

# Advances in Battery Technologies for Electric Vehicles and Grid Storage

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# Market Drivers for Advances in Rechargeable Batteries



## Continued Growth of Wireless and Portable Electronics

- Transition to mobile computing and communications
  - Need for safe, energy dense battery storage

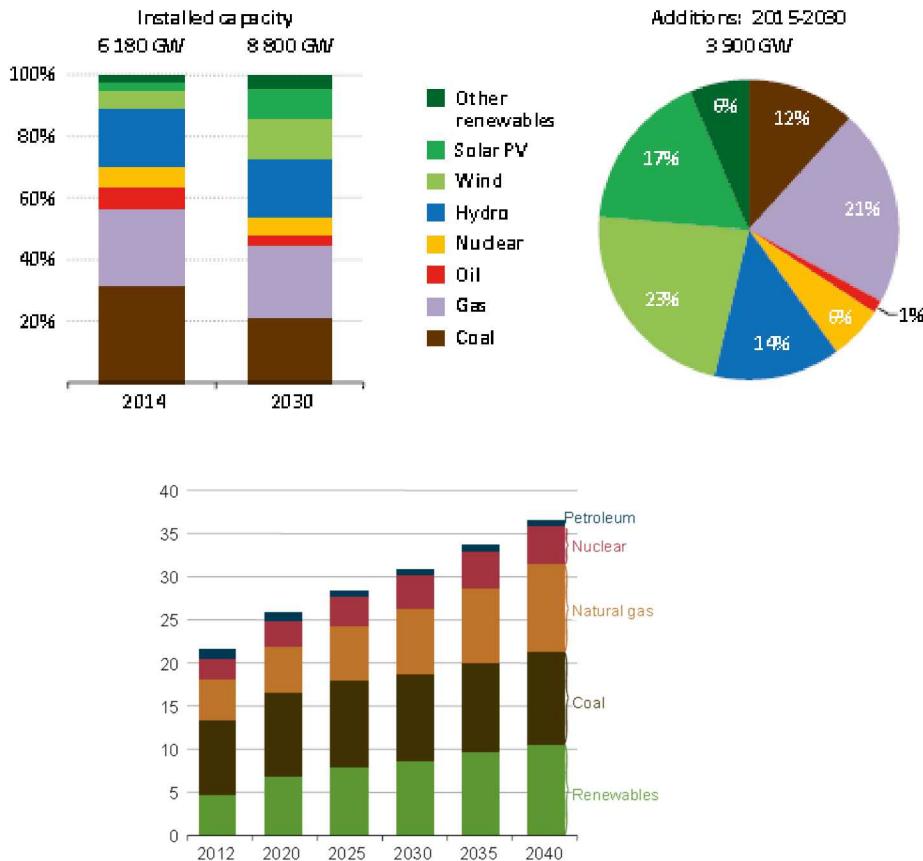
## Electrification of Transportation

- Need energy storage systems with higher energy and power densities
  - Improvements in costs, cycle life, safety and reliability
  - Lighter and faster recharge times

## Transformation of the Electricity Infrastructure

- Aging bulk grid, improving grid reliability and resiliency
- Transition to a distributed generation model, ability to handle intermittency
- Rapid transformation of the grid edge
- Increasing role of electronic loads
- Uncertainty in the utility business models
  - Need lower costs, systems scalable from kWh to 100's of MWh
  - Long cycle life and low operating costs

## Electric Grid: Are we at the cusp of a major transformation?



Source: International Energy Outlook, EIA, 2016

Of the 6 TW of worldwide generation capacity, renewables are reaching the 20% range in many markets.

- Installed solar and wind capacity reached 1 TW in 2018, penetration levels approaching 30-40% in some markets.

US Grid: 850 GW baseload, 1250 GW summer capacity.

- Installed solar and wind capacity reached 150GW in 2018

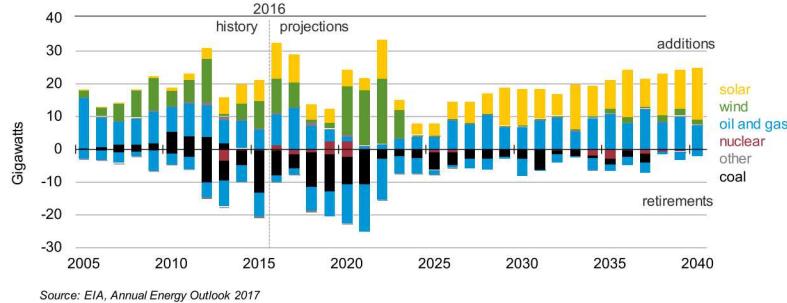
Handling intermittency is becoming a challenge in many markets

- High level integration of energy storage and hybrids, on a grand scale.

**In 2000**, the IEA forecast that by 2030, renewable energy would be 4.4% of the total mix  
**In 2018**, installed wind and solar capacity reached 1 TW, new generation is more renewable

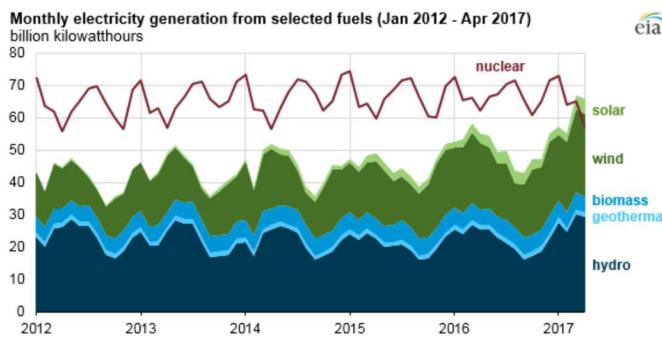
# Major Trends in Electricity Markets

## Capacity Additions and Retirements

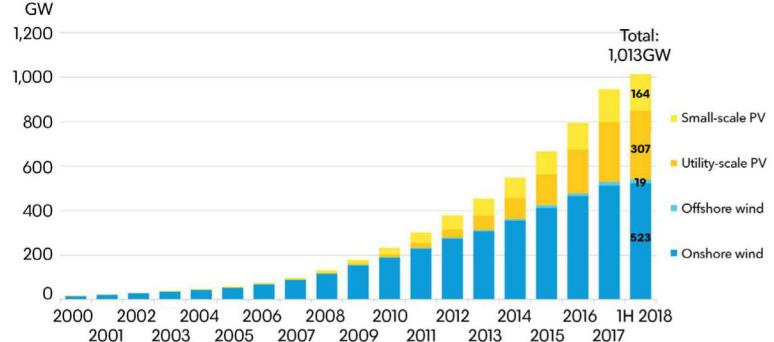


Coal-fired unit retirements driven by low NG prices (EIA, 2017)  
 In California by 2021, solar, storage and wind capacity additions will exceed natural gas (GTM Research)

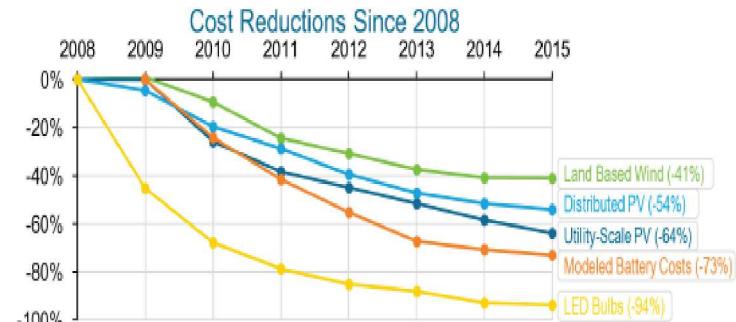
## Utility-scale Renewables Generation surpassed Nuclear Generation - April 2017



Global wind and solar installations, cumulative to June 30, 2018



Cost reductions primarily due to high volume manufacturing and large scale deployments



<http://energy.gov/eere/downloads/revolutionnow-2016-update>

# Grid Evolution - Centralized vs Distributed



We are beginning to see existing business models breaking down

Flat to declining electricity sales in OECD markets

- Investors struggling with poor returns due to long adoption cycles. \$2 Tn Asset Base in the US alone

Conservative regulated utility industry

- not open or reluctant to change business models
- IOUs and PUCs struggling to adapt to rapid change

Rapid change is bottom-up, with major transformation at the grid edge

- EVs, DER, Smart metering, microgrids, demand response, energy efficiency

Changes cuts across technology, economics, policy, and markets

Are we transitioning from a centralized to a decentralized power delivery model?

# Major Battery Technologies for EVs and Grid Storage



## Traditional Batteries

e.g. Lead-acid, Ni-Cd, Ni-MH, Zn-MnO<sub>2</sub>



## Lithium Batteries

e.g. Li-ion, Li-polymer, Li-metal, Li-S



## High-temperature Batteries

e.g. Na-S, Na-NiCl<sub>2</sub>



## Flow Batteries

e.g. Vanadium redox, Zn-Br



	World Wide Production Capacity	Cost and Performance Improvements
Lead Acid Batteries	350 GWh	2%/year (30 year data). \$80-150/kWh
Li-ion Batteries	100 GWh	5%/year (20 year data). Cell level price reaching \$150/kWh
NaS and NaNiCl	300 MWh	Mature, but no economies of scale
Flow Batteries	<200 MWh	Potential for lower cost. \$400/kWh. Reach \$270/kWh
Alkaline chemistries (Zn-MnO <sub>2</sub> , Zn-air)	<100 MWh	Not fully mature. Lowest cost BOM

# Energy Storage - Design and Application Aspects



## Cell Architecture

- Cell format
  - Cylindrical
  - Prismatic
  - Bipolar

## Thermal management

- Heating
- Cooling

## Safety

- Abuse resistance
- Flammability
- Toxicity
- Sustainability

## Plant Models

- Modular
- Centralized

## Power vs. Energy

- High-power, short-duration discharges
- High-energy, long-duration discharges

## Modularity and Scalability

- kW → MW
- kWh → MWh

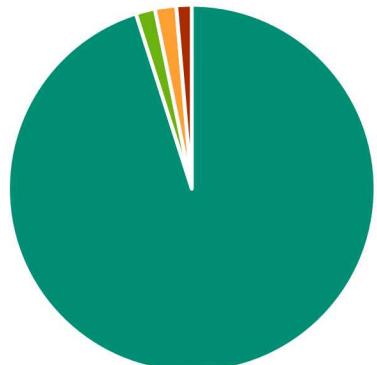
## Cycling capability

- Electrical
- Thermal

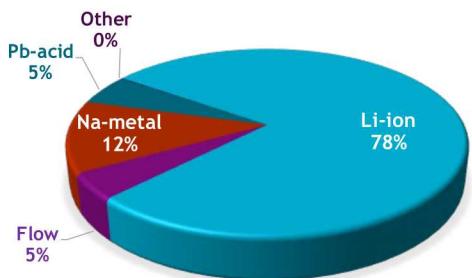
## Operational Aspects

- Round-trip efficiency
- Auxiliary power consumption
- O&M Costs

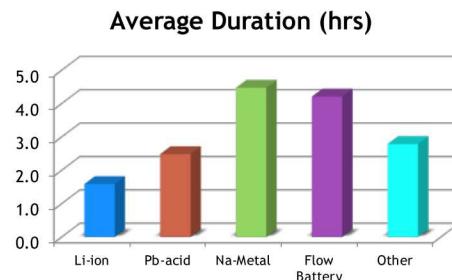
# Energy Storage in the Grid Today



Global Installed Storage Capacity



US Battery Energy Storage Deployed Reaching 2 GW in 2018



Numbers reflect projects reported to the DOE Global Energy Storage Database as of Nov 2017

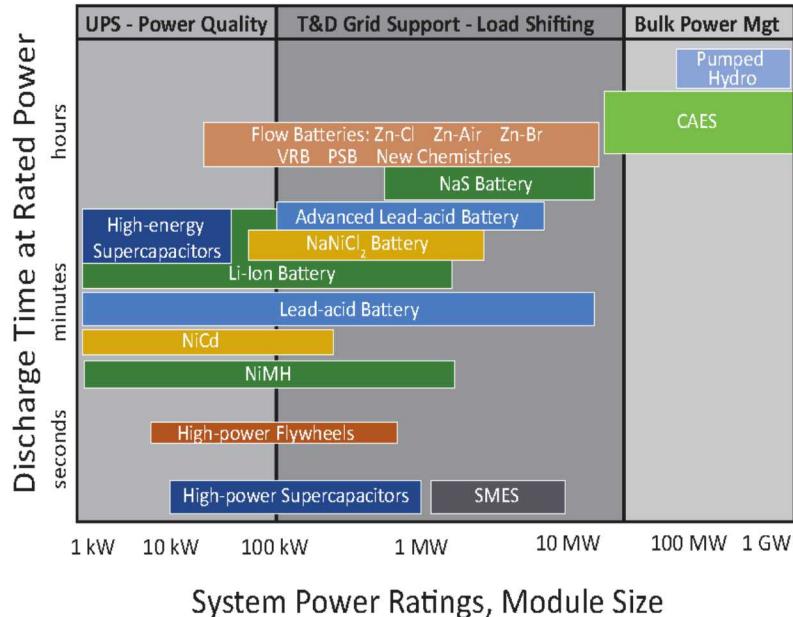
Technology Type	Projects	Rated Power (MW)
Electro-chemical	993	3,279
Pumped Hydro Storage	352	183,800
Thermal Storage	206	3,622
Electro-mechanical	70	2,616

US installed energy storage capacity of 32 GW represents 15 min ride through

Compared to the need, scale of energy storage deployments are insignificant.

