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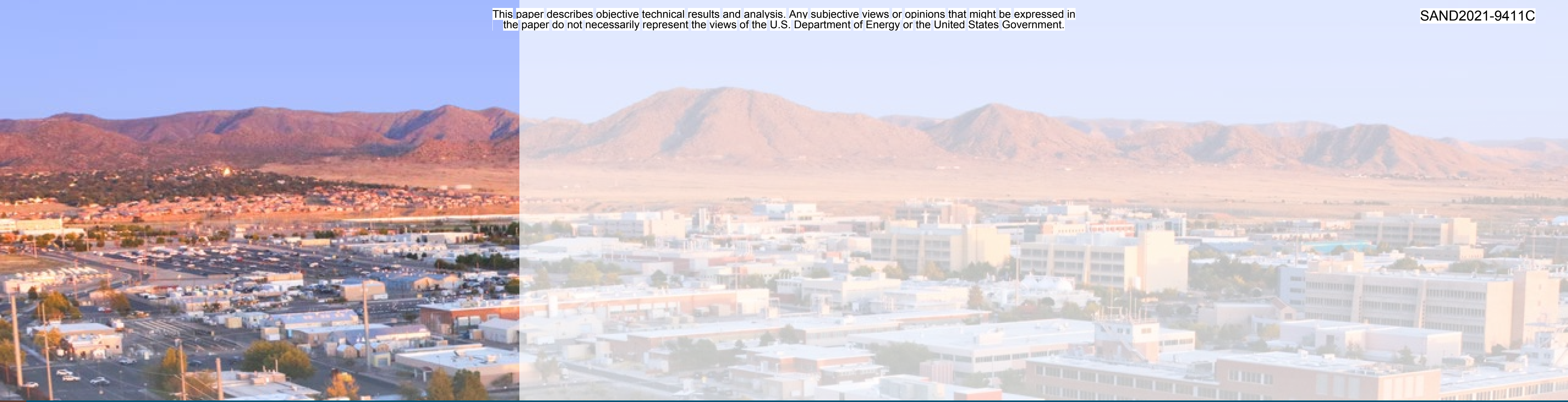

Energy Storage Technologies

Ray Byrne, Ph.D.

Sandia National Laboratories

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ENERGY STORAGE R&D AT SANDIA

BATTERY MATERIALS
Large portfolio of R&D projects related to advanced materials, new battery chemistries, electrolyte materials, and membranes.

DEMONSTRATION PROJECTS
Work with industry to develop, install, commission, and operate electrical energy storage systems.

CELL & MODULE LEVEL SAFETY
Evaluate safety and performance of electrical energy storage systems down to the module and cell level.

STRATEGIC OUTREACH
Maintain the ESS website and DOE Global Energy Storage Database, organize the annual Peer Review meeting, and host webinars and conferences.

POWER CONVERSION SYSTEMS
Research and development regarding reliability and performance of power electronics and power conversion systems.

GRID ANALYTICS
Analytical tools model electric grids and microgrids, perform system optimization, plan efficient utilization and optimization of DER on the grid, and understand ROI of energy storage.

SYSTEMS ANALYSIS
Test laboratories evaluate and optimize performance of megawatt-hour class energy storage systems in grid-tied applications.

Wide ranging R&D covering energy storage technologies with applications in the grid, transportation, and stationary storage

Reducing the Cost of Battery Energy Storage

Li-ion batteries

- Increase reliability and cycle life
- Improve safety

Sodium batteries

- Lower temperature Na batteries
- Sodium ion batteries

Alkaline Zn-MnO_2 Batteries

- Make alkaline batteries fully chargeable

Li-ion Batteries

Family of electrochemical systems

Positive electrode
- Metal-oxides (e.g. LCO, NMC, NCA)
- Phosphates (e.g. LFP)

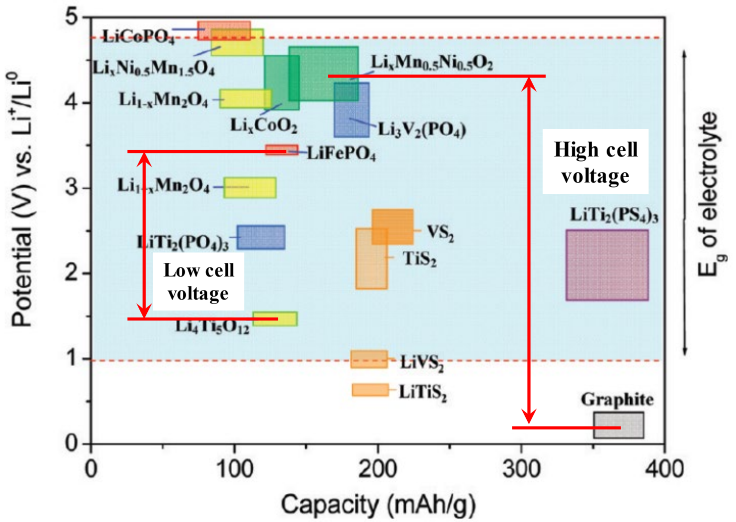
Negative electrode
- Graphite and other carbons
- Lithium titanate

