Other Energy Storage Technologies

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SAND No:

Sodium Metal Batteries (NaS, NaNiCl2..)

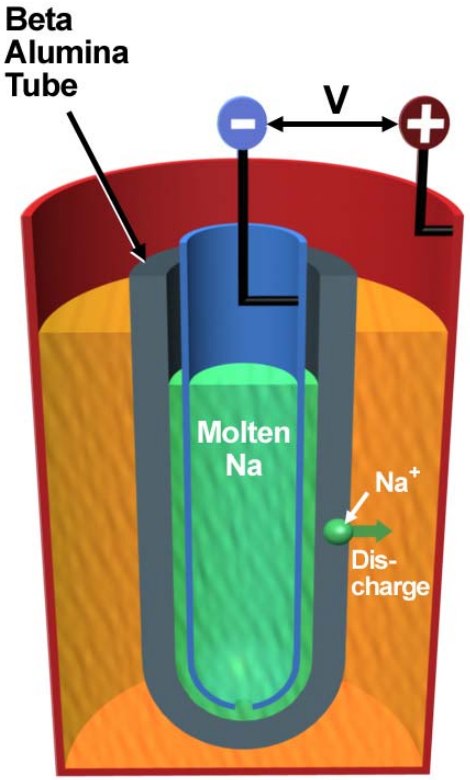
- Two primary chemistries
  - NaS, mature technology, deployed in grid applications
  - $NaNiCl_2$, mature, more stable than NaS
- NaS first developed by Ford Motor Co. in 1960's
  - Commercialized by NGK in Japan, most installed capacity
- NaNiCl2 (Zebra) developed in South Africa in 1980's
  - FIAMM in limited production
- Neither NaS nor $NaNiCl_2$ are at high volumes of production for economies of scale

NGK 34MW - 245 MWh NaS, Rokkasho, Japan

FIAMM Sonick Na-$NiCl_2$ Battery Module

Na-Metal Batteries

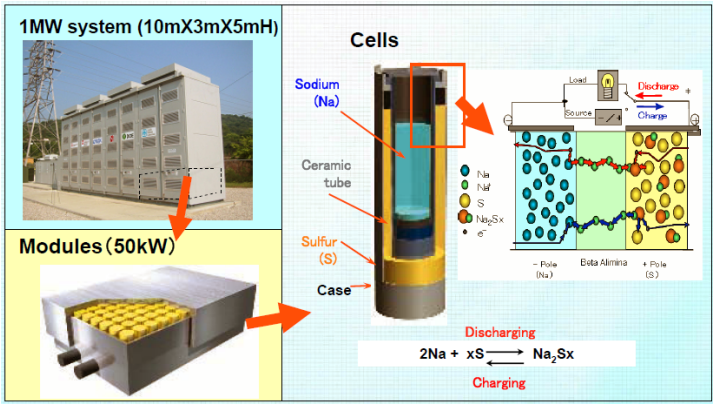
- Batteries consisting of molten sodium anode and β"-Al2O3 solid electrolyte (BASE)
  - Low cost starting materials
  - High specific energy density (120~240 Wh/kg)
  - Good specific power (150-230 W/kg)
  - Good candidate for energy applications
    - (4-6 hrs discharge)
  - Operated at relatively high temperature
    - (300~350°C)
- NaS battery
  - $2Na + xS \rightarrow Na_2S_x$ (x = 3~5)
    - E = 2.08~1.78 V at 350°C
- NaNiCl2 (Zebra) battery
  - $2Na + NiCl_2 \rightarrow 2NaCl + Ni$
    - E = 2.58V at 300°C
    - Use of catholyte (NaAlCl4)



NaS Batteries

- Most widely deployed of long duration batteries
- NaS Batteries
  - High energy density
  - Long discharge cycles
  - Fast response
  - Long life
  - 530 MW/3700MWh installed primarily in Japan
- Applications
  - Power quality
  - Congestion relief
  - Renewable integration
- Challenges
  - High operating temperature (250-300C)
  - Liquid containment issues

