From Concept through Product to Market: Rechargeable Zinc Manganese Dioxide Batteries

Sanjoy Banerjee

Distinguished Professor of Chemical Engineering,
Director, CUNY Energy Institute,
The City College of New York,
Founder & Chairman
Urban Electric Power Inc., NY
banerjee@ccny.cuny.edu

2020 DOE Office of Electricity
Energy Storage Program
Annual Peer Review
September 29th - October 1st, 2020

CUNY ENERGY INSTITUTE

The City College of New York

URBAN ELECTRIC POWER

MAIN TOPICS

Why develop rechargeable zinc-manganese dioxide batteries?

Alkaline zinc-manganese dioxide battery chemistry: proton insertion and conversion reactions

Battery development roadmap: Generation 1 (proton insertion) and Generation 2 (conversion reaction)

Generation 1 battery developments: Sandia-CCNY-UEP progress

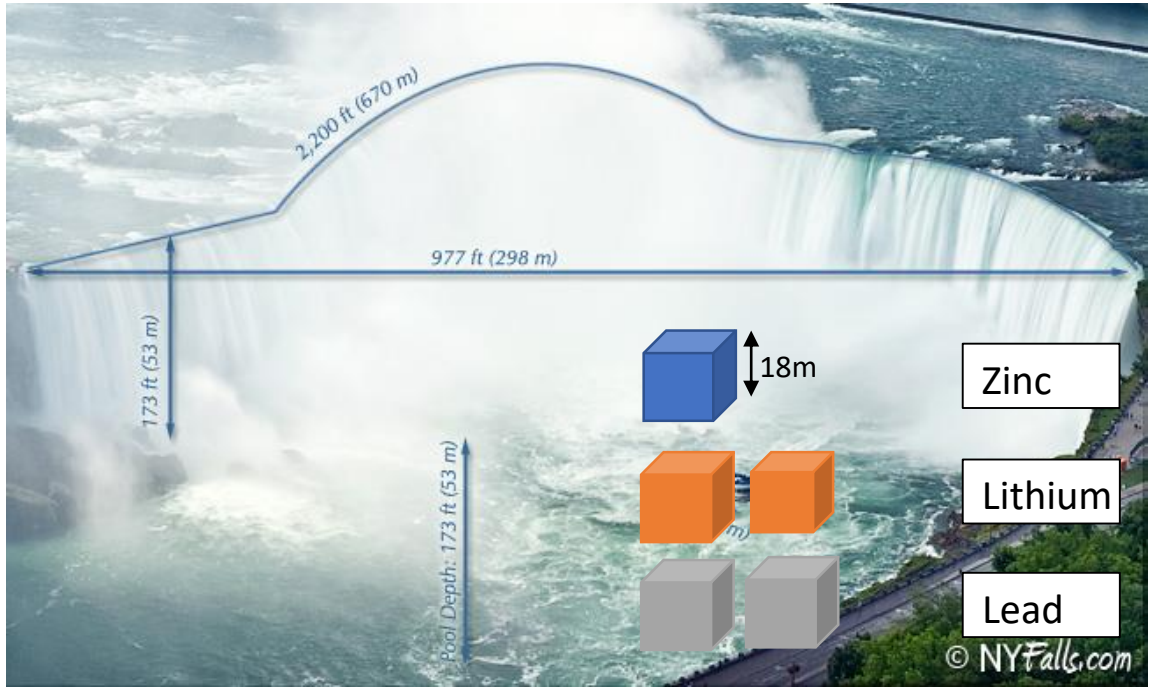
Generation 1 system deployments : power backup/UPS and solar systems

Generation 2 developments: Sandia-CCNY-UEP progress

ANODE MATERIAL CHARACTERISTICS

How much material is theoretically needed to store electricity produced by Niagara Falls in a day?

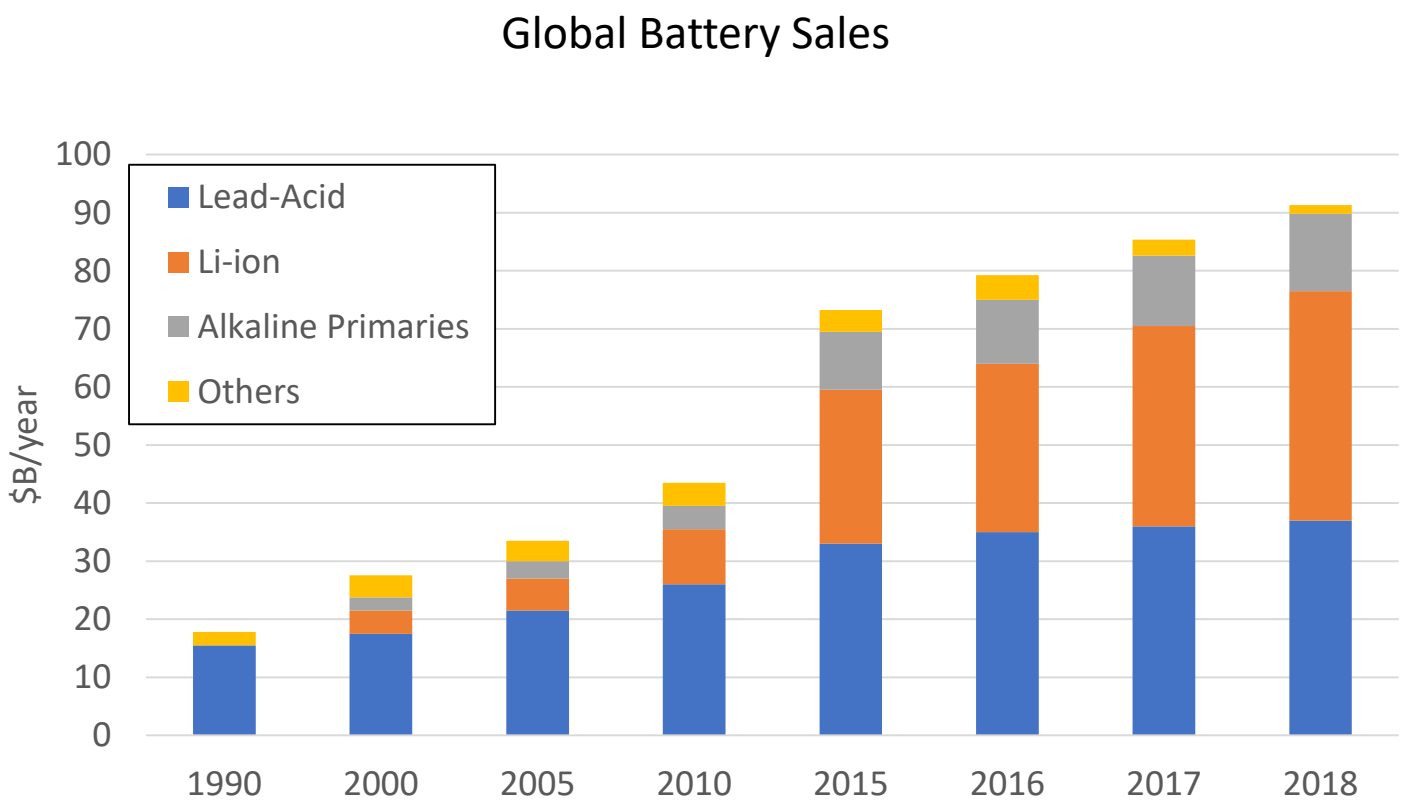
Niagara Falls: 60,000 MWh/day



Anode (*)	Cost $M	GHG Produced (Mt CO_2)	Volume (m^3)	Mass (tons)
Zinc	93	1.5	6,200	44,000
Lithium	370	6	10,200	5,300
Lead	230	4	12,000	120,000

(*) Based on the anode theoretical capacity against a hypothetical air cathode

ANNUAL SALES BY BATTERY TYPE



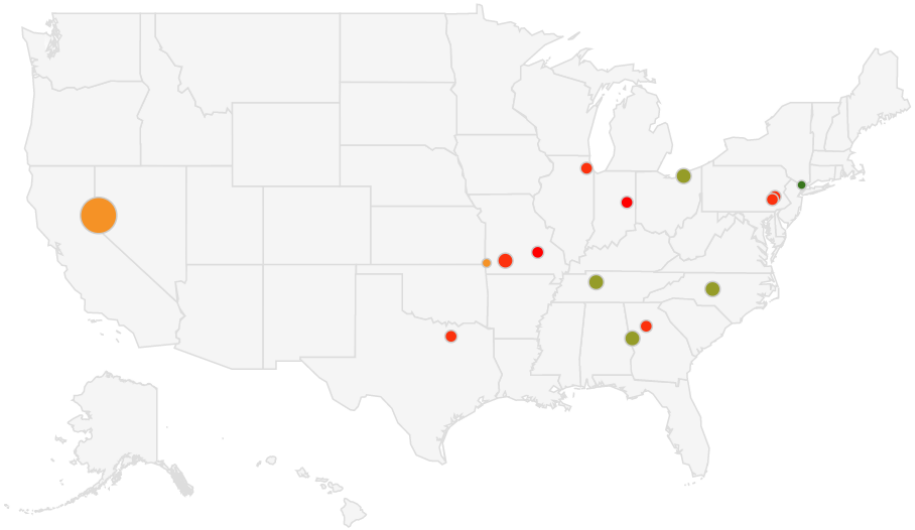
Where are we today?

- Li-ion sales ~$40B/yr growing
- Lead-Acid sales~$38B/yr stable
- Zn primary cell sales ~ $13B/yr growing
- Other battery sales (NiCd, NiMH, Flow batteries, NAS, …) ~$1.5B/yr decreasing

BATTERY MANUFACTURING IN THE US:

TECHNOLOGY, PLANT LOCATIONS & RELATIVE SIZES

Technology	Applications	Manufacturing & Supply chain	Material Cost ($/kWh)
Li-ion	EV, portable, Power applications	US supply chain? Only 2 plants in the US (9% of Worldwide capacity)	>$100 1000 cycles
Lead-Acid	SLI, Backup, UPS Some solar	Supply depends on price and availability of recycled lead	~$100 (mature) 1000 cycles
Zn Primary	Consumer electronics	$5B sales US. Established supply	~$5 (primary) 1 cycle
Zn rechargeable	Grid-Resilience & Recovery Evolving Grid	Established supply chain. Manufacturing investment required	Now: $200 (early) To: $15-$30 1000 cycles

