Alkaline Zn-MnO_2 Battery Development: A University-Private-Public Partnership

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The work is supported by the Department of Energy, Energy Storage Program, Dr. Imre Guyk

Battery Innovations: Incremental to Disruptive

Incremental	Intermediate	Disruptive	
Personal Electronics Start-stop & hybrid vehicles	Electric Vehicles Electric Grid	Electric Flight Autonomous Robots	**Application**
Lithium-ion: Si anodes, low Co cathodes Adv. Pb-acid: Pb-carbon Adv. rechargeable alkaline	Adv. Li: Li metal anode, Solid state electrolyte Zn metal: adv. MnO_2 cathodes Adv. Flow	Beyond Li-ion: Li-S, Li-O Mg & Al Ion High voltage Zn metal	**Technology**
Modest	Significant	High	**Risk**
Private	Public-Private	Public	**Funder**

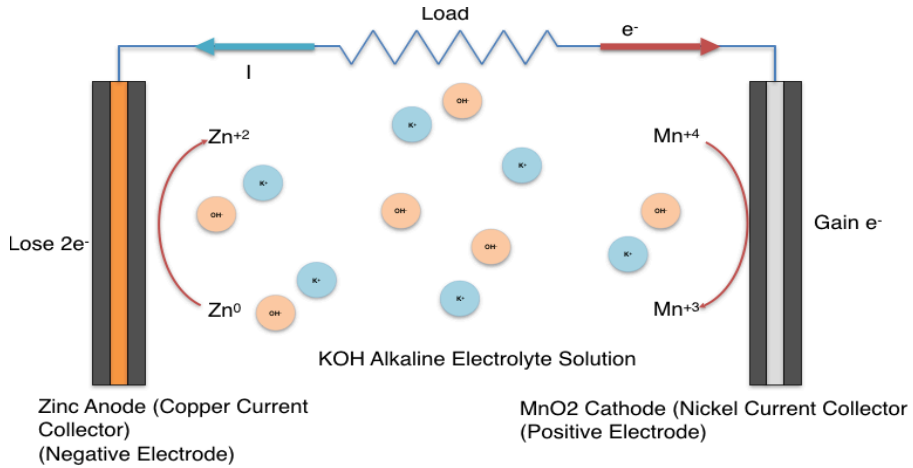
Rechargeable Alkaline Batteries

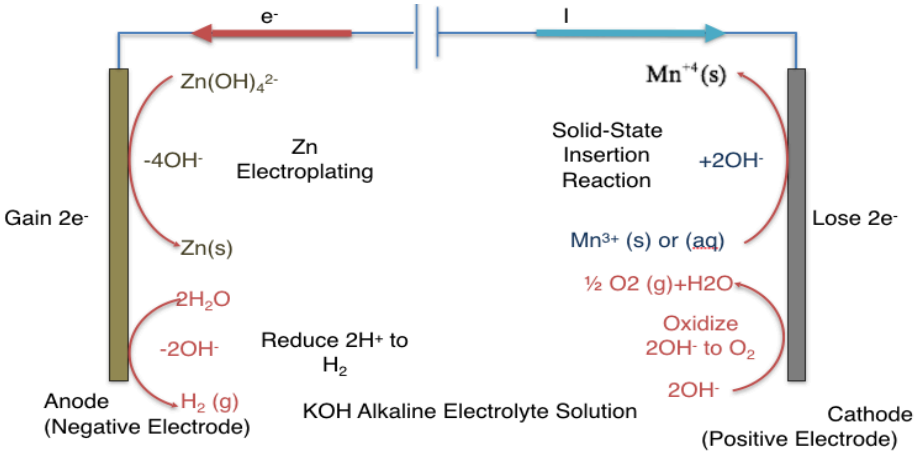
- A range of alkaline battery chemistries
  - NiMH
  - Ni-Fe
  - Ni-Cd
  - Zn-Ni
  - Zn-MnO_2
- Continues to be an active research area
- Among the alkaline chemistries for low cost grid storage applications, Zn-MnO_2 has compelling attributes

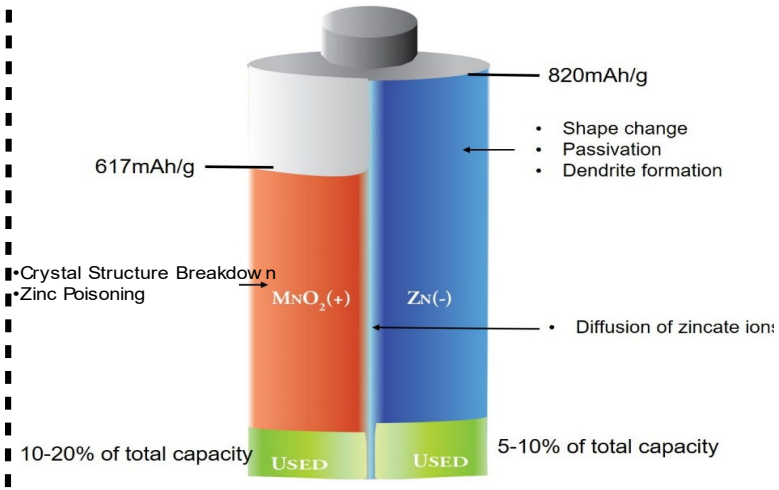
$Zn\text{-}MnO_2$ Batteries

- Traditionally primary batteries at $18-25/kWh with long shelf life
- Lowest bill of materials cost, low manufacturing capex
- 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
- Inherently safer, e.g. EPA certified for landfill disposal
- The ultimate challenge in $Zn\text{-}MnO_2$ batteries is rechargeability

