction algorithm to evaluate RUL of power devices and batteries, and to develop an integrated approach for predicting the BESS reliability.	Prediction algorithm to evaluate RUL of power devices and batteries for safe operation of BESS and model for overall reliability assessment.	Analytical capability of BESS RUL estimation with a prediction error of less than 500 hours

II. SOC Balancing Method

- For long life and reliable operation of BESS, the SoCs of battery modules need to be equalized through BMS.

❑ **We propose a self – BMS to perform SoC balancing among the battery modules using current controlled operation of cascaded H-bridge (CHB) interfacing converter.**

- Performs fast SoC balancing by operating the converter at rated current irrespective of the amount of power flow.
- Power transfer from a higher SoC battery module to a lower SoC battery module is achieved without compromising the amount of power flow among the BESS and the grid.

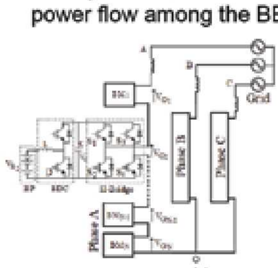


Figure (1)

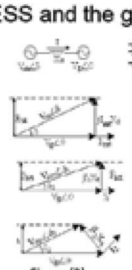


Figure (2)

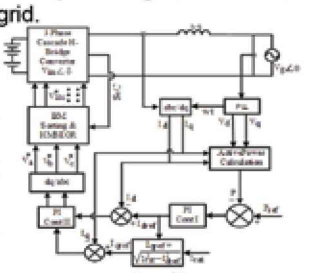


Figure (3)

Figure (1). Three-phase CHBC connected to the grid.

Figure (2). (a) Single line diagram of CHBC-grid system, (b) Rated power operation at UPF, (c) Actual power operation at UPF, (d) Actual power operation at rated current.

Figure (3). Block diagram implementing rated current operation of CHBC.

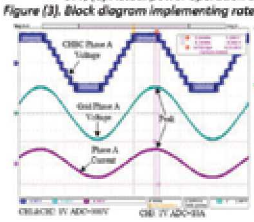


Figure (4)

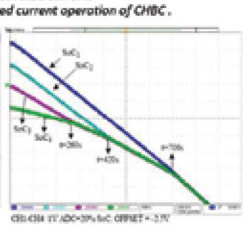


Figure (5)

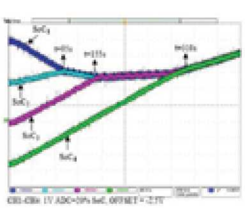


Figure (6)

Figure (4). Waveforms of CHBC voltage, grid voltage, and line current during 100kW power transfer from BESS to the grid at rated current operation

Figure (5). Variation of SoCs of the four BPs during 100kW power transfer from BESS to the grid at rated current operation.

Figure (6). Variation of SoCs of the four BPs during 50kW power transfer from the grid to BESS at rated current operation.

III. RUL Prediction for Li-ion Battery

- RUL prediction is critical to the implementation of condition based maintenance (CBM) and prognostics and health management (PHM) for battery system.
- A Particle Filter (PF) based algorithm for predicting the RUL of Li-ion battery to interface with converters for the safe operation of BESS is implemented.
- The estimated capacity of Li-ion battery is considered as the health condition indicator of Li-ion battery and used as the input of PF algorithm to predict the RUL of battery.

❑ **RUL estimation algorithm predicts the time to failure of BESS with certain probability to avoid unscheduled downtime.**

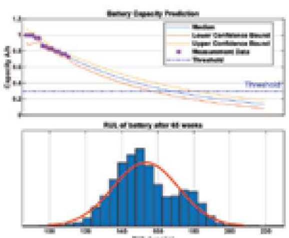


Figure (8)

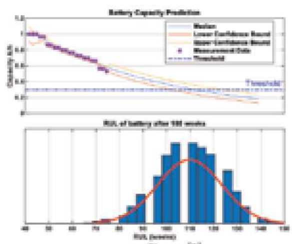


Figure (9)

Figure (8).The RUL distribution after the usage of battery for 65 weeks

Figure (9). The RUL distribution after the usage of battery for 105 weeks

IV. Ongoing Work – Hardware Evaluation

- Online SoC estimation through open circuit battery voltage calculation.
- Building hardware setup to implement rated current operation of CHB converter to perform SoC balancing among battery modules.

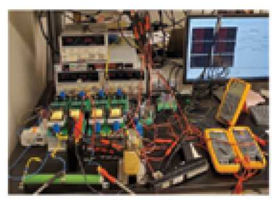


Figure (10)

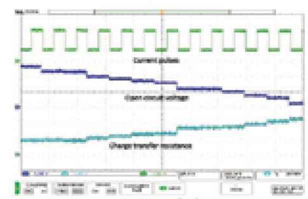


Figure (11)

Figure (10). Hardware set up for open circuit voltage calculation of a BM

Figure (11). The Waveform of open circuit voltage and charge transfer resistance of a BM.

V. Conclusion and Future Work

- Conventional battery systems use dedicated BMS for cell SoC balancing and module level balancing, which adds cost and control complexity. This can further affect the life of battery modules.
- Further, there is no existing technique to precisely predict the RUL of BESS, including the batteries and the power converters.
- In this project, we proposed a fast SoC balancing scheme with a self-BMS using interfacing modular converters for grid integration.
- We were able to achieve a **66 %** improvement in the rate of SoC balancing using rated current operation, when compared with conventional UPF operation at half the system power exchange.
- A 1 kW, 5-level hardware prototype is being set-up to implement the rated current operation for SoC balancing among BMs.
- A system-level health monitoring algorithm is being developed to predict BESS RUL with an error of less than **500 Hrs**. in about 20 years.

ACKNOWLEDGEMENT: The investigators gratefully acknowledge support for this work from *Dr. Imre Gyuk* and the Office of Electricity at U.S. DOE.

List of Publications from this project:

[1] Amir Hussain, Krishna Raj, Kaushik Rajashekara, Harish Krishnamoorthy, and Stanley Atcitty, "Minimum Voltage Operation of Cascaded H-Bridge Converter for Fast SoC Balancing in Grid Energy Storage," accepted for presentation at ECCE 2019 - Baltimore, MD.

[2] Amir Hussain, Krishna Raj, Kaushik Rajashekara, Harish Krishnamoorthy, and Stanley Atcitty, "A Voltage Droop Based SoC Control for Split Batteries in Modular Multilevel Converter for Grid Energy Storage Interface," accepted for presentation at IEEE IAS Annual Meeting 2019 - Baltimore, Maryland.

INDUSTRY ACCEPTANCE:

DEMONSTRATIONS

The DOE OE Energy Storage power electronics thrust area advances power conversion systems (PCS) for grid-tied and off-grid applications. This is driven by the development of new semiconductor switching circuits, as they determine the overall cost, reliability, and performance of the converter. Next generation PCS use advanced semiconductor materials known as wide band gap semiconductors (i.e. Silicon Carbide and Gallium Nitride) that allow for faster switching frequencies, improved voltage breakdown characteristics, and higher operating temperatures.

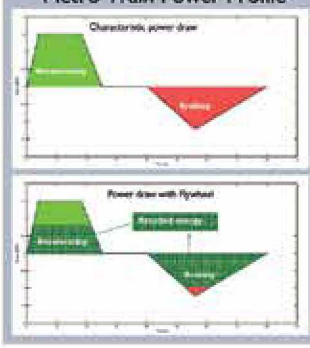
STRATEGIC OUTREACH

Sandia collects key information on current and future storage technologies and acts as a clearinghouse for the information so that it can be effectively disseminated among key stakeholders and the community. Outreach activities include conducting strategic communication initiatives, managing the Energy Storage Systems website, improving the DOE Global Energy Storage Database, updating the DOE Energy Storage Handbook, and organizing the Peer Review meeting and formerly the Electrical Energy Storage Applications and Technologies International Conference.

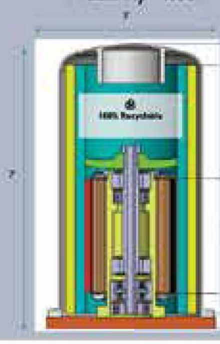
Helix Power: Technical Challenges for Energy Storage in Metro Rail Applications

Application: Metro train application is challenging due to MW+ power levels, short duration, high cycles, and space constraints.

Metro Train Power Profile

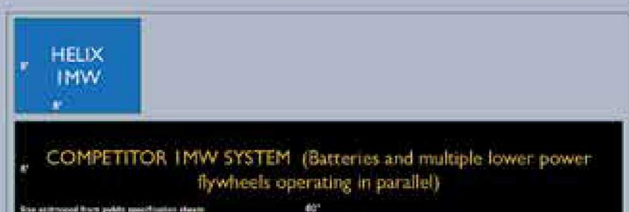


Helix Flywheel



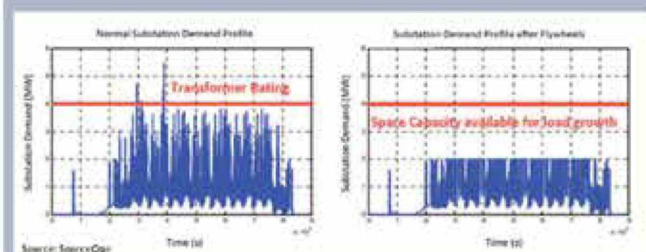
Technical specification: Meeting the technical specification drives the economics as fewer units are required.

Form factor comparison: Compact form factor is required for realistic systemwide deployment of the technology.



A systemwide wayside deployment with metro systems requires the ability to retrofit in space constrained areas.

Substation impact: Each 1MW unit has the potential to reduce peak demand at rush hour up to 500kW.

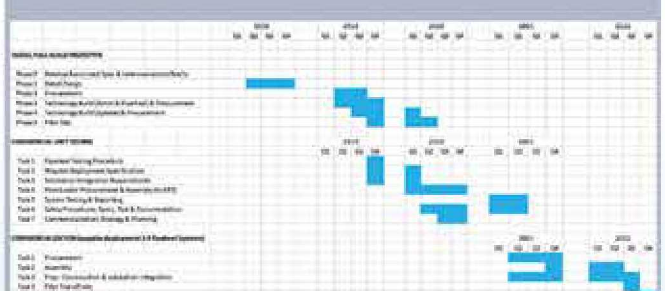


Metro train peak reductions will free substation capacity in urban areas.

Benefit summary: Flywheel energy storage has the potential to reduce metro train energy use by 35% (energy captured during braking can support 30-50% of the energy required for acceleration).* These benefits have not been realized to date because of the technical difficulty meeting the requirements of the application.

BENEFIT	BENEFIT PER 1 MW UNIT
Energy Savings	$200,000/year
Peak Demand Reduction	Up to 500kW
Greenhouse Gas Reductions	800 tons/year per unit
Substation Benefits	$667,000 - $1,000,000
Projected Payback Period	1-5 years**
Projected IRR	18-70%**

Path to commercialization: Helix Power plans to run a pilot test in 2020, a commercial unit test in 2021, and begin wayside deployment in 2022.



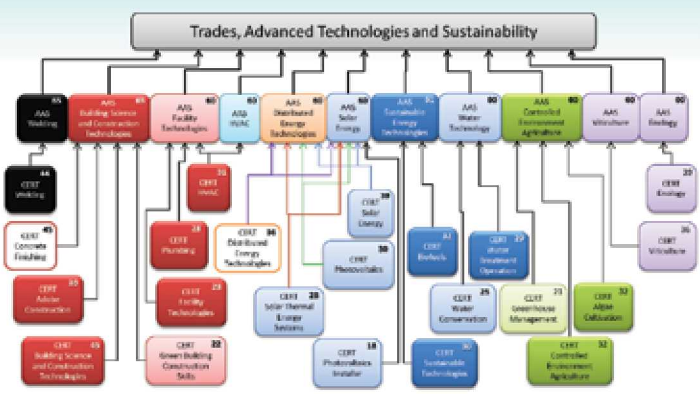
Sandia National Laboratories

The BEAM Training Center at Santa Fe Community College

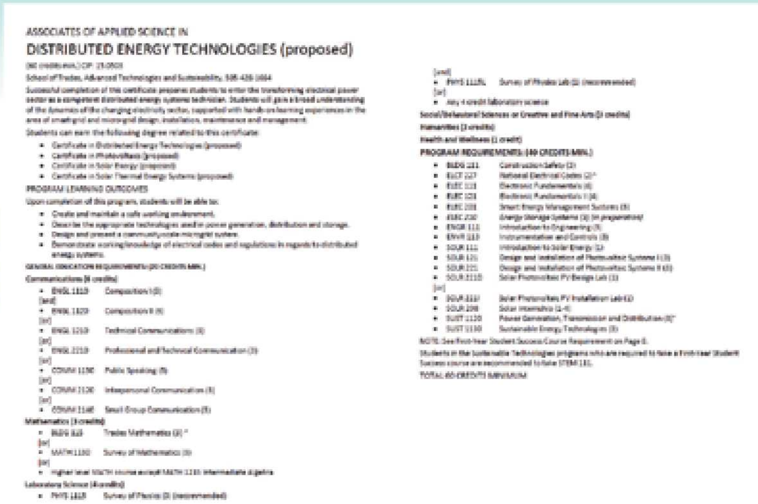
Stephen Gómez[1], Bill Kipnis[2], Frank Currie[3], Luke Spangenburg[1], Ondine Frauenglass[1], and Camilla Bustamante[1]

1 – Santa Fe Community College; 2 – Siemens; 3 – Sandia National Laboratories

Santa Fe Community College (SFCC) is an emerging leader in the implementation of distributed energy generation and in the development and delivery of educational and training programs to prepare students for coming changes in the energy sector. SFCC is currently implementing the Building Energy Automation and Microgrid (BEAM) Training Center partially funded through a grant from the U.S. Economic Development Administration. Support from NSF/NM-EPSCoR New Mexico SMART Grid Center is funding a faculty position to create degree programs to train students in installation, commissioning, data collection, and integration of clean energy assets and energy storage systems into operational microgrids.



Reorganization of Trades, Advanced Technology, and Sustainability Department to accommodate new Distributed Energy Technologies degree and certificates



ASSOCIATES OF APPLIED SCIENCE IN

DISTRIBUTED ENERGY TECHNOLOGIES (proposed)

PROGRAM REQUIREMENTS

Proposed catalog entry for AAS in Distributed Energy Technologies.

The new faculty member will oversee the BEAM-TC consisting of two student training centers offering the first community college curriculum providing students with a comprehensive energy education.

- New Faculty hire — October 2019
- 1st Training Center - B.E.S.T. Laboratory
  - a new program supported by the National Science Foundation. It consists of HVAC equipment and automation hardware and software.
- 2nd Training Center - 11,000 ft^2 aquaponics greenhouse "nanogrid"
  - powered by natural/bio-/syn-gas, solar PV, and biofuels
  - nested within the campus microgrid
  - managed with a METASYS building automation system in combination with a Siemens microgrid management system.

Once the SFCC microgrid is operational, it will serve as integral training tool in the BEAM Training Center and will include energy storage curricula developed in cooperation with Sandia National Laboratories

This project is supported by EDA BEAMTC Grant #: 08-01-05191, the National Science Foundation EPSCoR Program under Award #OIA-1757207 and in-kind contributions from Siemens Industry

New Mexico EPSCoR SIEMENS Ingenuity for life NNSA National Nuclear Security Administration

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

The Nanogrid at Santa Fe Community College

Stephen Gómez[1], Henry Mignardot[1], Luke Spangenburg[1], Bill Kipnis[2], Frank Currie[3], Nazar Al-Khayat[2], and Dan Borneo[3]

1 – Santa Fe Community College; 2 – Siemens; 3 – Sandia National Laboratories

SFCC CONTROL ENVIRONMENT AGRICULTURE

The SFCC Microgrid Has Four Distinct Purposes:

1. Utility and operations cost savings
2. Resiliency from power interruptions and outages
3. Islanding from the utility grid
4. Student Education

Santa Fe Community College (SFCC), Sandia National Laboratory (SNL), and Siemens are leading the effort in the development, design, installation, and commissioning of a microgrid system for the operation of a 11,000 ft^2 aquaponics greenhouse ("the nanogrid"). The Production Greenhouse is powered by campus alternative power systems including: solar PV, solar thermal, and natural gas/biogas/pyrolysis gas; in addition, using reclaimed wastewater and biodigester compost for growing media.

- The DOE-Office of Electricity provided partial funding, managed by SNL, to provide a permanent battery energy storage system.
- The nanogrid will operate, *and be nested within* the campus microgrid, with the both microgrids capable of bi-directional power management.
- The purpose is to demonstrate resiliency in food production, critical load protection, and peak shaving to reduce energy demand charges.
- There is no intention to export power to the grid from the battery.
- SFCC Plant and Operations staff will manage campus utilities using a METASYS building automation system in combination with a Siemens microgrid management system.
- SFCC will provide a framework to facilitate DOE-OE/SNL projects in the context of its energy storage test bed.

Summary of Microgrid Energy Savings

	Current Electric Usage		After Microgrid		Usage Savings	
	Billed Demand	Energy	Billed Demand	Energy	Billed Demand	Energy
Month	kW	kWh	kW	kWh	kW	kWh
January	944	276,787	500	231,395	444	45,393
February	1,062	260,461	500	218,129	532	42,332
March	983	245,769	500	218,149	483	27,640
April	944	276,264	500	217,266	444	58,998
May	947	256,535	500	226,426	447	30,509
June	1,082	302,992	500	260,570	582	42,321
July	1,080	322,778	500	278,577	580	44,201
August	1,012	300,650	500	248,487	512	52,969
September	1,122	297,697	500	248,291	622	49,406
October	1,074	284,213	500	246,697	574	37,516
November	1,026	294,600	500	239,444	526	55,156
December	980	270,326	500	231,230	480	39,096
Total	12,133	3,400,992	6,000	2,892,655	**6,133**	**509,737**
	Current Total Cost		Cost After Microgrid		Total Electric	After 80%
Total	Demand	Energy	Demand	Energy	Savings	Safety Factor
Charges	$ 226,573	$ 153,156	$ 113,254	$ 125,843	$140,633	$114,906
					Annual Fuel Cost	With Safety Factor
					(326,760)	(332,118)
					Net Savings	**$82,788**

The new 11,000 ft^2 greenhouse will be powered by a nanogrid—a smaller microgrid nested within the full campus microgrid. The nanogrid will be capable of providing and receiving power from the campus microgrid

Scenarios

One : Power Interruption

- Solar PV is disconnected from the SFCC grid for protection purposes.
- The BESS is signaled to smoothly provide power within milli-seconds of the interruption.
- Solar PV or natural gas generator are dispatched to provide power to meet the campus load.
- In response to a prolonged power interruption, MGMS may disconnect parts of the campus load determined in advance to be non-critical.

Two: Operating the Microgrid in Low Greenhouse Emissions Mode

- SFCC operators change operating from "low cost" mode to "low emissions" mode.
- MGMS is programmed with the data on PNM's resource mix of coal, wind, etc.
- MGMS evaluates on campus solar and BESS availability, and campus load.
- MGMS determines that the campus natural gas generator creates lower emissions per kW than the utility.
- MGMS operates the campus in islanding mode, or to minimize utility power, subject to meeting the load requirements.

