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Optimization of Hydrogels for Non-spillable Zn|MnO_2 Rechargeable Batteries Allowing for the 2nd Electron MnO_2 cycling

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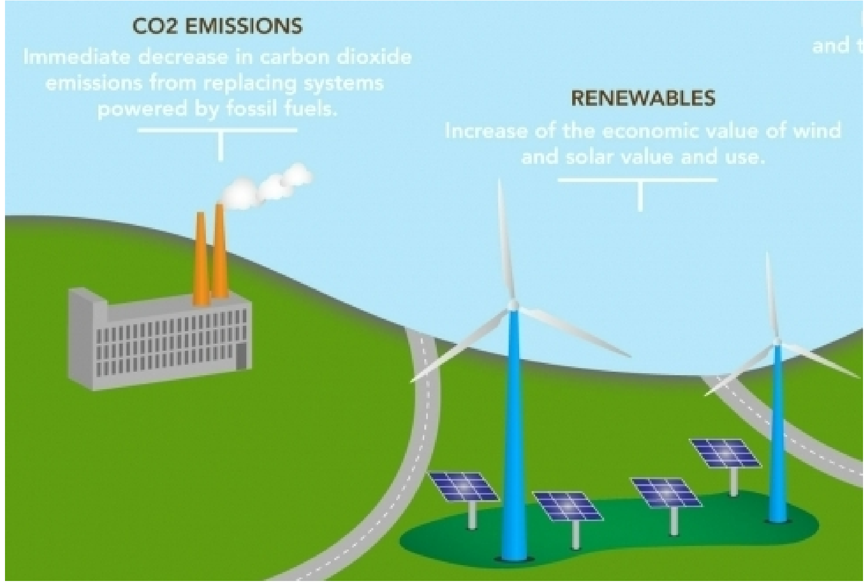
Need for Energy Storage

- To combat climate change further penetration of renewable sources of energy like solar and wind are required, which can be improved by energy storage devices like batteries

- Two most dominant battery chemistries: Lead acid and Lithium-ion

- Both are unfortunately toxic, expensive and unsafe



Why Zn|MnO_2 battery?

Cheap

Zn: \$4.1 kg^{-1}
MnO_2: \$1.58 kg^{-1}
KOH: \$1.97 kg^{-1} (1)

Abundant

Identified
Mn ~ 0.86 million tons
Zn ~1.9 billion tons(2)

Safe

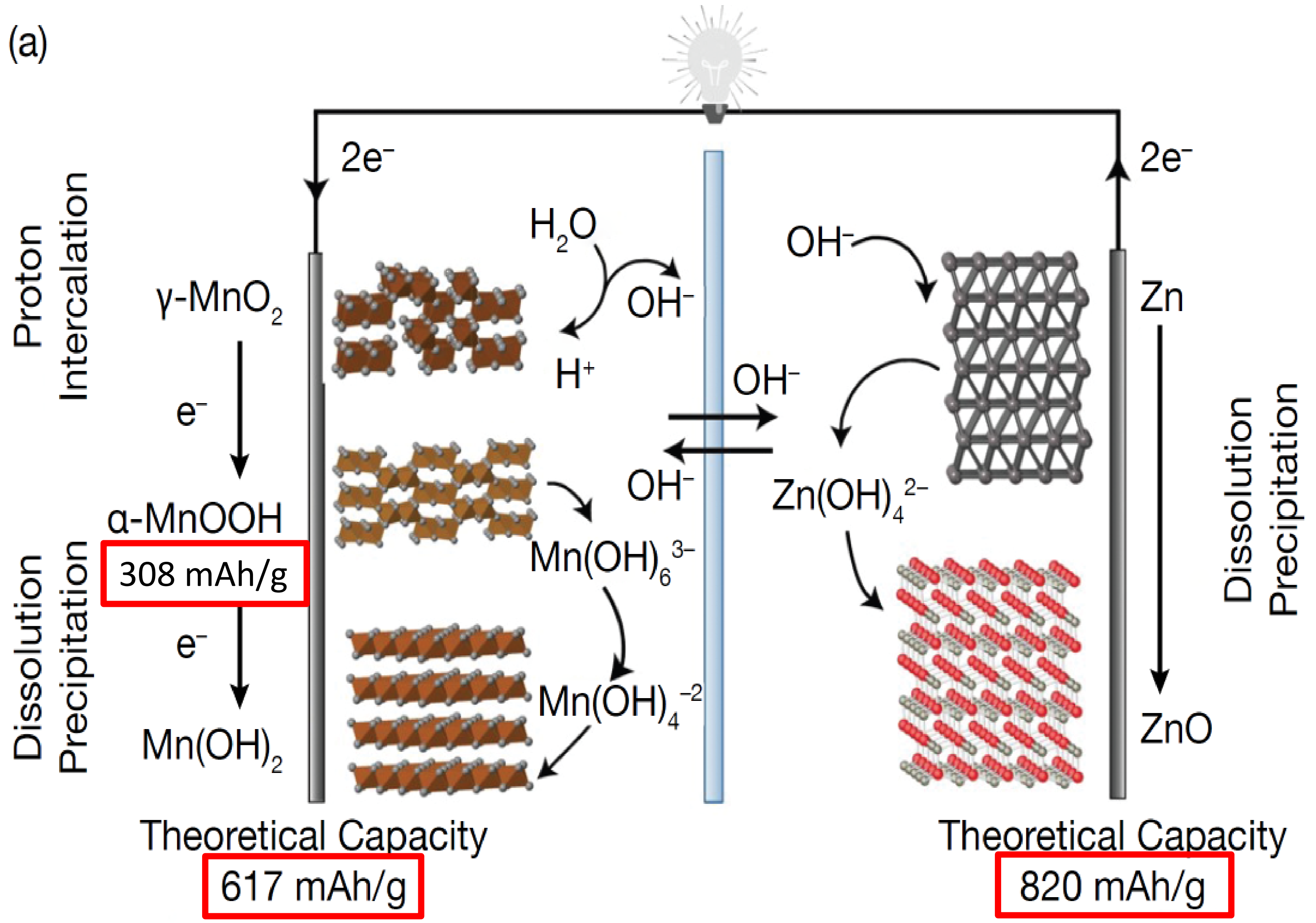
Non-flammable
Compatible in aqueous electrolyte

High energy density

>400Wh/L

(1) N.D. Ingale et al, *J. of Power Sources*, 276 (2015)
(2) Mineral commodity summary data used from U.S. Geological Survey

