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ACES Lab
Analysis of Complex
Electrochemical Systems

Development of High Capacity Cathodes for Rechargeable Alkaline Zinc Batteries

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Background

As global energy production becomes increasingly dependent on renewable sources, the development of improved energy storage systems has become a mission of global importance. **Rechargeable alkaline batteries** have the potential to meet the demanding cost and safety requirements for grid storage, i.e. **Zn-MnO₂** and **Zn-CuO**. The cathodes of these cells are metal oxides that can deliver 2 electrons per transition metal. The simplified cathode half-cell reactions are below:

Mn^{IV} to Mn^{III} reaction (1st electron):
 $\text{Mn}^{\text{IV}}\text{O}_2 + \text{H}_2\text{O} + \text{e}^- \leftrightarrow \text{Mn}^{\text{III}}\text{OOH} + \text{OH}^-$

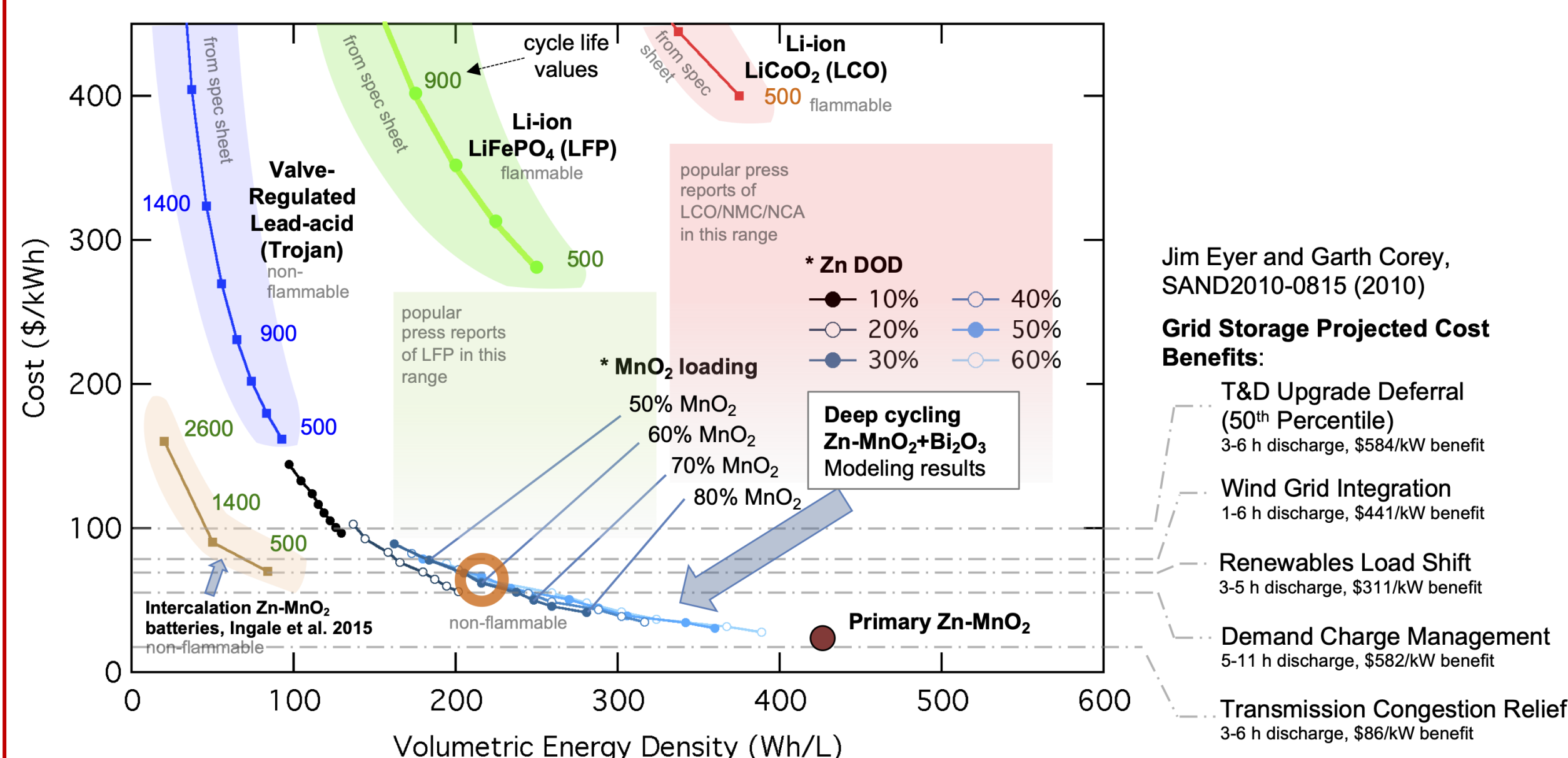
Cu^{II} to Cu^I reaction (1st electron):
 $2\text{Cu}^{\text{II}}\text{O} + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow \text{Cu}_2\text{O} + 2\text{OH}^-$