This project is supported by National Technology and Engineering Solutions of Sandia, LLC subcontract 1981686,0, EDA BEAMTC Grant #: 08-01-05191, and in-kind contributions from Siemens Industry

SIEMENS *Ingenuity for life*

NNSA National Nuclear Security Administration

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

Sandia National Laboratories

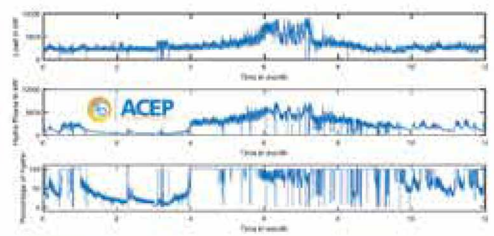
Exceptional service in the national interest

Applications that Reduce the Use of Diesel Gensets

Sponsored by: Dr. Imre Gyuk,
Director of Energy Storage Research, Department of Energy Office of Electricity

Background:
- Cordova Electric Cooperative owns and operates an islanded microgrid.
- 18 Megawatts of total generation capacity
- One diesel plant, 2 run-of-river hydroelectric projects - no storage!
- Deflect 750kW of hydro for frequency control.
- Growing seafood industry requiring more energy.
- Cordova Electric Cooperative achieves 100% hydro generation, 60% of the time.
- Goal: 100% renewable

Cordova, AK
- 60°32' 37" N 145°45 '07" W
- Population: 2500 / 5000 (Winter / Summer)
- Total hydro capacity: 7.25 MW
- Total diesel capacity: 11 MW
- 2017 Residential power rate: $/kWh 0.3735



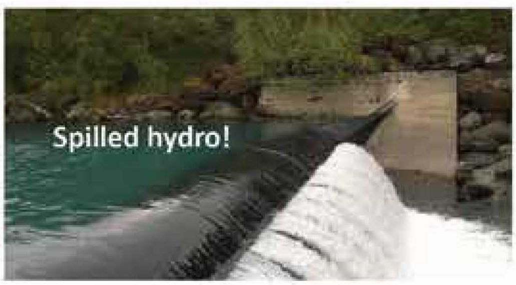
Problem:
- Water not immediately utilized for generation is spilled.
- Spilled hydro = 3-4 gWh per year!

Solution:
- Demand management- utilize hydro when its available.
- Power to Heat- heating community swimming pool and power house "keep warm" boilers used to allow quick starting large diesel generators.
- Utilize excess hydro to charge grid-scale battery.

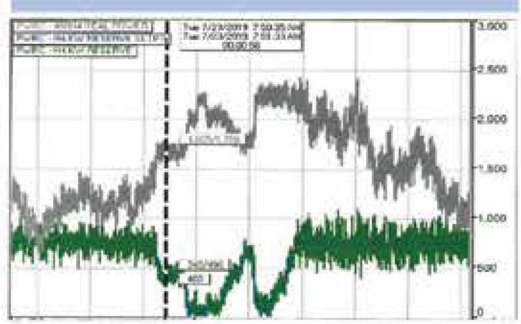
Spinning Reserve:
- Cordova Electric maintains 750kW spinning reserve for sudden load changes.
- Spinning reserve is maintained either by diesel or hydro.

The Spinning Reserve Problem:
Once below 750 kW of available spinning reserve on a hydro plant, a diesel engine is started and base loaded to 400 kW. This 400 kW is "removed" from the hydro and transferred to the diesel thereby leaving 1150 kW of unused hydro.

Solution:
- Utilize grid scale battery to control spinning reserve and system frequency.
- Charge battery during times of excess hydro.

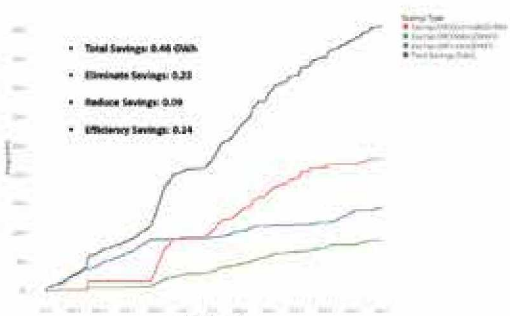


Solution:
- Balance the CEC Grid with lithium-ion Battery Energy Storage System (BESS) and strategically charge/discharge to maximize diesel fuel savings
- CEC has commissioned and operated the CEC BESS in isoc (as the prime mover) on the CEC grid, maximize hydro and go "diesel off" for a full day (July/Sep 2019)

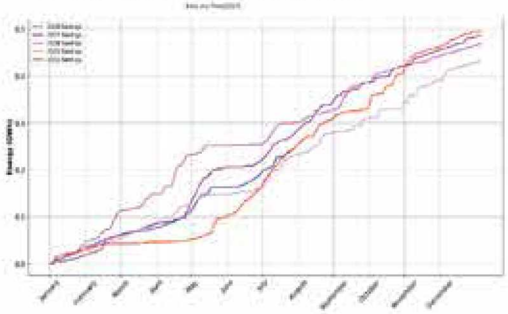


Additional Benefits:
A Battery Energy Storage Solution will deliver additional benefits such as emergency power to critical loads (hospital), charge and discharge arbitrage between $0.06/kWh hydro and $0.37/kWh diesel, reduce diesel start and stops.

Multifaceted Benefits:
- A grid scale battery opens the door for solar, which is currently being assessed and strongly considered with our partners.
- Liberate 500kW of hydro rather than deflecting.
- Improve diesel efficiency
- Allow more diesel-off conditions



Project Champions:
- Department of Energy, Office of Electricity, Energy Storage Research
- Cordova Electric Cooperative
- Sandia National Laboratories
- Alaska Center for Energy and Power



U.S. DEPARTMENT OF ENERGY

NNSA

Global Energy Storage Database (GESDB) Updates

S. Roberts, J. Hernandez, Sandia National Laboratories

The **DOE Global Energy Storage Database (GESDB)** is a go-to source for unbiased, accurate, and up to date information on energy storage projects and policies. The free database, managed by Sandia National Laboratories, is publicly accessible and simple to use. The GESDB provides an open-access resource for detailed energy storage project technical characteristics and applications. This resource allows individuals to contribute data through a third-party vetting process. View the database at www.energystorageexchange.org.

The GESDB is vital to the energy storage industry. This research-grade tool is widely used by industry, policymakers, academia, and investors around the world. No other source of information matches the international credibility of the DOE-backed GESDB, or provide the private data sources with energy infrastructure data appear to use the GESDB with respect to deployment information.

Functionality

Projects

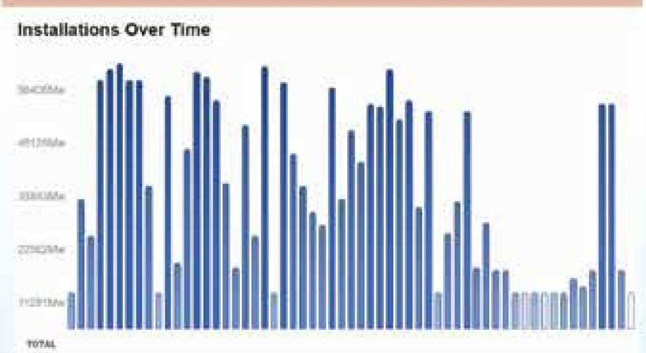
Navigate energy storage projects with the export-ready results appearing on the page's map. Narrow your search results by: *Technological Data, Financial and Ownership Data*, and *Geographical Data*. These three menus provide you with data points to further narrow or broaden their search results.

Policies

Our new State Energy Storage Policy pages feature state energy offices, and public utilities commissions information, and comprehensive energy storage policy analysis for each state, as well as Federal Energy Regulatory Commission or FERC policies.

Data Visualization

Users may use this page to visualize various aspects of the projects in the database, such as *Installations Over Time, Projects by Ownership and ISO/RTO, Top 10 Countries by Installed Capacity*, and *Use Cases*. Additionally, you can filter by technology type, status, and country to further refine their search requests.



Current Tasks

Verification/Validation

- Migration / complete rebuild of database
- Fixing of various HTML encoding and character encoding errors
- Fixing incorrect Announcement, Commissioning, Construction, Decommissioning dates
- Normalization of Rated Power, Capacity, & Duration values
- Vetting additional ~500 projects for inclusion in the database

New Developments

- Released new comprehensive FERC Policy / Energy Storage Policy Pages
- Released Australian Energy Storage Portal (AESDB)

Future Developments

- Collaboration with QuESt on new ISO/RTO tool
- Improvements on Data Visualization Page / Site Speed
- GESDB Operating Manual – All purpose manual for users, administrators & developers of the database

Acknowledgments: This work was supported by Dr. Imre Gyuk through the Department of Energy Office of Electricity.

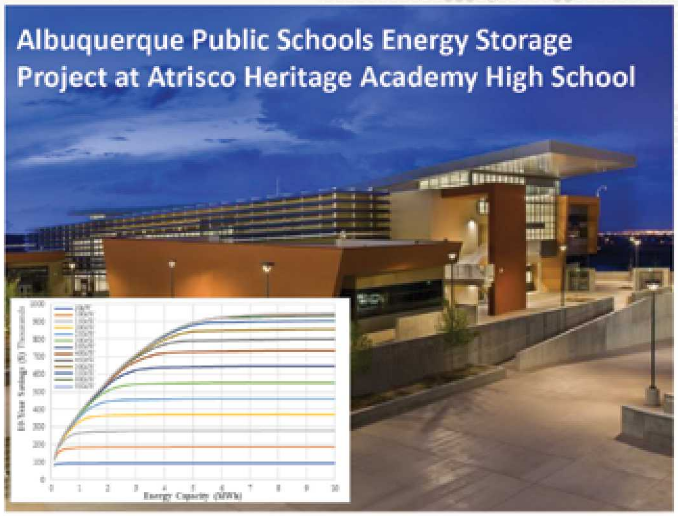
CESA Energy Storage Technology Advancement Partnership

The Energy Storage Technology Advancement Partnership (ESTAP) is a federal-state funding and information sharing project, managed by CESA, that aims to accelerate the deployment of electrical energy storage technologies in the US. ESTAP is funded by US DOE-OE through a contract with Sandia National Laboratories.

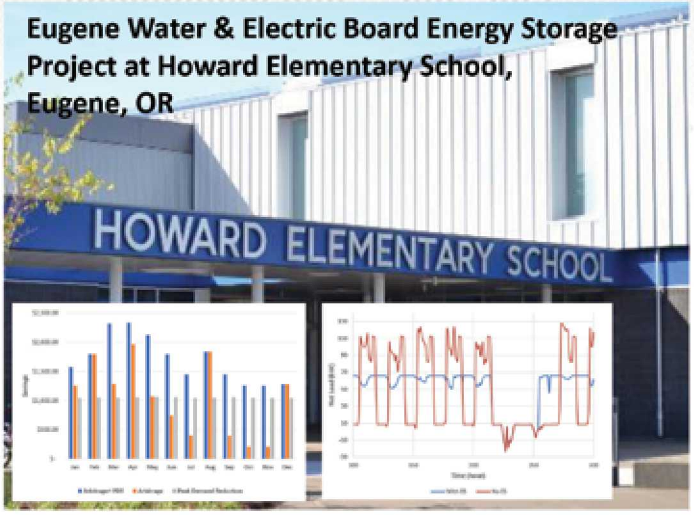
Examples of CESA Deployment Projects

Clean Energy States Alliance

Albuquerque Public Schools Energy Storage Project at Atrisco Heritage Academy High School



Eugene Water & Electric Board Energy Storage Project at Howard Elementary School, Eugene, OR



Examples of CESA State Energy Storage Policy Support

- CESA states energy storage policy working group (CA, CO, CT, DC, IA, IL, MA, MD, ME, MI, MN, NH, NJ, NM, NY, OR, PA, RI, VA, VT, WA, WI)
- Utility-run customer battery programs in five states (CT, MA, NH, RI, VT)
- CT Green Bank, CT DEEP – support battery rebate design, microgrids grant program
- MA DOER, MassCEC – resiliency and battery grant program technical assistance, EE plan technical assistance
- MN Department of Commerce – review storage study proposals, support study
- NH Public Utility Commission - present at conferences, support utility customer program regulatory review
- NM EMNRD – present at ES working group, support state policy efforts
- OR DOE – support storage grant program, write policy brief for Energy Trust of OR
- RI Office of Energy Resources – present at microgrids summit
- VT Department of Public Service, Legislature, PUC – contribute to ES study, present to legislative committee, participate in PUC docket
- WA State Energy Office - review grid modernization grant proposals

ESTAP Current Project and Policy Locations

Webinar Title	Date	Attended	Webinar Recording Views to date	TOTAL Views
Energy Storage in the Clean Peak Standard	11/8/2018	294	200	494
Oregon's New Energy Storage Project for Resiliency and Cost Savings	12/18/2018	182	143	325
State of the US Energy Storage Industry: 2018 Year in Review	2/28/2019	416	243	659
Energy Storage 101, Part 1: Battery Storage Technology, Systems and Cost Trends	3/26/2019	601	504	1,105
Massachusetts' Municipal Utility Energy Storage Projects: Examples from Sterling, Templeton and Wakefield	6/25/2019	235	84	319
Energy Storage 101, Part 2: Best Practices in State Policy	7/23/2019	413	110	523
New York's Energy Storage Roadmap and Other Initiatives	8/21/2019	277	306	583
FERC 841 Compliance Update	10/1/2019			
TOTALS		2,418	1,590	4,008

Upcoming webinars, webinar recordings, presentations, blogs, reports may be found at https://www.cesa.org/projects/energy-storage-technology-advancement-partnership/

State Energy Storage Deployment Projects:

AK: Cordova hydro-storage project, Homer Electric storage project
CO: Gunnison Rural Electric Coop storage project
IA: Alliant energy storage project
MA: Sterling Municipal Lighting District islandable storage project
MN: Minnesota Power battery storage project
NM: Albuquerque Public Schools Atrisco Heritage Academy HS project
OR: Eugene Water & Electric Board microgrid
Puerto Rico: Villalba municipal microgrid project
VT: Green Mountain Power Stafford Hill microgrid, McKnight Lane redevelopment

Exceptional service in the national interest

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY NNSA

Eugene Water and Electric Board / Korean Consortium Energy Storage Project

Kendall Mongird[1], Patrick Balducci[1], Jan Alam[1], Di Wu[1], Xu Ma[1], Vanshika Fotedar[1], and Will Price[2]
[1]PNNL , [2]EWEB

Pacific Northwest NATIONAL LABORATORY

Project Overview

The Eugene Water and Electric Board (EWEB) / Korean Consortium Energy Storage Project is a multi-national initiative including EWEB and a group of Korean partners - Hyosung, Shinsegae Engineering and Construction, and BlueSigma - that incorporates the deployment of three lithium-ion batteries at EWEB's Roosevelt Operations Center (ROC) in Eugene, Oregon. In exchange for funding the storage systems, the Korean Energy Technology Evaluation and Planning (KETEP) group is seeking information as to how U.S. energy markets and utilities function in order to better inform future investment opportunities. Pacific Northwest National Laboratory (PNNL) was engaged by the U.S. Department of Energy to work with EWEB and the Korean partners in evaluating the techno-economic performance of the energy storage system (ESS).

Objective and Approaches

Objective: To inform on potential economic opportunities and the variety of use cases the asset is capable of providing to both the utility and the customer.

Approaches:

- PNNL worked with all the project partners to discuss and define use cases applicable to the location and collect the necessary data to evaluate them.
- Methods and inputs were defined and refined for use case evaluation so that all benefits and costs could be accurately captured.
- PNNL's Battery Storage Evaluation Tool (BSET) was employed to simulate a year of battery operation and derive economic benefit of multiple co-optimized use cases across numerous scenarios.

Energy Storage System

The ESS will be lithium-ion. It will consist of three components offering a combined 1 MW / 2 MWh of power and energy capacities, respectively. The expected usable life of the system is 10 years.

The three systems and their locations at the ROC are designated as follows:

- 750 kW/1.5 MWh unit at the administrative facility;
- 125 kW/250 kWh unit at the warehouse facility; and
- 125 kW/250 kWh unit at the fleet building.

The two smaller 125 kW units will be held for resiliency purposes only, leaving the 750 kW battery to seek additional economic benefit streams.

Computer Rendition of 125 kW Storage Component

Computer Rendition of 750 kW Storage Component

Energy Storage System Services Evaluated

The following services were evaluated within the preliminary economic assessment from a variety of perspectives and across multiple scenarios:

1. Energy Arbitrage
2. Bonneville Power Administration (BPA) Balancing Cost Reduction
3. Capacity/Resource Adequacy
4. Demand Charge Reduction
5. Transmission Charge Reduction
6. Demand Response (DR)
7. Energy Imbalance Market (EIM) participation
8. Resiliency/Outage Mitigation

Battery Storage Evaluation Tool (BSET)

BSET was used to run a one-year simulation of energy storage operations at the ROC. The model was used to perform a look-ahead optimization hourly to determine the battery base operating point. The simulation was then used to determine the actual unit's operation. BSET determines the annual value of each service and the number of hours the system would optimally be engaged in providing each service.

Control Strategy Development

As part of the technology demonstrative initiative, PNNL is also developing control capabilities for the battery system. To bundle multiple use cases, a rule-based control and coordination strategy is being considered at this phase of the project. As more information is gathered and data collected, optimization-driven control strategies will be used.

Results of Preliminary Economic Analysis

- When optimization from the customer's perspective, there is approximately $9,500 in annual benefits to the customer and little impact on EWEB.
- Under the base case, which optimizes for EWEB's benefit under currently observed conditions, the total benefit is $18k annually to the utility.
- When EIM participation is also considered, total annual benefits increase to $36k.
- Seven different day-ahead DR scenarios were modeled and the annual DR value, on average, was found to be between $9,214 and $15,357 per year.
- By enabling continued operations for 8 hours, energy sales would increase by $227,373.

Next Steps

- After installation, begin performing battery testing.
- Calculate resiliency benefits to customers.
- Evaluate tradeoffs between the customer and the utility along Pareto-optimal paths.
- Finalize economic assessment.

Kendall Mongird
Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99352
(971) 940-7102
kendall.mongird@pnnl.gov

Acknowledgements
This work was supported by Dr. Imre Gyuk from the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is operated by Battelle for the DOE under contract DE-AC05-76RL01830.

