The City University of New York

CUNY ENERGY INSTITUTE

Sandia DOE Peer Review

URBAN ELECTRIC POWER

Engineering an Aqueous Energy Dense MnO_2|Zn Battery to Challenge Li-ion's Dominance

By

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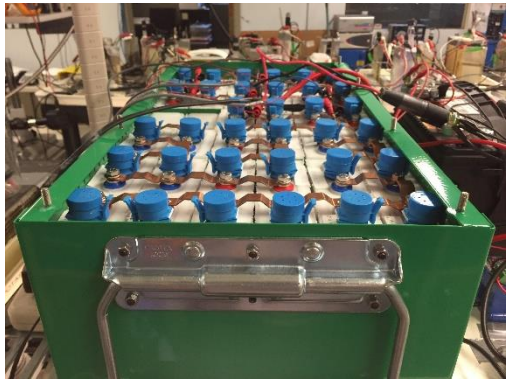


September 30th, 2020

Closer to Home …..Let’s Break Bad!

So if any Sandian’s are stuck in the desert….

Manganese Dioxide - Soil

Graphite – Brake pads

Zinc – Nuts, bolts, screws, etc

Dirt cheap!

How will we get out, Mr White?

By making a Battery!

Mr. White proceeds to make a cell

A sponge to soak up the electrolyte

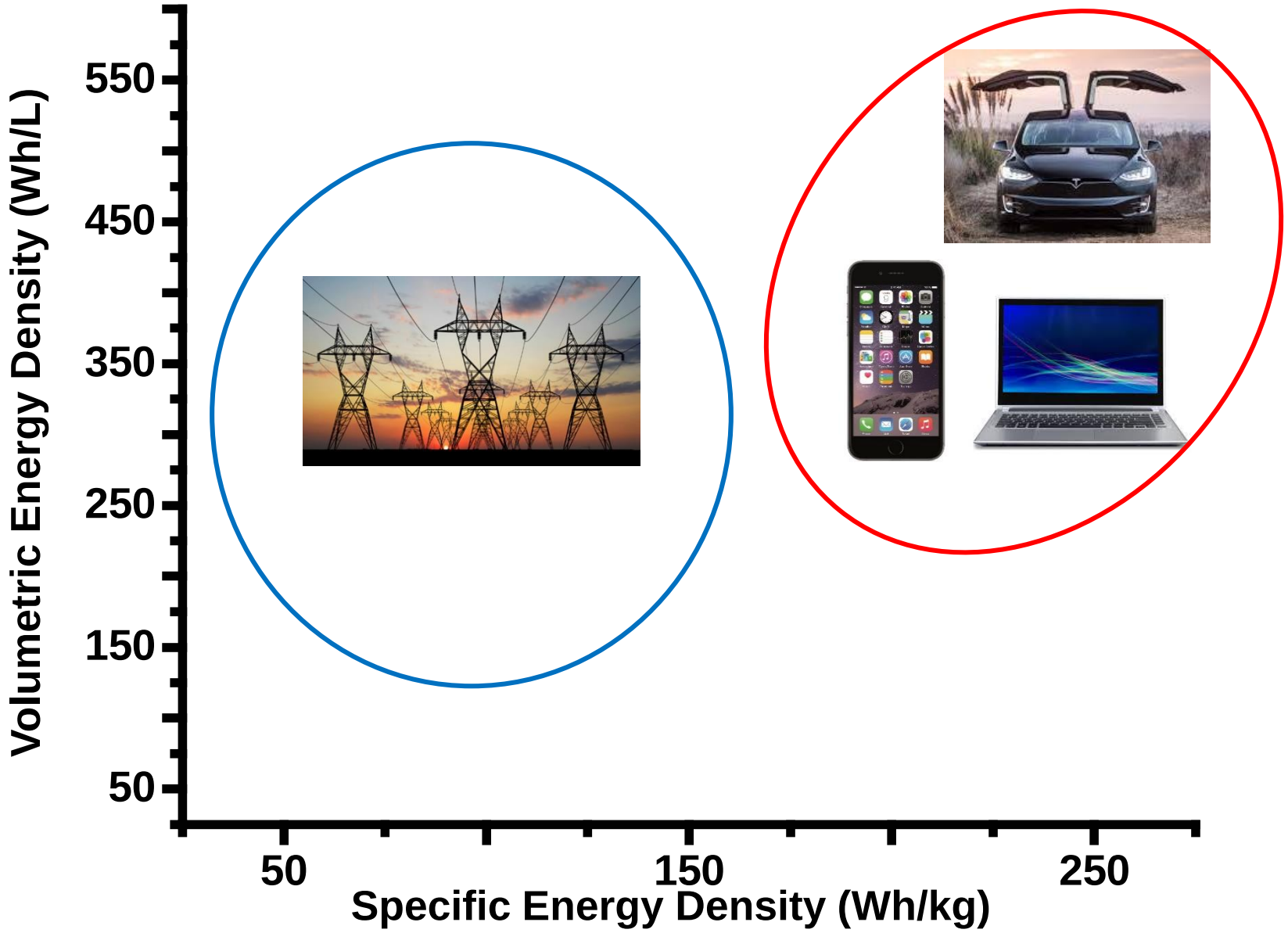
Zinc

Separator/ Electrolyte

Cathode with Graphite

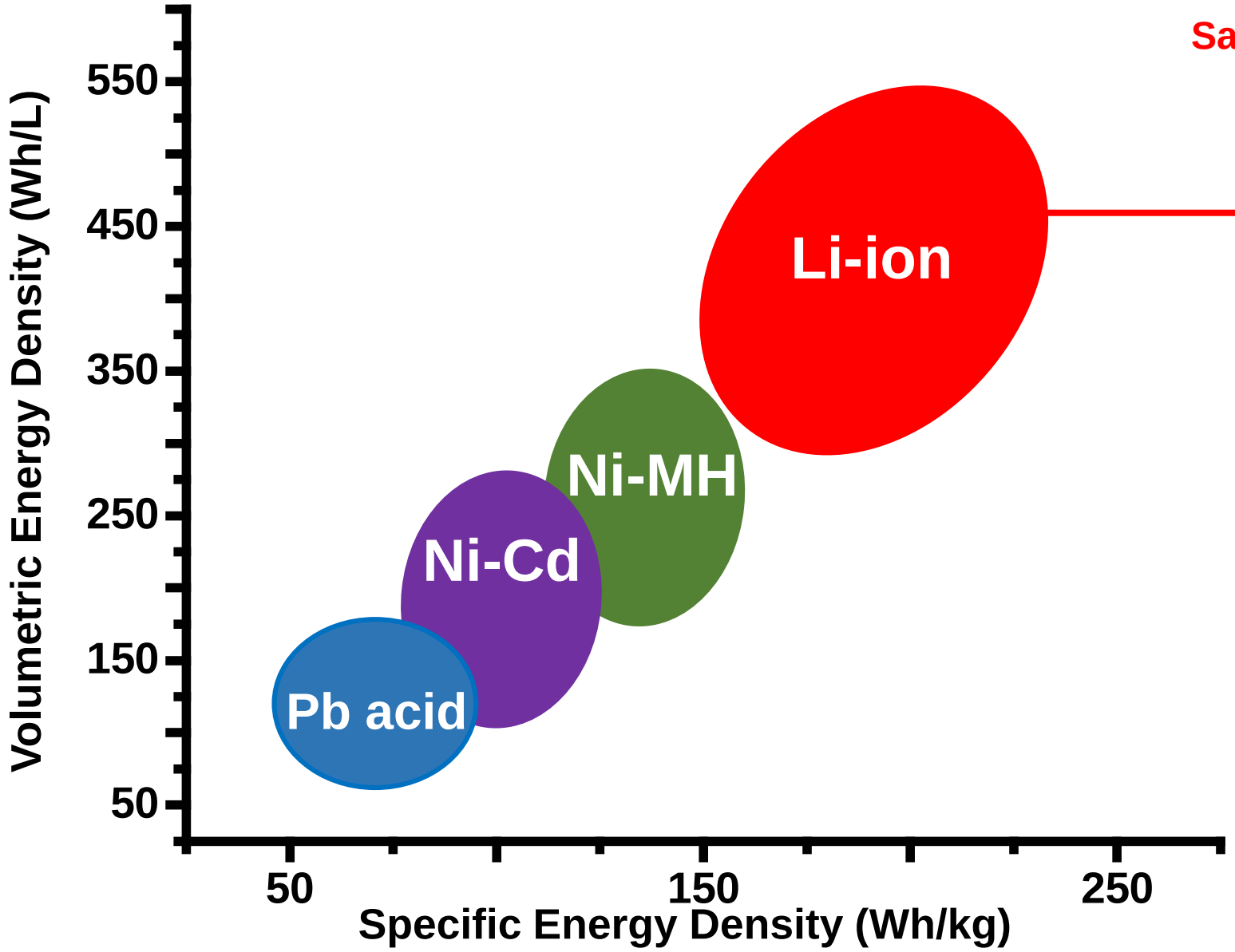
Citation: BREAKING BAD (2008)

Need for Energy Dense Batteries



Citation: G.G. Yadav (2019), Univ. Washington CEI

The Lithium Advantage



Safety is a Big Concern with Li-ion

Citation: G.G. Yadav (2019), Images taken from Google

Alkaline MnO_2|Zn Battery

MnO_2 (+)

+ Cheap
+ Abundant
+ Safe
+ ~$1/lb

Separator/Electrolyte (KOH)

* Cheap
* Abundant
* Aqueous-based
* Much safer than organic electrolytes

Zn (-)

- Cheap
- Abundant
- Safe
- ~$0.9/lb

Citation: Gautam G. Yadav (2014)

