

Meir Weiner<sup>1</sup>, Aditya Upreti<sup>1</sup>, Gautam G. Yadav<sup>1\*</sup>, Jinchao Huang<sup>1</sup>, Timothy N. Lambert<sup>2</sup>, Sanjoy Banerjee<sup>1</sup>:

\*Corresponding Author: [gautam@urbanelectricpower.com](mailto:gautam@urbanelectricpower.com)

1. Urban Electric Power Inc., Pearl River, 2. Sandia National Laboratories

## Introduction

- Recent discovery of safe and aqueous high voltage (2.45 to 2.8V) of zinc (Zn)|manganese dioxide ( $\text{MnO}_2$ ) batteries<sup>a</sup> has spurred interest in its usage for applications like personal electronics, e-mobility and the grid.
- The fundamental concept behind these high voltage batteries lies in the pairing of Zn anodes in alkaline electrolyte and access their highest redox potentials.
- Gelling of the alkaline electrolyte allows for the use of standard cellulose-based separator like cellophane rather than an ion-selective membrane, which makes it a highly economical battery. Schematic diagram of this battery is shown in Figure 1.
- While the Zn anode in alkaline liquid electrolyte is a well studied topic, its performance in hydrogels is another area of collaboration between UEP and Sandia.
- The electrochemical mechanism of  $\text{MnO}_2$  in acidic electrolyte is not a well understood topic. The mechanism behind electrodeposition and stripping of Mn ions, its stability and relation to  $\text{MnO}_2$  phase formation is scant.
- In this work, we present our preliminary data on the effect of acidity on the stability of Mn ions and  $\text{MnO}_2$ , and its eventual application in a long lived rechargeable high voltage Zn|MnO<sub>2</sub> battery