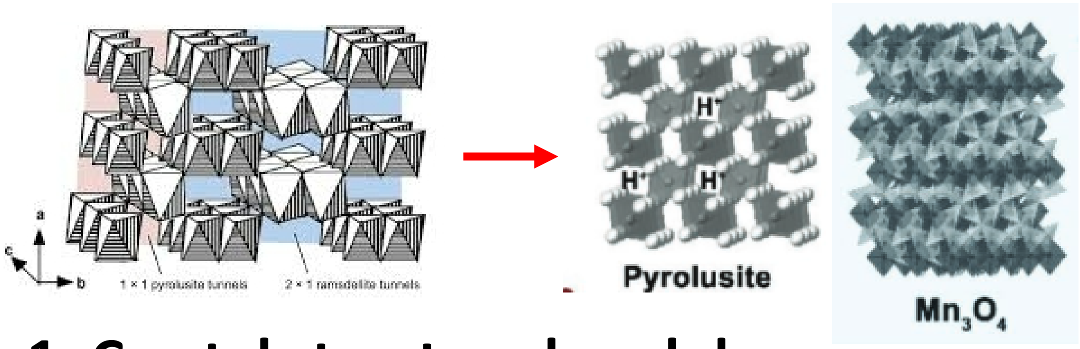
Fundamental Electrochemical Reactions of Zn and MnO_2



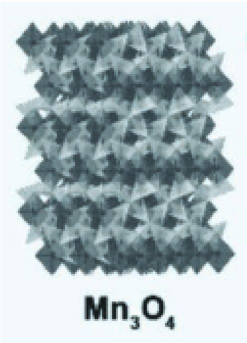
Yadav et al, Chemical &Engineering News, 98 (19) 41-47

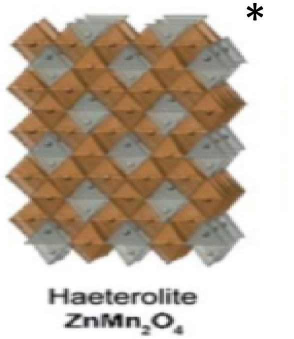
Challenges of Zn|MnO_2 Rechargeable Batteries

MnO_2



1. Crystal structure breakdown





*

2. Form inactive phases from soluble Mn^{3+} ions
3. Poisoning by dissolved Zn ions
4. Loss of active Mn ions

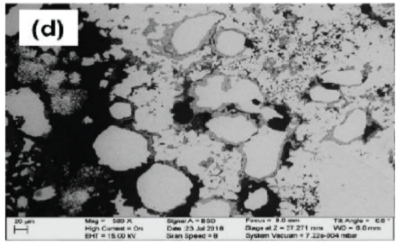
Aqueous KOH

Evaporation
Safety

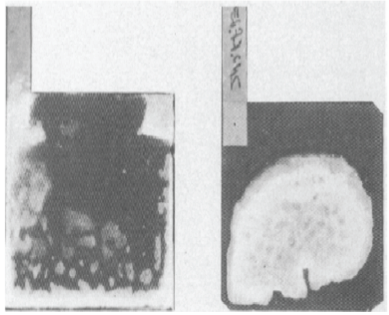
Zn

Pore Plugging

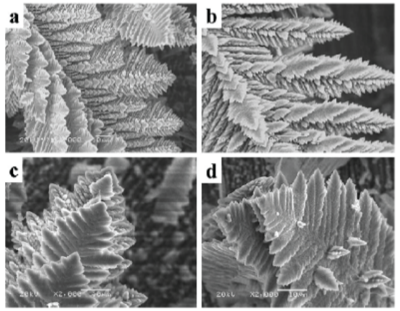
Passivation



Shape Change



Dendrite



Loss of capacity related to Zn redistribution and unpredicted cycle life due to dendrites shorting the cell

* Yadav et al, J. Mater. Chem. A, 2017, 5, 15845-15854

Motivation of the Development of Hydrogel Electrolytes

- Hydrogel electrolytes are being considered an alternative to liquid electrolytes for non-spillable Zn|MnO_2 alkaline batteries

  - protect active materials eventually leading to long cycle life

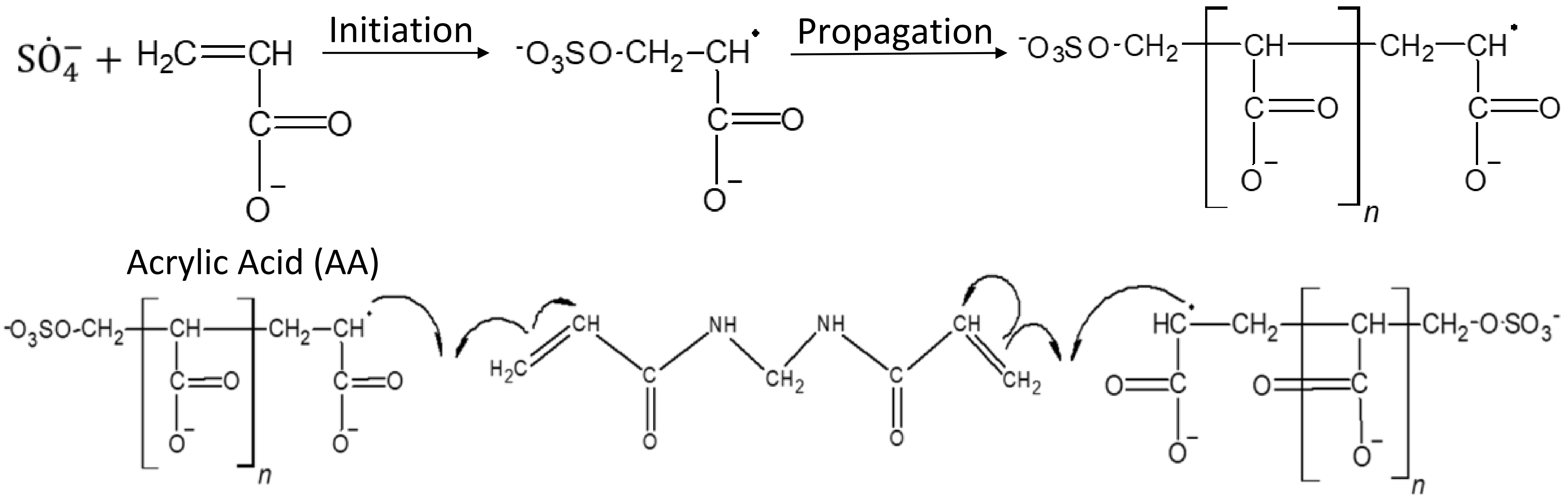
  - keep safety from high pH electrolyte leaks

- It is necessary to develop hydrogel electrolytes not only to have high ionic conductivity but also to allow high utilization of active materials

- The objective is to improve the maintainability and transportability of the current rechargeable Zn|MnO_2 alkaline battery system

