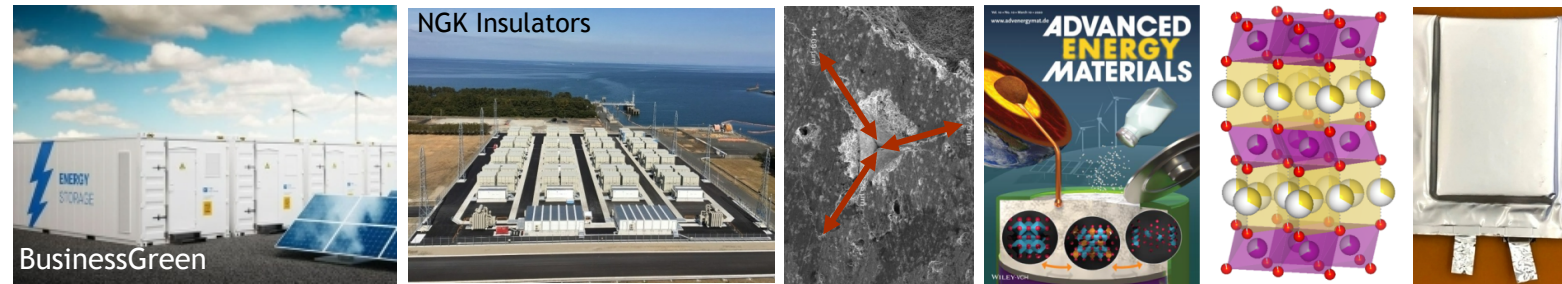




# Sodium-Based Batteries



PRESENTED BY

Erik D. Spoerke, Ph.D.

DOE Office of Electricity Virtual Peer Review 2021  
October 26-28, 2021

This work at Sandia National Laboratories is supported by Dr. Imre Gyuk through the U.S. Department of Energy Office of Electricity.

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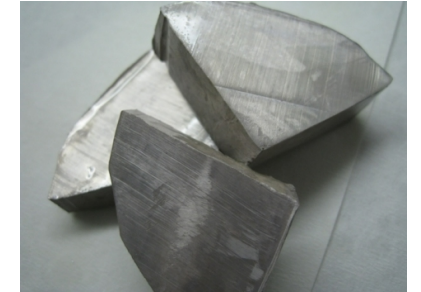
SAND No.:

# Sodium Batteries: Diverse Technologies



Sodium batteries...

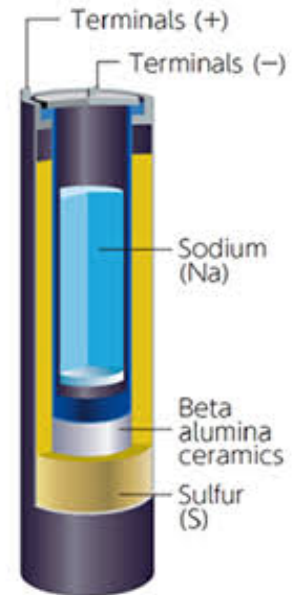
- Take advantage of globally abundant sodium...
  - 6th most abundant element in Earth's crust and 4<sup>th</sup> most abundant in the oceans.
  - 5X the annual production of aluminum
- Offer potential for safe, versatile, cost-effective energy storage
  - Grid-scale and backup power
  - Portable or vehicle storage



Sodium Metal

There are a number of sodium battery technologies in development or production:

1. Molten sodium (Na) batteries
  - A. Sodium Sulfur (NaS)
  - B. Sodium Metal Halide (Traditional ZEBRA Batteries)
2. Sodium Ion Batteries (NaIBs) - *PNNL, ORNL*
  - A. "Li-Ion Analogs"
  - B. Prussian Blue Analogs
  - C. Salt-Water Batteries
3. Solid State Sodium Batteries (SSSBs)
4. Sodium Air Batteries (Na-O<sub>2</sub>)



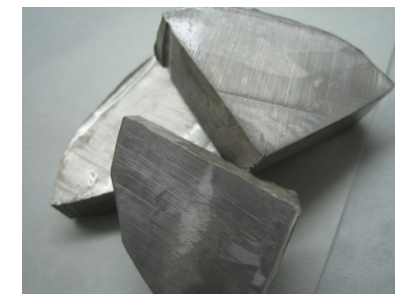
- Sodium Image from Dnn87 at English Wikipedia. - Transferred from en.wikipedia to Commons., CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=3831512>
- NaS battery schematic from NGK Insulators.