DOE Global Energy Storage Database  
<http://www.energystorageexchange.org/>

# Energy Storage System Needs and Applications



Range of applications and storage system needs [Source: DOE/EPRI Electricity Storage Handbook in Collaboration with NRECA, 2013]

Energy Applications	Power Applications
Arbitrage	Frequency regulation
Renewable energy time shift	Voltage support
Demand charge reduction	Small signal stability
Time-of-use charge reduction	Frequency droop
T&D upgrade deferral	Synthetic inertia
Grid resiliency	Renewable capacity firming

## Energy storage application time scale

- “Energy” applications – slower times scale, large amounts of energy
- “Power” applications – faster time scale, real-time control of the electric grid

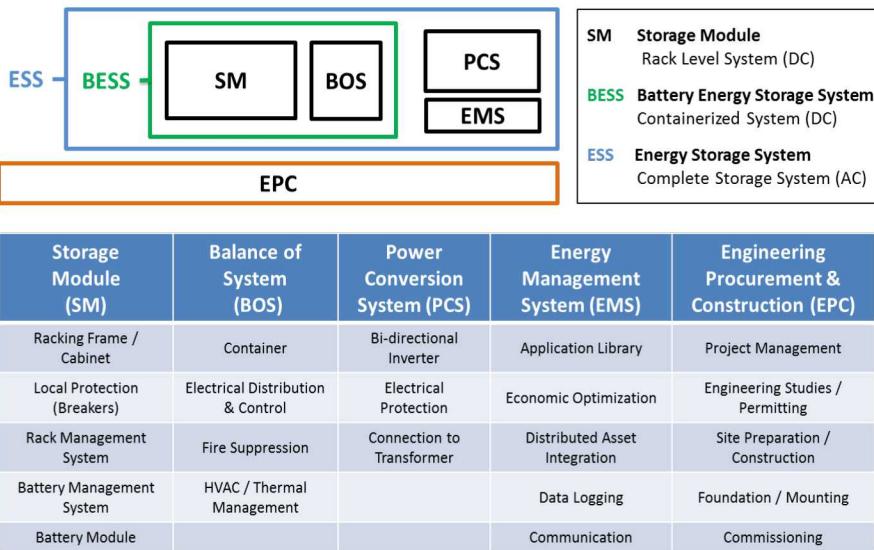
## The grid needs energy storage – right now there are several barriers

- Expensive, especially in energy markets
- Electricity markets/utilities do not properly allocate payments/costs for services provided

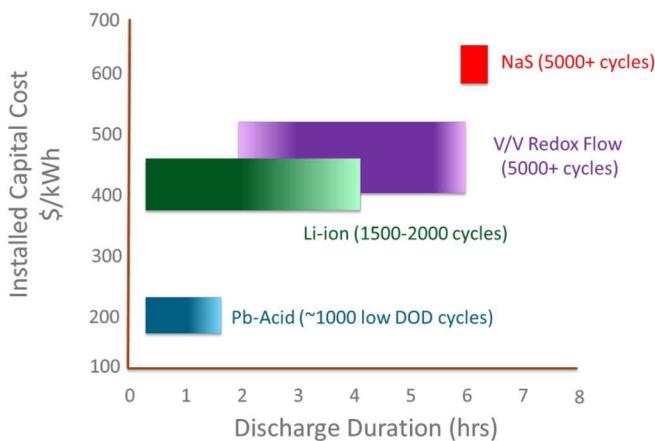
## The future ....

- Higher energy prices – storage starts looking better
- Lower technology costs – storage starts looking better
- Efficient market design – helps pay for storage costs

# Cost of Grid Storage - Not just Batteries, it is a Complex System



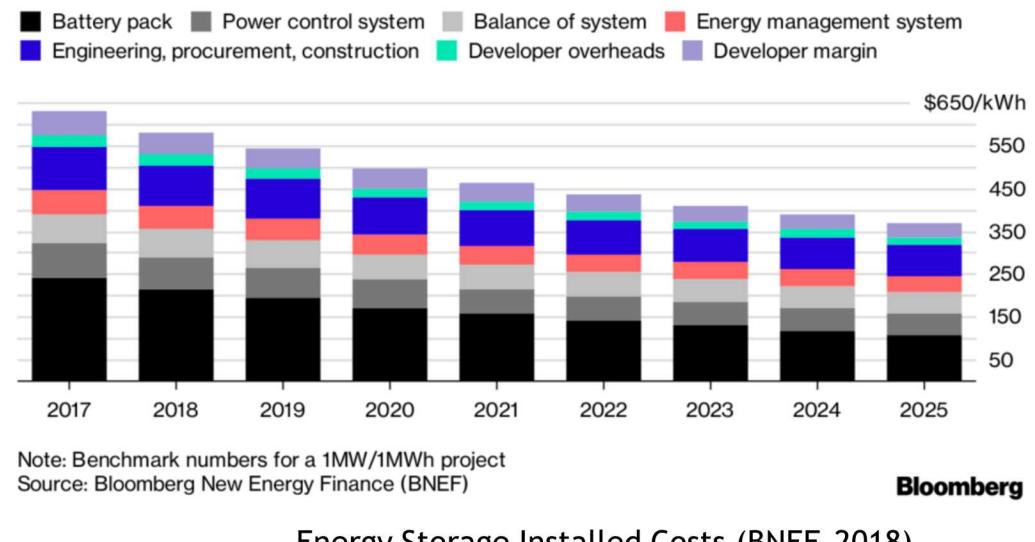
Source: R. Baxter, I. Gyuk, R.H. Byrne, B.R. Chalamala, IEEE Electrification, Aug 2018



Source: V. Sprengle, PNNL, 2017

**Cell to Battery to a Storage System**  
 Doubling in cost, \$250/kWh battery  
 leads to \$500-\$700/kWh at the  
 System level

- Energy Storage is competitive in power markets such as regulation
- Expensive in most energy markets



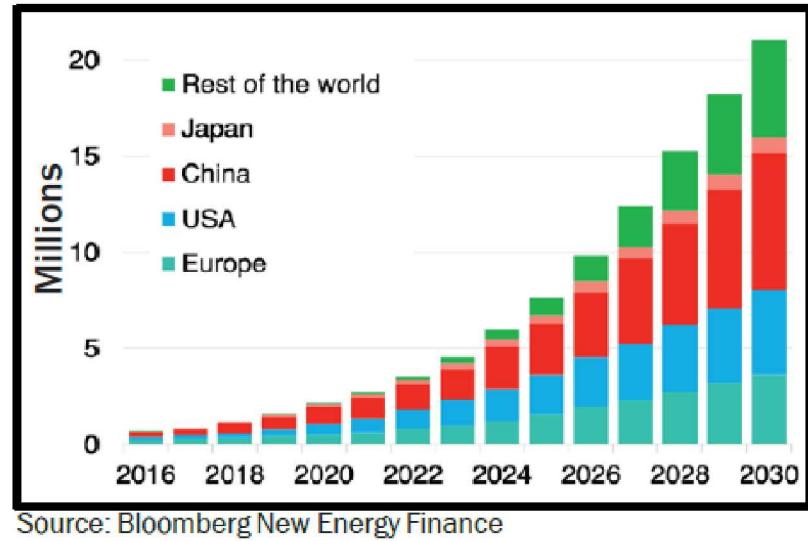
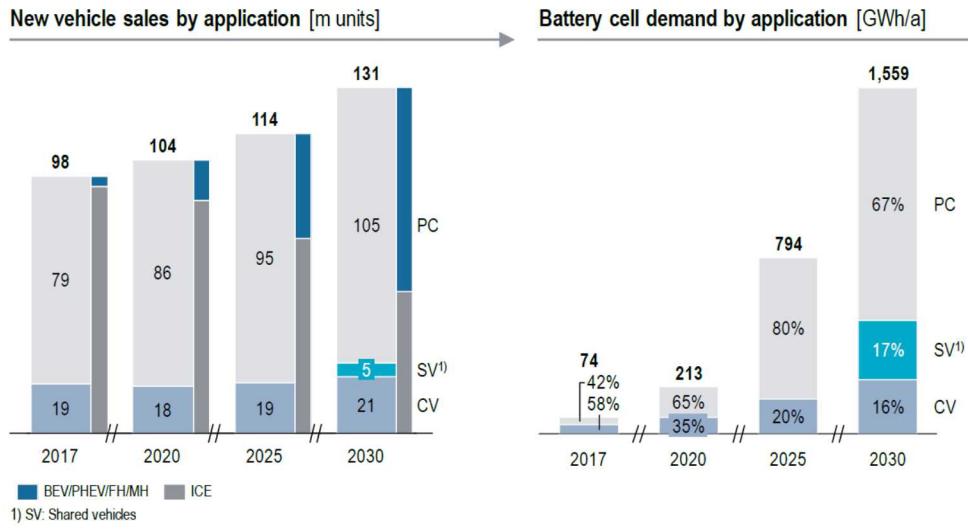
Energy Storage Installed Costs (BNEF, 2018)

# Electrification of Transportation



IEA, IHS, Bloomberg projections for annual production of electric vehicles reaching 20 Million by 2030 and a fleet of 130 Million vehicles (mostly passenger vehicles) on road as base case, 230M vehicles optimistic case'