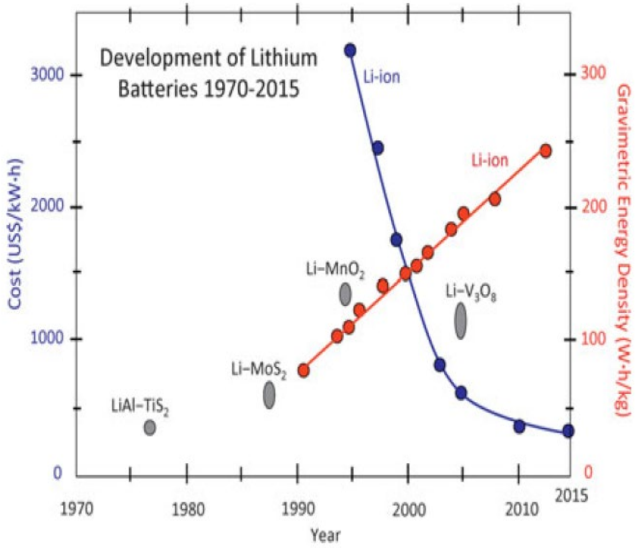
SOA EV batteries - Specific energies near 250 Wh/kg

330-350 Wh/kg possible near term with composite anodes (Si-based anodes)

500 Wh/kg as a longer term goal based on significant improvements in electrode design and composition (e.g., lithium anodes), electrolyte formulations, and separator innovations.

Safety continue to be a significant concern





Source: Crabtree, Kocs, Trahey, MRS Bulletin, Dec 2015

Large Commercial Li-ion Deployments

AES 30 MW / 120 MWh ESS, Escondido, CA
Peaker replacement

Tesla 100 MW / 129 MWh ESS
Australia - Grid stability

Saft 6 MW / 4.2 MWh ESS
Kauai - Grid Stability

Li-ion Batteries – Challenges for Power and Energy Applications

Battery safety is very important for applications where high power is required.

Heat generation during high power usage must be managed

- Dictates smaller form factor
- Higher production costs

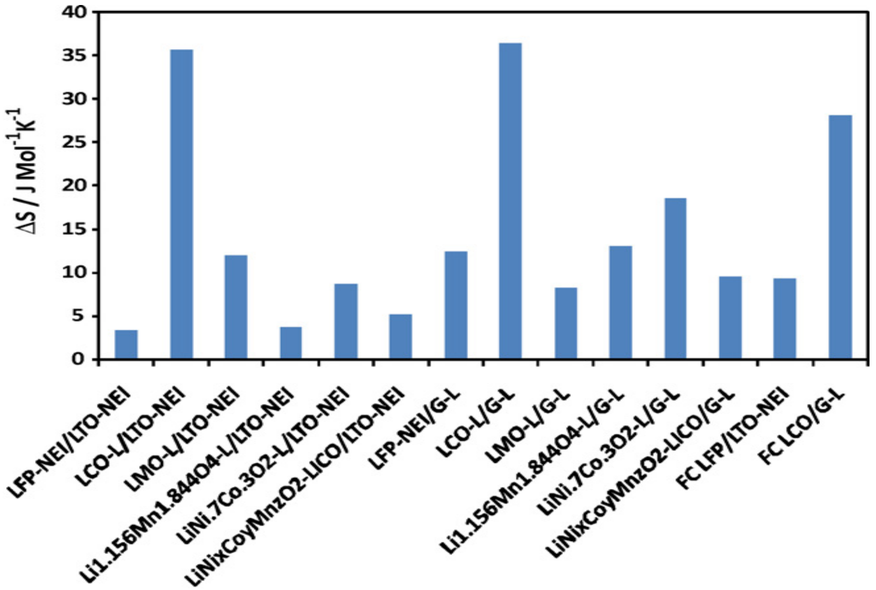
High Temperature

- Typical operating window 0-50°C
- Operation above this temperature can lead to organic electrolyte decomposition and flammable gas, rapid internal pressure build-up

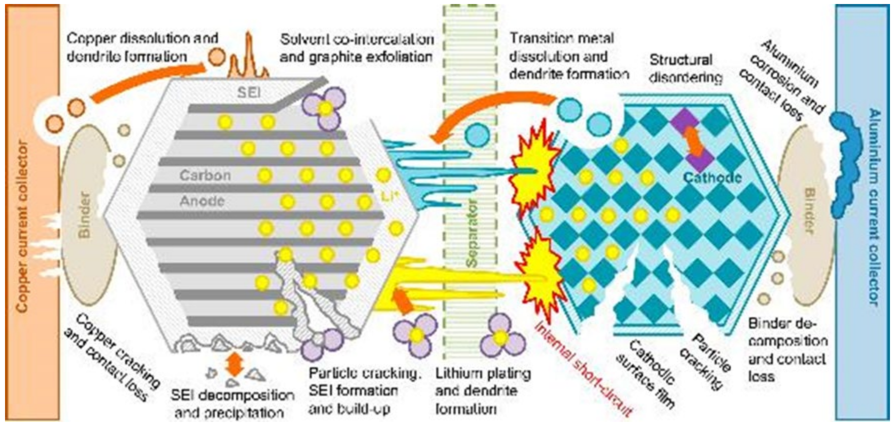
Overcharging

- Overcharging can lead to Li metal plating on anode, potential for short

Need better understanding of the degradation pathways and engineering to control thermal runaway