Reactions for (1 & 2 Electron) Capacity Utilization







History of Rechargeable Zn-MnO_2

Primary
Low Power

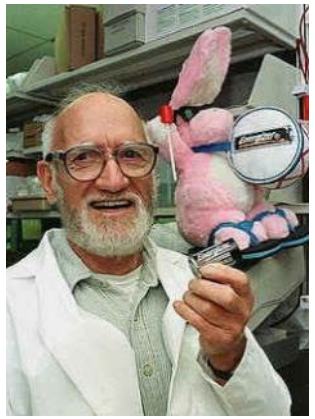
1866

1st Zn- MnO_2 battery

Primary

1950

Alkaline Zn-MnO_2 battery



Limited Capacity
Poor Energy Density

1970

5% Rechargeable Capacity

Potentiodynamic
Poor Cycle Life

1980

60-80% Rechargeable Capacity, Low Cycle Life

Ford

Halina Wroblowa

Stabilized full-cycling MnO2

2010-2016

2010-2014: CUNY Energy Institute 10-20% capacity

2014-2016
Stabilized full-cycling (2 electron capacity) MnO_2

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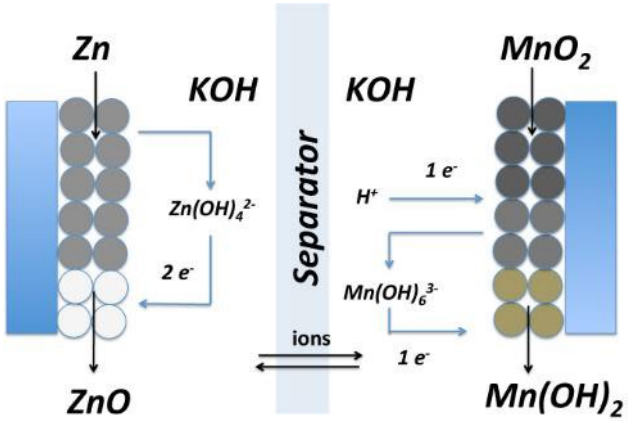
CUNY Energy Institute

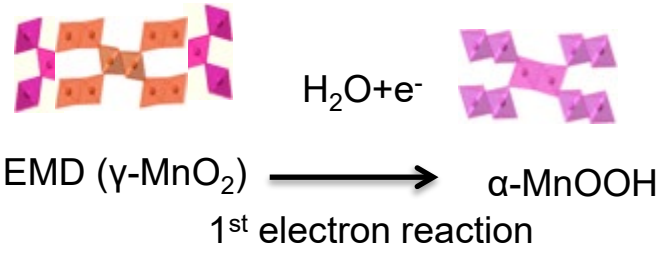
S. Banerjee, Symposium on Grid Energy Storage, MRS Spring Meeting, 2015
G. Yadav, CUNY Energy Institute, 2018