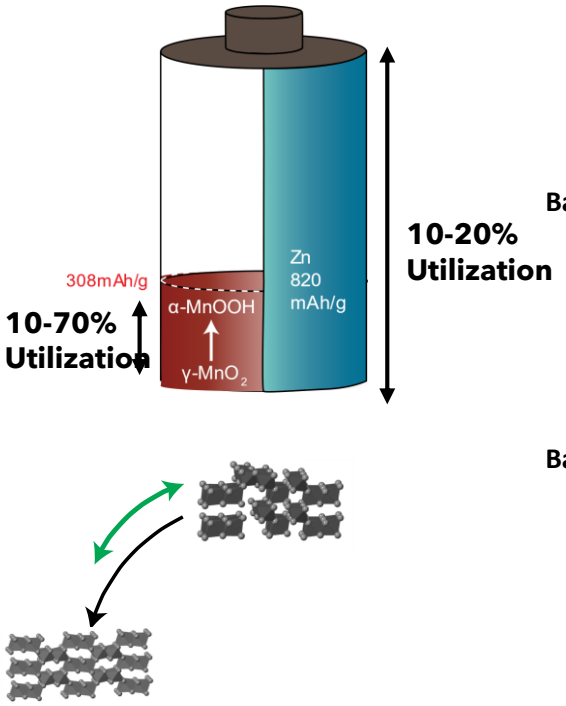


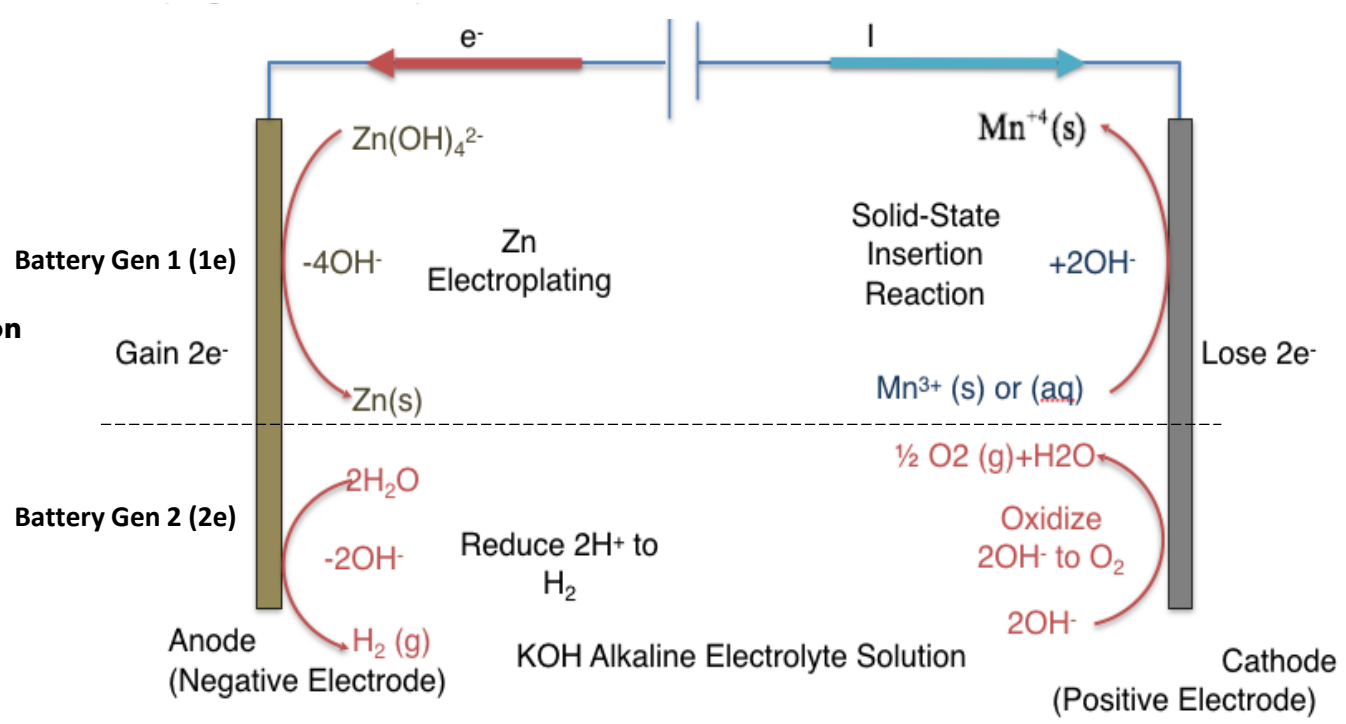
Urban Electric Power	Secondary Alkaline
Duracell	Primary Alkaline
Duracell	Primary Alkaline
Energizer	Primary Alkaline
Zochem, Inc	Zinc Battery Recycle
Tesla	Li-ion
Eagle Picher	Li-ion

Northstar	Lead Acid
Trojan Battery	Lead Acid
East Penn Manufacturing	Lead Acid
Exide Technologies	Lead Acid
EnerSys, Inc	Lead Acid
Crown Battery	Lead Acid
Exide Recycling	Lead Acid Recycle
Doe Run's	Lead Acid Recycle

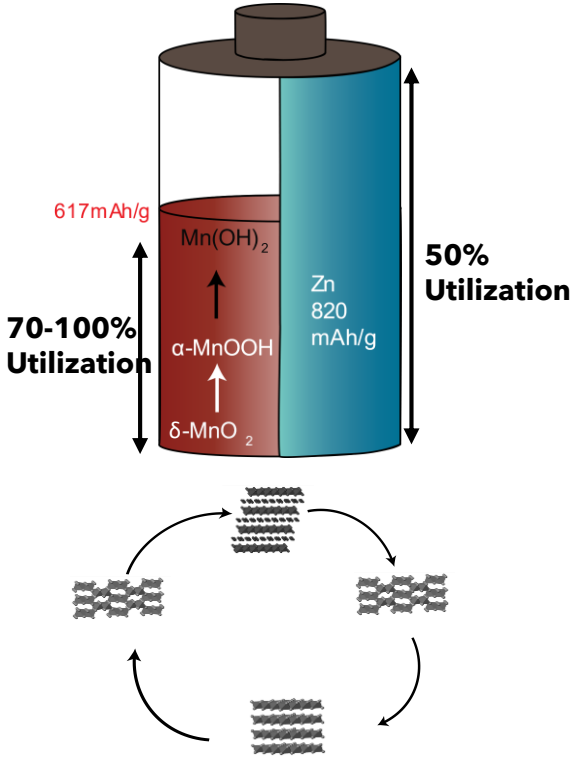
ALKALINE ZINC-MANGANESE DIOXIDE BATTERY CHEMISTRY

GEN 1
Proton Insertion Battery





GEN 2 Low Voltage
Conversion Battery



- Analogous to the Li-ion intercalation chemistry.
- Rechargeable utilization till 70% of proton insertion chemistry.
- Inactive spinel formation beyond 70% utilizations.

- Analogous to the Li-ion's Silicon conversion anodes that promise higher energy density.
- UEP's conversion battery can access energy densities comparable to Li-ion.

BATTERY DEVELOPMENT ROADMAP

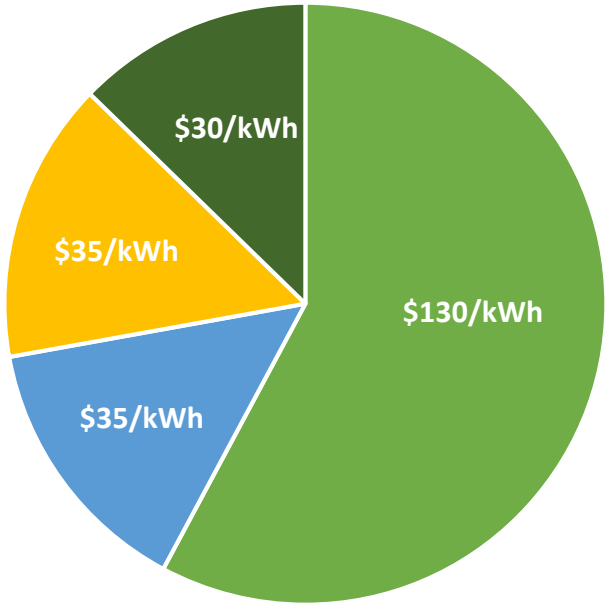
Basis of comparison: 300 cycles / 4h charge / 4h discharge (Peak shaving application)

GEN 1

GEN 2

2020

BATTERY 1: $230/KWH



- Proton insertion battery
- 20% MnO_2 (1e) / 10% Zn (2e)
- $230/kWh Manufactured Cost

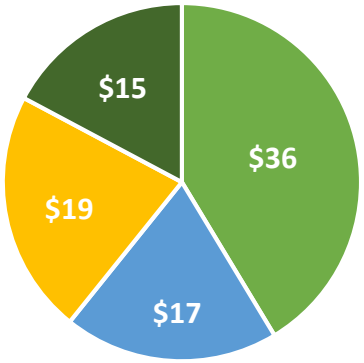
Raw Material Consumption

MnO_2: 15 MT/MWh

Zn: 10 MT/MWh

2021

BATTERY 2: $87/KWH



- Proton insertion battery
- 40% MnO_2 (1e) / 20% Zn (2e)
- $87/kWh Manufactured Cost

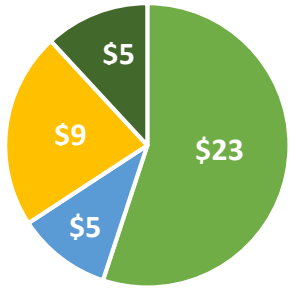
Raw Material Consumption

MnO_2: 7.5 MT/MWh

Zn: 5 MT/MWh

2023

BATTERY 3: $42/KWH



- Conversion battery
- 75% MnO_2 (2e) / 50% Zn (2e)
- $42/kWh Manufactured Cost

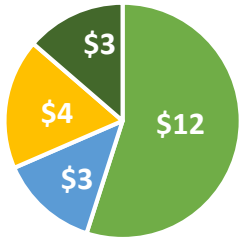
Raw Material Consumption

MnO_2: 2.2 MT/MWh

Zn: 2.4 MT/MWh

2025

BATTERY 4: $22/KWH



- Dual-electrolyte battery
- 100% MnO_2 (1e) / 50% Zn (2e)
- $22/kWh Manufactured Cost

Raw Material Consumption

MnO_2: 1.4 MT/MWh

Zn: 1 MT/MWh

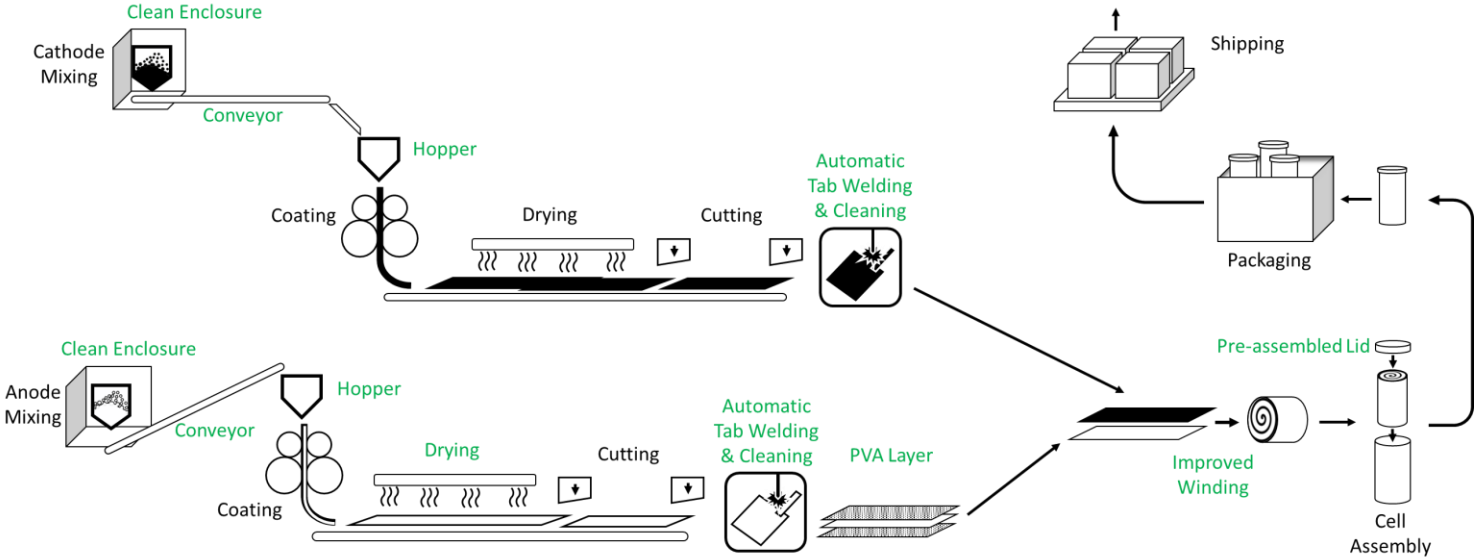
- Inactive Materials
- MnO2
- Zn
- Manufacturing cost