Inherent Heat Generation of Electrodes



J. Power Sources, **2017**, 341, 373

Future Developments in Li-based Batteries

Higher-voltage positive (cathode) materials

- Lithium manganese phosphate
- Lithium cobalt phosphate

Higher-capacity negative (anode) materials

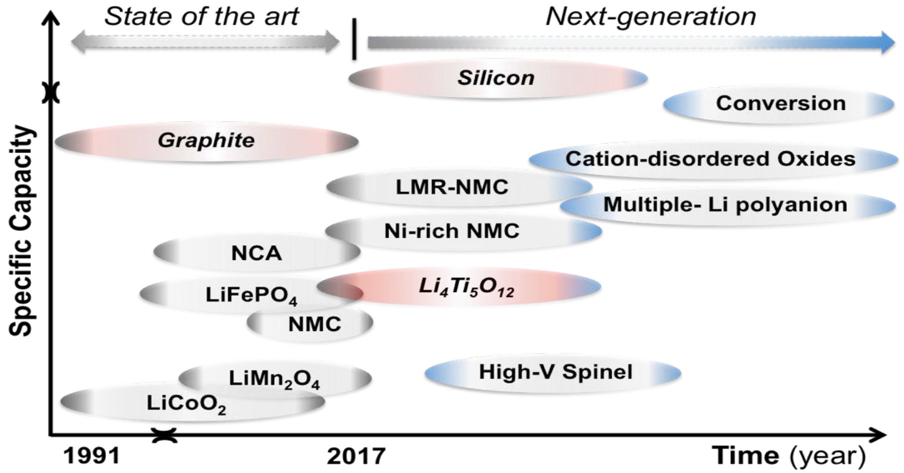
- Silicon-based

Safer electrolytes

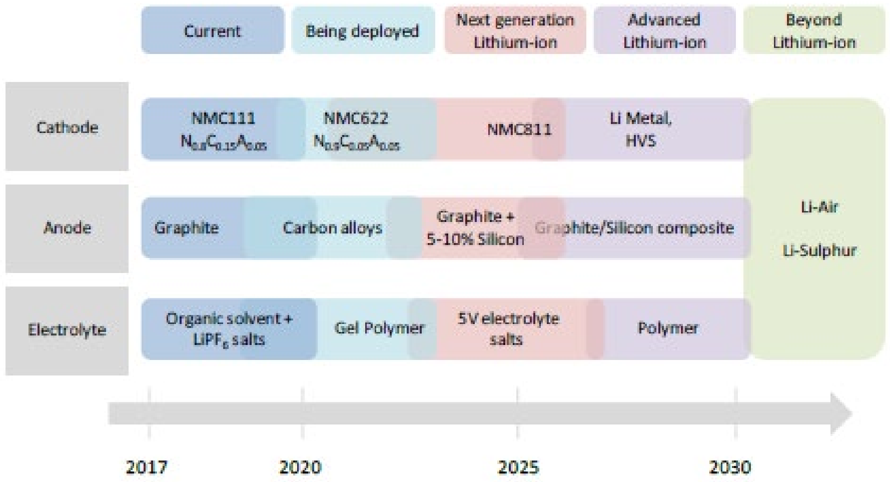
- Inorganic
- Solid-state electrolytes

Other Li chemistries

- Lithium-sulfur



DOE Basic Research Needs Report on Energy Storage
DOE Office of Science, 2017



Global EV Outlook Report, IEA 2018
Based on DOE-VTO and NEDO Projections

High Energy Density Li-S and Metal Air Batteries

Li-S: high theoretical energy density (>2700 Wh/kg), prototype cells ~ 400Wh/kg

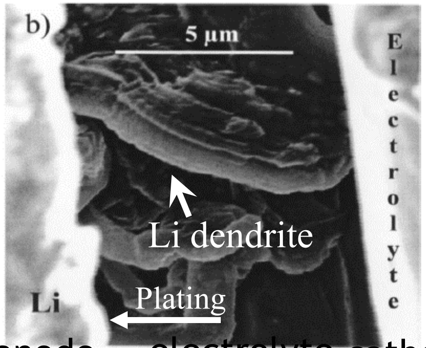
- Suffers from self discharge and poor life
- Breakthroughs needed with Li electrodes
- Managing the Sulphur shuttle reactions

Metal air batteries (Li-air, Zn-air)

- Potential to deliver high energy densities at low cost. Challenges with recharging have so far precluded commercialization of the technology.
- Not mature, many years away
- Potential fundamental problems

Li-Air combines difficulties of air and lithium electrodes

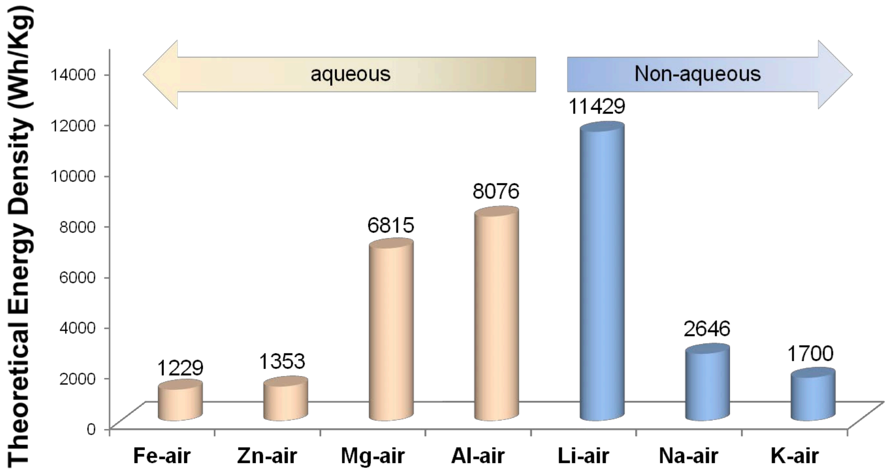
- Breakthroughs needed in cheap catalysts, more stable and conductive ceramic separators
- Developing a robust air electrode is a challenge, need major breakthroughs



