

Engineering Zn and Mn Anodes for Aqueous Batteries

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Project Overview

- **Project Goal:** We aim to develop low-cost, high-energy batteries by using manganese and zinc metal electrodes in non-flammable water-based electrolytes.
- **Current Practice:** Today's metal-based batteries pair manganese oxide with zinc but suffer from short cycle life, high cost, and limited specific energy.
- **Why Georgia Tech:** Expertise on aqueous batteries, cutting-edge materials labs, and strong partnerships with DOE national labs and user facilities.
- **Innovation:** We will create novel metal electrode designs and customize the battery electrolyte to stop material loss and extend battery life.
- **Impact:** Success will yield affordable, durable batteries for backup power and grid storage that rely on abundant, non-critical materials.
- **Alignment:** This work directly supports DOE Office of Electricity goals by advancing long-duration, resilient energy storage for a flexible and reliable power grid.

Project Team



Zhitao Chen



Dr. Timothy N. Lambert
Sandia



Dr. Jason Huang
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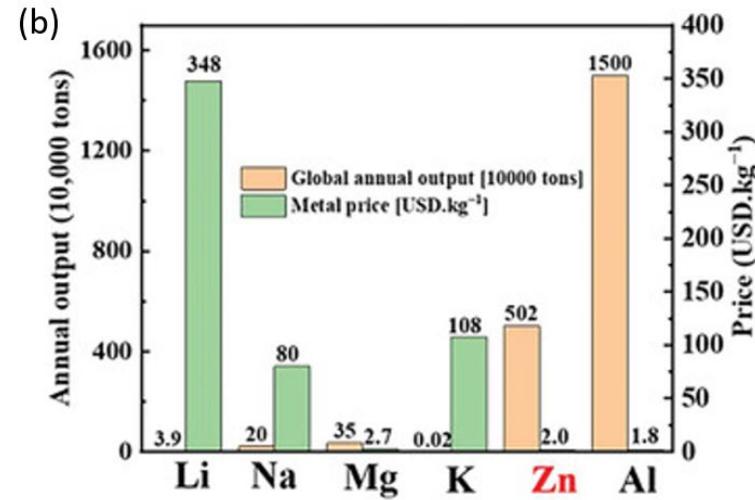
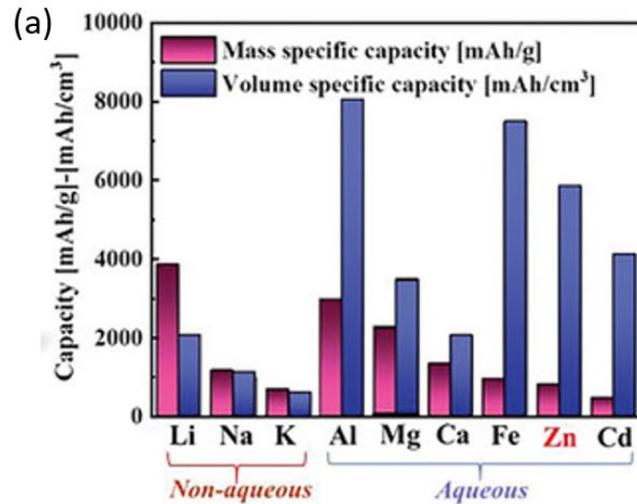


Dr. Calvin D. Quilty
Sandia



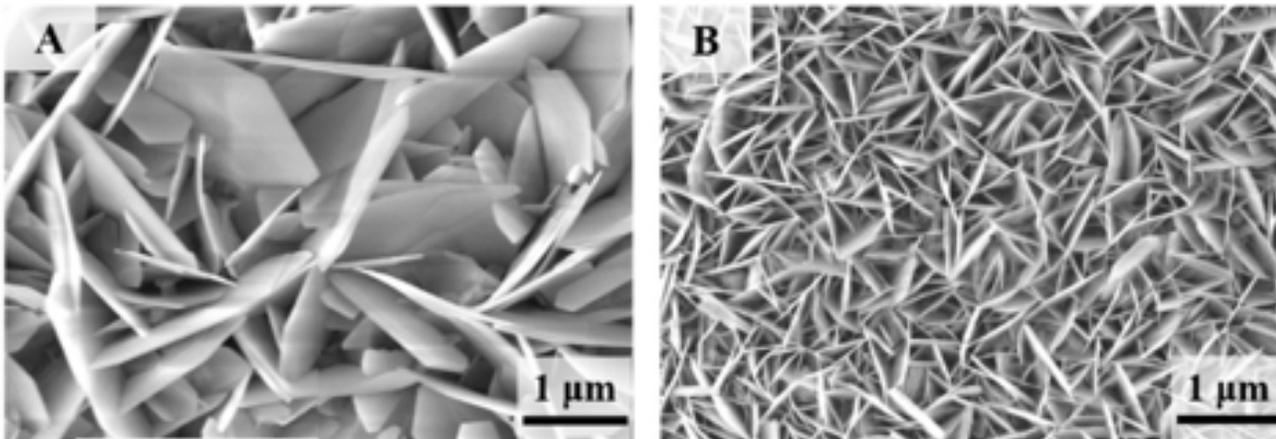
Dr. John Watt
CINT

Zinc metal anode in neutral/mild acidic



Small 16, 2000730-2000758 (2020)