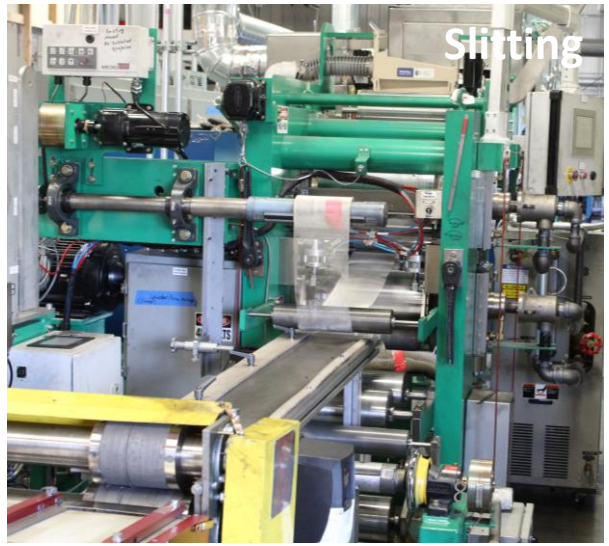
Material prices used:

MnO_2: $2.2/kg

Zn: $4.07/kg

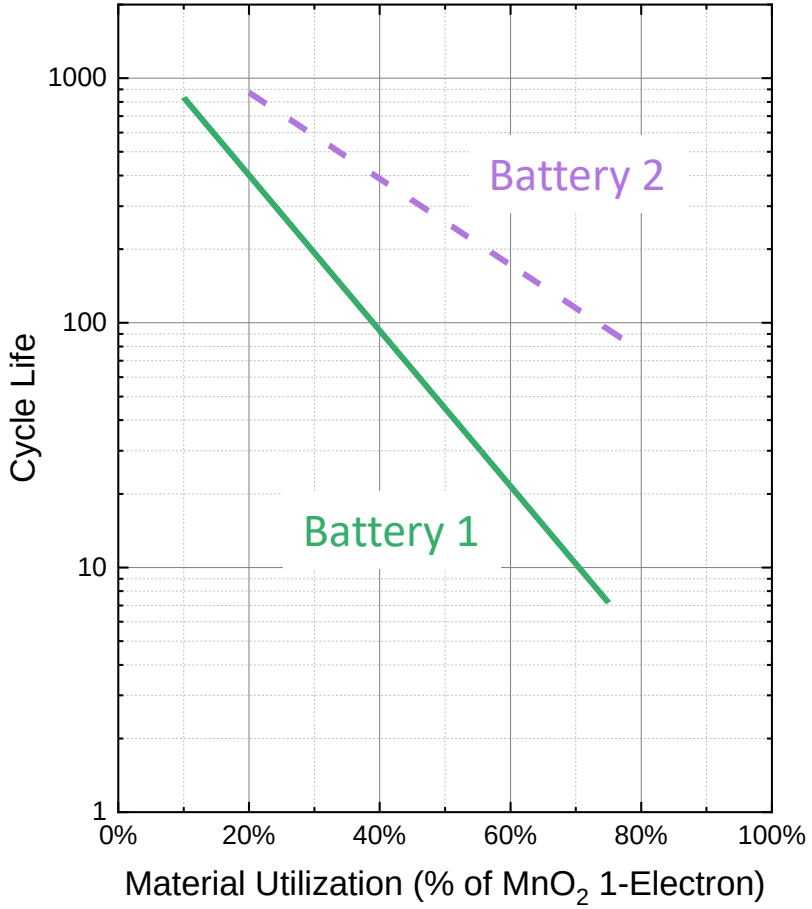
BATTERY MANUFACTURING PROCESS SCHEMATIC





BATTERY CYCLING PERFORMANCE
Battery 1 & 2

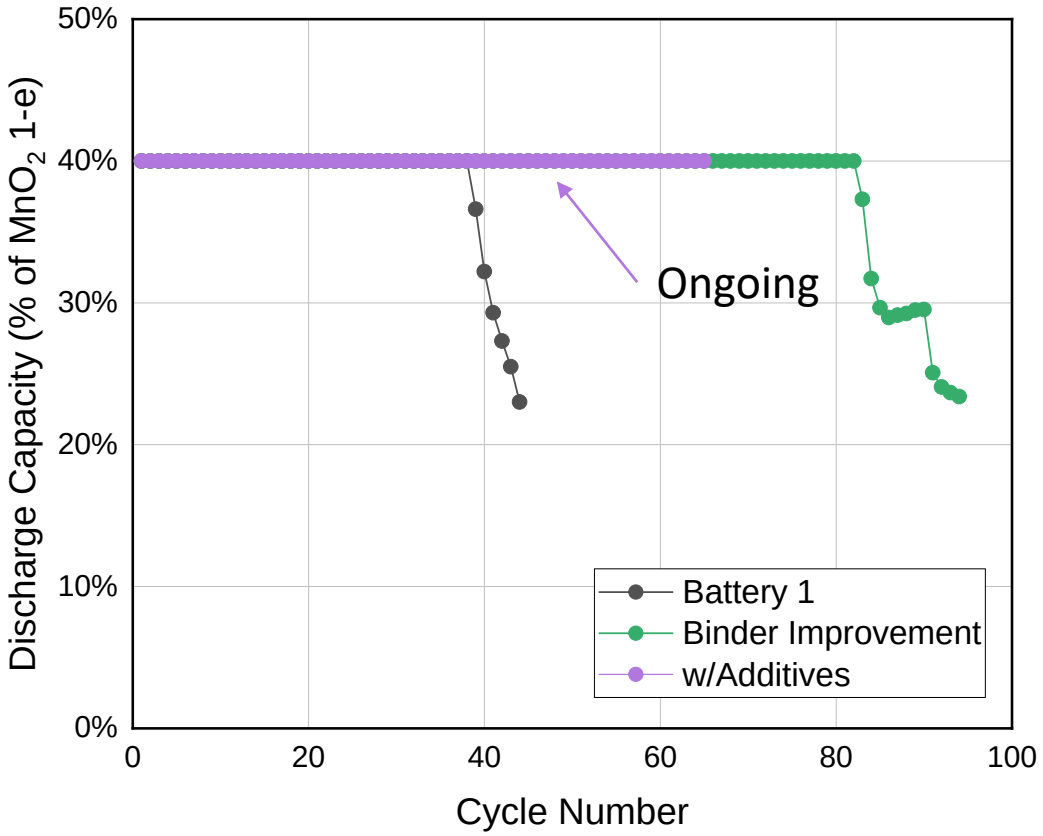
Battery 1 & 2
MnO_2 1-e Capacity: 350 Ah
Nominal Voltage: 1.30 V



- Battery 1 can achieve 300+ cycles at 20% utilization of MnO_2 1-e capacity and 10% utilization of Zn 2-e capacity
- Battery 2 is under development to achieve similar cycle life while doubling the utilization of active materials.

BATTERY 2 DEVELOPMENT PROGRESS

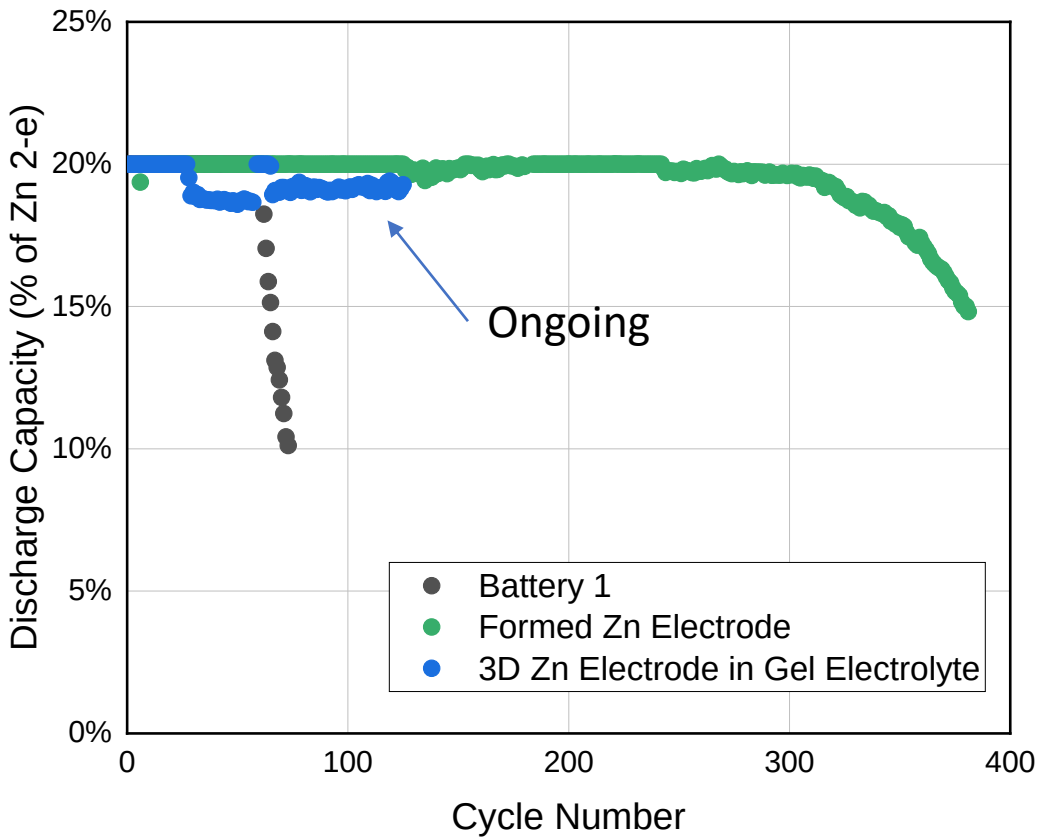
Cathode Development



- Development of the cathode is underway to achieve 40% utilization of the MnO_2 full 1-electron capacity for a long cycle life.
- Progress has been made on the material research on the electrolytic manganese dioxide (EMD) material, the current collector, the carbon conductive matrix, the binder materials and the additives.

BATTERY 2 DEVELOPMENT PROGRESS

Anode Development



- Development of the anode is underway to achieve 20% utilization of the Zn full 2-electron capacity for a long cycle life.
- Progress has been made by modifying the Zn electrode structure, studying the additive materials and improving the electrolyte.

COMPARISON OF BATTERY 1, 2 AND OTHER BATTERIES

Comparison of UEP Battery 1 & 2 with lead acid AGM, LFP and lithium ion batteries under IEC 61427-1 cycling protocol.

	Zn-MnO2		**Lead acid AGM**	**Lithium Iron Phosphate**	**Lithium Ion**
Battery	UEP Battery 1	UEP Battery 2	Trojan 27-AGM	Dakota LFP Battery	Panasonic NCR18650B
Nameplate Capacity (Ah)	123	210	82	100	3.2
Norminal Voltage (V)	12	12	12	12.8	3.6
Volumetrc energy density (Wh/L)	97	165	78	102	676
Gravimetric energy density (Wh/kg)	44	76	34	88.3	243
Cycle life	5-year life	5-year life	8-year life	8-year life?	5-year life?
Operating temperature (°C)	-20 to 60	-20 to 60	-20 to 50	-30 to 50	-20 to 60
Retail price	$380	$380	$270	$900	$6
Cost per kWh	$257	$151	$274	$703	$520

Note:
- Energy densities are battery level data.
- Cost and performance data are based on IEC 61427-1 solar protocol.
- Each year of life is equivalent to 150 cycles under IEC 61427-1 solar protocol at 40 °C.
- The LFP battery and the lithium ion battery have not been tested under IEC solar protocol. Their cycle life numbers are estimated from the life data in the specs.