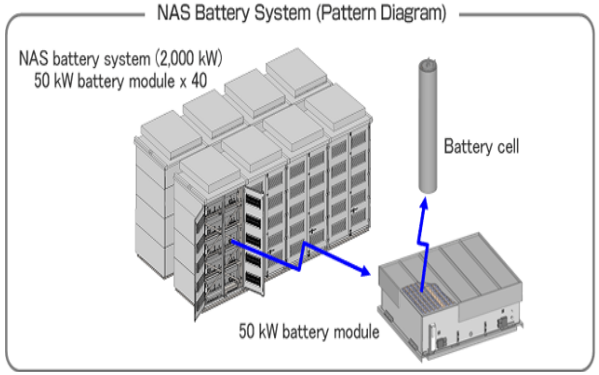
Los Alamos, NM. 1 MW, 6MWh

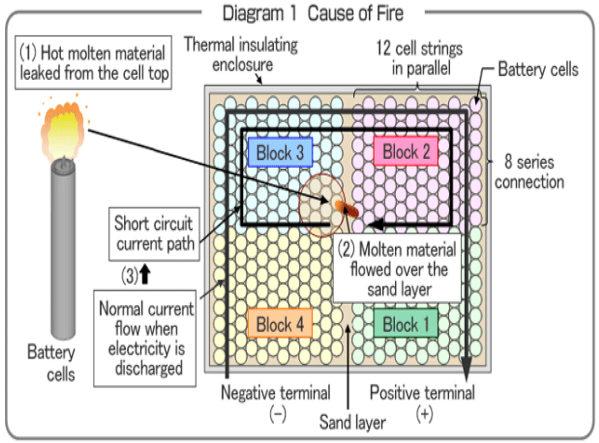


Source: NGK

NaS - Status

- NGK is the only committed manufacturer
- Battery is assembled fully charged, presents a major safety/handling issue
- System need to maintained at temperature
- Recent work on lower temp NaS utilizing NaSiCON solid electrolytes



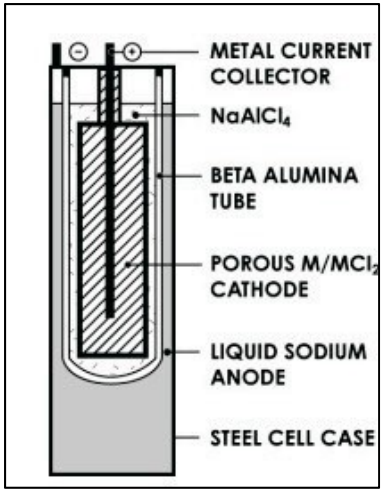


Na-Metal Batteries: Advantages/Issues

- **Temperature**
  - Less over temperature concerns, typical operating window 200-350°C. additional heaters needed when not in use.
  - At < 98°C, Na metal freezes out, degree of distortion to cell dictated by SOC of battery (amount of Na in anode)
- **Charging/Discharging Limitations**
- **Safety Concerns**
  - Solid ceramic electrolyte keeps reactive elements from contact. Failure in electrolyte can lead to exothermic reaction (Na-S)

$NaNiCl_2$ (Zebra) Batteries

- Large cells and stable chemistry
  - Lower temperature than NaS
  - Cells loaded in discharge mode
  - Addition of NaAlCl4 leads to a closed circuit on failure
- High efficiency, low discharge
- Long warm up time (16 hr)
- Only one major manufacturers
  - FIAMM
  - Limited deployments



FIAMM 222-kWh System Duke Energy Rankin Substation

Lower Temperature Na-based Batteries

- Low temperature, safe, nonflammable alternatives to Na-S batteries.
- Enabled by low to intermediate temperature (<200oC) ceramic Na-ion conductor (NaSICON)
  - Robust physical barrier - no electrode crossover
  - Reduced operating costs
  - Lower cost materials/seals
  - Enables new cathode chemistries
- Engineered safe
  - Fully inorganic, no volatile organic electrolytes
  - Robust ceramic separator isolates anode and cathode
  - Cross-reaction generates benign byproducts

- Sodium-air
- Sodium-ion
- Aqueous Redox Flow
- Low temperature sodium-sulfur

- Sodium-bromine: $Na + \frac{1}{2} Br_2 \leftrightarrow Na^+ + Br^-$
- Sodium-iodine: $Na + \frac{1}{2} I_2 \leftrightarrow Na^+ + I^-$
- Sodium-nickel chloride: $Na + \frac{1}{2} NiCl_2 \leftrightarrow Na^+ + Cl^- + Ni(s)$
- Sodium-copper iodide: $Na + CuI_2^- \leftrightarrow Na^+ + 2I^- + Cu(s)$