U.S. DEPARTMENT OF ENERGY

www.pnnl.gov

Sizing Tool for a Cost-effective and Resilient Microgrid

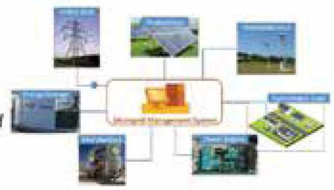
Pacific Northwest NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

Di Wu, Sen Huang, Xu Ma, Patrick Balducci, Tao Fu, Vanshika Fotedar, Avijit Das

PROJECT OVERVIEW

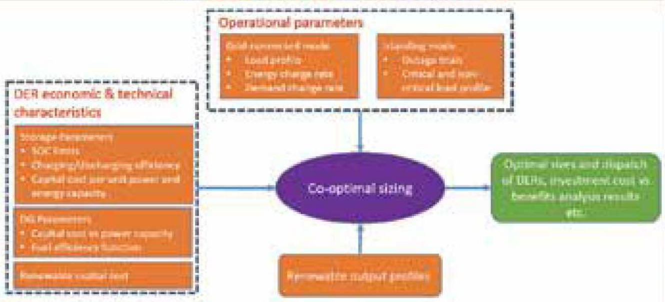
Microgrid design and operational concepts, including distributed energy resources (DERs) selection and sizing, have received increasing attention in recent years. This project considers a microgrid planning/expansion problem. The objective is to develop a method and tool for determining the optimal investment of DERs considering both economic benefits and resiliency performance. The outcome of this project will be an open-source web-based *modeling and analytics* tool that will directly contribute to 1) *electric grid modernization and resiliency of energy infrastructure* and 2) a *resilient, reliable, and flexible electricity system.*



METHODOLOGY AND INNOVATION

- The optimal sizes are determined considering both economic benefits and resiliency requirements
- The tool models various DER technologies (including energy storage, renewable, and dispatchable distributed generation) with different economic and technical characteristics
- The co-optimal sizing method simultaneously determines the optimal sizes of different DERs
- Diversified system conditions in both grid-connected and islanding modes are captured
- The interdependency between optimal size and dispatch is explicitly modeled
- Using the piecewise linearization technique, the optimal sizing problem is formulated using linear programing that can be efficiently solved with a large number of operation conditions.

CO-OPTIMAL SIZING FORMULATION

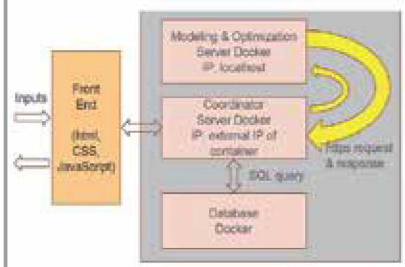


Objective Function min (capital cost + operational cost – operational benefits)

Models & Constraints

- Resiliency requirement
- Microgrid power balancing in grid-connected mode
- Microgrid power balancing in each of outage scenarios
- Power output from renewables as a function of their sizes
- Dispatchable generator power output limits
- Dispatchable generator fuel consumption and cost
- Energy storage power and energy limits
- Energy storage energy state dynamics

TOOL ARCHITECTURE



- The web-based application minimizes dependencies on operating systems
- The modular structure facilitates maintenance and expansion
- The encapsulated environment with Docker eliminates the need for customized settings
- The dedicated Database Docker and SQL query improves data security

TOOL FRONT-END

FUTURE WORK

- Develop multi-objective optimization and generate the Pareto front to better explore the trade-off between system cost/benefits and resiliency level
- Separate lumped load into critical and non-critical load to improve resiliency analysis
- Model generator failure and capture the impacts on system economics and resiliency
- Incorporate additional practical constraints such as budget limits and on-site fuel storage capacity
- Collaborate with industrial partners to use the tool for planning studies, and resiliency and economic analysis on microgrid systems

Acknowledgements
This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. We are particularly thankful to Dr. Imre Gyuk, manager of the Energy Storage Program of DOE, Office of Electricity for his leadership and financial support.

U.S. DEPARTMENT OF ENERGY

Contact: **Di Wu**
Staff Engineer
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: di.wu@pnnl.gov; Tel: (500) 375-3975

www.pnnl.gov

Washington Clean Energy Fund (CEF) Grid Modernization Projects: Economic Results

P. Balducci[1], K. Mongird[1], J. Alam[1], D. Wu[1], V. Fotedar[1], V. Viswanathan[1], A. Crawford[1], Y. Yuan[1], G. Labove[2], S. Richards[2], X. Shane[2], and K. Wallace[3]

[1] Pacific Northwest National Laboratory, [2] Puget Sound Energy, [3] Avista Utilities, [4] Snohomish Public Utility District

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

INTRODUCTION

The Washington Clean Energy Fund (CEF) provided $14.3 million in funding to three Washington-based utilities for the purchase of four battery energy storage systems (BESSs) with a total investment of $43 million. Pacific Northwest National Laboratory (PNNL) was engaged to evaluate the economic benefits of these systems to the utilities and the customers they serve. PNNL developed an extensive taxonomy for estimating the value of benefits realized through transmission, distribution, bulk energy, and ancillary services. PNNL then modeled the benefits of each of these use cases specific to each utility at each site. This poster highlights the results of this economic analysis, which includes several innovations such as the evaluation of a broad set of use cases, non-linear performance of battery operations, the performance of BESS control systems, and the benefits of using the Modular Energy Storage Architecture (MESA).

CEF Projects

1. **Puget Sound Energy:**
   Glacier, Washington
   2 MW / 4.4 MWh Lithium-ion ESS
2. **Snohomish Public Utility District:**
   Everett, Washington
   2 MW / 1 MWh Lithium-ion ESS
   2 MW / 8.8 MWh Vanadium-Redox Flow ESS
3. **Avista:**
   Pullman, Washington
   1 MW / 3.2 MWh Vanadium-Redox Flow ESS

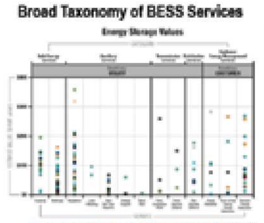
PROJECT OBJECTIVES

1. Collaborate with states, utilities, and energy storage providers to help elucidate storage benefits and integration challenges.
2. Define the services or use cases the Washington CEF BESSs could provide and evaluate associated economic benefits when the BESSs are operated in an optimal manner.
3. Evaluate the technical performance of the BESSs using battery-specific and grid-specific measurements when engaged in economic operation.
4. Evaluate the cost savings associated with deploying BESSs using MESA.

BESS Services

1. Energy arbitrage
2. Capacity/resource adequacy
3. Primary frequency response
4. Regulation up and down
5. Conservation voltage reduction
6. Load shaping services
7. Demand response
8. Outage mitigation

Broad Taxonomy of BESS Services



Washington CEF Use Case Matrix

Category	Use Case	PSE	Avista	SnoPUD
Bulk Energy Service	Capacity or Resource Adequacy	✔	✔	✔
	Arbitrage	✔	✔	✔
Ancillary Services	Frequency Regulation	✔	✔	
	Frequency Response	✔		
Distribution Services	Conservation Voltage Reduction		✔	
Utility Bill Management	Load Shaping Services			✔
	Demand Response			✔
Customer Services	Outage Mitigation	✔	✔	

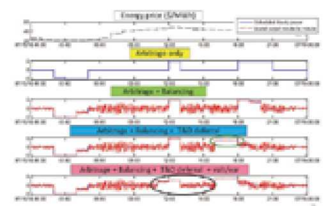
KEY CHALLENGES

1. Developing value taxonomy
2. Valuing non-market services
3. Financial/performance data acquisition
4. Valuing benefits for utilities of varying structures
5. Establishing data pipeline for tests
6. Development of non-linear BESS model

BATTERY STORAGE EVALUATION TOOL

BSET was used to run a one-year simulation of energy storage operations. The model was used to perform a look-ahead optimization hourly to determine the battery base operating point. The simulation was then used to determine the actual battery operation. BSET determines the annual value of each service and the number of hours the ESS would optimally be engaged in providing each service.

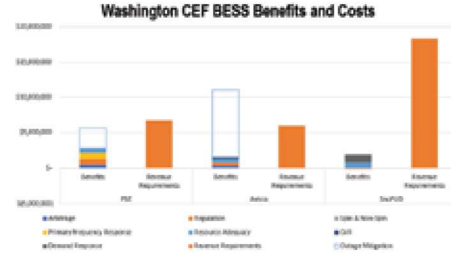
Bundling Services



RESULTS OF ECONOMIC ANALYSIS

1. From a utility perspective, all three projects fall short of generating positive net benefits under the base case scenario.
2. When outage mitigation is included as a benefit, the Avista Turner BESS project generates a positive net return and the PSE BESS shows a large increase in benefits.
3. Outage modeling indicates that the Avista Turner BESS could mitigate all voltage sags affecting Schweitzer Engineering Laboratory (SEL); however, it is not currently functional.
4. A study on the effects of using MESA standardization show cost reductions as high as 50% were identified in equipment procurement, electrical design, and commissioning costs.

Washington CEF BESS Benefits and Costs



ADVANCES IN THE STATE OF THE ART

- ❑ Development of detailed BESS value taxonomy and advances in methods used to estimate economic benefits of BESS operations.
- ❑ Most extensive set of use cases ever co-optimized in a non-market setting.
- ❑ Data analysis provides unique insight into BESS performance across multiple systems.
- ❑ Economic and test program can be model for analysis of other grid-scale systems.
- ❑ Non-linear battery performance woven into BESS economic optimization engine.

PUBLICATIONS / ACHIEVEMENTS

1. Project has resulted in 23 presentations, 3 conference papers/journal publications, 1 pending patent and 8 reports (https://energystorage.pnnl.gov/publications.asp)
2. Pacific Northwest National Laboratory (PNNL) is currently supporting energy storage demonstration projects at 8 utilities in the Pacific Northwest
3. Washington CEF has been extended into two additional rounds of investment with PNNL providing analytical support for seven of the nine projects selected under the CEF Grid Modernization Program.

Acknowledgements

This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. We also wish to acknowledge program leadership provided by Dr. Imre Gyuk, Director of Energy Storage Research at DOE.

U.S. DEPARTMENT OF ENERGY

Contact: **Patrick Balducci**
Chief Economist
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: Patrick.balducci@pnnl.gov; Tel: (503) 417-7540

www.pnnl.gov

Nantucket Island Energy Storage System Economic Assessment

Vanshika Fotedar, Xu Ma, Patrick Balducci, Jan Alam, Tom McDermott, Di Wu, Bilal Bhatti, Kendall Mongird, Bishnu Bhattarai, Alasdair Crawford, Sumitrra Ganguli

Pacific Northwest NATIONAL LABORATORY

PROJECT OVERVIEW

Nantucket Island, located off the coast of Massachusetts, has a fairly small resident population of approximately 11,000, which swells to 50,000 during summer. In order to meet the rise in energy demand in summer, as well as to improve reliability, National Grid will be deploying a 6 MW/48 MWh lithium-ion energy storage system (ESS), and replacing an on-island combustion turbine generator (CTG) with a new CTG capacity varying between 10 MW and 16 MW. Currently, Nantucket's electricity is supplied by two submarine supply cables (shown in the figure) with a combined capacity of 71 megawatts (MW) and two small CTGs. In the event that one of the supply cables fails (i.e., an n-1 contingency is triggered), the island would face outage threats during a small number of days during peak summer months. The total value will be generated through a variety of use cases or services, which have been developed by Pacific Northwest National Laboratory (PNNL) in consultation with National Grid.

PROJECT OBJECTIVES AND CHALLENGES

1. Evaluate the technical and financial benefits of ESS and its impact on the Nantucket system
2. Develop control strategies to maximize financial benefits while achieving resilience goals
3. Understand market rules, obtain verified network data, and validate system model results
4. Challenge in managing multiple use services within a single optimization engine
5. Model the benefits with AGC regulation and imperfect foresight using DAM and RTM data

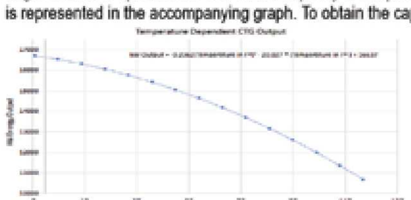
TESLA BATTERY ENERGY STORAGE SYSTEM

The Nantucket ESS is a 6 MW/48 megawatt-hour (MWh) lithium-ion Powerpack 2 system procured from Tesla, Inc. The total system will include the battery packs, a power conversion system (PCS), and a site-level controller. The ESS will be deployed at National Grid's Bunker Road Substation located on Nantucket Island. The system as designed is expected to have an economic life of 20 years with preventative maintenance being conducted throughout to ensure its reliability. The expected Round-Trip Efficiency (RTE) for the ESS was calculated based on the average daily temperature in 2016 for Nantucket Island. This resulted in average yearly RTE of 87.77% at Beginning of Life (BOL) and 83.44% over 10 years of life.

Tesla Powerpack 2 Lithium-ion BESS

COMBUSTION TURBINE GENERATOR

National Grid will soon be replacing two 3 MW generators, which will be disconnected once the larger turbine is operational. The CTG's capacity is temperature dependent and this relationship is represented in the accompanying graph. To obtain the capacity curve of the generator throughout the year, the hourly temperature data for the year 2016 is used to generate the temperature-dependent CTG rating. For Nantucket Island, the capacity range goes from 13.28 MW to 16.67 MW, with a year-round average of 14.88 MW.



BENEFITS OF ESS AND CTG

Local Operations

1. Transmission Deferral
2. Outage Mitigation
3. Conservation Voltage Reduction/Volt-VAR

Market Operations

1. Forward Capacity Market
2. Arbitrage
3. Regulation
4. Spinning Reserves

MARKET OPERATIONS BENEFITS

No Perfect Foresight Assumptions: Daily market operation is based on forecast prices while revenue results from market clearing prices. Thus, this evaluation does not assume perfect foresight but rather reflects the impacts of prediction error. PNNL used Gradient Boosting Machine Model (GBM) infused with ARIMA time series model as well as Day-Ahead Locational Marginal Prices (DALMP) as predictors for Real Time Locational Marginal Prices (RTLMP).

Arbitrage and Regulation Revenue by Year by Prediction Method

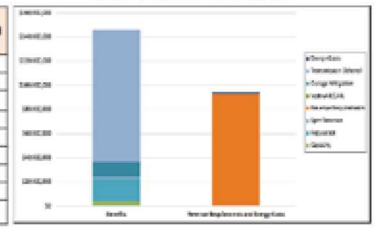
Market/Prediction Method	2016	2017	2018	Average
GBM Prediction of DALMP	1,275,790	1,358,226	1,295,250	1,309,755
Prior Day's DALMP as Predictor of DALMP	1,275,790	1,358,226	1,295,245	1,309,754
GBM Prediction of RTM	1,275,648	1,355,728	1,294,895	1,308,757
DALMP Prediction of RTM	1,275,648	1,355,686	1,294,895	1,308,743

CO-OPTIMIZED BENEFITS

Benefit and Cost Values by Element

Element	Benefits	Revenue Requirements and Energy Costs
Capacity	$4,060,124	
Regulation	$18,757,805	
Spin Reserves	$1,195,419	
Volt-VAR/CVR	$80,043	
Outage Mitigation	$12,313,206	
Transmission Deferral	$109,490,163	
Energy Costs		$657,898
Revenue Requirements		$93,264,355
Totals	$145,896,759	$93,922,253

Base Case Benefits and Costs



CONCLUSIONS

1. The total 20-year present value of ESS and CTG operations at $145.9 million exceed revenue requirements and energy costs at $93.9 million with a benefit-cost ratio of 1.55.
2. Benefits are largely driven by the transmission deferral use case, which provides nearly $109 million in present value terms. This is about 75% of the total benefits.
3. An additional $18.8 million results from regulation services, which comprise 12.9% of the benefits making it the second largest benefit stream.
4. Regulation service dominates the application hours, with the ESS engaged in the provision of this service 7,900 hours each year.

NEXT STEPS

1. PNNL will deliver research findings to the National Grid Leadership Team
2. Nantucket Island ESS/CTG ribbon cutting ceremony on October 8th
3. PNNL is aiding in development of real-time control systems and has proposed load and price prediction model to assist with bidding operations
4. PNNL will seek to publish the findings of the economic assessment and will continue to assist National Grid with transmission modernization

ABOUT

Pacific Northwest National Laboratory

The Pacific Northwest National Laboratory, located in southeastern Washington State, is a U.S. Department of Energy Office of Science laboratory that solves complex problems in energy, national security, and the environment, and advances scientific frontiers in the chemical, biological, materials, environmental, and computational sciences. The Laboratory employs nearly 5,000 staff members, has an annual budget in excess of $1 billion, and has been managed by Ohio-based Battelle since 1965.

For more information on the project you see here, please contact:

Vanshika Fotedar / Xu Ma
Pacific Northwest National Laboratory
P.O. Box 999,
Richland, WA 99352
(971) 940-7106 / (509) 372 4912
vanshika.fotedar@pnnl.gov / xu.ma@pnnl.gov

ACKNOWLEDGEMENTS

This work is supported by Dr. Imre Gyuk, U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830.

U.S. DEPARTMENT OF ENERGY

www.pnnl.gov

Battery State of Health Model

Alasdair Crawford, Vilayanur Viswanathan, Daiwon Choi, Vineet Joshi, Di Wu, Jan Alam, Kendall Mongird, Patrick Balducci

Pacific Northwest National Laboratory, Richland, WA 99352

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

Introduction:

Lithium-ion battery performance degradation depends on ambient & operating temperature, rate, depth of discharge, number of cycles, and duration at various states of charge and temperature. Very few models exist that take into account multiple modes of degradation or include the effect of temperature changes during operation. This electrothermal model addresses these gaps.

Objectives:

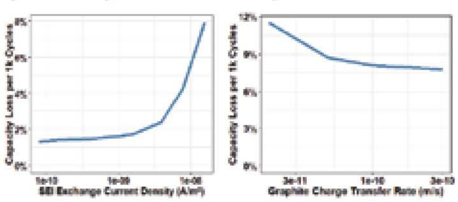
- Develop electrothermal model based on first principles taking into account multiple degradation pathways to predict performance and degradation
- Identify the most important design and operating parameters that affect battery state of health
- Find suitable electrode architecture & cell design for various grid services
- Enhance battery management systems to optimize battery throughput
- Inform the top down model with key findings from electrothermal model
- Enable Battery Storage Evaluation Tool (BSET) to incorporate degradation cost into market transactions – improve net benefits over useful battery life

Approach:

- Pseudo-2d model using COMSOL Multiphysics 5.4
- Model validation done using literature and in-house data
- Solid Electrolyte Interphase (SEI) formation on already formed SEI
- SEI formation on freshly exposed graphite upon SEI film cracking
- Graphite active material loss due to fracture
- Lithium plating and cathode dissolution
- SEI formation effect on electrode porosity and electrolyte effective conductivity and diffusivity
- Effect of ambient & operating conditions, electrode architecture & cell design

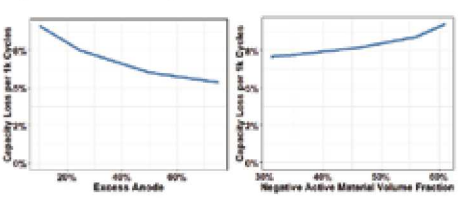
Results and Discussion:

a) Exchange current density / reaction rate constant



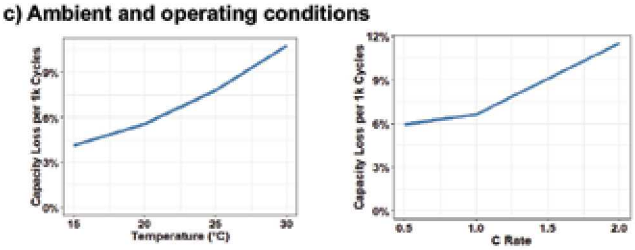
- Losses increase as SEI exchange current density increases and charge transfer rate constant decreases.
- Ratio of SEI and charge transfer rate constant is a key metric.

b) Cell balancing and electrode architecture



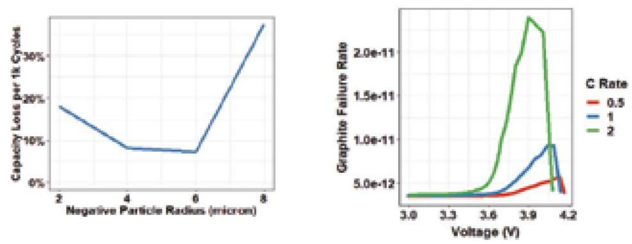
- With excess anode, electrode potential at end of charge less negative – lower driving force for SEI formation.
- Higher active material fraction increases tortuosity.

c) Ambient and operating conditions



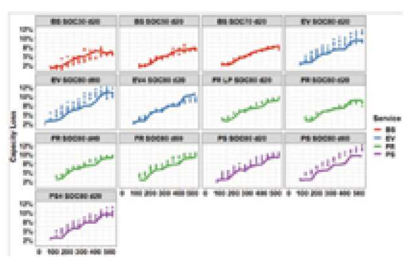
- Degradation rate increases at higher temperature
- High temperature increases SEI formation and cathode dissolution rate
- High C rates lead to higher temperature, higher stress on SEI film and graphite particles
- Greater loss of lithium and active material capacity

d) Particle size and V/I effect on structural mechanics



- Optimum radius is 6 microns. Particle stress increase at radius > 6 microns
- High current (I) and high cell voltage (V) contribute to higher stress levels

e) Top down model results for various duty cycles



- In-house 18650 NMC-Gr data
- Key degradation mechanisms from electrothermal model used as input
- Active material loss, cumulative discharge energy, square root of total SEI formed, cathode dissolution, age most important
- Capacity loss predicted within 10% after 500 cycles

Future Work:

- Model multi-electrode pouch and cylindrical cells
- Model multi-cell modules
- Predict safety behavior of cells and modules with changing SOH

Acknowledgements

This work was supported by Dr. Imre Gyuk from the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is operated by Battelle for the DOE under contract DE-AC05-76RL01830.