anode electrolyte cathode

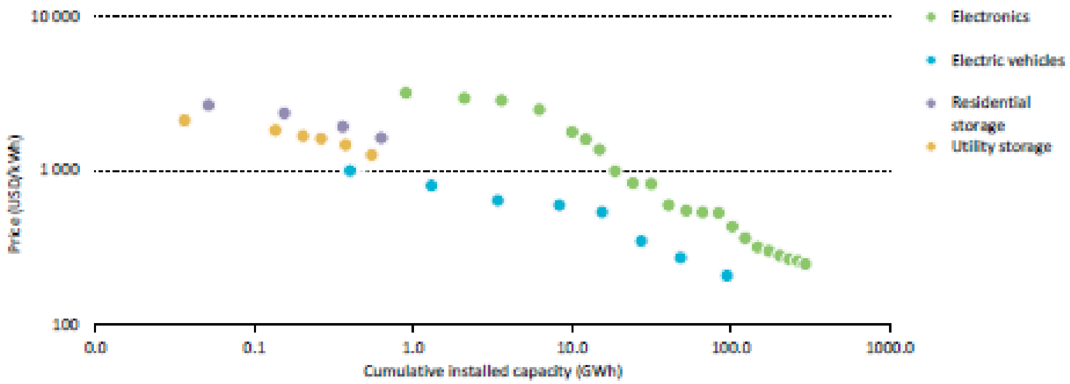
Li dendrite growth

H. Pan, et. al, Adv. Energy Mater., 2015



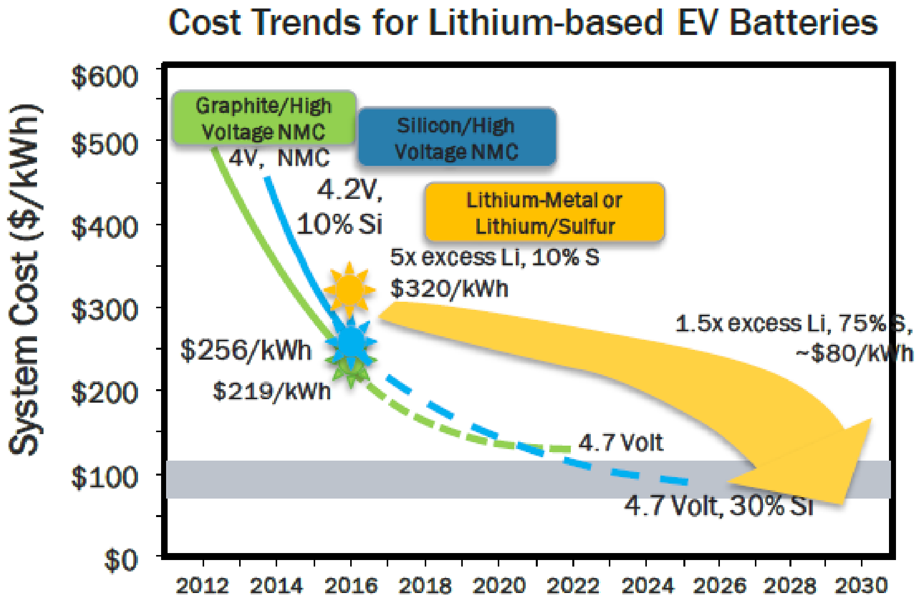
Y. Li and J. Lu, “Metal-Air Batteries: Future Electrochemical Energy Storage of Choice?,” PNNL, 2017

Manufacturing Scale and Cell/System Costs



Li-ion storage technology price with manufacturing volume
Source: IEA, 2018

Future cost projections predicated on stable commodity prices, significant improvements in energy density and cell performance



Cost trends for Li-based EV Batteries (pack level)
Source: David Howell, DOE VTO, 2018

Lead-Acid Batteries

Overall Reaction
- $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
- OCV ~ 2.0 V

Flooded lead-acid
- Requires continuous maintenance
- Most common

Sealed lead-acid
- Gel and Absorbed Glass Mat (AGM)
- More temperature dependent

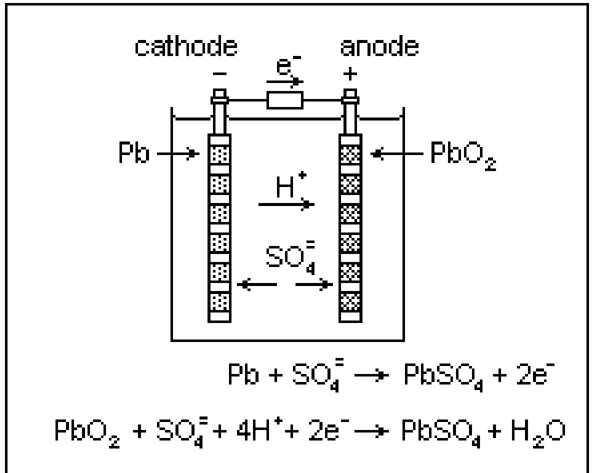
Advanced Lead Acid Energy Storage
- Carbon plates significantly improve performance