- Typical battery pack: 100 kWh/80kW, 500 mile



**Projected battery capacity needs for EVs in 2030**

- 1.5 - 2.5 TWh of manufacturing capacity

# 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

## High energy density

Better cycle life than Lead - Acid

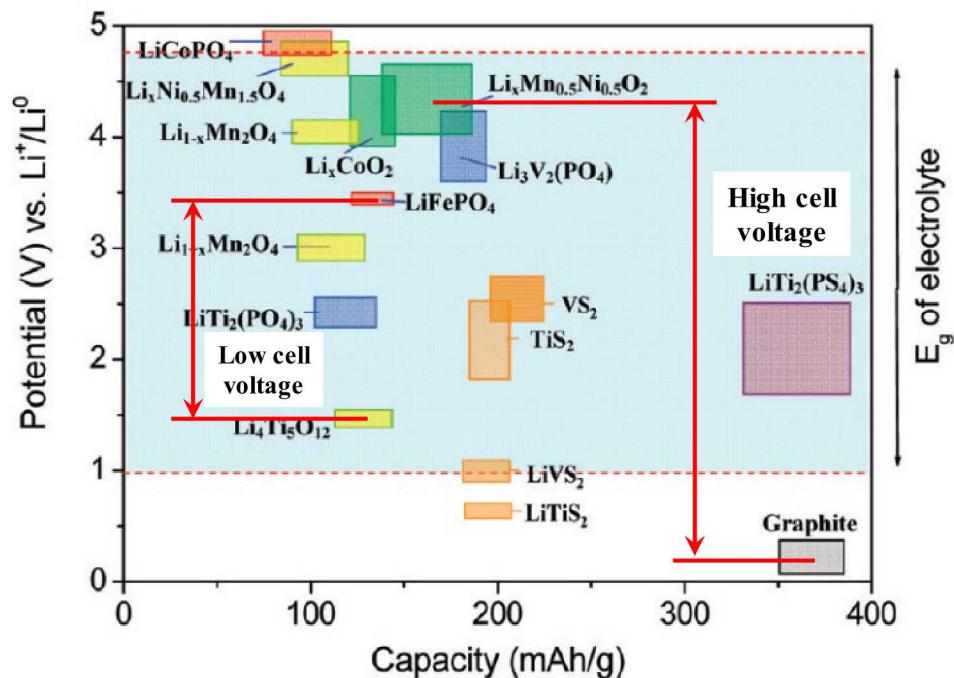
## Decreasing costs

## Ubiquitous – Multiple vendors

## Fast response

## Higher efficiency

No single type is best for all applications



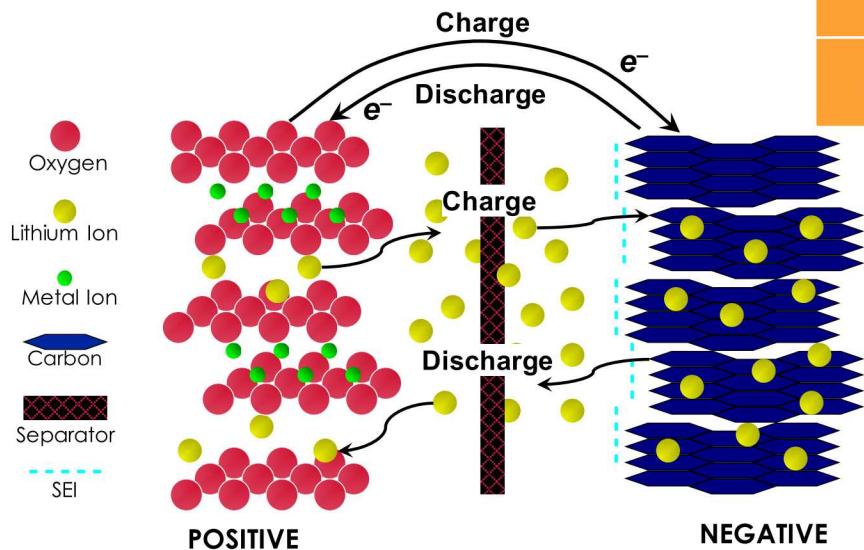
# Li-ion: Basic Chemistries

## Anodes

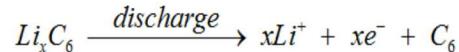
Chemistry	Specific Capacity	Potential vs. Li <sup>+</sup> /Li
Soft Carbon	< 700	< 1
Hard Carbon	600	< 1
Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub>	175 / 170	1.55
TiO <sub>2</sub>	168 / 168	1.85
SnO <sub>2</sub>	782 / 780	< 0.5
Sn	993 / 990	< 0.5
Si	4198 / < 3500	0.5 ~ 1

## Cathodes

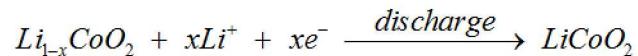
Chemistry	Specific Capacity	Potential vs. Li <sup>+</sup> /Li	
LiCoO <sub>2</sub>	273 / 160	3.9	Consumer Electronics
LiNiO <sub>2</sub>	274 / 180	3.6	
LiNi <sub>x</sub> Co <sub>y</sub> Mn <sub>z</sub> O <sub>2</sub>	~ 270 / 150~180	3.8	NMC - LG/Volt
LiNi <sub>x</sub> Co <sub>y</sub> Al <sub>z</sub> O <sub>2</sub>	~ 250 / 180	3.7	NCA - Tesla
LiMn <sub>2</sub> O <sub>4</sub>	148 / 130	4.1	
LiMn <sub>1.5</sub> Ni <sub>0.5</sub> O <sub>4</sub>	146 / 130	4.7	
LiFePO <sub>4</sub>	170 / 160	3.45	LFP
LiMnPO <sub>4</sub>	171 / 80~150	4.1	
LiNiPO <sub>4</sub>	166 / -	5.1	
LiCoPO <sub>4</sub>	166 / 60~130	4.8	



Anode:



Cathode:



# Li-ion Batteries - SOA

First two generations driven by consumer electronics, newer chemistries geared for automotive applications

- LiCoO<sub>2</sub> continues be the dominant technology for consumer electronics
- 2nd Generation Li-Ion Chemistries offering better performance, wider temp range, improved safety and lower cost. NMC, NCA preferred for EVs

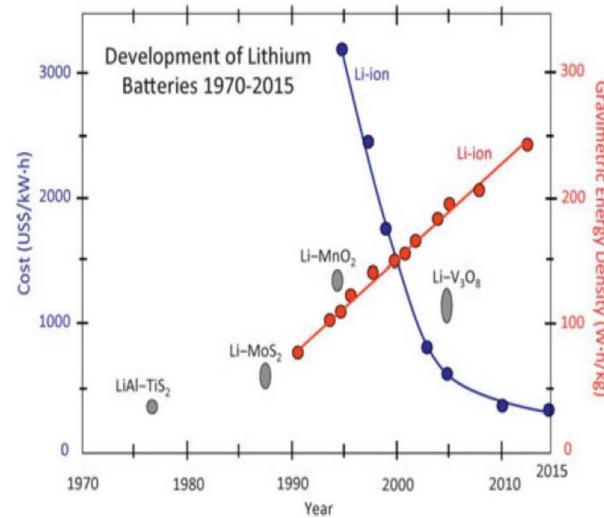
Rapid growth of application beyond frequency regulation and power quality to energy applications. Large plants in the 100 MW are being built.

Capacity improvements are becoming incremental

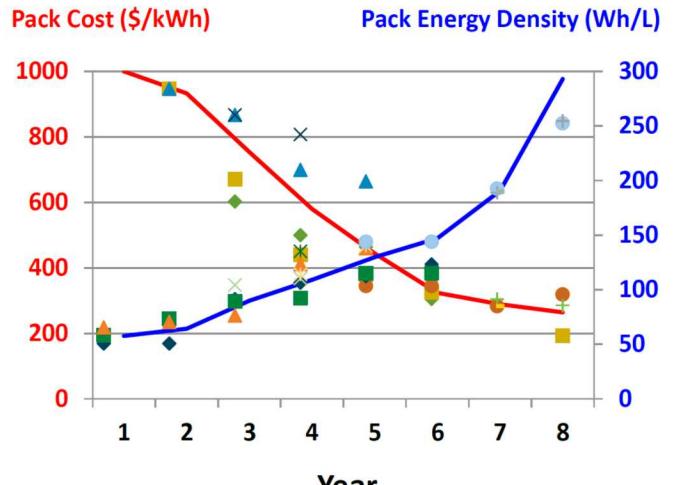
- 8% for LIB (1992-2007); BOM is 80-85% of cell costs, Scaling down materials cost proving difficult
- Engineering larger cells (>100 Ah) is not still economical

Safety and reliability continue to be significant concerns

Deep discharge cycle life issues for energy applications (1000 cycles for automotive)

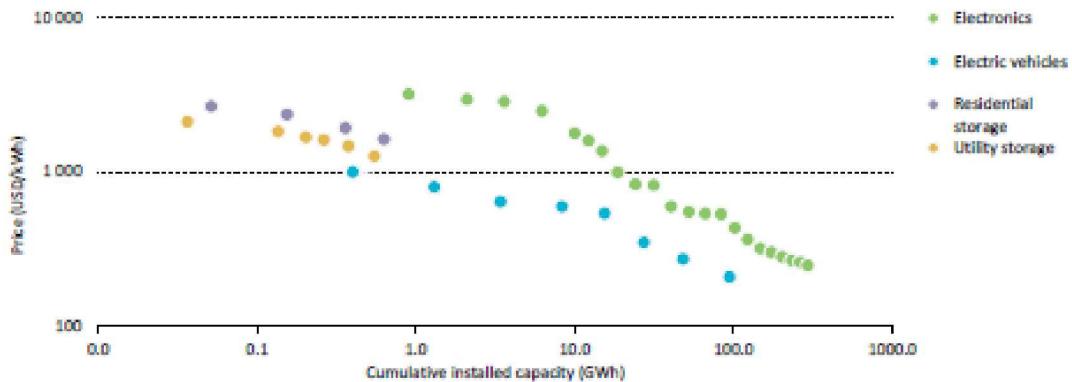


Source: Crabtree, Kocs, Trahey, MRS Bulletin, Dec 2015



Source: David Howell, DOE VTO, 2017

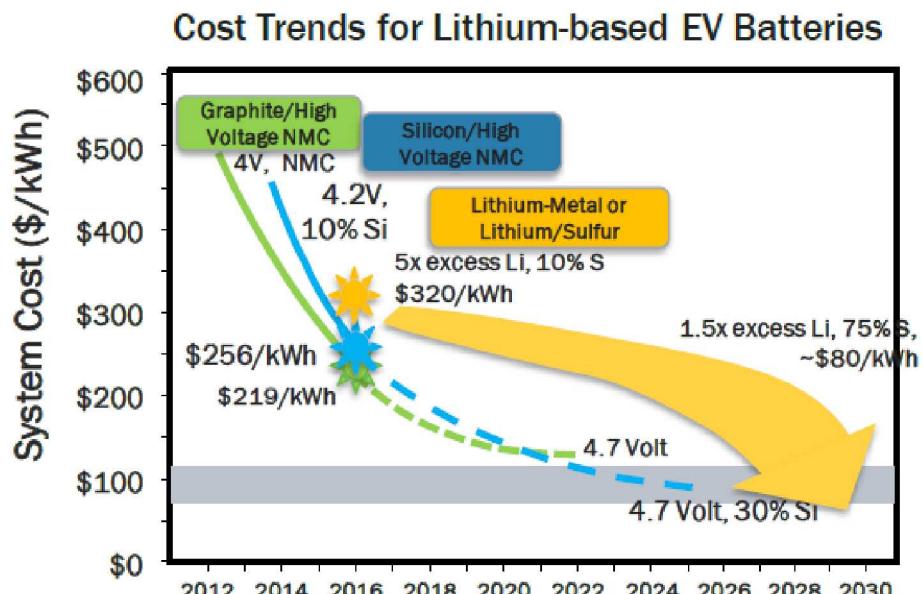
# Manufacturing Scale and Cell/System Costs



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



## Heat Generation

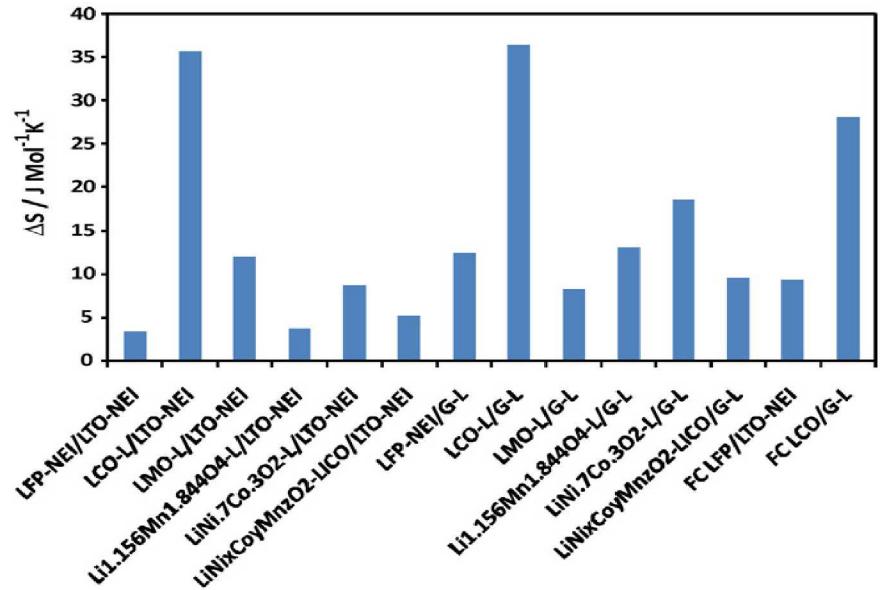
- Dictates smaller form factor
- Higher production costs.