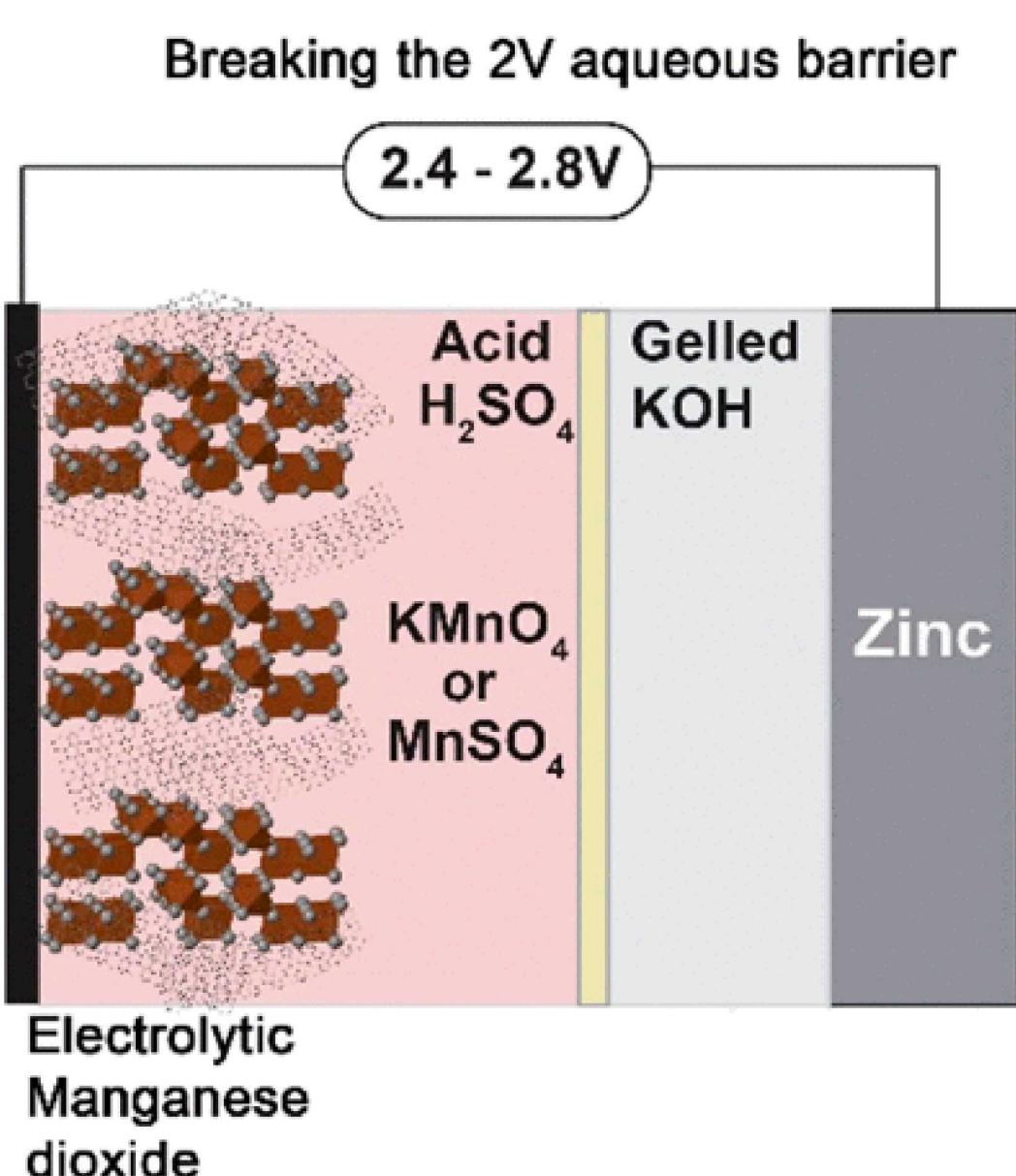


Figure 1. Schematic Diagram of the Dual Electrolyte High Voltage Zn|MnO<sub>2</sub> Battery

## Incomplete View of the Reaction Mechanism

- Most literature reports on the reaction mechanism have a simplistic view of the  $\text{MnO}_2$  stripping and redeposition reaction as shown below:
$$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \quad E=1.22\text{V vs SHE}$$
- The dissolution (stripping) and redeposition reactions of  $\text{MnO}_2$  are dependent on the proton concentration present in the electrolyte as shown in the above reaction.
- Understanding on the role of  $\text{Mn}^{2+}$  ions on the repeated redeposition for thousands of cycles is not well understood. Especially, its stability in the presence of acid and the efficiency of its plating with change in pH on repeated charge cycles.
- We present preliminary data on the effect of acid and  $\text{Mn}^{2+}$  concentration on the efficiency of the above reaction, average discharge potential and stability.