U.S. DEPARTMENT OF ENERGY

Dr. Vilayanur Viswanathan
Engineer
Electrochemical Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: Vilayanur.Viswanathan@pnnl.gov
Tel: (509) 372-4745

www.pnnl.gov

Energy Storage Control Capability Expansion at Portland General Electric's Salem Smart Power Center

J. Alam[1], P. Balducci[1], D. Wu[1], V. Viswanathan[1], A. Crawford[1], K. Mongird[1], V. Fotedar[1], K. Whitener[2], S. Cox[3]

[1] Pacific Northwest National Laboratory, [2] Portland General Electric, [3] Nikos, Inc.

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by **Battelle** *Since 1965*

INTRODUCTION

Value proposition of energy storage systems (ESS) is a key topic for creating and advancing its acceptance within the electric power sector, particularly for electric utilities. While ESS as a technology is gaining popularity within the electric utility industry, its anticipated value streams are not fully understood, quantified, or demonstrated. Unavailability of suitable demonstration sites/projects, lack of deep understanding of available economic opportunities, and deployment complexities associated with pursuing those opportunities are some of the reasons that complicate value demonstration processes. This poster reports a transformative project aimed at enhancing the control capabilities of a Portland General Electric (PGE)-owned 5 MW/1.25 MWh ESS located at Salem Smart Power Center (SSPC), Salem, Oregon, USA toward achieving better techno-economic value. Lessons learned from this project are summarized for the benefit of the wider ESS community.

Battery Blocks | Inverters | Controller

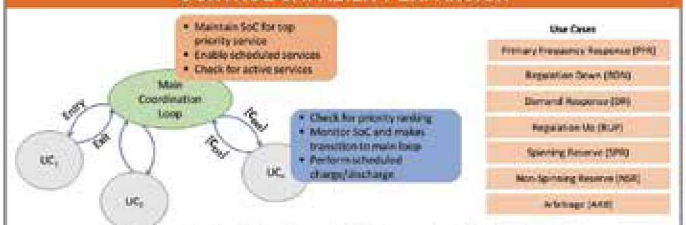
- 5 Blocks, 4 Racks/Block, 18 Drawers/Block, 4 Modules/Drawer
- 2x125 kVA Eaton Power Xpert Inverters per Rack
- PLC based BMS and control system

- Was used only for Primary Frequency Response and Demand Response
- Sitting idle over a significant amount of time over the year
- Could be used for additional economic opportunities

PROJECT OBJECTIVES

1. Understand available economic opportunities and refine use cases to be pursued.
2. Develop control strategies and refine through discussion with stakeholders.
3. Implement, test, and refine control strategies and proposed innovative features.
4. Share results and lessons with the wider energy storage community.

CONTROL CAPABILITY EXPANSION



Control Strategy Development by Integrating Multiple Use Cases

Implementation via PLC | EMS Integration

KEY CHALLENGES

1. Identifying use cases to pursue
2. Obtaining stakeholder input
3. Testing and validating with external signal
4. Integration with utility's central operation scheme

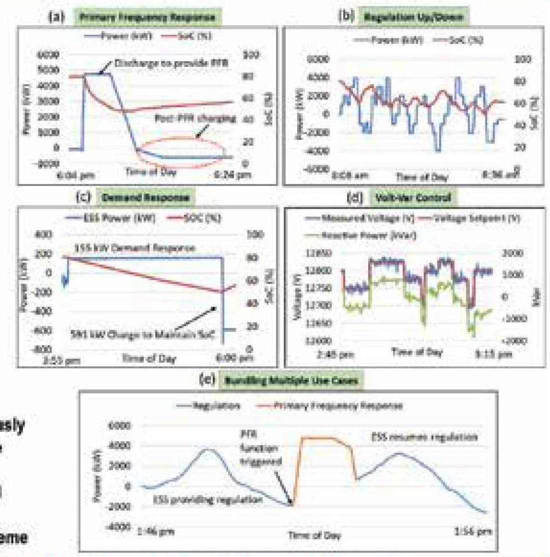
KEY INNOVATIVE FEATURES

Day in the Life of the ESS | Financial Value Tracking | Animated Flowchart

SSPC ESS IN OPERATION

Various use cases operating individually

Two simultaneously enabled use cases are coordinated through a priority scheme



ADVANCES IN THE STATE OF THE ART

- ❑ Advanced the knowledge of ESS control with multiple use cases via demonstration
- ❑ Important lessons generated for utilities intending to install ESS
- ❑ Demonstrated an approach to expand capabilities of existing control systems
- ❑ Explored ESS integration with a utility's system operation platform

PUBLICATIONS / ACHIEVEMENTS

1. Project has resulted in 3 presentations, 1 conference paper, 1 journal article (under consideration) (https://energystorage.pnnl.gov/publications.asp)
2. A more impactful ESS control/coordination project has been launched with PGE based on the outcome of this project
3. Led to ESS control/coordination effort at multiple utilities across the nation (National Grid, Eugene Water and Electric Board, Orcas Power and Light Co-op, Energy Northwest, Tacoma Power, and Puget Sound Energy)

Acknowledgements
This work is supported by Energy Storage Program, Office of Electricity, U.S. Department of Energy (DOE) under the guidance of Dr. Imre Gyuk.

U.S. DEPARTMENT OF ENERGY

Contact: **Jan Alam**
Power Systems Engineer
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: Jan.Alam@pnnl.gov; Tel: (509) 372-4972

www.pnnl.gov

Energy Storage Analysis for Regional Demonstration Projects

Alexander Headley, Tu Nguyen, Ray Byrne - Sandia National Laboratories

Overview

In FY19, we performed analyses to assist with planning, project development, and valuation for: the Eugene Water & Electric Board in OR, Atrisco Heritage High School in Albuquerque, NM, Minnesota Power, BQ Energy in NY, and the NELHA research campus in HI. In these analyses, we optimize the benefits from energy storage for the customers for different grid applications such as peak demand charge reduction, PV utilization, and time-of-use rate structures. Below is analysis from two particularly interesting cases.

Community Distributed Generation in NY

Background

Recent changes to pricing in NY include updates to increase the value of energy storage. BQ Energy, a community distributed generation developer in NY, requested analysis of three different solar projects for energy storage integration.

Unique Considerations

Value Stacking in NY

- Six value streams
- Time-of-generation windows
- Generation requests

System Configurations

- DC vs. AC coupling

Proposed Solar Projects

	A	B	C
MW DC	7.5	3.0	0.75
MW AC	5	2	0.577
Fixed Values (2018)			
E - $/kWh	0.02741	0.02741	0.02741
DRV - $/kWh	0.01765	0.00417	N/A
LSRV - $/kW	2.56	N/A	14.08
CC - $/kWh	0.0225	N/A	0.12

Analysis

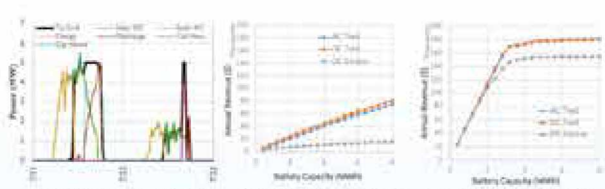
- PV modeled with PVLib
- AC-tied, DC-tied, DC excess charging

Optimization Framework

$$\max \sum_{t=1}^{T} P_{dis,t} \cdot (ACap_t + DRV_t + LSRV_t + E + CC + LBMP_t)$$
$$\text{subject to } SOC_t = SOC_{t-1}\eta_s + \Delta t(P_{c,t}\eta_c - P_{dis,t})$$
$$P_{dis,t} + \eta_{inv}(P_{PV,t} + P_{dc} - P_{c,t} - P_{curtail,t})$$
$$P_{c,t} \le P_{PV,t} - P_{PV,t}$$

Results

- Value from coincident peak discharge (38%), scheduled calls (30%), and LBMP arbitrage (24%)
- AC / DC tied similar value in low energy applications



Project A optimal ESS dispatch schedule | Project B 2-TPM Capacity Option | Project B Coincident Peak Capacity Option

Project Status

- BQ Energy soliciting energy storage proposals for Projects A & B

Energy Storage and Large Scale Hydrogen Production – NELHA Research Campus

Background

The NELHA campus will soon support a large water electrolysis facility generating hydrogen for three fuel cell buses. Early tests of the facility more than doubled the peak demand for the campus.

Unique Considerations

Hydrogen Production

- 250kW electrolyzer
- Flexible operation from 10-100%

Analysis

- Time-of-use and flat rate options
- With and without hydrogen facility

Research Campus — Demand and Energy Charges; Battery SOC Model

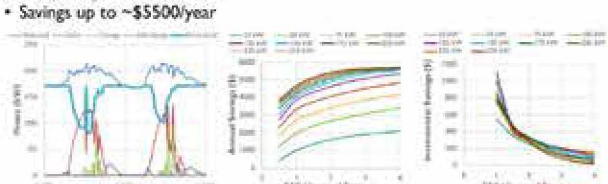
Hydrogen Facility — Hydrogen Storage Model; Operation Limits

$$\min \; P_{peak} \cdot C_{Dem} + \sum_{t=1}^{T} P_{N,t} \frac{\Delta t}{60} (C_{E,t} + C_{fixed}) + \frac{\sum_{k=1}^{K} S_k + S}{K}$$
$$\text{subject to } SOC_t = SOC_{t-1} + \frac{\Delta t}{60}(P_{c,t}\eta_c - P_{d,t})$$
$$SOE_{H,t} = SOE_{H,t-1} + \frac{\Delta t}{60} P_{H,t} - D_{H,t}, \quad 0 \le SOE_{H,t} \le SOE_{H,max}$$

Results

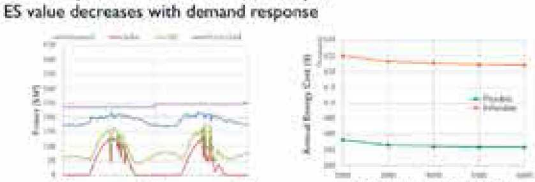
No Hydrogen Production

- Savings up to ~$5500/year



With Hydrogen Production

- Flexible operation would save ~$25000/year
- ES value decreases with demand response



Project Status

- NELHA / HNEI investigating hydrogen facility interface and control to lower demand increases
- Continued work on microgrid development which may incorporate more energy storage

Acknowledgements

This work was supported through the Energy Storage Program managed by **Dr. Imre Gyuk** within the US Department of Energy's Office of Electricity. Also, a special thanks to collaborators Laurence Sombardier and Keith Olson from NELHA as well as Mitch Ewan at HNEI.

Safety Considerations for BESS: Before, During and After Commissioning

-

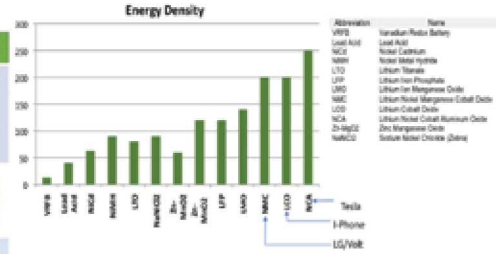
Susan Schoenung, Longitude 122 West, Inc.
Dan Borneo, Sandia National Laboratories

Abstract:
Safety is a significant factor in the use of battery energy storage, as the desirable high energy density has the disadvantage of fire risk. While the commissioning process is intended to check for both satisfactory system performance and safety features, attention to other considerations both before and after commissioning are needed to ensure long life and safety of the system.

Design and Construction

Elements of the Battery Energy Storage system (BESS)

Choosing the right battery



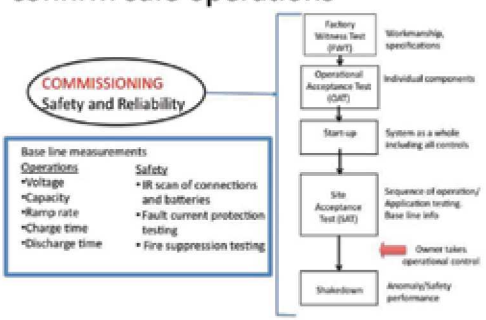
Design safety into the system

System considerations
- ✓ Battery types
  - Energy density of batteries
  - Hybrid batteries
- ✓ BMS should have fail-safe mechanisms
  - Predictive maintenance tools within BMS
  - Temperature feedback / sensors
  - Charge/Discharge rates controls
- ✓ Energy isolation means at module, rack or cell level
- ✓ Cooling approach / thermal management
- ✓ Adequate Fire protection: Today's suppression systems may be false security
  - ➢ Chemistry and duration of suppressant?
  - ➢ Is Gas Monitoring needed for Li-ion?
  - ➢ Adequate Ventilation

Codes and standards: Need to be clear and implementable
- ➢ NFPA 68, 69, 855; IEEE 1547; UL 9540A

Commissioning

Commissioning/testing to confirm safe operations



Battery Management

- The Battery management system (BMS) controls the charge and discharge of the battery.
- The BMS measures cell voltages, currents, temperatures, and balances cells.
- BMS adjusts charge voltage – Charging to a lower Voltage limit allows extended operation at partial SOC.
- The BMS monitors cell health and detects and annunciates cell and module failures.
- Module and rack safety isolation approach
- The BMS is part of the overall safety system.

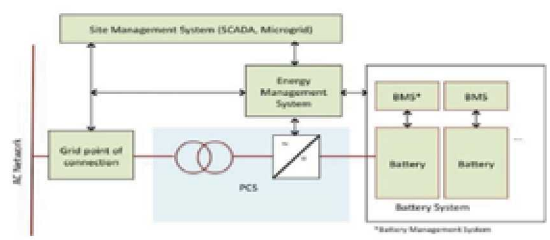
CHECK during Commissioning:
- ✓Lower and upper state of charge, i.e. 10-90%
- ✓Charge current
- ✓Safety and operational set points
- ✓Annunciation means
- ✓Fail safe operation, to the extent possible

Energy Management

The Energy Management System (EMS):
- Monitors grid voltage
- Manages energy flow to/from grid (ramp rate)
- Controls current or voltage source mode of operation of inverter
- Controls the Energy Storage System (ESS)
  - •Communicates with inverter
  - •Communicates with BMS
  - •Communicates with customer interface
- Controls balance of plant – HVAC, emergency stop, fire protection
- Insures inverters operate batteries within the battery parameters

Check during Commissioning:
- ✓Needs to operate ESS based on grid needs
- ✓Application control testing

Power and Energy Configuration



Site Management System (SMS)

The SMS interfaces with the ES energy management system, distributed energy resources and the grid and acts as the Master Controller
- Monitors Grid: Measures grid electrical conditions – voltage, current, frequency, Power
- Event logging
- Data Management , including historical records
- *Controls Sensors, Breakers, re-closers, Power Measurement Unit (PMU)*
- Operates BESS and Distributed Energy Resources (DER)

CHECK during Commissioning:
- ✓Sequence of operations controlling multiple DER
- ✓System shutdown and restart
- ✓Cyber Security
- ✓Load management

Balance of Plant

Balance of plant functions:
- •HVAC: battery temperature operations (10-40 C for Lithium-ion)
- •Fire protection: water sprinklers; Suppression material; gas detection; smoke alarms; fail-safe shut-down controls; emergency off; exhaust
- •Electrical distribution: Over-current protection, i.e., coordinated breakers / fused disconnects,
- •Communications
- •Site work: pad, fencing, conduit / wiring

Check during Commissioning
- ✓Ambient Temperature control within equipment specs.
- ✓Fail safe fire system operation
- ✓Annunciation

Operations / Maintenance

Controls and Maintenance for Safety

Controls :
- •Maximum charge and discharge rates
- •State-of-charge range (per vendor specification)
- •Depth-of-discharge (per vendor specification)
- •Ambient temperature (high / low)
- •Adequate time to cool down between cycles (charge/discharge).
- •BMS adequate to monitor and equalize charge.

- •Periodic IR scanning
- •Periodic Physical inspection
- •Battery Capacity Measurements (Annual)
- •Check BMS to insure (within spec):
  - -Cell voltages are within spec
  - -Temperatures
  - -Review operational parameter
- •Circuit Breaker testing per NFPA 70B, NECA (multiple)
- •Cable insulation testing (power cables)
- •Manufacturer maintenance recommendations

Acknowledgments:
This work was supported by Dr. Imre Gyuk through the Department of Energy Office of Electricity Delivery and Energy Reliability.

State Regulatory Commission Energy Storage Outreach and Education

Howard Passell, SNL

Energy storage technologies (ES) and their importance in the grid are advancing faster than policy makers and regulators can keep up. ES economics and valuation are complex and challenging. Reaching out to states' regulatory commissions and offering them educational workshops on topics associated with ES is an important way to increase and enhance ES adoption across the country.

PROJECT OBJECTIVES, METRICS & MILESTONES

OBJECTIVES OF THE PROJECT

- To make contact with regulatory commissions in each state and offer educational workshops
- To design workshops to meet specific needs in each state or group of states
- To provide access for the states to expertise from a variety of national labs and institutions
- To open channels between states and experts for future contact and continued assistance

METRICS

- Number of workshops and number of participants

FUTURE MILESTONES

- 3-4 workshops per year

PROJECT RESULTS

RESULTS

- Grid Energy Storage Introductory Training for the Hawaii PUC, Honolulu, Dec. 7, 2018, ~40 participants
- California Energy Commission (CEC)
- Energy Storage Academy, Sacramento, June 14, 2019, ~30 participants
- Southeast Energy Storage Symposium and PUC Workshop, Birmingham, July 17-18, 2019, ~100 participants overall, with 8 PUCs represented and 25 PUC commissioners or staff

WHAT CAME OUT OF THE WORK?

