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 improve rechargeability 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 (started Jan 2025)

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Georgia Tech

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Sandia

Dr. Jason Huang
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Dr. Calvin D. Quilty
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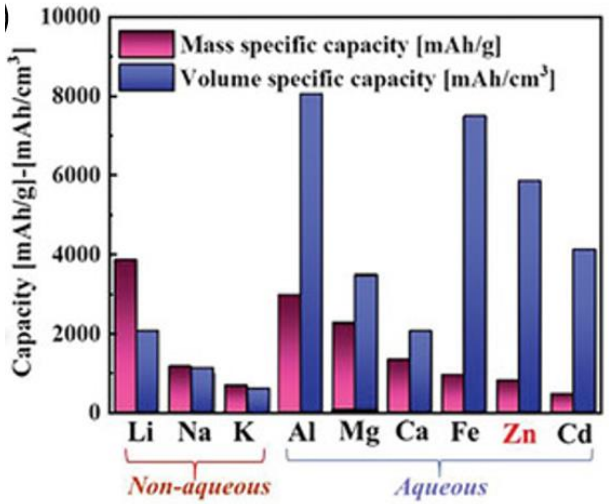
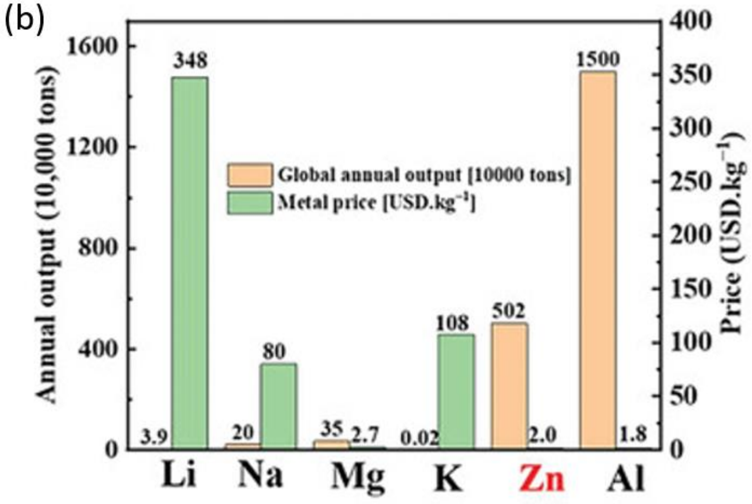
Dr. John Watt
CINT

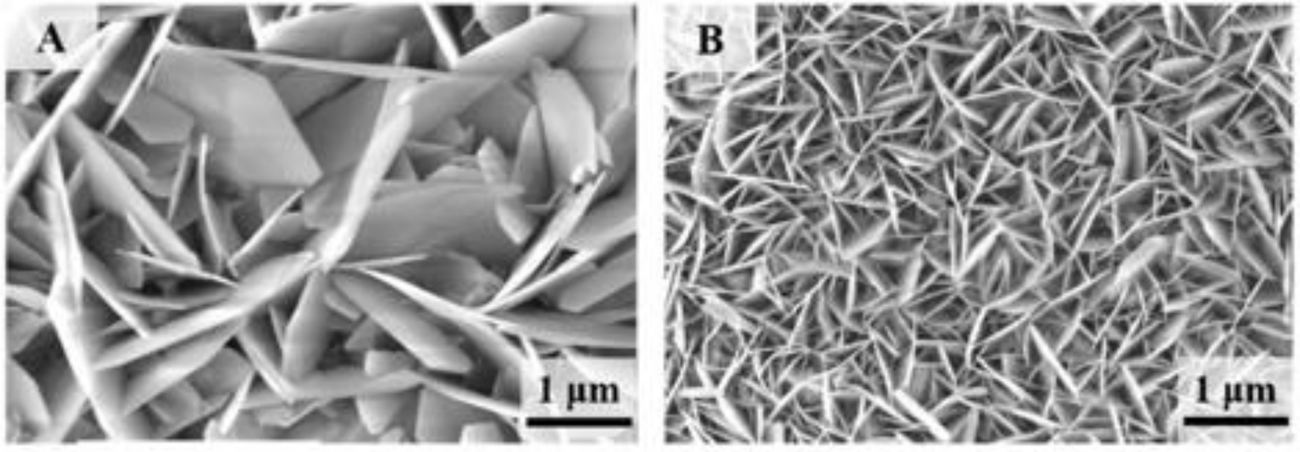
Zinc anode in neutral/mildly acidic electrolytes





Small **16**, 2000730-2000758 (2020)

Morphology of electrodeposited zinc:



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

Zinc anode:

- **Nonflammable aqueous electrolyte**
- **Low (but not too low) redox potential (slightly under HER)**
- **High theoretical specific capacity (820 mAh/g, 5854 mAh/cm^3)**
- **Low cost**

Challenges:

- **Water reduction (HER)**
- **μm-scale: non-uniform deposition**

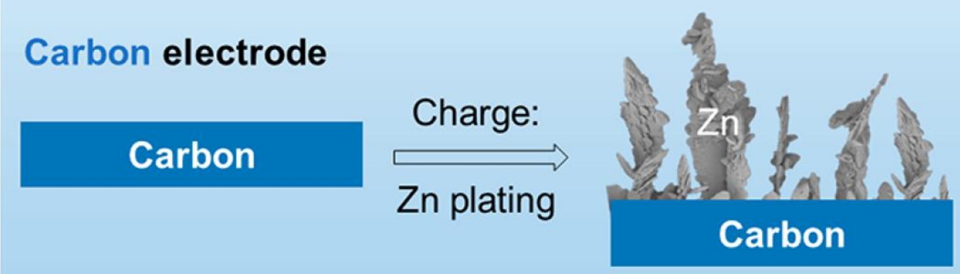
  Solutions:

  - Electrolyte additives
  - Electrode coating & doping (e.g. In, Sb)

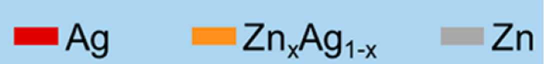
- **mm-scale: migration of active materials**

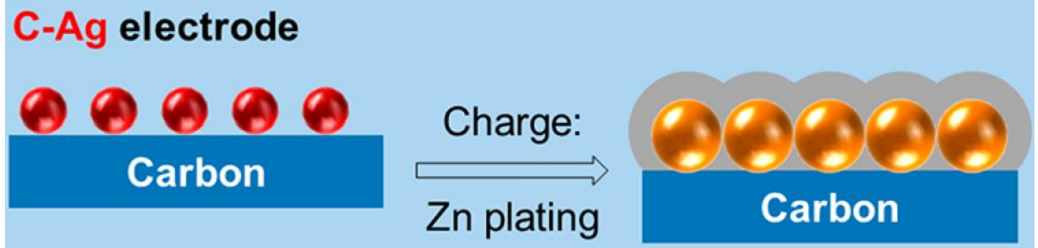
  (thick electrodes, high areal capacity)

Shape change of Zn anodes; Spatial regulation of soluble Zn species



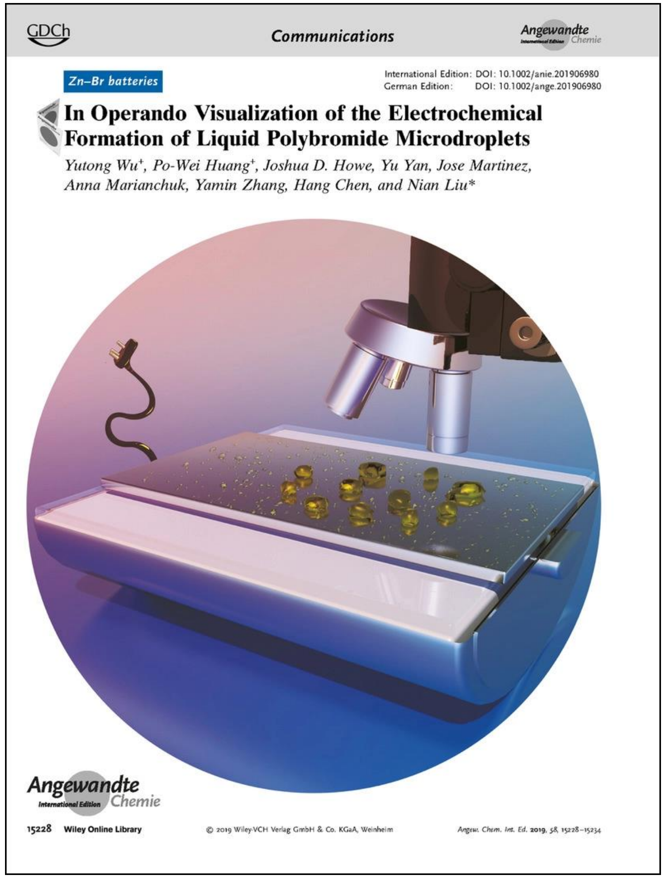
Y. Zhang, N. Liu* et al.
ACS Energy Lett.
2021, 6 (2), 404–412