# Sodium Batteries: Diverse Technologies



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## 1. Molten sodium (Na) batteries

A. Sodium Sulfur (NaS)

B. Sodium Metal Halide (Traditional ZEBRA Batteries)

- ✓ *New ZEBRA Batteries (Ni-free, operate below 200°C) - PNNL*
- ✓ *Low Temperature (~100°C) Na-NaI Batteries - SNL*

## 2. Sodium Ion Batteries (NaIBs) -

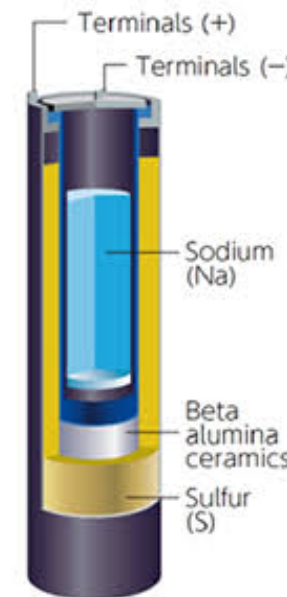
A. *"Li-Ion Analogs" PNNL, ORNL*

B. Prussian Blue Analogs

C. Salt-Water Batteries

## 3. Solid State Sodium Batteries (SSSBs)

## 4. Sodium Air Batteries (Na-O<sub>2</sub>)



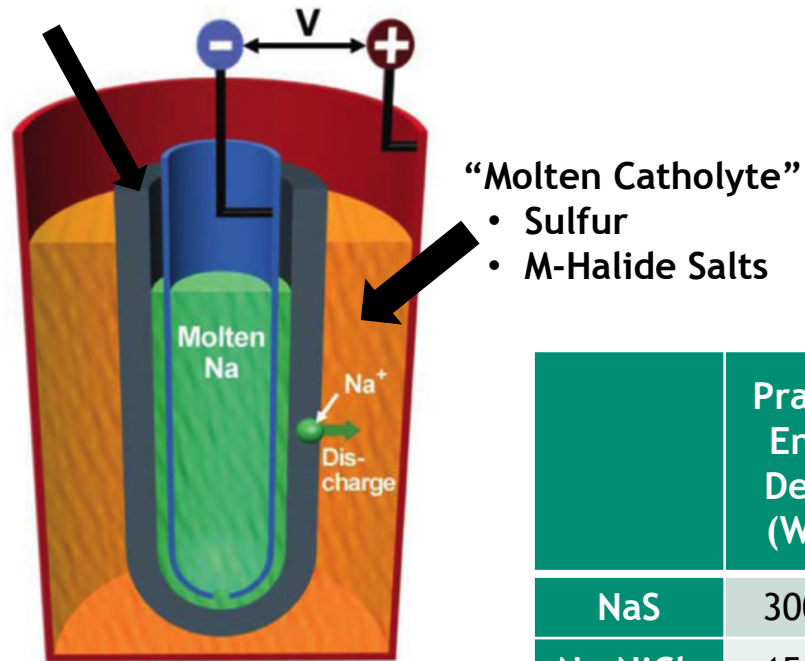
- Sodium Image from Dnn87 at English Wikipedia. - Transferred from en.wikipedia to Commons., CC BY-SA 3.0, <https://commons.wikimedia.org/w/index.php?curid=3831512>
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# Molten Sodium Batteries: Where Does the Industry Stand?

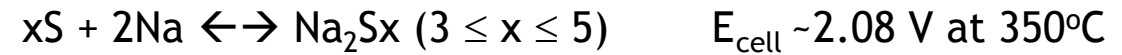


## Molten Sodium Battery Basics

Ion Conducting  
Ceramic Separator

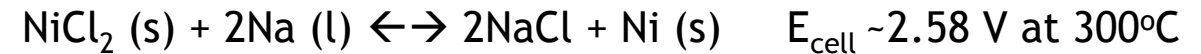


### Na-S



✓ 600 MW/4.2 GWh of deployed storage in over 200 sites globally

### Na-NiCl<sub>2</sub>



✓ Approximately 130MWh deployed storage globally

	Practical Energy Density (Wh/L)	Expected Cycle Life (cycles at 80% DOD)	Expected Lifetime (years)	Operating Temperature (°C)	Suitable Ambient Temperature (°C)	Discharge Duration (at rated power)	Round Trip Efficiency
NaS	300-400	4,000-4,500	15	300-350	-20 to + 40	6-7 hours	80%
Na-NiCl <sub>2</sub>	150-190	3,500-4,500	20	270-300	-20 to +60	2-4 hours	80-85%

- Na-S takes advantage of low cost materials, but introduces some safety concerns.
- Na-NiCl<sub>2</sub> is a safer, greener chemistry, but high cost of Ni is a challenge.

*NaS and Na-NiCl<sub>2</sub> batteries are used today for Renewables Integration, Grid Services, Consumer Applications, and Microgrids*