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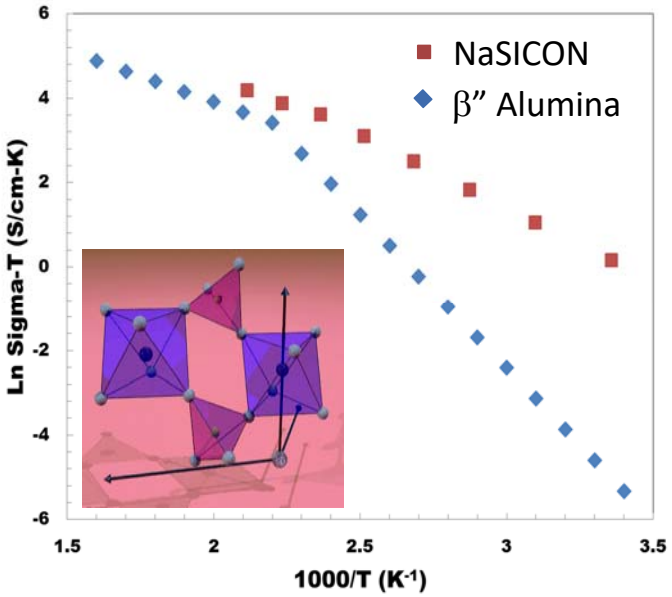
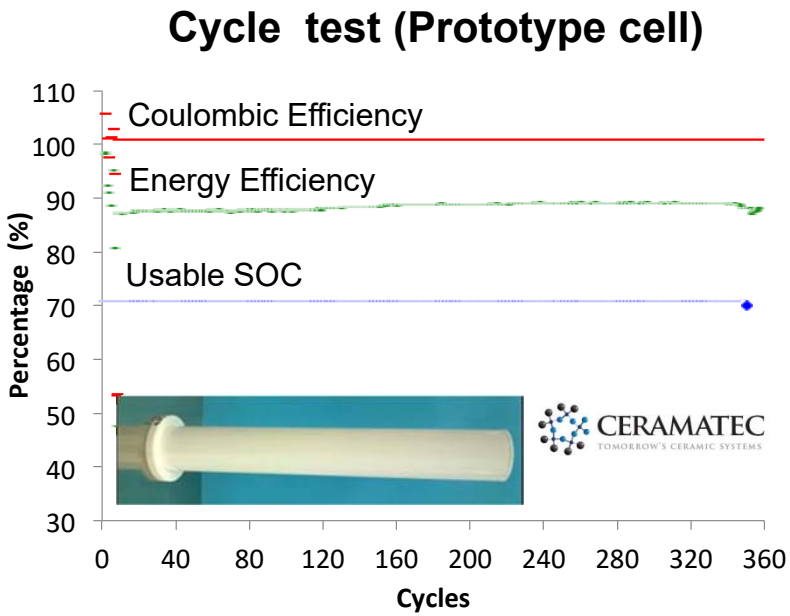
NaSICON Lower Temperature Electrolyte

NaSICON (Na Super Ion CONductor): $Na_3Zr_2PSi_2O_{12}$



Engineered materials chemistry and advanced, scalable processing (Ceramatec, CoorsTek) make NaSICON a *chemically/mechanically stable, low temperature, high conductivity (>10^{-3} S/cm @RT)* separator technology.



13 Wh Na-NiCl2 (NaX) Cell operation for 9+ months. 70% Depth of Discharge, >85% energy efficiency at 65 mA /cm2 Charge/Discharge NaSICON current density

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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

Further Away: Other Li-like Chemistries

- Na/NaxCoO_2 and Na/NaxMnO_2 attracting a lot of attention
  - Na/NaxCoO2: 440 Wh/kg, 1600 Wh/l
  - Na/NaxMnO2: 420 Wh/kg, 1410 Wh/l

- Na and Mg Chemistries potentially lower cost
  - Intercalation chemistry similar to Li ion
  - New class of electrolytes, separators needed
  - Very early stage, metal anodes vs. insertion materials

Rechargeable Alkaline Batteries

Primary Chemistries

- NiMH
- Ni-Fe
- Zn-Ni
- Zn-MnO_2

For low cost grid storage applications, Zn-MnO_2 has compelling attributes

Zn-MnO_2 Batteries

- Zn/MnO_2 alkaline batteries
- Traditionally primary batteries
- Lowest bill of materials cost, lowest manufacturing capital expenses
- Established supply chain for high volume manufacturing
- Readily be produced in larger form factors for grid applications
- Do not have the temperature limitations of Li-ion/Pb-acid
- Are inherently safer, e.g. are EPA certified for landfill disposal.
- Until recently reversibility of Zn/MnO2 has been challenging

History of Rechargeable Zn-MnO2 Batteries

- Long history of research on making Zn-MnO_2 rechargeable.
  - Several commercial products based on cylindrical formats (Rayovac, BTI).
  - All focused on cylindrical designs for consumer markets.