## Acknowledgements

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## Preliminary Results

### 1. Effect of Acid on Cycling Potential

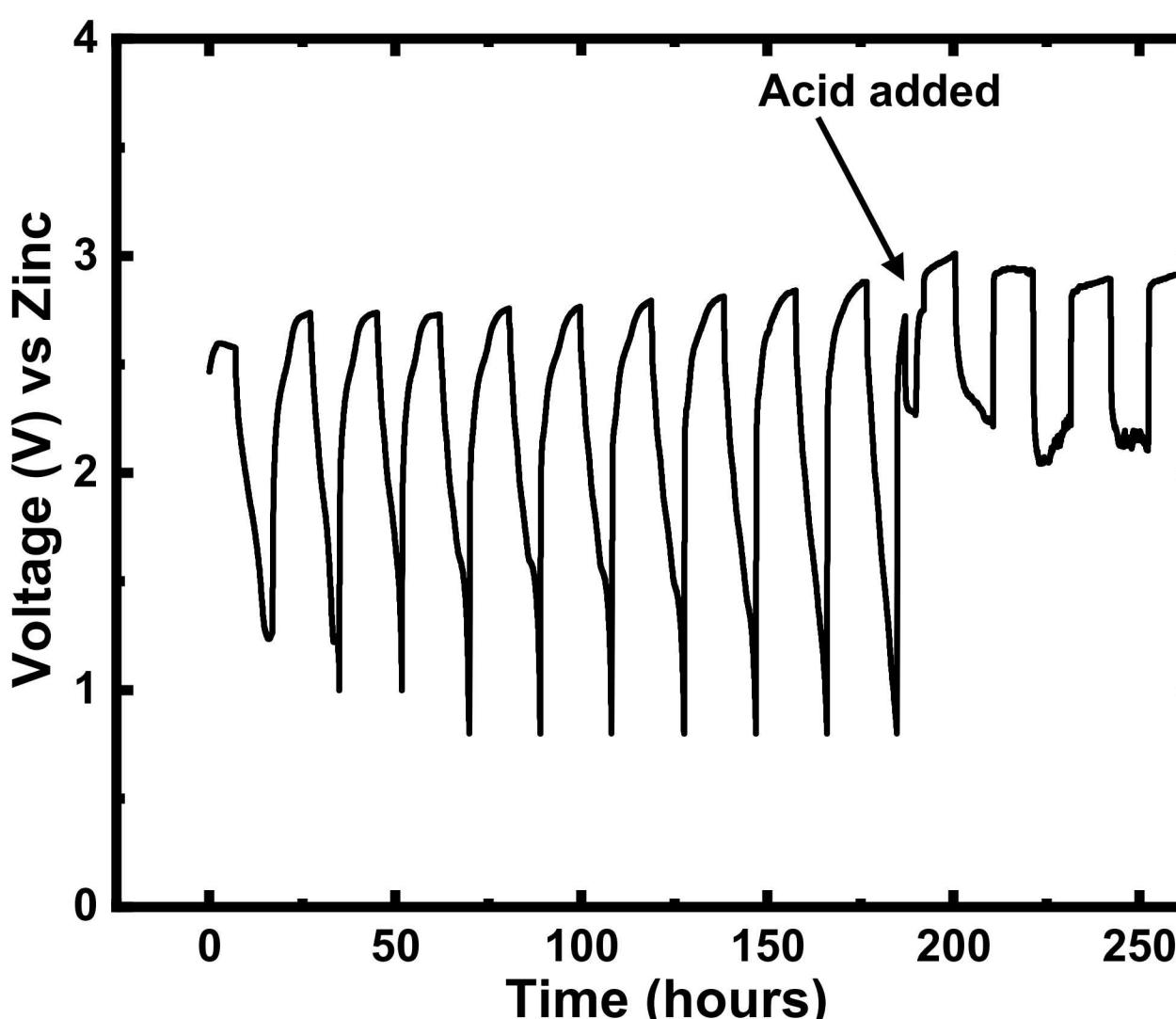


Figure 2. Operation of a cell without acid initially (till 200hrs of operation) and after acid is added.

### 2. Effect of Acid on Average Discharge Potential & Reversibility

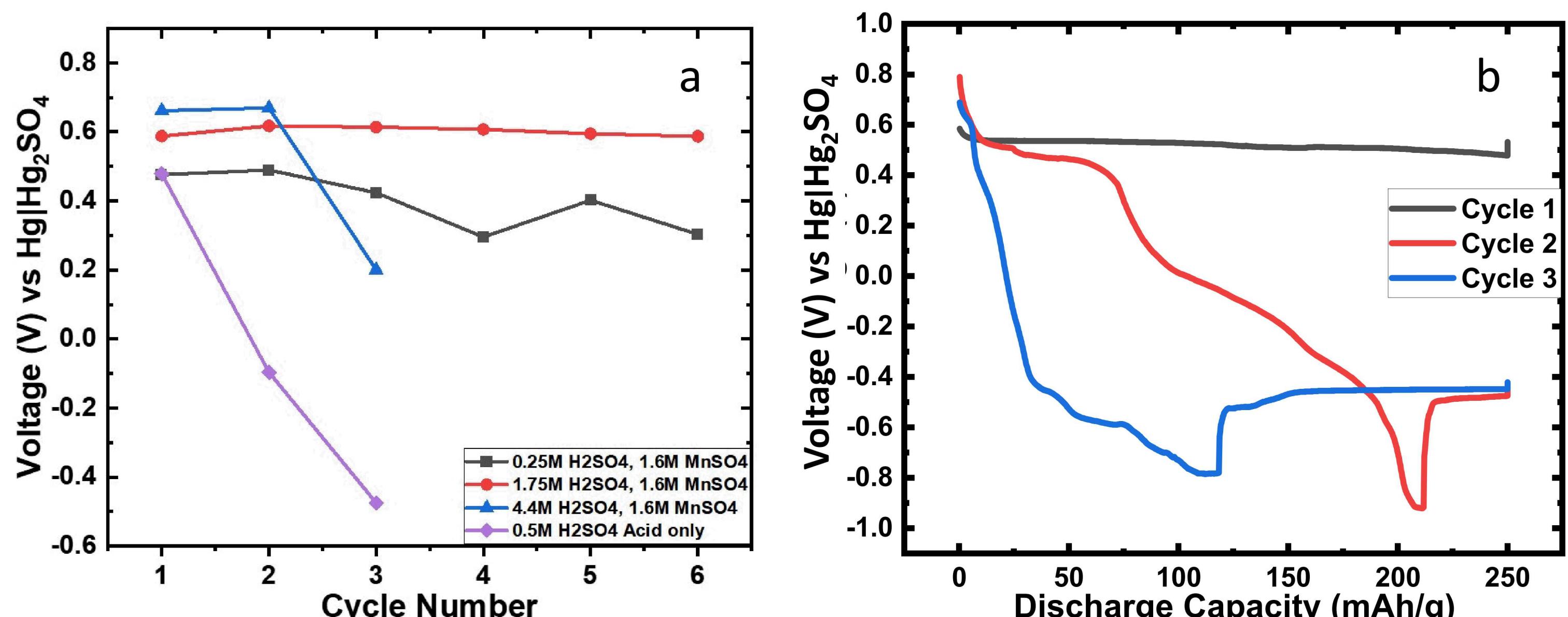


Figure 3. (a) Effect of acid concentration and  $\text{Mn}^{2+}$  on average discharge potential (b) Effect of absence of  $\text{Mn}^{2+}$  ions in acid only electrolyte on the reversibility of the cathode reaction

- High acid concentration increases the average discharge potential but its effect on the reversibility is drastic (Figure 3a), where it loses potential in the 3<sup>rd</sup> cycle.
- Presence of  $\text{Mn}^{2+}$  ions in solution is necessary for reversibility. (figure 3b).