Electrodeposition morphology of zinc



ACS Appl Mater Inter 13, 32930-32936 (2021)

Metallic zinc anode

- High theoretical specific capacity (820 mAh/g, 5854 mAh/cm³)
- Aqueous electrolyte
- Low redox potential
- Low cost
- **Dendrite formation**
- **Parasitic reactions**

Existing effort

- Electrolyte additives
- Zn electrode coating including CNT coating, graphene coating, ion-sieving carbon nano shells
- Zn electrode additives including Bi, In, Pb

Soluble zincate: Passive encapsulation → Active management

Carbon electrode

Carbon

Charge:
Zn plating



Carbon

Y. Zhang, N. Liu* et al.
ACS Energy Lett.
2021, 6 (2), 404–412

Ag Zn_xAg_{1-x} Zn

C-Ag electrode

Carbon

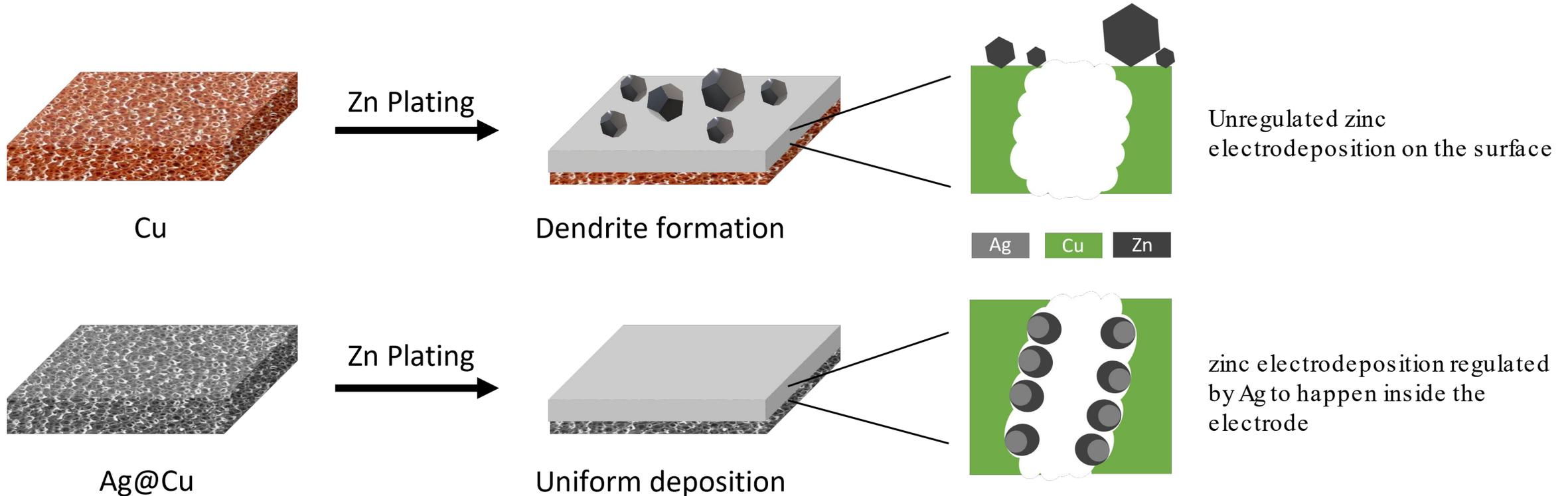
Charge:
Zn plating



Carbon



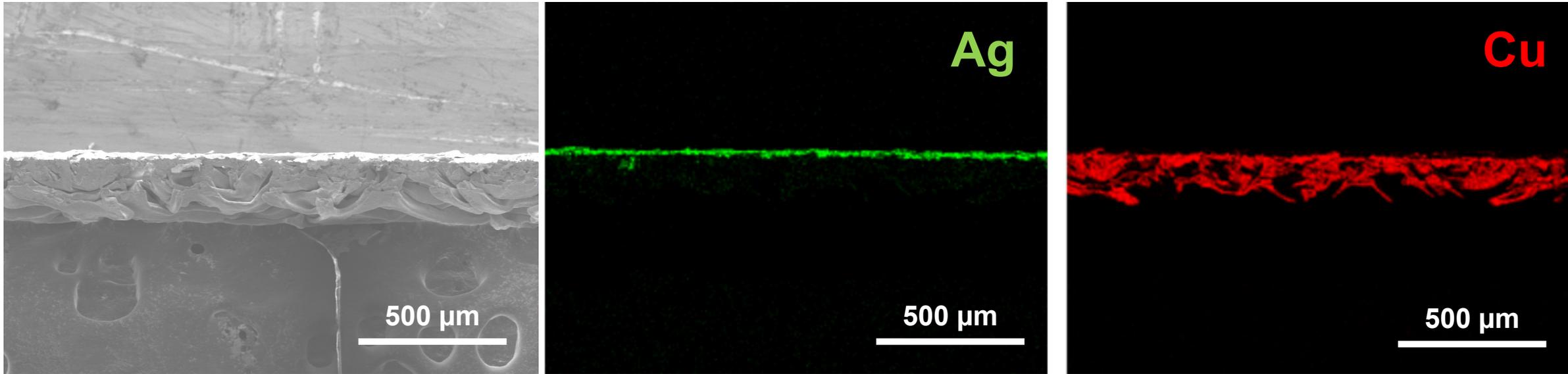
Alloy Seeded Host (ASH) Zinc Anode



3D structure-zinc electrodeposition throughout the electrode in neutral electrolyte

- Alloy seeded host (ASH) Zn anodes have a conductive host material such as super P carbon, that is decorated with zinc-alloying metal, Ag, as seed on the 3D substrate, Cu foam.
- The host accommodates the zinc during electrodeposition process, and the Ag decoration spatially controls the zinc deposition to happen inside the host to achieve uniform and dendrite-free zinc electrodeposition in a 3D structure.