Cylindrical cells

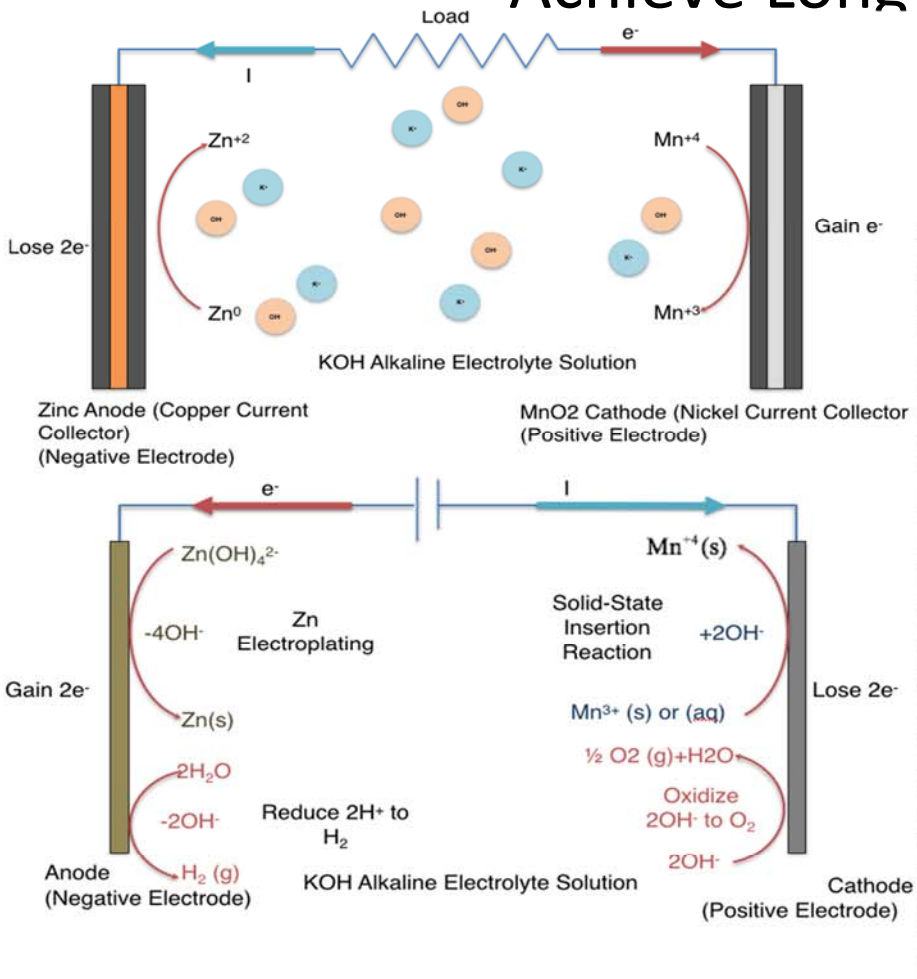
No flexibility to change criticalparameters.

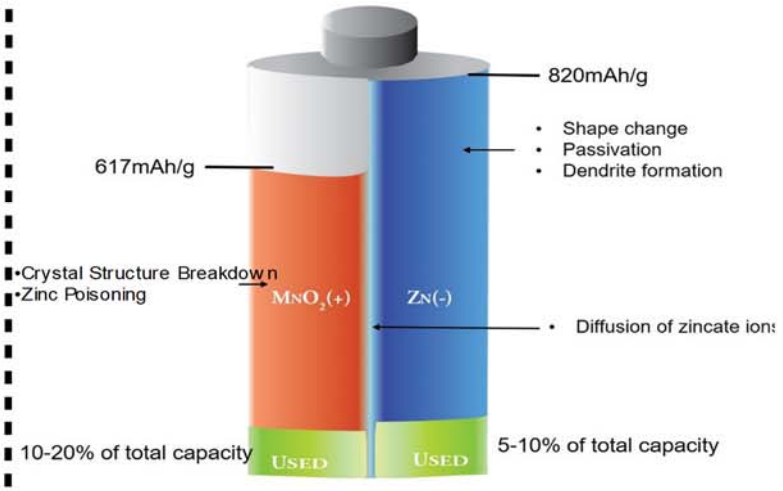
Year	Event
1882	Probably first description of an alkaline MnO_2 cell in German patent 24552 of G. Leuchs
1903	Description of another "wet alkaline cell" in US Patent 746,227 of S. Yai
1912	First alkaline "dry cells" described in German patent 261,319 of E. Aschenbach
1952	W.S. Herbert introduced first commercial alkaline MnO2 "crown" cell for low drain
1960	US patent 2,960,558 of K. Kordesch, P. Marsal and L. Urry describes the invention of the "modern" alkaline cell w/ sleeve type pelletized cathode on the outside in contact w/ the can
1962	US patent 3,024,297 of L. Urry describes a method of forming a cathode depolarizer mix for a rechargeable alkaline cell
~1970	First commercial rechargeable alkaline cells introduced by Union Carbide Corp. and Mallory Corp., but soon withdrawn.
~1980	Research on rechargeable alkaline manganese chemistry was intensified at the TU Graz under the leadership of Prof. Dr. K. Kordesch
1981	Kordesch et al studied the rechargeability of 12 International Common Samples
1983	US patent 4,384,029 of K. Kordesch and J. Gsellman describes a new cell design w/ the cathode constrained by a metal cage.
1985	Titanium doped electrolytic manganese dioxide for improved cycle life described in German patent 3,337,568 of K. Kordesch and J. Gsellman
1986	Battery Technologies Inc. (BTI) founded w/ the mission to commercialize rechargeable alkaline manganese (RAM™) technology
1990	US patent 4,925,747 of K. Kordesch and K. Tomantschger describes the internal pressure management of sealed cells via hydrogen recombination by catalytic means
1991	Ph.D. Thesis of J. Daniel-Ivad on Rechargeable Alkaline Manganese Cells focusing on mercury-free designs
1992	US patent 5,108,852 of K. Tomantschger and C. Michalowski describes a basic rechargeable alkaline cell w/o constraining the cathode
1993	US patent 5,108,852 of R. Flack describes an improved separator bottom seal
1993	Rayovac Corporation launched BTI licensed RAM™ cells manufactured and sold under their trademark RENEWAL™ in the United States