- Southeastern energy Storage Seminar and Workshop: Report on Proceedings and Lessons Learned. Twitchell, J.B., H.D. Passell, R.S. O'Neil. PNNL
- Ongoing collaboration with PNNL, ORNL, CESA, Quanta Technologies

LOOKING FORWARD

2019-2020 Prospective Workshops

- A series of 2-hour workshops with NM PRC begins in Oct. 2019
- Day-long workshop scheduled with Nevada PUC for Jan. 2020
- Early planning underway with
  - Iowa Utilities Board
  - New Jersey Board of Public Utilities
  - Texas PUC
  - California Energy Commission (a second workshop)

PROJECT TEAM – Partners & Collaborators

INSTITUTIONS

- Sandia National Labs
- Pacific Northwest National Lab
- Oak Ridge National Lab
- Southern Research
- Clean Energy States Alliance (CESA)
- Quanta Technologies

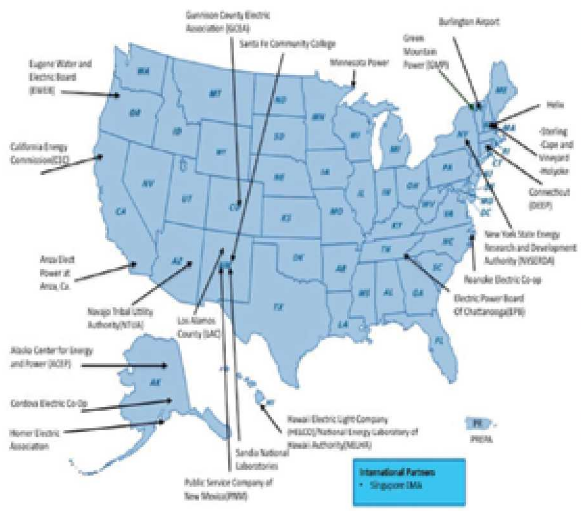
PEOPLE

- Howard Passell, SNL
- Jeremy Twitchell, PNNL
- Michael Starke, ORNL
- Bert Taube, Southern Research
- Todd Olinsky-Paul, CESA
- Ralph Masiello, Quanta Technologies

Sandia National Labs Demonstration Summary

Benjamin Schenkman, Sandia National Labs
Dan Borneo, Sandia National Labs

Objective: *Energy storage is a key to enabling modernization of the electricity grid, including the successful integration of renewable and distributed energy resources. The DOE OE Energy Storage Program uses it Demonstrations Team at Sandia National Laboratories to address multiple challenges to the widespread deployment of energy storage: cost, creation of an equitable regulatory environment, safety and reliability, and industry acceptance. The team supports development, deployment, and research across multiple storage technologies and applications from transmission constrained regions in Alaska to hurricane-prone Puerto Rico, and from the off-grid rural corners of the Navajo Nation to the leading edge of emerging educational programs.*



Project	Technology Development	Analytics (Economic / Technical)	RFP / Commissioning	Data Collection / Performance Evaluation
ACEP		✓		
Albuquerque Public Schools			✓	
ANZA			✓	
Burlington Airport			✓	
California Energy Commission				✓
Cordova Electric Coop				✓
CUNY	✓			
EWEB				✓
EPB			✓	
GMP				✓
Gunnison		✓		
HELCO			✓	
Helix	✓			
HOMER		✓		
Los Alamos		✓		
Minnesota Power		✓		
NTUA	✓			
PNM			✓	
Roanoke		✓		
Sandia				✓
SPCC				✓
Singapore				✓
SMUD				✓
Villalba		✓		

Demonstration Milestones in FY19

- Engineering and manufacturing drawings are complete for the prototype 1MW/25kWh flywheel and building the flywheel has been initiated
- Controls for Urban Electric Power ZnMnO2 for grid tied applications has been completed and will be deployed in Navajo Tribal Utility Authority territory
- Economic Analysis has been completed for Homer Electric Association (Alaska), Gunnison Electric Cooperative (Colorado), Minnesota Power (Minnesota), Roanoke Electric Cooperative (North Carolina) and Villalba (Puerto Rico)
- Completed RFP development and issuance for energy storage system based on Sandia economic analysis for Albuquerque Public Schools (New Mexico), ANZA (California), and Electric Power Board (Tennessee)
- Commissioned 1MW/1MWh energy storage system in Cordova, AK for increasing hydroelectric capacity
- Collected and collecting energy storage data to refine models, develop degradation algorithms and evaluate performance from Cordova Electric Cooperative (Alaska), Green Mountain Power (Vermont), Sterling Municipal Lighting Department (Massachusetts), Eugene Water and Electric Board (Oregon), Sandia (New Mexico), Santa Fe Community College (New Mexico) and Energy Market Authority (Singapore)

Demonstrations and Analysis Coming Online

- Alliant Energy in Iowa installing a 2 MW / 2.8 MWh energy storage system to increase renewable production capacity
- City College of New York demonstrating a 50kW / 160kWh Zinc Manganese Dioxide system for peak shaving
- Three off-grid Urban Electric Power systems for Native American residential loads in the Navajo Tribal Utility Authority territory
- Seminole Tribe of Florida procuring solar plus storage for 8 buildings to offset daily electric costs
- Energy storage utilization in a resilient microgrid using the campus of Santa Fe Community College
- Evaluate using Sandia analytics to determine the tradeoff between PV curtailment and energy storage within NELHA campus
- Increase analytic capabilities to include an energy storage siting tool

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
SAND No. SAND2019-10891 C

SAND2019-10891 C

Sandia National Laboratories

Rechargeable Solid-State Copper Sulfide Cathodes for Alkaline Batteries: Importance of the Copper Valence State

Jonathon Duay, Timothy N. Lambert, Maria Kelly and Ivan Pineda-Dominguez*

Department of Photovoltaics and Materials Technology, Sandia National Laboratories; Albuquerque, New Mexico, USA, 87185

*e-mail: tnlambe@sandia.gov

Background

Batteries for grid storage applications must be inexpensive, safe, reliable, as well as have a high energy density. Sulfur is abundant, produced at low cost in high quantities and has high theoretical capacity; however, it has not been previously applied to a rechargeable alkaline battery system.

Objective

Utilize the high capacity of sulfur (S) (**1675 mAh g^{-1}**, based on the idealized redox couple of S^{2-}/S) in order to demonstrate for the first time, a reversible high capacity solid-state S-based cathode for alkaline batteries.

To maintain S in the solid-state, it is bound to copper (Cu), initially in its fully reduced state as the sulfide. Upon charging, the sulfide is oxidized to a polysulfide species which is captured and maintained in the solid-state by the Cu ions.

Success would open the way to a new class of energy dense grid storage batteries based on high capacity solid-state S-based cathodes.

Sulfur Electrochemistry in Alkaline

HS^- is known to have the following redox chemistry in alkaline electrolyte:

$$S_5^{2-} + 5H_2O + 8e^- \leftrightarrow 5HS^- + 5OH^- \quad 0.003\text{ V vs. SHE}$$

$$S_4^{2-} + 4H_2O + 6e^- \leftrightarrow 4HS^- + 4OH^- \quad 0.033\text{ V vs. SHE}$$

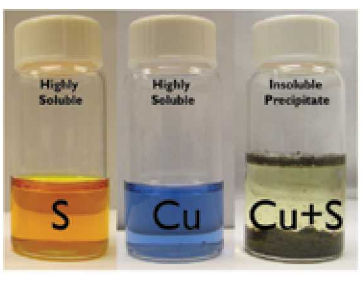
$$S_3^{2-} + 3H_2O + 4e^- \leftrightarrow 3HS^- + 3OH^- \quad 0.097\text{ V vs. SHE}$$

$$S_2^{2-} + 2H_2O + 2e^- \leftrightarrow 2HS^- + 2OH^- \quad 0.298\text{ V vs. SHE}$$

Theoretical performance metrics of polysulfide reductions in alkaline solutions

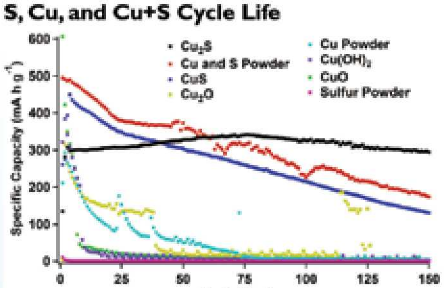
Chemical Reduction Equation	Polysulphide Species	# of e⁻ per S atom	Potential vs. Zinc (V)	Specific Capacity (mA h g^{-1} S)	Specific Capacity (mA h g^{-1} Cu_2S)
(1)	S_5^{2-}	1.60	1.202	1340	268
(2)	S_4^{2-}	1.50	1.232	1256	251
(3)	S_3^{2-}	1.33	1.296	1117	223
(4)	S_2^{2-}	1.00	1.497	838	168

Maintaining Solid State



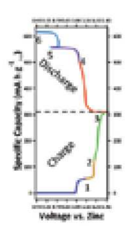
5 wt. % solution of Sulfur in 8.5 M KOH, saturated solution of Copper in 8.5 M KOH, and their mixed product in 8.5 M KOH

S, Cu, and Cu+S Cycle Life

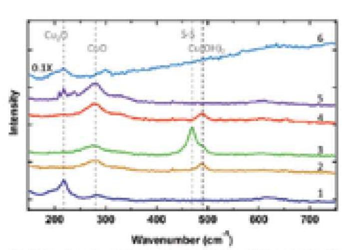


Specific capacity (based on mass of active material) versus cycle number for a variety of Cu and S materials as the active materials in the cathode versus a Zn anode.

Characterized by Raman Spectroscopy

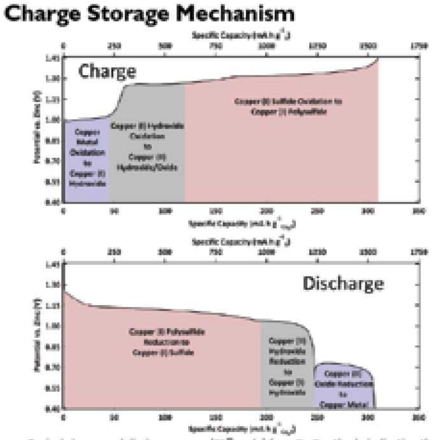


Representative charge/discharge curve with numeric figures indicating positions along the curve where Raman spectra was taken



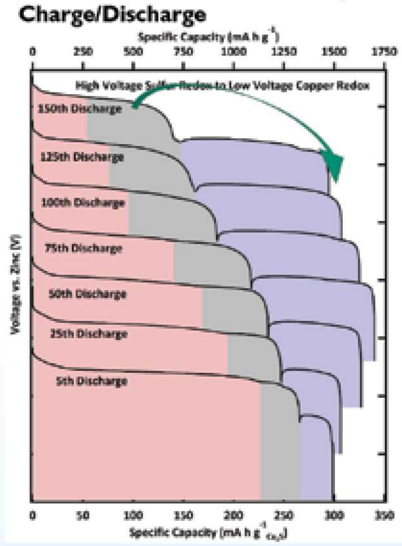
Ex Situ Raman spectra of electrodes taken along their charge/discharge profile at the different numeric points indicated in graph at left

Charge Storage Mechanism



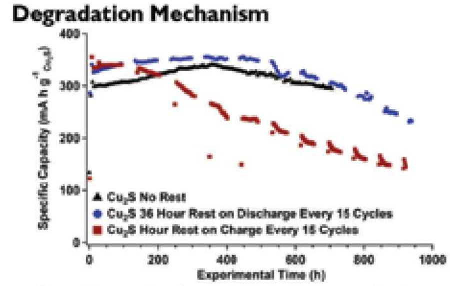
Typical charge and discharge curve (25[th] cycle) for a Cu_2S cathode indicating the phase transitions inferred by the Raman spectroscopy above.

Failure Mechanism of 100% Depth of Charge/Discharge



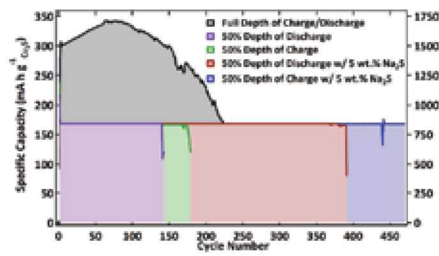
Discharge curves of Cu_2S at a 0.4 C rate (note: based on S^{2-}/S redox; however, the rate is 0.2 C based on Cu/Cu^{2+} redox) from cycle 5 to the 150[th] cycle with the three redox reactions represented by shading;

Chemical versus Electrochemical Degradation Mechanism



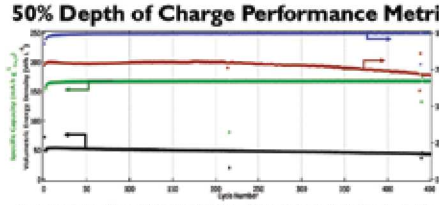
Specific capacity versus time of a Zn/Cu_2S battery with no rest and resting every 15 cycles for 36 hours upon discharge (to 0.4 V vs Zn) or upon charge (to 1.45V vs Zn).

Adjusting Depth of Charge/Discharge and Electrolyte Chemistry



Cu_2S cathode cycling at various charge discharge protocols: full depth of charge (black), 50% depth of discharge with no additive (purple), 50% depth of charge with no additive (green), 50% depth of discharge with 5 wt. % Na_2S in the electrolyte (red), and 50% depth of charge with 5 wt. % Na_2S in the electrolyte (blue).

50% Depth of Charge Performance Metrics



Performance metrics of Cu_2S electrode cycled at 50% depth of charge with 5 wt. % Na_2S added to the electrolyte over 450 cycles.

Conclusions

- First example of a rechargeable solid-state sulfur cathode in an alkaline battery (Zn/Cu_2S battery is demonstrated)
- The nominal voltage of this battery is **> 1.202 V** with a derived empirical capacity (see table 1) of **≥ 168 mA h g^{-1}** based on the mass of Cu_2S (**≥ 838 mA h g^{-1}** based on the mass of S)
- S cycles best when bound to Cu ions in the 1$^+$ valence state, forming Cu_2S as a discharge product
- The failure mechanism of these cells was found to be a slow conversion from S redox to Cu redox chemistry with a subsequent rapid decline in capacity upon the full conversion from the S to Cu redox chemistry

Publications/Presentations/Patents

- J. Duay, T. N. Lambert et al. "Rechargeable Solid-State Copper Sulphide Cathodes for Alkaline Batteries: Importance of the Copper Valence State" J. Electrochem. Soc. 2019 166 (4), A687-A694. DOI: 10.1149/2.0261904jes.
- Invited Talk: J. Duay et al. "Advances in Alkaline Storage Batteries and their Potential Impact for Society" to be presented at the 9th WMRIF Symposium and General Assembly, Budapest, Hungary, June 17-20, 2019.
- T. N. Lambert and J. Duay, United States of America Patent Application filed

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government. Dr. Imre Gyuk, Director of Energy Storage Research, Office of Electricity is thanked for his financial support.

Sandia National Laboratories

PARTNERSHIPS

The Department of Energy's Office of Electricity (DOE OE) energy storage research program relies on collaboration and partnerships with a range of stakeholders, including other national laboratories, universities, electric utilities, industry, federal and state agencies, and international consortia. These partnerships help enable the rapid adoption of new R&D and provide guidance for developing appropriate policy and regulatory framework.

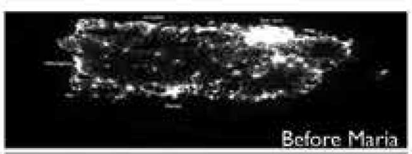
Using Hydro and Energy Storage for Resiliency in Puerto Rico

Frank Currie, Alexander Headley, Dan Borneo

Municipality	Population (2010)	Area (mi²)
Utuado	33,149	115
Jayuya	16,642	39.4
Ciales	18,782	66.5
Morovis	32,610	38.7
Orocovis	23,423	71.1
Villalba	26,073	37.7
Barranquitas	30,318	33.2
Totals	**180,997**	**401.6**

Abstract:

Municipalities in the interior of Puerto Rico went *months* without power after hurricane Maria. This work focuses on using energy storage and existing hydroelectric facilities to create an independent mountain region minigrid that would require no transmission ties to PREPA baseload generation assets. An optimization minimized energy storage and PV requirements as a function of hydroelectric capacity factor. The results show that hydro and energy storage can be used cooperatively to increase resilience and vastly reduce future capacity investments.



Source: NOAA National Environmental Satellite, Data, and Information Service (NESDIS)

Future Study:

- Use a hydro **rehab cost estimate** to improve resource optimization
- Improve **hydro model** to include reservoir dynamics
- Improve **load profile** using historic load data for the specific municipalities
- Improve **solar profile** to reflect municipalities-specific differences
- Integrate ReNCAT to modify load profile to reflect load criticality

Acknowledgements: Funding provided by US DOE Energy Storage Program managed by Dr. Imre Gyuk of the DOE Office of Electricity Delivery and Energy Reliability.

Current plans call for PV + ES, but the total cost of new capacity can be significantly reduced by using existing hydroelectric facilities.