Carbon fiber paper:

- Dendritic Zn deposition
- Dead Zn left behind results in capacity decay


GDCh Communications Angewandte Chemie

Zn–Br batteries

International Edition: DOI: 10.1002/anie.201906980
German Edition: DOI: 10.1002/ange.201906980

In Operando Visualization of the Electrochemical Formation of Liquid Polybromide Microdroplets

*Yutong Wu[+], Po-Wei Huang[+], Joshua D. Howe, Yu Yan, Jose Martinez, Anna Marianchuk, Yamin Zhang, Hang Chen, and Nian Liu**

Angewandte Chemie International Edition

15228 Wiley Online Library © 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim *Angew. Chem. Int. Ed.* 2019, 58, 15228–15234

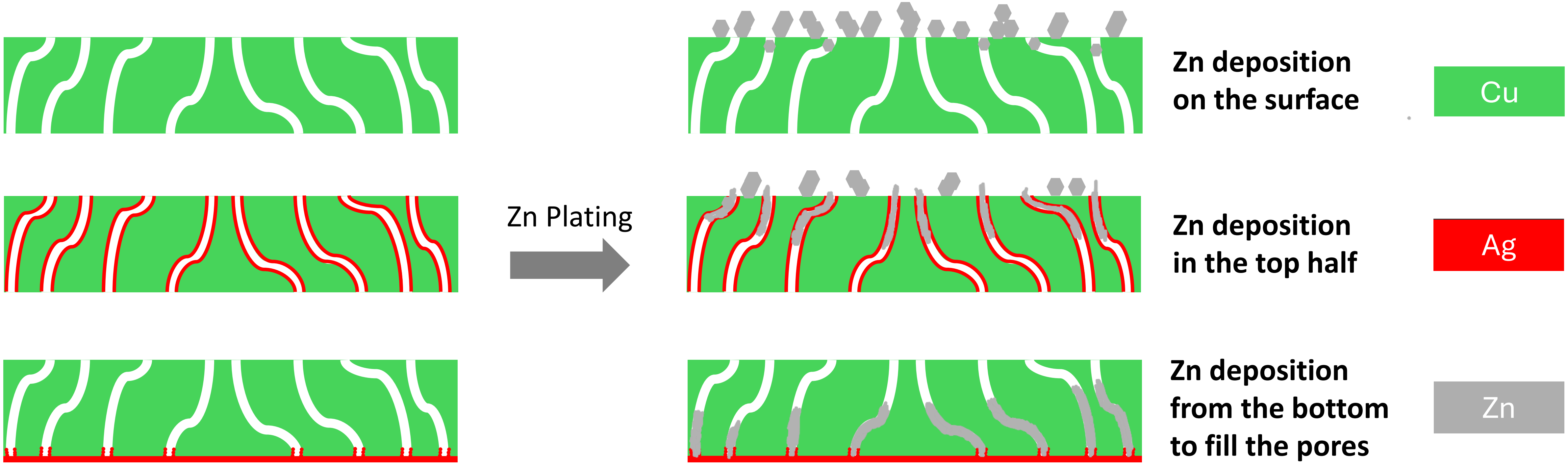
In operando Optical Microscopy for Visualizing Battery Local Dynamics

Angew. Chem. Int. Ed. 131 (43), 15372-15378 (2019)

Proc. Natl. Acad. Sci. U.S.A 116 (3), 765-770 (2019)

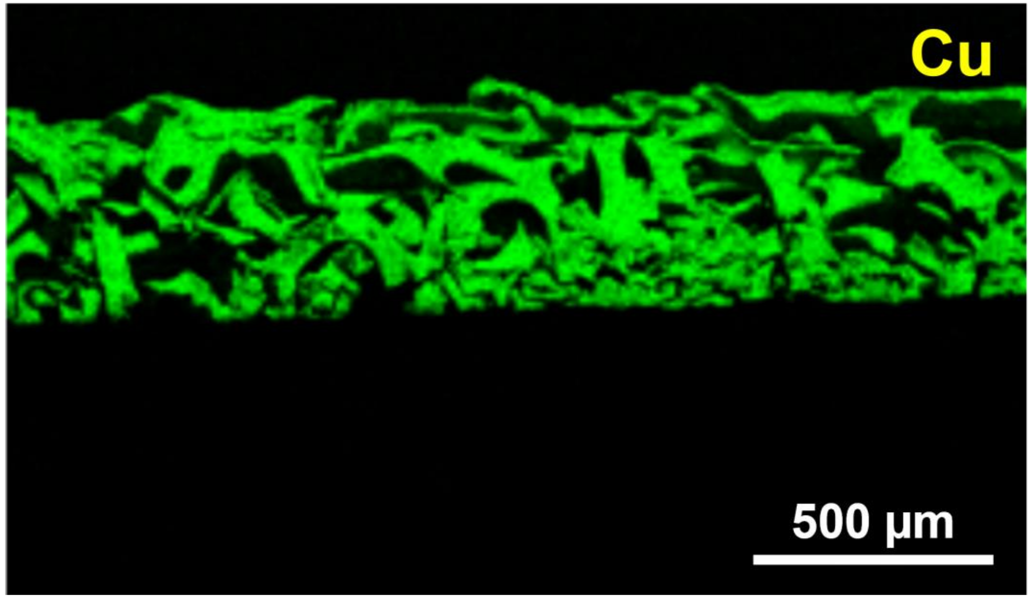
Nature Communications 11, 606 (2020)

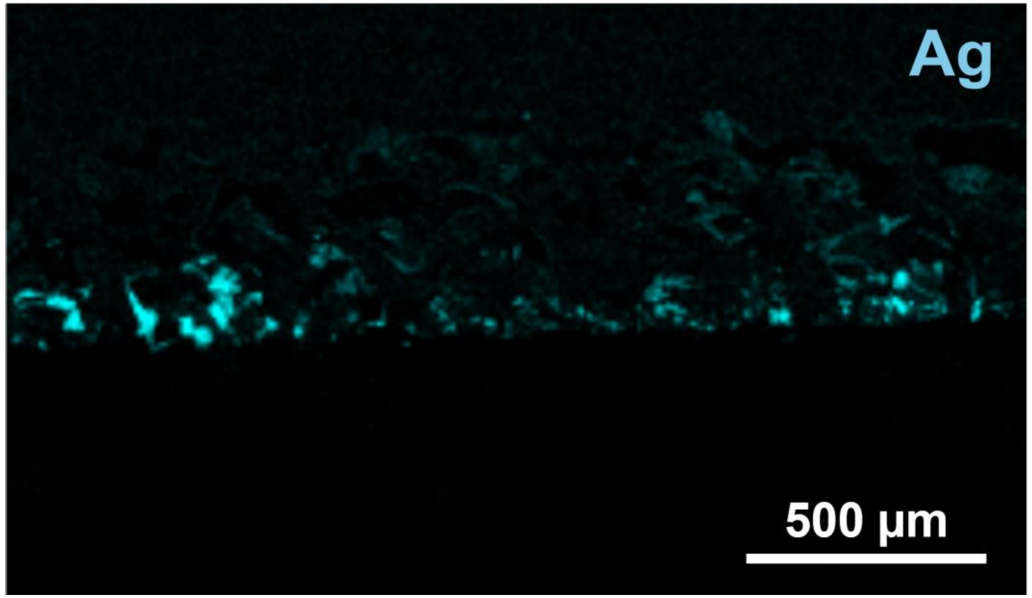
Design of Ag@back Cu foam

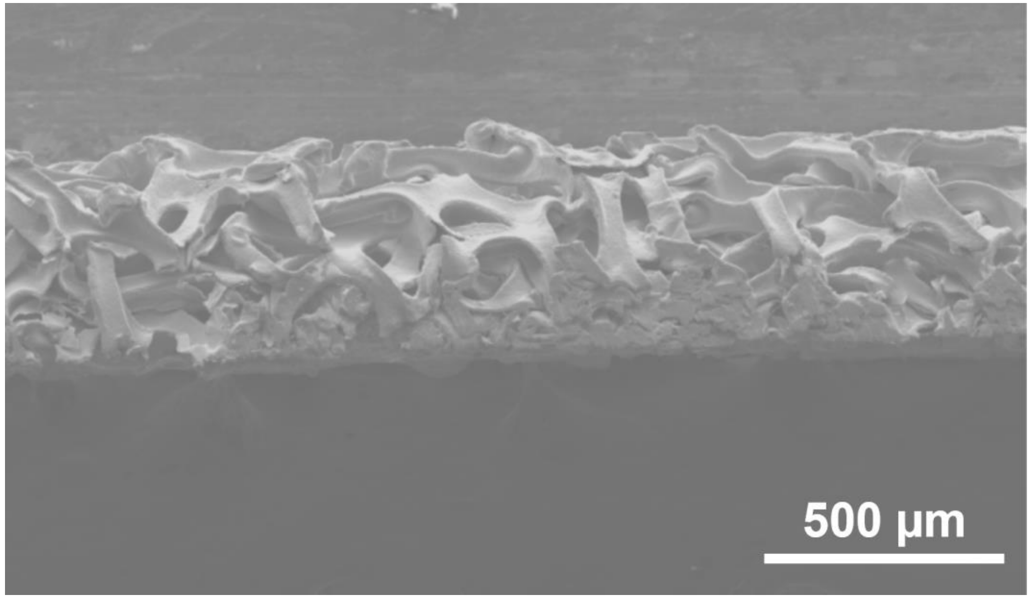


- Ag is sputtered on one side of Cu foam
- Before cycling, Zn will be electrochemical loaded into Ag@Cu foam
  - unsputtered side faces towards Zn foil counter electrode, "Ag@back Cu foam"
- Zn will preferentially deposit on Ag-rich side and fill the pores inside Cu foam
  - Zn deposition preference (Ag > Zn > Cu)
- This design can achieve stable cycling at high areal capacity
  - has enough porosity to host 120 mAh/cm^2, tested up to 30 mAh/cm^2)