Year	Event
1994	US patent 5,281,497 of K. Kordesch, J. Daniel-Ivad and R. Flack describes a mercury-free rechargeable cell w/ an anode having gas release properties and a hydrogen recombination system to limit in-cell gas pressure
1994	Pure Energy Battery Corporation launched BTI licensed RAM™ cells manufactured under their trademark PURE ENERGY™ in Canada. Cells are mercury-free.
1995	US patent 5,424,145 of J. Daniel-Ivad, J. Book and K. Tomantschger describes a basic rechargeable cell w/ specific anode to cathode Ah-balance to achieve satisfactory performance in consumer use/misuse.
1995	Rayovac's RENEWAL™ cells become mercury-free
1996	US patent 5,626,988 of K. Tomantschger, J. Book and J. Daniel-Ivad describes a mercury-free rechargeable cell w/ a special anode process for reliable performance
1996	Young Poong Corporation launched BTI licensed RAM™ cells manufactured under their trademark ALCAVA™ in South Korea
1997	AccuCell started to sell BTI licensed RAM™ cells in Germany
1998	Grand Batteries Technologies launched BTI licensed RAM™ cells manufactured under their trademark GRANDCELL™ in Malaysia
1998	Single-use alkaline cell producers introduce cells capable of higher drain rates
1999	BTI released 1st Generation High-Rate RAM™ cell specifications for production
1999	Endurance cycling breakthrough of RAM™ cells in Cordless Phone test: 6500 cycles for 5 minute call, then recharge in cradle
2000	"Marathon" RAM™ cell research to extend the deep discharge stability from 25 to 50 cycles initiated
2000	US patent 6,099,987 of J. Daniel-Ivad, J. Book and E. Daniel-Ivad describes a cylindrical cell w/ a cup seal for improved cumulative performance
2001	BTI acquired the Dema Group, a Swedish distribution company, and launched Demacell™ RAM™ cells in an effort to promote a European expansion of the technology.

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

Limiting the Depth of Discharge to Achieve Long Cycle Life

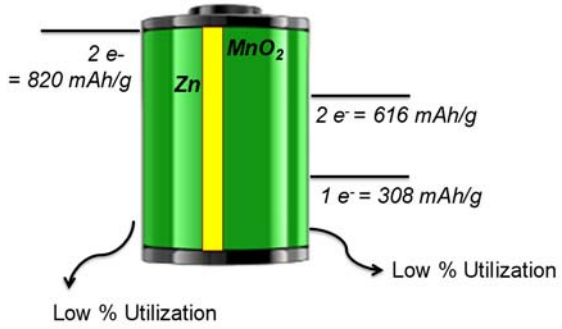




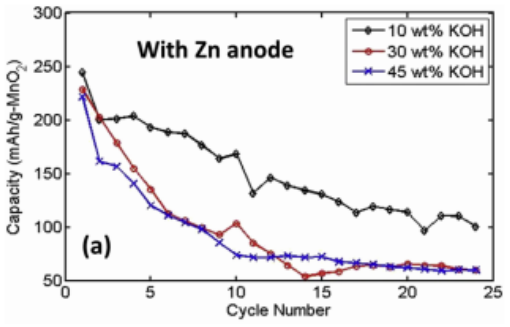
Source: CUNY Energy Institute

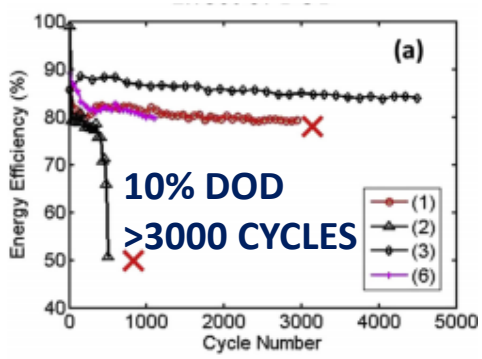
Low DOD discharge makes for a highly viable technology