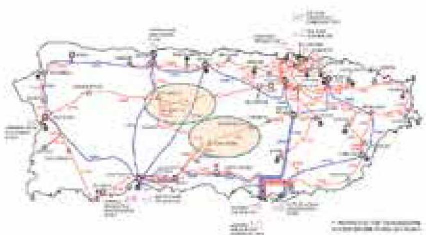
North Central: Includes the cities of Ciales, Morovis, Utuado, and Jayuya

<u>**Approximate peak loads:**</u>

Ciales:	6 MW
Morovis:	9 MW
Utuado:	15 MW
Jayuya:	8 MW
	38 MW

<u>**Generation:**</u>

Caonillas 1:	18 MW
Dos Bocas:	15 MW
Caonillas 2:	4 MW
	37 MW



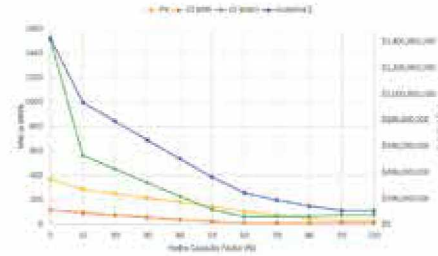
South Central: Includes the cities of Villalba, Orocovis, and Barranquitas

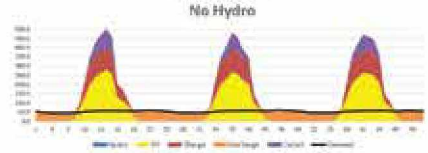
<u>**Approximate peak loads:**</u>

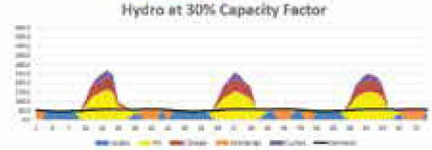
Villalba:	10 MW
Orocovis:	6 MW
Barranquitas:	10 MW
	26 MW

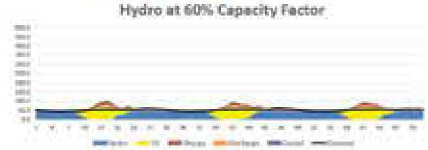
<u>**Generation:**</u>

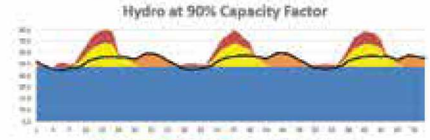
Toro Negro 1:	9 MW
Toro Negro 2:	2 MW
	11 MW

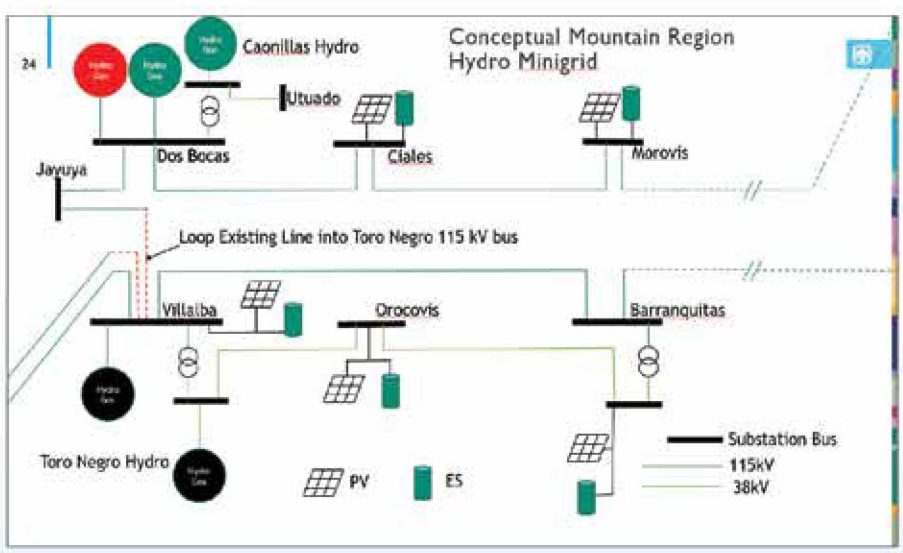












DOE OE PEER REVIEW
Albuquerque, New Mexico | September 23-26, 2019

Update on the Natural Energy Laboratory of Hawaii Authority ESS and Microgrid Projects

Laurence Sombardier, Gregory Barbour, Keith Olson, Natural Energy Laboratory of Hawaii Authority (NELHA)
Daniel Borneo, Benjamin Schenckman, Alexander Headley, Sandia National Laboratories

NELHA'S ENERGY OBJECTIVES

- State of Hawaii Goal: 100% Clean Energy by 2045.
- Test small and large scale ESS systems on Hawaii grid to provide enhancements to resiliency, circuit level frequency, voltage and VAR support, renewable energy dispatching capabilities.
- Test ESS in tropical and marine environments.
- Microgrid development.
- Facilitate development of new clean energy technologies.

MICROGRID DEVELOPMENT

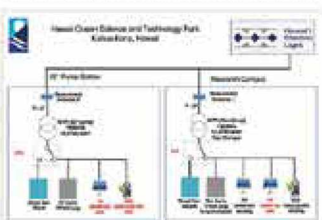
UH HAWAII NATURAL ENERGY INSTITUTE STUDY

- 1 year study starting September 2019
- Develop conceptual designs for power generation, energy storage, and power management and control technologies over a 10-year planning horizon to assist NELHA in becoming carbon-neutral by 2030.

JOINT KOREAN US MICROGRID DEMONSTRATION PROJECT

Development and field verification of an artificial intelligence based microgrid operation platform.

Equipment to be used in KETEP NELHA microgrid



Microgrid Components and overall concept. Red items are new components.

Milestones	Date
Design Completion	January 15, 2020
Construction Completion	December 1, 2020
Microgrid Commissioning	January, 15 2021

GRID SCALE -UET 100KW ESS

UET UniEnergy Technologies

- 100kW/500kWh modular ReFlexTM ESS.
- Advanced vanadium flow technology.
- System will be owned by local utility, Hawaii Electric Light Company.

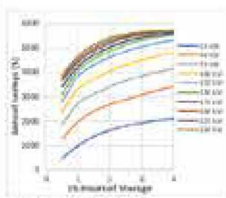
ESS installation early December 2018

Inauguration Dec 6, 2018

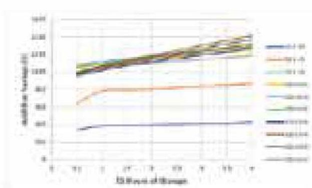
System experienced a catastrophic failure and UET shut the ESS down on February 9, 2019. The failure included a rupture in primary electrolyte tank. 30 gallons of electrolyte were spilled into the secondary containment. System is in the process of being replaced with 13 UET ReFlex units.

SANDIA QUEST ESS STUDY

- Purpose of study: investigate use of ESS and scheduling of the production of hydrogen to realize savings in NELHA's research campus.
- Study utilized Sandia National Laboratories QUEST open source software and was primarily carried out by Alexander Headley.



Annual Savings from ESS alone



Annual Savings from ESS with scheduled H2 Production

CONCLUSIONS:

- Model shows that savings may be realized by reducing monthly peak demand.
- A 150 kW/2 hour system could be expected to yield ~$5,000/year in savings. This assumes no H2 production or scheduling.
- Scheduling the H2 facility will flatten the demand and lead to $26,000/year savings (versus unscheduled daily H2 production). An additional 150kW/2 hour battery will save an additional $1,200/year.

CAMPUS PV INSTALLATION

- Installed 170 KW PV on rooftops of two campus buildings.
- Power Purchase Agreements with Greenpath Technologies LLC.
- $0.18/kW, no escalator over 20 years. Utility rate is ~$0.32/kW.
- Testing and inspection completed July 2019.
- Systems started producing August 1, 2019.
- With existing 36kW, total PV is campus is at 206kW DC.
- Campus load is 150 kW to 220kW, not counting Hydrogen generation and distribution facility (250kW).

OUR PARTNERS

Sandia National Laboratories
ENCORED
Advanced Grid Research
KETEP
ulupono INITIATIVE
Hawai'i Electric Light
LG
HNEI
GREEN PATH TECHNOLOGIES, Inc.

ACKNOWLEDGEMENTS

Special Mahalo to Dr. Imre Gyuk from DOE Office of Electricity without whom the NELHA ESS projects would not be possible.

Energy Storage Valuation at San Carlos Apache Tribe

Rodrigo D. Trevizan, Tu Nguyen and Stan Atcitty

Abstract: San Carlos Apache Tribe (SCAT) is located in a sparsely populated region that has limited power generation and transmission resources. Currently, the energy tariffs are high and the system suffers from frequent power interruptions. In this study, we have analyzed the benefits of Energy Storage Systems (ESS) to reduce costs and improve power quality for the tribe. We have conducted two case studies evaluating behind-the-meter ESSs for a casino and a hospital. Results show that energy storage has the potential to reduce electricity costs and provide backup power for critical loads during several hours.

Challenges at SCAT

- Population: around 10,000 people
- Area: 2,900 sq. miles (2x Rhode Island)
- Scattered loads – three power providers:
  - San Carlos Irrigation Project (SCIP)
  - Arizona Public Service (APS)
  - Graham County Electric Cooperative
- Limited electric power resources
  - Small solar PV, utility-scale planned
- Limited transmission
  - Only 1 69kV transmission line (SCIP)
- Reliability issues
  - Average 100 outages per year
  - Could affect 4,000 to 6,000 people
- Cost of electricity above state average

Project Goal:

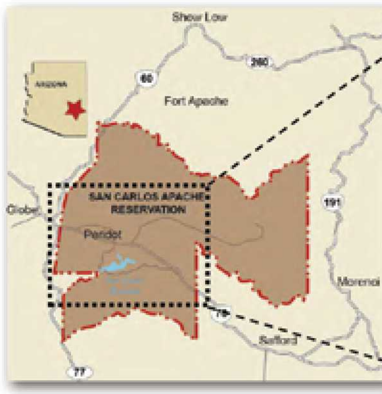
- Provide technical assistance to the Tribe to enable informed decision making with respect to future planning of Renewable Energy Portfolio and show how ESS can enhance system reliability

Benefits of Energy Storage

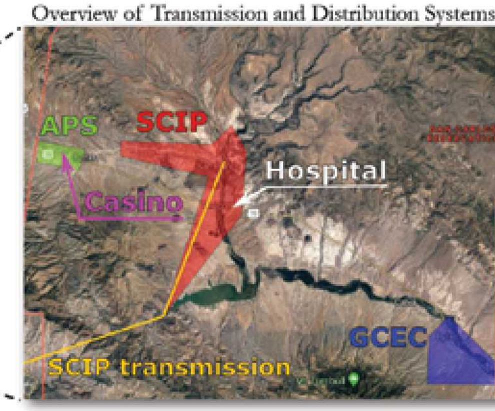
- Increase reliability for critical loads
- Reduce electricity costs
- Behind-the-meter (BTM) cost savings
  - Time of use (TOU) energy
  - Demand
  - Increase value of solar

Case Studies

- Two BTM applications for ESS
- Case 1 – Apache Gold Casino/Resort
  - APS –TOU (E-35) Primary
- Case 2 – San Carlos Apache Healthcare
  - SCIP – Large commercial



Overview of Transmission and Distribution Systems



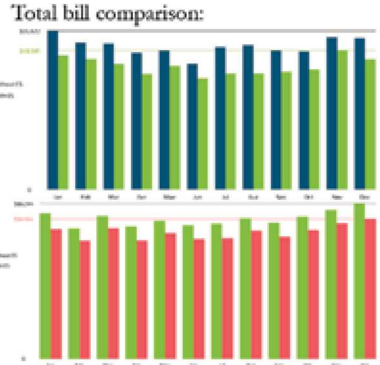
- Assumptions:
  - No hourly load data available - estimates
  - Backup power by ESS only
- Assuming 2 cases for backup power:
  - Reduction of load to 20% or 40%
- Case 1 - Apache Gold Casino/Resort
  - Planned 1,100 kW solar PV
- Case 2 - San Carlos Apache Healthcare Hospital
  - Planned 2,000 to 3,000 kW solar PV
- Techno-economic analysis using QuESt BTM

Preliminary Results

Total bill comparison:

Case 1

Case 2



Demand charges:

Case 1

Case 2

Case	Solar power	ESS power	ESS capacity	Backup time @ 20% load	Backup time @ 40% load	Yearly charges	Total yearly savings	Savings demand	Reduction peak demand
Case 1 - Casino	1,100 kW	500 kW	1,000 kWh	5.87 h	2.93 h	$601,080.77	$83,959.77	$83,867.93	47.23 kW (3.5%)
Case 2 - Hospital	2,000 kW	500 kW	2,000 kWh	8.65 h	4.33 h	$716,013.93	$69,365.13	$73,742.20	478.26 kW (30.13%)

Conclusions

- ESS can reduce costs and improve reliability of critical load centers in SCAT
- Apache Gold Casino/Resort
  - 500 kW/1,000 kWh system can reduce costs with electricity in about 14%
  - Up to 5.8 hours of backup power
- San Carlos Apache Healthcare Hospital
  - 500 kW/2,000 kWh system can reduce annual costs with electricity in about 10%
  - Up to 8.6 hours of backup power
- Future work
  - Obtain load data - Hospital & Casino
  - BTM analysis for other sites
  - Front-of-the-meter analysis (Utility-Scale)

Acknowledgement: Funding was provided by the US DOE OE Energy Storage Program managed by **Dr. Imre Gyuk** of the DOE Office of Electricity.

Sandia National Laboratories

MATERIALS I

The Pacific Northwest National Laboratory (PNNL) Electrochemical Materials and Systems group comprises materials scientists, ceramists, metallurgists, and mechanical engineers engaged in research and formulation of advanced cost-effective lightweight materials, power generation sources, engine exhaust remediation, advanced manufacturing processes, prototype devices, and pilot-scale process development. Their program aims to develop and demonstrate novel energy storage technologies that can meet economic and performance targets for broad market penetration. Research areas include emissions, fuel cells, high-temperature electrochemistry center, transportation materials, and vehicle and transportation technologies.

Sandia National Laboratories

Exceptional service in the national interest

Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge

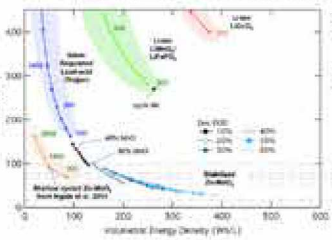
Matthew B. Lim[1], **Elijah I. Ruiz**[2], **Timothy N. Lambert**[2,*], **Gautam G. Yadav**[3], **Damon E. Turney**[3], **Sanjoy Banerjee**[3]

[1]*Energy Storage Technology & Systems Department, Sandia National Laboratories, Albuquerque, NM 87185, USA*
[2]*Photovoltaics & Materials Technologies Department, Sandia National Laboratories, Albuquerque, NM 87185, USA*
[3]*The CUNY Energy Institute at the City College of New York, Department of Chemical Engineering, New York, NY 10031, USA*

***Email:** mlambe@sandia.gov

Background and Objectives

Zn/MnO$_2$ batteries for the grid: Energy-dense, safe, abundant, low-cost materials

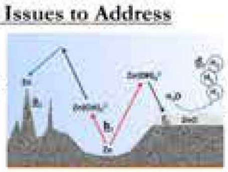


DE Turney and GG Yadav, City University of New York (2019).
Jim Eyer and Garth Corey SAND2010-0815, 2010

- Up to 400 Wh/L, 150 Wh/kg and ~$18/kWh as primary cell
- Commercialized by Urban Electric Power, ***but only under limited depth-of-discharge (DOD) conditions***
  - ~100 Wh/L, $200/kWh

Anode Issues to Address

- Shape change
- Dendrite formation
- Passivation
- H_2 evolution



J. Fu et al., *Adv. Mater.* 29, 1604685 (2017)

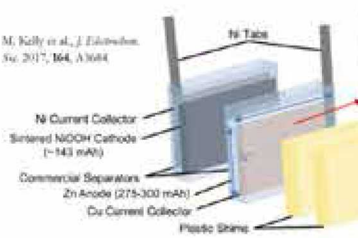
Objectives

- **Increase achievable cycle life and energy density by pre-saturating electrolyte with ZnO to inhibit dissolution and migration of zinc from the anode.**
- **Study effect of ZnO saturation at different depths of discharge, *relative to total zinc species in the system*, and at different KOH concentrations in a more commercially relevant limited-electrolyte system.**

Experimental Plan

Due to the sensitivity of MnO$_2$ to Zn(OH)$_4^{2-}$, use NiOOH as the cathode material instead to examine the effect of ZnO saturation at different Zn DOD.

M. Kelly et al., *J. Electrochem. Soc.* 2017, 164, A3684



- 3 mL 25%, 32%, or 45% KOH electrolyte with/without saturated ZnO
- Cycled between 1 and 1.93 V vs. Zn at C/10 relative to full anode capacity ≈ **75 mA/g$_{anode}$**
- Zn DOD limits of 14%, 21%, 35% **relative to all Zn+ZnO in system**
- Cells considered failed when discharge capacity fell below 80% of DOD limit

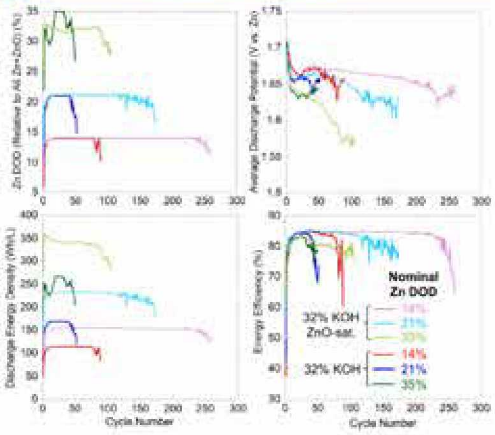
Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. The views expressed herein do not necessarily represent the views of the U.S. Department of Energy or the United States Government. Dr. Imre Gyuk, Director of Energy Storage Research, Office of Electricity is thanked for his financial support. The authors also thank Bonnie McKenzie at Sandia National Laboratories for SEM characterization, and Michael Nyce at the CUNY Energy Institute for providing sintered NiOOH electrodes.

SAND No. SAND2019-11032 E

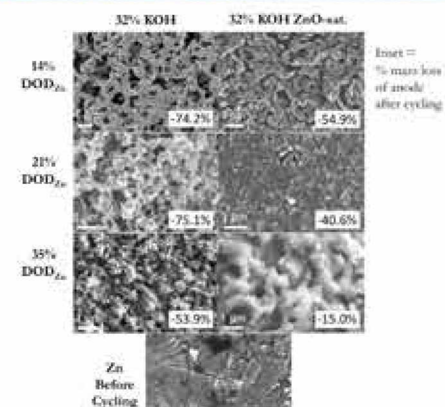
LDRD U.S. DEPARTMENT OF ENERGY NNSA

Cycling Results

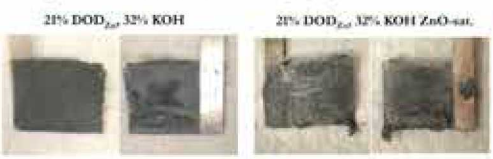


Cells with saturated electrolyte last significantly longer with no energy losses due to voltage and similar energy efficiency compared to cells with regular electrolyte cycled at same DOD, ***even when including dissolved ZnO in capacity***

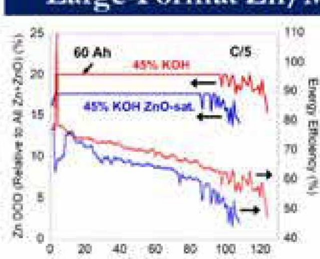
Post-Cycling Characterization



- Anodes in ZnO-saturated electrolyte yield more compact Zn deposits indicating more homogeneous current density
- They also lose less mass during cycling despite significant Zn deposition on the bottom and through separator.