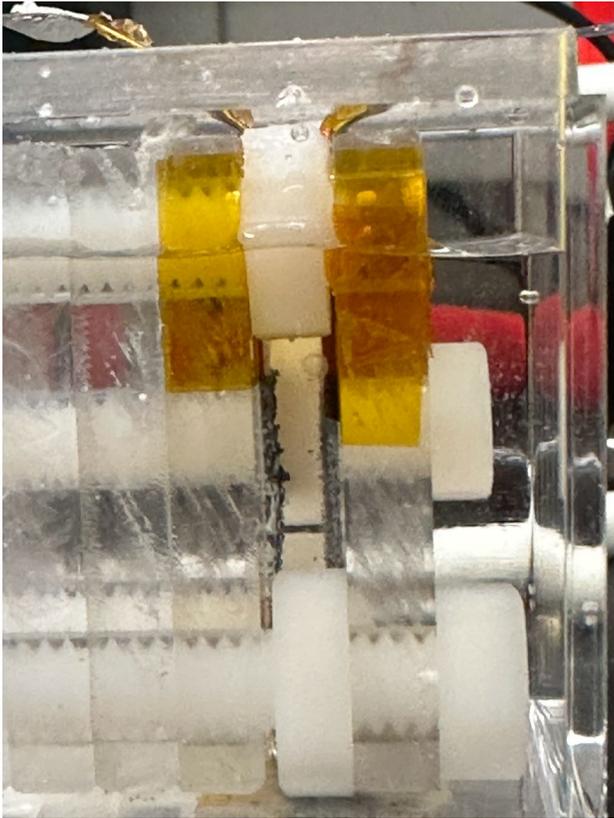
Ag decorated Cu foam



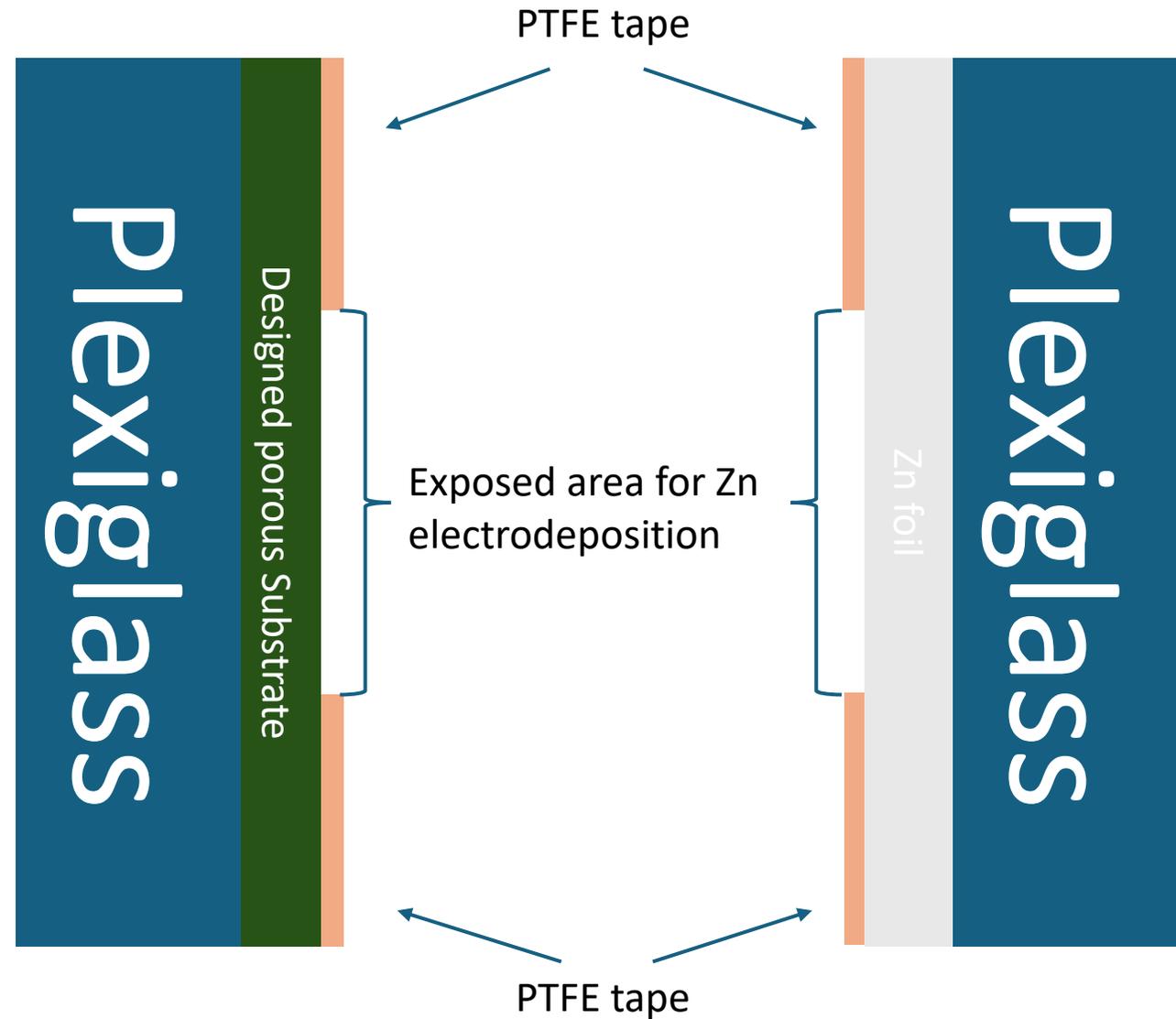
Ag decorated Cu foam

- Ag-rich side is created by using Ag sputtering
- Cu-rich side will be placed facing towards Zn foil counter electrode
- Zn will preferentially deposit on Ag-rich side and fill the porous structure of Cu foam
 - Zn deposition preference (Ag>Zn>Cu)
- This can realize ultrahigh Zn mass loading and areal capacity