Mature technology

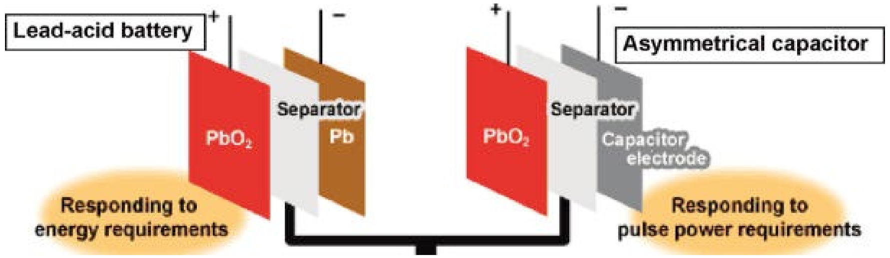
High recycled content

Good battery life

Advantages/Drawbacks
- Low cost/Ubiquitous
- Limited life time (5~15 yrs)/cycle life (500~1000 cycles) and degradation w/ deep discharge (>50% DoD)
- New Pb/C systems > 5,000 cycles.
- Low specific energy (30-50 Wh/kg)
- Overcharging leads to H2 evolution.
- Sulfation from prolonged storage



Lead-Acid Storage Cell



http://www.ultrabattery.com/

Lead Acid Batteries – Deployment for Grid Services

3 MW/3 MWh advanced lead acid battery system for utility applications (Source: EastPenn, East Lyons, PA)

Solar plus ultrabattery storage (Source: PNM Albuquerque, NM

1.3MW/1.9 MWh advanced lead acid battery system providing support for a 68MW solar farm in Alt Daber, Germany (Source: BAE Batteries, 2018)

Redox Flow Batteries

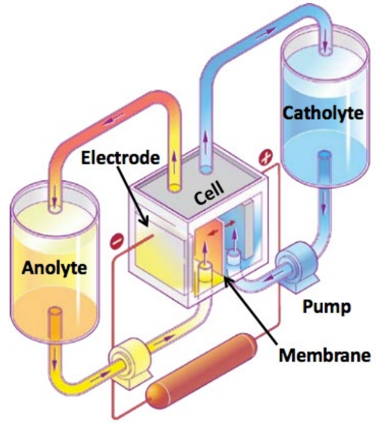
Energy storage technology utilizing redox states of various species for charge/discharge purposes

Key Aspects

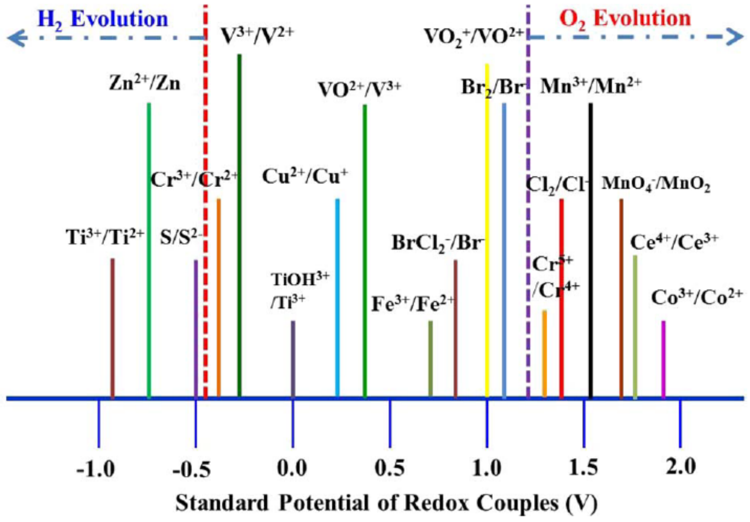
- Power (kW) and energy (kWh) separation
- Greater flexibility and safety
- Modular and scalable across a wide range of power and energy
- Long cycle life
- Low energy density ~ 30 Wh/L

Range of redox chemistries

- Fe-Cr, Zn-Br, V-V are most studied and large systems demonstrated
- Most large commercial flow batteries are based on V-V chemistry, and Zn-Br



Source: Travis Anderson, Sandia National Laboratories, 2013



B.R. Chalamala, et.al., Proc IEEE, vol. 102, pp. 976-999, June 2014

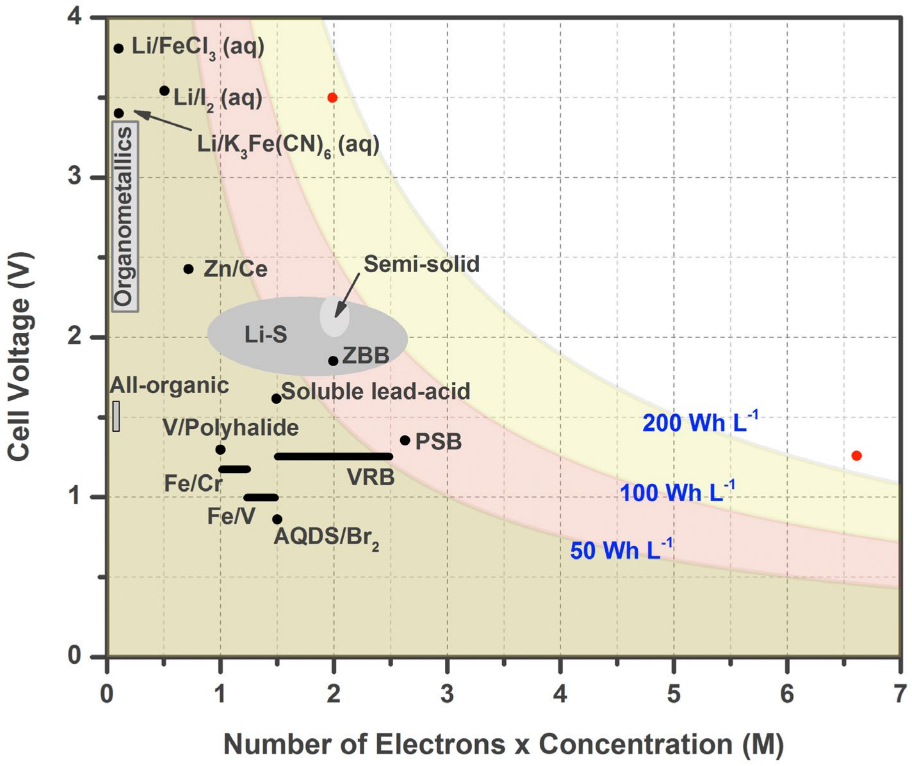
Redox Flow Batteries – Technical Challenges