Fabrication & characterization of Ag@back Cu foam

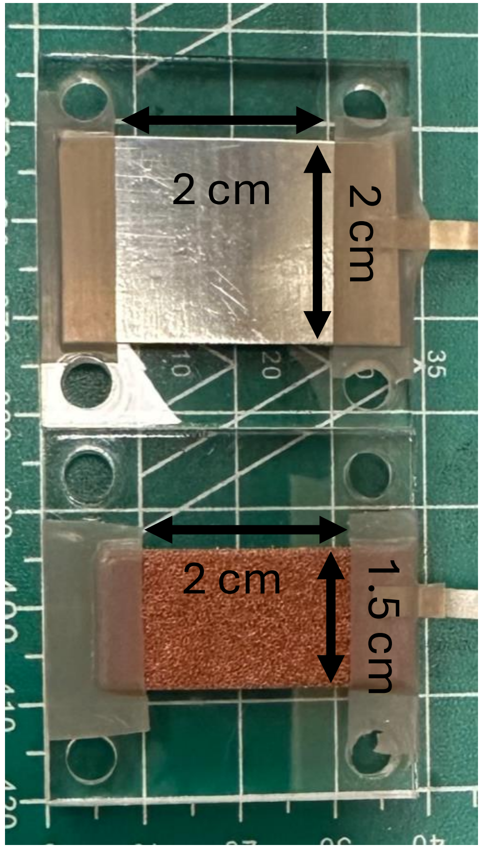


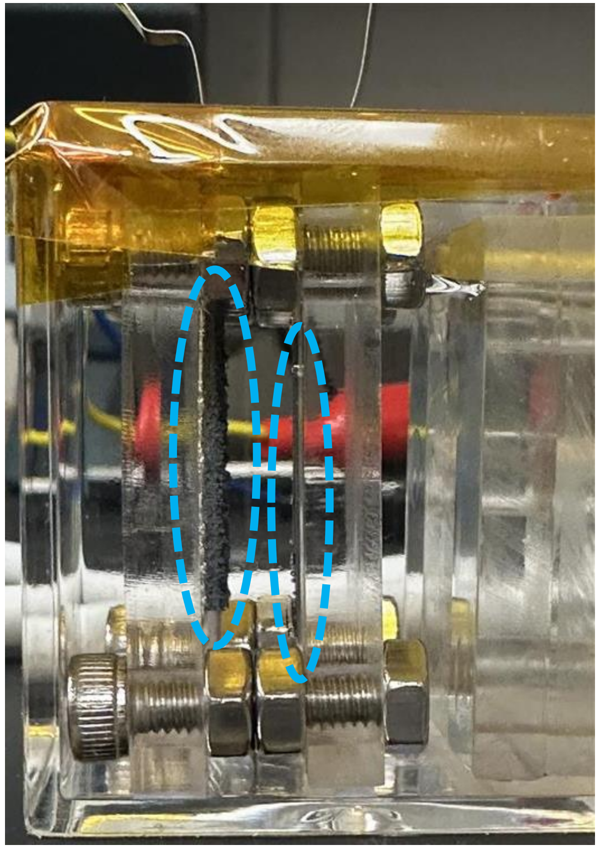


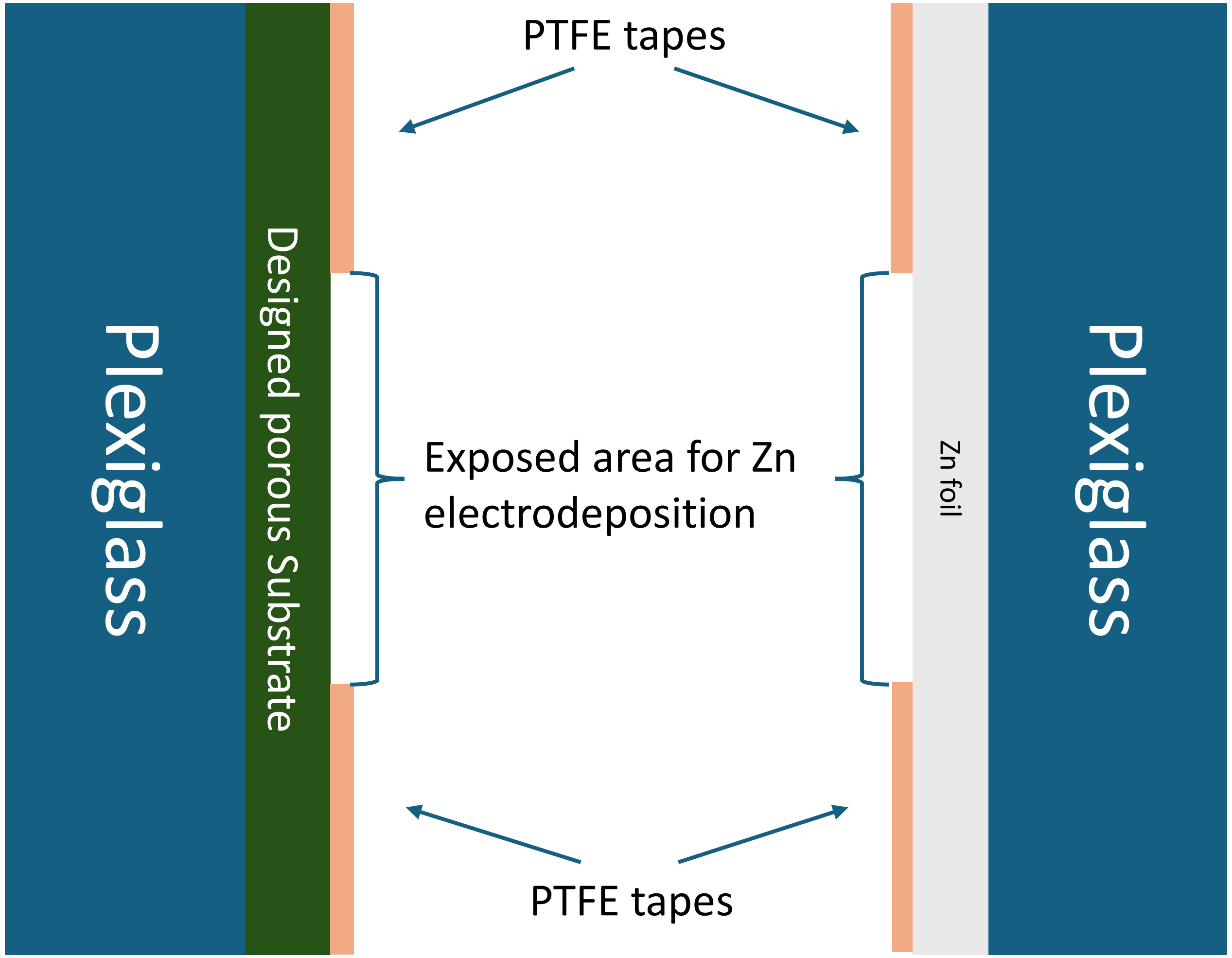


2 um of Ag was deposited by DC magnetron sputtering at a rate of 50 nm/min at a pressure of 5 mT