Single-use Alkaline Battery $23/kWh

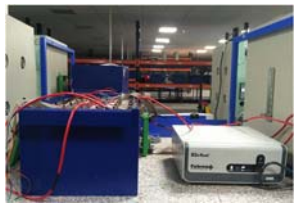


Gen 1 Alkaline Battery
Projected cost: $100/kWh in volume



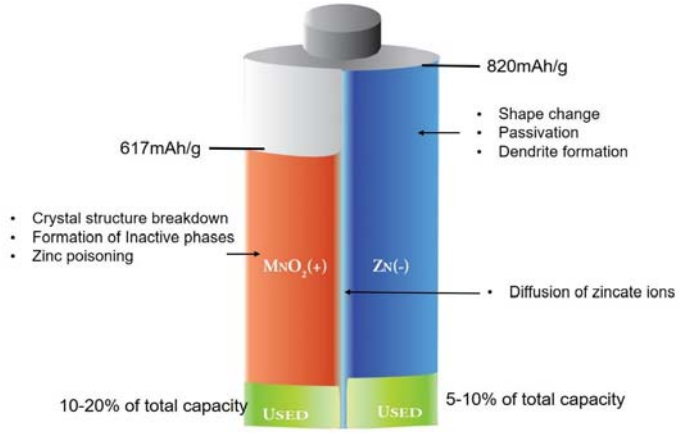


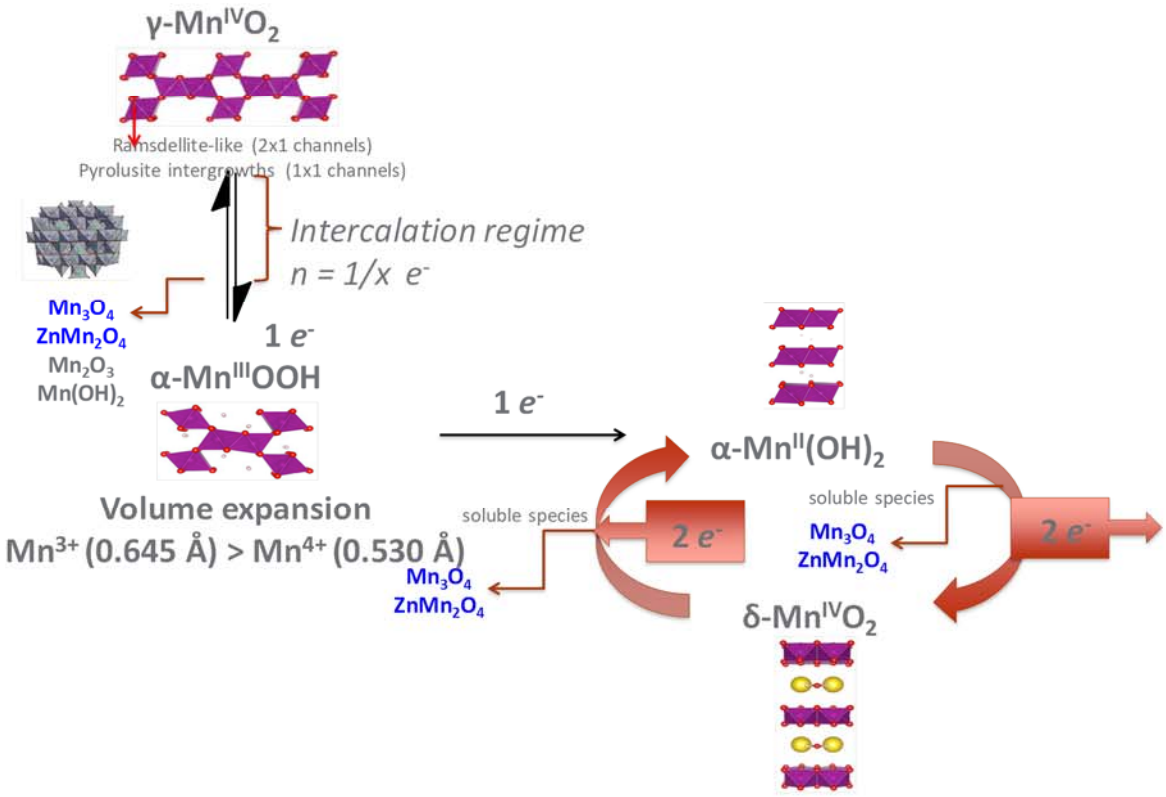
RAPID CELL DEATH >30% DOD



http://www.urbanelectricpower.com

Utilization of 2e in MnO_2
Enabling Zn-MnO_2 to Reach Li-ion in Energy Density