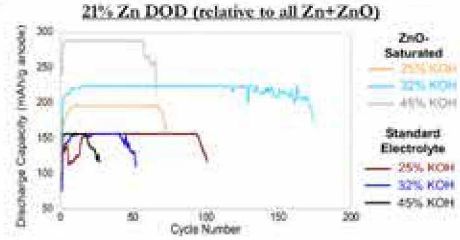
Large-Format Zn/MnO$_2$ Cell



- Cells with saturated electrolyte last >100 cycles, though slightly less than cells with 45% KOH only, and lower energy efficiency
  - Zinc clogs separator, creating soft short-circuit

Effect of KOH Concentration

21% Zn DOD (relative to all Zn+ZnO)



- Cells with 45% KOH fail more quickly with more zinc growth outside electrode than cells with less concentrated electrolyte
- ZnO saturation *reduces* cycle life in 25% KOH at 21% Zn DOD

Initial wt% KOH	mol/L Zn(II) at Saturation	mAh in Dissolved ZnO
25	0.45	72.4
32	0.74	119
45	1.50	241

J. Electrochem. Soc. 1967, 114, 1045.
J. Chem. Soc. Faraday Trans. 2, 1974, 70, 1958.

Cycled Cells with ZnO-Saturated Electrolyte

Bottom view (front of cell facing down)

Conclusions and Future Work

- Pre-saturating electrolyte with ZnO increases lifetime of Zn/Ni cells at high Zn utilization (≥14% DOD) without energy losses, but only at higher KOH concentrations
  - 32% KOH appears to be optimal concentration
- ZnO saturation has no benefit on Zn/MnO$_2$ cells with commercial separators → **Need to develop zincate-blocking separators** to isolate zincate in anode and suppress deposition away from anode
  - Should be **flexible and conductive**
  - Potential for >250 Wh/L and <$100/kWh
  - Ongoing collaboration with City College of New York
- Further reduce electrolyte usage to reduce material cost
  - Want **~2 mL/mL anode** (ours ~ 40 mL/mL anode)
  - Electrolyte is effectively saturated with zincate in operando

Research Output

Publications

- MB Lim, TN Lambert, EI Ruiz. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge", *to be submitted Sep-Oct 2019.*

Talks

- MB Lim, M Kelly, J Duay, IV Kolesnichenko, TN Lambert. "Improving Cycle Life and Active Materials Utilization for Rechargeable Alkaline Zn–MnO$_2$ Batteries". 235[th] Electrochemical Society Meeting, Dallas, TX (May 28, 2019).
- MB Lim, TN Lambert. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge". 31[st] Rio Grande Symposium on Advanced Materials, Albuquerque, NM (Sep 16, 2019).
- MB Lim, IV Kolesnichenko, DJ Arnot, TN Lambert. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zn–Ni and Zn–MnO$_2$ Batteries at High Zinc Depth-of-Discharge". 236[th] Electrochemical Society Meeting, Atlanta, GA. (Oct 15, 2019).

Poster

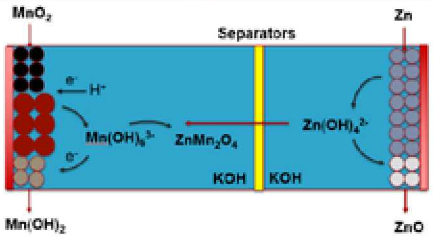
- MB Lim, IV Kolesnichenko, DJ Arnot, TN Lambert. "Effect of ZnO-Saturated Electrolyte on Rechargeable Alkaline Zinc Batteries at High Depth-of-Discharge". Los Alamos National Laboratory Postdoc Research Symposium, Los Alamos, NM (Aug 27, 2019).

Sandia National Laboratories

Zincate-Blocking Polymeric Separators for Zn/MnO_2 Batteries

Igor Kolesnichenko,[1] David Arnot,[1] Matthew Lim,[2] Timothy N. Lambert,[1]*
Gautam Yadav,[3] Jungsang Cho,[3] Michael Nyce,[3] Sanjoy Banerjee[3]
[1]Department of Photovoltaics & Materials Technologies, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA
[2]Department of Energy Storage Technology & Systems, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA
[3]Department of Chemical Engineering, The CUNY Energy Institute at the City College of New York, Steinman Hall Room 316, 160 Convent Avenue, New York, New York 10031, USA
***Email:** tnlambe@sandia.gov

Background and Objectives



Cathode Failure Mechanisms:

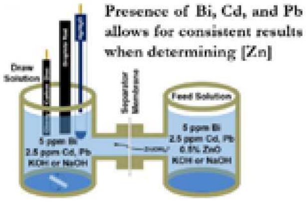
- Formation of irreversible Mn_3O_4.
- Formation of irreversible $ZnMn_2O_4$.
- Passivation from an insulating ZnO layer.

Caused by $Zn(OH)_4^{2-}$ crossover

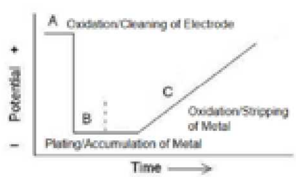
Objectives:

- Synthesize separators selective for blocking zincate, while allowing for crossover of hydroxide
- Cast membranes with thicknesses similar to those of commercial separators and establish the aforementioned selectivity outside of cells
- Implement into prototype cells and demonstrate an improvement in battery performance

Zinc Diffusion Analysis



Presence of Bi, Cd, and Pb allows for consistent results when determining [Zn]



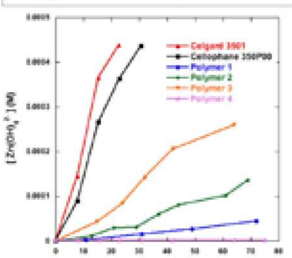
A. J. Bard, L. R. Faulkner, Electrochemical Methods, (2001) 458–466.

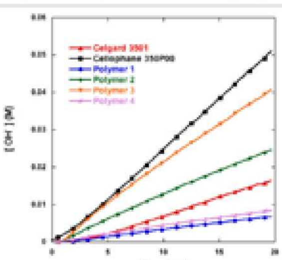
Anodic stripping voltammetry (ASV) allows for much faster screening of separators compared to ICP-MS, with similar limits of detection.

ASV Analysis of Zn performed for the first time in alkaline conditions.
J. Duay, T.N. Lambert, R. Aidun, *Electroanalysis*, 29 (2017) 1-8.

Polymeric Separators

Separator	Hydroxide Diffusion Coefficient (cm²/min) *10 [illegible]	Zincate Diffusion Coefficient (cm²/min) *10 [illegible]	Selectivity	Water Uptake (%)	Thickness (µm)	Conductivity (mS/cm)
Celgard 3501	6.74	5.7	1.18	68	25	12.2
Cellophane 350P00	17.4	2.0	8.70	96	25	13.8
Polymer 1	2.48	0.049	50.6	11	30	5.83
Polymer 2	9.43	0.17	55.5	17	30	7.19
Polymer 3	15.4	0.42	36.7	47	30	8.79
Polymer 4	3.08	≤ 0.000032	10,000	14	25	Approx. 1-4



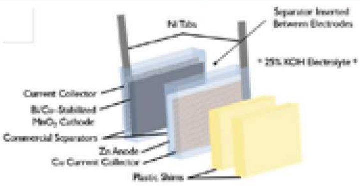


Polymers 1-3 show a greatly improved selectivity ratio over commercial separators for screening out zincate, while allowing for hydroxide crossover. Polymer 4 has an even higher selectivity ratio, but is also far less conductive, resulting in lower practical cycling rates.

Future Goal:

Attain a selectivity ratio on par with Polymer 4, while retaining a conductivity similar to those of commercial separators

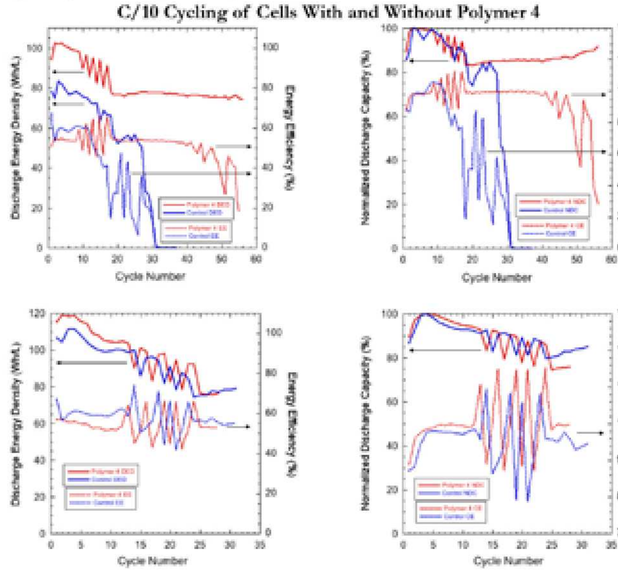
Battery Assembly and Cycling



Journal of Power Sources, 395 (**2018**) 430-438

Control cells are assembled by wrapping both the anode and cathode in 3 layers of Cellophane, while the cells containing Polymer 4 are assembled by wrapping only the anode in 3 layers of Cellophane, inserting Polymer 4 between the electrodes (as shown to the left) and using the cathode as received from CUNY, with no additional wrapping.

C/10 Cycling of Cells With and Without Polymer 4



Conclusions and Research Output

- Prepared flexible polymeric membranes that are resistant to zincate, while maintaining hydroxide permeability on par with commercial separators
- Conductivity constraints limit the rates at which functional batteries containing the fabricated separators can be cycled → **Need to improve upon conductivity**
- Preliminary data from $Zn–MnO_2$ cells shows cycling at C/10 rates that is on par with cells using commercial separators

Publications

- Kolesnichenko, I. V.; Arnot, D. A.; Lim, M. B.; Lambert, T. N. "Zincate–Blocking Functionalized Separators for Secondary Zn/MnO_2 Batteries" *in final preparation*
- Arnot, D. A.; Lim, M. B.; Kolesnichenko, I. V.; Lambert, T. N. "Development of Zincate–Blocking Separators and Their Application in Zinc–Manganese Oxide Batteries" *in preparation*

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Electricity, and the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-program laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. Department of Energy or the United States Government. Dr. Imre Gyuk, Director of Energy Storage Research, Office of Electricity is thanked for his financial support. The views expressed herein do not necessarily represent the views of the U.S.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
SAND No. [illegible]

Sandia National Laboratories

Effects of Water-Soluble Binders on Electrochemical Performance of Manganese Dioxide Cathode in Mild Aqueous Zinc Batteries

Hee Jung Chang[1], Matthew R. Fayette[1], Ismael Rodriguez Perez[1], Huilin Pan[1], Daiwon Choi, Xiaolin Li[1], Vincent L. Sprenkle[1] and David Reed[1*]

[1]Electrochemical Materials and Systems Group, Pacific Northwest National Laboratory (PNNL), Richland, Washington, USA

Pacific Northwest NATIONAL LABORATORY

Proudly Operated by Battelle Since 1965

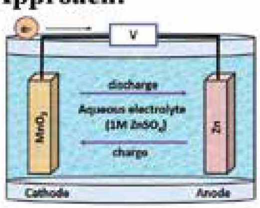
Introduction: Stationary electric energy storage has become a growing worldwide interest due to increased global market needs. With demand growing fast, conventional lithium ion battery (LIB) technologies have a limited portfolio for stationary applications due to use of high cost materials and limited life cycle.

In recent years, intensive studies of aqueous Zn-based batteries have been reported due to its wide availability, low-cost nature, and recyclability. With respect to LIB, current electrode processing for aqueous battery systems is based on the use of fluorine-containing polymers, such as polyvinylidene difluoride (PVDF) which requires toxic N-methyl-2-pyrrolidone (NMP) solvent.[1] Therefore, PNNL investigates various water-soluble binders for Zn/MnO_2 systems to develop a fully sustainable, cost-effective and environmentally friendly electrochemical energy storage device.

1. Breuer et al. Energy & Environmental Science 11 11 (2018) 3096-3127

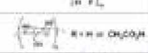
Objective: The goal of this program is to enhance the electrochemical performance of Zn/MnO_2 aqueous batteries by using low cost and environmentally friendly binders

Approach:

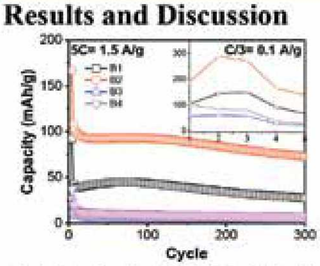


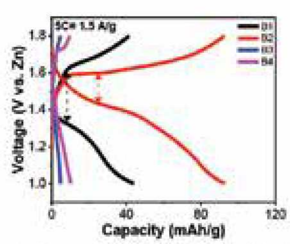
Cell preparation

- Cathode : 70% EMD (γ- MnO_2) + 20% acetylene black + 10% binder
- Anode: metallic Zn
- Electrolyte: 1M $ZnSO_4$
- Separator: glass fiber
- Theoretical capacity=308mAh/g for 1e⁻

No.	Binders	Solvent	Structures
B1	5 wt% Polyvinylidene fluoride (PVDF)	NMP	
B2	2.5 wt % Carboxymethyl cellulose (CMC)	Water	
B3	2.5 wt% Alginic acid, sodium salt	Water	
B4	2 wt% CMC +Polyvinyl alcohol (PVA) (1:1 wt%)	Water	

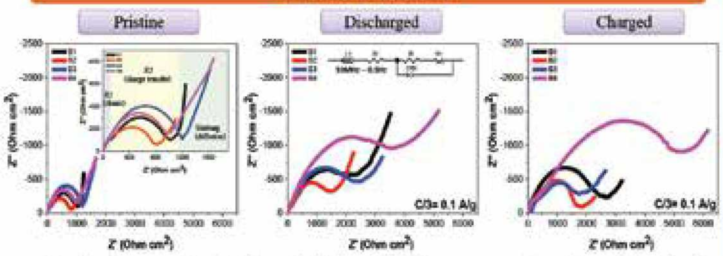
Results and Discussion





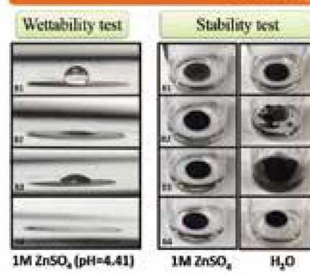
- The MnO_2-Zn cell with B2 binder (CMC) achieved higher cell capacity of 166 mAh/g at 5C and 288 mAh/g at C/3 (inset data) for 300 cycles than the rest of the cells including PVDF.
- The 50th voltage profile displays the cell with CMC showing smaller cell overpotential.

EIS measurement



- Smaller charge transfer (R2, the semicircle in middle frequency range) was observed for the cell with the aqueous B2 binder (CMC) before and after cycling than the cell with PVDF.
- In the low frequency region, the cell with B1 binder (PVDF) displays steeper slope (Warburg line), which implies slower diffusion near the surface.

Wettability and Stability test

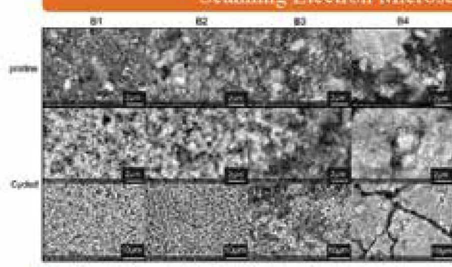


- Sessile drop technique demonstrates that sluggish diffusion near the surface for the cathode with PVDF is associated with high surface tension.
- All of the cathodes with different binders seem very stable in 1M ZnSO4 over 6 months. However, significant dissolution in excessive water was observed for the aqueous binders B2 and B3 .
- ICP results support aqueous binders can be stable in the electrolyte without dissolution.

ICP test of B3 binder

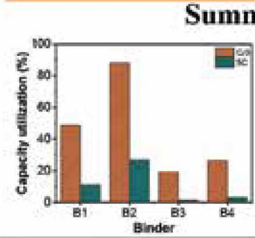
		ICP results: ppm			Conc. M/L		
Sample ID#	dilute times	Zn	Na	S	Zn	Na	S
1M ZnSO4	10000	6.154	0	3.53	0.94112	0	1.10071
1M ZnSO4+B3	10000	6.227	0.602	3.63	0.95229	0.0008	1.13189

Scanning Electron Microscopy (SEM)



- Similar cathode particle sizes and distribution on the surfaces were observed for all cathodes except B4 before and after cycling.
- Significant cathode particle aggregation was detected for the cell with B4 binder after electrode slurry processing.

Summary and Perspective



- We observed water-soluble binder CMC can be stable and offer desirable adhesion at certain pH levels (3.5~5) without any decomposition.
- Our work suggests that the implementation of water-soluble binders can lead to substantial improvements for efficient and cost-effective electrode manufacturing for aqueous battery systems.
- In order to fully assess the applicability of aqueous binders, further test for validation on a larger scale will be conducted.

U.S. DEPARTMENT OF ENERGY

Contact: Hee -Jung Chang
Battery Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: heejung.chang@pnnl.gov
Tel: (509) 372-4072

Acknowledgements This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is a operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830

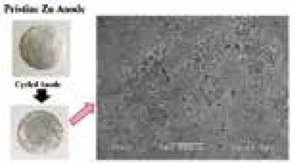
Development of Zinc-Based Anodes for Aqueous MnO_2/Zn based Batteries

Matthew R. Fayette[1], Hee-Jung Chang[1], Ismael A. Rodriguez-Perez[1], Xiaolin Li[1] and David Reed[1]*
[1]Battery Materials and Systems Group, Pacific Northwest National Laboratory (PNNL), Richland, Washington, USA

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

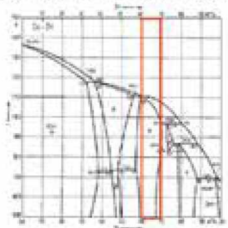
Introduction: The development of alternative energy sources (i.e. batteries) has garnered much attention in the past few years. In particular, stationary energy storage devices have become a major focus for research and development in order to make electrical storage cheaper, and more environmentally friendly than traditionally used sources (i.e. fossil fuels).[1]

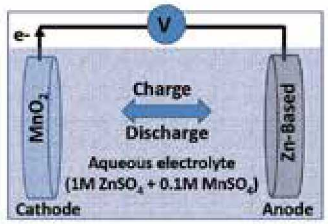
Within the past decade, Zinc (fourth-most mined material on the Earth) has attracted much attention because it is abundant, inexpensive, and re-usable. Moreover, as Zinc-based batteries can be manufactured with a water-based electrolyte, this allows for competition with Lithium-ion batteries, but with the advantage of enhanced safety.



Zinc-based batteries (i.e. alkaline Zinc/MnO_2) have previously been commercialized and are one of the dominant technologies in the primary battery market. However, the alkaline Zinc/MnO_2 system is not currently considered re-chargeable owing to formation of zinc dendrites, and low cathode capacity.[2]

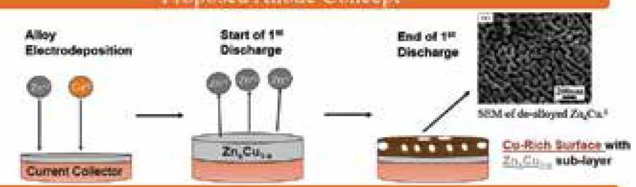
Objective: Mitigation of dendrites in zinc-based anodes for mildly acidic aqueous Zn-MnO_2 battery technology for stationary energy applications.


Zinc-Copper Phase Diagram



Approach: Develop Zinc-based Anodes using an electrochemical-based method.