Cell configuration

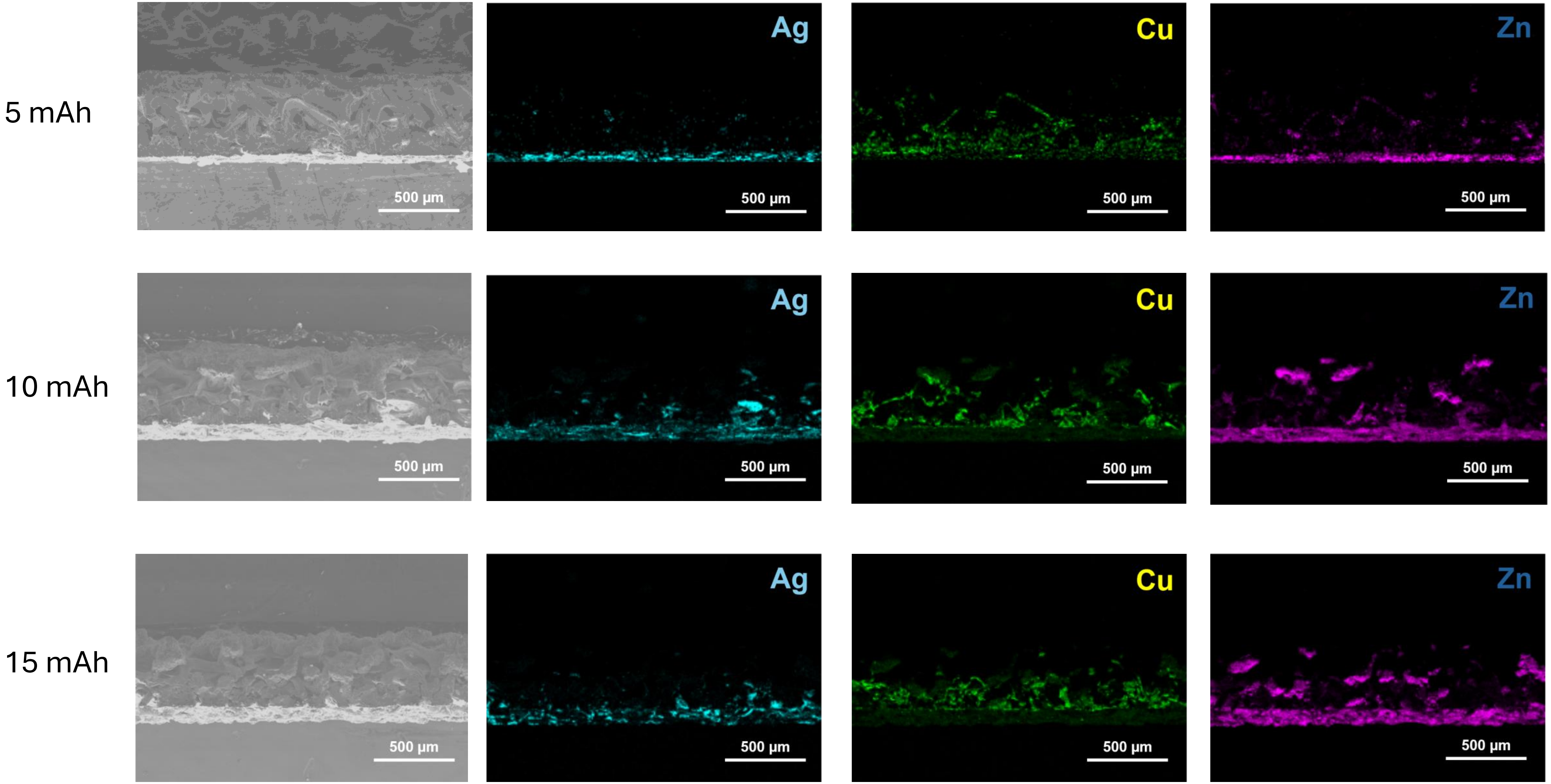




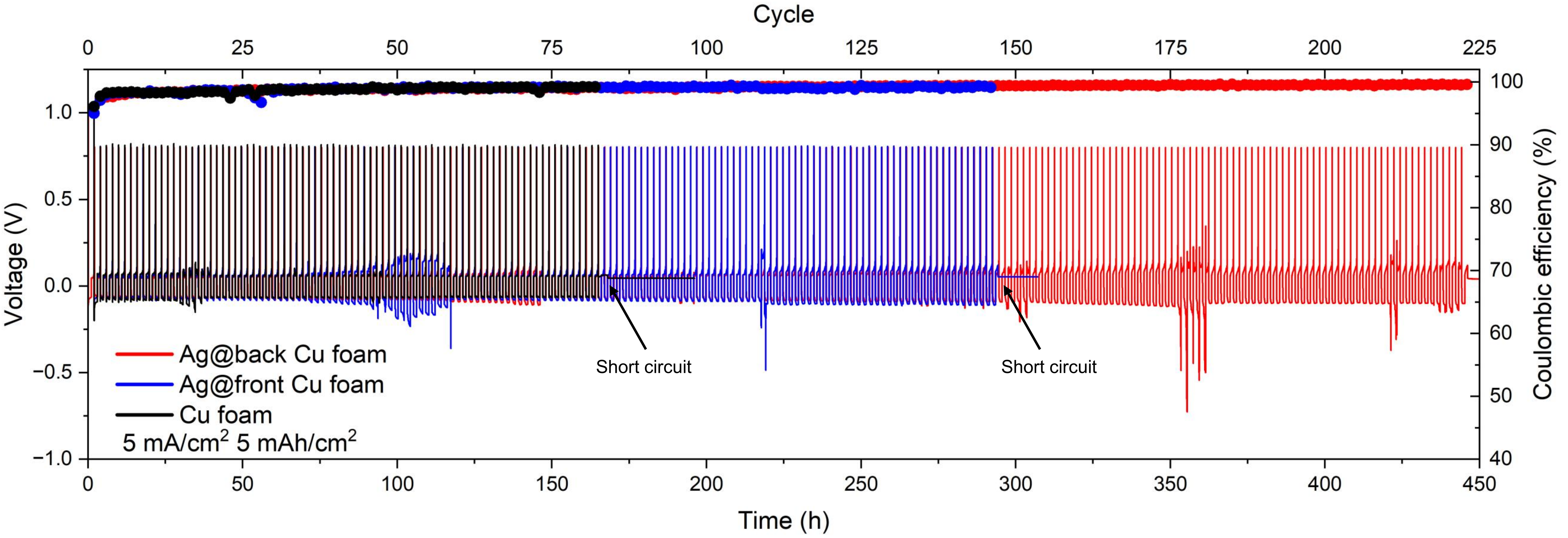


- The battery cell is exposed to vacuum for 1 h and then rest for 2 h before adding 2 M $ZnSO_4$ electrolyte
- Electrolyte is added until exposed area are fully immersed
- The distance between two electrodes is controlled to be ~4mm
- Using slightly larger Zn foil to mitigate dendrite formation on Zn foil side

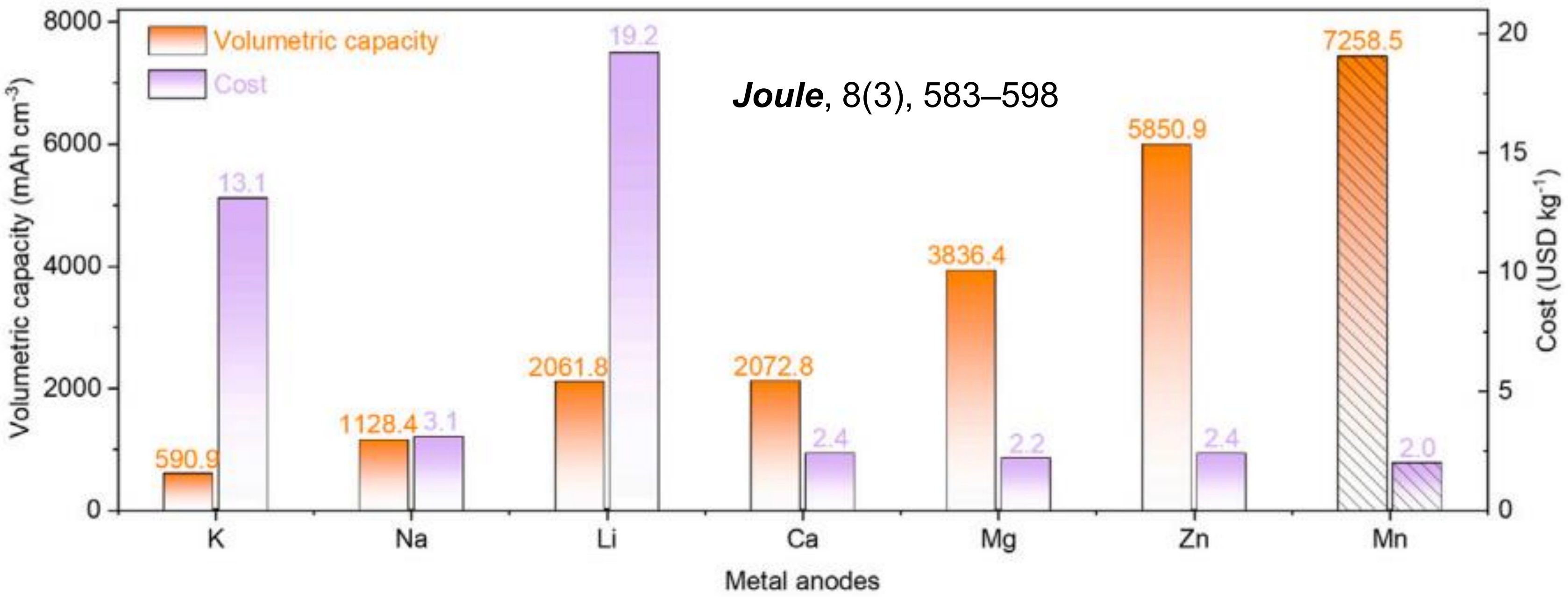
Zn electrodeposition morphology



Cycling performance (half cell against Zn foil)