Chemistry Behind MnO_2|Zn Battery

Voltage Problem: Low Compared to Competitors

VOLTAGE ~1.2V

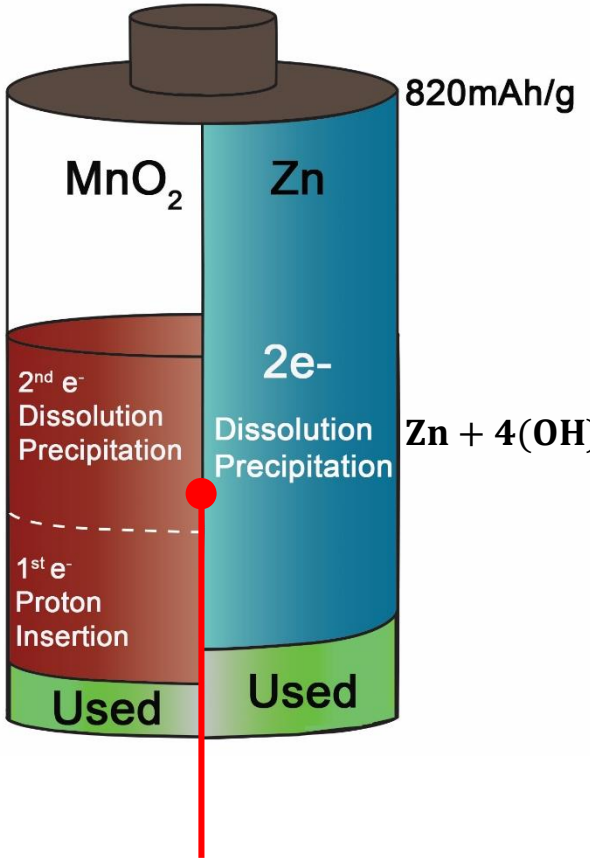
Cathode Problems

- Side Reactions
- Zinc Poisoning
  - Inactive $Mn_3O_4/ZnMn_2O_4$ Formation

- Crystal Structure Breakdown
- Zinc Poisoning
  - Inactive $Mn_3O_4/ZnMn_2O_4$ Formation

$$\mathbf{MnOOH + H_2O + e^- \rightarrow Mn(OH)_2 + OH^-}$$

$$\mathbf{\gamma - MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^-}$$



$$\mathbf{Zn + 4(OH)^- \rightarrow Zn(OH)_4^{2-} + 2e^-}$$

Anode Problems

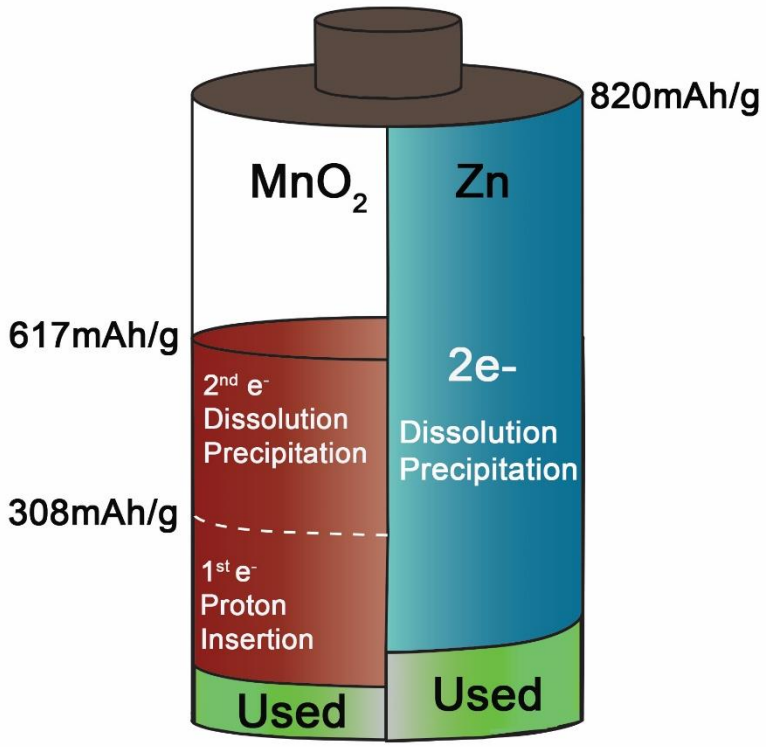
- Side Reactions
  - Hydrogen Formation
  - Passivation
  - Dendrite Formation

Separator Problems

- Block Zinc Ions from Poisoning the cathode

Citation: Gautam G. Yadav (2014)

Program Objectives



OBJECTIVE 1:

1] Obtain >75% utilization of the MnO_2 2e capacity
2] Discover new conversion cathodes
3] Obtain >20% utilization of Zn anodes

OBJECTIVE 2:

1] Develop transportable battery that are non-spillable that fit Department of Transportation regulations
2] Development of Gel Batteries

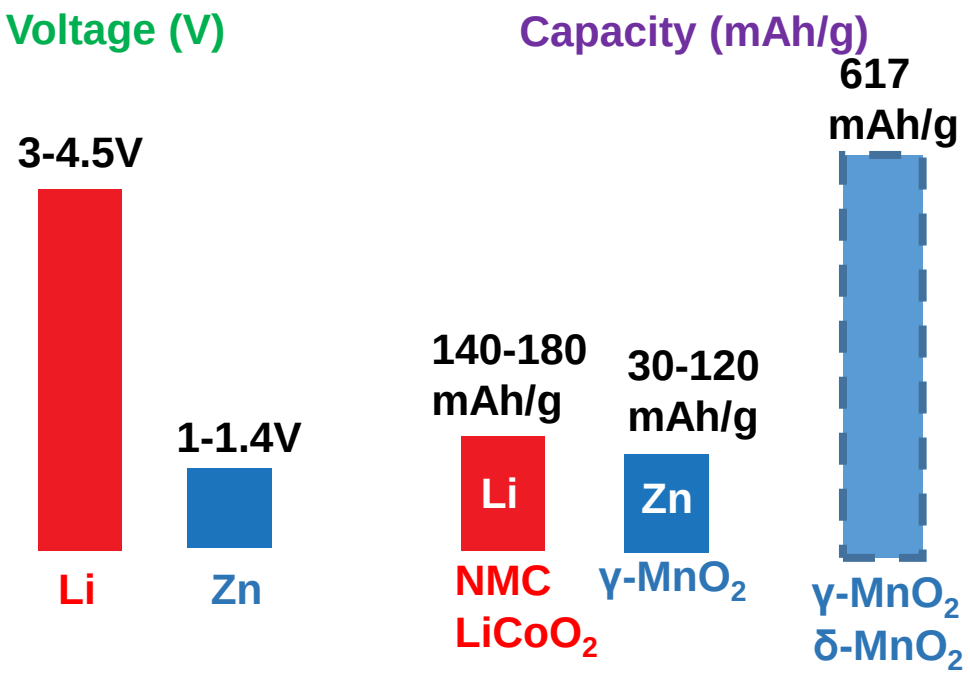
OBJECTIVE 3:

1] Increase the voltage of the Zn|MnO_2 battery >2V
2] Develop prototype versions of the high voltage Zn|MnO_2 Battery.

ULTIMATE OBJECTIVE: Create a Zn|MnO_2 battery that competes with Lithium

How Can We Compete with Lithium?

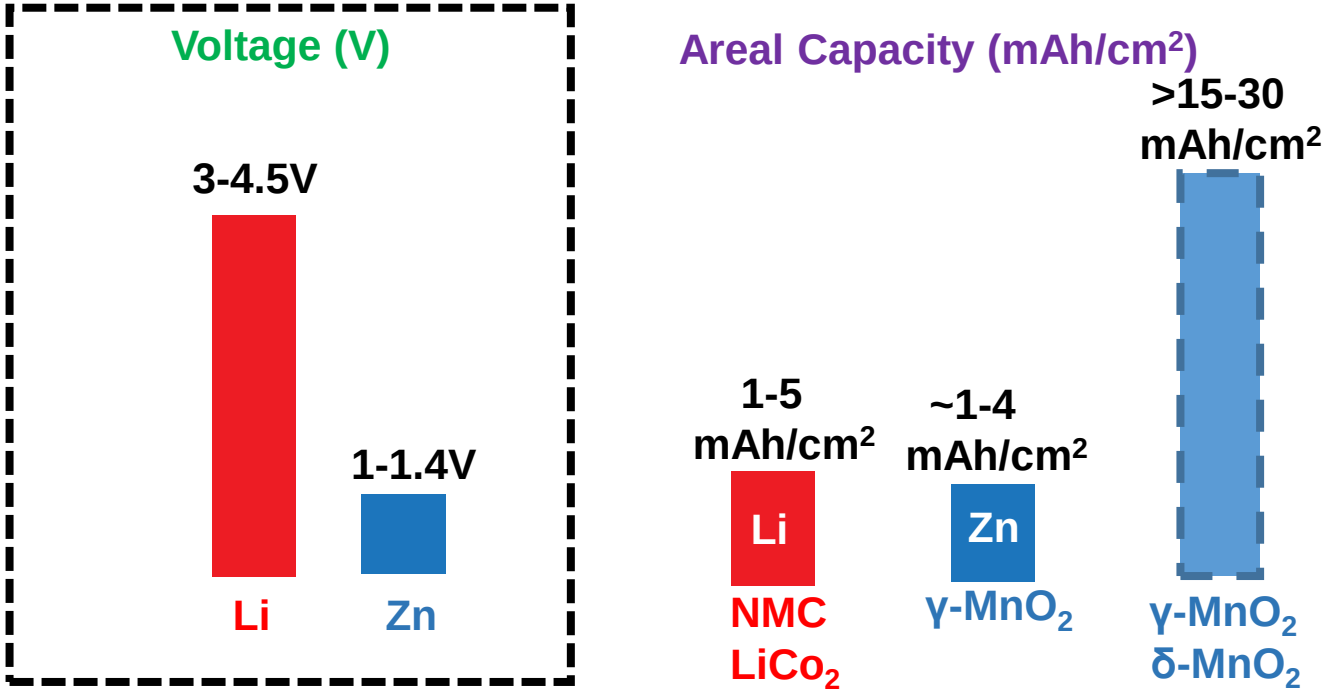
Energy = Voltage (V) x Capacity (mAh/g)



***Lithium** wins Easily!*

Unless High Capacity Can be Accessed

Energy = Voltage (V) x Areal Capacity (mAh/cm²)



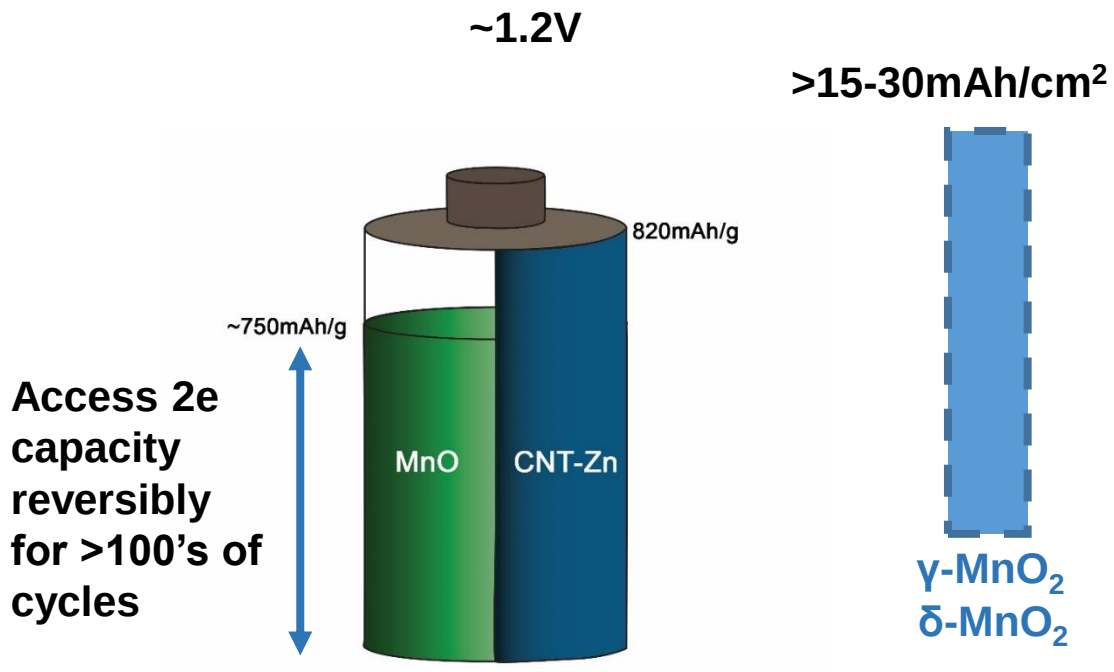
Can We Break the Voltage Barrier for Aqueous Zn Batteries?