## 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

- Max voltage depends on materials, overcharging can lead to Li metal plating on anode, potential for short



Inherent Heat Generation of Electrodes



Electric EV batteries are primarily NCA and NMC

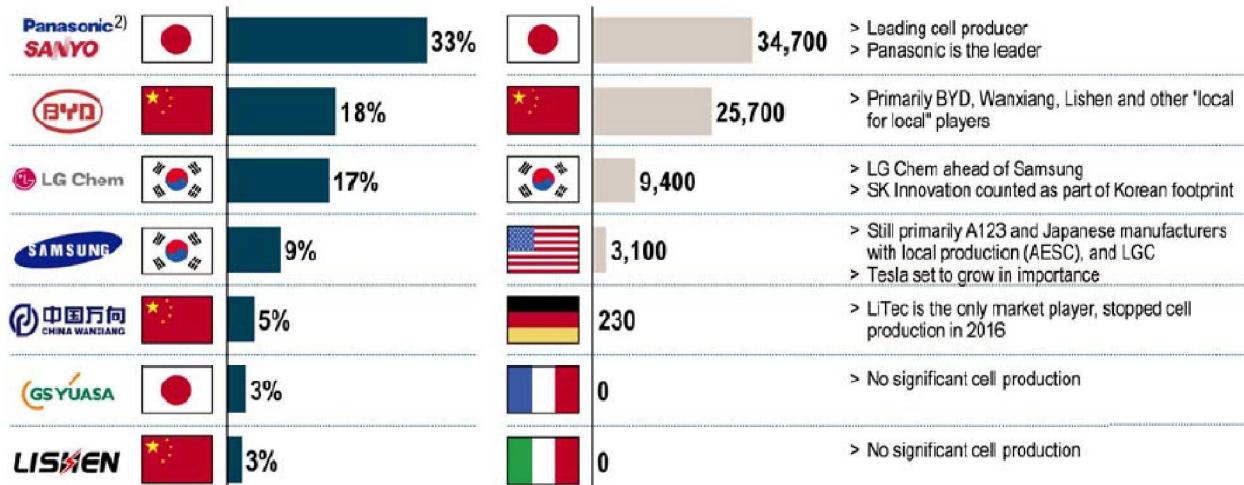
Except for Tesla which uses NCA in 18650 format, all other EV companies use NMC in large format pouch cells

Electric buses most use LFP cells

### Most new capacity coming online is primarily for EVs

Projected global market share, 2018<sup>1))</sup>

Domestic cell production, 2014-2018 [MWh]



1) 2018 market value in USD calculated as follows: 280 USD/kWh for PHEVs and 200 USD/kWh for EVs; shift from single to dual sourcing strategies expected mid-term  
 2) Including Primearth's market share

# Li-ion Batteries for Grid Applications

Technology – wider range than EV needs, lower costs, longer cycle life and simpler packaging

Already a dominant technology for Power Applications in the grid

Expanding range of deployments

- Behind the meter, regulation, ramping products

Advantages

- High energy density
- Better cycle life than Lead - Acid
- Decreasing costs – Stationary on coattails of increasing EV.
- Ubiquitous – Range of vendors
- Fast response
- Higher efficiency

Challenges

- Intolerance to deep discharge
- Cycle life for energy applications
- Sensitive to
  - Over temperature
  - Overcharge
  - Internal pressure buildup



SCE Tehachapi plant, 8MW, 32MWh

# Large Commercial Li-ion Deployments



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



Saft 6 MW / 4.2 MWh ESS  
Kauai - Grid Stability



Tesla 100 MW / 129 MWh ESS  
Australia - Grid stability

# Future Developments in Li-based Batteries

## Higher-voltage positive (cathode) materials

- Lithium manganese phosphate
- Lithium cobalt phosphate

## Higher-capacity negative (anode) materials

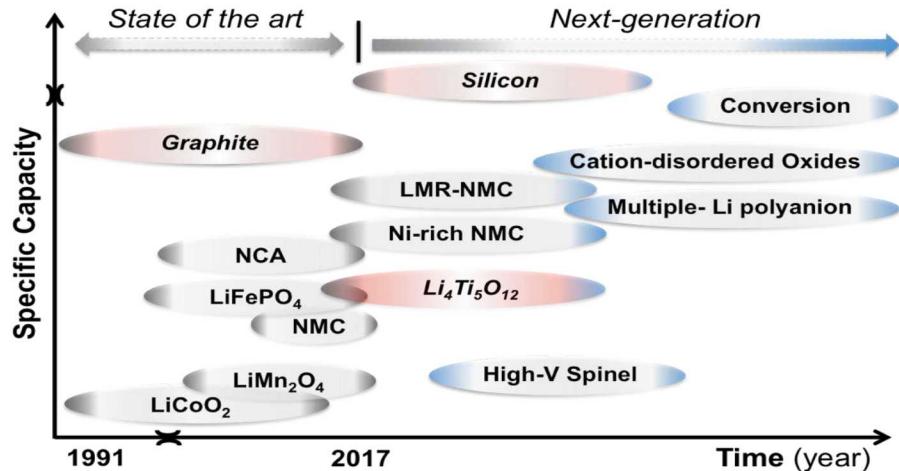
- Silicon-based

## Safer electrolytes

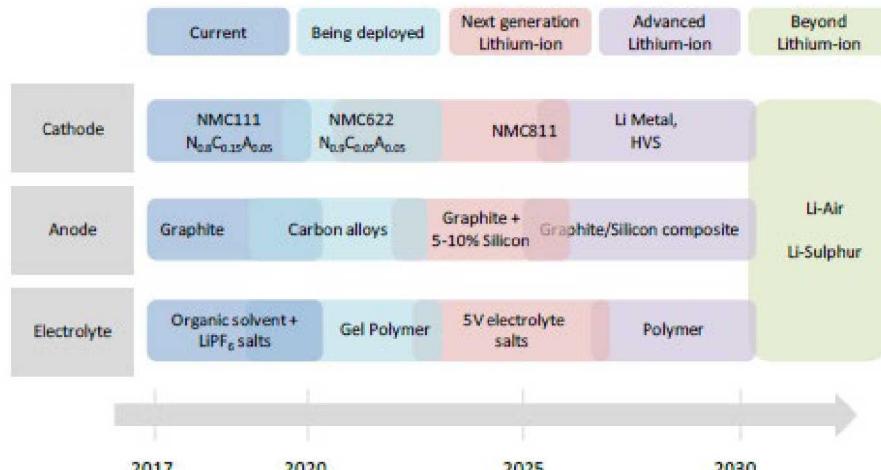
- Inorganic
- Solid-state electrolytes

## 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 and Metal Air Batteries

All metal air batteries (Li-air, Zn-air) have the potential to deliver high energy densities at low cost. Challenges with recharging have so far precluded commercialization of the technology.

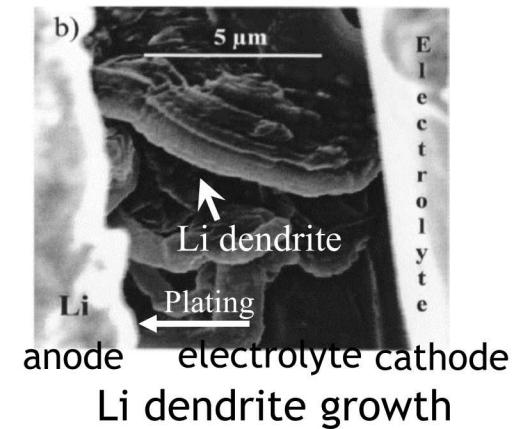
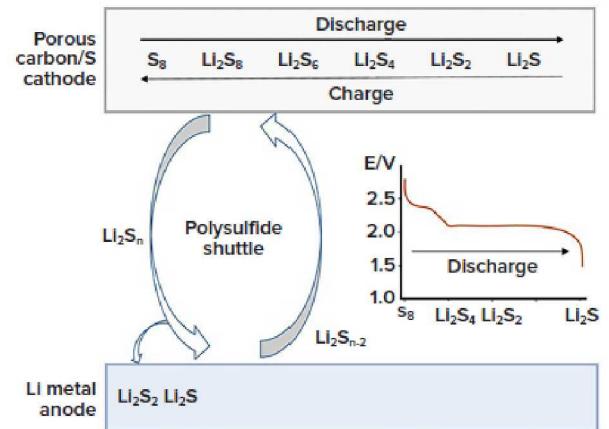
- Lot of startup activity in Metal-Air batteries
- Technology not mature, decade or more away
- Potential fundamental problems

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

Li-S suffers from major problems of self discharge and poor life

- Breakthroughs needed for life of Li electrode, low cost separator



# Lead-Acid Batteries

## Overall Reaction

- $\text{Pb(s)} + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$
- OCV  $\sim 2.0$  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

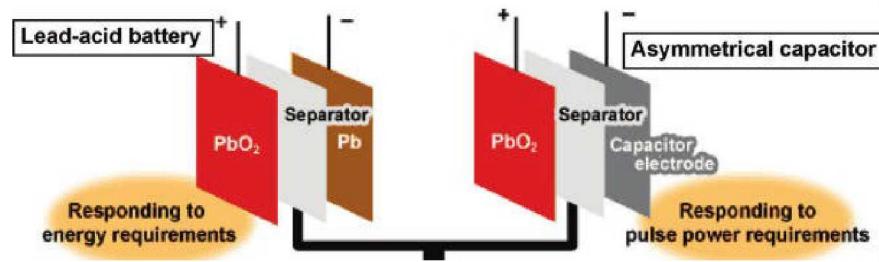
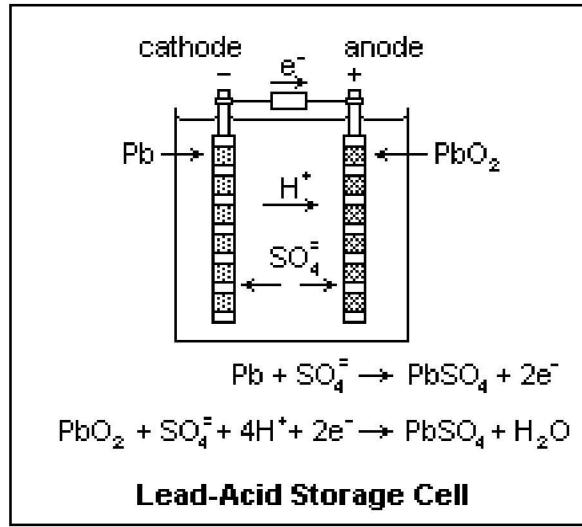
## Mature technology

## 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 H<sub>2</sub> evolution.
- Sulfation from prolonged storage



<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

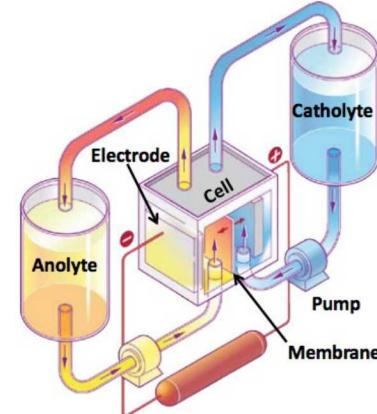
Energy storage technology utilizing redox states of various species for charge/discharge purposes