Mn as an anode material for aqueous batteries



- Mn anode has the highest volumetric capacity and lowest cost, among all the elements listed in the table
- The standard electrode potential is 0.42V lower than Zn, leading to higher cell voltage
- Promise of an all-Mn aqueous battery (2 Mn (II) ↔ Mn (IV) + Mn (0), assemble at symmetric/discharged state, 1.5V → 1.9V, 33% higher theoretical specific energy than Zn-MnO_2 chemistry)

However, Mn anodes suffer from:

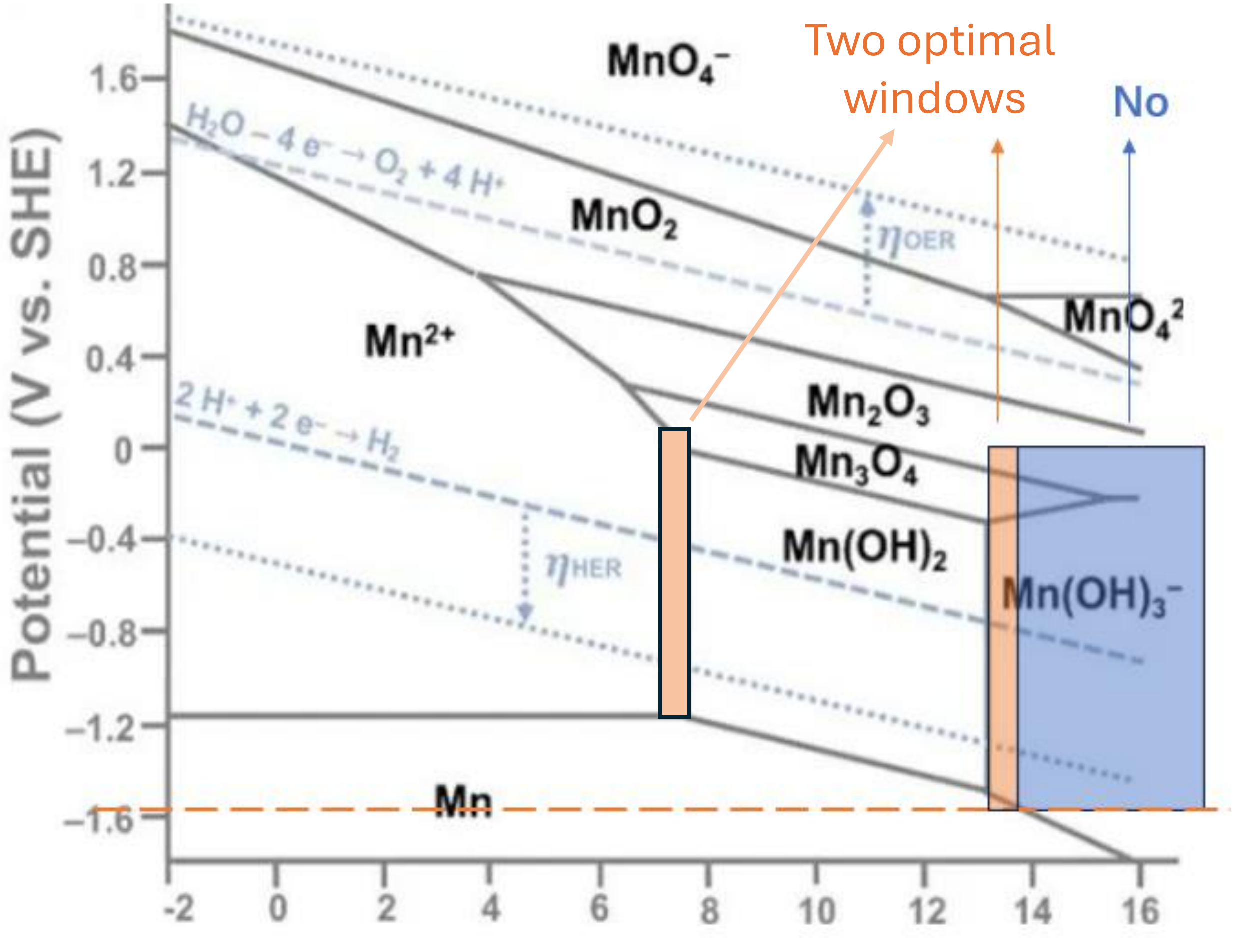
- More severe hydrogen evolution reaction (as compared to Zn, due to the lower potential)
- Poor reversibility of plating/stripping reactions (similar problems in Zn have been tackled)

Our initial design of electrolyte (v1.0)

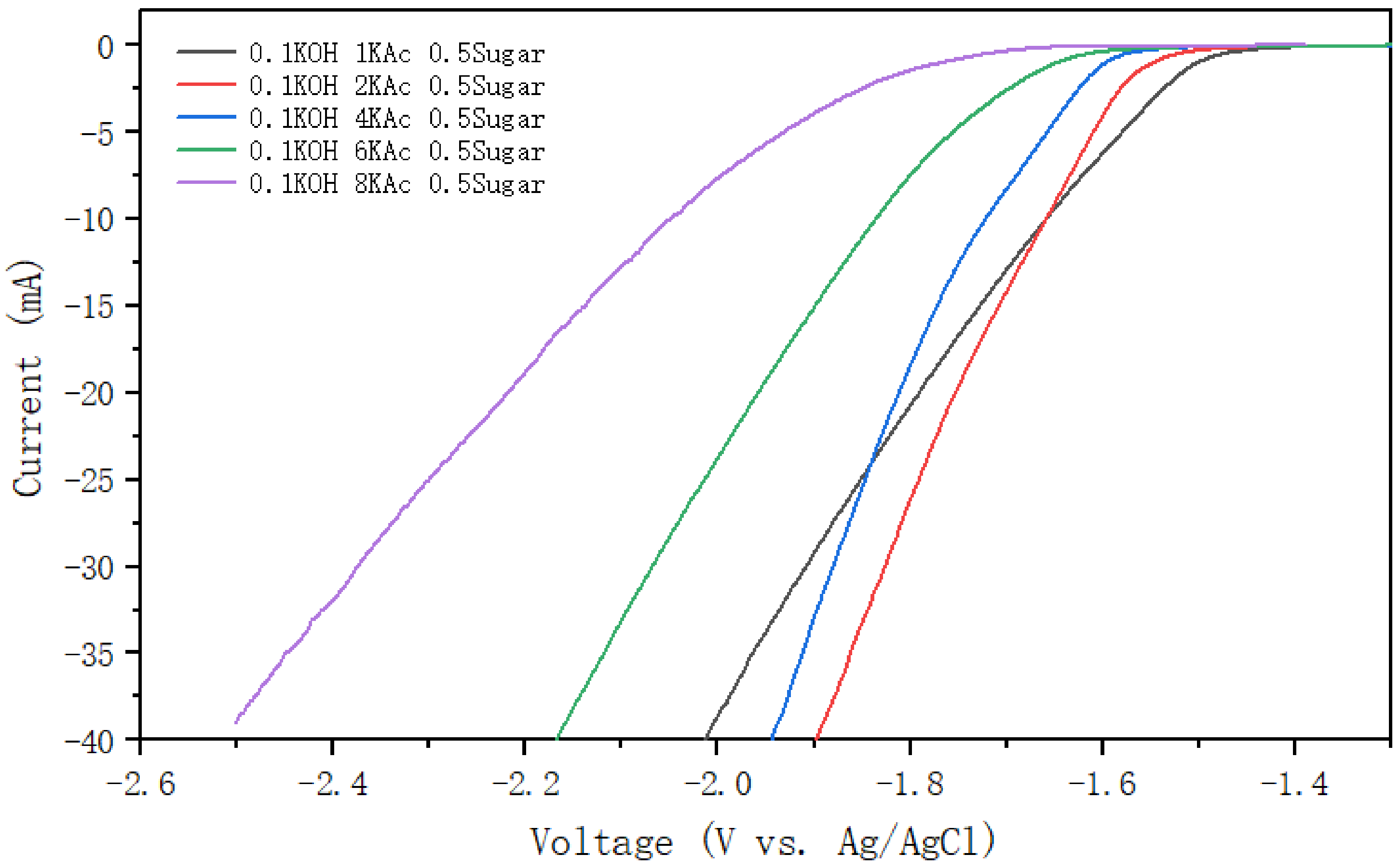
- Suppress water activity
  by adding potassium acetate (KAc) and sucrose
- Avoid passivating discharge product, $Mn(OH)_2$
  by controlling pH < 8 or > 13
- Ease the plating of Mn (as compared to HER)
  by controlling 7 < pH < 14
- Electrolyte v1.0:
  KAc + Sucrose + 0.1M KOH