Mn^{III} to Mn^{II} reaction (2nd electron):
 $\text{Mn}^{\text{III}}\text{OOH} + \text{H}_2\text{O} + 3\text{OH}^- \leftrightarrow \text{Mn}^{\text{II}}(\text{OH})_6^{3-}$
 $\text{Mn}^{\text{III}}(\text{OH})_6^{3-} + \text{e}^- \leftrightarrow \text{Mn}^{\text{II}}(\text{OH})_2 + 4\text{OH}^-$

Cu^{II} to Cu^I reaction (2nd electron):
 $\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \leftrightarrow 2\text{Cu}^0 + 2\text{OH}^-$

Being able to reversibly cycle 2 electrons imparts high specific capacity to these materials: MnO₂ being **617 mAh/g** and CuO being **674 mAh/g**. These large capacities rely on dissolution of intermediate materials and is enabled by the alkaline electrolyte. This work seeks to maintain these capacities over many cycles, to develop successful batteries for the grid.

Economic Analysis of MnO₂ Cathodes



Alkaline electrolyte systems enable cathodes that can reversibly cycle 2 electrons in depth. The plot above shows analysis of the alkaline Zn-MnO₂ system using materials cost (\$/kWh) on the y-axis and energy density (Wh/L) on the x-axis.¹ In general, energy density will be highly limited by the cathode capacity. The **red circle** shows a design target for grid batteries with cost <60 \$/kWh and energy density >200 Wh/L.