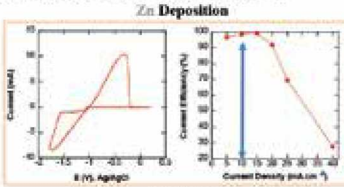
Proposed Anode Concept



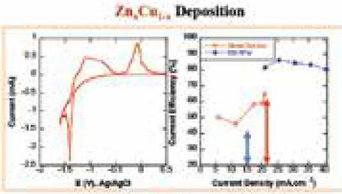
SEM of de-alloyed Zn_xCu.[3]

Results and Discussion:

Zn Deposition



Zn_xCu_{1-x} Deposition



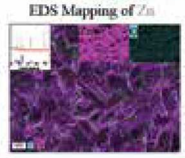
Zn Films

Zn_xCu_{1-x} Films

- Both Zinc and Zn_xCu_{1-x} can be deposited onto current collectors at efficiencies of at least 80%
- For the Zn_xCu_{1-x}, a brass-colored deposit is obtained at the same current density relative to pure Zn solution. Higher current densities result in a silver-like deposit indicative of Zinc-rich brass

X-ray Diffraction (XRD)/ Energy Dispersive X-Ray Spectroscopy (EDS)

EDS Mapping of Zn

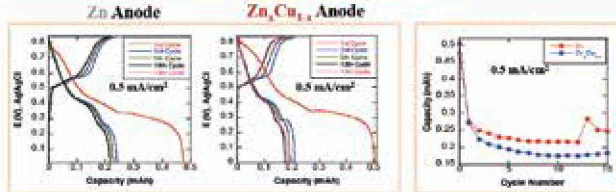


- EDS/XRD confirms that the Zinc film is polycrystalline and metallic (PDF Card #: 01-078-9364).
- EDS results show that the surface composition of the Zn_xCu_{1-x} alloy is $Zn_{0.35}Cu_{0.65}$

EDS Mapping of Zn_xCu_{1-x}

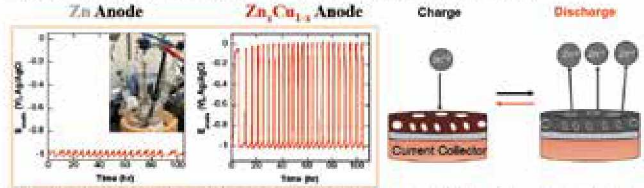
Electrochemical Performance

Zn Anode — Zn_xCu_{1-x} Anode



- At 0.5 mA/cm², full cells with Zn and Zn_xCu_{1-x} film anodes have similar initial electrochemical capacity.
- Over the course of 15 cycles, the pure Zn anode has a slightly higher capacity compared to Zn_xCu_{1-x}. This slight capacity difference may be due to stability against dendrites.

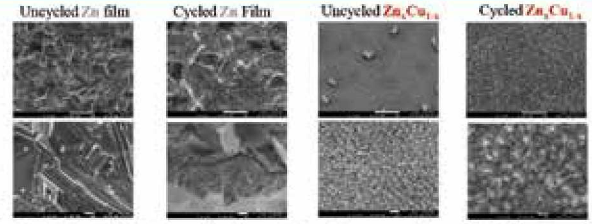
Zn Anode — Zn_xCu_{1-x} Anode — Charge — Discharge



- While the Zn thin film has a stable potential, the Zn_xCu_{1-x} potential varies by nearly 1V. This is due to removal of Zn from the alloy, leaving a copper rich surface during discharge. Upon charging, the potential slowly returns to a pure Zinc potential, indicating possible Zinc diffusion into the copper pores.

Scanning Electron Microscopy (SEM)

Uncycled Zn film — Cycled Zn Film — Uncycled Zn_xCu_{1-x} — Cycled Zn_xCu_{1-x}



- Zn_xCu_{1-x} film anode has improved tolerance to dendrites compared to pure Zn film.

Summary and Perspective

- In general, both Zn and Zn_xCu_{1-x} alloys can be electrodeposited directly onto current collectors and act as a self-standing electrode without the need to binding agents.
- Preliminary results show that Zn_xCu_{1-x}–MnO_2 cells give similar capacity performances compared to pure Zinc–MnO_2 cells with an improved tolerance to dendrites.
- Further optimization and analysis will be carried out to conditions (composition, thickness, and deposition conditions) for Zn_xCu_{1-x} anode in the Zn-MnO_2 battery.

Acknowledgements
This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. 57558. PNNL is a operated by Battelle Memorial Institute for the DOE under contract DE-AC05-76RL01830

U.S. DEPARTMENT OF ENERGY

Contact: Matthew R. Fayette
Battery Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: matthew.fayette@pnnl.gov
Tel: (509) 372-4848

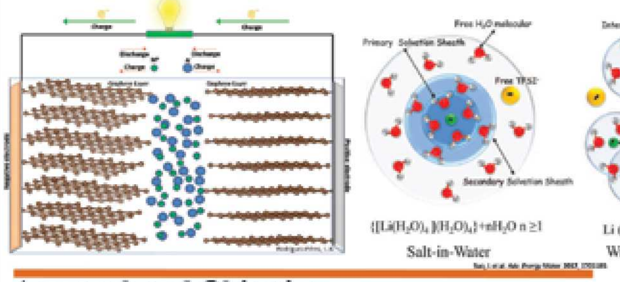
References:
1. Dunn et al. *Science*. 334, 928 (2011)
2. Xu et al. *Angewandte*. 51, 933 (2012)
3. Cheng, I. C.; Hodge, A. M.. *Advanced Engineering Materials*, *14*(4), 219 (2012)

Enabling Natural Graphite in High Voltage Aqueous Zinc-Graphite Dual-Ion Batteries

Ismael A. Rodríguez-Pérez[a]*, Tobias Placke[c], Maria Sushko[b], Xiaolin Li[a], David Reed[a], Vince Sprenkle[a]
[a]Battery Materials & Systems Group, Pacific Northwest National Laboratory Richland, WA 99352
[b]Physical Sciences Division, Pacific Northwest National Laboratory Richland, WA 99352
[c]*University of Münster, MEET Battery Research Center, Corrensstr. 46, 48149 Münster, Germany.*

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle *Since 1965*

Introduction: A new energy storage technology that is attracting attention for grid-level applications is the Dual-ion battery (DIB). DIBs operate having anions and cations simultaneously intercalate at the cathode and anode, respectively, upon charge. Water-in-salt electrolytes (WiSE) have expanded the electrochemical stability window of water based electrolytes, allowing graphite to store charge in aqueous media.



Approach and Objective:

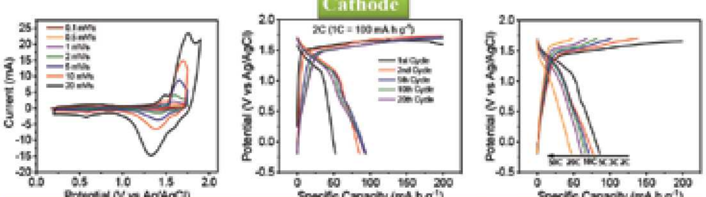
- Choosing a high voltage low cost material and a WiSE electrolyte to expand the water stability window.
- To explore DIBs as an alternative energy storage technology for grid-level applications. DIB advantages are cost, modest performance and safety

Results and Discussion:

Natural graphite has been successfully enabled in an aqueous system at high oxidation potentials. A suite of characterization techniques have been employed to prove and elucidate the anion storage mechanism into the graphite

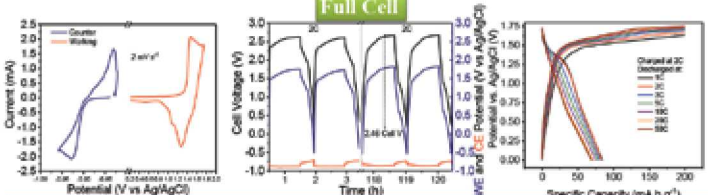
a) Electrochemical Characterization

Cathode



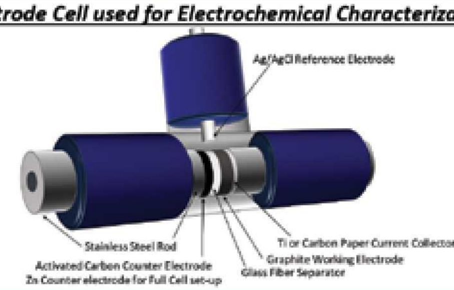
- Clear reversible redox peaks are observed; clear peaks remain even at fast rates
- GCD reveals the remarkable capacity of anion storage in graphite using WiSE

Full Cell



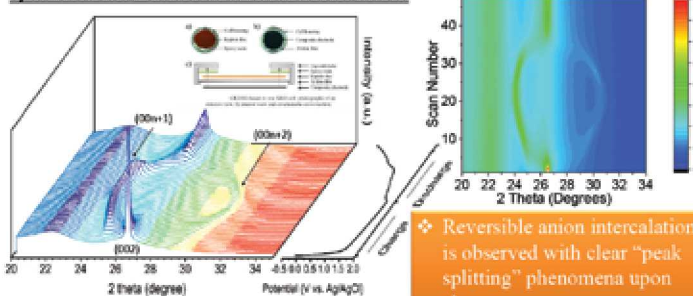
- Three-electrode cell CV tests reveal the reversible plating and tripping of Zn metal in parallel to anion intercalation/deintercalation into the graphite cathode
- Three electrode full cells show the stable, reversible record high cell voltage

b) Three-electrode Cell used for Electrochemical Characterization



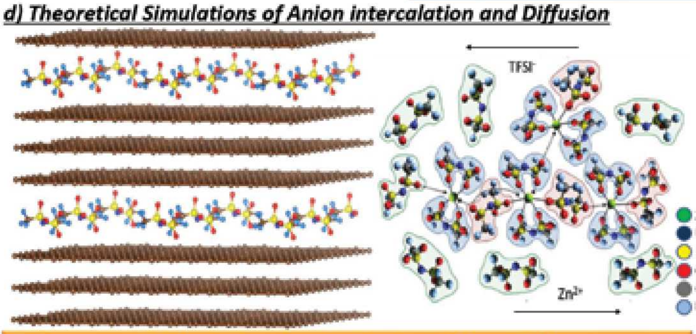
- This set-up allows us to see the stable cycling of both electrodes in a full cell

c) In-Situ XRD Structural Characterization



- Reversible anion intercalation is observed with clear "peak splitting" phenomena upon charge.

d) Theoretical Simulations of Anion intercalation and Diffusion



- Plane-wave DFT simulations showing the charged Stage-3 GIC
- Insights into the anion storage mechanism into graphite point towards a driving force preferential to intercalation of TFSI⁻ anions vs. FSI⁻ anions

Future Work:

- Investigate the bulk electrolyte and the electrolyte electrode interface
- Optimize graphite cathode and electrolyte to achieve longer cycling
- Investigate capacity decay and impact of binder on cycling and self discharge

Acknowledgements

The research described in this poster **was conducted under the Laboratory Directed Research and Development Program at Pacific Northwest National Laboratory**, a multiprogram national laboratory operated by Battelle for the U.S. Department of Energy. I.A.R.P is grateful for the support of the Linus Pauling Distinguished Postdoctoral Fellowship program. I.A.R.P is grateful for the support from MEET for in situ measurement, and support from the physical sciences division for simulations

U.S. DEPARTMENT OF ENERGY

Contact: **Ismael A. Rodriguez-Pérez**
Linus Pauling Distinguished Postdoctoral Fellow
Battery Materials & Systems Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: ismael.rodriguezperez@pnnl.gov
Tel: (509)–375–2097

References:

1. Rodriguez-Pérez, I. A. & Ji, X. Anion Hosting Cathodes in Dual-Ion Batteries. *ACS Energy Lett.* 1762–1770 (2017). doi:10.1021/acsenergylett.7b00321
2. Suo, L. *et al.* "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* **350**, 938–943 (2015).
3. Zhang, C. *et al.* A ZnCl2 water-in-salt electrolyte for a reversible Zn metal anode. *Chem. Commun.* **54**, 14097–14099 (2018). **4.** Placke, T. *et al.* Intercalation of Bis(Trifluoromethanesulfonyl) Imide Anion into Various Graphites for Dual-Ion Cells. *ECS Trans.* **50**, 59–68 (2013).

The following posters were not available at time of printing this report, organized by thrust area:

Equitable Regulatory Environment & Analytics

Opportunities for Energy Storage + Solar in CAISO
Ray Byrne, Sandia National Laboratories

Materials II

Materials and Membranes for High Energy Density Nonaqueous Redox Flow Batteries
Jagjit Nanda, Oak Ridge National Laboratory

Power Electronics

GLIDES: Delivering Efficient, Flexible Energy Storage
Ayyoub Momen, Oak Ridge National Laboratory

Advanced Power Electronics for Grid Storage
Satish Ranade, New Mexico State University

Advanced Capacitors for Future Power Conversion System
Bruce Gnade, Southern Methodist University

Advanced Power Conversion Systems featuring SiC MOSFETs with In-Situ Restoration Capabilities
Ranbir Singh, GeneSiC Semiconductor

Design and Fabrication of High-Temperature Octocoupler for High-Density Power Module
Zhong Chen, University of Arkansas

Materials I

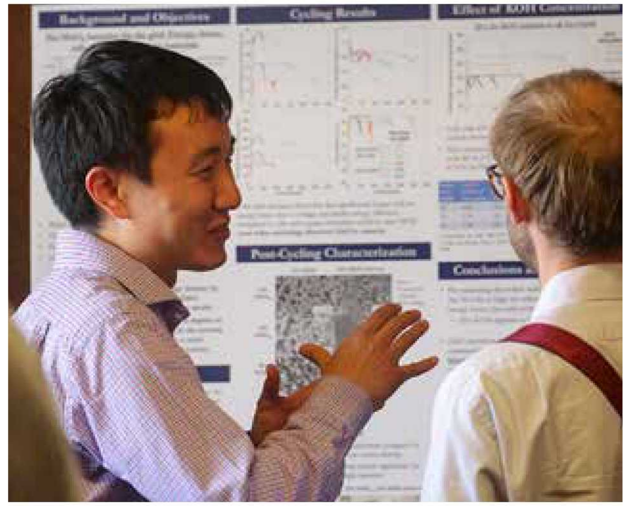
Rechargeable Zinc-Manganese Dioxide Batteries: From Concept to Product
Jinchao Huang, Urban Electric Power

Real-time Identification and Understanding of Zinc Compound in Rechargeable Zinc Electrodes
Brendan Hawkins, City College of New York

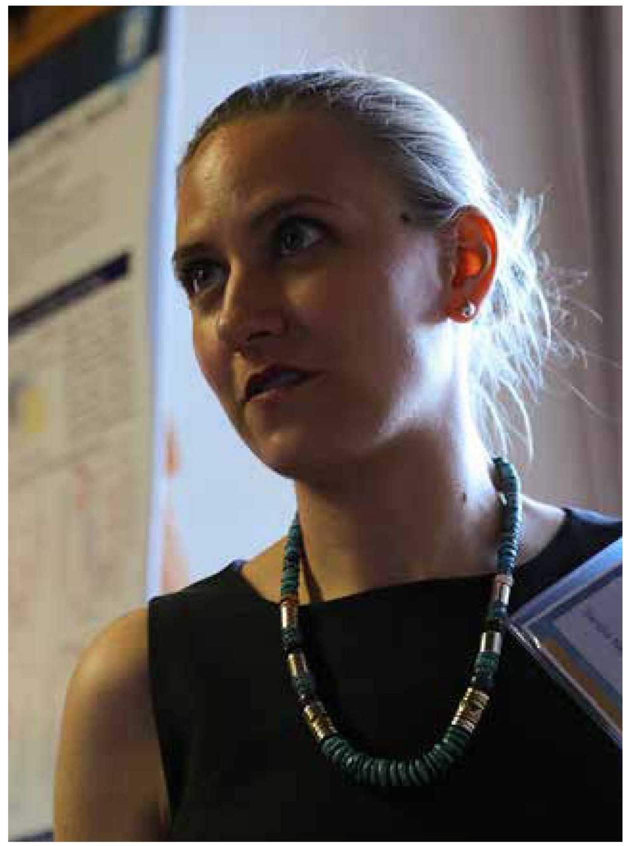
Theoretical Studies of the Electrochemical Properties of Bi- and Cu-Modified d-MnO2 Electrodes in Rechargeable Zn/MnO2 Batteries
Birendra Ale Magar, New Mexico State University

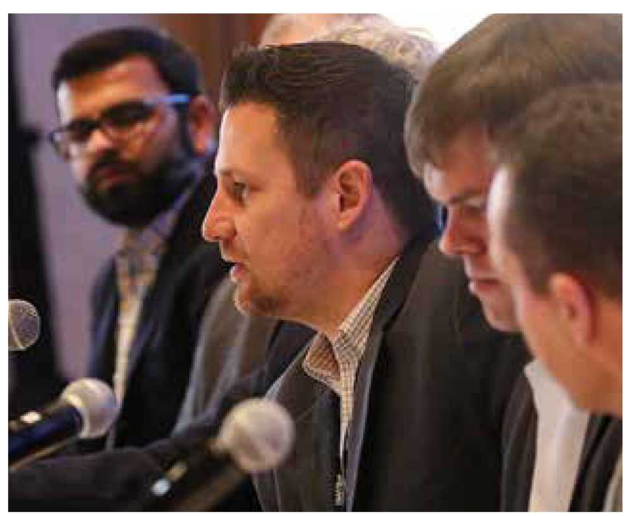
Electrochemically Produced Zinc Oxide Electrode in Rechargeable Alkaline Batteries
Snehal Kolhekar, City College of New York

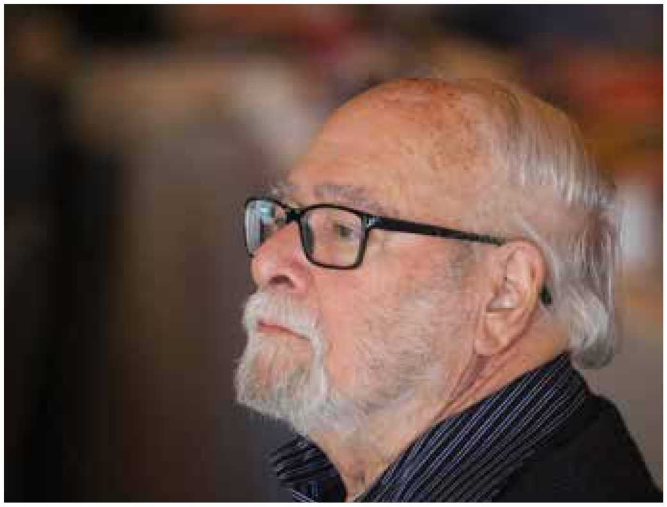
PHOTOS



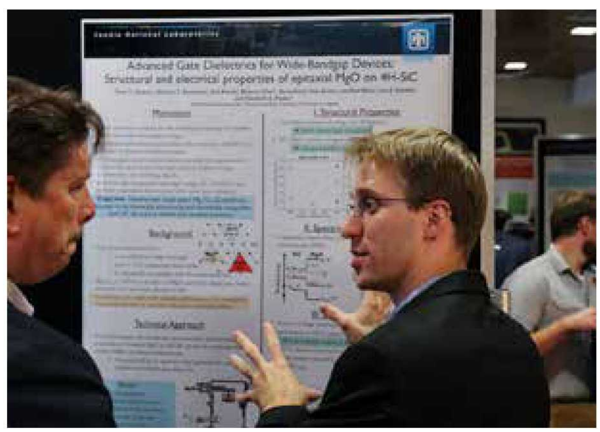
The DOE OE Energy Storage Peer Review event took place at the Hotel Andaluz in Albuquerque, New Mexico September 23-26, 2019. Here is a selection of photos of plenary speakers, poster presenters and peer reviewers.








Hyungjin Choi


Advanced Gate Dielectrics for Wide-Bandgap Devices:
Structural and electrical properties of epitaxial MgO on 4H-SiC
Background
Technical Approach

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.