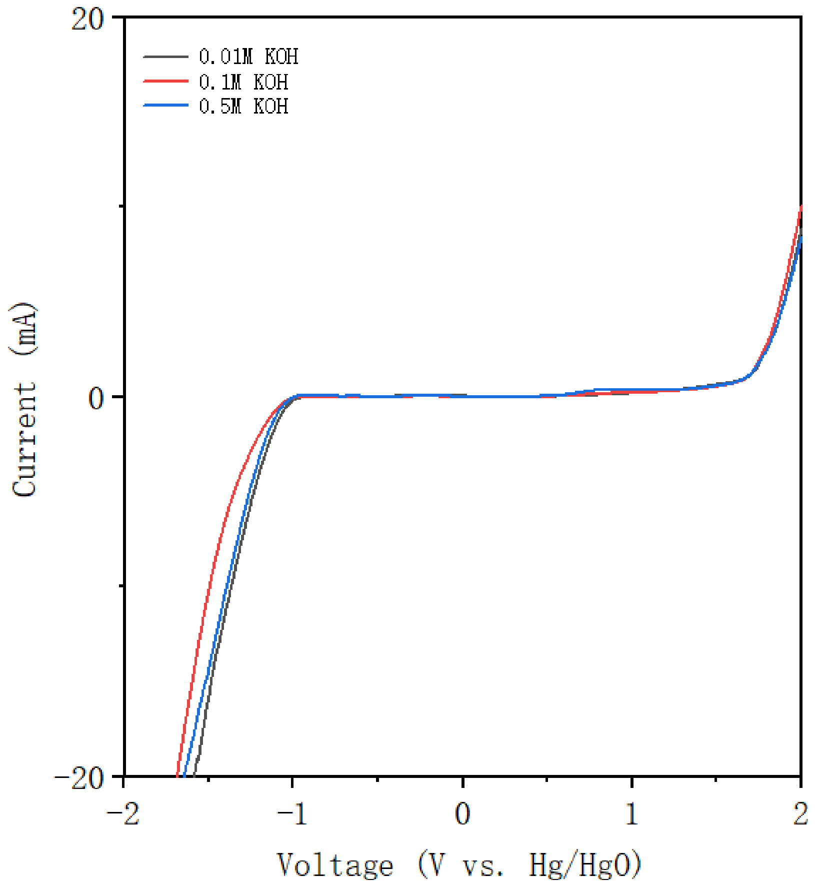
We will test the following characteristics of electrolyte

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



Widened stability window (suppressed HER)

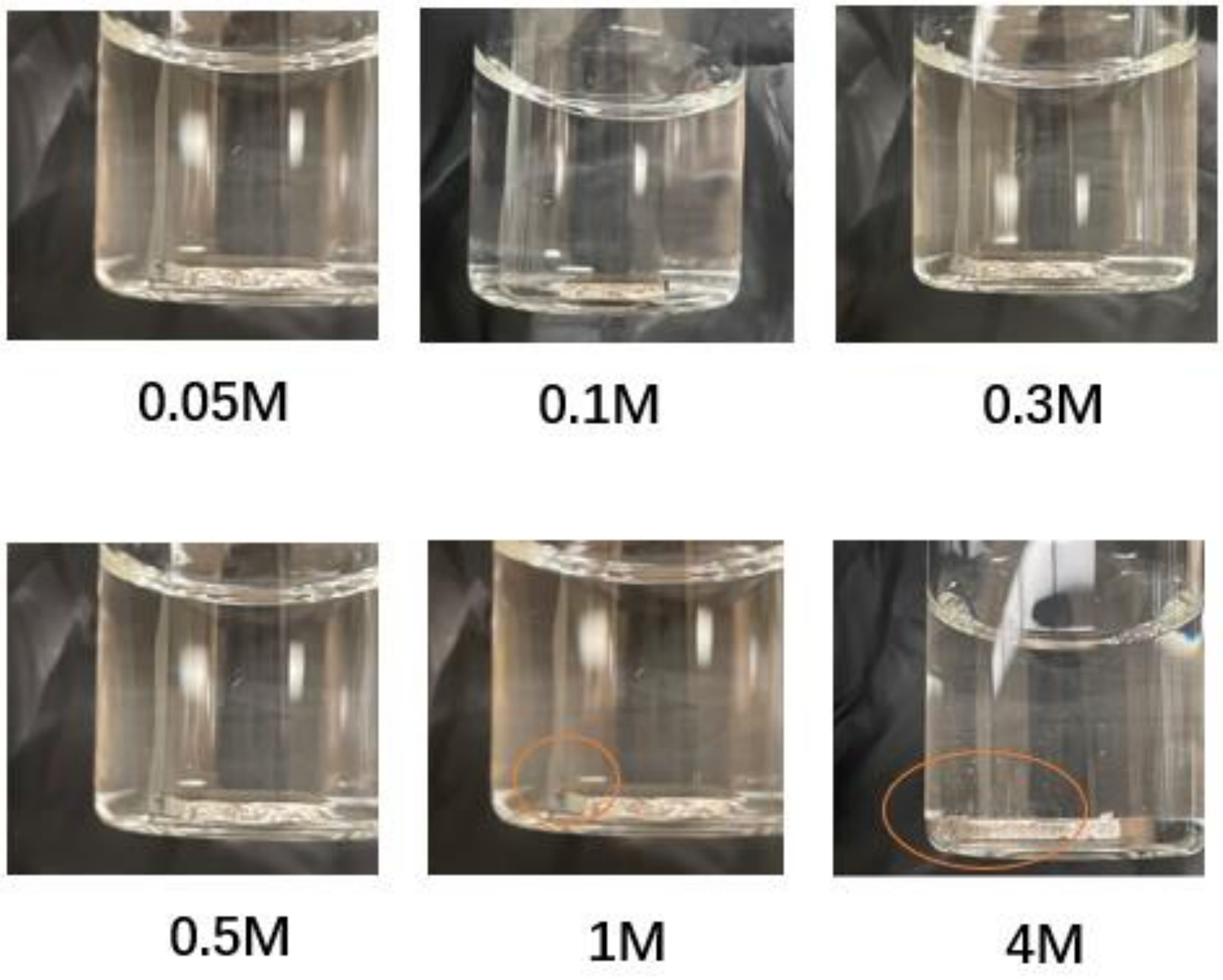




- Potential window of electrolyte with same concentration of KOH and sucrose but different KAc concentrations
- More KAc, wider the stability window of electrolyte