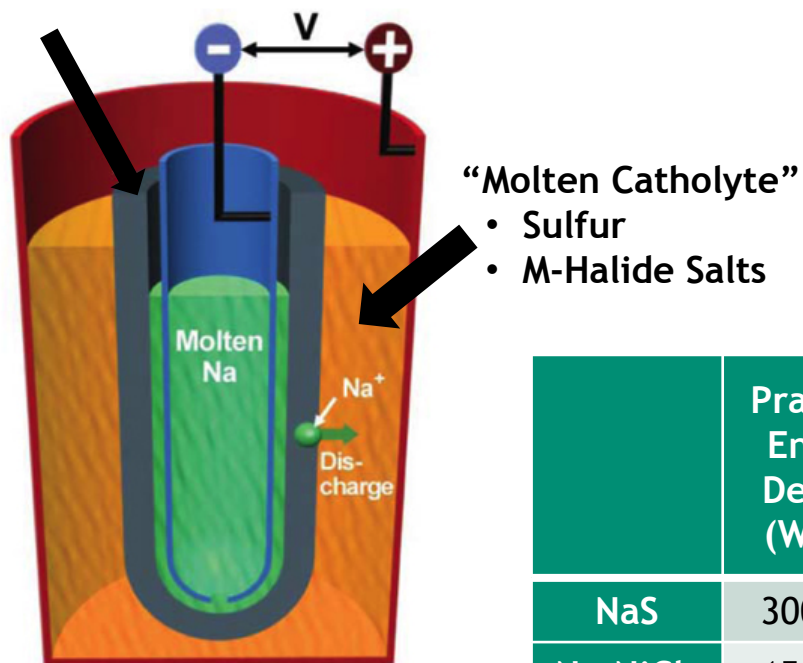


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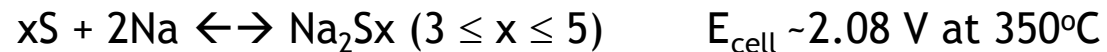


## Molten Sodium Battery Basics

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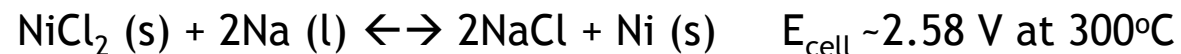


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# Lowering Battery Operating Temperature to Drive Down Cost

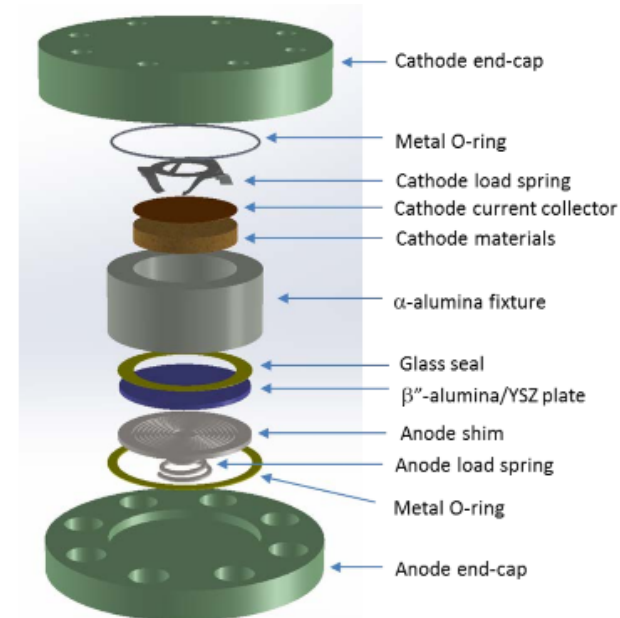


Our Collective OE Objective: A safe, reliable, molten Na-based that eliminates costly reagents (e.g., Ni) and operates at reduced temperatures (below 200°C).

- Improved Lifetime
  - Reduced material degradation
  - Decreased reagent volatility
  - Fewer side reactions
- Lower material cost and processing
  - Seals
  - Wiring!
  - Cell body
  - Polymer components?
- Simplified heat management costs
  - Operation
  - Freeze-Thaw

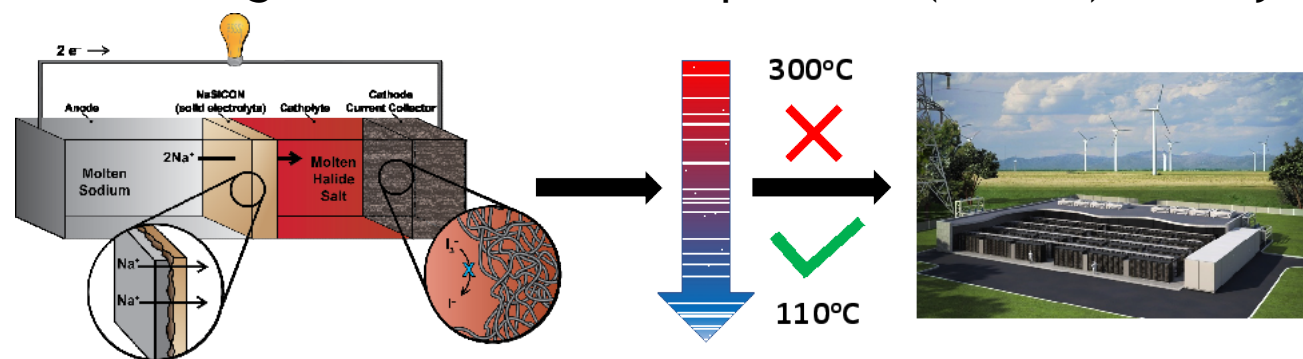
PNNL intermediate temperature (<200°C) planar Na-MH battery design.

FY21 focus on using low cost cathode materials (Fe, etc) to replace Ni.



Li, G, et al. *Nature Commun.* 2016, 7, 10683.