Mature battery chemistries

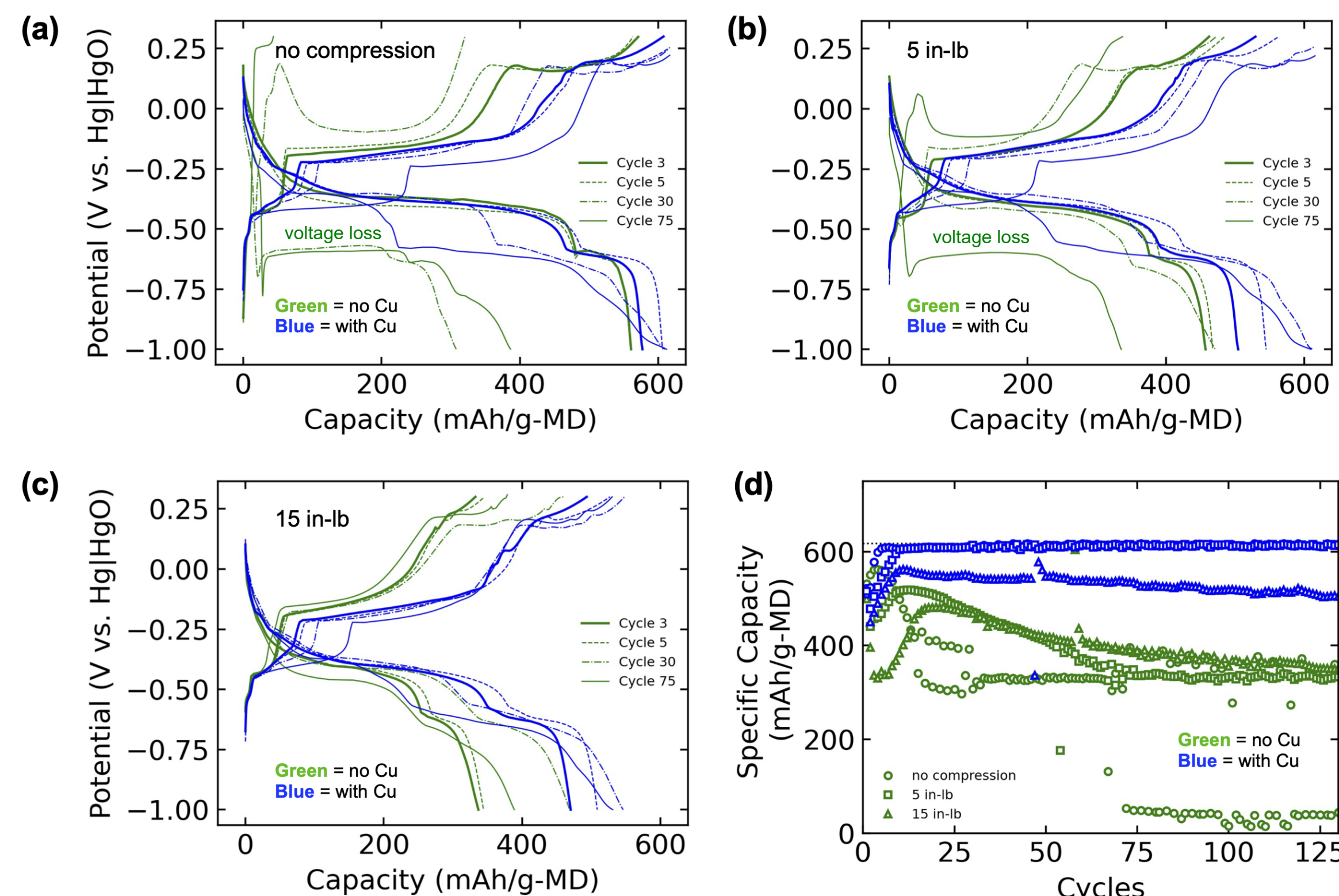
- Lead-acid, LFP Li-ion, and LCO Li-ion are mature technologies. Calculations for these were based on available battery specifications.
- There is generally a trade-off between *cycle life* and *cycled depth of discharge (DOD)*. Cycling to a higher DOD results in lower cost and higher energy density, but also lowers the expected cycle life.
- Reports of lower-cost Li-ion cells originating from China are indicated by the colored boxes.

Deep cycling Zn-MnO₂+Bi₂O₃

- Assuming 100% DOD of the MnO₂, there are two important variables: *wt% loading of MnO₂* in the cathode and *cycled DOD of the Zn anode*. These are systematically varied in the model above.
- At 10% DOD of Zn, the battery is a low-cost competitor to lead-acid.
- At 30% DOD of Zn, the battery can potentially have high energy density, competitive with LFP Li-ion.

1. Turney, Yadav, and Gallaway et al.; *Energy-Sustainable Advanced Materials*, Edited by Alston and Lambert. Springer, 2021