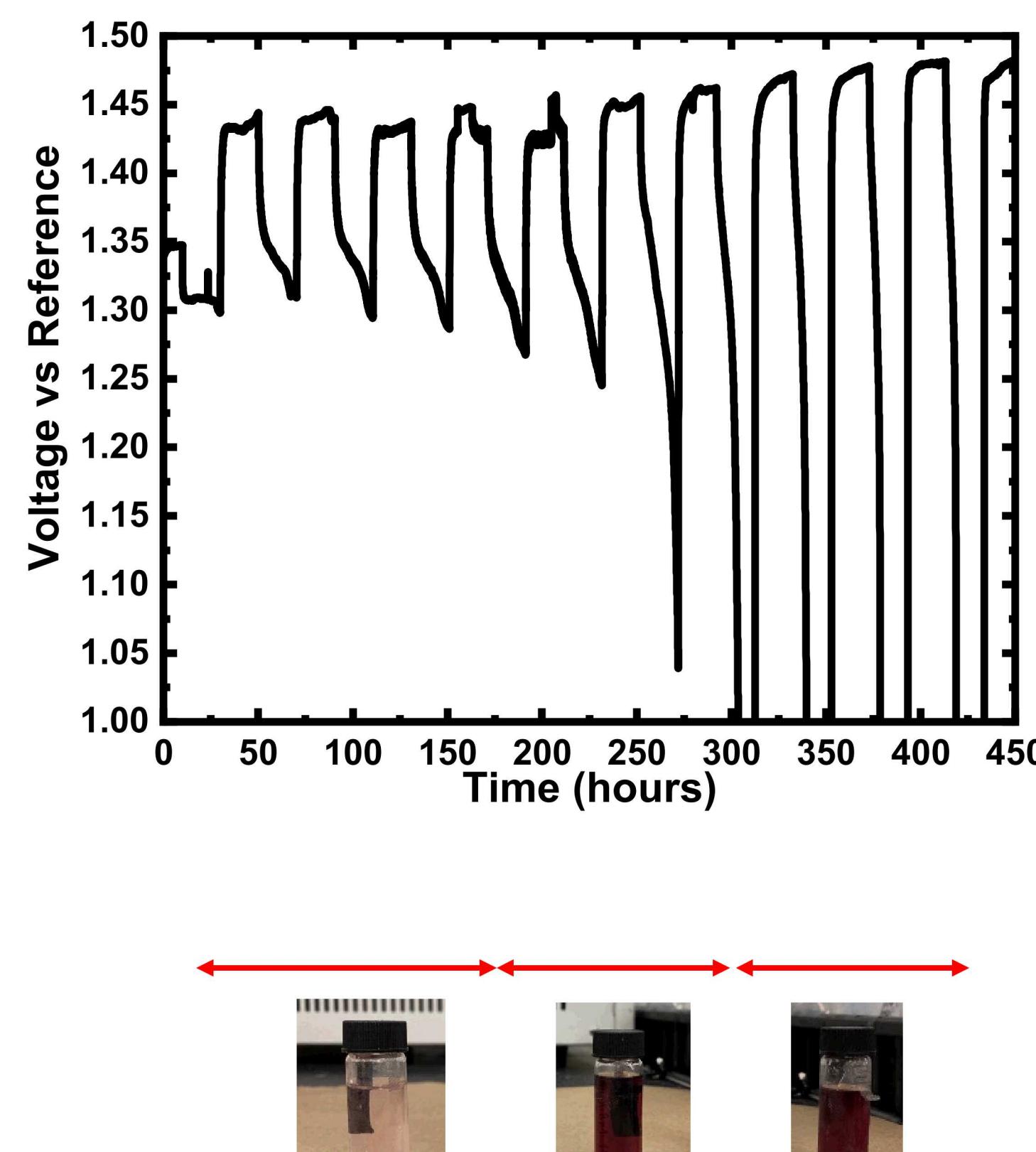


Figure 4. High acid concentrations immediately affect the reversibility of the cathode.

## Conclusions & Future Work

- An optimized electrolyte solution balancing the capacity fade and retaining the average discharge potential has been identified.
- Prototype cell designs are being currently manufactured at UEP for a wide range of applications.
- A manuscript has been submitted for peer-review and another one is in preparation for review

## References

- Gautam G. Yadav\*, Damon Turney, Jinchao Huang, Xia Wei and S. Banerjee, *ACS Energy Lett.*, 2019, 4, 9, 2144-2146.

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