SNL design for Na-NaI low temperature (~100°C) battery



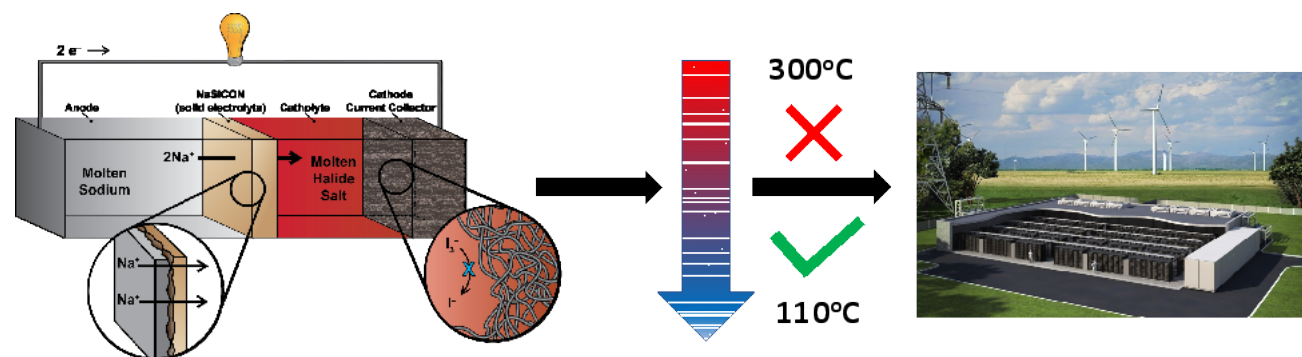
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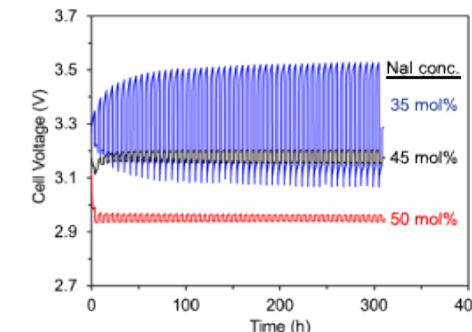
SNL design for Na-NaI low temperature (~100°C) battery.



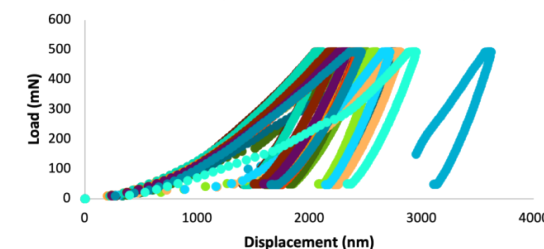
## FY21 Focus Areas:

- Realizing high performance with lower-cost catholytes
- Improving NaSICON Production/Performance
- Exploring mechanical properties of NaSICON (U. Kentucky, Prof. YT-Cheng)

Cycling with new catholytes



Load vs. Displacement – 50 gf (grey spots)



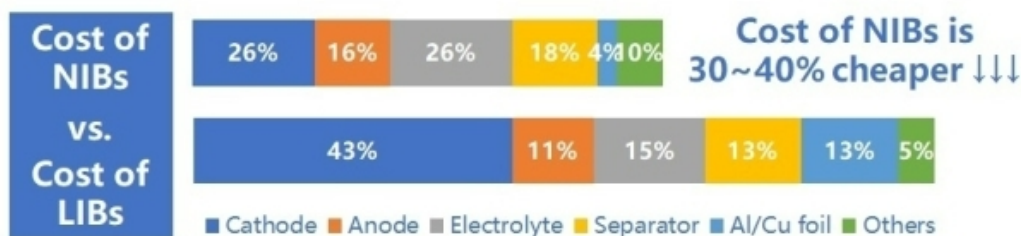


# Considerations in Na-Ion Battery Development



Resource		Crustal Abundance	Distribution	Price US\$/kg
	Na	2.75%	Everywhere	0.3 ( $\text{Na}_2\text{CO}_3$ )
	Li	0.0065%	75% in Americas	20 ( $\text{Li}_2\text{CO}_3$ )

Current Collector	<p>NIBs: Al foil (cheap) for both positive and negative electrodes</p> <p>LIBs: Cu foil (expensive) for negative and Al foil for positive</p>
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Tips: NaCuFeMnO and Soft-Carbon are used in NIBs; LiFePO<sub>4</sub> and Graphite are used in LIBs.

	LABs	SIBs	LIBs
Energy Density	30~50 Wh/kg	100~150 Wh/kg	150~250 Wh/kg
Voltage	~2.1 V	2.8~3.5 V	3.0~4.5 V
Life	~300 cycles	2000+ cycles	3000+ cycles

Tips: The above parameters of different materials varies.

NIBs can be fully discharged for shipping, LIBs must be maintained at 30% SOC.