Low energy density
- Limited voltage window of aqueous electrolyte solutions (< 1.5 V)
- Large form factor/footprint

Limited electrolyte stability
- Low solubility of redox species in aqueous electrolytes
- Capacity decay during cycling
- Narrow temperature range

Corrosion of membranes and electrode materials by acidic electrolyte solutions
- Long-term reliability

Opportunities to Reduce Materials Cost
- New redox chemistries, new electrolytes under development
- Lower cost of membranes
- Increased current density and lower cost stack design



Wei Wang, et. al., Adv. Funct. Mater., , **23**, 970, 2013

RFB Stack Sizes Continue to Grow – Large Plants being built

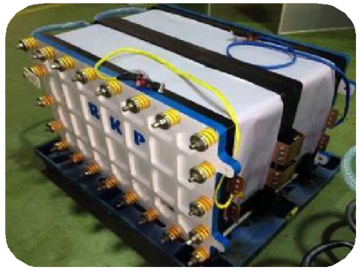
Rapid progress in the development of large utility class redox flow battery systems

Rapid development of new electrolytes to replace Vanadium species

Further potential to reduce the size of the stacks and to increase energy density

Containerized Systems

UniEnergyTechnologies, 1MW/4MWh



32 KW Stack
Rongke Power/UET
120 mA/cm2
Meter size stack

Flow battery power plants

Sumitomo Electric, 15MW/60MWh

Stack room

Sodium Batteries (NaS and $NaNiCl_2$)

Abundant low cost materials (Na, S, …)

Offer potential for safe, versatile, cost-effective energy storage

Molten sodium batteries - Two primary chemistries

- NaS, mature technology, deployed in grid applications
- $NaNiCl_2$, mature, more stable than NaS
- Neither NaS nor $NaNiCl_2$ are at high production volumes and the economies of scale needed

Early Stage Technologies

- Sodium Ion Batteries (NaIBs)
- Solid State Sodium Batteries (SSSBs)
- Sodium Air Batteries (Na-O2)

NaS batteries

Batteries consisting of molten sodium anode and β"-Al_2O_3 solid electrolyte (BASE)

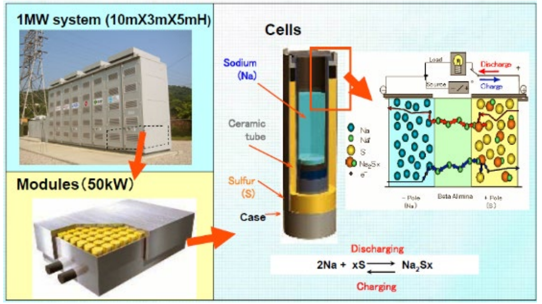
- High specific energy density (120~240 Wh/kg)
- Good specific power (150-230 W/kg)
- Long duration batteries, with 4-6 hr discharge
- Operated at relatively high temperature (300~350°C)

Originally developed at Ford Motors, later commercialized by NGK Insulators in Japan

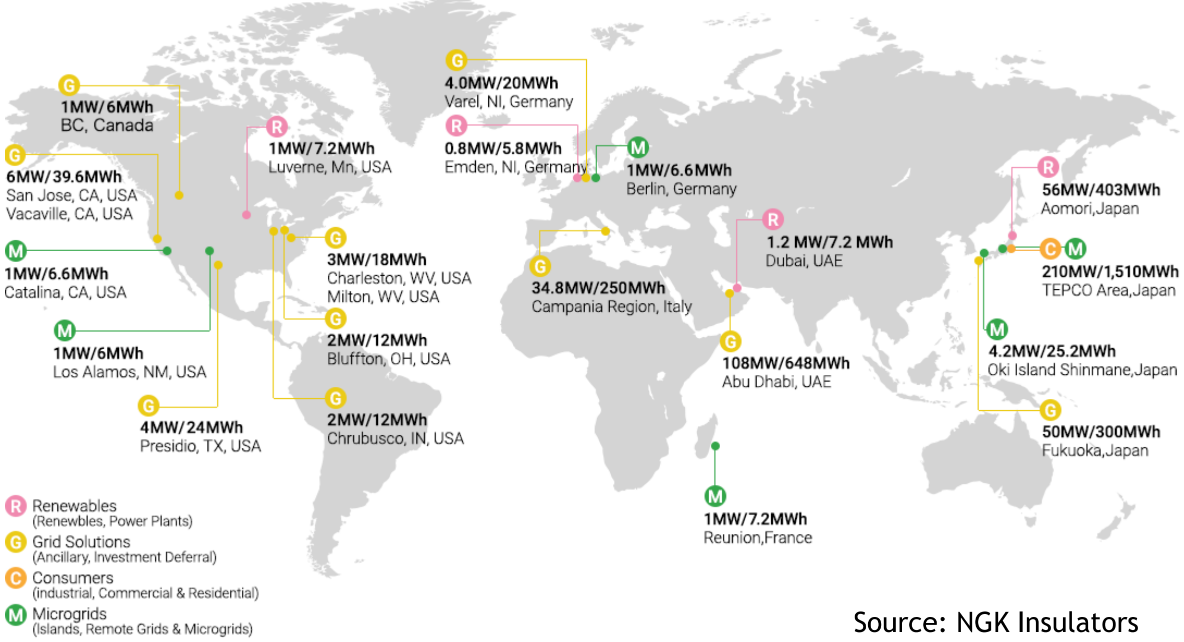
NGK has deployed ~ 580 MW/4 GWh of storage, primarily in Japan