SYSTEM COST COMPARISON

Price Comparison includes Battery Cells and Inverter

SYSTEM	Energy (kWh)	Power (kW)	Price ($)	$/kWh
UEP Battery 1 System	**13**	**4**	**$5,053**	**$389**
Tesla Powerwall Li-ion	13.5	5	$6,500	$481
LG RESU10H Li-ion	9.8	4	$5,250	$536
ElectriQ Li-ion	11	6	$8,998	$818
Outback Power Lead-Acid AGM 800RE-24	30	8	$15,379	$513

Sources	
Outback:	https://www.solar-electric.com/outback-power-systemedge-830re-inverter-storage-system.html?gclid=Cj0KCQjwvvj5BRDkARIsAGD9vlJEpcQ3Fa5tqyzjV_AY21DyjSxrQ2Gw0-_nwHwnGwKXmLLCt2_z2p8aAnlWEALw_wcB
LG:	https://www.solaris-shop.com/lg-chem-resu10h-9-8kwh-primary-lithium-ion-battery/
ElectriQ:	https://electriqpower.com/specs/
Tesla:	https://www.tesla.com/powerwall

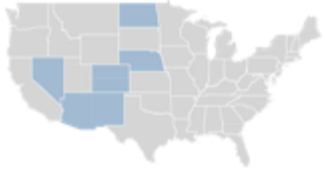
CURRENT Battery 1 PROJECTS: 2021

Project	Usecase	Est Completion Date	Value
San Diego Supercomputer Center Backup (San Diego, Californa)	High Rate UPS	Jan.-June 2021	$ 500,000
CCNY Grid Modernization center (Manhattan, New York)	Grid storage (demand response/ demand charge) Solar microgrid High Rate UPS	Jan.-June 2021	$ 1,000,000
BMCC Energy Storage System (Manhattan, New York)	Grid storage (demand response/ demand charge)	Sep. 2021	$ 350,000
Dairy Farm Power Backup System (New York)	Low Rate UPS	Jan.-Feb. 2021	$ 245,000
Navajo Nation Microgrid (New Mexico)	Solar Microgrid	Mar. 2021	$ 85,000
UT-Austin High-Voltage Microgrid (Austin, Texas)	Solar Microgrid	Dec. 2020	$ 187,000
Total			**$ 2,367,000**

THE NEED FOR POWER BACKUP/UPS SYSTEMS

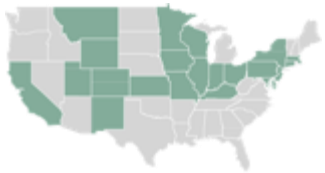
US Outages Widespread

130M households experience outages exceeding **2 hours annually**



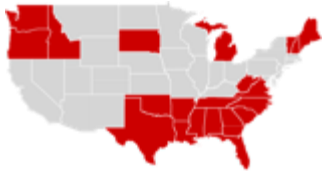
- **Avg. outage per household:** <2 Hours
- **No. of states:** 6
- **Households:** ~6M

Short Duration



- **Avg. outage per household:** 2-4 Hours
- **No. of states:** 21
- **Households:** ~70M

Medium Duration



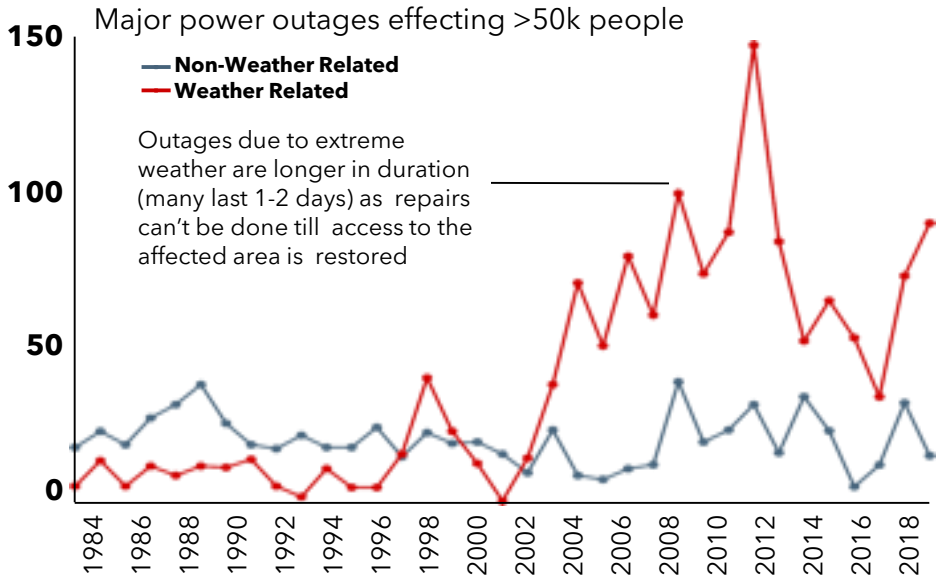
- **Avg. outage per household:** >4 Hours
- **No. of states:** 21
- **Households:** ~70M

Long Duration

Major outages due to extreme weather over the last decade are 2-3x higher versus the 1990s

- UEP Gen 1 batteries are a safe and low self discharge solution, ideally suited for addressing backup power needs indoors.
- Lead-acid requires float charge adding cost and toxicity hazards.
- Lithium-ion requires complex BMS to manage flammability hazard, adding cost to manage safety concerns.

UEP Gen 1 B1 Addressable

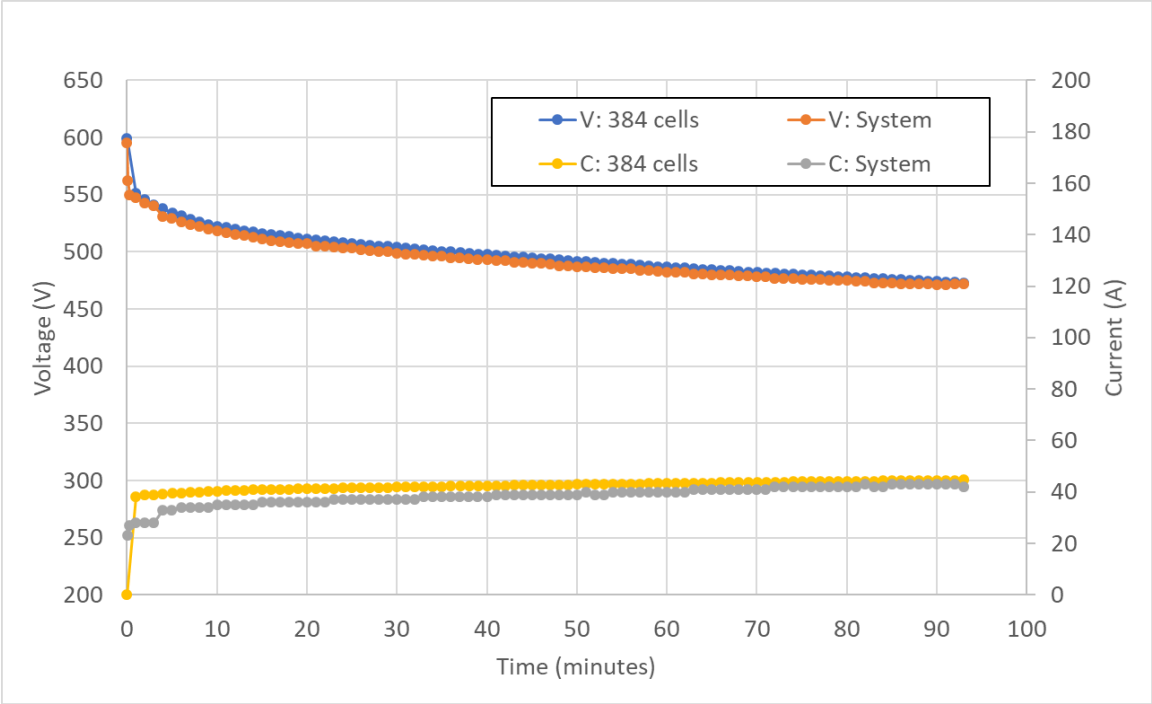


Total US Market Greenfield Potential of ~$95B

	Long duration outage states w/ access to gas	**Long duration** outage states w/o access to gas	**Mid duration** outage states w/ access to gas
Total no. of households	~ 47M	~ 13M	~ 53M
Single, detached, owner occupied households	~ 25M	~ 7M	~ 26M
Households with annual income >60k	~ 11M	~ 3M	~ 10M
Total market potential	~ $43B	~ $12B	~ 40B

25KW SDSC RACK TESTING AT CUNY

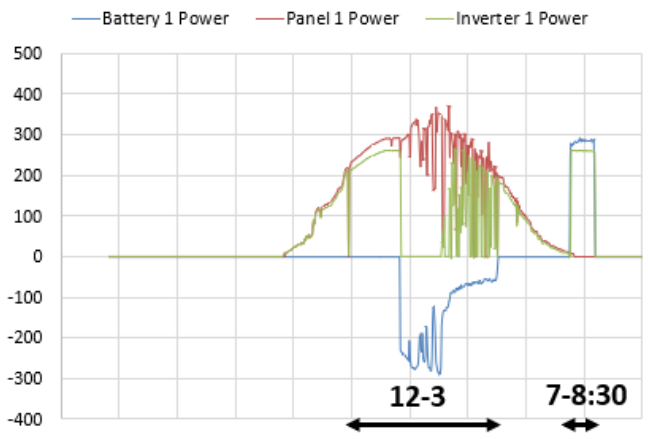
Mitsubishi invertor and a rack of 384 cells



- Confirmed system performance.
- Tested cell-to-cell and battery-to-battery connections.
- Tuning the charging protocol of the Mitsubishi inverter.