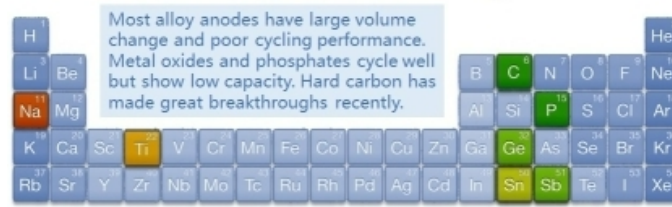
## Anode Materials for NIBs

Transition Metals Are Dispensable for Anodes.

100+ Anode materials have been reported:

- Carbon (e.g. hard/soft carbon)
- Alloy (e.g. Sn, Sb, SnSb)
- Transition Metal Oxides (e.g.  $\text{Na}_{0.66}\text{Li}_{0.22}\text{Ti}_{0.78}\text{O}_2$ )
- Transition Metal Phosphates (e.g.  $\text{NaTiOPO}_4$ )

Longer Cycling Life  
Lower Cost  
Faster Charge/Discharge



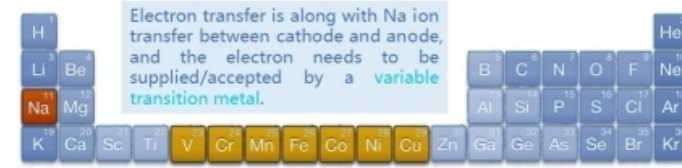
## Cathode Materials for NIBs

Different Structure, Indispensable Transition Metals

100+ cathode materials have been reported:

- Transition Metal Oxides (e.g.  $\text{NaMnO}_2$ )
- Transition Metal Phosphates (e.g.  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ,  $\text{Na}_2\text{MnP}_2\text{O}_7$ )
- Transition Metal Sulfates (e.g.  $\text{Na}_2\text{Fe}_2(\text{SO}_4)_3$ )
- Transition Metal Cyanates (e.g.  $\text{Na}_2\text{FeFe}(\text{CN})_6$ )

Higher Energy Density  
Longer Cycling Life  
Lower Cost



## Application of NIBs

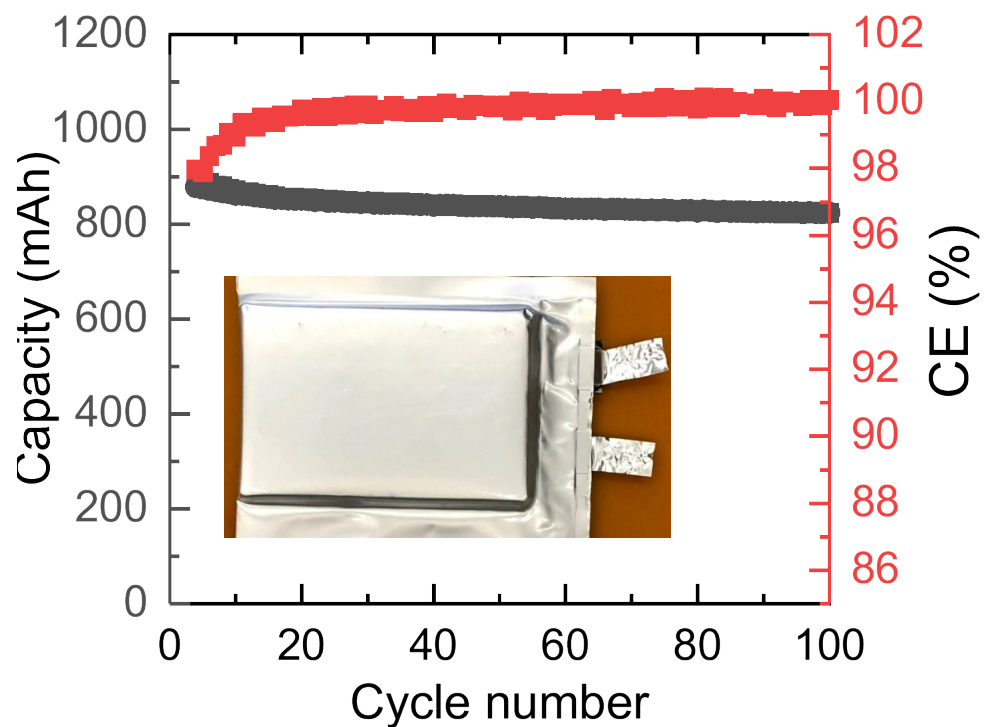


- Global sodium-ion batteries market has been estimated to reach USD 1.01 billion in 2021.
- Projected to grow at a CAGR of 19.3% during the forecast period from 2021-2030.