High Areal Capacity is a Must!

Citation: Gautam G. Yadav et al Chemical & Engineering News (2020)

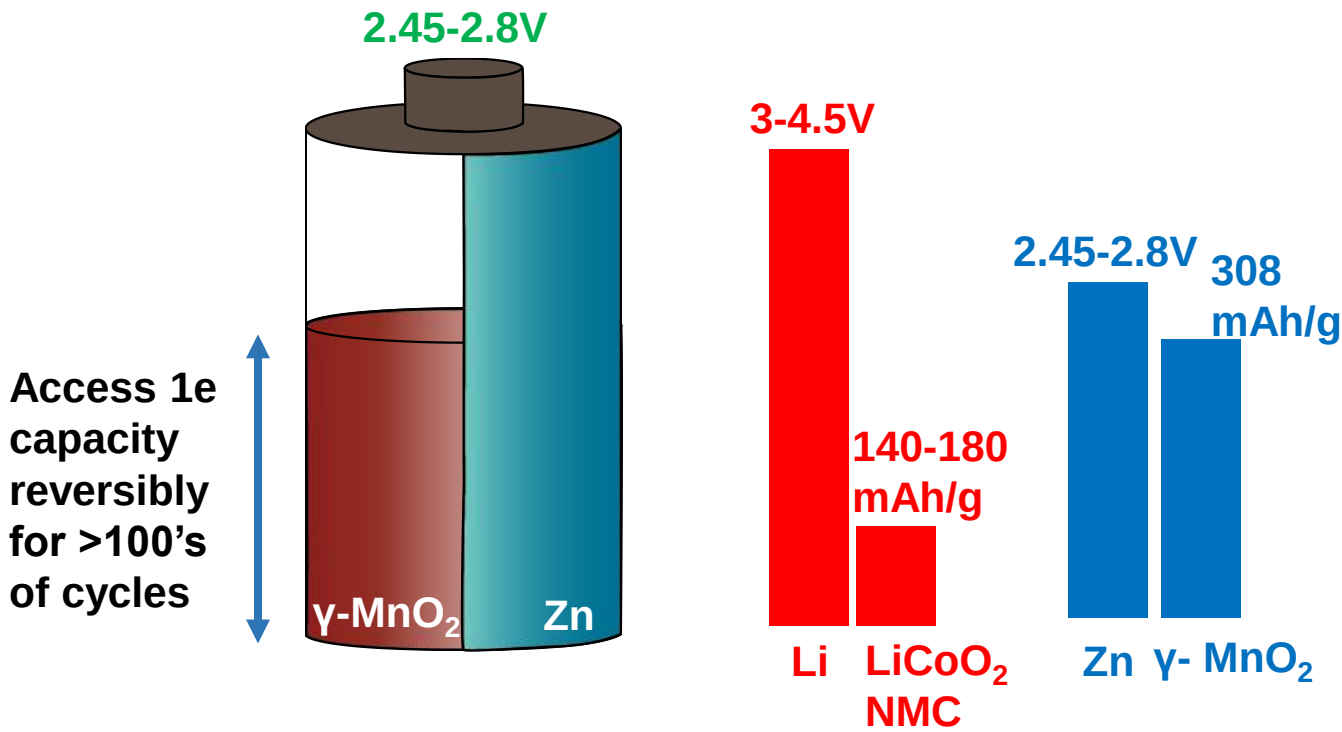
The Battery Wars

Part 1: Accessing the 2nd electron capacity of MnO_2 or other conversion electrodes at High Areal Capacities



Published in:
1] Nature Communications (2017)
2] Journal of Materials Chemistry A (2017)
3]Materials Today Energy (2018)
4] International Journal of Hydrogen Energy (2018)
5] Advanced Energy Materials (2019)

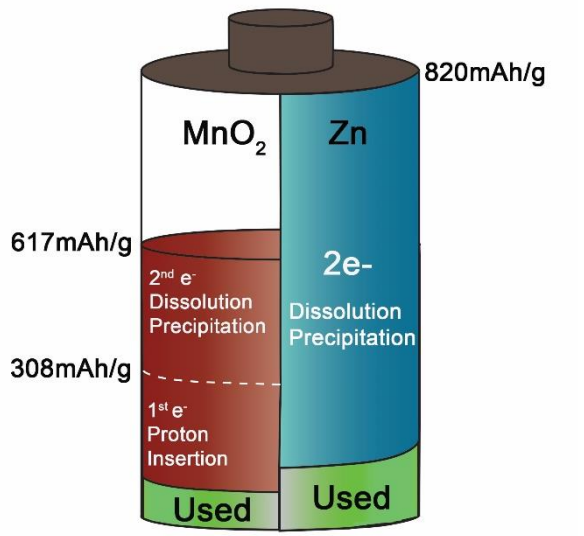
Part 2: Breaking the 2V Barrier in Aqueous Zinc anode Batteries Making Zinc the new Lithium



Published in:
1] ACS Energy Letters (2019)
2] Chemical Engineering & News Invited Review (2020)
3] Submitted for Peer Review (2020)
4] Submitted for Peer Review (2020)
5] Invited Review, Manuscript in preparation for Carbon Energy (2020)

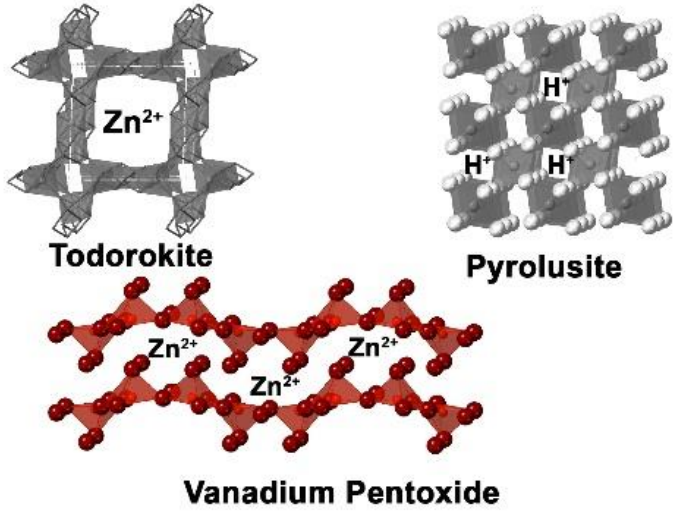
Going Beyond Intercalation Capacity

Current Status Quo of Alkaline MnO_2/Zn Batteries



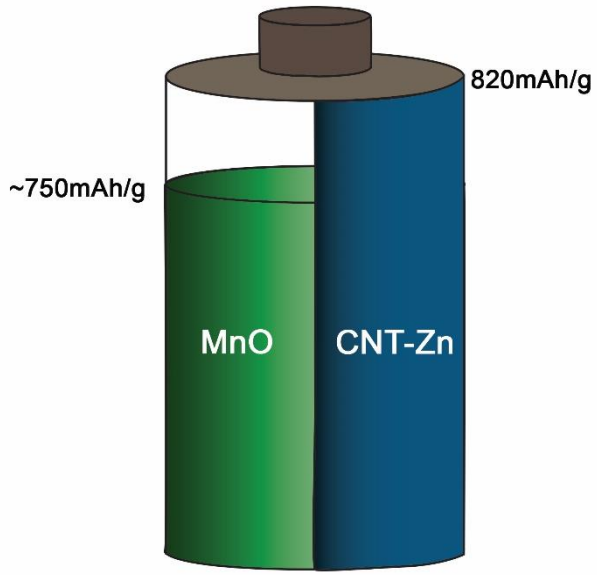
Capacity used in Commercial Rechargeable Cells

Capacity Limitation of Zn and Proton Intercalation Systems



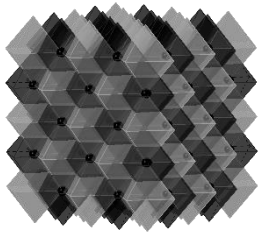
Limited Capacity
Excess Intercalation can lead to structure breakdown

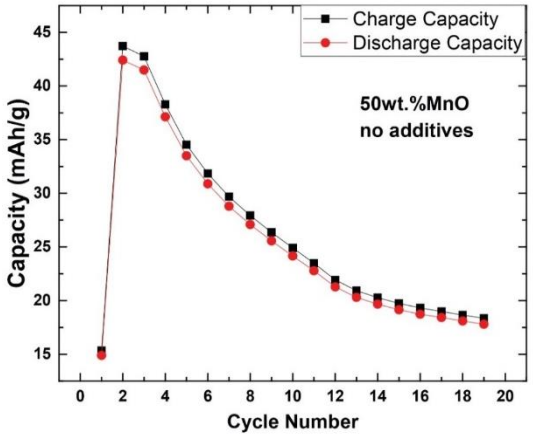
Proposed Conversion-based High Capacity & Energy Dense MnO/CNT-Zn Batteries

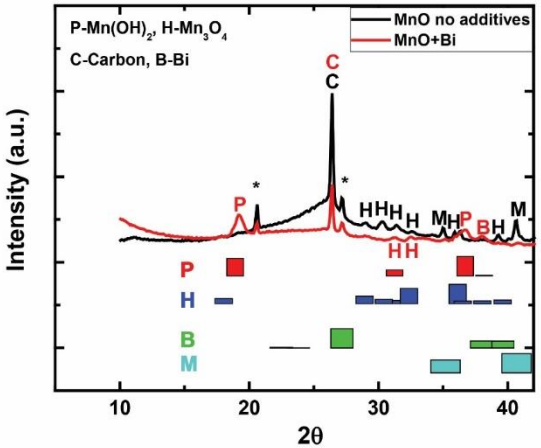


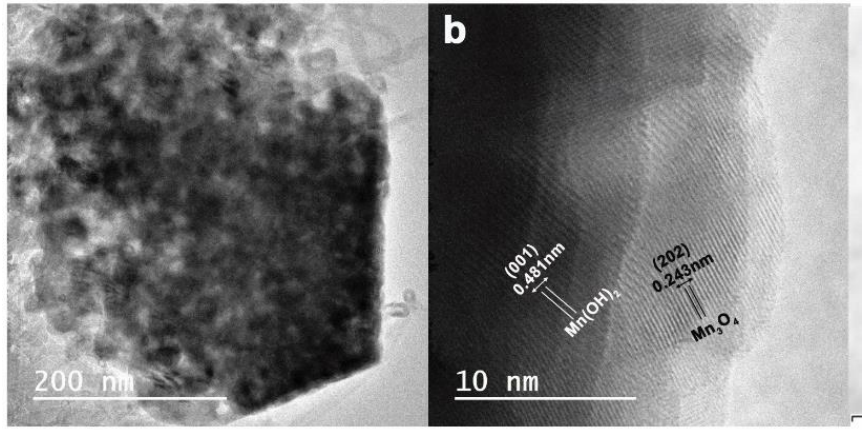
Citation: G. G. Yadav et al., Nature Communications (2017), G. G. Yadav, et al. Advanced Energy Materials (2019)

