Scaling up inorganic flow-assisted long duration energy storage chemistries based on lead, manganese, and copper

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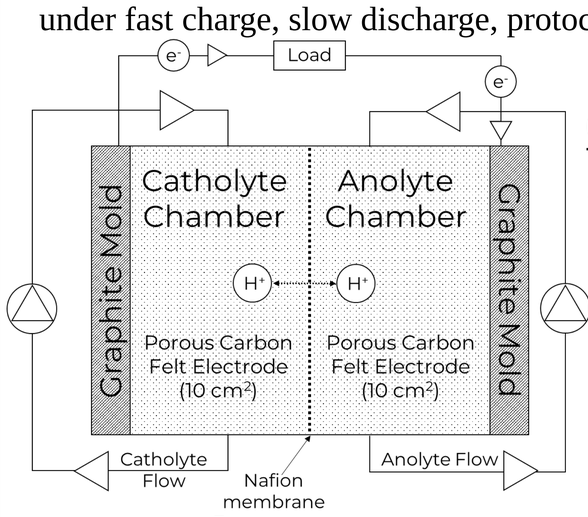
Introduction: Long duration energy storage (LDES) encompasses an array of technologies potentially capable of providing cheap and reliable power to the modernizing electrical grid. One promising technology is aqueous redox flow batteries (ARFB), utilizing decoupled catholyte/anolyte redox reactions, which can deliver safe and affordable power based on abundant elements.

The path from lab to market for ARFB requires the evaluation of specific combinations of redox couples, electrolyte composition, and electrochemical cycling parameters. Here, aqueous acidic electrolytes (pH < 2) are evaluated in 10 cm^2 flow cells. The Cu^{2+}/Cu anode reaction is paired with either an MnO_2- or PbO_2-based cathode reaction. The electrochemical performance of the two chemistries are presented and discussed.

Objective: Evaluate the performance of 10 cm^2 aqueous redox flow cells under fast charge, slow discharge, protocols.



Catholyte reactions

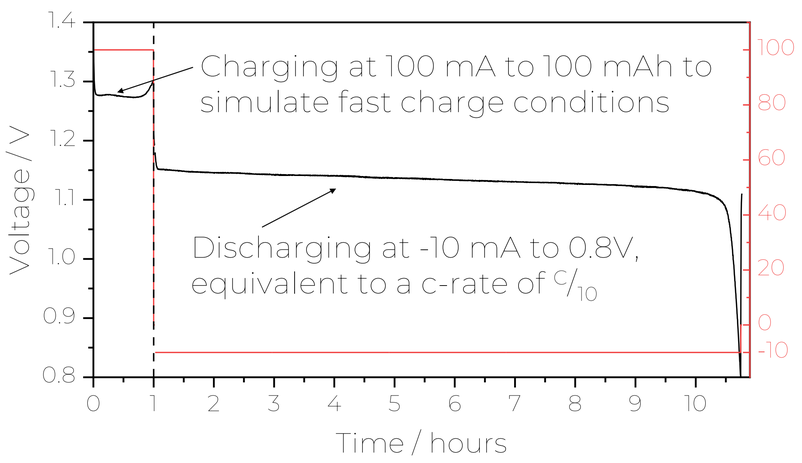
$Pb^{2+} + 2H_2O \leftrightarrow PbO_2 + 2e^- + 4H^+$, $E^o = +1.67\ V\ (vs\ SHE)$

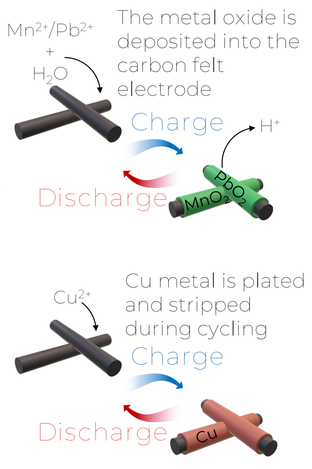
$Mn^{2+} + 2H_2O \leftrightarrow MnO_2 + 2e^- + 4H^+$, $E^o = +1.23V\ (vs\ SHE)$