Challenges

- Battery is assembled fully charged, presents a major safety/handling issue
- System needs to be maintained at temperature
- High temperature operation, safety and containment challenges
- Relatively expensive



50 MW system at a solar farm Fukuoka, Kyushu, Japan (NGK)



Source: NGK Insulators

$NaNiCl_2$ Batteries

NaNiCl2 battery

- 2Na + NiCl2 → 2NaCl + Ni
  - E = 2.58V at 300°C

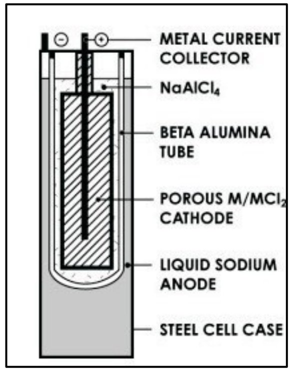
Large cells and stable chemistry

- Lower temperature than NaS
- Cells loaded in discharge mode
- Improved safety compared to NaS. Addition of catholyte $NaAlCl_4$ leads to a closed circuit on failure

High efficiency, low discharge

Long warm up time (16 hr)

Supply chain concerns. Only one major manufacturer (FIAMM). Limited deployments



FIAMM 222-kWh System Duke Energy Rankin Substation

620 V 1.4 MWh (400 kW)

Sodium Ion Batteries on the Horizon

While not yet commercially mature, several types of NaIBs are in development or early production

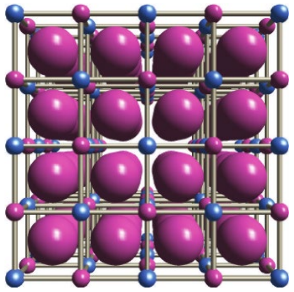
Prussian blue analogs (PBAs)

- Utilize ferric ferrocyanide salts as electroactive materials (mostly cathodes)
- Natron Energy is developing NaIBs with PBAs aimed at 8kW units for data server backup power.

Li-Ion “Analogs” – possibly manufacturable on Li-ion production lines?

“Salt-water batteries”

- Carbon-titanium phosphate composite Anode, sodium perchlorate aqueous electrolyte, manganese oxide cathode.



Y. Moritomo, *Adv. Cond. Matt. Phys.* (2013) 539620.

https://www.bluesky-energy.eu/en/greenrock-home-2/

Rechargeable Alkaline Batteries

Range of alkaline battery chemistries
- NiMH, Ni-Fe, Ni-Cd, Zn-Ni, Zn-MnO2

$Zn\text{-}MnO_2$ shows most promise for grid storage

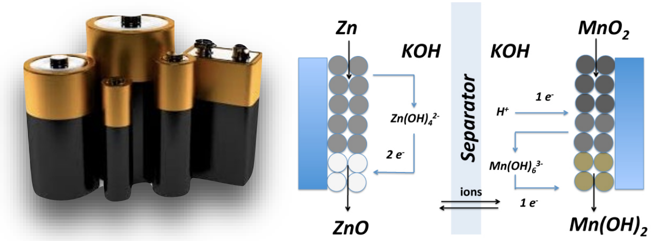
Cost
- Traditional primary batteries, low cost ($18-20/kWh primaries)
- Low-cost materials and manufacturing
- Established supply chain

Safety
- Aqueous chemistry
- Non-flammable
- EPA certified for landfill disposal

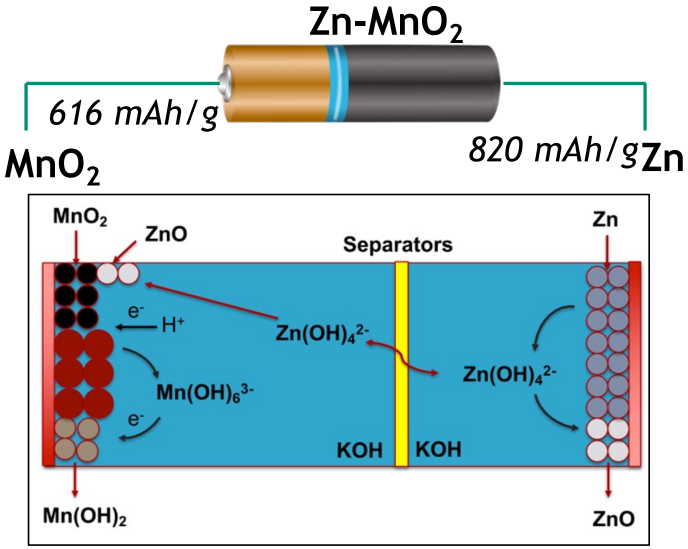
Reliability
- Long shelf-life
- Limited thermal management required