NEW MEXICO STATE UNIVERSITY: EXTREME SOLAR PANEL

Data from one week of operation of two systems in New Mexico



Detailed Daily Profile

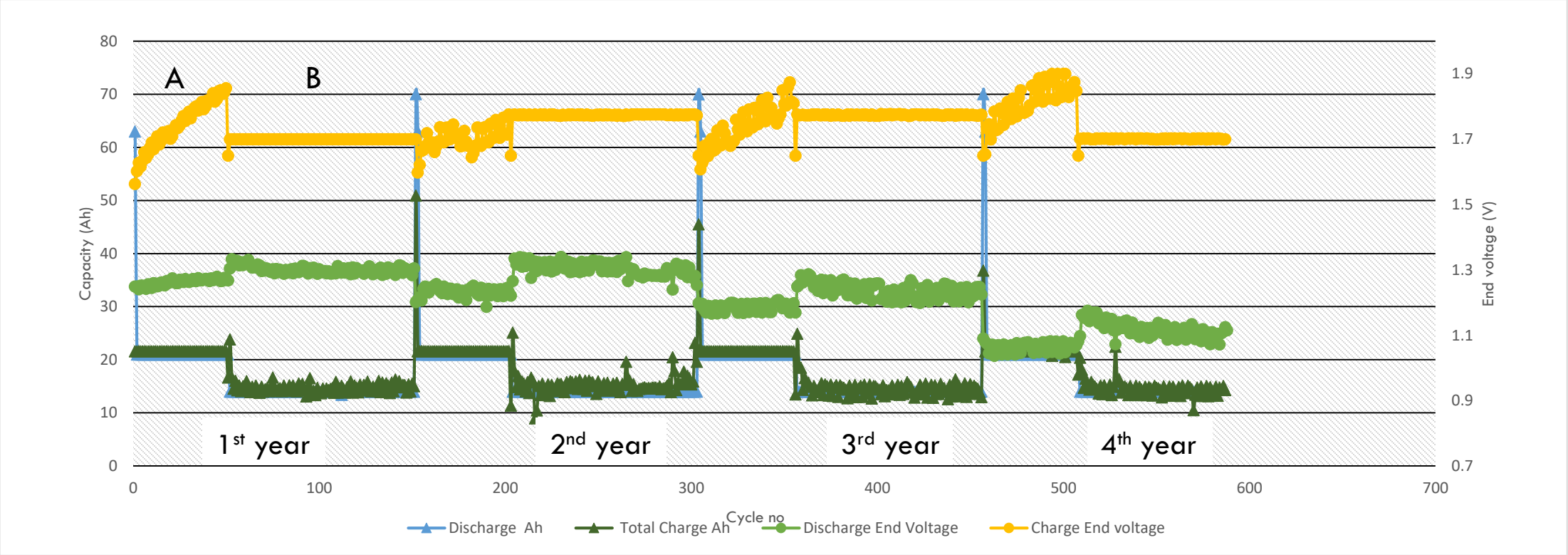
The blue curve is the battery power (negative is charging and positive is discharging).
The Green curve is the Inverter Power (standard Enphase IQ7+).
The Red curve is the solar power.
The solar is used to charge the batteries between 12PM and 3PM and the batteries provide power to the Enphase Inverter between 7 PM and 8:30 PM.

Solar integrated batteries

- Direct pairing of batteries and solar panels on the DC side with low-cost (<$50) electronics
- Batteries are also used to hold the panels down
- Product made possible by the ability of the $ZnMnO_2$ batteries to charge in 4-6 hours with a wide range of constant current/power values and to work at high temperature
- Future step is to add the battery electrodes flat under the panels to make 24-7 solar panels

PERFORMANCE : SOLAR MICROGRID FOR 5 YEAR WARRANTY

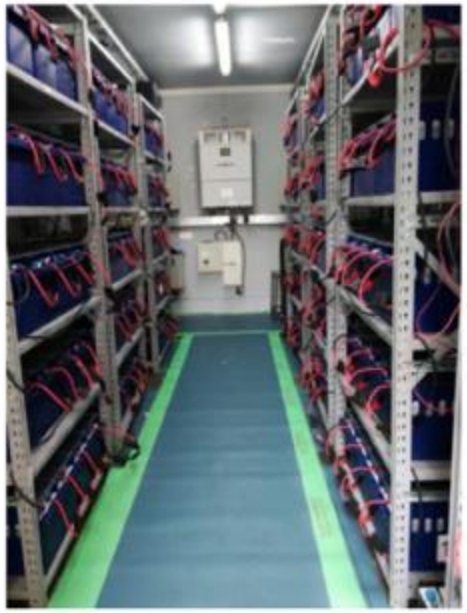
UEP Battery can cycle under IEC 61427-1 protocol (international standard for secondary cells and batteries for renewable energy storage) to give 5-year warranty for solar microgrid application. The test below has completed 4 years and is still running.

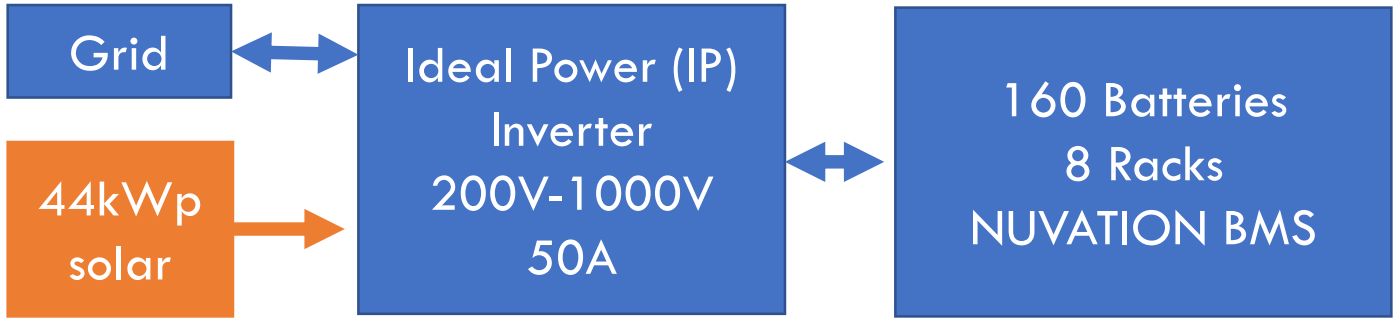


Test Protocol is in 2 Successive Phases:

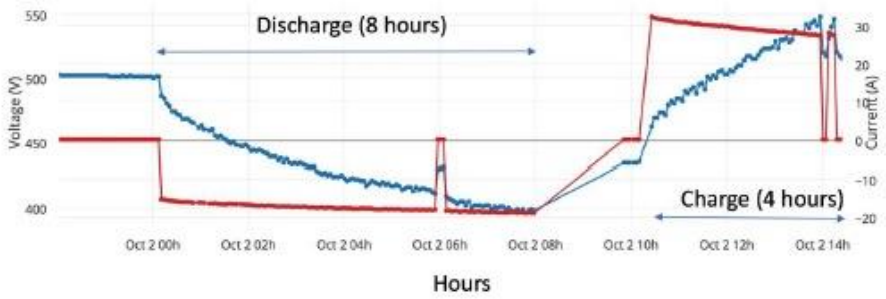
- Phase A: 3h C/10 charge and 3h C/10 discharge cycling at low state of charge for 50 cycles.
- Phase B: 6h charge and 2h C/8 discharge cycling at high state of charge for 100 cycles.
- If on completion of these two phases 80% of initial capacity is retained, then the battery is deemed to have completed a year of service in a solar microgrid successfully.

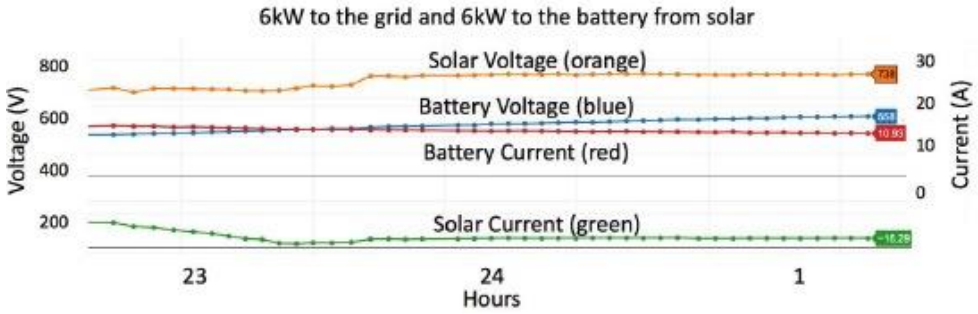
CONTAINERIZED GRID-TIED SOLAR-TIED SYSTEM IN G&B INDIA





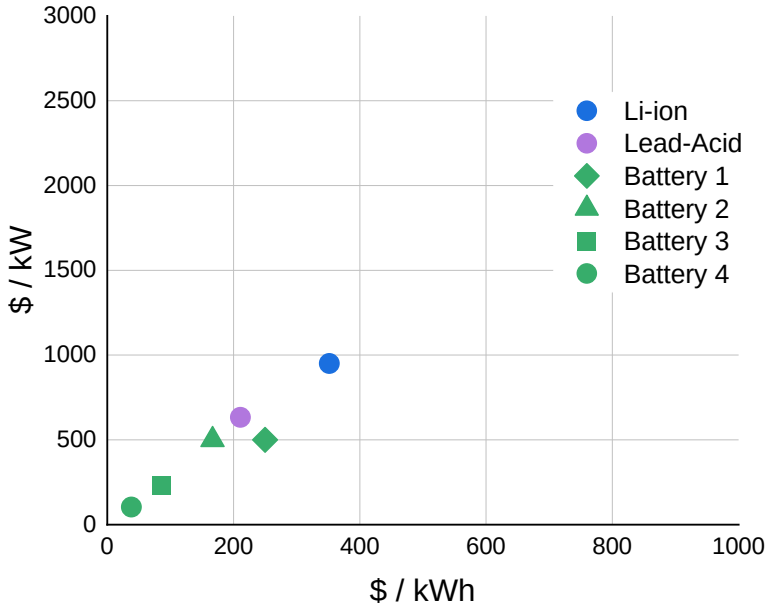
- System built in 2016 with G&B
- Use standard off-the-shelf BMS from NUVATION and Ideal Power grid-tied inverters
- Operates between 400V and 800V DC
- 30kW inverter with 44 kWp of solar



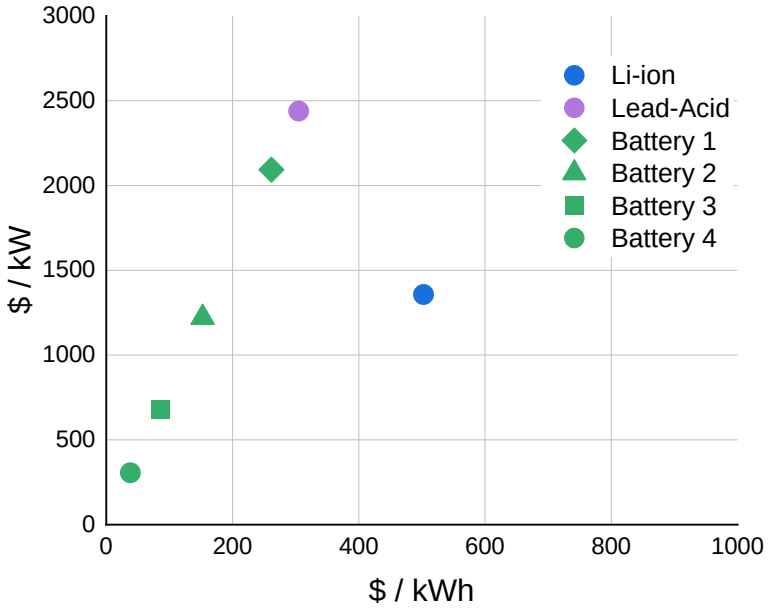


ZINC-MANGANESE DIOXIDE BATTERY APPLICATION: PRICE COMPARISON

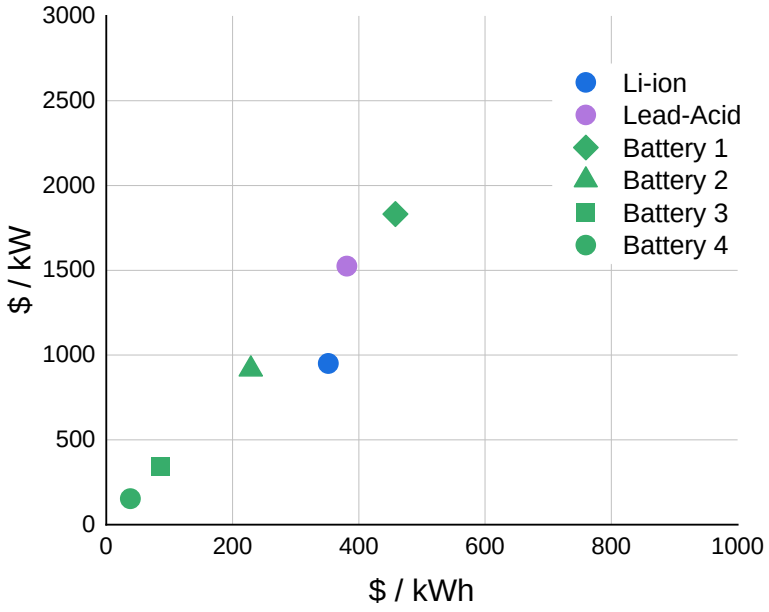
UPS/Telecom
2-3 hours, 20 cycles, 5 years