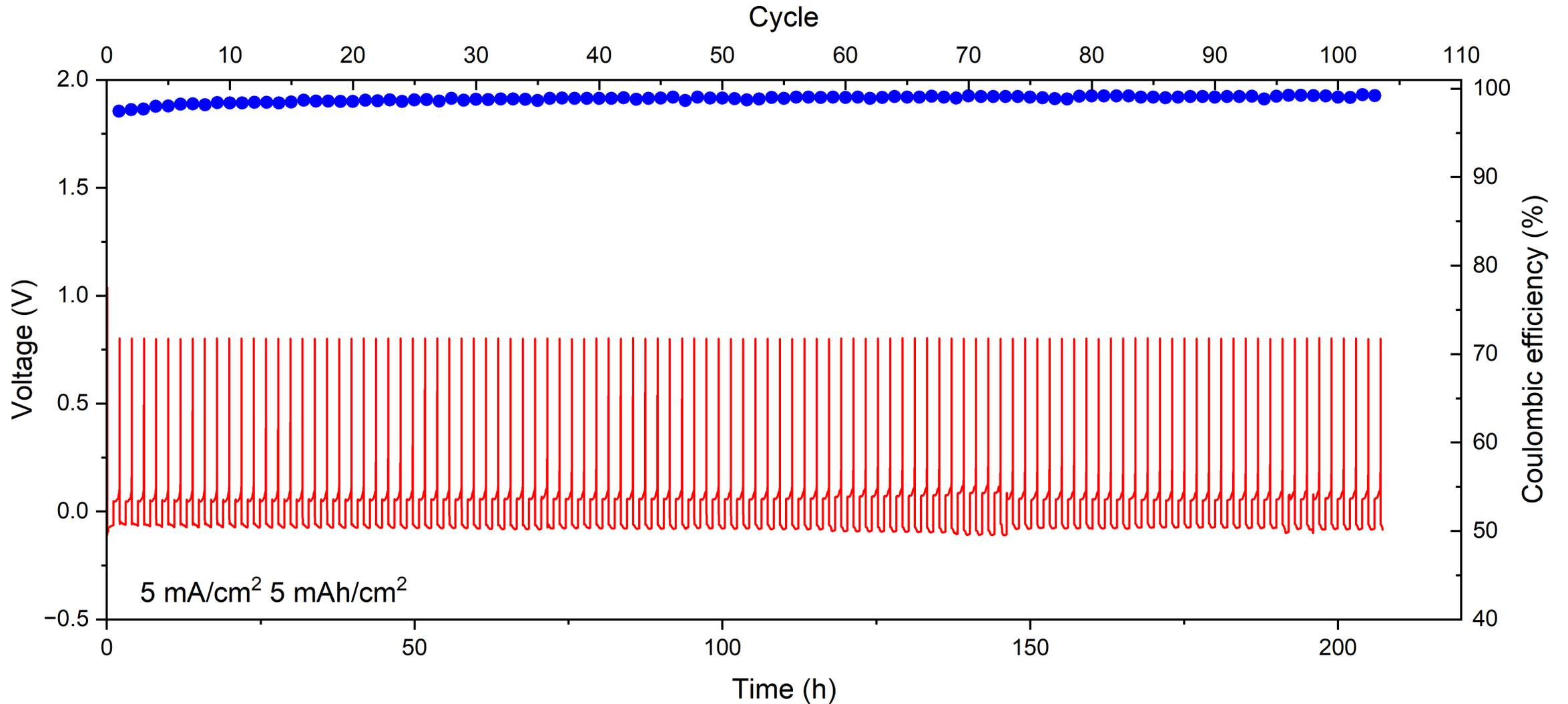
Configuration of beaker-type cell



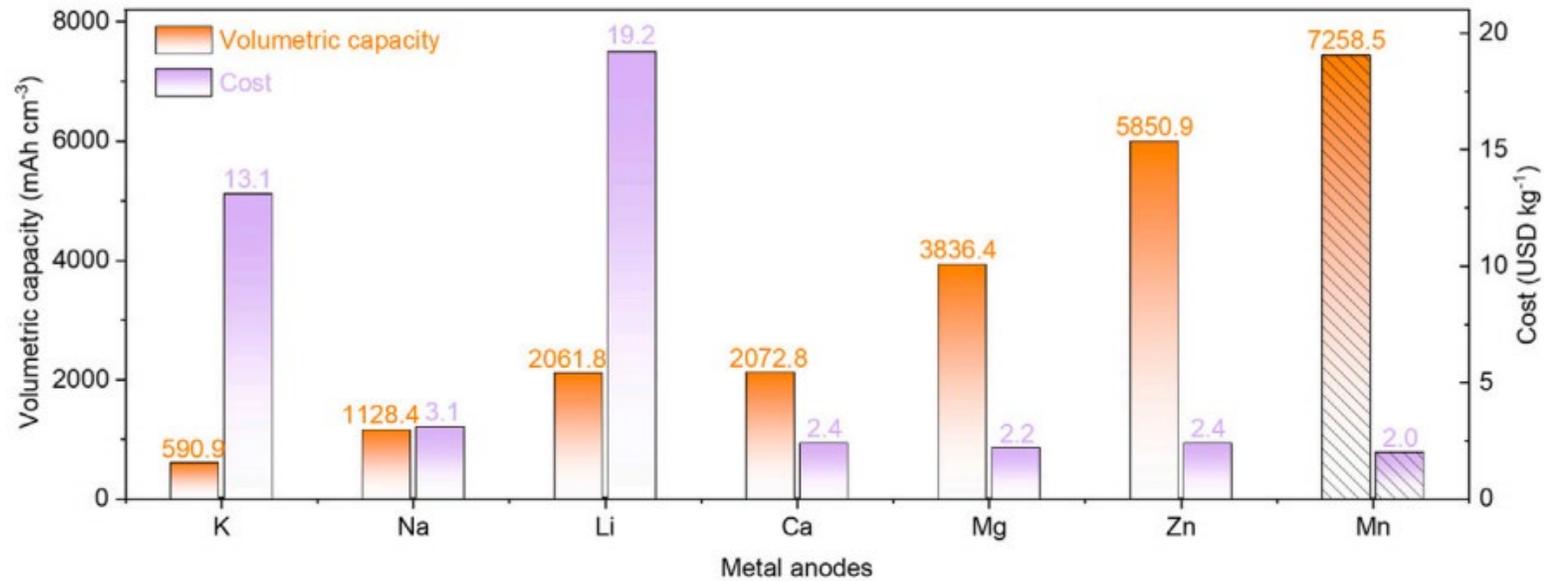
The battery will be vacuum soaked for 1 h and then rest for 2 h before testing



Cycling performance



Overview of Mn anode



Joule, 8(3), 583–598

- Mn anode has highest volumetric capacity but lowest cost, exceling all the elements listed in the table
- The redox potential is even lower than Zn, leading to higher discharge voltage

However,

- Mn anode suffers from hydrogen evolution reaction
- The main problem is the reversibility of plating/stripping reactions of Mn/Mn²⁺ on Mn anode