## Key Aspects

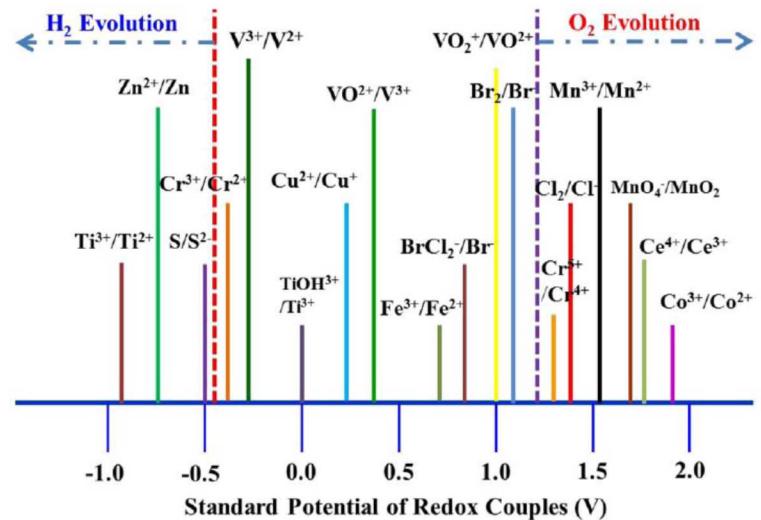
- Power (kW) and energy (kWh) separation
- Greater flexibility and safety
- Modular and scalable across a wide range of power and energy
- Long cycle life
- Low energy density  $\sim 30$  Wh/L

## Range of redox chemistries

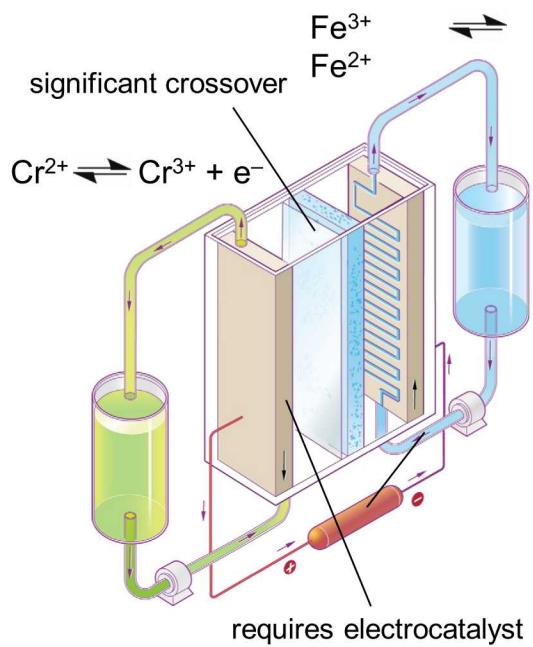
- Fe-Cr, Zn-Br, V-V are most studied and large systems demonstrated
- Most large commercial flow batteries are based on V-V chemistry, and Zn-Br



Source: Travis Anderson, Sandia National Laboratories, 2013

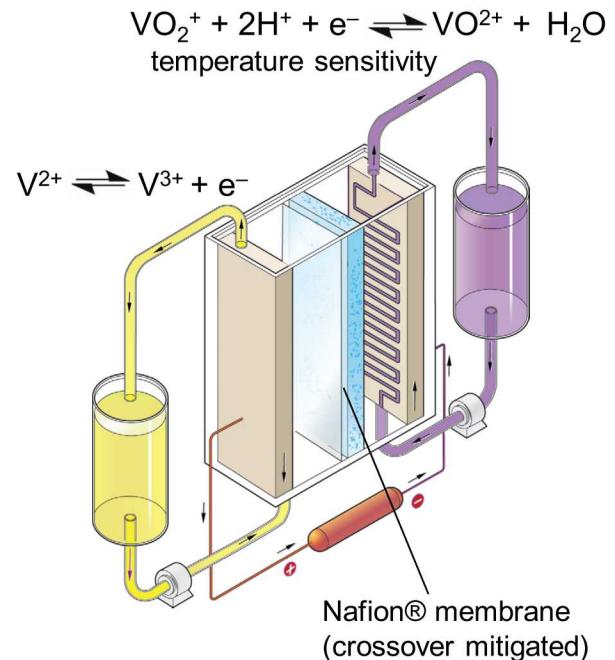


# Early Development (Aqueous)



Open Circuit Potential (OCP)<sup>1</sup> **1.2 V**

<sup>1</sup>Skyllas-Kazacos, M. J. *Electrochem. Soc.*, 158 (8) R55-R79 (2011)



Open Circuit Potential (OCP)<sup>2</sup> **1.3 V**

<sup>2</sup>Li, L. *et al.*, *Adv. Energy Mater.* 2011, 1, 394–400

# 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

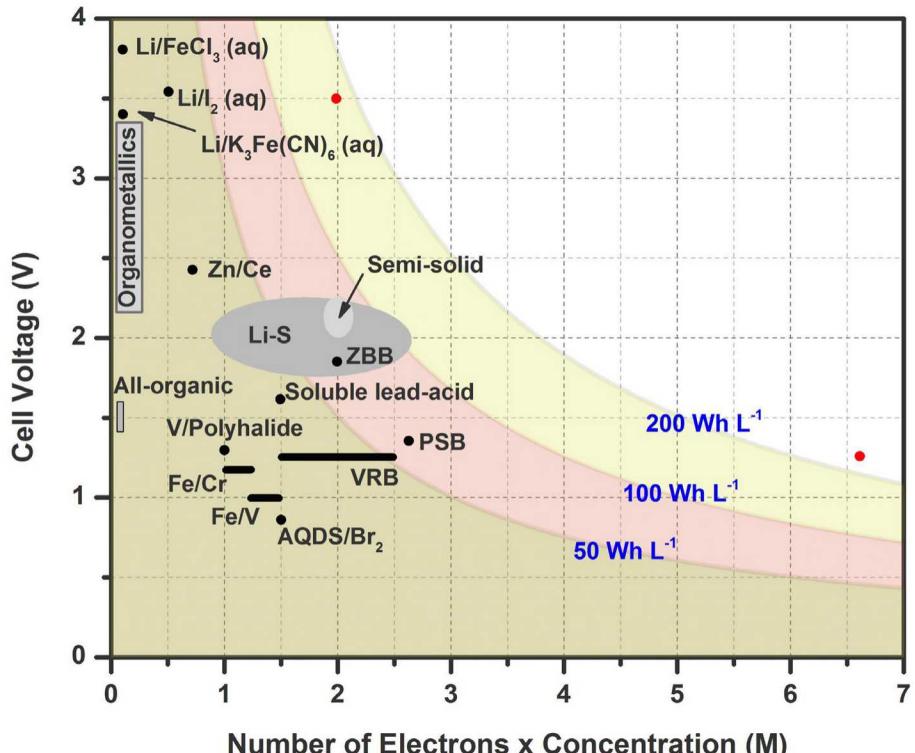
- Low solubility of redox species in aqueous electrolytes
- Capacity decay during cycling
- Narrow temperature range

## Corrosion of membranes and electrode materials by acidic electrolyte solutions

- Long-term reliability

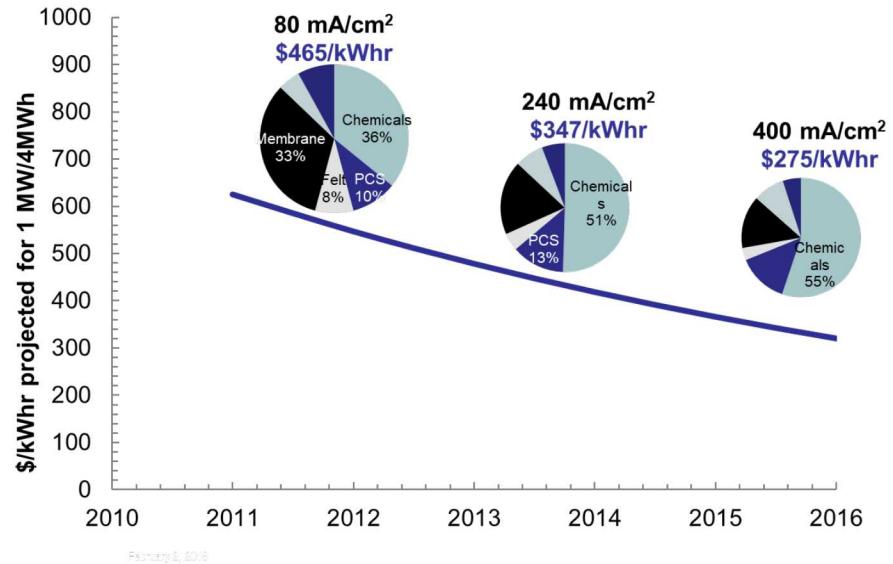
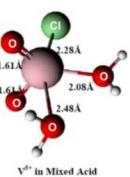
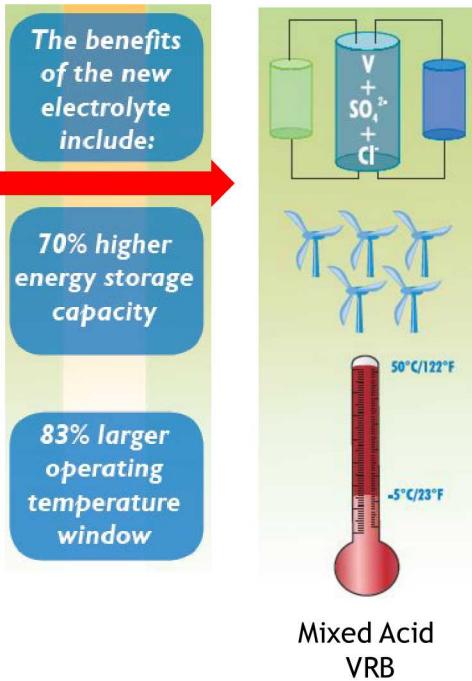
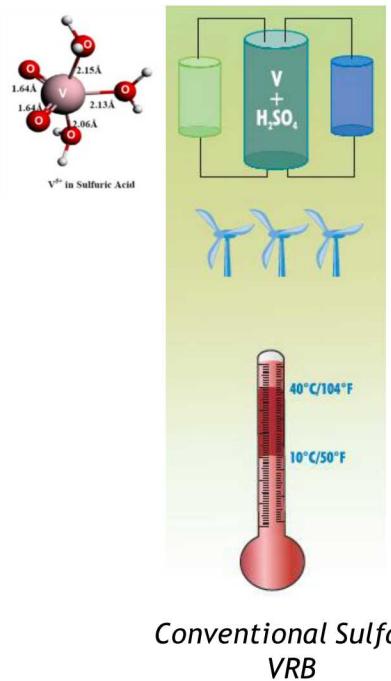
## Opportunities to Reduce Materials Cost

- 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

# Vanadium Mixed Acid Electrolyte



Source: V. Sprengle, PNNL, 2018

Increased energy density and larger temperature window  
 Continued cost reductions in materials and system costs

# 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/cm<sup>2</sup>  
Meter size  
stack

Flow battery power plants



Sumitomo Electric, 15MW/60MWh



Stack room

# Next Generation Flow Batteries

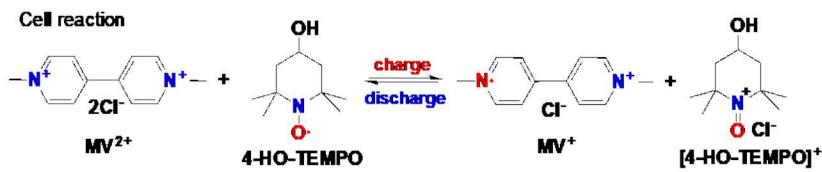
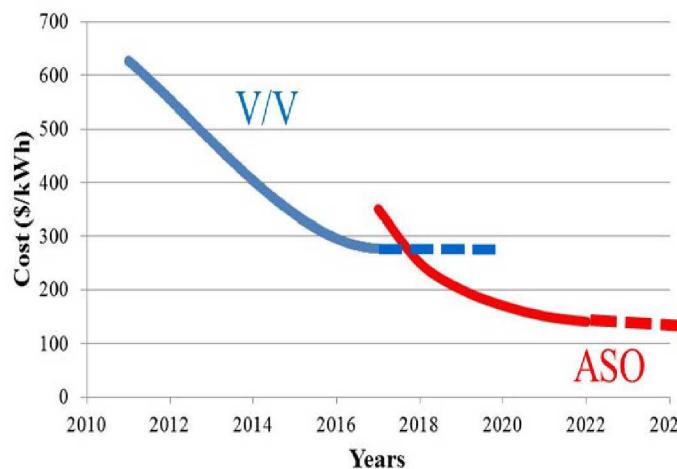


## Aqueous Organic Electrolytes

Aqueous soluble organic electrolytes showing promise as drop-in replacement to current V/V systems.