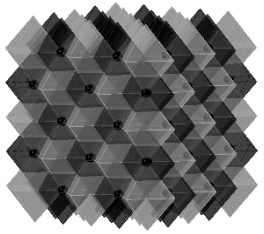
Cycling Rocksalt MnO

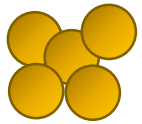


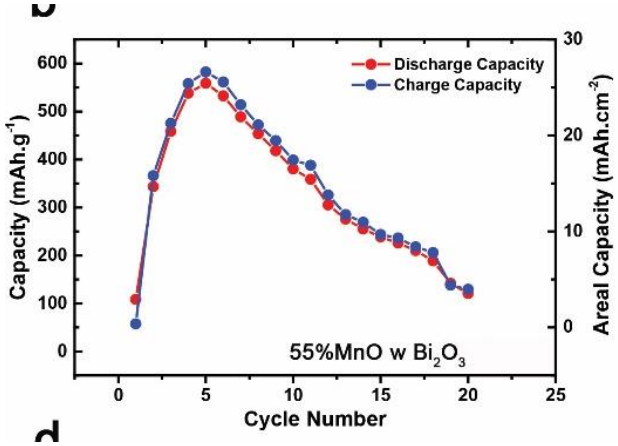


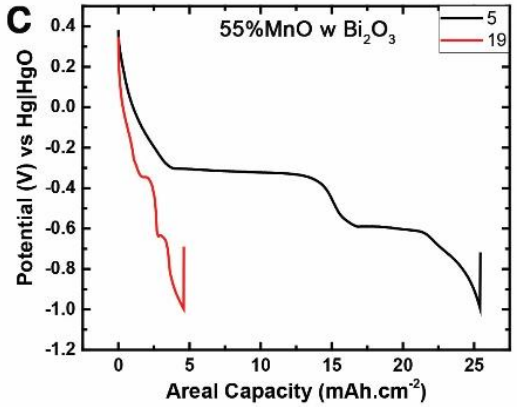


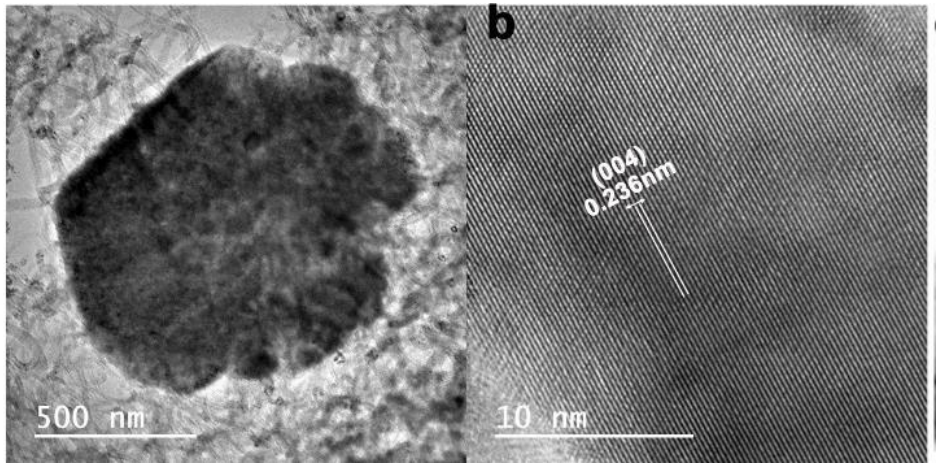






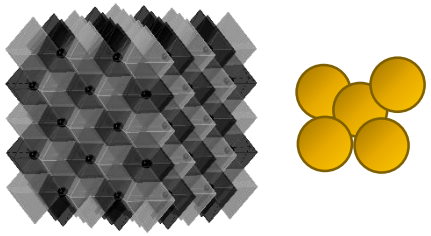






Citation: G. G. Yadav, et al. Advanced Energy Materials (2019)

Rechargeable Rocksalt MnO: Accessing the Conversion Capacity



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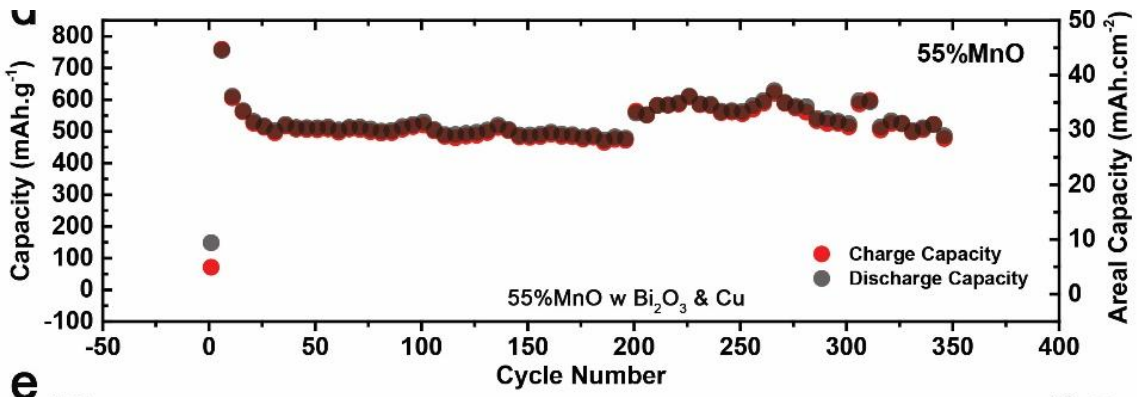
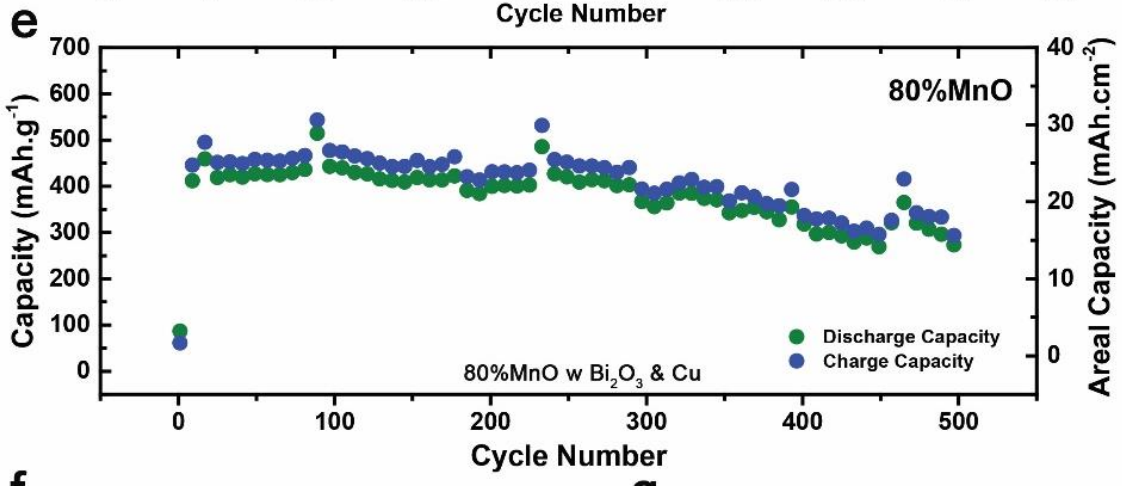
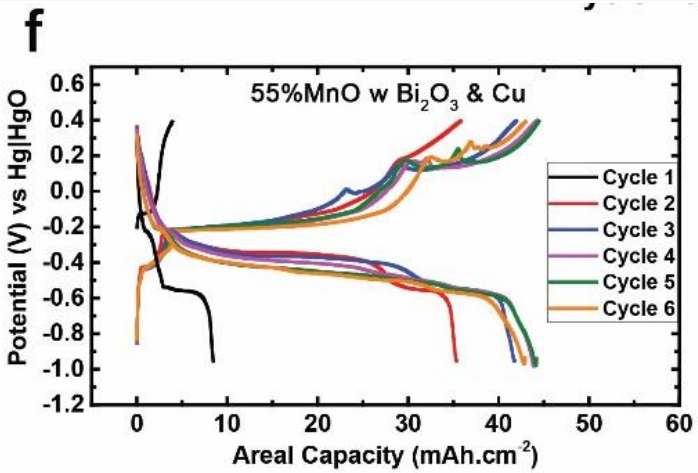
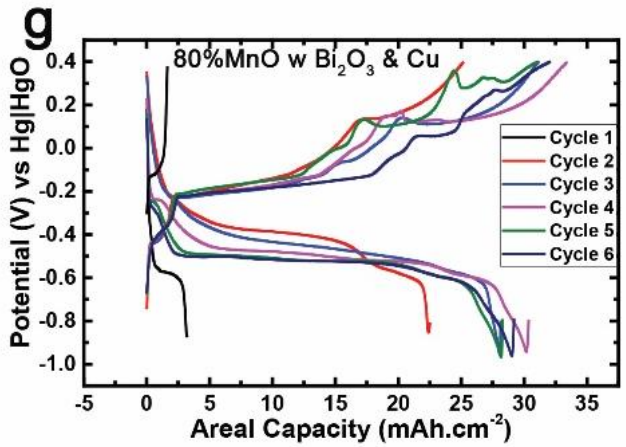