Anolyte reactions

$Cu^{2+} \leftrightarrow Cu_{(s)} + 2e^-$, $E^o = +0.34\ V\ (vs\ SHE)$

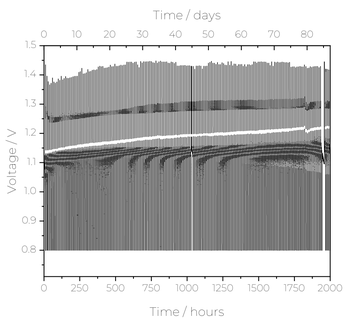
Approach: Develop metal oxide – metal couples for aqueous redox flow cells

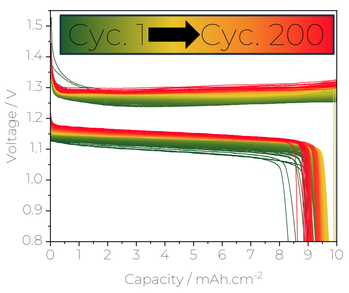


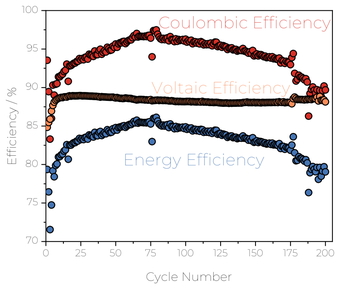


Results and Discussion:

Pb-Cu at 10 mAh.cm^{-2} areal loading

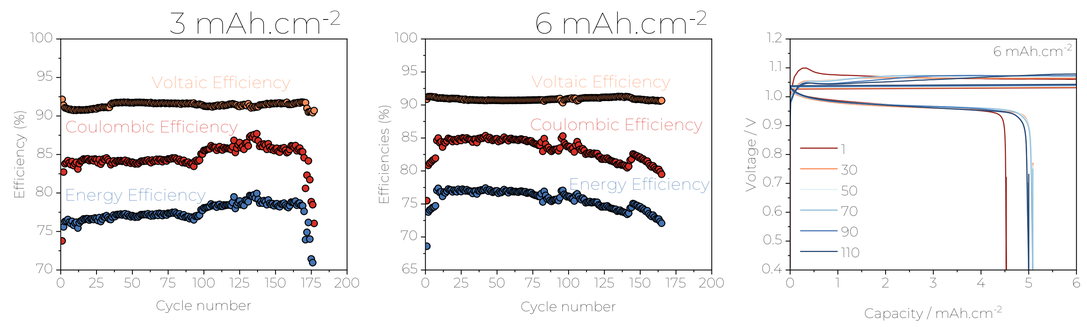






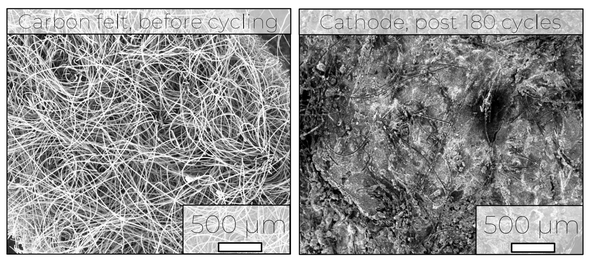
- Acidic electrolyte containing Pb^{2+}, and Cu^{2+}, 1C charge – C/10 discharge, 9.5 % DoD
- Using the asymmetric cycling protocol, the retains a CE above 90% for 200 cycles (2000 hours)
- A high average discharge voltage of ca. 1.15 V was achieved