Hydrogel Electrolyte Synthesis: Free Radical Polymerization

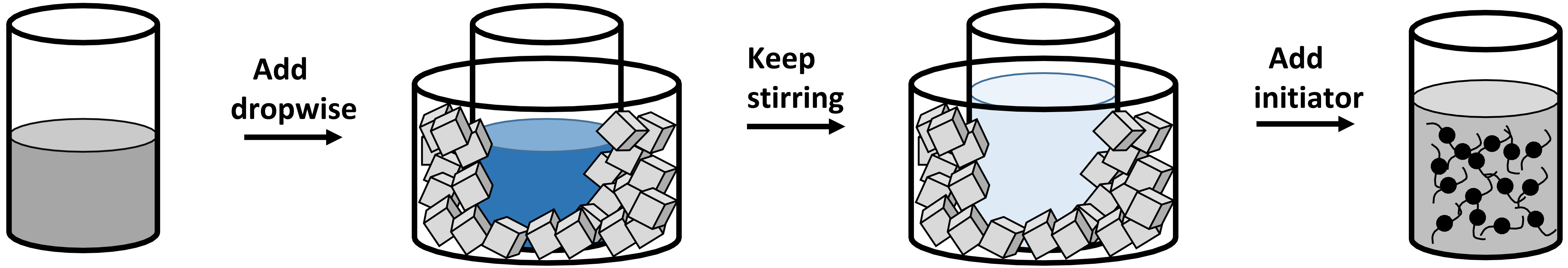
Initiator: $S_2O_8^{2-} \rightarrow 2S\dot{O}_4^-$



N,N'-methylene bisacrylamide
(MBA, cross-linker)

- A poly(acrylic acid)-potassium hydroxide (PAA-KOH) hydrogel was investigated and optimized as the electrolyte due to its high hydrophilicity and high ionic conductivity.
- Chemicals: Potassium persulfate ($K_2S_2O_8$, initiator), Potassium hydroxide (KOH), Acrylic acid (C_2H_3COOH, monomer), N,N'-Methylenebisacrylamide (cross-linker)