Source: CUNY Energy Institute

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

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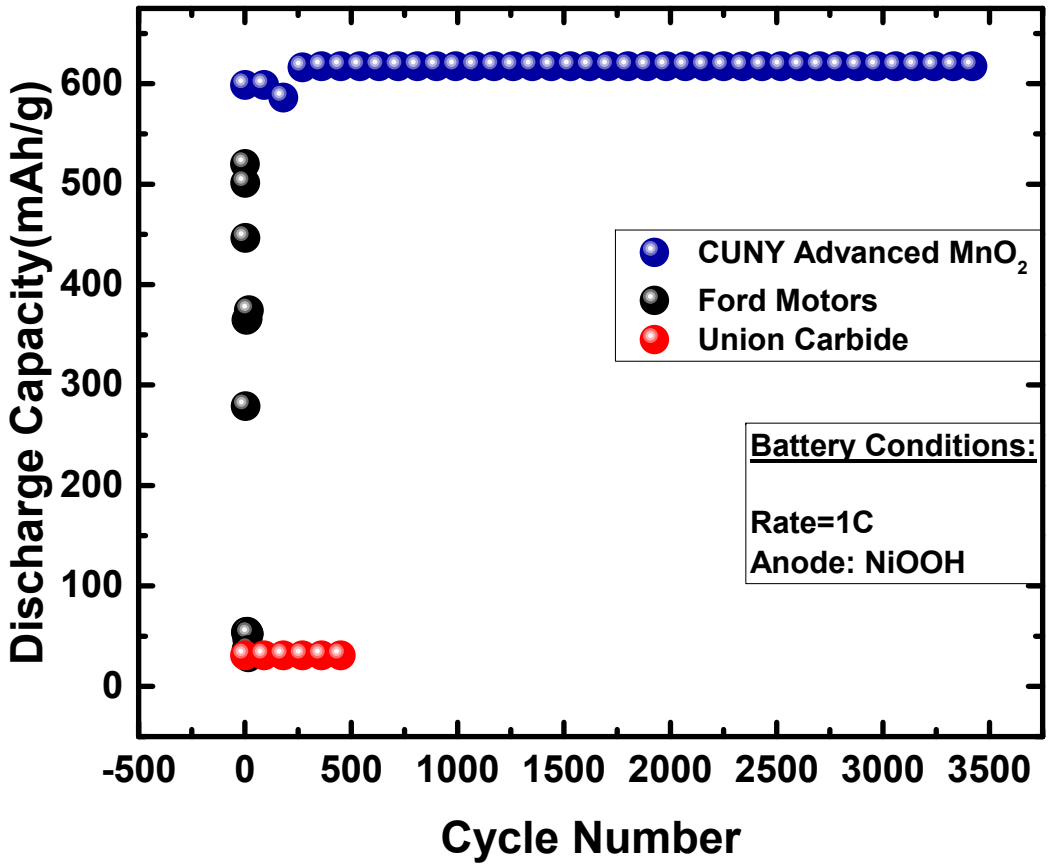
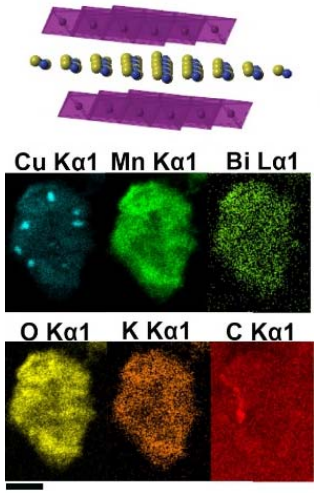
CUNY Breakthrough Advancement

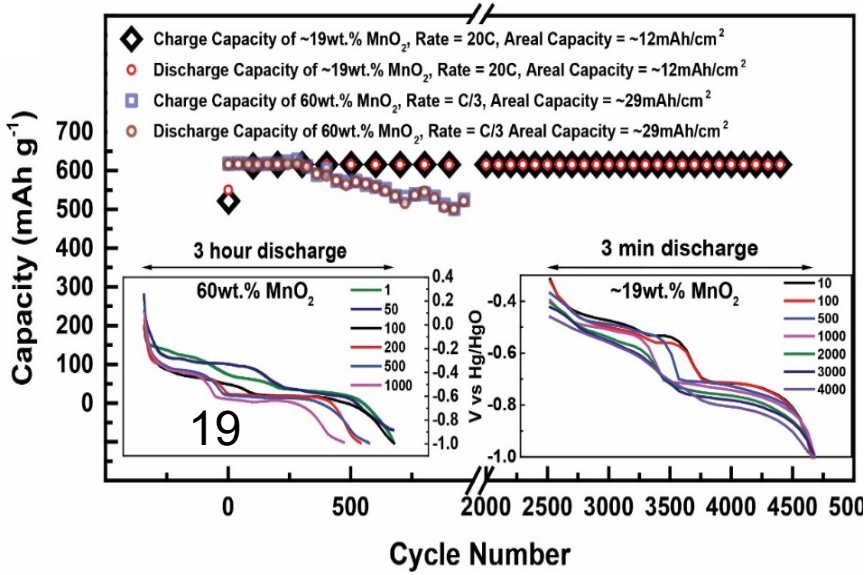


- With full utilization of 2e in MnO_2, we have the possibility of safe, ~$50/KWh rechargeable batteries