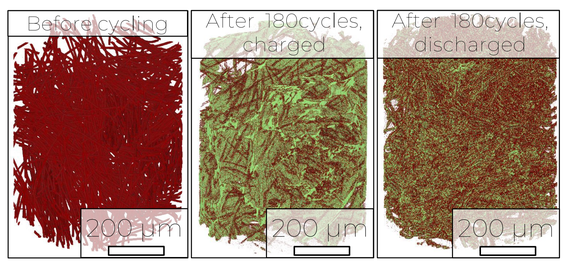
Mn-Cu at 3 and 6 mAh.cm^{-2}



- Acidic electrolyte containing, Mn^{2+}, and Cu^{2+}, 1C charge – C/10 discharge, 1.4% DoD
- MnO_2/Mn^{2+} cathode provides shorter cycle life, lower coulombic efficiency, and lower discharge voltage (0.95 V) compared to PbO_2/Pb^{2+} cathode (1.15 V)

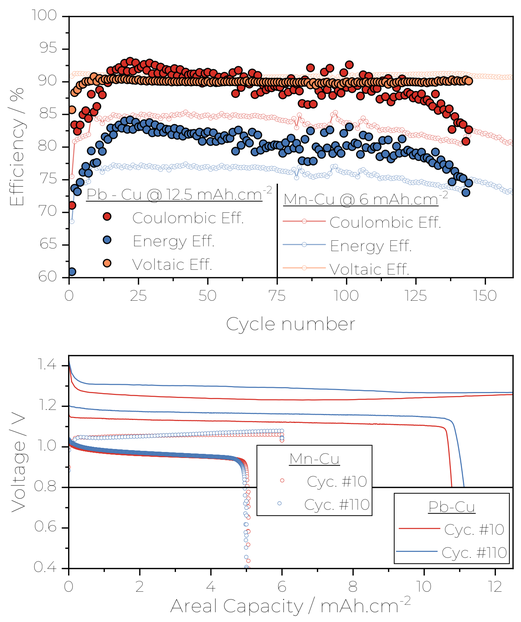
Ex-situ Characterization of Mn-Cu flow cells





- Due to inherent inefficiency MnO_2 deposits accumulate in cathode carbon felt
- Accumulated MnO_2 is non-conductive, depletes active source of Mn from electrolyte, and modifies the flow of catholyte through the reaction chamber
- Mn – green, carbon – red
- µCT measurements of cycled Mn-Cu cathode felts illustrate 3D deposition morphology of oxide within porous carbon framework

Comparing Pb-Cu at 12.5 mAh.cm^{-2} to Mn-Cu at 6 mAh.cm^{-2}



- To compare the limitations of the two chemistries, a representative high loading cell of each are plotted at left
- PbO_2 exhibits nearly metallic electronic conductivity[1,2] while MnO_2 is only semiconducting (~ 1-1000 Ω.cm)[3,4]. We hypothesize that this enables the higher areal capacities in the PbO_2 chemistry versus the MnO_2 chemistry
- In addition to the higher areal capacity, the 12.5 mAh.cm^{-2} Pb-Cu cell exhibits a higher discharge voltage and higher coulombic efficiency (~90% at cycle 100) compared to the 6 mAh.cm^{-2} Mn-Cu cell (85% at cycle 100)

Summary and Perspective

- Two redox flow cell cathode-anode combinations were presented: (1) Pb-Cu and (2) Mn-Cu
- Both cells relied on the reversible plating/stripping of Cu^{2+}/Cu on the anode carbon felt
- The cell using the Mn^{2+}/MnO_2 cathode reaction demonstrated high stability but failed consistently around 170 cycles for both 3 mAh.cm^{-2} and 6 mAh.cm^{-2} areal loadings.
- The cell employing a Pb^{2+}/PbO_2 cathode reaction showed more fluctuation from cycle to cycle but was able to achieve high areal loadings of 10 mAh.cm^{-2} and 12.5 mAh.cm^{-2} for over 140 cycles.

Acknowledgements

This work is supported by the U.S. Department of Energy (DOE) Office of Electricity under contract No. DE-AC05-76RL01830, through Pacific Northwest National Laboratory Project No. 70247 (Long Duration & Cost Competitive Energy Storage).

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