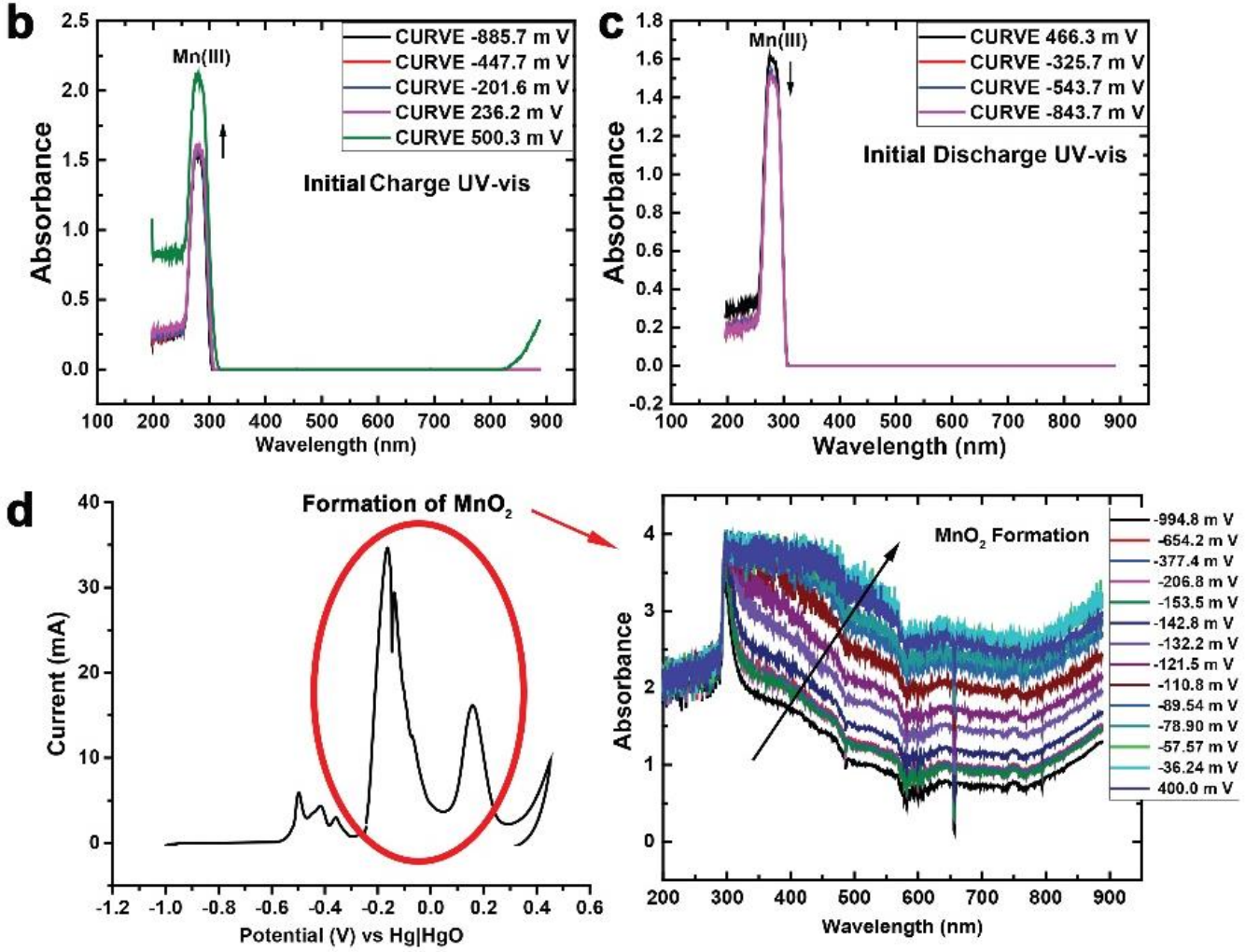






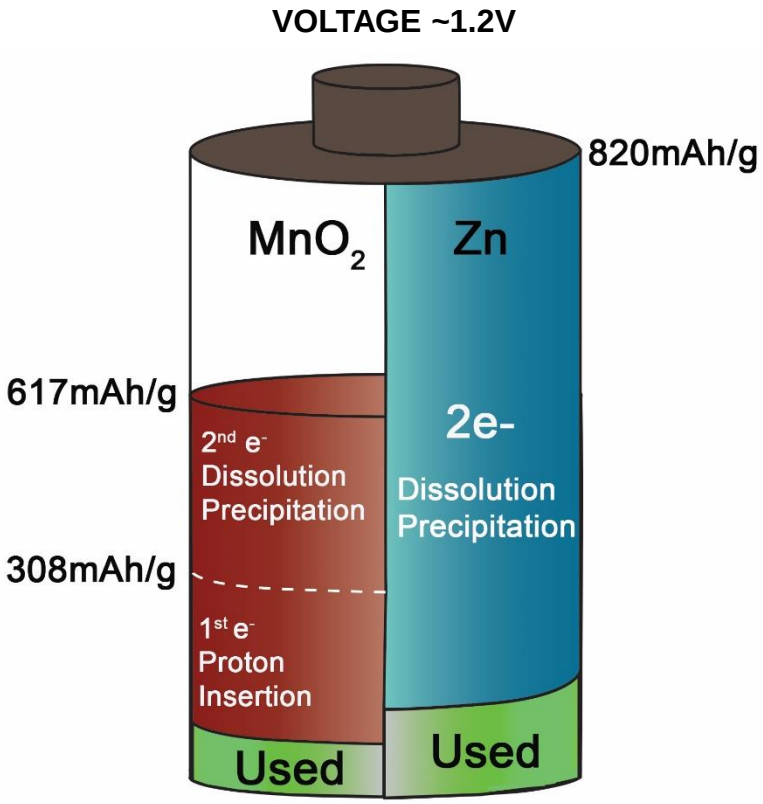
Citation: G. G. Yadav, et al. Advanced Energy Materials (2019)

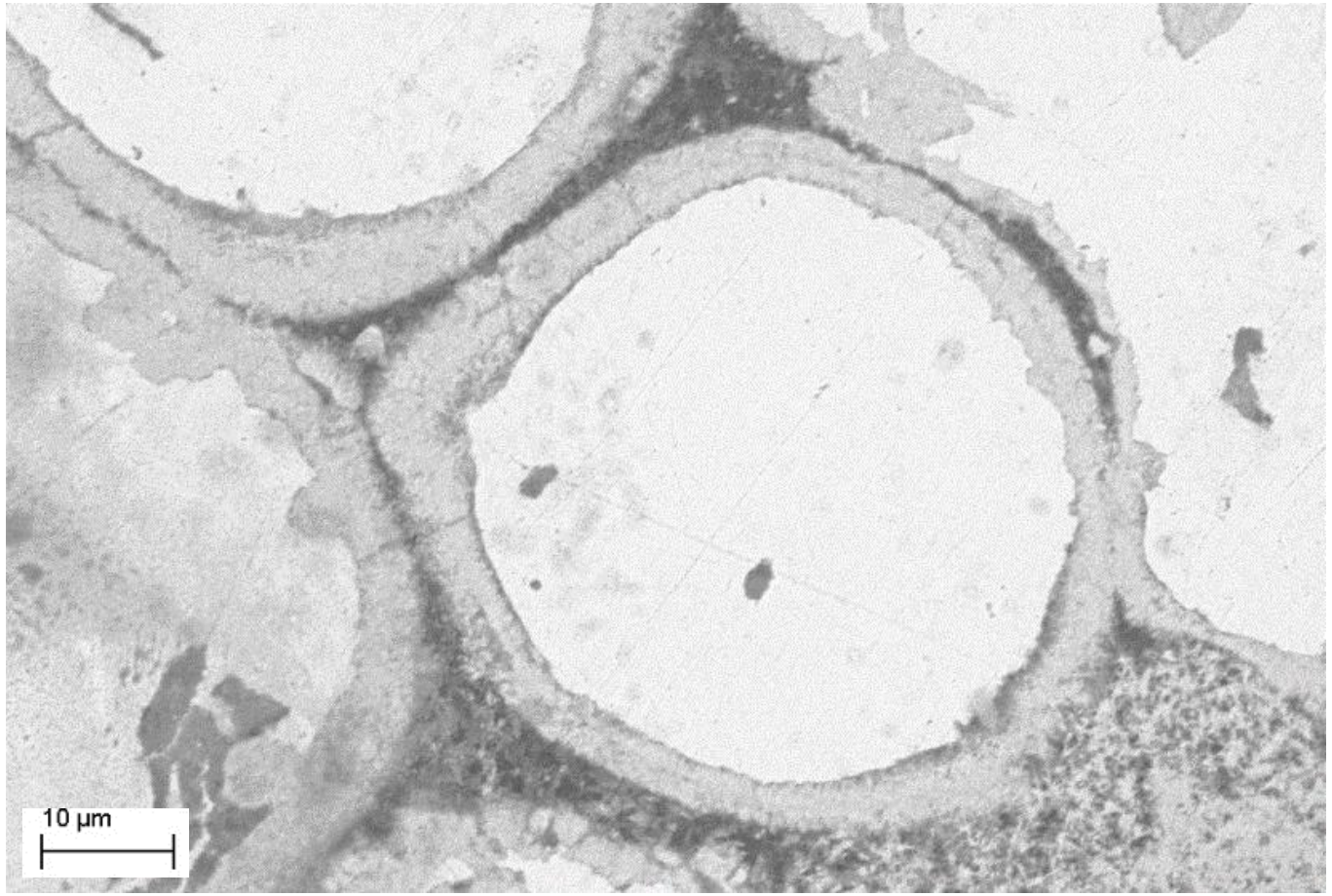
Real Time In-Situ Microscopy



Citation: G. G. Yadav, et al. Advanced Energy Materials (2019)