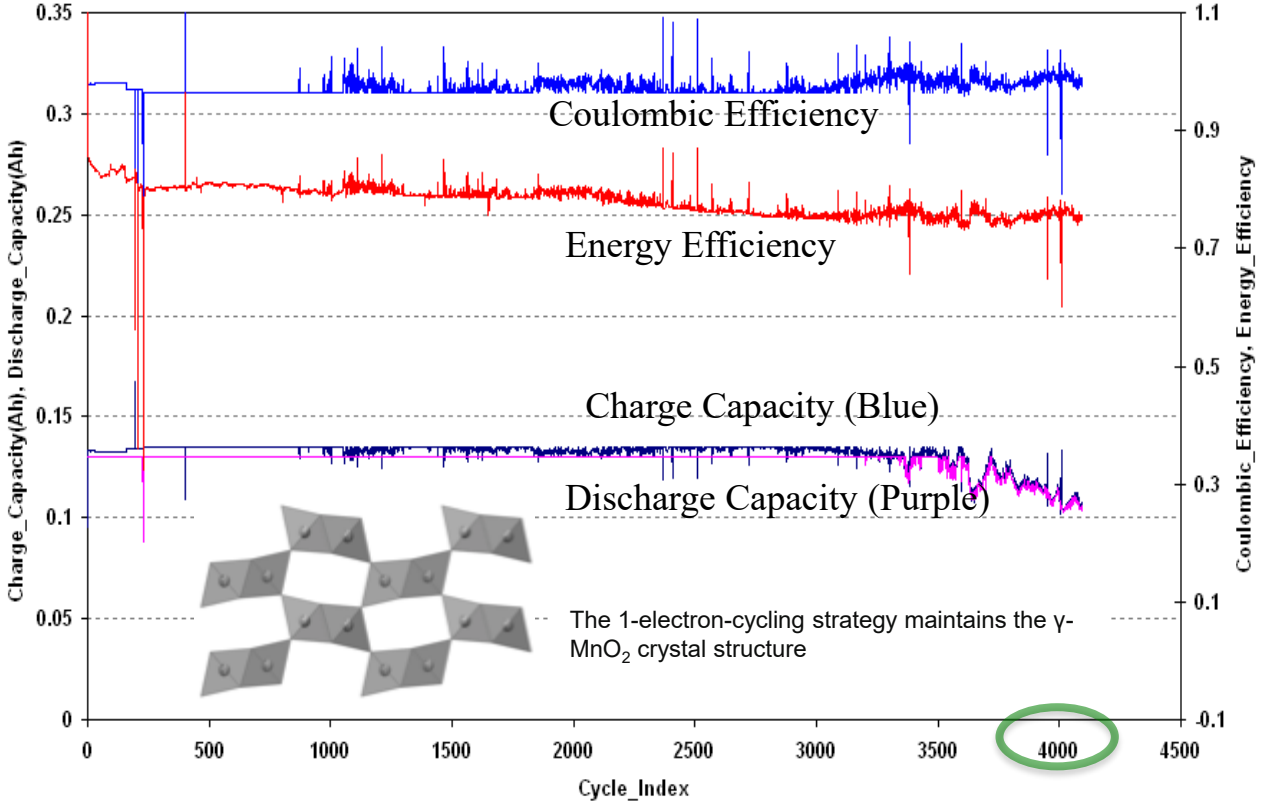
Making Zn-MnO_2 Rechargeable

- Earlier approaches to make rechargeable Zn-MnO_2 cells not successful
  - Dendrite formation, passivation and shape change on cycling Zn anode; crystal structure collapse and formation of inactive species (hausmanite) on cycling MnO2 cathode
- CUNY approach for long cycle life at 10-20% utilization
  - Innovations for anode: charging protocol, electrode additives, electrolyte composition, and zinc metal anode coating/binding/pore structure to mitigate shape change, passivation and pore plugging
  - Innovations for cathode: electrode composition, coating procedures, electrolyte composition, controlled porosity and conductivity, and charge/discharge protocol

Shallow-Cycled 1-e Zn-MnO2 Retains Long-Cycle Capacity



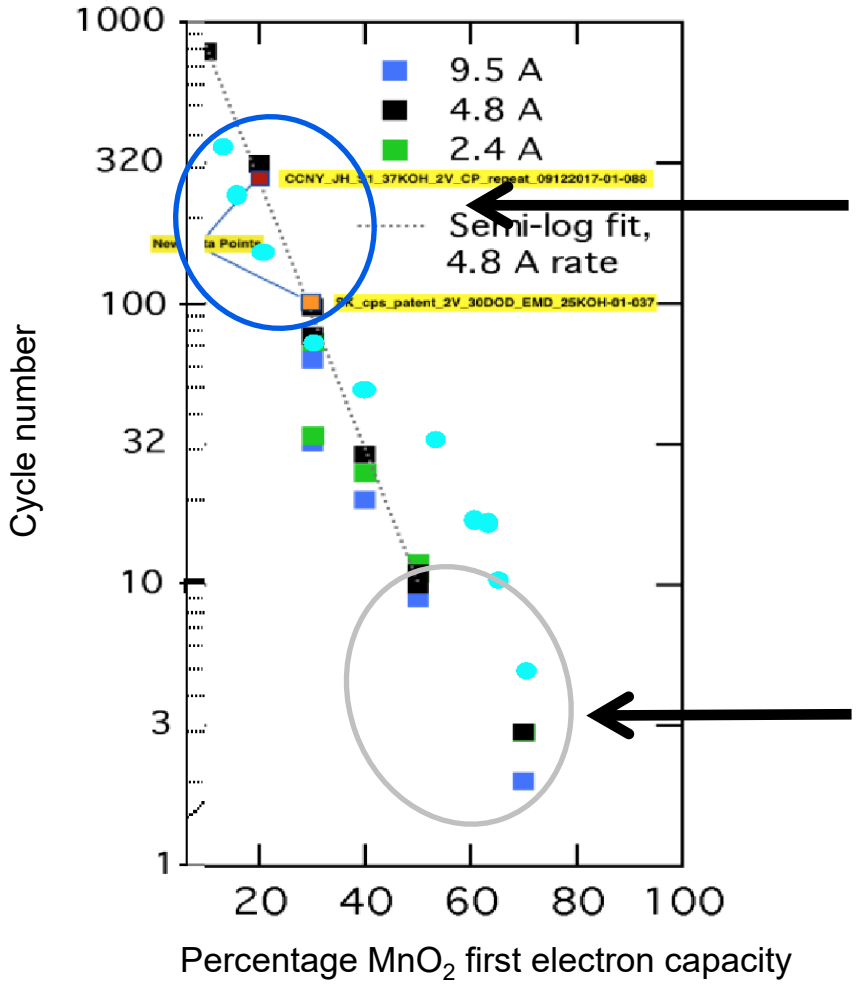




1-electron Zn-MnO_2 cells with 4000 cycles led to first products by Urban Electric Power

Ingale et al, Journal Power Sources 2015

Cell Cycle Life vs. MnO2 Utilization



Many cycles with low capacity utilization
For areas with no power or frequent outages

Use Cases:

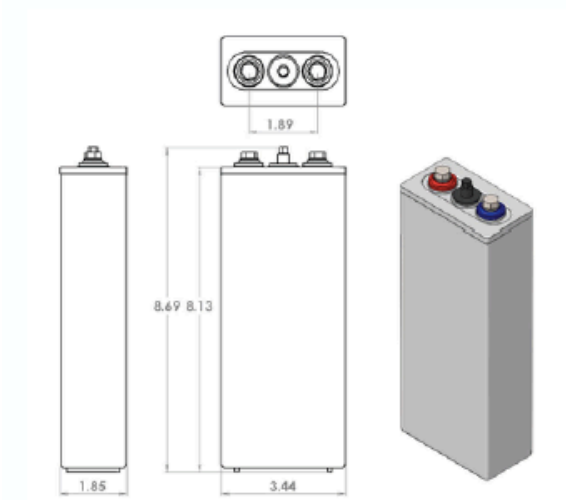
- Solar capacity enhancement
- Grid/microgrid support
- Home inverter market in India and Central America