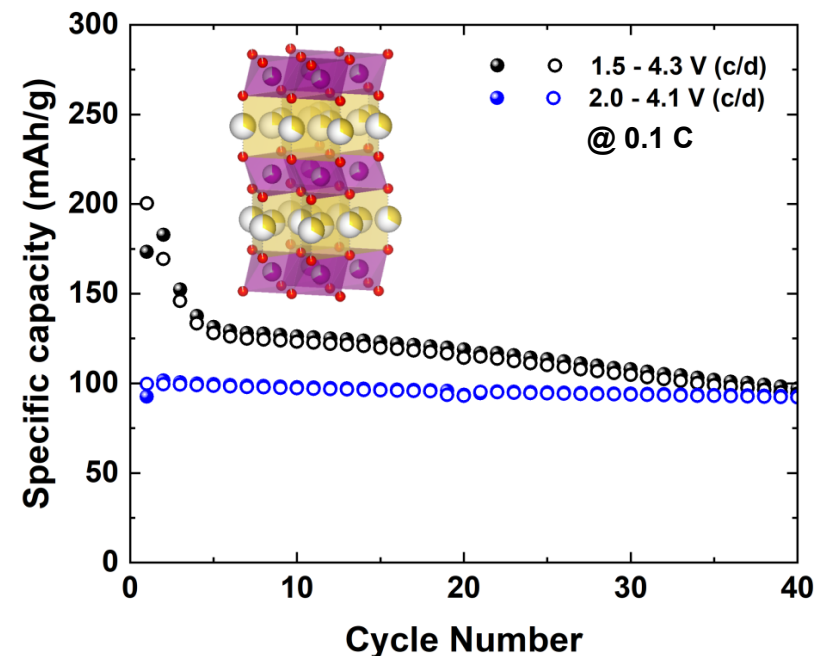
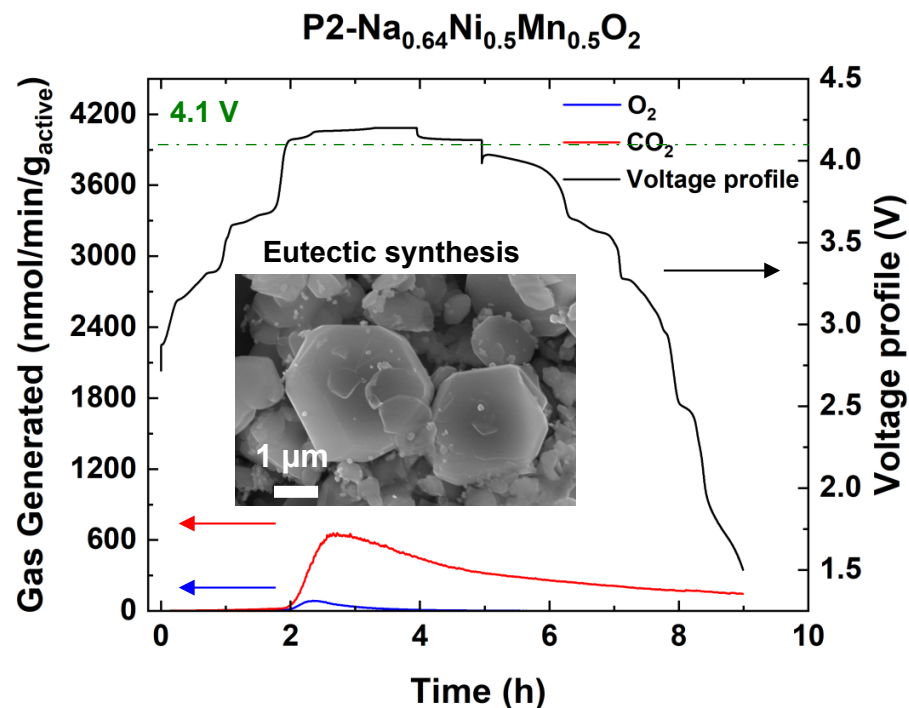




## Project Highlights



- Gen 2 (Ni-rich NMC cathode) material synthesis scaled up to 1 kg/batch level, multi-layer pouch cell assembly was scaled up to ~ 1Ah.
- Gen 3 (Ni-low, Co-free cathode) material synthesis scaled up to 50g/batch, single-layer pouch cell assembly achieved 50 mAh.
- Discovered new mechanisms for promoting cathode performance.




- ORNL's Belharouak team developed novel eutectic synthesis for sodium transition metal layered oxide cathodes.
- Gassing studies were performed to evaluate the oxygen anion redox in different kinds of cathodes in pouch cells and seek engineering routes towards longer duration storage and stable cycling performances.


# Looking to a Future with Long-Duration Energy Storage




## Long Duration Storage Shot



Reduce storage costs  
by **90%\***...