Hydrogel Electrolyte Synthesis: In Situ Polymerization

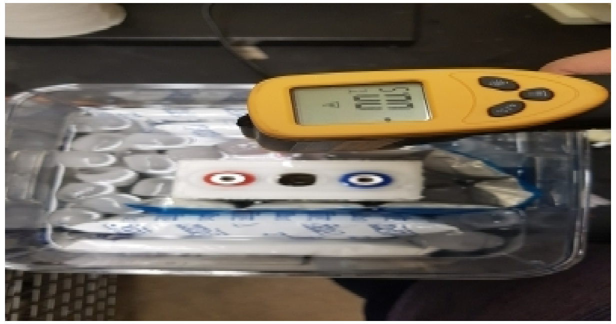


Acrylic Acid

MBA & KOH solution cooling down at 0°C in the ice bath

Gel electrolyte solution

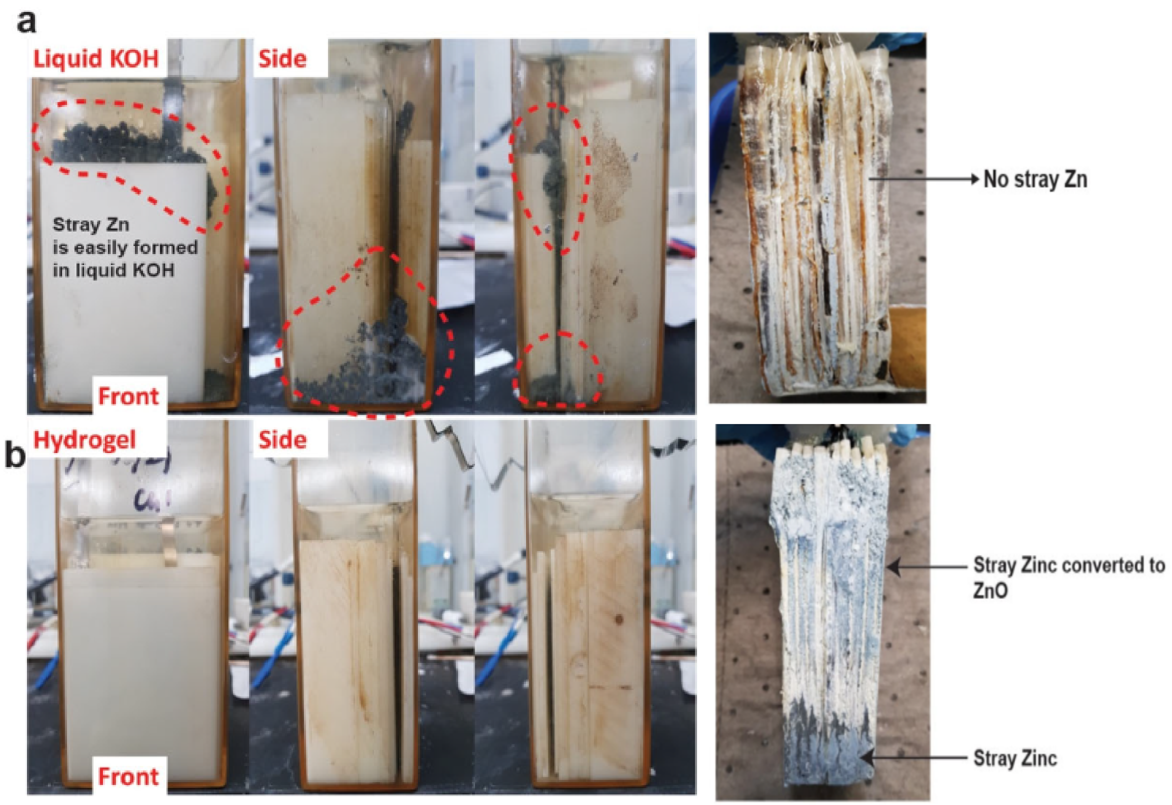
Fill cells

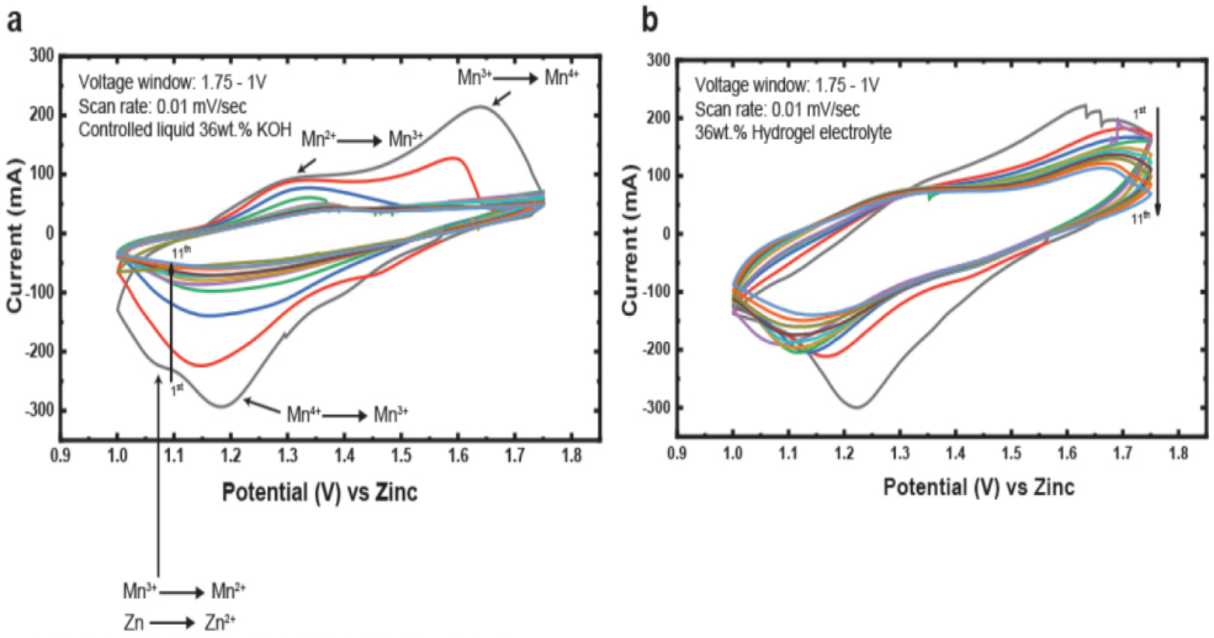


Pull the vacuum
Let it soak and gel
Start Cycling

- To delay polymerization reaction kinetics, the temperature was kept at 0 °C
- It ensures enough time to soak porous Zn and MnO_2 electrodes

Current Findings under the 1st electron technology





The "hump" peak signifies the beginning of the 2nd electron reaction of MnO_2. It also signifies Zn ions influence on the electrochemical discharge of MnO_2 which ultimately leads to spinel formation (Mn_3O_4 and $ZnMn_2O_4$) that lead to capacity fade because of its inactivity.

- Hydrogel reduced zincate migration and the formation of stray Zn, which is a cause of dendrite formation and eventually short circuits
- Hydrogel reduced manganese dissolution and mitigated inactive spinel formation stemming from zincate

Cho et al, Poymers, 2022, 14 (3), 417

Targeting the 2nd electron MnO_2 cycling

- Need to improve the utilization under the 2nd electron reaction for more energy ensuring transportation and safety

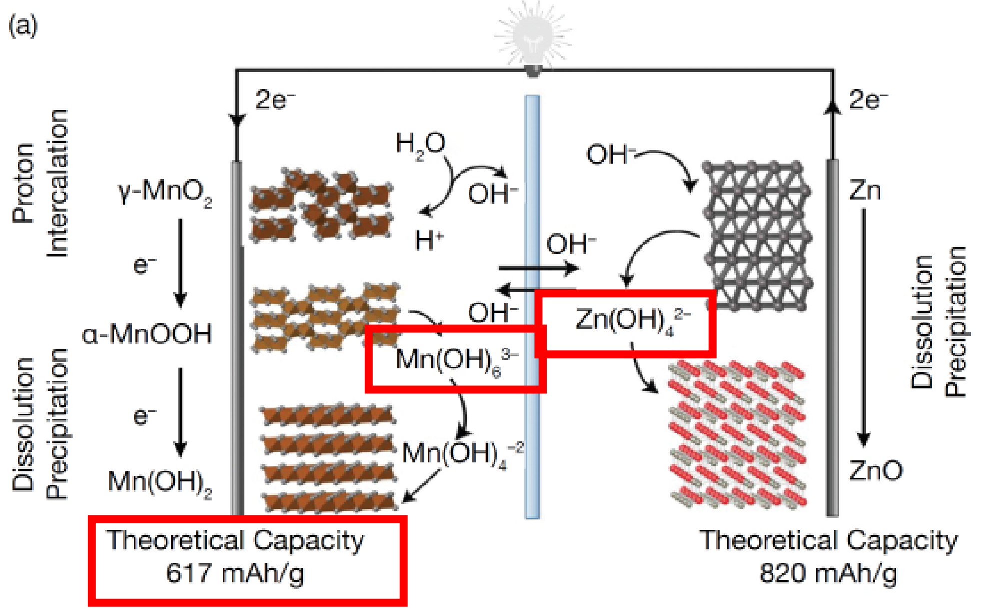
- Key is to keep active Mn ions

 - prevent Zn poisoning to active Mn ions

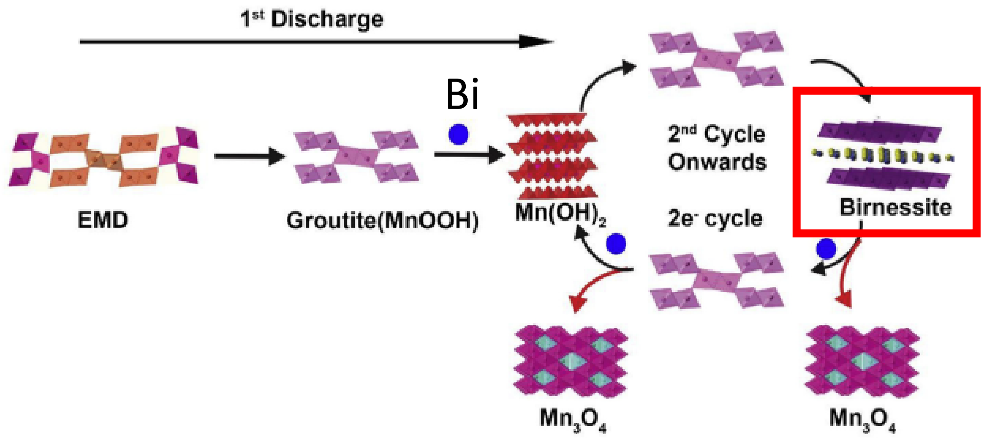
 - the reversibility of a layered δ-MnO_2 morphology, Birnessite

- Cu makes Bi- δ-MnO_2 complex stable by intercalation into Mn's layered morphology while cycling*

 - Used this cathode material for the following experiment with the same effective OH- concentration