Few cycles with high capacity utilization
For areas with reliable electrical service

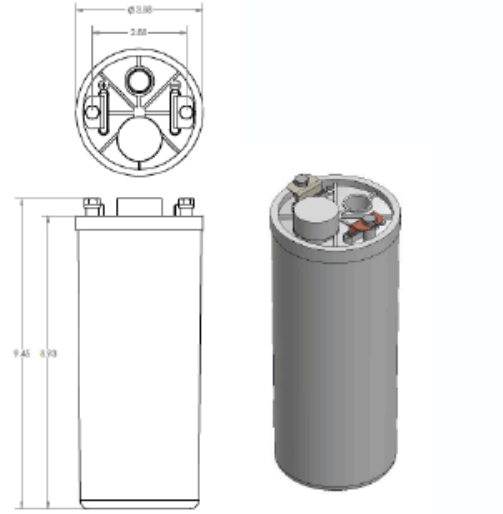
Use Cases:

- Data center backup
- Home power assurance in U.S. and Europe

UEP Product Evolution: 100Ah Prismatic to 400Ah Cylindrical



Width inches (mm)	Height inches (mm)	Weight lbs (kg)
1.85 (46.9)	8.69 (220.7)	3.52 (1.6)



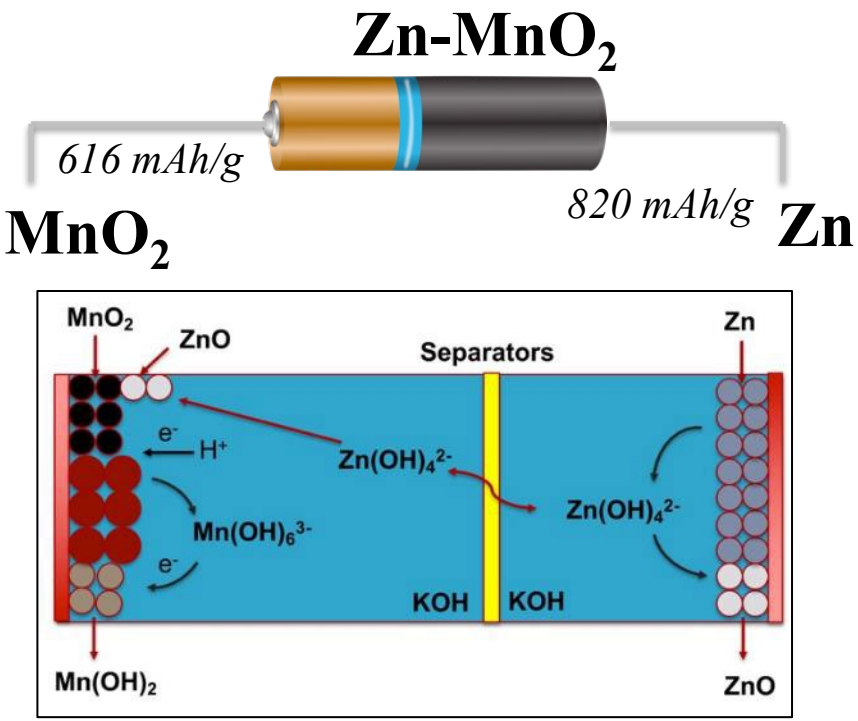
Diameter inches (mm)	Height inches (mm)	Weight lbs (kg)
3.88 (98.6)	9.45 (240)	5.82 (2.64)

- Two prismatic cells are equivalent to one cylindrical cell in capacity
- Electrodes and separators have identical thicknesses and compositions
- More data currently available on prismatic cell as cylindrical cell recently introduced
- Performance characteristics of both types are very similar

UEP 400Ah Cell is Economically Competitive

	Lead Acid		$ZnMnO_2$ 2019	
	Home Inverter	Solar	Home Inverter	Solar
Number of Cells	6	12	8	8
Estimated BOM/Cell (USD)	$18.18	$16.00	$15.00	$15.00
Nameplate Capacity (Ah)	150	110	400	400
Nominal Voltage (V)	12	24	11.2	11.2
Nameplate Energy Capacity (kWh)	1.80	2.64	0.90	0.67
Charge Time (hours)	10	4	4	4
Delivered Energy Capacity in WOS tests (kWh)	0.79	0.92	0.90	0.67
BOM/delivered kWh (USD)	$138	$208	$134	$179
Number of Cycles	300	500	300	500
BOM/Delivered kWh/Cycle (USD)	$0.46	$0.42	$0.45	$0.36

Zn-MnO2 Cell: 2e – Utilization Challenges



On the MnO_2 Cathode

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

Separator:

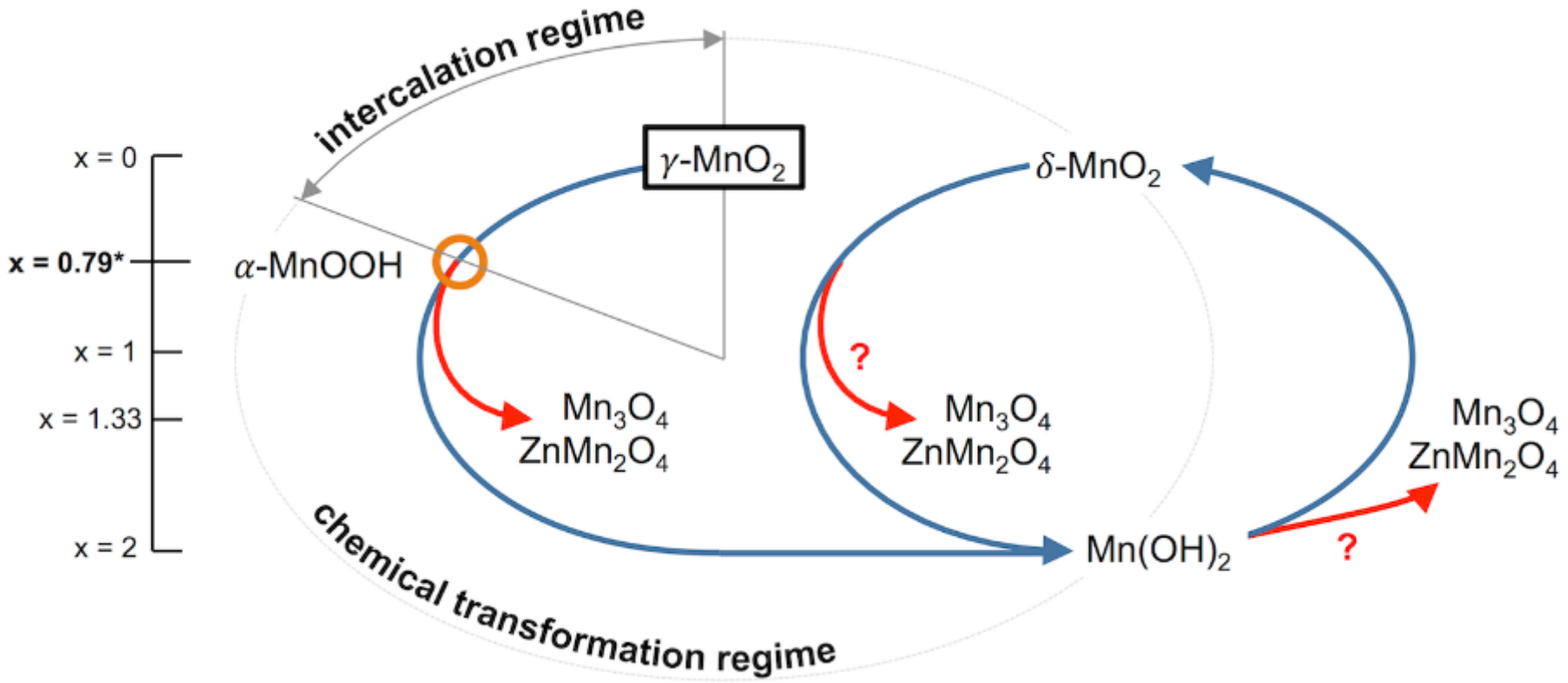
- Reduce Zincate crossover

On the Zn Anode:

- Control shape change
- Passivation
- Reduce dendrite formation

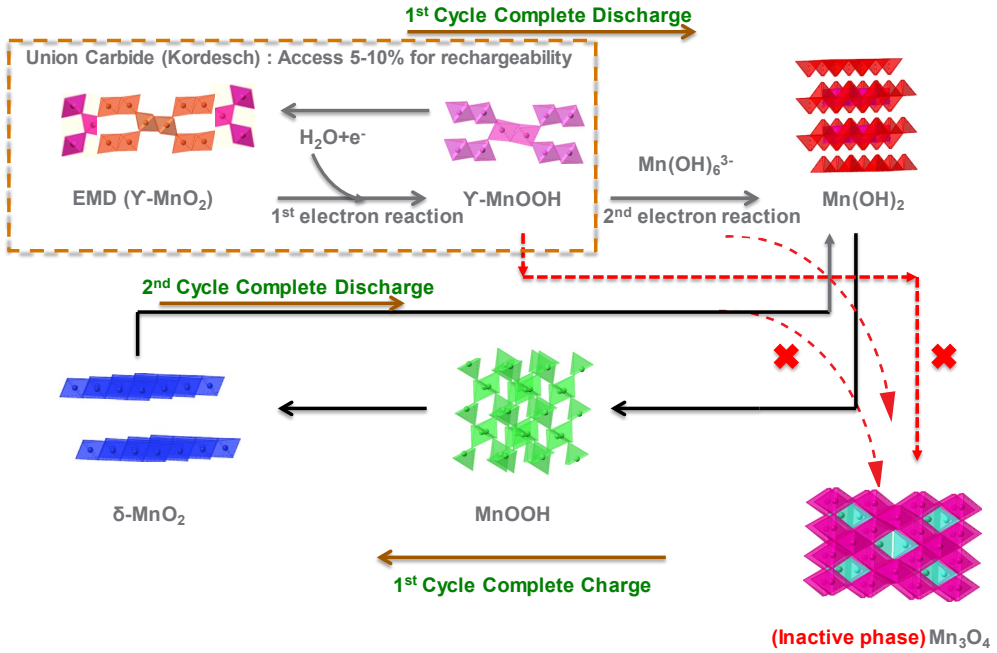
Need improvements in materials utilization, process optimization and engineering of large format cells