Electrolyte design strategy

□ Design strategy scheme

- **Low water activity**

Using potassium acetate (KAc) and sucrose to alter the solution structure

- **pH-control** Balance between Solubility of $\text{Mn}(\text{OH})_2$

Mn reduction potential Vs. HER

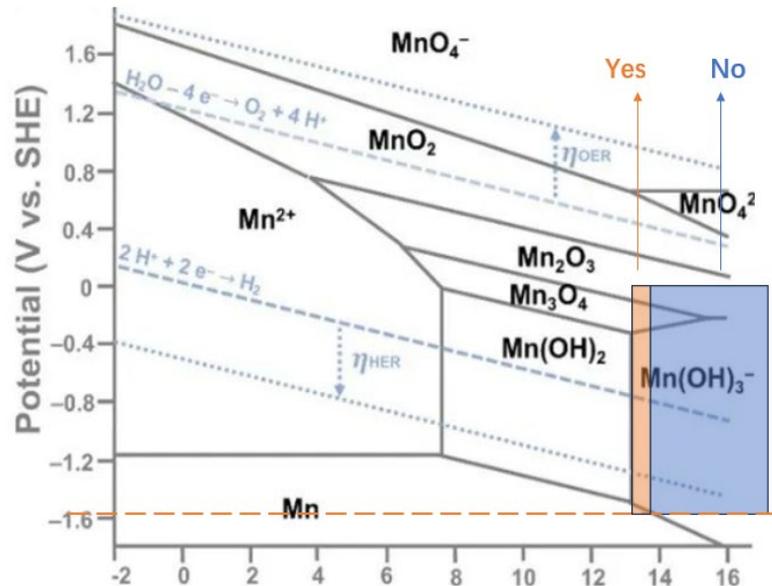
Water activity

- KAc + sucrose

Adding different concentration of KOH

pH-control

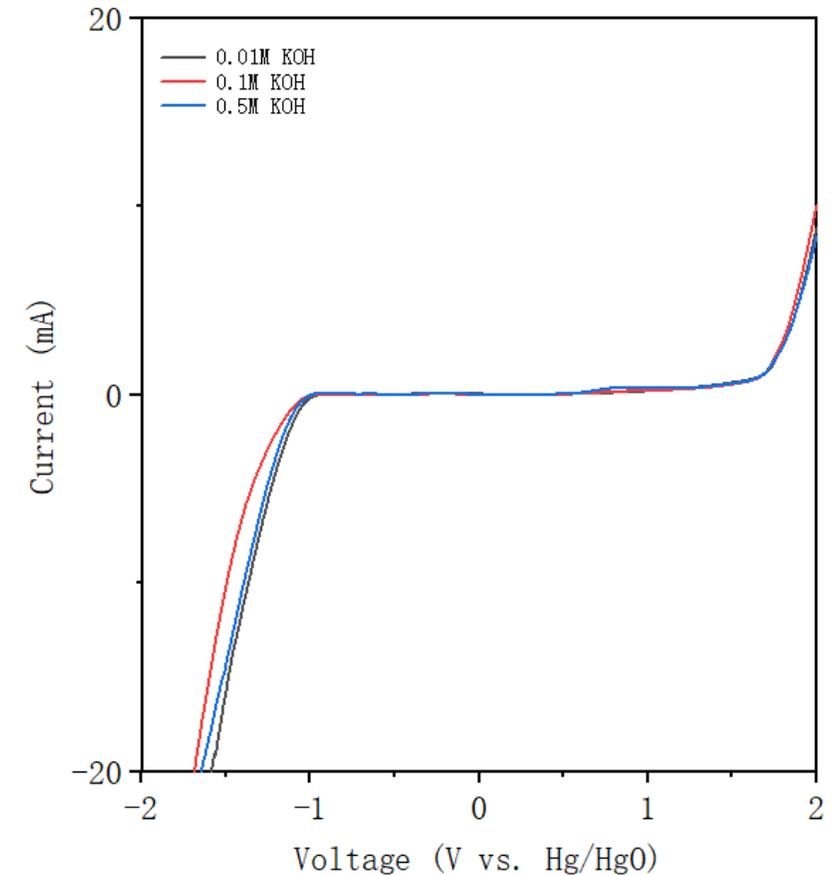
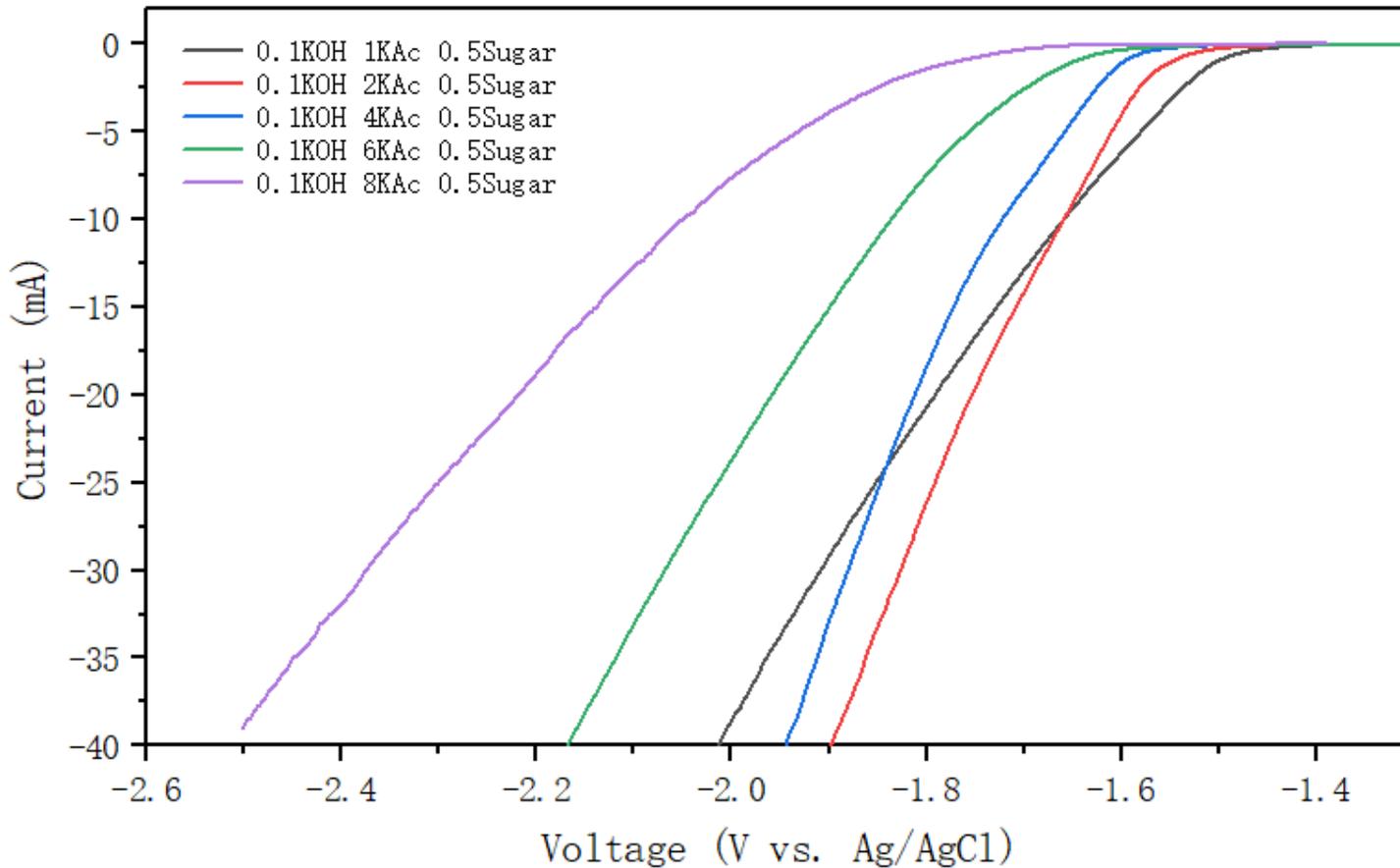
- KAc + Sucrose + KOH



We will test the electrolyte in four main aspects

- Electrochemical window
- Ionic conductivity
- Solvation structure
- Compatibility with Mn anode

Potential window



- Potential window of electrolyte with same concentration of KOH and sucrose but different KAc concentrations
- It can be clearly seen that the potential window is wider in the electrolyte with 0.1M KOH + 8M KAc + 0.5M sucrose and suppress HER

- 0.1M KOH demonstrates the widest potential window compared to other concentrations