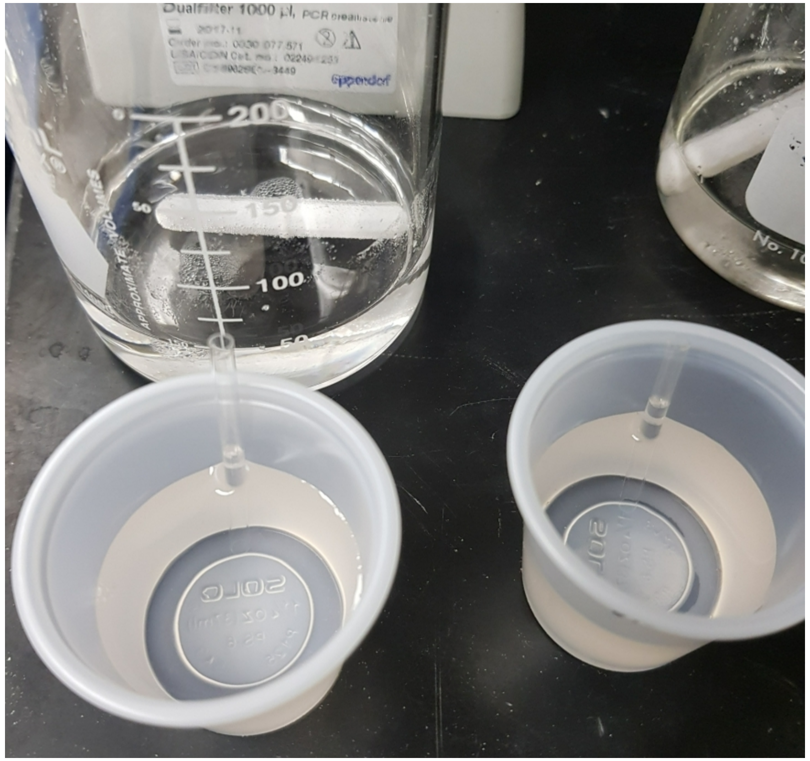


G.G. Yadav et al. / Materials Today Energy 6 (2017) 198–210



* Yadav et al, Nature communication

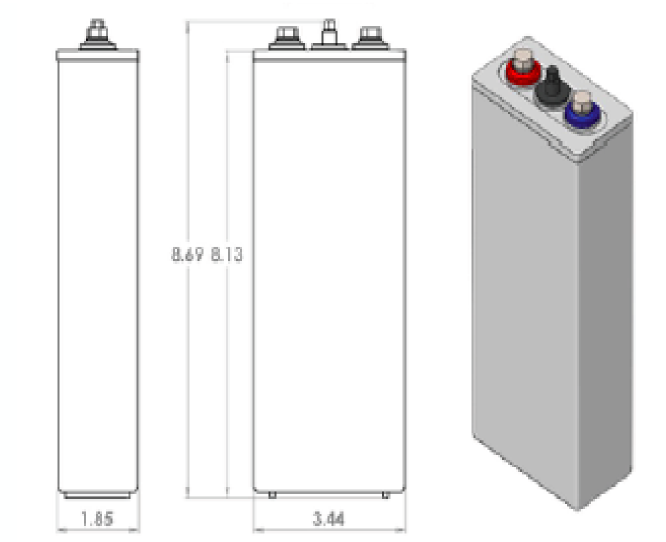
Gel Electrolyte Optimization



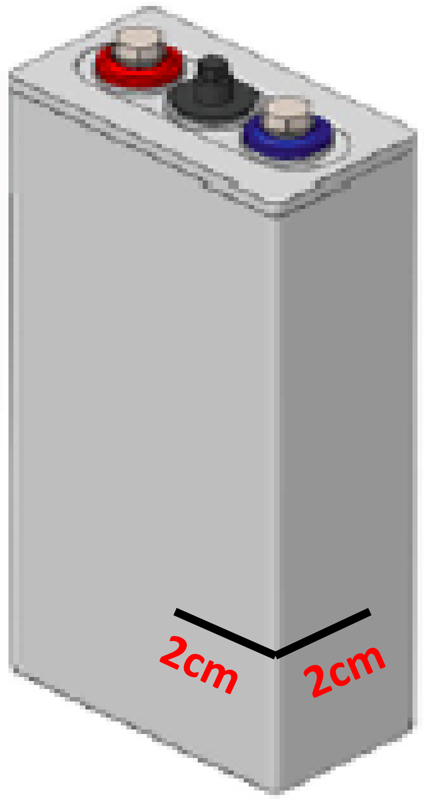
Mole fraction MBA:H_2O	Flow from ~1 mm gap	Flow from ~75 mm gap
2.61E-5	Flow	Flow
3.4E-5		
3.92E-5	No Flow	
4.7E-5		
5.2E-5		
6E-5		
6.5E-5		No flow
7.3E-5		
7.8E-5		

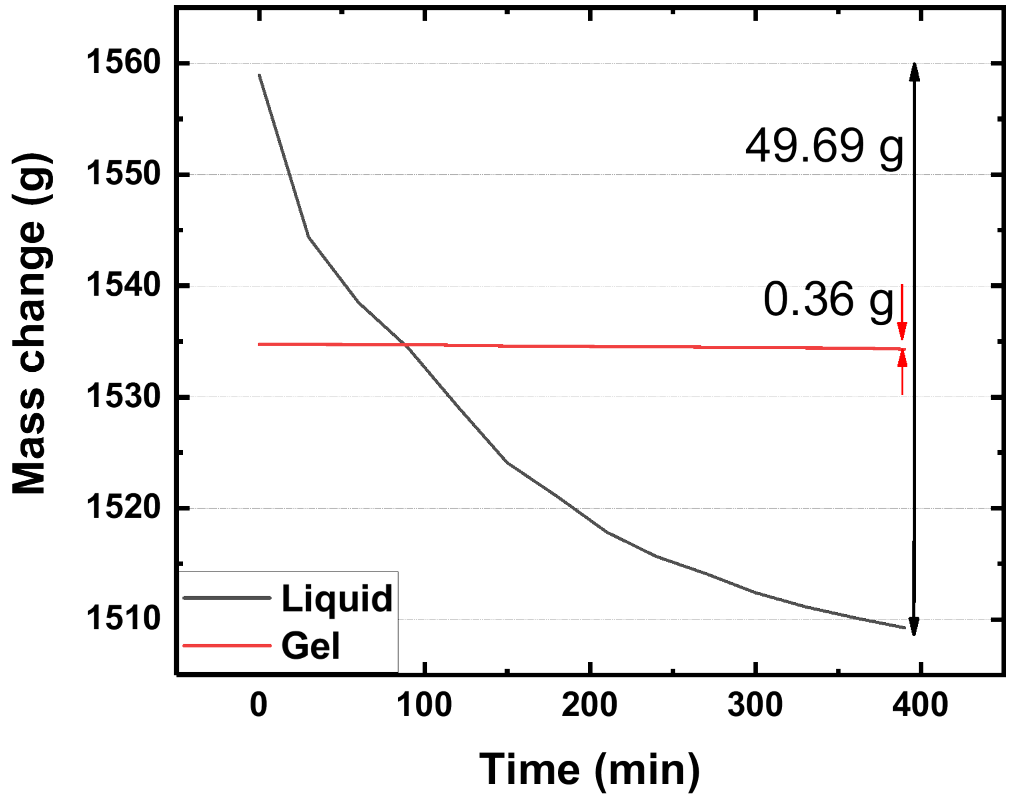
- DOT regulation: no leaks allowed for non-spillable batteries from cracks/ruptures
- Find a sweet spot to satisfy making gel and ensuring ionic conductivity
- 3.95 10-5 mole fraction is determined
- All samples remained its gel shape, not behaved as water