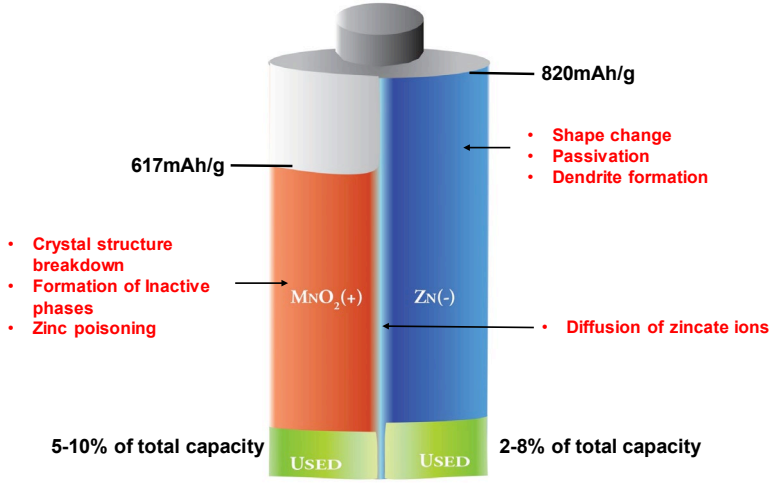
Failure Mechanisms of Cathode



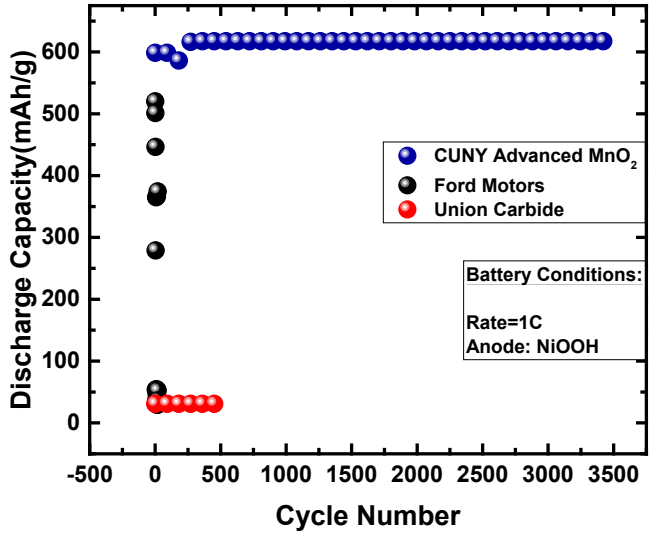
1. Instability of Mn(III) resulting in formation of irreversible **Mn_3O_4**
2. Zn poisoning forming irreversible **$ZnMn_2O_4$**

Making MnO_2 Fully Rechargeable





- Chemistry relies on formation of a **layered** birnessite MnO_2 structure and **stabilizing** this structure for thousands of cycles
- MnO_2 goes through a complete regeneration process during each cycle

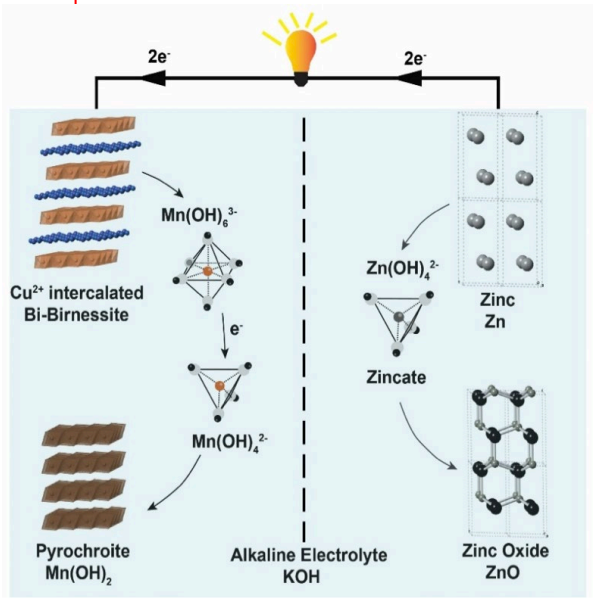


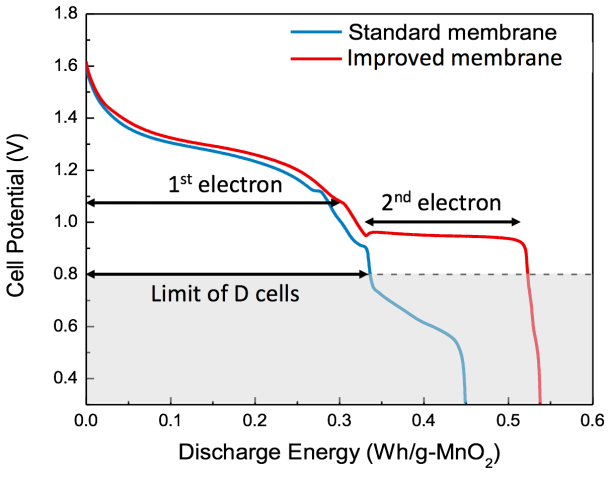
MnO_2 cycling data against reference anode