Potential for  $\frac{1}{2}$  cost reduction if performance and stability targets can be obtained.

No resource constraints



Advanced Energ

## Non-Aqueous Organic Electrolytes

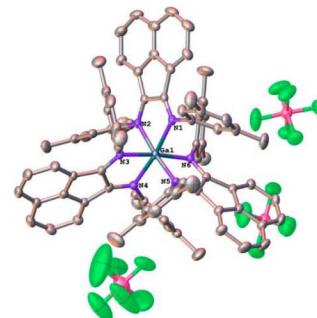
Wider voltage window, Potentially higher energy density

Decreased temperature sensitivity

Potentially favorable cost projections

Metal coordinated redox couple

- Metal coordination complexes (UMich)
- Metal-based ionic liquids (Sandia)
- Semi-solid lithium flow battery (MIT)
- Li-redox flow battery (UTexas/JAIST)
- Li-S flow battery (Stanford/MIT/PNNL)
- Metal-organic hybrid RFB (PNNL)



Mitch Anstey, 2016  
DOE Energy Storage Peer Review

# Sodium Batteries (NaS and NaNiCl<sub>2</sub>)

Batteries consisting of molten sodium anode and  $\beta''\text{-Al}_2\text{O}_3$  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)

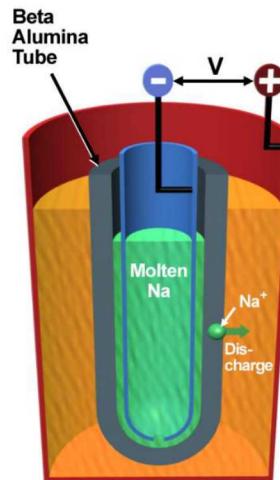
Two primary chemistries

- NaS, mature technology, deployed in grid applications
- NaNiCl<sub>2</sub>, mature, more stable than NaS

NaNiCl<sub>2</sub> (Zebra) developed in the 1980's

- FIAMM in limited production, GE no longer in manufacturing

Neither NaS nor NaNiCl<sub>2</sub> are at high production volumes and the economies of scale needed



# NaS Batteries

Most widely deployed of long duration batteries

NaS first developed by Ford Motor Co. in 1960's

- Commercialized by NGK in Japan
- 530 MW/3700 MWh of installed capacity, primarily in Japan

NaS battery

- $2\text{Na} + x\text{S} \rightarrow \text{Na}_2\text{S}_x$  ( $x = 3\sim 5$ )
- $E = 2.08\sim 1.78 \text{ V}$  at  $350^\circ\text{C}$

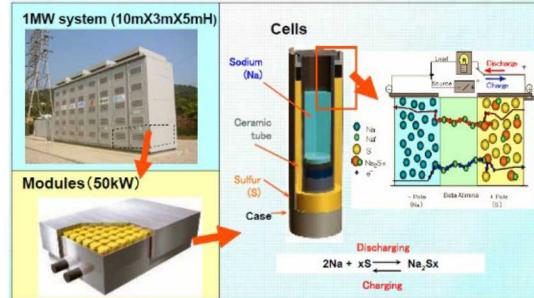
Applications

- Power quality, Congestion relief
- Renewable integration

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

NGK is the only committed manufacturer



Source: NGK



34MW /245 MWh NAS at a wind farm  
Rokkasho, Aomori, Japan (Source: NGK, 2017)



Los Alamos, NM. 1 MW, 6MWh

# NaNiCl<sub>2</sub> Batteries

## NaNiCl<sub>2</sub> battery

- $2\text{Na} + \text{NiCl}_2 \rightarrow 2\text{NaCl} + \text{Ni}$
- $E = 2.58\text{V}$  at  $300^\circ\text{C}$

Large cells and stable chemistry

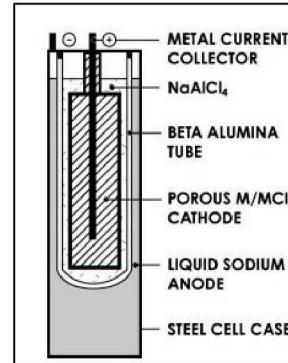
- Lower temperature than NaS
- Cells loaded in discharge mode
- Improved safety compared to NaS. Addition of catholyte  $\text{NaAlCl}_4$  leads to a closed circuit on failure

High efficiency, low discharge

Long warm up time (16 hr)

Supply chain concerns. Only one manufacturer  
FIAMM. GE no longer in this business

- Limited deployments



FIAMM 222-kWh System Duke Energy Rankin Substation

# Molten Na Batteries - Engineering Challenges



## **Low cost active materials, but challenging systems engineering**

- Need for high temperature operation, kinetics driven by the solid ceramic electrolyte
- Typical operating window 250-350°C. Need for continuous thermal management even when not in use. At lower T, Na metal freezes out, degree of distortion to cell dictated by SOC of battery
- Safety concerns related to membrane rupture. In NaS, failure can lead to exothermic reaction
- Need hermetic seals
- Charging/discharging limitations

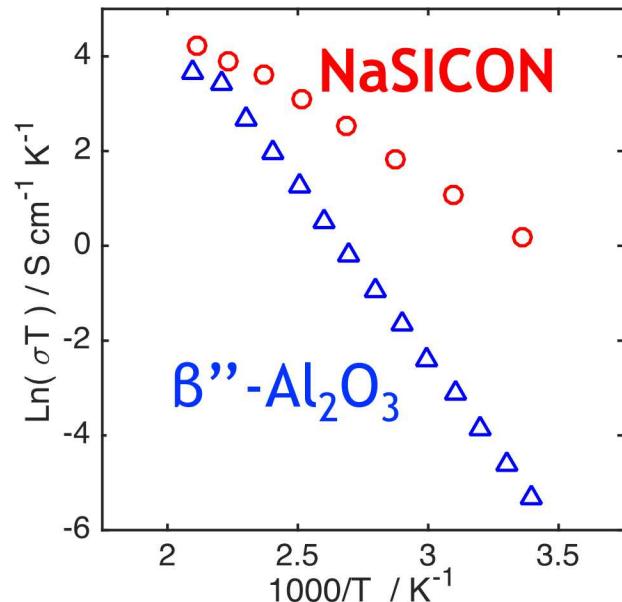
## **Engineering cells that operate at lower T (150°C or lower) remains a challenge. Low Temperature Operation of a Molten Na Battery is Tremendously Enabling**

- Improved Lifetime
  - Reduced material degradation, Decreased reagent volatility, Fewer side reactions
- Lower material cost and processing
  - Seals, Separators, Cell body
  - Polymer components become realistic!
- Reduced operating costs
- Simplified heat management costs

# Low Temperature NaSICON Electrolyte Enables Multiple Na-Battery Chemistries

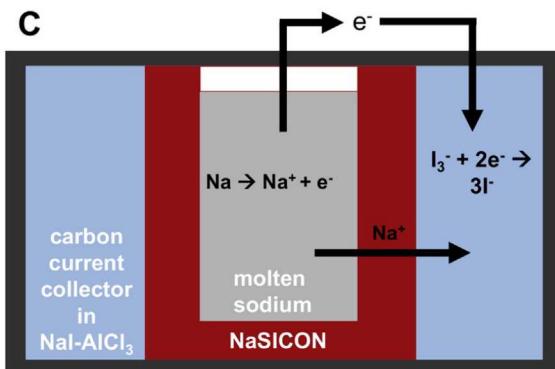
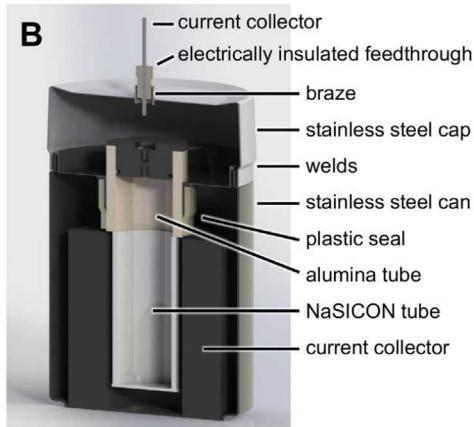
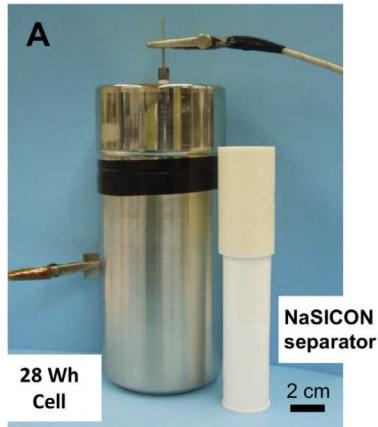


NaSICON (Na Super Ion CONductor):  $\text{Na}_3\text{Zr}_2\text{PSi}_2\text{O}_{12}$



NaSICON is chemically/mechanically stable and has high conductivity ( $>10^{-3} \text{ S/cm}$  @RT) at lower temperatures. This opens the possibilities for a range of cell chemistries.

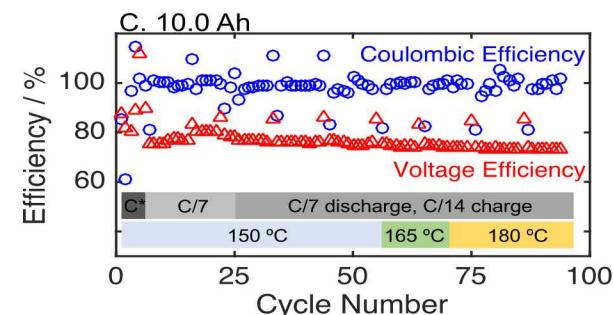
# Early Demonstration of Na-NaI Battery (150-180°C)



