Investigating Electrochemical Reactions of MnO_2 and Mn Ions in Acidic Electrolyte

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Introduction

1. Recent discovery of safe and aqueous high voltage (2.45 to 2.8V) of zinc (Zn)|manganese dioxide (MnO_2) batteries[a] has spurred interest in its usage for applications like personal electronics, e-mobility and the grid.
2. The fundamental concept behind these high voltage batteries lies in the pairing of Zn anodes in alkaline electrolyte and access their highest redox potentials.
3. 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.
4. 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.
5. The electrochemical mechanism of 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 MnO_2 phase formation is scant.
6. In this work, we present our preliminary data on the effect of acidity on the stability of Mn ions and MnO_2, and its eventual application in a long lived rechargeable high voltage Zn|MnO_2 battery

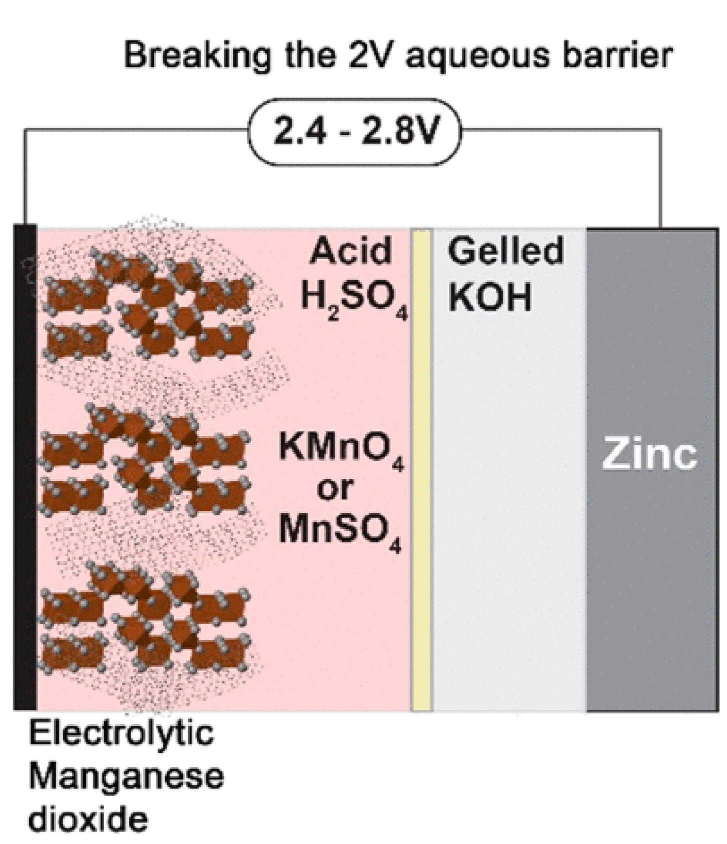

Figure 1. Schematic Diagram of the Dual Electrolyte High Voltage Zn|MnO_2 Battery

Incomplete View of the Reaction Mechanism

1. Most literature reports on the reaction mechanism have a simplistic view of the MnO_2 stripping and redeposition reaction as shown below:

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \qquad E=1.22V \text{ vs SHE}$$

2. The dissolution (stripping) and redeposition reactions of MnO_2 are dependent on the proton concentration present in the electrolyte as shown in the above reaction.
3. Understanding on the role of 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.
4. We present preliminary data on the effect of acid and Mn^{2+} concentration on the efficiency of the above reaction, average discharge potential and stability.