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

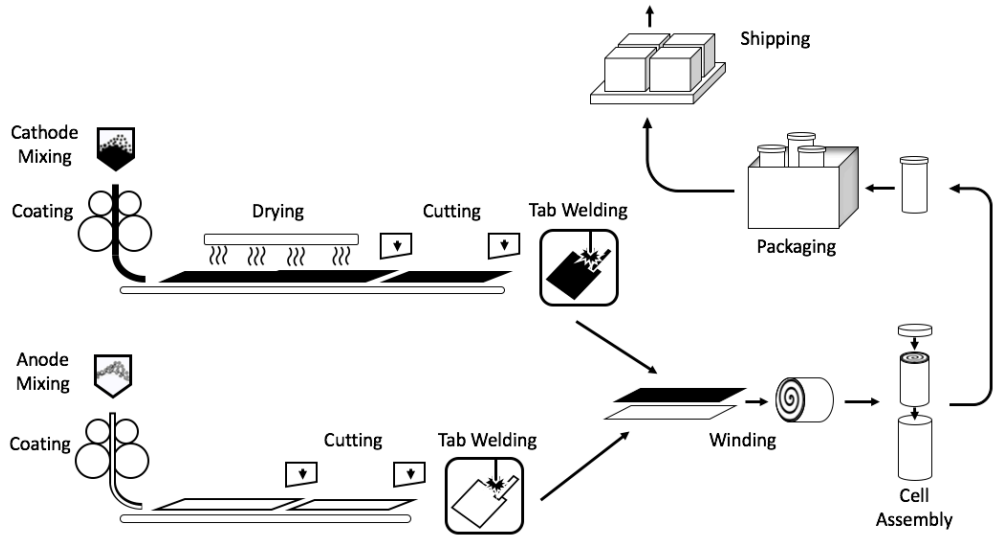
R&D to Products and Systems: Collaboration with Sandia National Labs