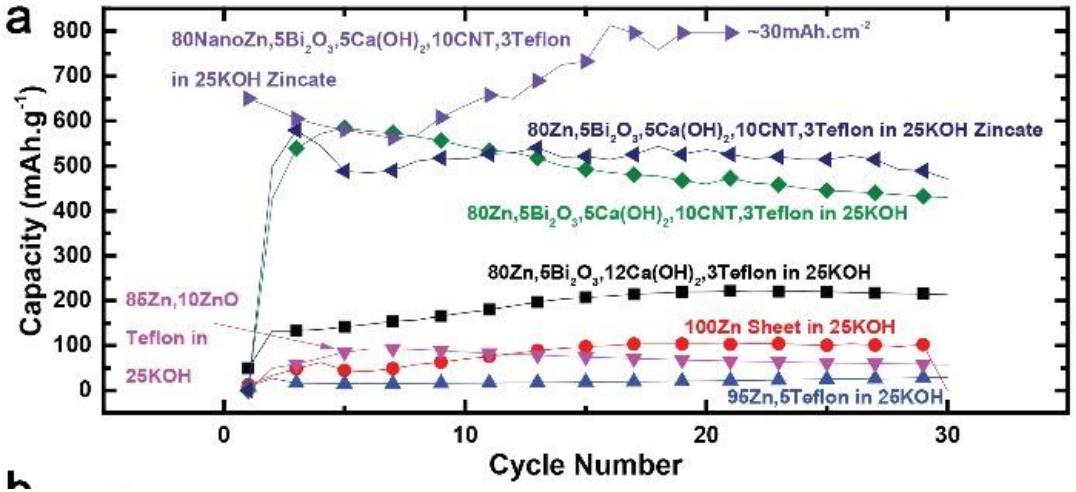
Challenges With The Zinc Anode

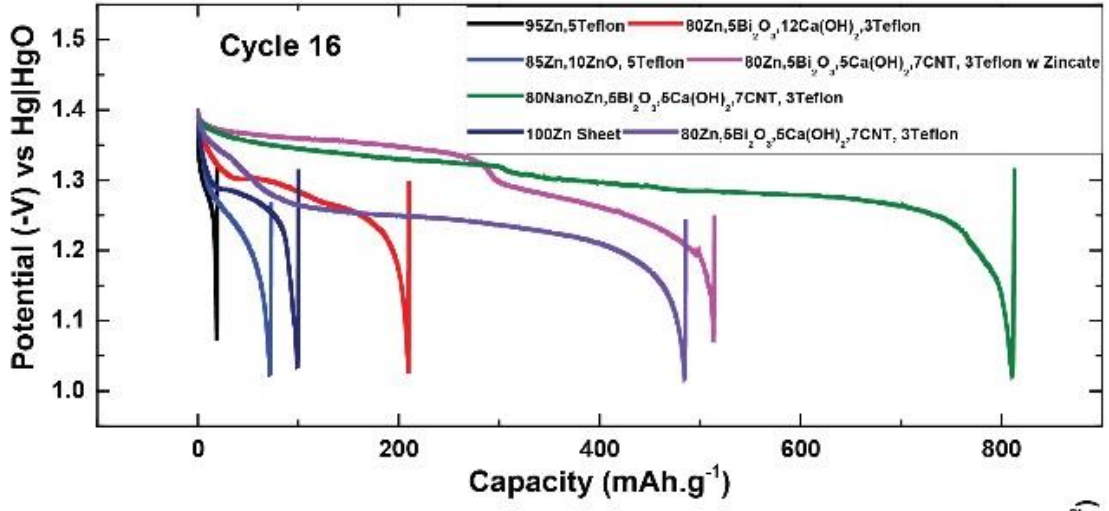


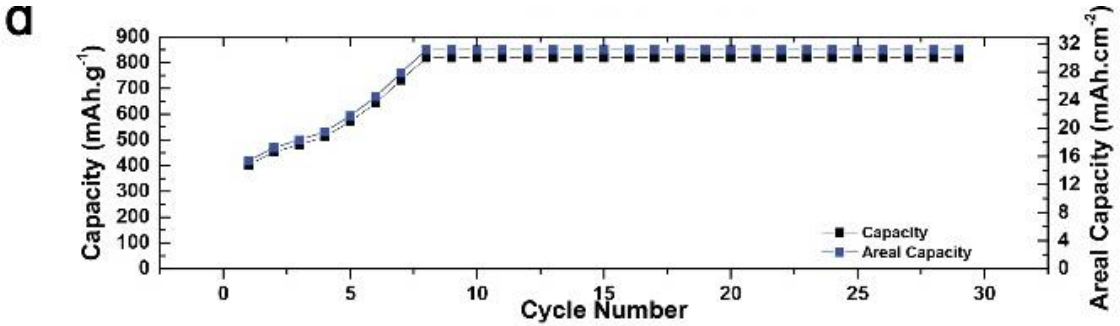


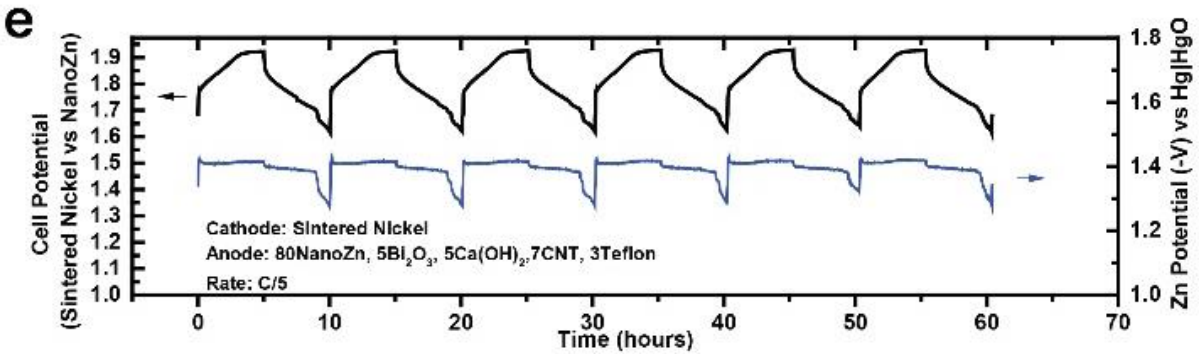
Citation: Jinchao Huang, Thesis (2018)

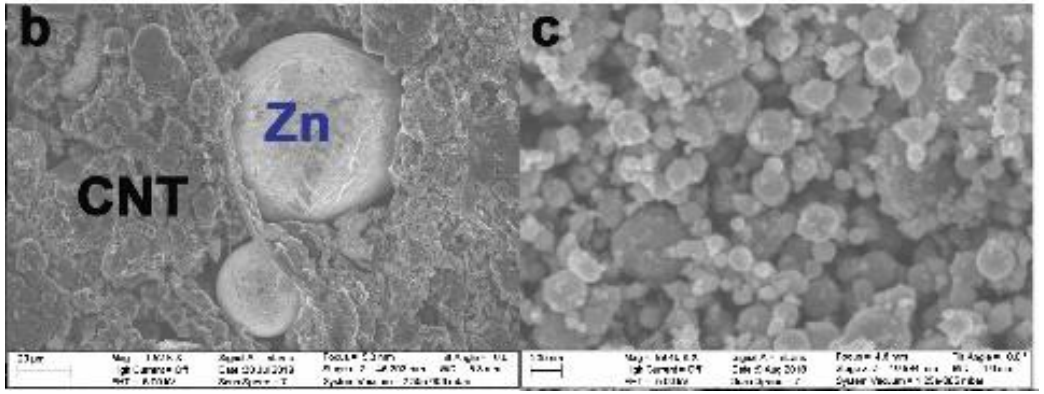
Solving the Zinc Anode Problem





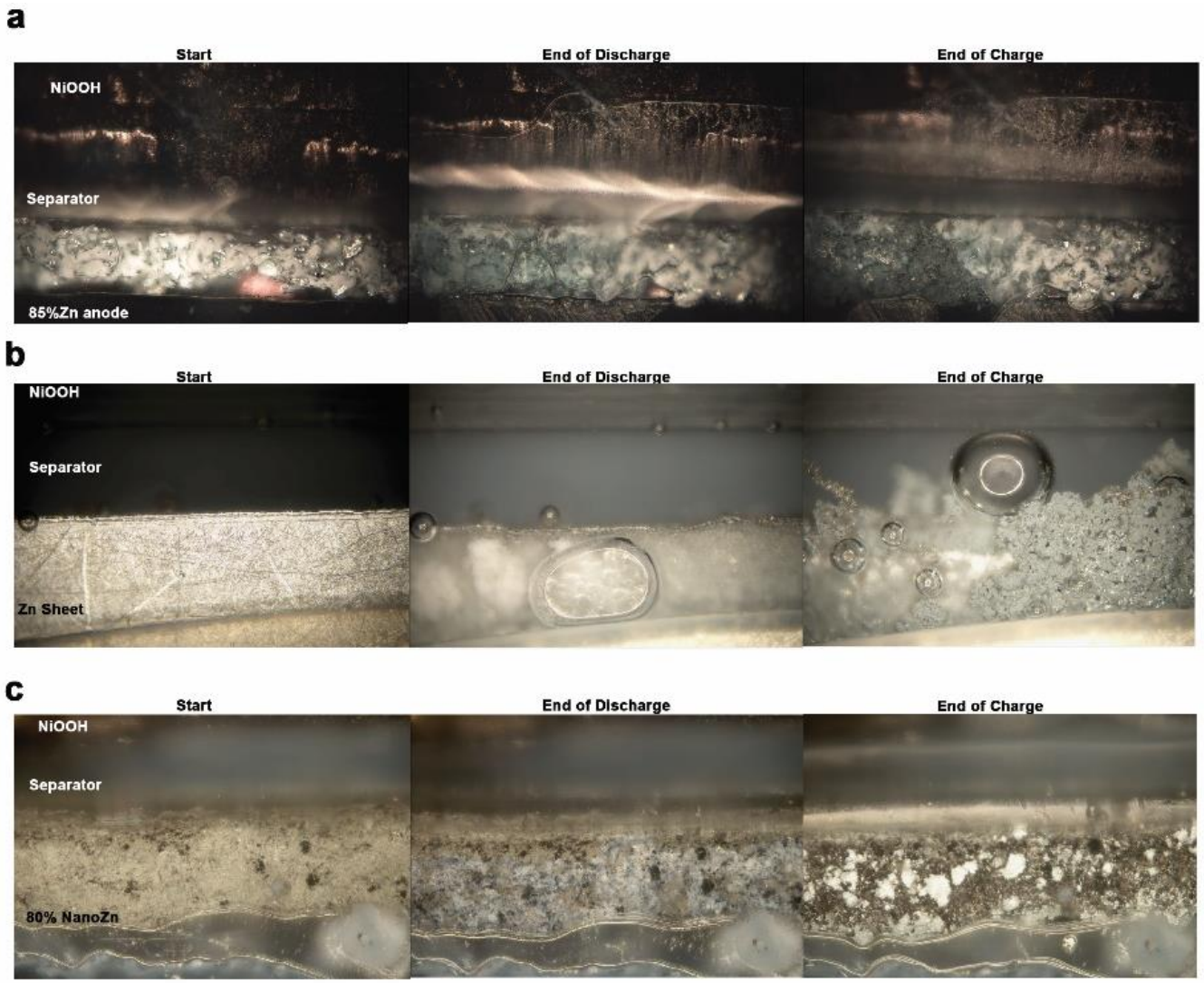


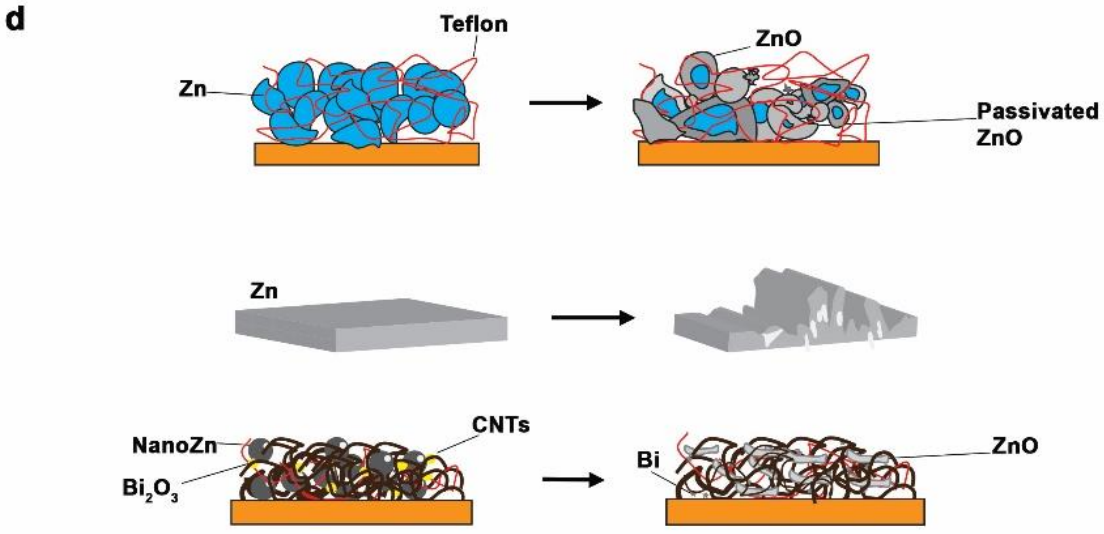


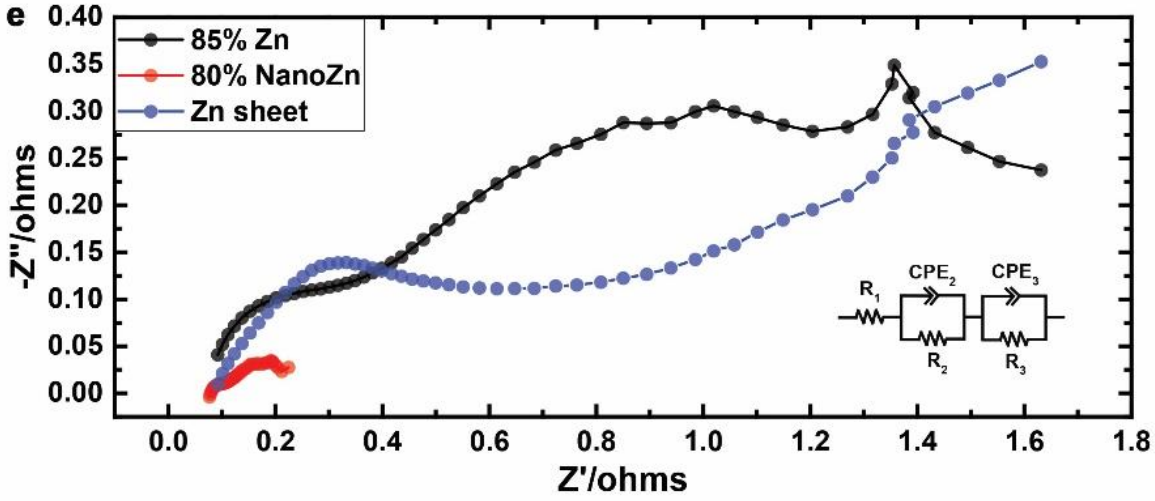


Citation: G. G. Yadav, et al. Advanced Energy Materials (2019)