0.850 Ah

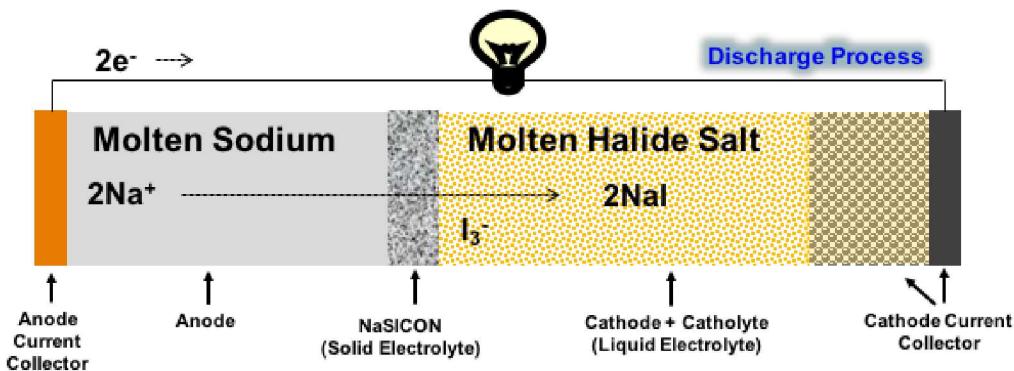
150 °C

B. 3.00 Ah

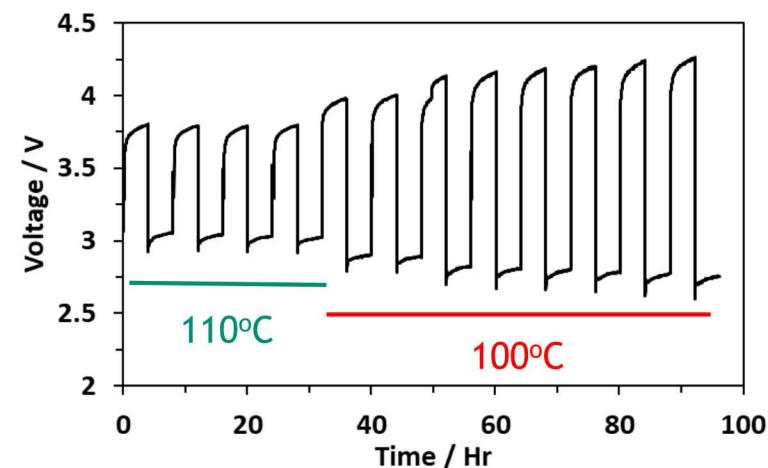
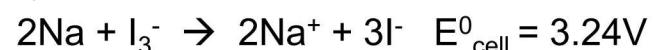
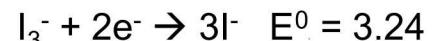
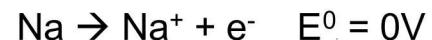


The catholyte is 60 mol%  $\text{NaI}-\text{AlCl}_3$  (with 5-10 mol%  $\text{NaI}$  added) – Significant undissolved solids at 150°C.

# Lower Temperature Sodium Halide Batteries

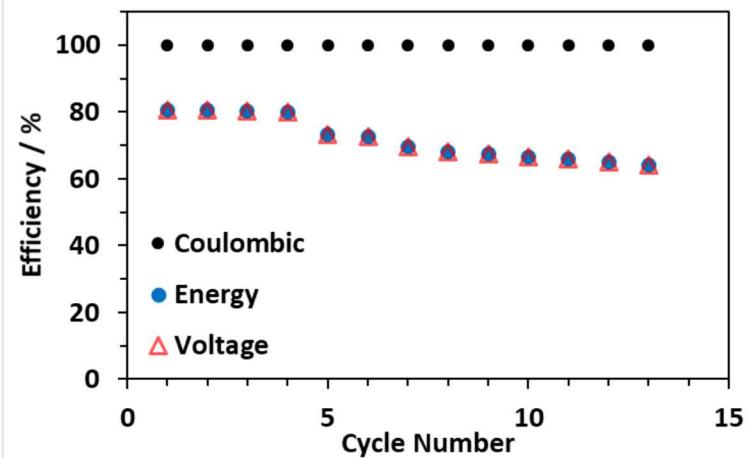


## Na-Nal battery:



**Battery cycling  
at 100°C!**

25 mol% NaI-AlBr<sub>3</sub>  
with NaSICON  
separator.



Source: E. Spoerke, Sandia National Labs  
2018 DOE Energy Storage Program review

# Rechargeable Alkaline Batteries

## Range of alkaline battery chemistries

- NiMH, Ni-Fe, Ni-Cd, Zn-Ni, Zn-MnO<sub>2</sub>

## Zn-MnO<sub>2</sub> shows most promise for grid storage

### Cost

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

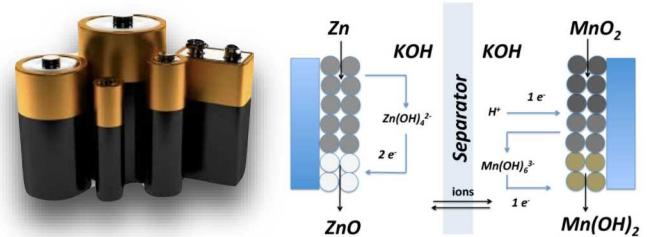
### Safety

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

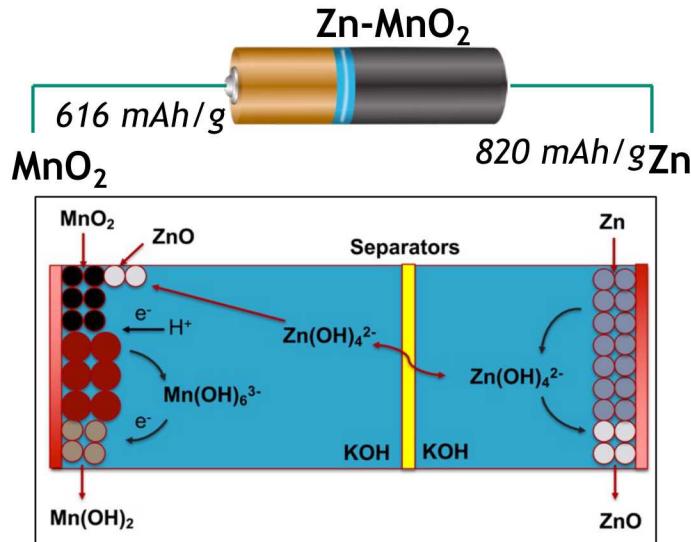
### Reliability

- Long shelf-life
- Limited thermal management required

**Reversibility and cycle life have been the primary technical challenges**



Single-use Alkaline Battery \$25/kWh



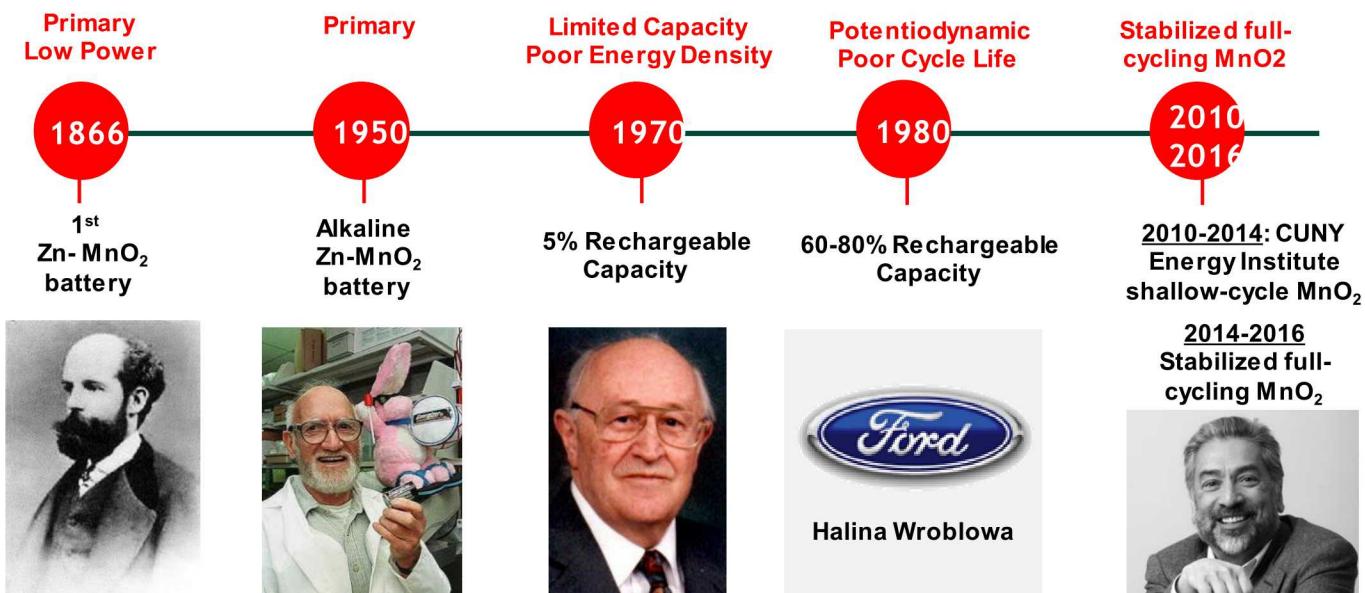
Source: S. Banerjee, CUNY Energy Institute

# History of Rechargeable Zn-MnO<sub>2</sub> 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



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

# Full Utilization of 2e

## On the $\text{MnO}_2$ Cathode

- Regeneration of cathode structure on solution/dissolution/precipitation cycle
- Formation of Inactive phases
- Reducing susceptibility to Zinc poisoning

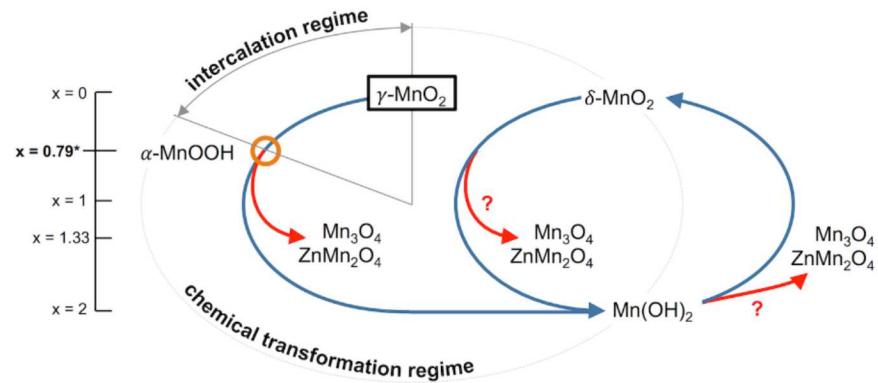
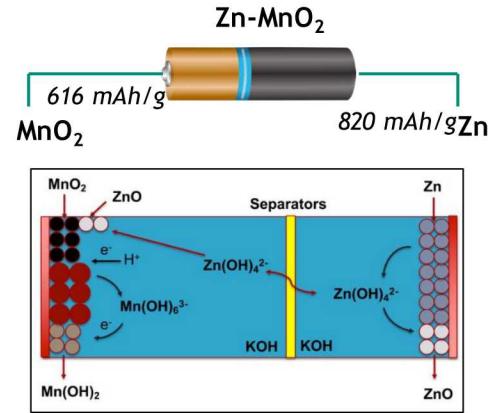
## Separator