Leakage Experiment



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

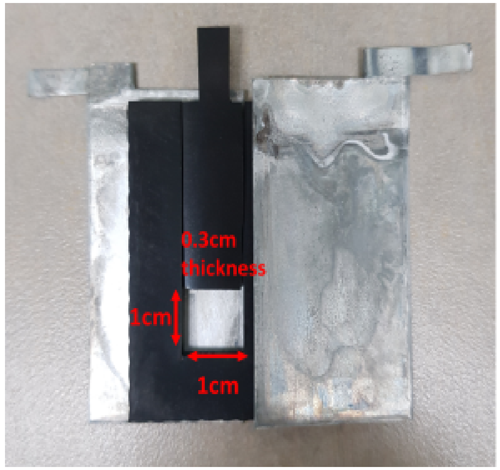


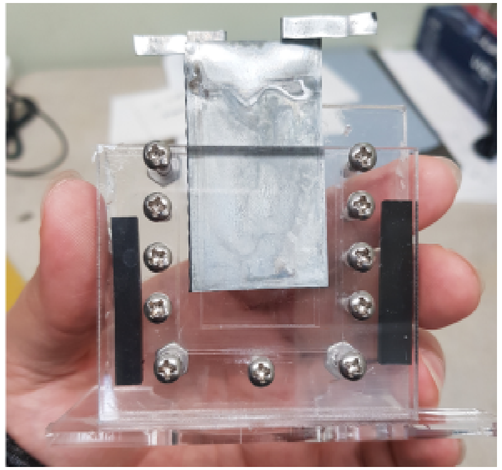


- Prismatic cell description and experimental set up. Once the crack was produced, the total mass change was measured every 30 minutes

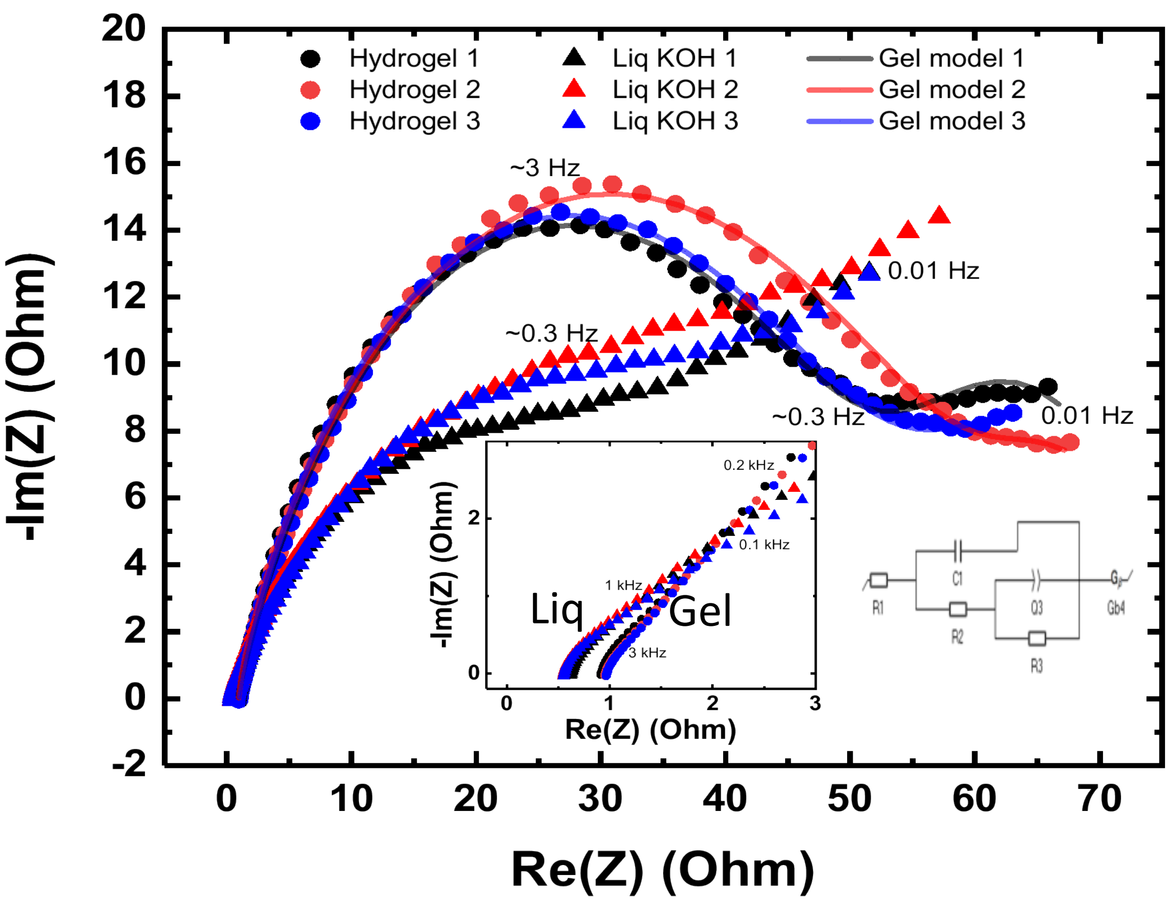
- The gel proved much safer than liquid from spills but it still has room for the improvement to be non-spillable

EIS Measurement for Zn Foil Symmetric cell: Zn diffusion





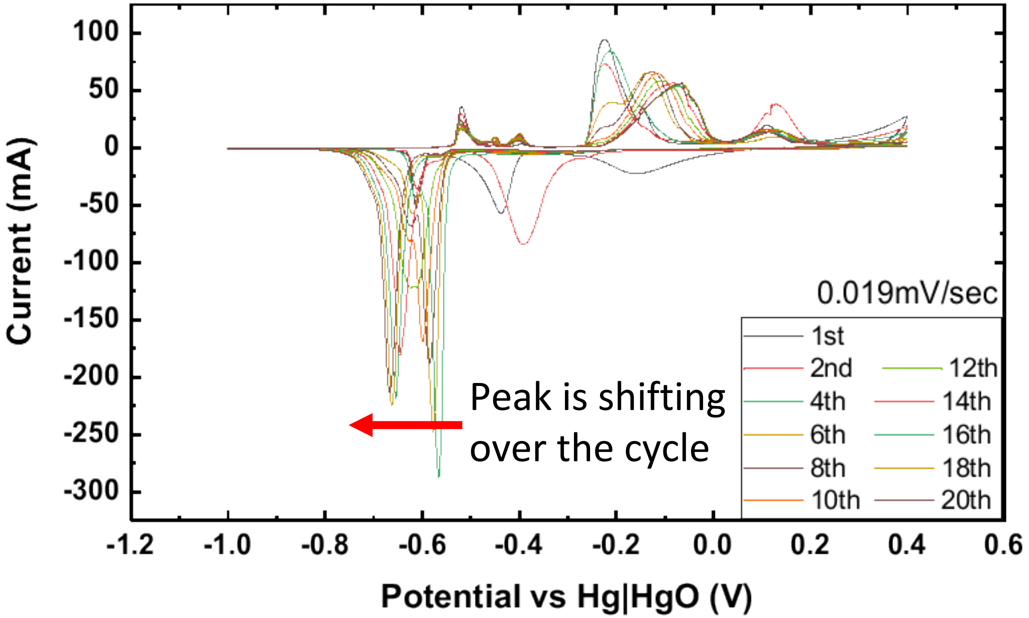
Experimental set up for Zn foil EIS measurement. The gel electrolyte was put into the square area from the top of the rubber gasket. Then, each Zn foil was assembled