ESS – Solar Microgrid
8-10 hours, 5 years warranty



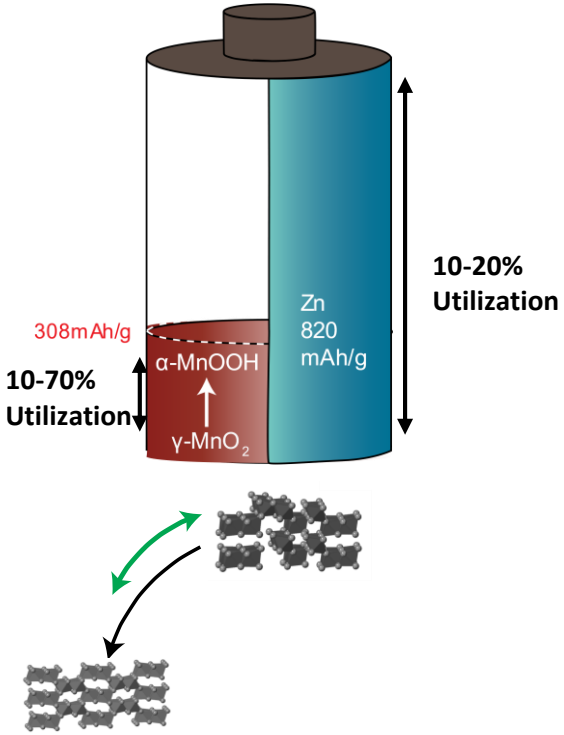
ESS – Grid Storage
(Peak shaving)
4 hours, 300 cycles, 5 years



** Prices shown above are actual selling prices for three different applications*

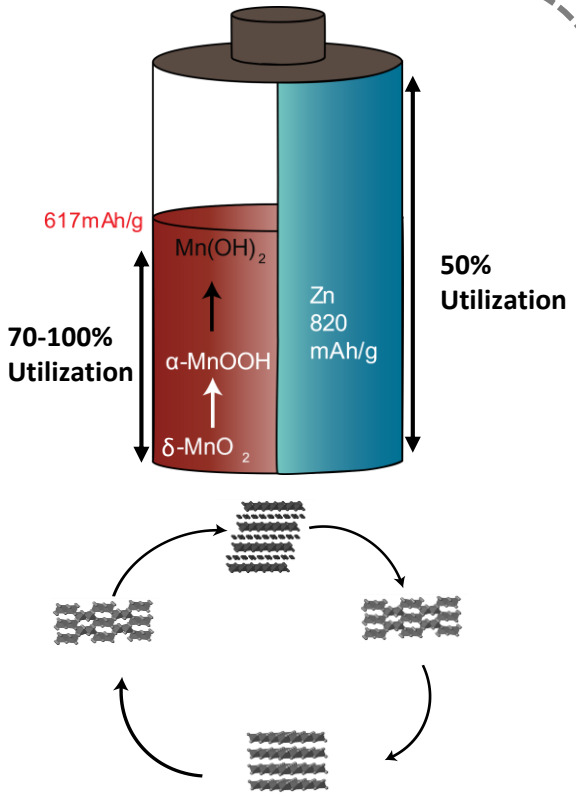
KEY DEVELOPMENTS OF ZN-MNO_2 BATTERIES

Battery 1 and 2
Proton Insertion Battery



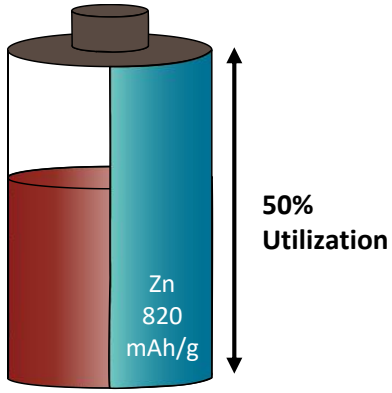
- Analogous to the Li-ion intercalation chemistry.
- Rechargeable utilization till 70% of proton insertion chemistry.
- Inactive spinel formation beyond 70% utilizations.

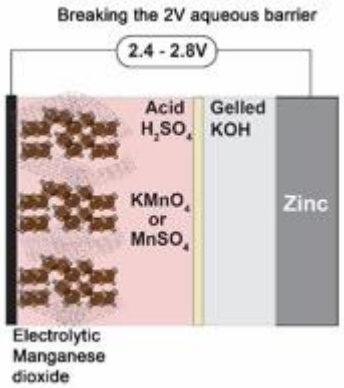
Battery 3
Conversion Battery



- Analogous to the Li-ion's Silicon conversion anodes that promise higher energy density.
- UEP's conversion battery can access energy densities comparable to Li-ion.

Battery 4
The Li-ion Competitor
High Voltage 2.45-2.8V Zn-MnO_2



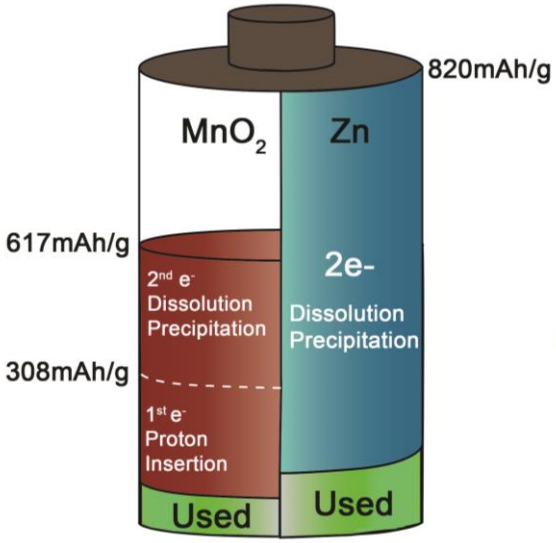


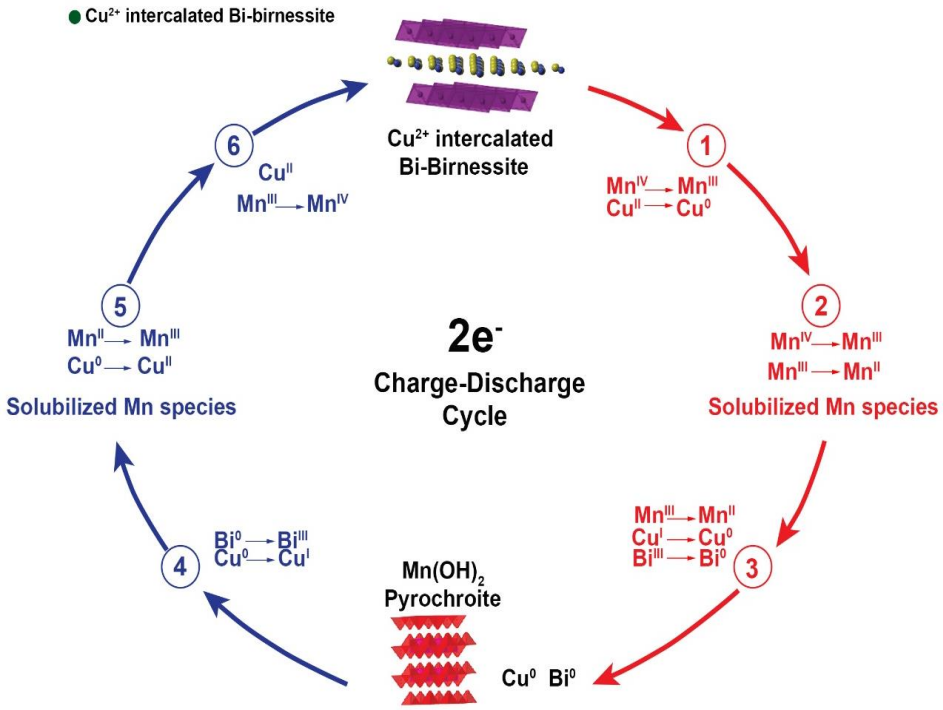
- Breakthrough accessibility in >2.4-2.8V & 100% utilization of 308mAh/g of MnO_2 allows higher energy density than Li-ion.

SANDIA-CCNY-UEP PROJECT:

Developing 2nd Electron Cells

Birnessite Cathode Capable of Accessing 100% of 2e





Key Challenges

MnO_2 Cathode

- Crystal structure breakdown
- Formation of Inactive phases
- Susceptibility to Zinc poisoning

Separator

- Reduce zinc crossover

Zn Anode

- Control shape change
- Passivation
- Dendrite formation

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

SANDIA-CCNY-UEP PROJECT:

Developing 2nd Electron Cells – Objectives and Strategies

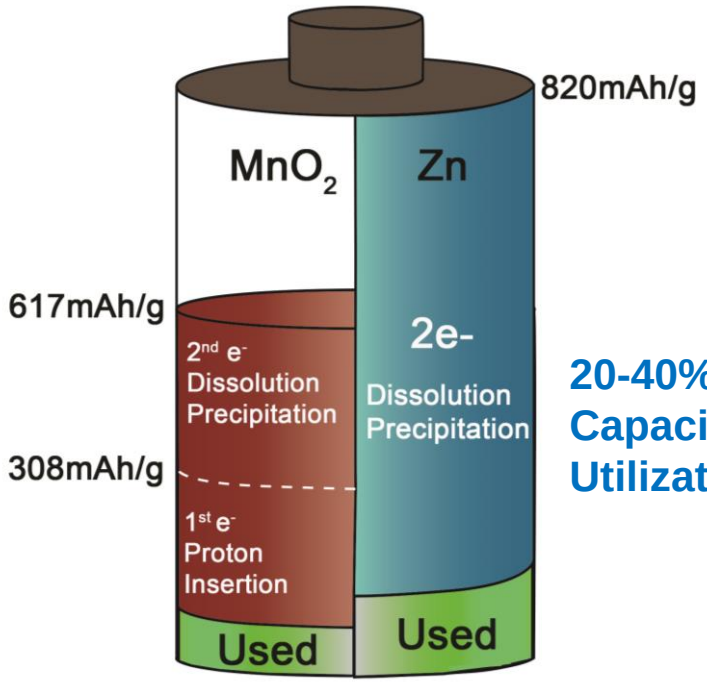
Research Objectives:

- Achieve >75% utilization of the MnO_2 2-electron capacity
- Achieve 20-40% utilization of the Zn 2-electron capacity
- Create a manufacturable cell in either a D-cell or 18650 format that delivers 300 full cycles at a bill of materials in volume production of ~$75/kWh (at 75% MnO_2 utilization and 20% Zn utilization).

Strategies:

- Develop polymer gel electrolyte to mitigate zinc redistribution and manganese active materials loss issues;
- Investigate hydrophilic and conductive binders to improve electrodes performance;
- Develop 3D Zn electrode to improve Zn utilization;
- Develop Zn blocking separators to prevent Zn poisoning;
- Increase active materials loading and reduce inactive components to reduce cost.