Compatibility between electrolyte and Mn anode



0.05M



0.1M



0.3M



0.5M



1M

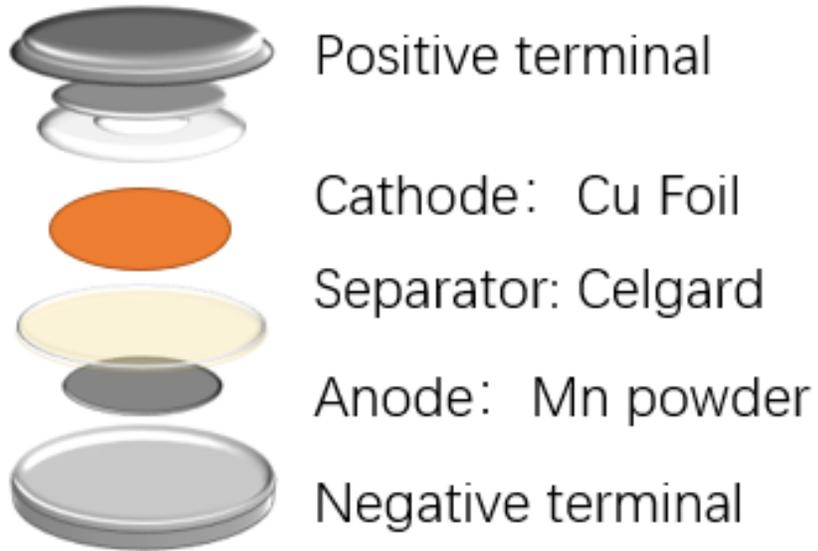


4M

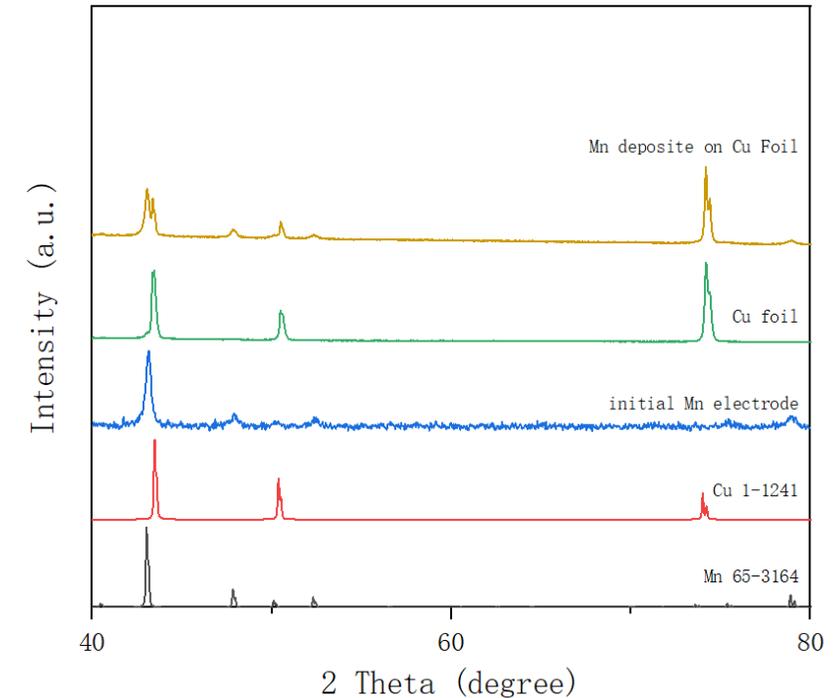
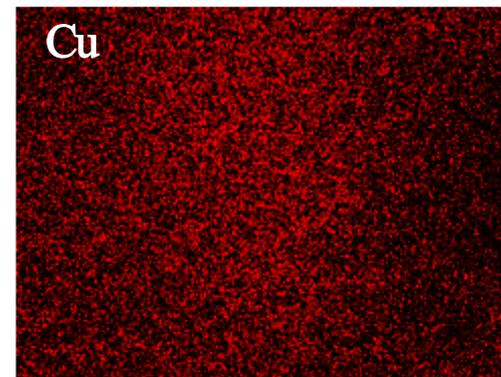
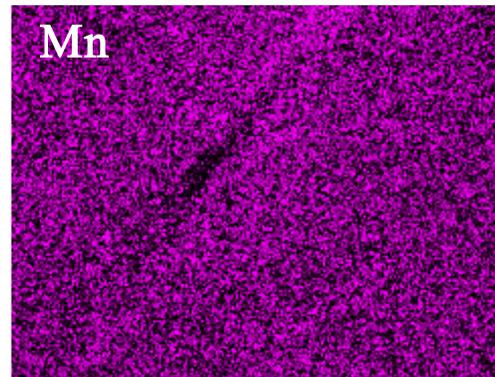
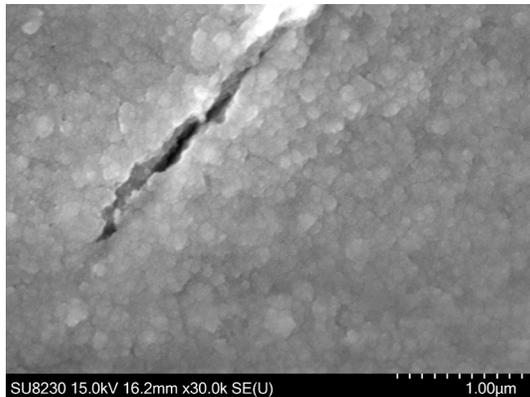
Base electrolyte: 8M Kac + 0.5M sucrose

- Experimental result
 - A small Mn plate is placed in electrolyte with different concentration of KOH
 - There is bubble formation in the electrolyte with KOH concentration higher than 1M

Mn deposition in Mn-Cu coin cell



- Electrolyte- 0.1M KOH, 8M KAc, 0.5M sugar with sat MnCl_2
- 0.1mA/cm^2 , 0.01mA/cm^2



Acknowledgment

- This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.