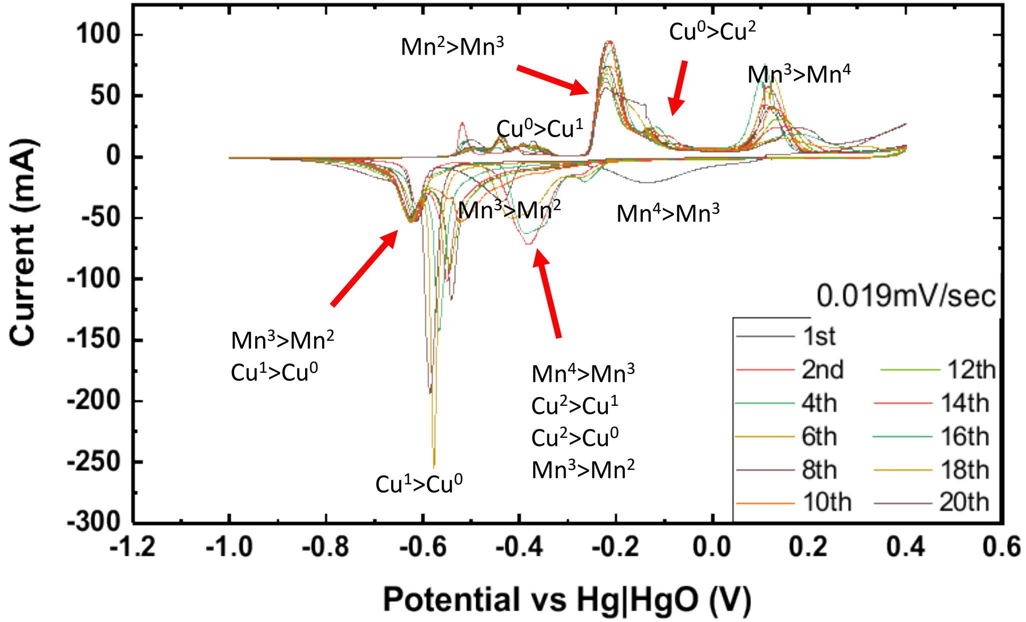
- As the gel has a network structure, resistance is higher than the liquid
- Ionic conductivity is close to each other (inset)