>75% Capacity Utilization

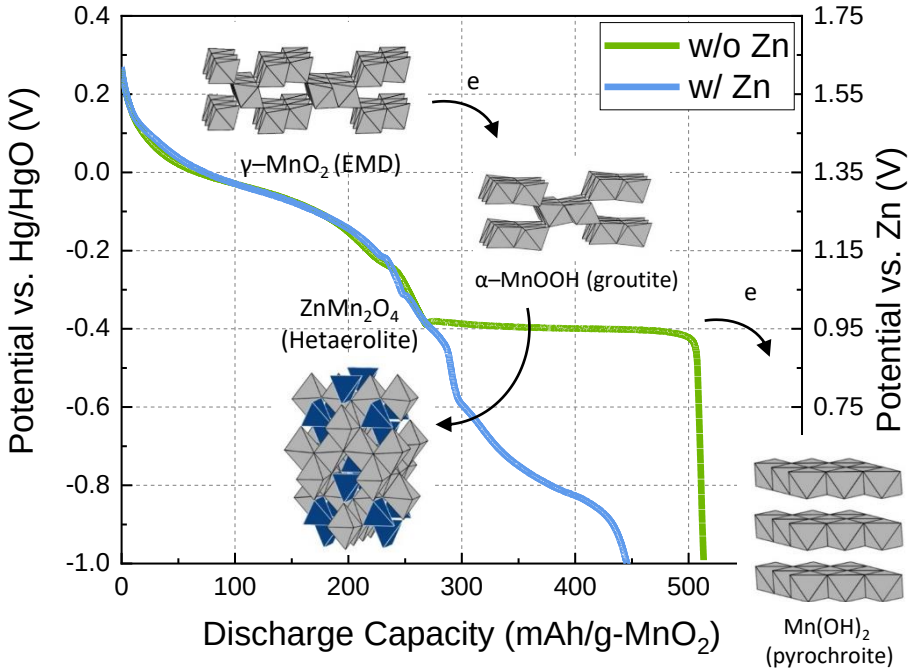


20-40% Capacity Utilization

SANDIA-CCNY-UEP PROJECT:

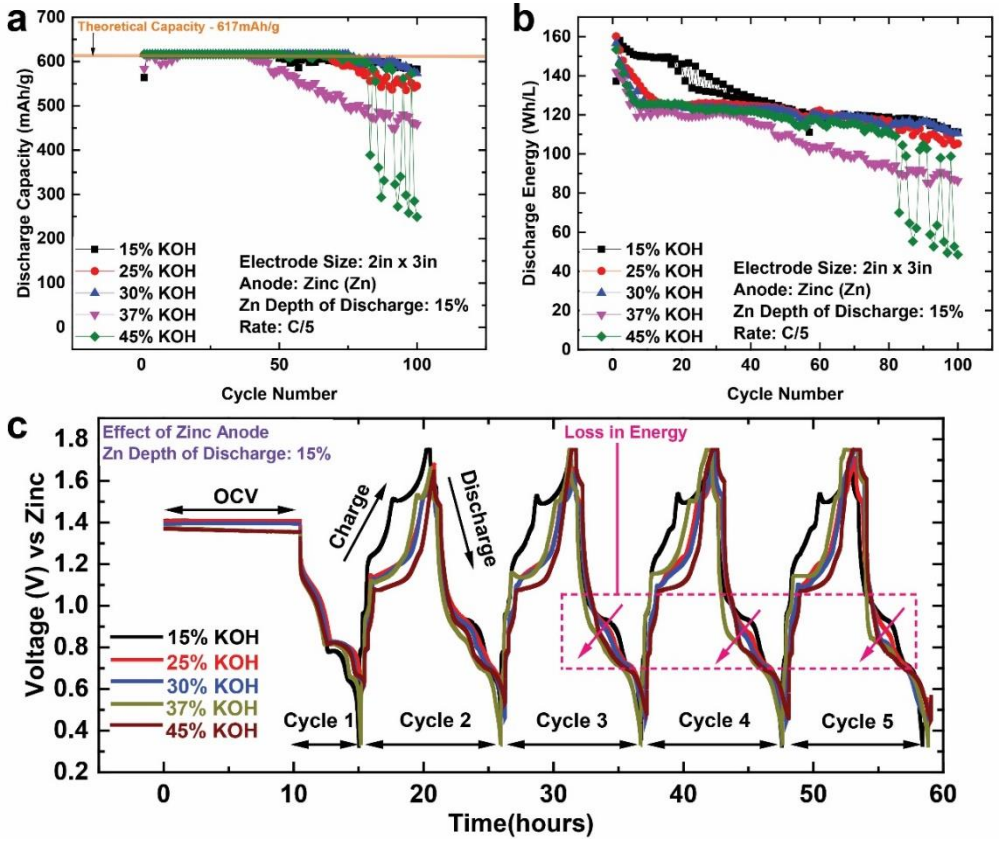
Effect of Zinc Crossover

Zinc effect on full discharge of EMD (2-e)

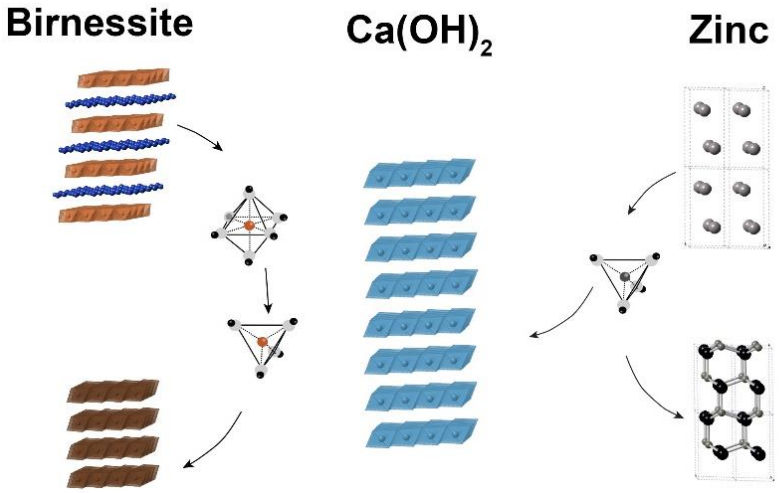


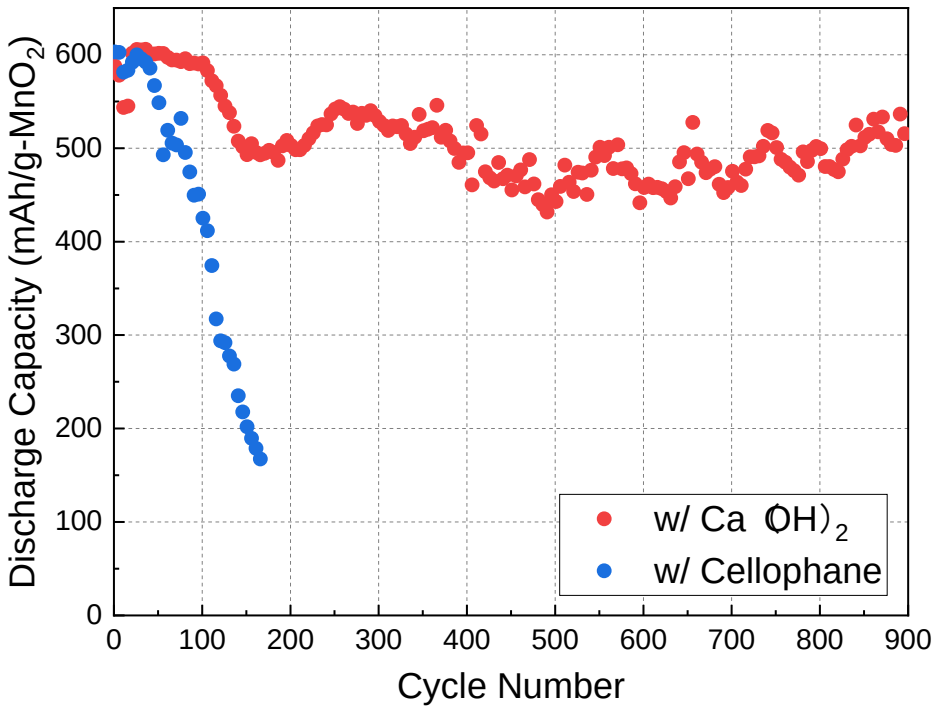
$$2MnOOH + Zn(OH)_4^{2-} \rightarrow ZnMn_2O_4 + 2H_2O + 2OH^-$$

Zinc effect on 2-e cycling of CUNY doped-birnessite cathode



SANDIA-CCNY-UEP PROGRAM:
Zinc Blocking with $Ca(OH)_2$ Interlayers



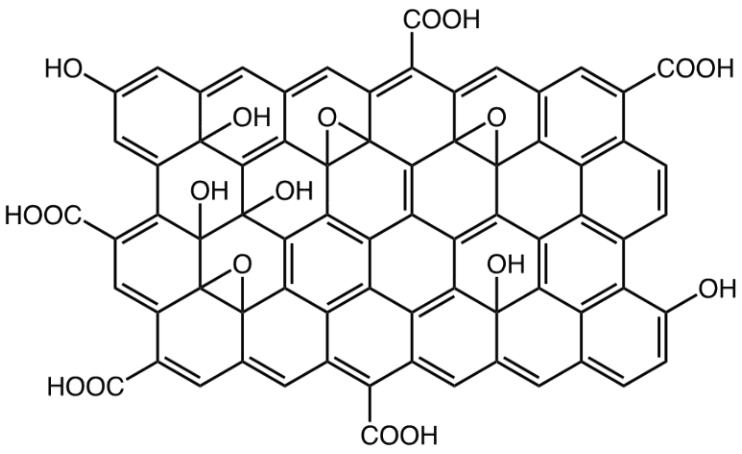


- The $Ca(OH)_2$ interlayer captures zincate ions by forming an insoluble compound $Ca(OH)_2 \cdot 2Zn(OH)_2 \cdot 2H_2O$ (calcium zincate) and extends the cell's cycle life with stabilized capacity and energy (80% retention of the full 2-electron capacity).