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

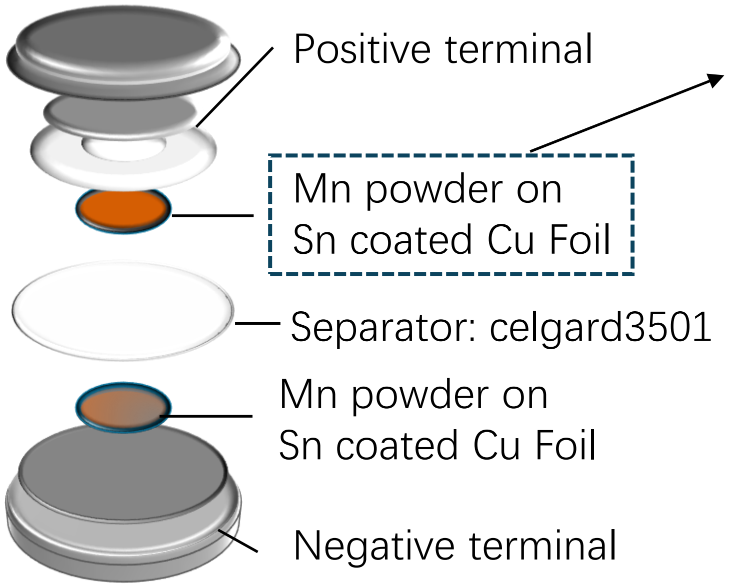
Stability of Mn metal in electrolyte

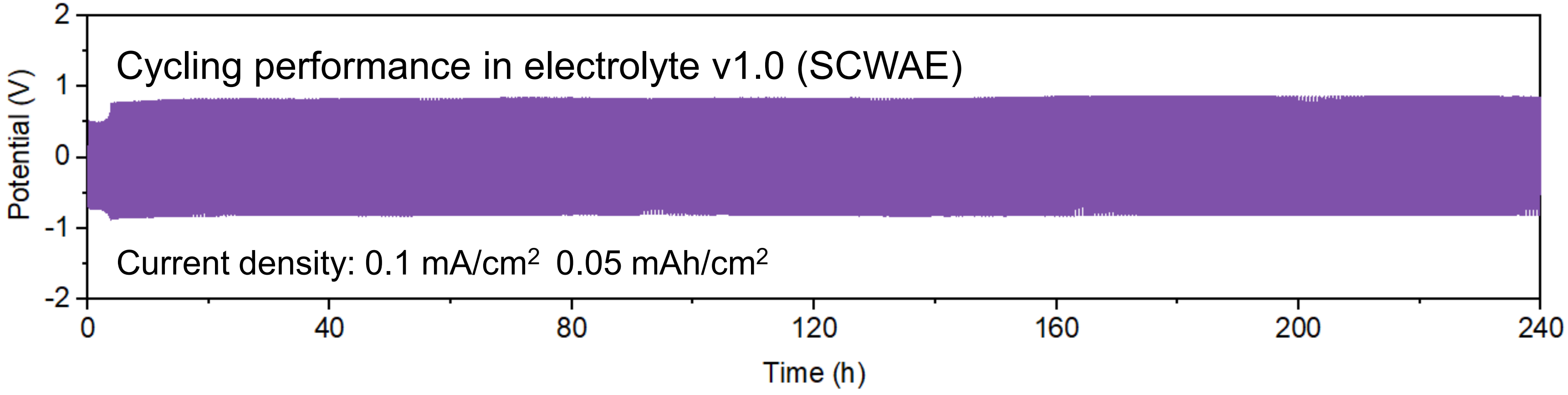


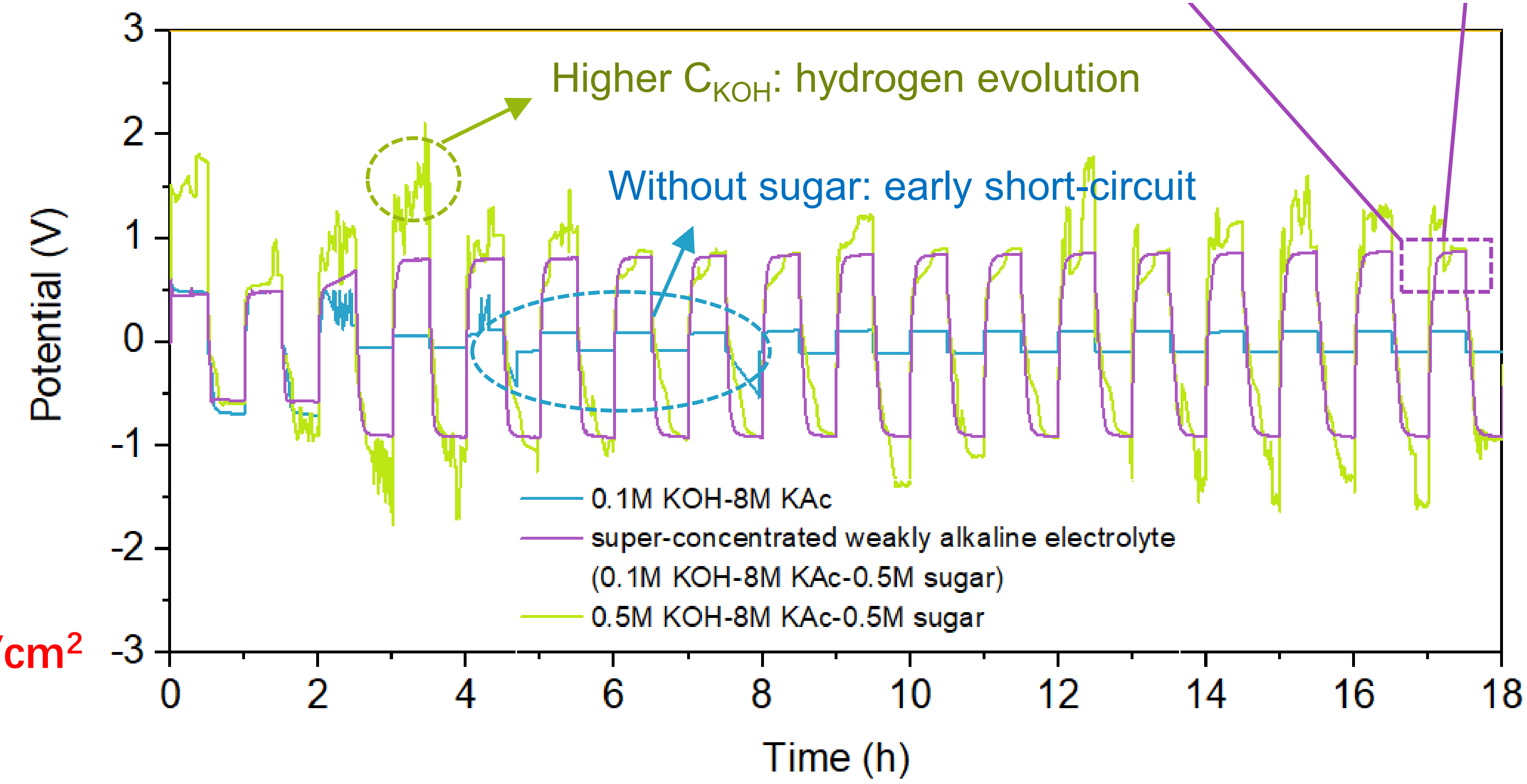
Base electrolyte: 8M KAc + 0.5M sucrose

- Small pieces of Mn is placed in electrolytes containing different concentrations of KOH
- Bubbles form in the electrolyte with > 1M KOH concentration