Cyclic Voltammtry Results with Liquid and Gel Electrolyte

Liquid



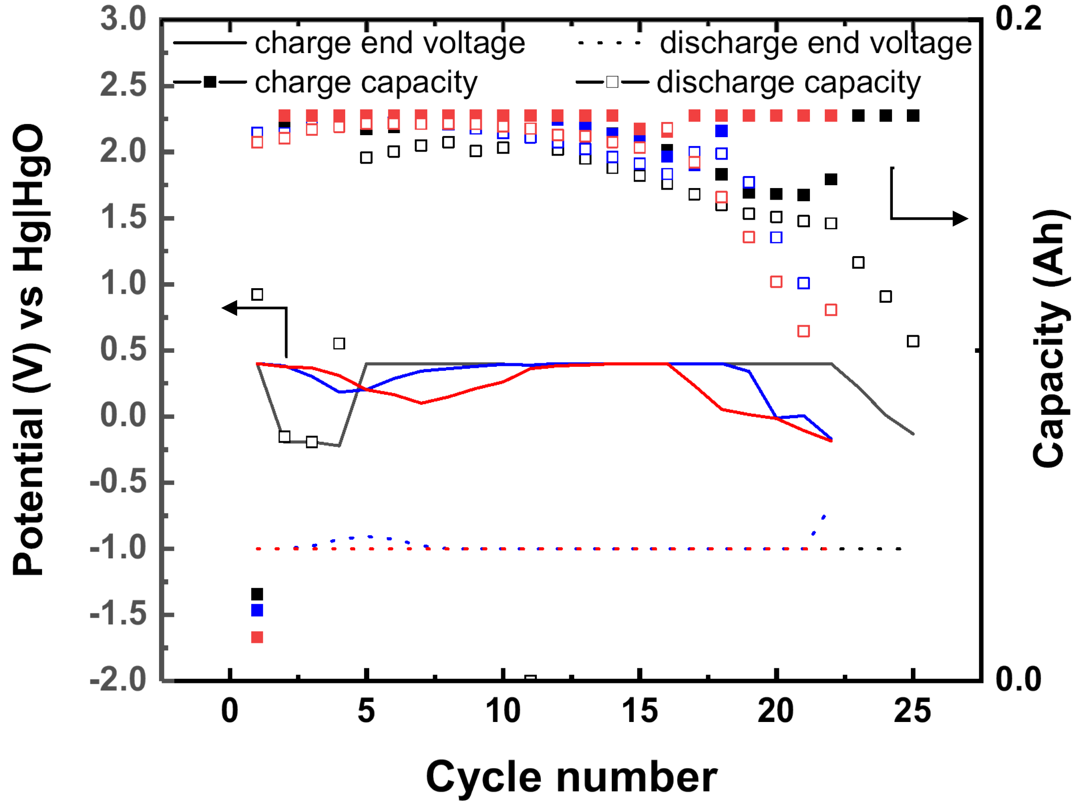
Gel



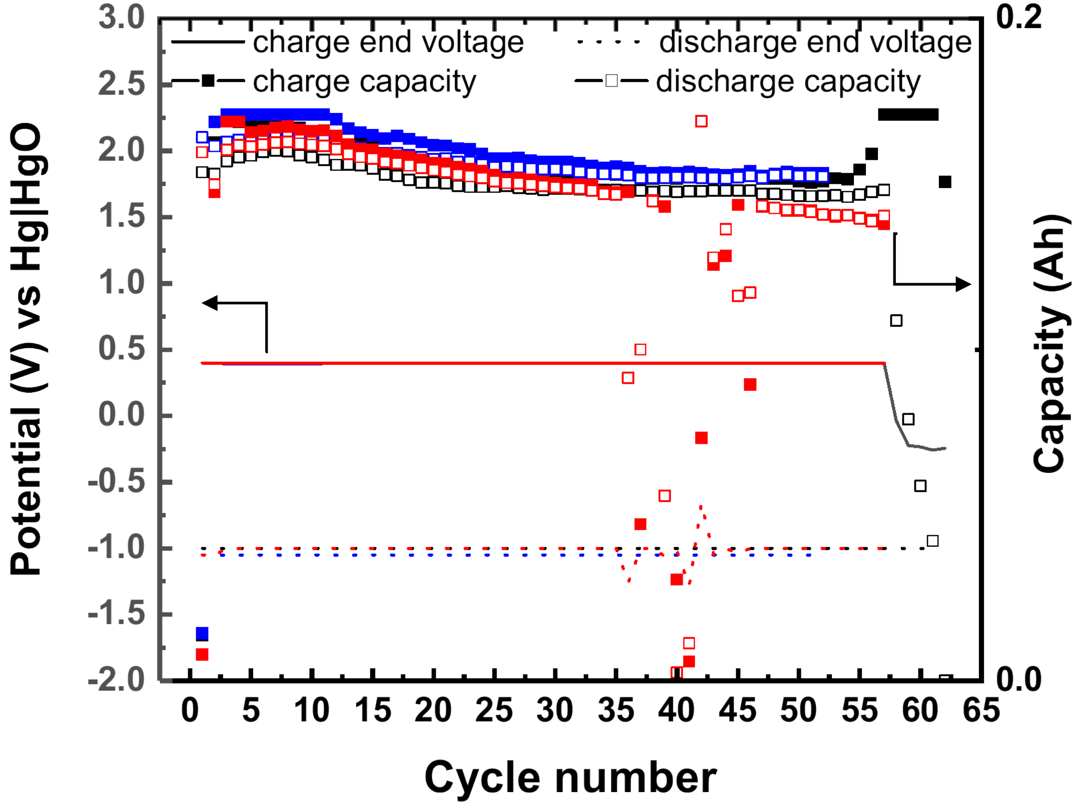
- The liquid electrolyte cell has the two Cu peaks faded at -0.6 V and -0.25 V over the cycle, while gel electrolyte cell showed all peaks for all cycles
- Using the gel electrolyte is hypothesized to localize Cu and limit Cu diffusion so that it makes [(Cu-Bi)Mn] complex formation reversible, leading stable performance
- Currently, two cathode samples stopped at -0.6 V and -0.7 V are investigated

Cycling Performance with the Hydrogel Electrolyte

(a) traditional liquid electrolyte cycles

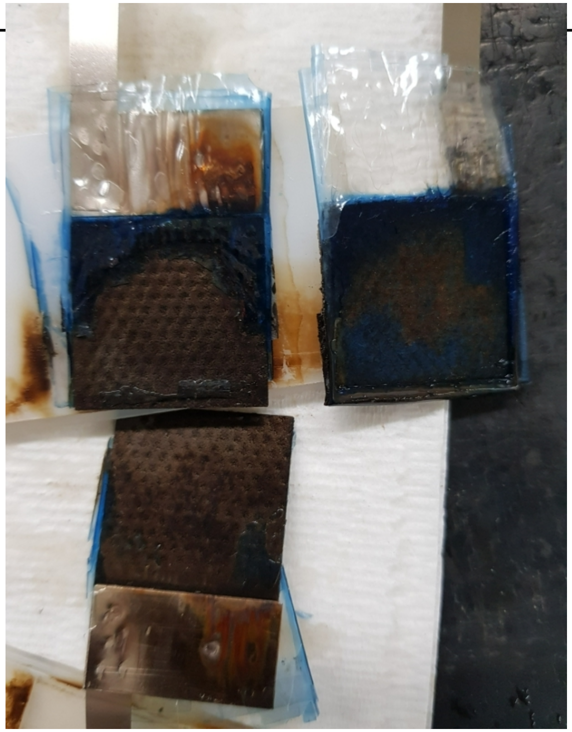
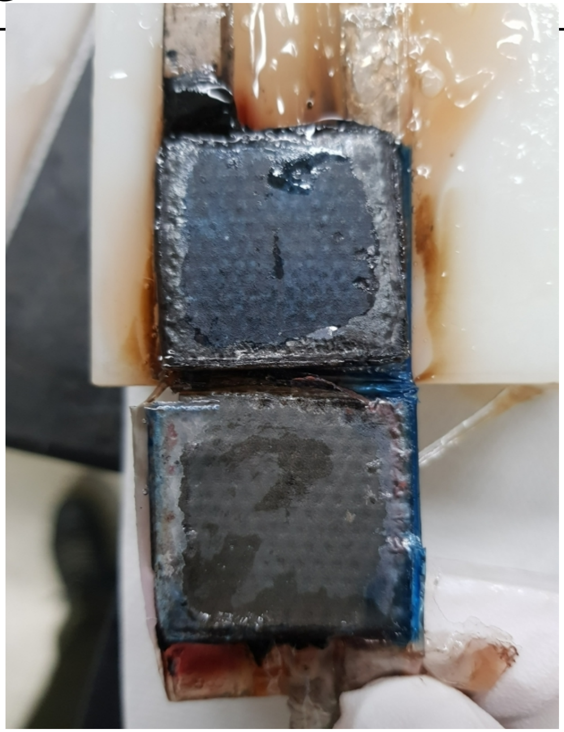


(b) gel electrolyte cycles



- Cycling performances of MnO_2 cathode vs NiOOH with a Hg|HgO reference electrode at C/20 charge and discharge (C is based on the 2nd electron MnO_2 capacity). All cell construction is identical and repeated three times
- Gel electrolyte cells are ongoing and outperforming

Dissecting the Cells After Galvanostatic Performance

(a) C/20 charge and discharge with liquid at 18th cycle	(b) C/20 charge and discharge with gel at 57th cycle
	

- The failure mechanism for the liquid electrolyte cell was due to short circuit caused by Cu deposition all around the separator, while Cu is limitedly diffused in the gel cell

Conclusions

- The crosslinked gel electrolyte was incorporated into Zn|MnO_2 rechargeable batteries making sure the ionic conductivity and safety

- The gel electrolyte limited Cu ion diffusion and mitigated Cu ion loss

- It is assumed that the gel electrolyte makes stable [(Cu-Bi)Mn] complex, leading long cycle life

Acknowledgements

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- Dr. Timothy Lambert

- Michael Nyce and lab mates


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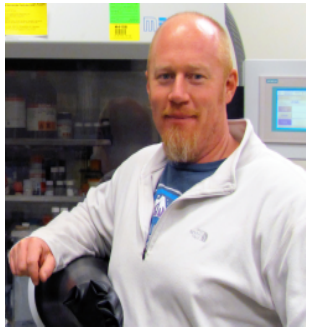

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Thank you