Real Time In-Situ Imaging of Zinc Anodes

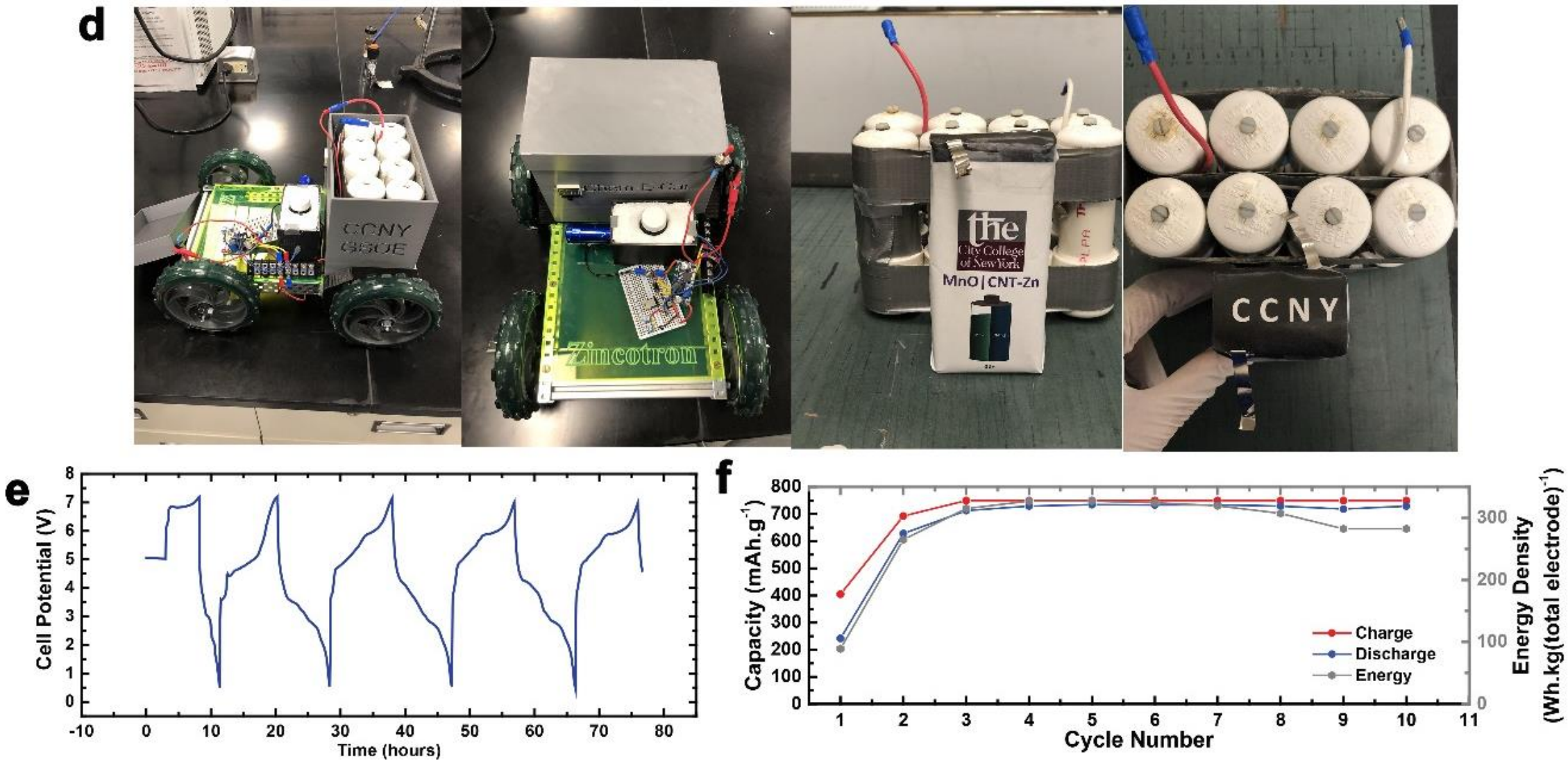






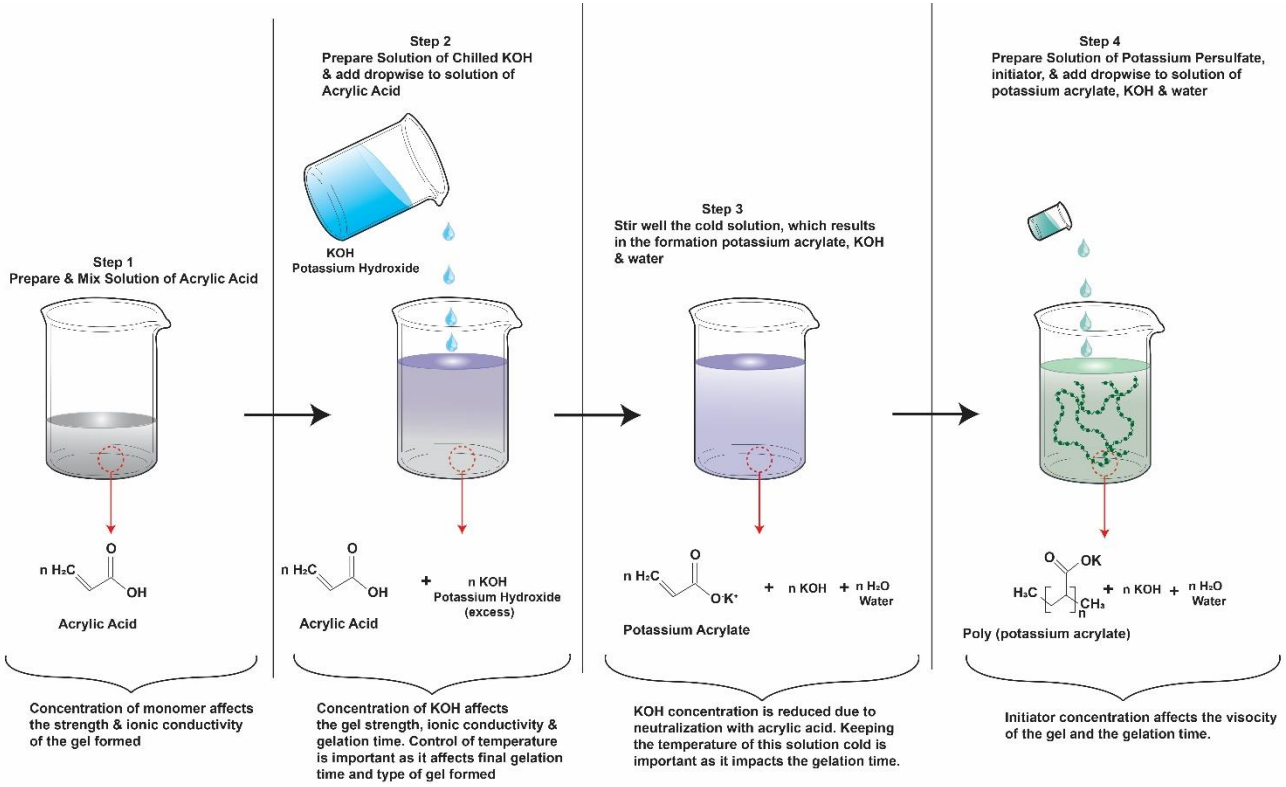
Citation: G. G. Yadav, et al. Advanced Energy Materials (2019)

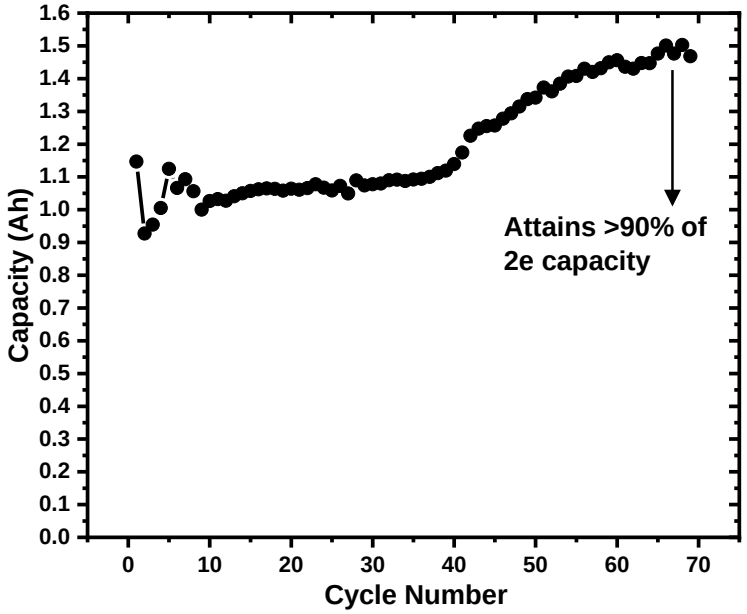
Application of The New Battery



Citation: G. G. Yadav, et al. Advanced Energy Materials (2019)