Reversibility and cycle life have been the primary technical challenges

Recent breakthroughs, promising potential for <$50/kWh



Single-use Alkaline Battery $25/kWh



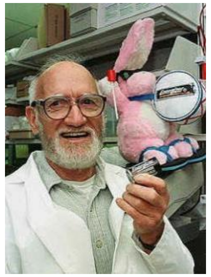
Source: S. Banerjee, CUNY Energy Institute

History of Rechargeable Zn-MnO_2 Batteries

- Early commercial products based on cylindrical formats (Union Carbide, Rayovac, BTI, ...)
  - Focused on consumer markets, rapid development of Li-ion batteries made small cell business not competitive
- Resurgence in the field for stationary storage

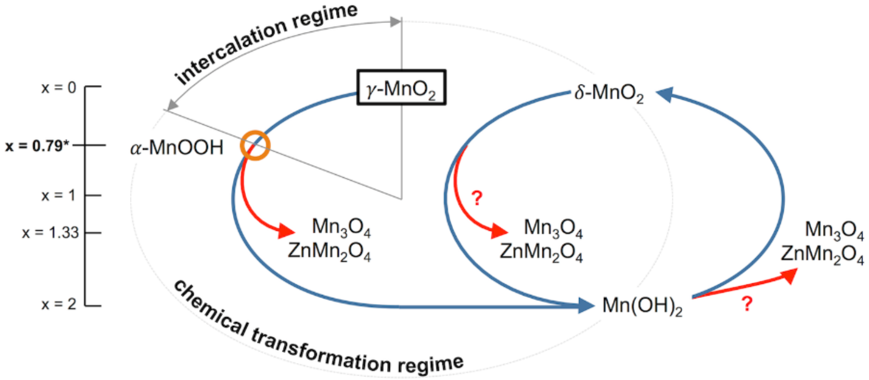
J. Daniel-Ivad and K. Kordesch, "Rechargeable Alkaline Manganese Technology: Past-Present-Future," ECS Annual Meeting, May 12-17, 2002

1866	1950	1970	1980	2010 2016
Primary Low Power	Primary	Limited Capacity Poor Energy Density	Potentiodynamic Poor Cycle Life	Stabilized full-cycling MnO2
1st Zn-MnO_2 battery	Alkaline Zn-MnO_2 battery	5% Rechargeable Capacity	60-80% Rechargeable Capacity	**2010-2014**: CUNY Energy Institute shallow-cycle MnO_2 **2014-2016** Stabilized full-cycling MnO_2



Halina Wroblowa

S. Banerjee, Symposium on Grid Energy Storage, MRS Spring Meeting, 2015
G. Yadav, CUNY Energy Institute, 2018



Failure Mechanisms of Cathode

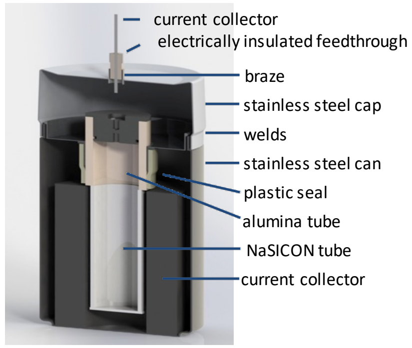
Instability of Mn(III) resulting in formation of irreversible Mn_3O_4
Zn poisoning forming irreversible $ZnMn_2O_4$

Grid Storage needs Large Format Cells

Engineering costs are significant for small format cells. Large format cells are needed to reduce overall system costs.

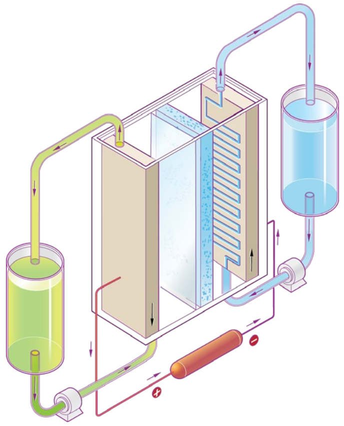
Large format cells also allow for tighter integration of power electronics, sensors, SOH monitoring at the cell level.

High Conductivity Separators for Low Temperature Molten Sodium Batteries



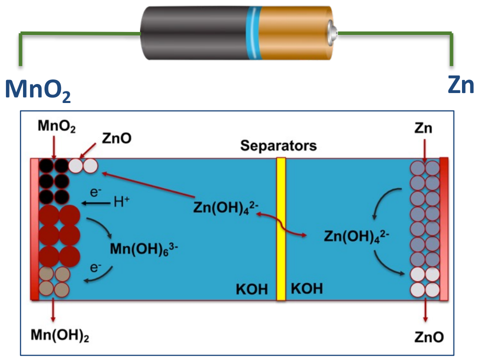
Robust ceramic separators exhibit low Na^+ conductivity at lower, more cost effective temperatures (120-180 °C).

Crossover in Redox Flow Batteries



Cross over of the electroactive species through the separator leads to severe capacity decay in flow battery systems.

Zincate poisoning of MnO_2 in Zn/MnO_2 Batteries



Zincate diffusion and subsequent poisoning of MnO_2 impairs reversibility and significantly decreases lifetimes.

Acknowledgements

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