Preliminary Results

1. Effect of Acid on Cycling Potential

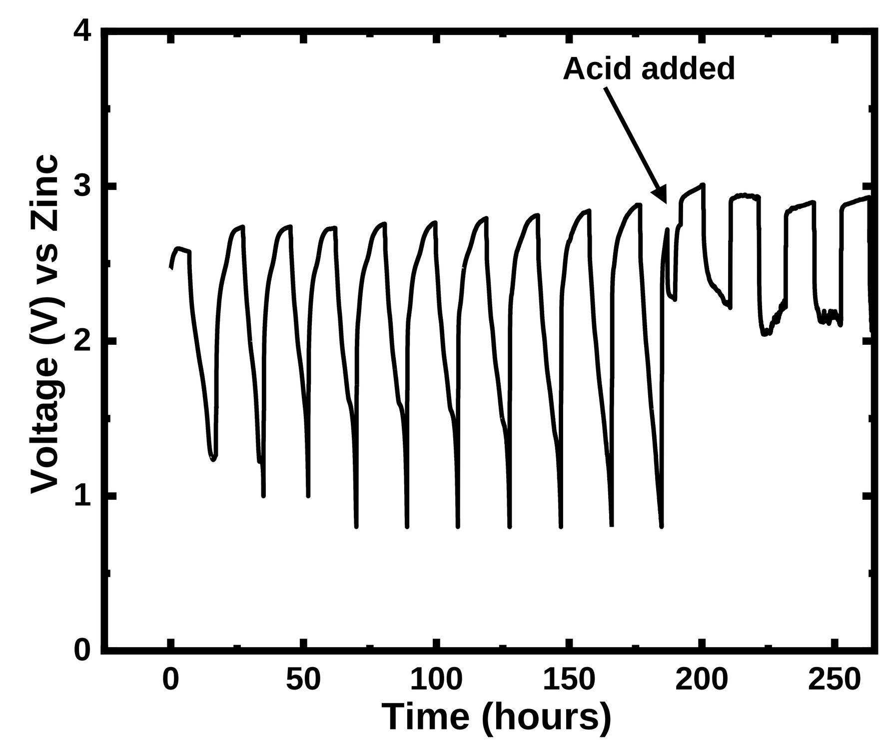

Figure 2. Operation of a cell without acid initially (till 200hrs of operation) and after acid is added.

1. A high voltage Zn|MnO_2 cell cycling with no acid or neutral solution yields poor average discharge potential and has less energy density (Figure 2, ~0 to 200hrs of operation).
2. Adding dilute acid at 200hrs leads to a significant bump in average discharge potential.

2. Effect of Acid on Average Discharge Potential & Reversibility

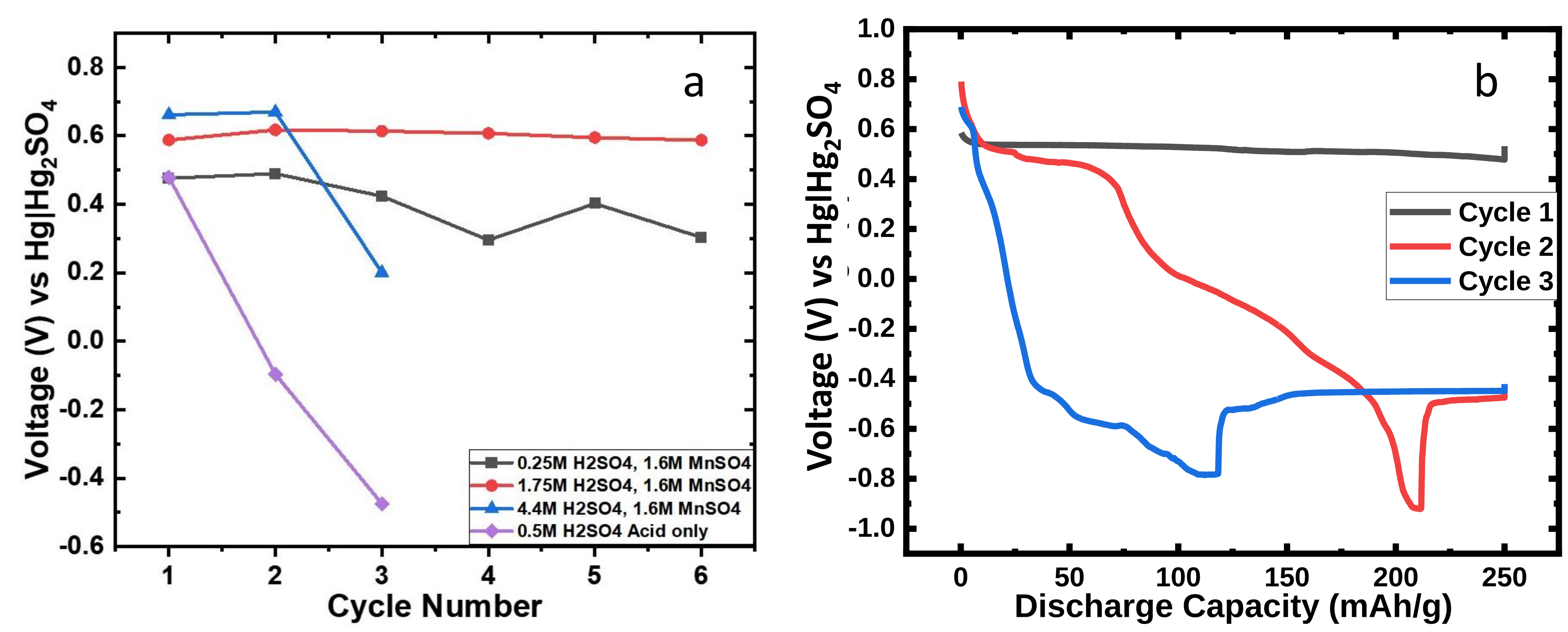

Figure 3. (a) Effect of acid concentration and Mn^{2+} on average discharge potential (b) Effect of absence of Mn^{2+} ions in acid only electrolyte on the reversibility of the cathode reaction