Source: S. Banerjee, CCNY

MATERIALS ENGINEERING OF MnO_2 FOR ACCESSING 100% DOD

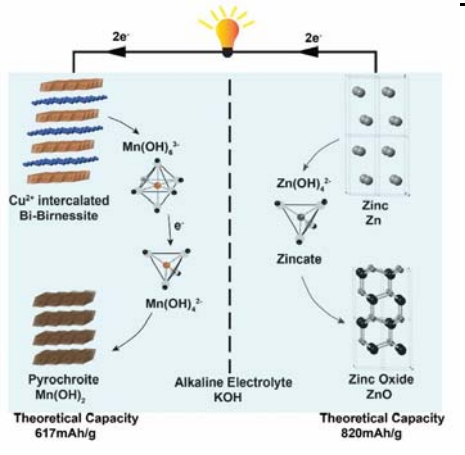




Source: CUNY Energy Institute

HIGHLY ENERGY DENSE BIRNESSITE/Zn BATTERY

A CONVERSION BATTERY CHEMISTRY

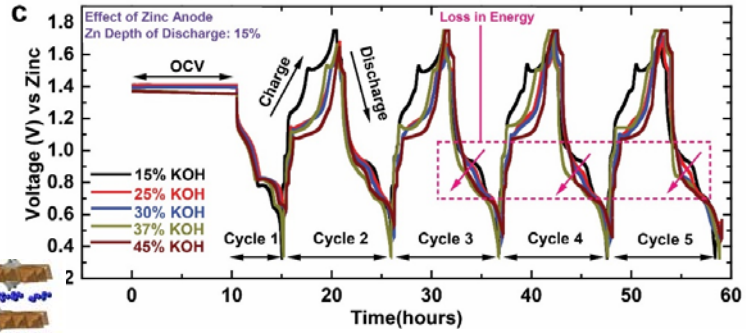


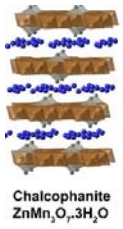
NYSERDA GOALS

- >160Wh/l
- 500 CYCLES

NEED TO HAVE >15% Zn DOD TO HIT TARGETS

Zn POISONING OF THE BIRNESSITE

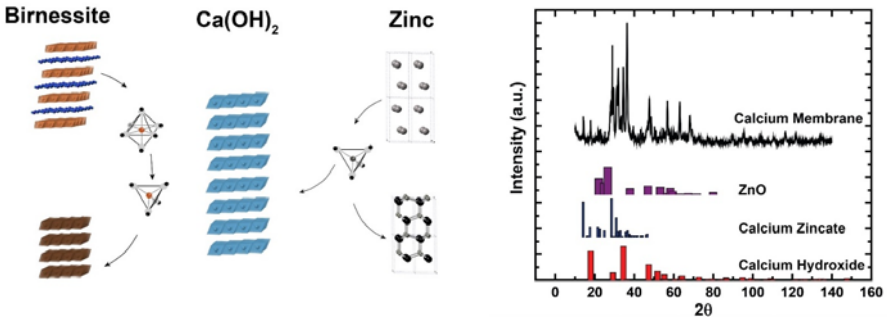


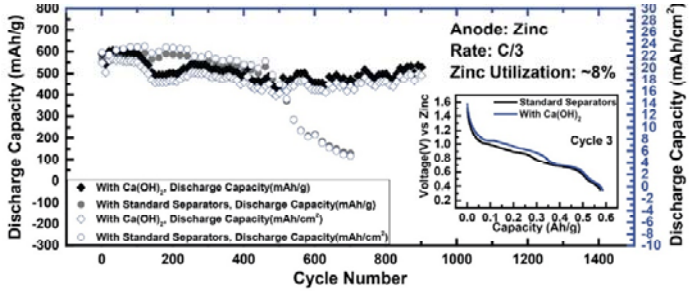


Zn AFFECTS ENERGY

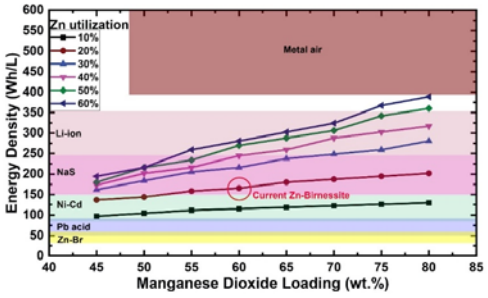
Zn- BIRNESSITE IS RESISTIVE

SEQUESTER Zn THROUGH COMPLEXATION





HIGHEST CYCLE LIFE REPORTED IN LITERATURE



CURRENT CELLS GET 160Wh/L

BUILDING & TESTING LARGE CELLS

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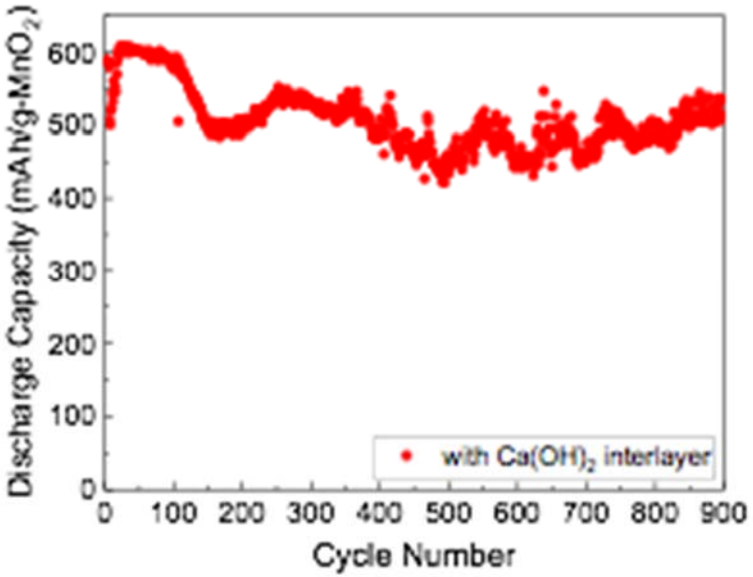
Utilization of 2e in MnO_2 -



- Current CUNY testing results
- Highest cyclone recorded in literature to date

Large format cells under test

Current university research targets:

- 180Wh/L
- 500 Cycles
- 40% Fade
- <$50/kWH
- Disrupt Li-FePO 4

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URBAN ELECTRIC POWER

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CUNY Roadmap for Zn-MnO_2