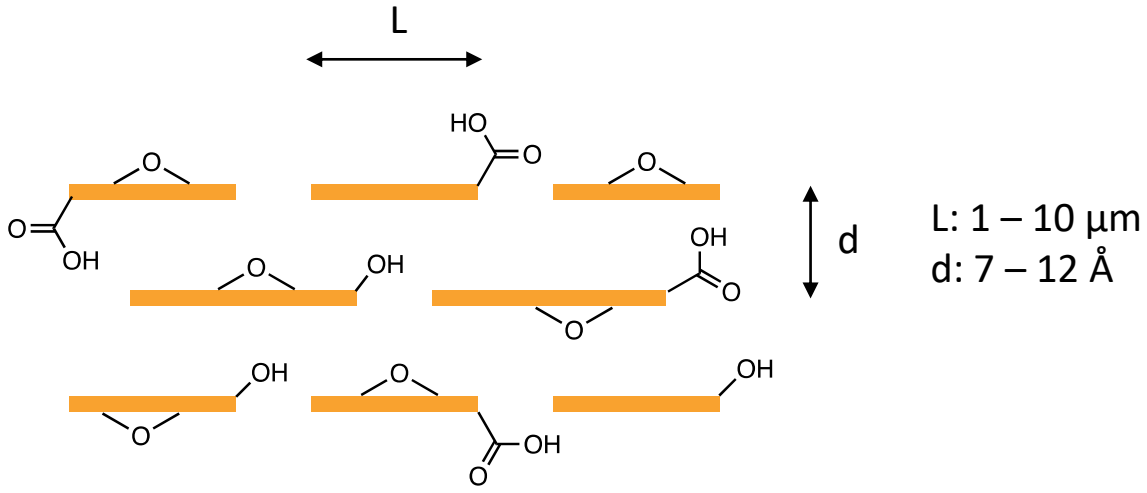
Yadav, G. G. et al. *J. Mater. Chem. A*, **2017**, 5, 15845

SANDIA-CCNY-UEP PROGRAM:
Zinc Blocking with Graphene Oxide (GO) Membrane

Graphene Oxide



Graphene Oxide Membrane

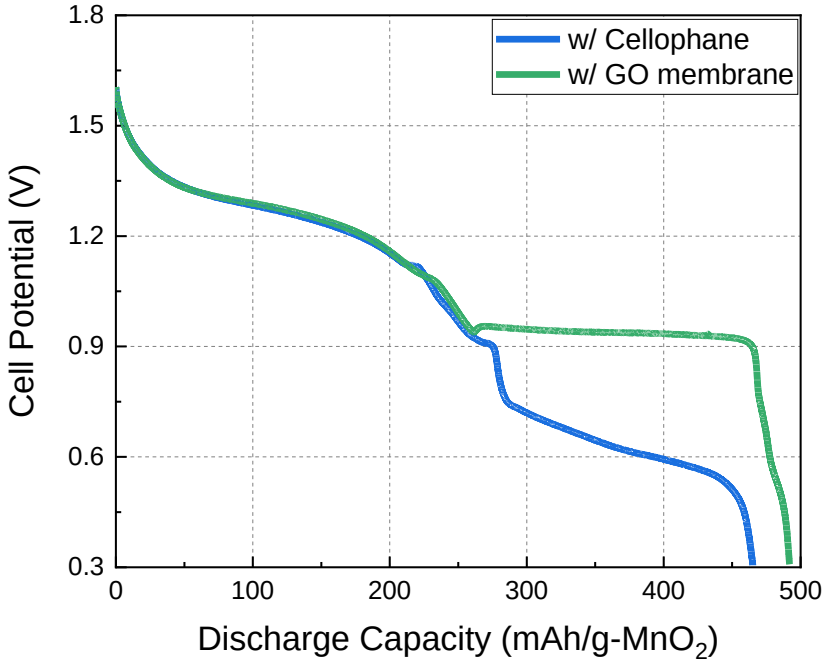


L: 1 – 10 µm
d: 7 – 12 Å

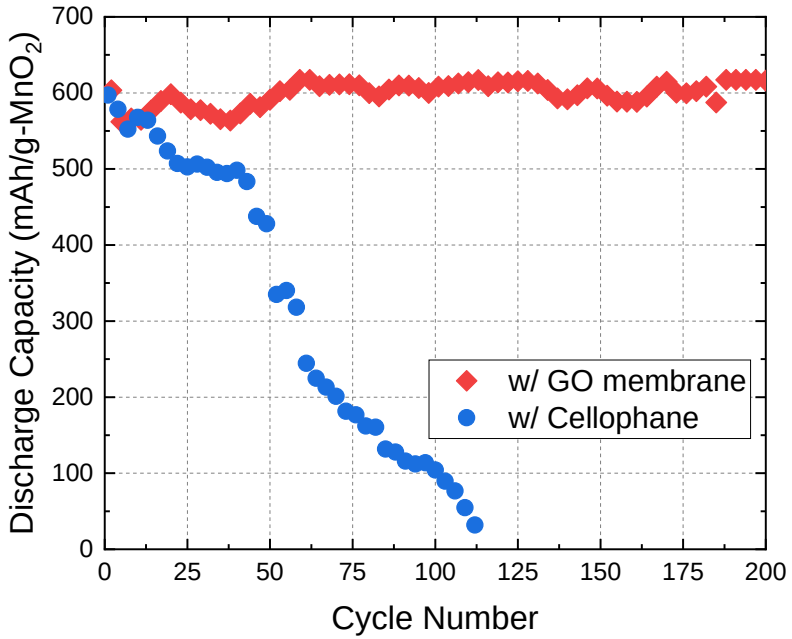
Graphene oxide membrane:
Stacked GO monolayers with narrow interlayer spacing and distinct laminar structures.

SANDIA-CCNY-UEP PROGRAM:
Zinc Blocking with Graphene Oxide (GO) Membrane

Full discharge of EMD cathode

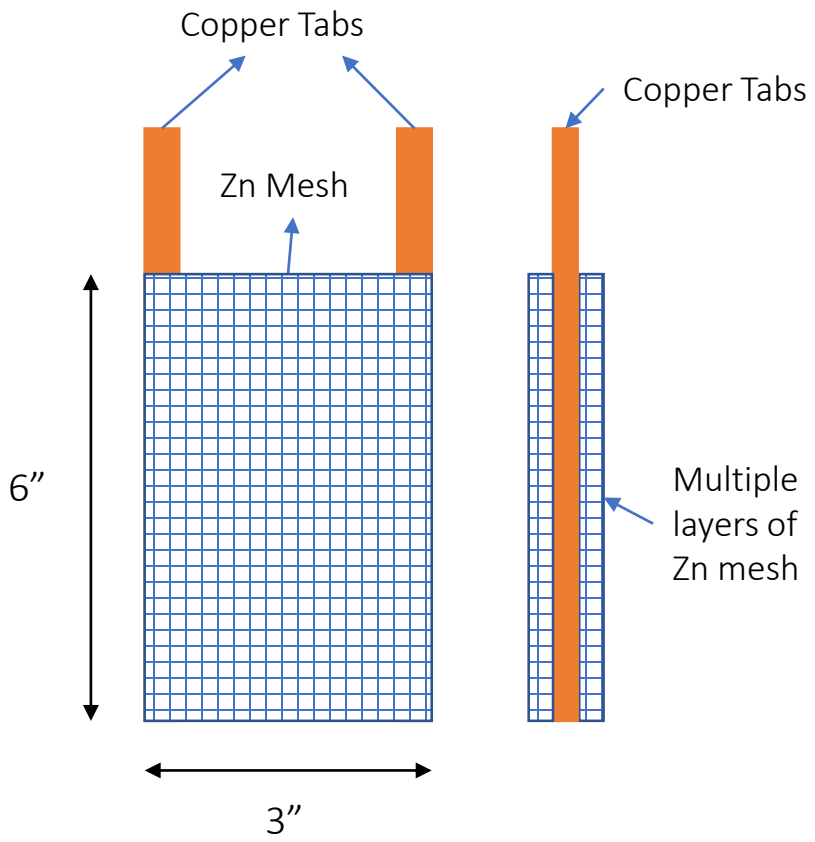


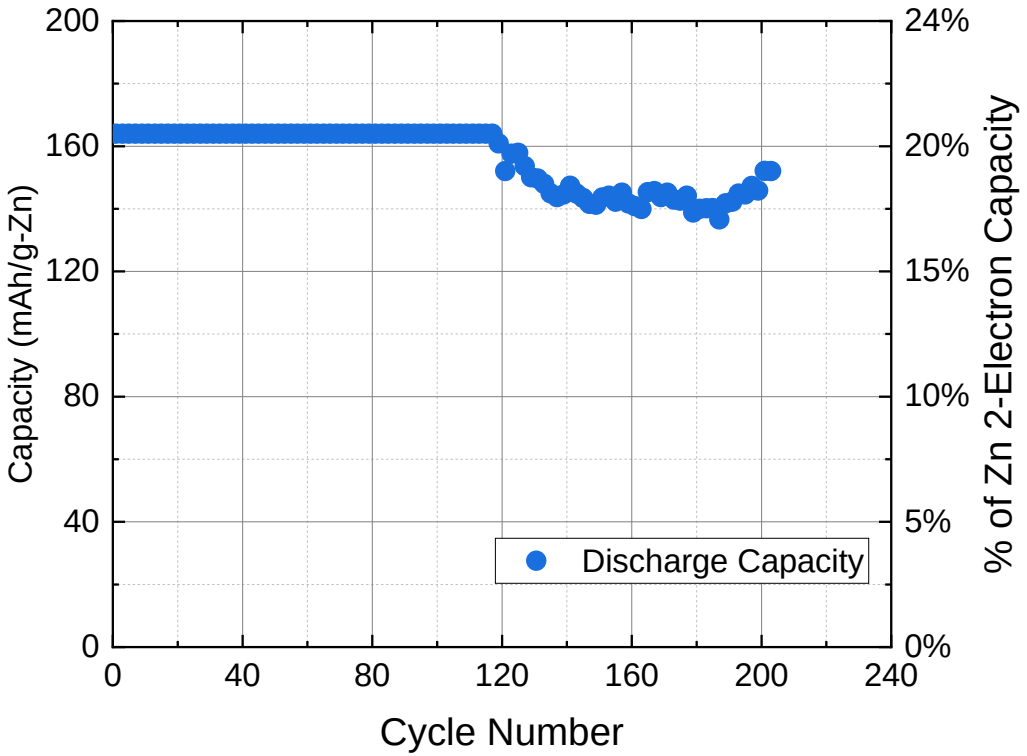
Cycling of doped birnessite cathode with 2-electron capacity



- GO membrane helps to preserve the 2nd electron potential plateau in a full discharge test, and almost doubles the achievable capacity above 0.9 V;
- The Cu^{2+} intercalated Bi-birnessite electrode achieves more than 200 cycles without any capacity fade with the application of a GO membrane.

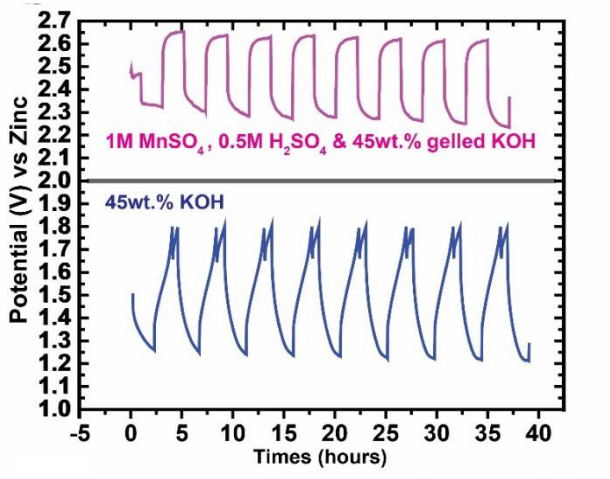
SANDIA-CCNY-UEP PROGRAM:
Increasing Anode Utilization with 3-D Zn-Mesh Electrodes

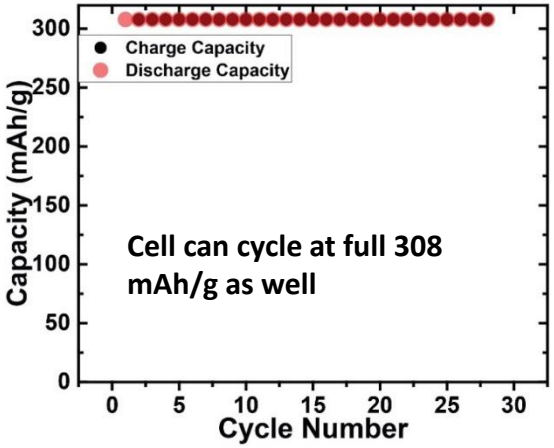




SANDIA-CCNY-UEP PROGRAM:

High Voltage Battery Cycling Performance





- Battery 4 can cycle at 100% of MnO_2 1-electron capacity with ~2.4V average potential.

ACKNOWLEDGEMENT

Thank you to Dr. Imre Gyuk, Director of the Energy Storage Program, Office Of Electricity, Department of Energy.

Thank you to the teams at CCNY, NMSU, SNL, BNL, LLNL, and UEP.

Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY | OFFICE OF ELECTRICITY