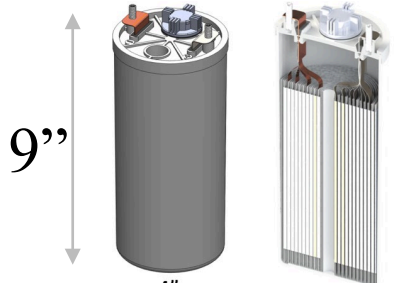
2nd electron R&D at the CUNY EI





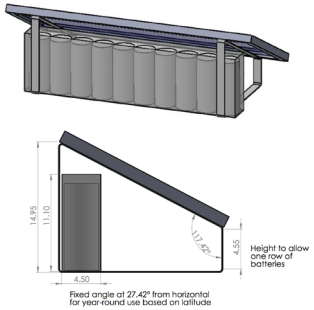
Roll-to-roll manufacturing at UEP



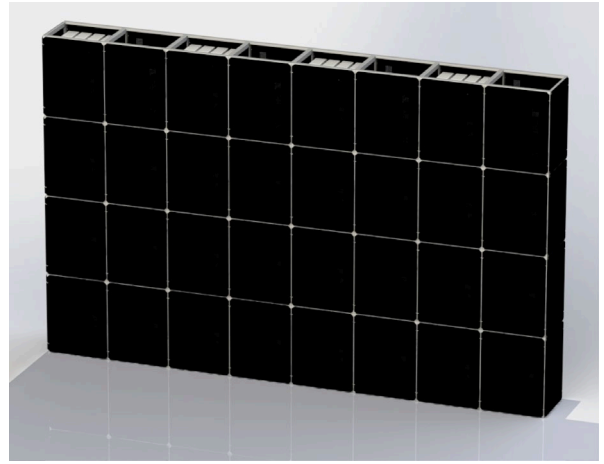


1.5V
400Ah

Field test in New Mexico and NYC

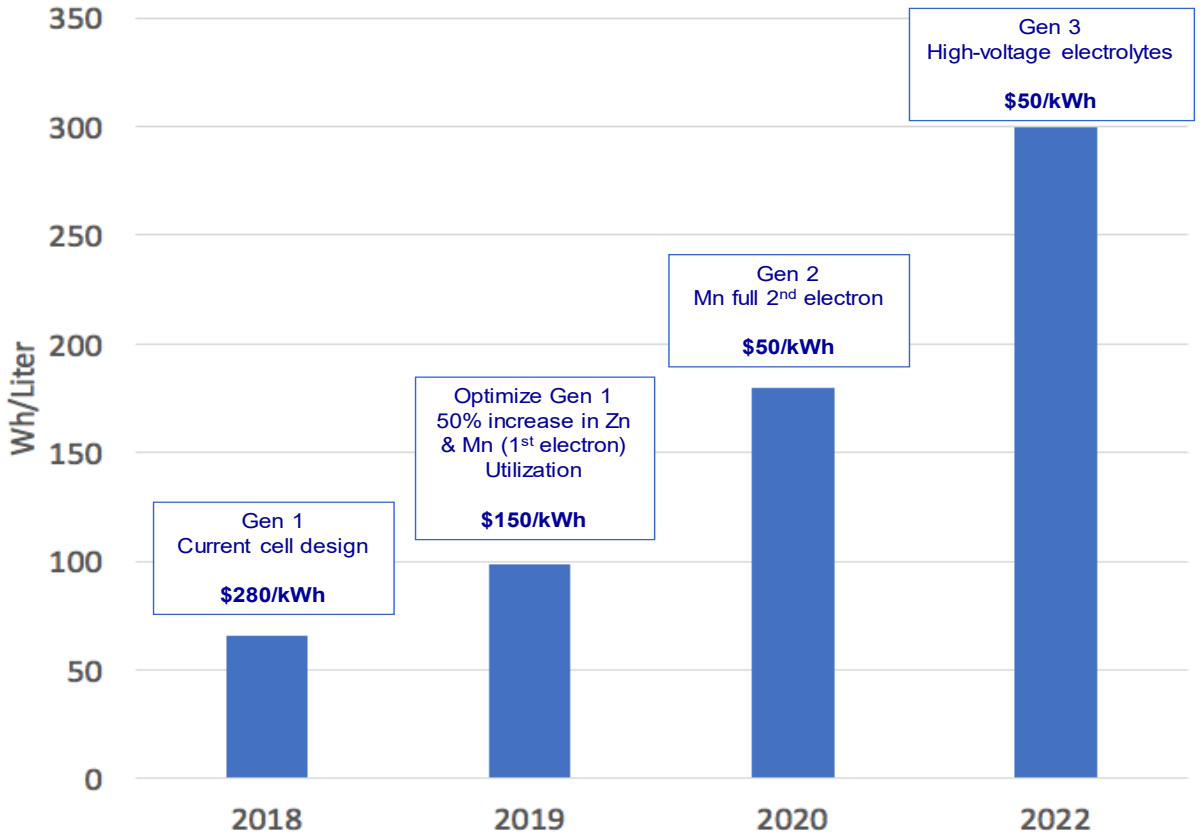


Solar/storage systems



800kWh/200kW grid-system

Potential for Zn-MnO_2 Cells at $50/kWh



Source: CUNY Energy Institute

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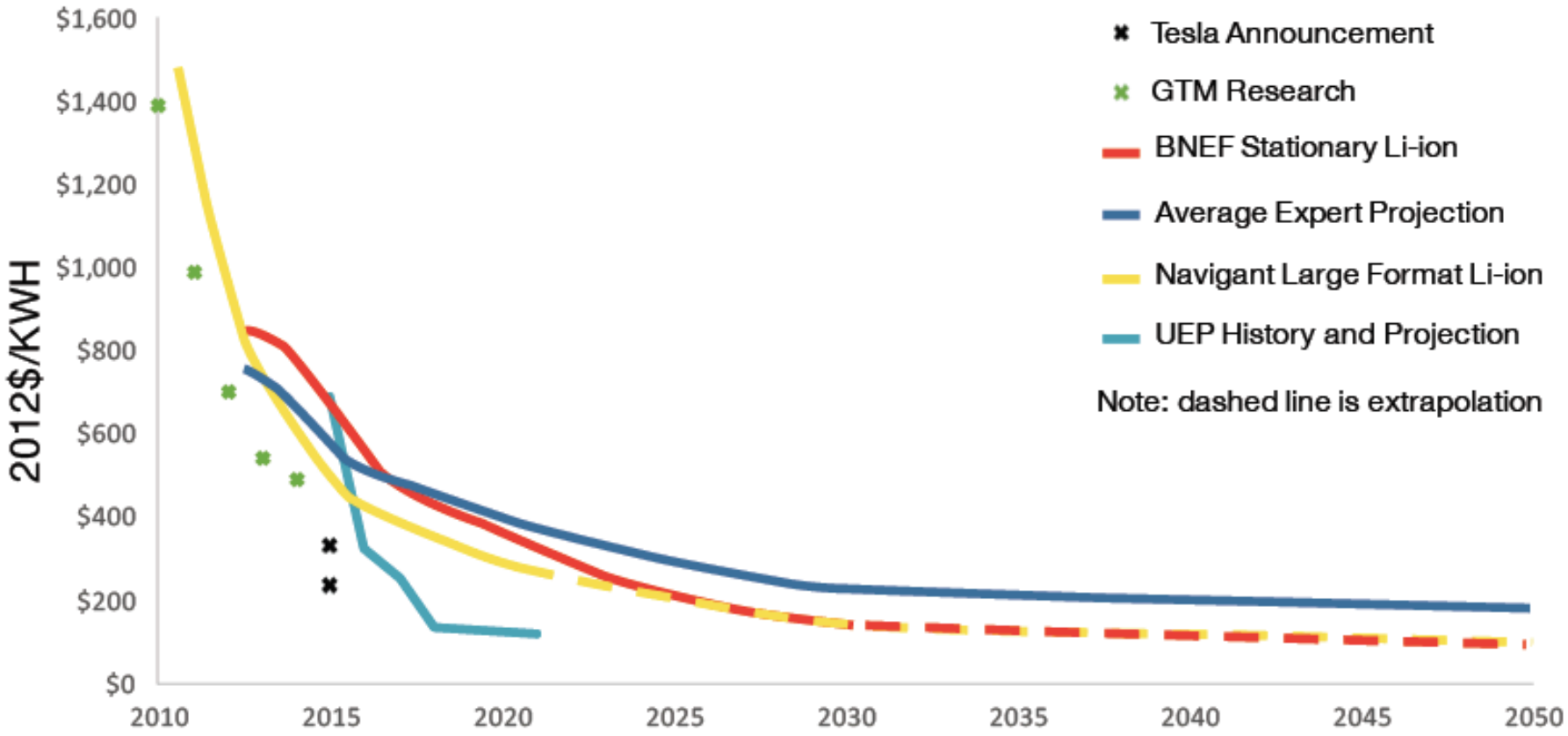
- Recent breakthroughs in making MnO_2 fully rechargeable. Based on the formation of a layered birnessite MnO_2 structure and stabilizing this structure for thousands of cycles.
- Improvement in energy density and cost by improvement in zinc utilization
- Cathode degradation mitigation by improvements controlling Zn migration across separator
- Potential for $50/Wh cells with high cycle-rechargeability of Zn-MnO_2

A Prescient 2015 Cost Projection