Hydrogels for 2nd Electron Batteries

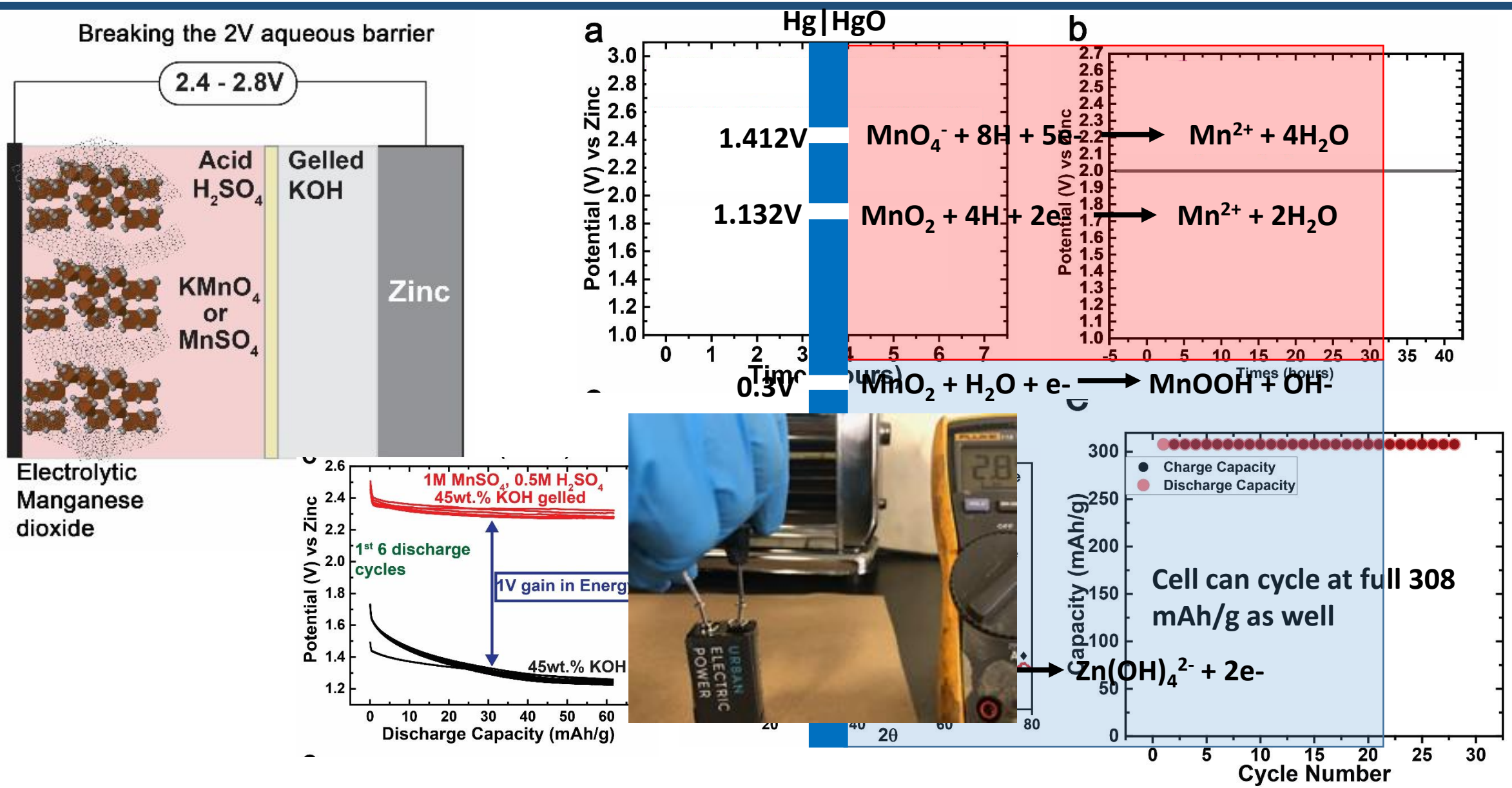




UEP's next generation of batteries will hydrogels to make non-spillable batteries. These hydrogels have been optimized to give the 2nd electron capacity of MnO_2

Citation: G. G. Yadav, et al. submitted for peer review (2020)

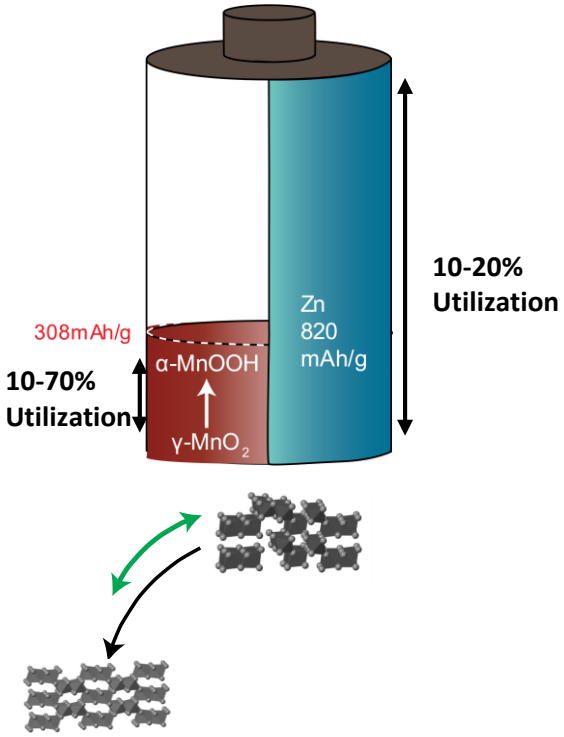
PART 2: Breaking the 2V Barrier in Zinc Anode Batteries



Citation: G. G. Yadav et al., ACS Energy Letters (2019), G. G. Yadav et al. submitted for peer review (2020)

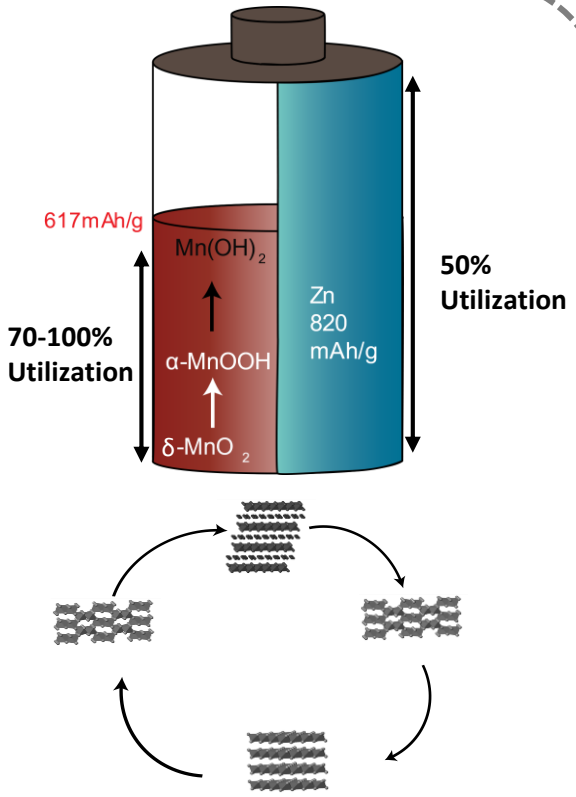
Classification of MnO_2|Zn Batteries

Battery 1 and 2
Proton Insertion Battery



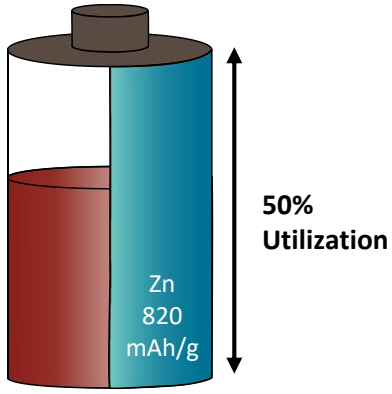
- Analogous to the Li-ion intercalation chemistry.
- Rechargeable utilization till 70% of proton insertion chemistry.
- Inactive spinel formation beyond 70% utilizations.

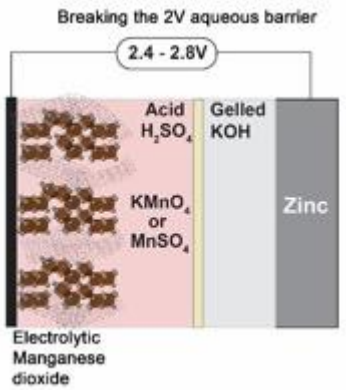
Battery 3
Conversion Battery



- 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.

Citation: Gautam G. Yadav, in peer review (2020), G. G. Yadav et al. Chemical Engineering & News (2020)

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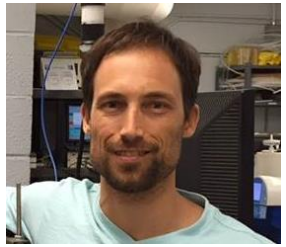

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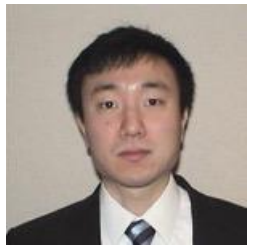

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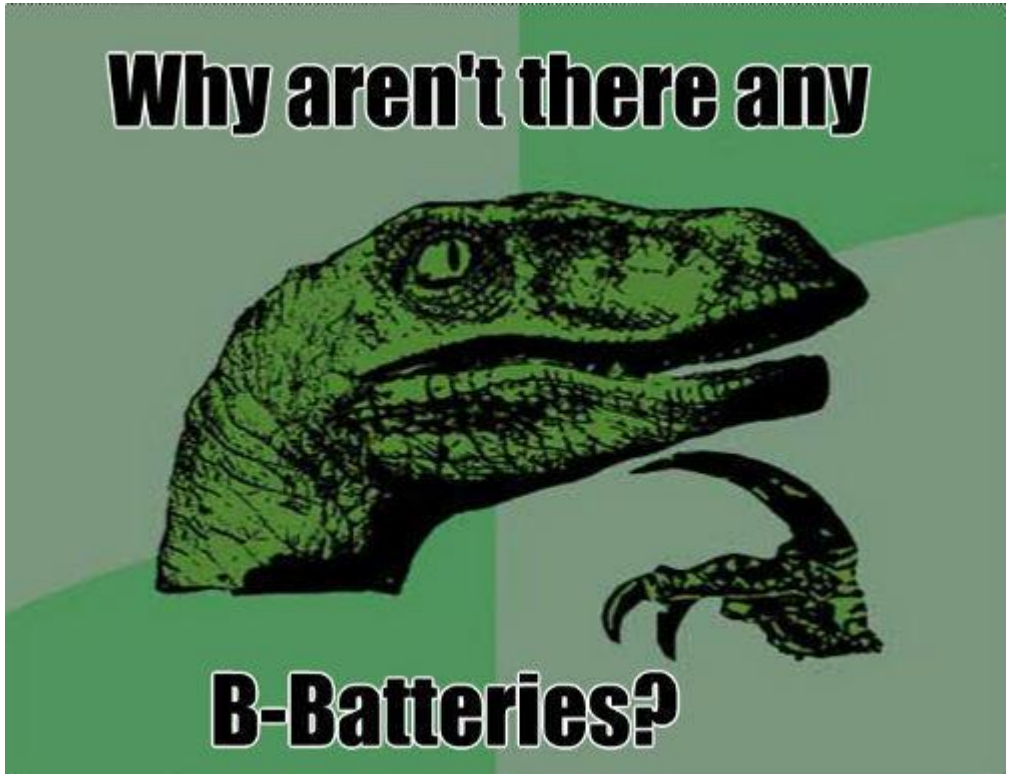
nyserda Energy. Innovation. Solutions.

Thank You!

Questions?