- Reduce Zinate crossover

## On the Zn Anode

- Control shape change
- Passivation
- Reduce dendrite formation

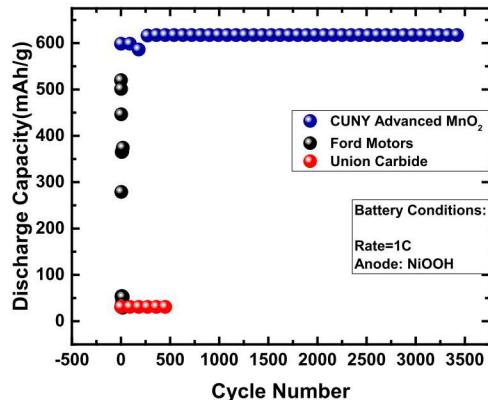
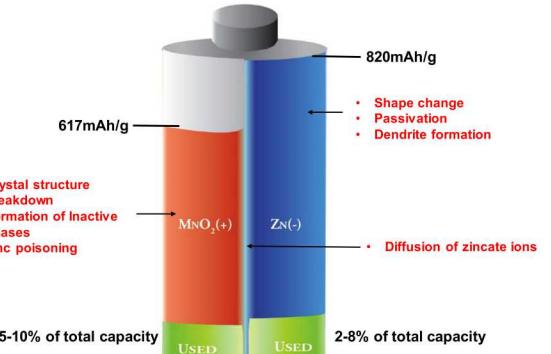
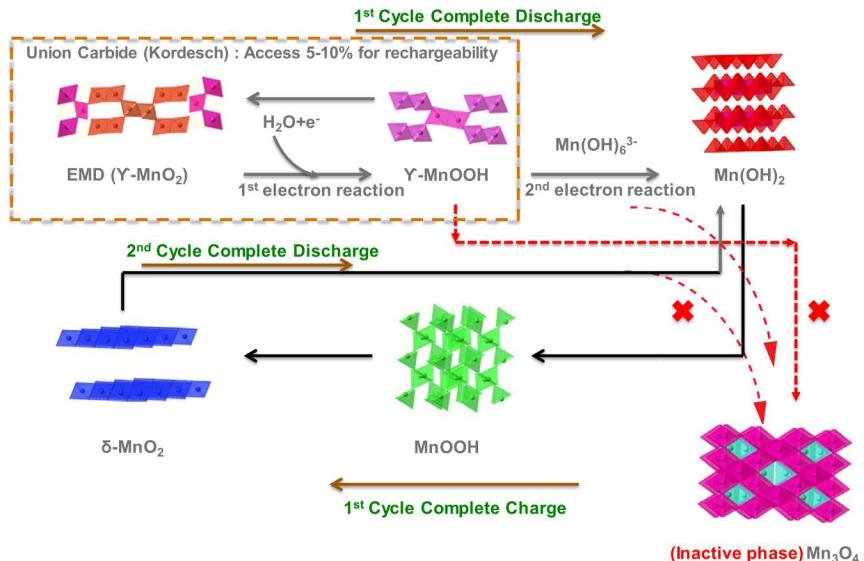
Need improvements in materials utilization, process optimization and engineering of large format cells



## Failure Mechanisms of Cathode

Instability of Mn(III) resulting in formation of irreversible  $\text{Mn}_3\text{O}_4$   
Zn poisoning forming irreversible  $\text{ZnMn}_2\text{O}_4$

# Making $\text{MnO}_2$ Fully Rechargeable



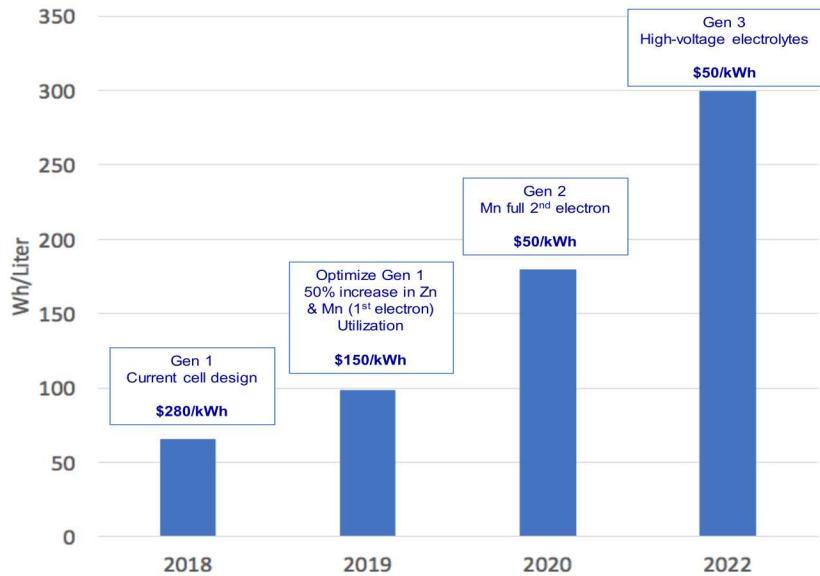
G.G. Yadav, J.W. Gallaway, D.E. Turney, M. Nyce, J. Huang, X. Wei and S. Banerjee, Nature Communications, vol. 8, 14424 (2017). doi:10.1038/ncomms14424

$\text{MnO}_2$  cycling data against reference anode

# Potential for Zn-MnO<sub>2</sub> Cells at \$50/kWh



- Recent breakthroughs in making MnO<sub>2</sub> fully rechargeable. Based on the formation of a layered birnessite MnO<sub>2</sub> structure and stabilizing this structure for thousands of cycles.
- Improvement in energy density and cost by improvement in zinc utilization
- Cathode degradation mitigation by improvements controlling Zn migration across separator
- Potential for \$50/Wh cells with high cycle-rechargeability of Zn-MnO<sub>2</sub>



Source: CUNY Energy Institute

# Grid Storage needs Large Format Cells

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

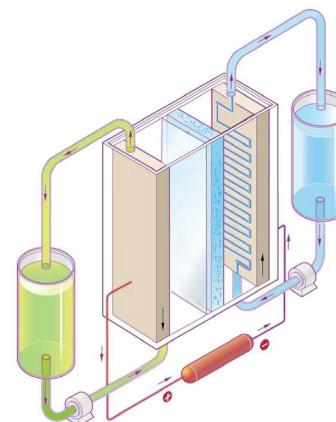
Large format cells also allow for tighter integration of power electronics, sensors, SOH monitoring at the cell level.

## High Conductivity Separators for Low Temperature Molten Sodium Batteries



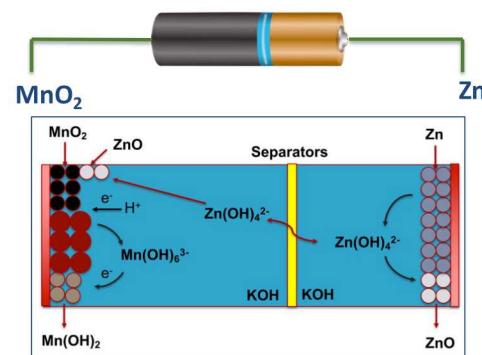
Robust ceramic separators exhibit low  $\text{Na}^+$  conductivity at lower, more cost effective temperatures (120-180 °C).

## Crossover in Redox Flow Batteries



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

## Zincate poisoning of $\text{MnO}_2$ in $\text{Zn}/\text{MnO}_2$ Batteries



Zincate diffusion and subsequent poisoning of  $\text{MnO}_2$  impairs reversibility and significantly decreases lifetimes.

# Safety of Battery Storage Systems

Ensuring safety of battery storage systems remains a major concern

Need significant advances at materials, engineering and systems level

Development of  
Inherently Safe Cells



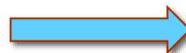
- Safer cell chemistries
- Non-flammable electrolytes
- Shutdown separators
- Non-toxic battery materials
- Inherent overcharge protection

Safety Devices and  
Systems



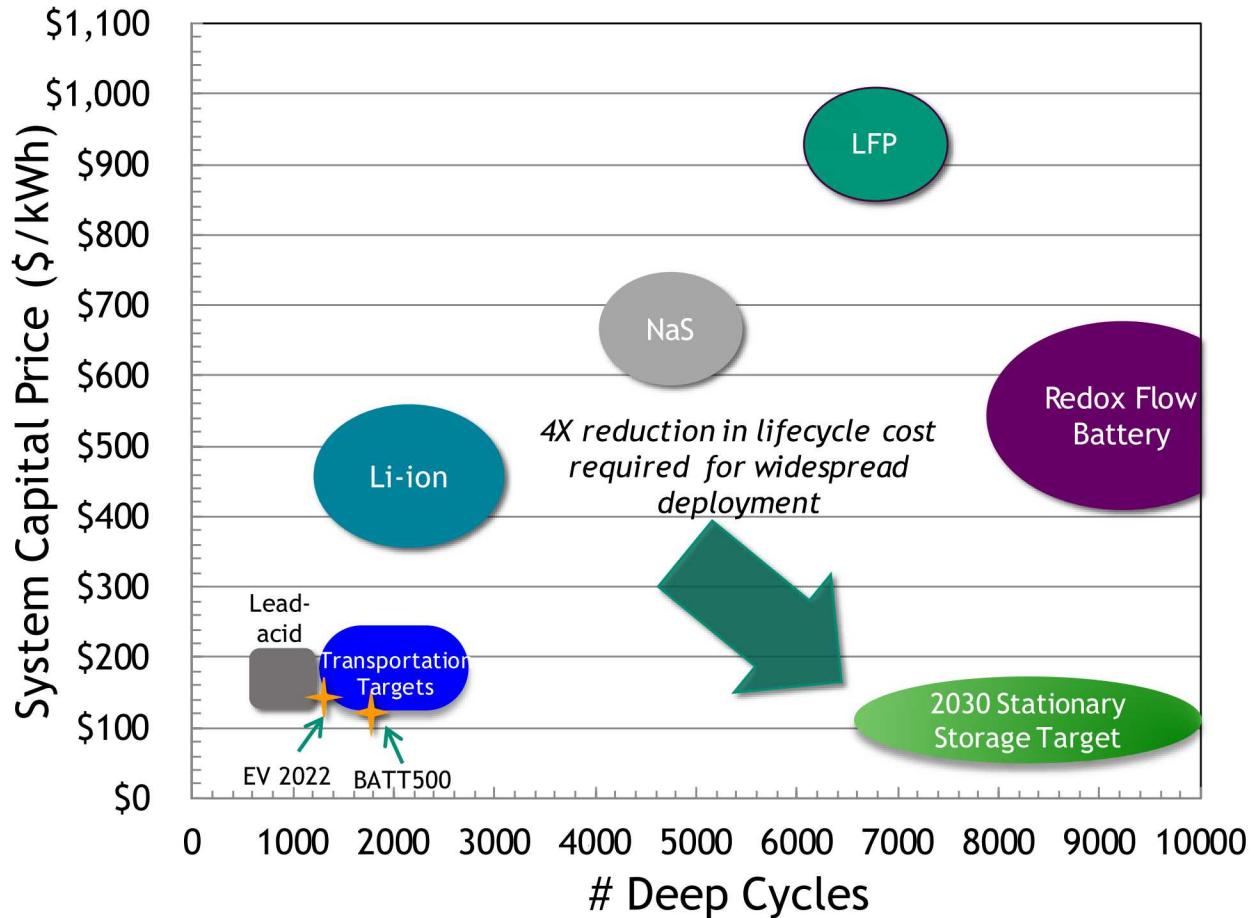
- Cell-based safety devices
  - current interrupt devices
  - positive T coefficient
  - Protection circuit module
- Battery management system
- Charging systems designed

Effective Response to  
Off-Normal Events



- Suppressants
- Containment
- Advanced monitoring and controls

# Future of Energy Storage Technologies



<sup>1</sup>Energy Storage Systems Cost: GTM/ESA US Energy Storage Monitor: Q2 2016

# Future of Energy Storage



Application	Consumer Electronics, Hybrid EVs	Electric Grid Electric Vehicles	Electric Flight
Advance Technologies	Incremental Li-ion: Si anodes, low Co cathodes Adv. Pb-acid: Pb-carbon Adv. rechargeable alkaline	Significant Adv. Li: Li metal anode, Solid state electrolytes Zn metal: adv. MnO <sub>2</sub> cathodes Adv. Flow	Breakthroughs Beyond Li-ion: Li-S, Li-Air Mg & Al Ion Zn-Air High voltage Zn Metal
Technology Risk	Modest	Significant	Major

Adapted from G. Crabtree's presentation at Xlab, 2018

# Summary



Battery technologies for electric vehicles and grid applications are advancing rapidly.

Engineering energy storage systems with higher energy and high power capacities while keeping safety and reliability remains a challenging task

Technical gaps - key questions:

- How do we manage the universal tradeoff between energy and power due to a combination of electrical, ionic, structural and chemical effects?
- How to improve energy capacity without sacrificing safety and life?
- How do we optimize power and energy at multiple length scales, large format cells?
- How do we enable fast ion and electron transport without sacrificing energy density, while maintaining long life and safety?
- How do we design materials to realize high energy and power simultaneously?
- How to achieve high reversibility, with low capacity loss, and low over-potentials

Market gaps

- Existing battery technology solutions remain expensive for many applications
- Technologies not scalable to cover all markets and applications

## Acknowledgements



This work was supported by  
US DOE Office of Electricity Delivery  
Energy Storage Systems Program