Mn-Mn symmetrical cell



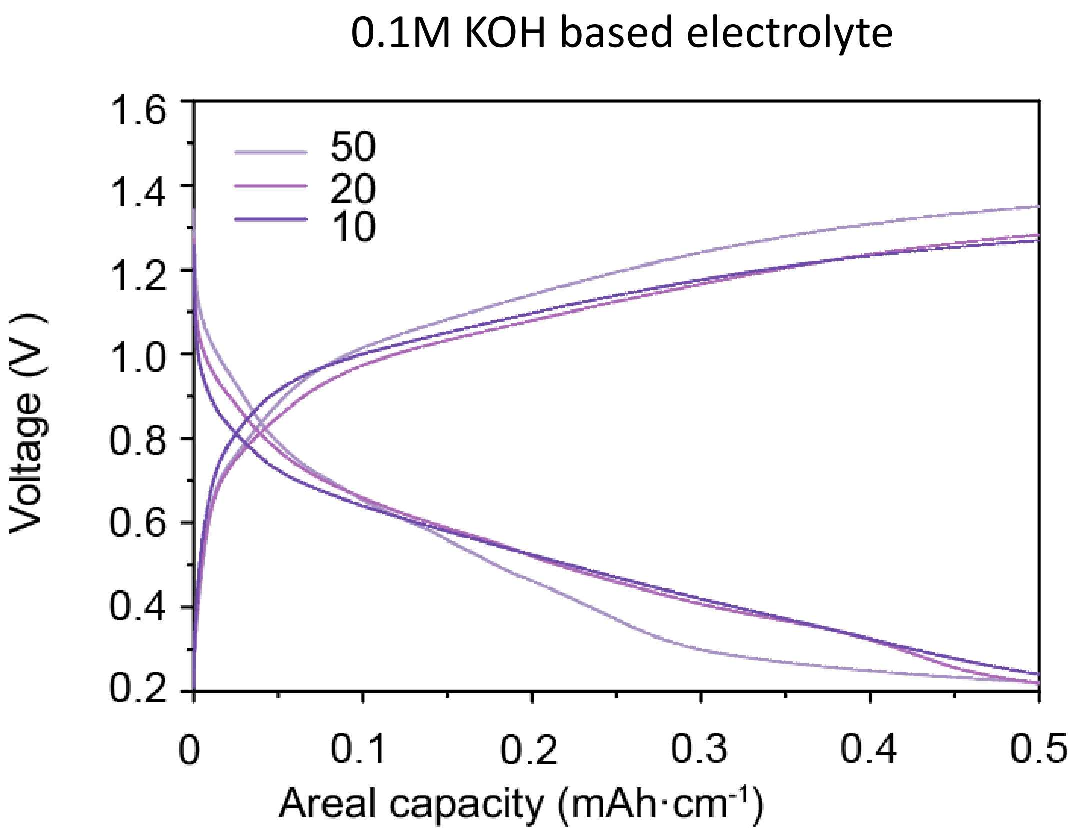


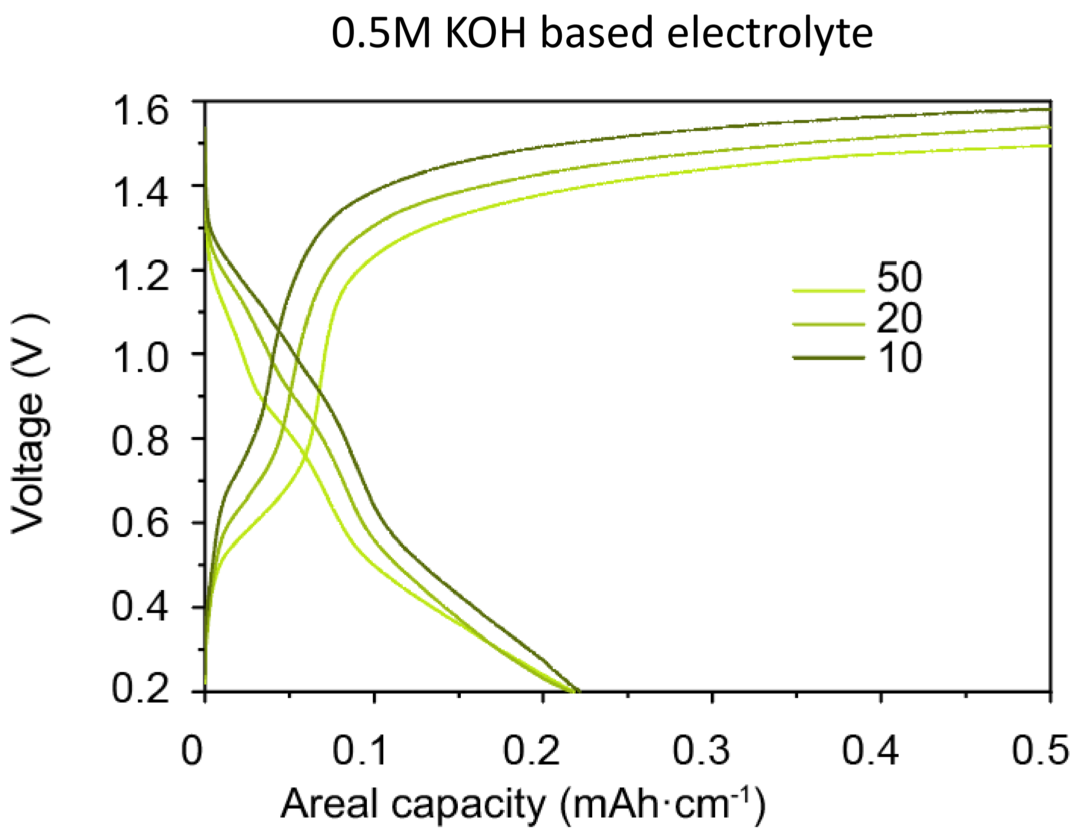


- Suppressed HER
- Suppressed Dendrite growth
- Prolonged the cycling life
- **0.8 V overpotential at 0.1 mA/cm²**

$Mn-MnO_2$ full cell

Testing condition: 0.1 mA/cm², 0.5 mAh/cm²

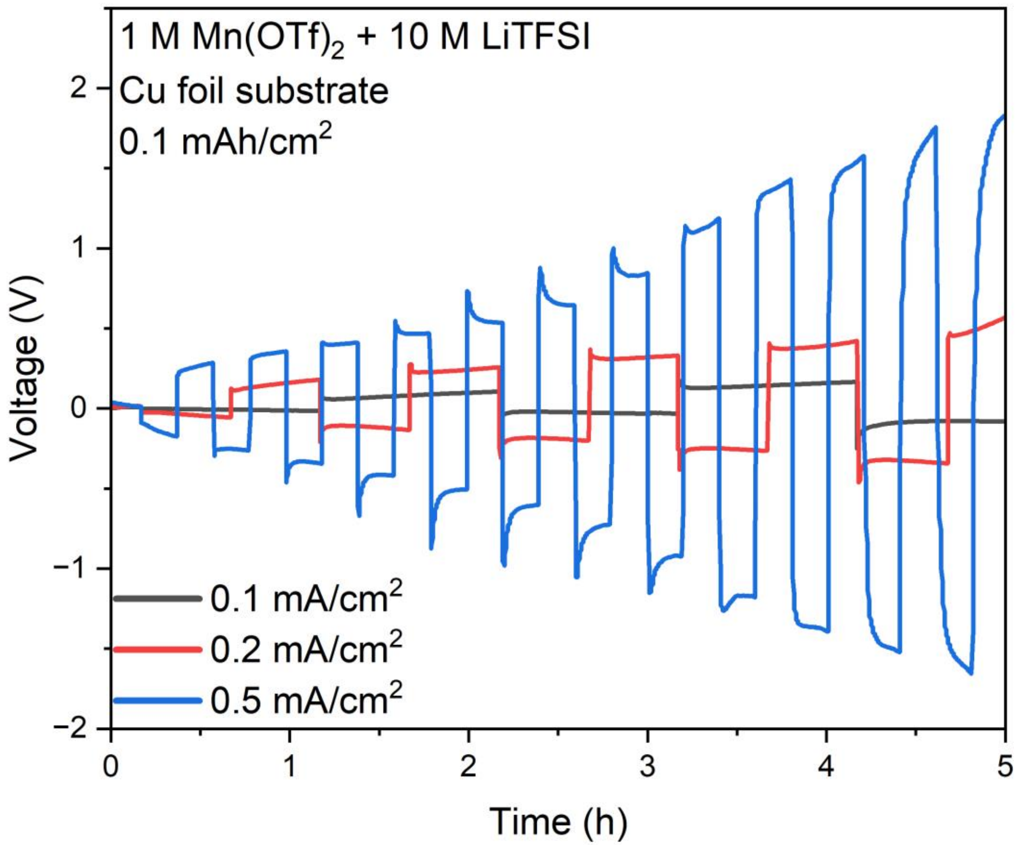


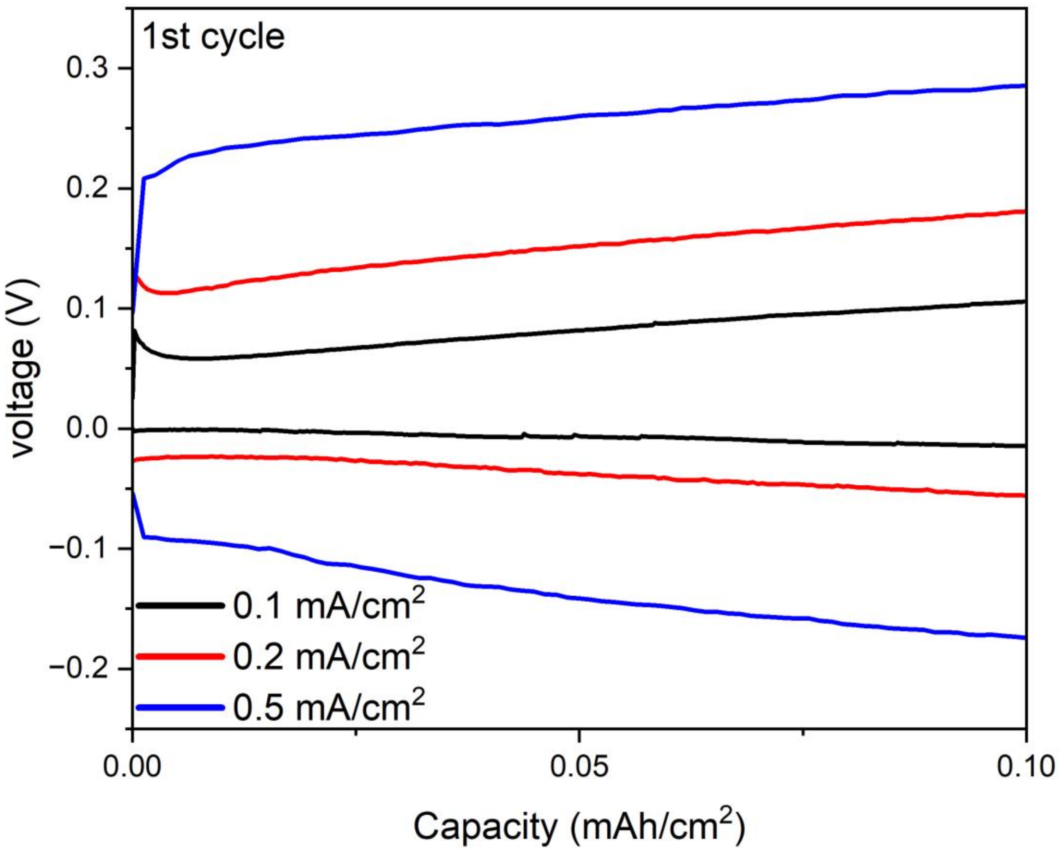


0.1M KOH based electrolyte: 0.1M KOH - 8M KAc - 0.5M sugar

0.5M KOH based electrolyte: 0.5M KOH - 8M KAc - 0.5M sugar

Electrolyte v2.0 (Mn-Mn symmetrical cell)





Overpotential at 0.1 mA/cm^2

0.8V → 0.1V

(v1.0) (v2.0)

Acetate anion has strong solvation to Mn^{2+}

TFSI anion has weaker solvation to Mn^{2+}

Acknowledgment

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- Sandia National Laboratories
- Contact me: nian.liu@chbe.gatech.edu