...in storage systems  
that deliver **10+** hours  
of duration



...in **1** decade

\*from a 2020 Li-ion baseline

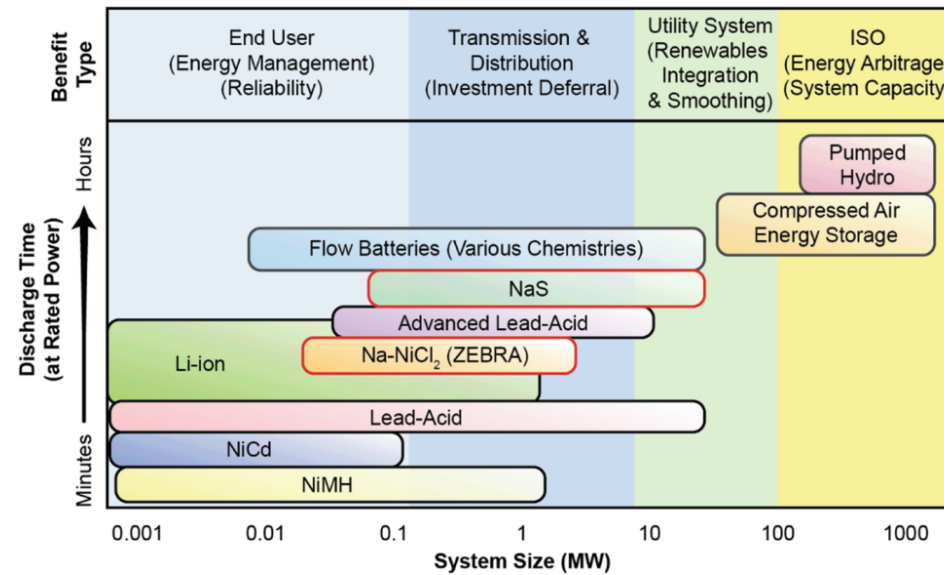
Clean power anytime, anywhere.

*Long-Duration Energy Storage (>10 hours) continues to be a growing priority for the DOE Office of Electricity's Energy Storage Research Program and across the DOE.*

# What are the Roles for Batteries in Long-Duration Energy Storage?



- Lithium-Ion Batteries
- Sodium-Based Batteries
- Zn-Based Batteries
- Flow Batteries
- Pb-Acid
- Metal-Air Batteries



Seasonal

Long-Duration

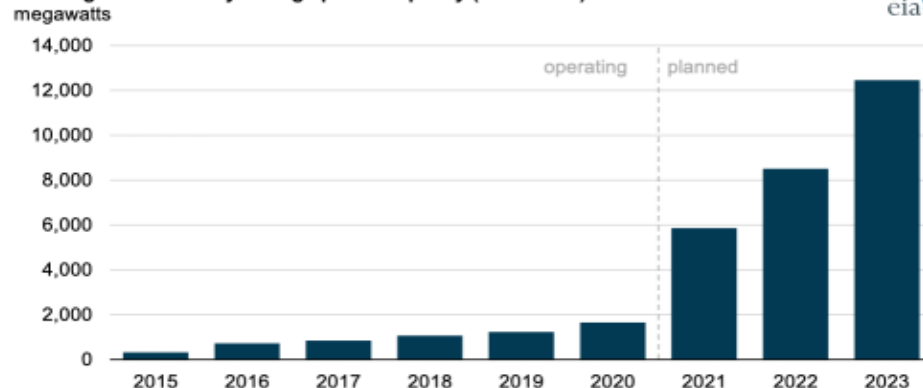
Medium-Duration

Short Duration

AUGUST 20, 2021

U.S. large-scale battery storage capacity up 35% in 2020, rapid growth set to continue

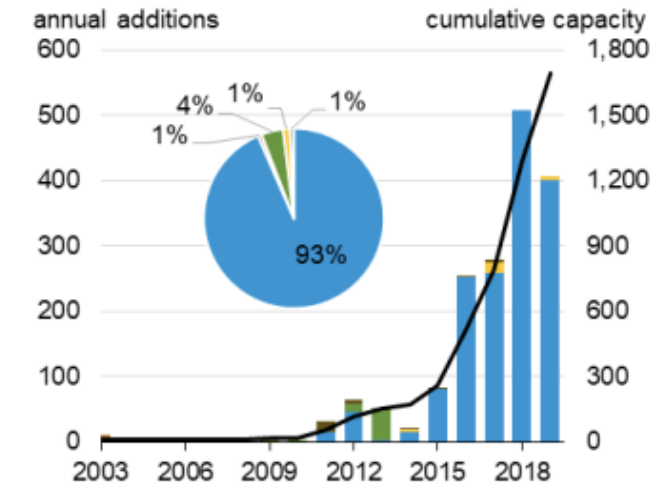
U.S. large-scale battery storage power capacity (2015–2023)



Source: U.S. Energy Information Administration, Preliminary Monthly Electric Generator Inventory, December 2020

energy  
capacity  
(MWh)