Compression Study of MnO₂ Cathodes

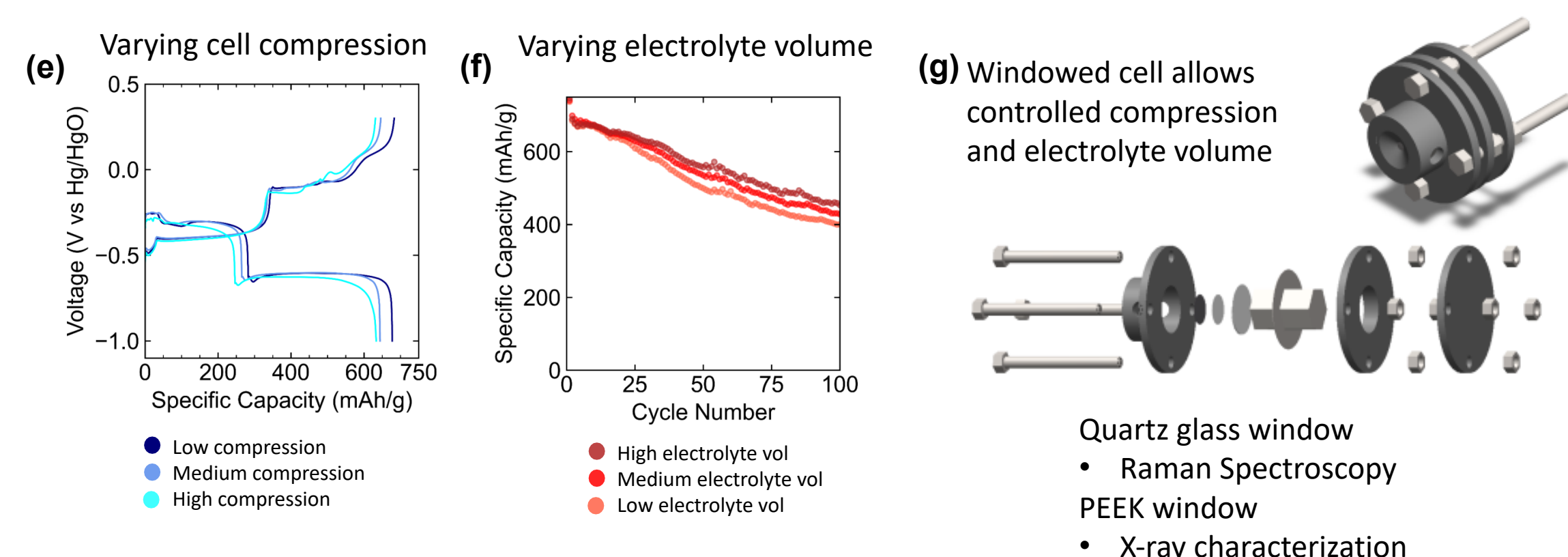


Compression is an important variable often overlooked in research on rechargeable alkaline batteries. We accomplished an analysis of the effect of compression on the alkaline MnO₂ cathode. Two sets of additives were considered: **MnO₂+Bi₂O₃** and **MnO₂+Bi₂O₃+Cu**. Including Cu has been shown to extend cycle life in the past.²

- The **MnO₂+Bi₂O₃** case showed large voltage loss at no compression (a) or moderate 5 in-lb bolt torque (b). However at 15 in-lbs the voltage profile was maintained (c), although ~25% of capacity was lost.
- The **MnO₂+Bi₂O₃+Cu** case showed better capacity at lower compression (d). This suggests the positive effect of adding Cu is partially a mechanical effect: volume expansion when converting to CuO provides compression. However, this effect is accompanied by additional capacity due to Cu electrochemistry. The 15 in-lb results indicate the additional capacity due to Cu is ~200 mAh/g-MD at cycle 75.

2. Yadav, et al. *Nature Communications*, 2017, 8, 14424.

Compression and Electrolyte Study of CuO



We have begun a corresponding study of the effect of compression (e) and electrolyte volume (f) on Zn-CuO cells developed at SNL. In parallel we are augmenting our previous findings on the CuO cycling mechanism with *operando* Raman spectroscopy experiments.³ These have required development of a windowed battery cell with controlled compression for spectroscopic characterization of alkaline systems (g).

- Applying compression to the cell housing during cycling decreases CuO electrode capacity and discharge voltage
- Increasing the amount of excess electrolyte improves capacity retention of the CuO electrode

3. Schorr, Bruck, Gallaway, Lambert et al.; *ACS Appl. Energy Mater.* 2021, 4, 7073–7082.

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