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

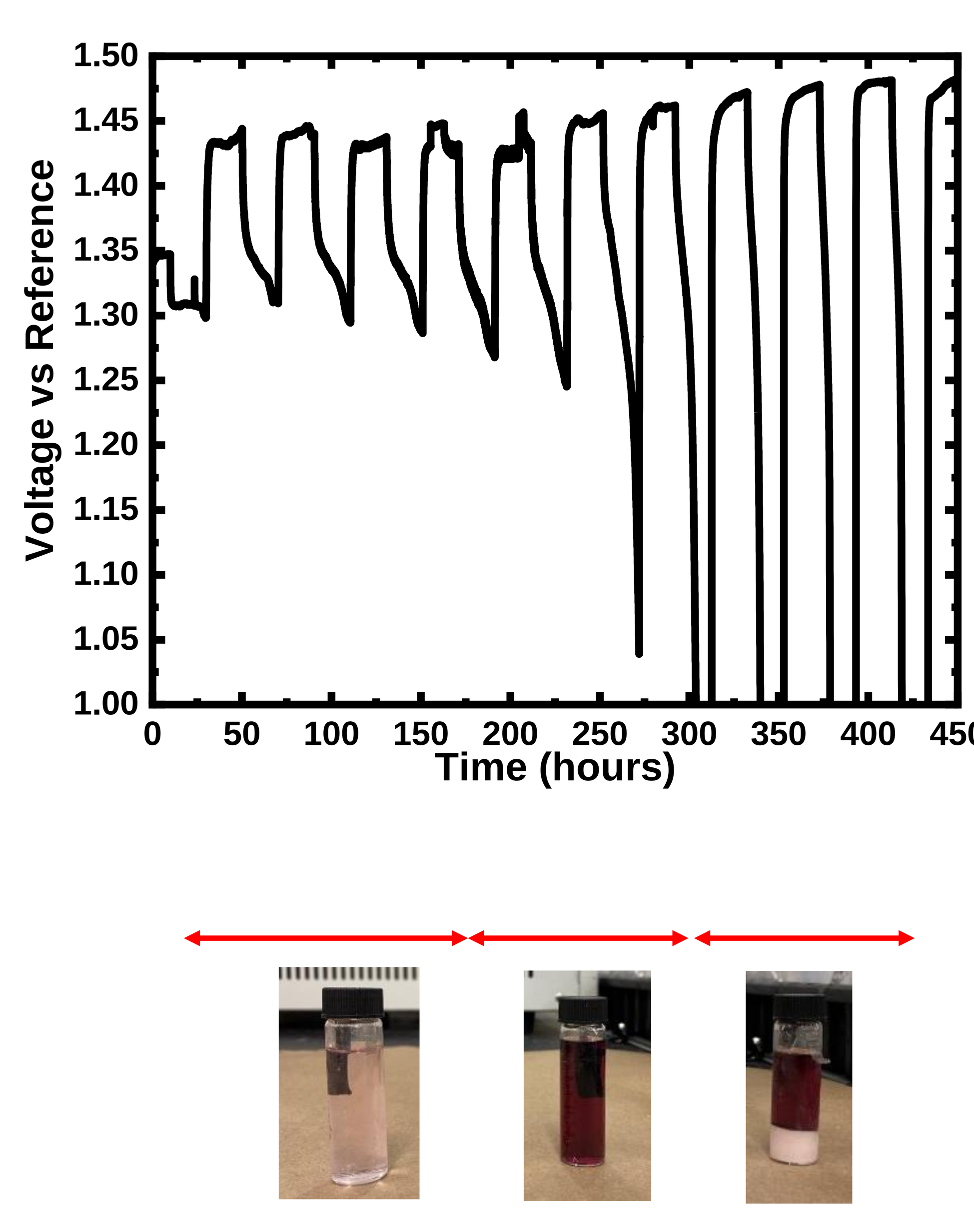

Figure 4. High acid concentrations immediately affect the reversibility of the cathode.

3. Medium acid concentration (1-2M) seems to be optimal for achieving both high discharge voltage and reversibility.
4. MnO_2 reaction shows that at high acid concentration the equilibrium is shifted which prevents the electrodeposition of MnO_2 on charge.
5. Mn^{2+} stability is also affected, where Mn^{2+} solubility is drastically curtailed and leads to the formation of Mn^{3+} ions that leads to immediate cathode failure (Figure 4).
6. For primary applications, electrolyte with only high acid concentration is recommended, while for rechargeable applications low to medium acid concentration with Mn^{2+} dissolved in the electrolyte is recommended to balance capacity fade and retain high average discharge potential.

Conclusions & Future Work

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

Acknowledgements
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