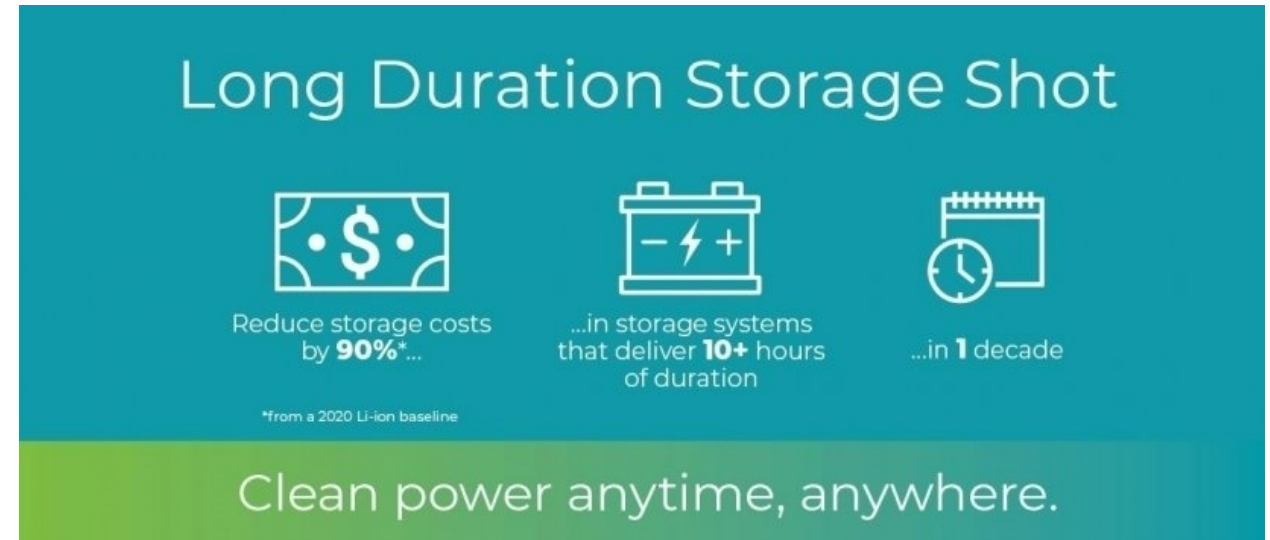
lithium-ion  
nickel-based  
sodium-based  
flow  
other



Source: U.S. Energy Information Administration, 2019 Form EIA-860, [Annual Electric Generator Report](#)



# Looking to a Future with Long-Duration Energy Storage



## Emerging Efforts:

- All Soluble Iron Flow Battery (PNNL)
  - all soluble Fe flow battery (intends to replace vanadium) for long duration and thermocycling battery (reduces self-discharge) for seasonal storage.
- Earth Abundant Molten Salt Batteries (SNL)
  - Utilize low-carbon approach to scalable molten salt batteries based on earth-abundant active materials.

*The DOE OE program has the opportunity to build on current programs to meet critical LDES needs!*



## DOE Long-Duration Energy Storage Workshop

### “BIG” Energy Storage: Priorities and Pathways to Long-Duration Energy Storage



*[longdurationstorage.sandia.gov](https://longdurationstorage.sandia.gov)*  
v

- Posted presentations
- Issue Brief on Long-Duration Energy Storage (as of late 2020)
- Recorded presentations available
  - Use Cases
  - Policy
  - Economics
  - Technologies

**Contact:**  
**[edspoer@sandia.gov](mailto:edspoer@sandia.gov)**

# On to the Main Show: Presentations



Sodium				
10:35 – 10:50 AM	<b>Program Overview</b>	<b>Erik Spoerke (Session Lead)</b>	<b>Sandia National Laboratories</b>	<b>300</b>
10:50 – 11:05 AM	Low Temperature Molten Sodium Batteries	Leo Small	Sandia National Laboratories	301
11:05 – 11:20 AM	Mechanical, Microstructural, and Electrochemical Characterization of NaSICON Sodium Ion Conductors	Yang-Tse Cheng	University of Kentucky	302
11:20 – 11:35 AM	(I) Intermediate Temperature Na Battery Technologies (II) Long Duration/Seasonal Battery Development	Guosheng Li	Pacific Northwest National Laboratory	303
11:35 – 11:50 AM	Na-ion batteries: Development and Scaling-up of Advanced Cathode Materials	Biwei Xiao	Pacific Northwest National Laboratory	304
11:50 AM – 12:05 PM	Deep Dive into the Oxygen Anion Redox in Na Layered Oxide Cathodes Synthesized by Eutectic	Ilias Belharouak	Oak Ridge National Laboratory	305
12:05 – 12:20 PM	<b>Break</b>			
12:20 – 01:00 PM	<b>Roundtable: Long Duration Energy Storage</b>			

## Please Don't Miss: Posters



Institution	Title	Authors
Sandia National Laboratories	Low-Temperature Molten Sodium Batteries	<u>Martha M. Gross</u> , Stephen J. Percival, Amanda S. Peretti, Joshua Lamb, Erik D. Spoerke, Leo J. Small
University of Kentucky/Sandia National Laboratories	Mechanical, Microstructural, and Electrochemical Characterization of NaSICON Sodium Ion Conductors	<u>Ryan C. Hill</u> , Jacob Hempel, Yang-Tse Cheng, Leo Small, Erik D. Spoerke, Martha M. Gross, and Amanda Peretti.
Pacific Northwest National Laboratory	Feasibility of Na-FeCl <sub>2</sub> Batteries for Long Duration Energy Storage Applications	<u>Evgueni Polikarpov</u> , Xiaowen Znan, Miller Li, J. Mark Weller, Keesung Han, David Reed, Vincent Sprenkle, and Guosheng Li
Pacific Northwest National Laboratory	Advancing Low Cost, Intermediate Temperature Na-Al Batteries for Scalable Long-Duration Energy Storage	<u>Jon (Mark) Weller</u> , Mark H. Engelhard, David M. Reed, Vincent L. Sprenkle, and Guosheng Li