Ionic diffusion in hydrogel electrolytes for two-electron Zn-MnO_2 batteries

SAND2023-10405C

Jungsang Cho[1], Damon E. Turney[1], Gautam G. Yadav[2], Michael Nyce[1], Timothy N. Lambert[3,4] and Sanjoy Banerjee[1]

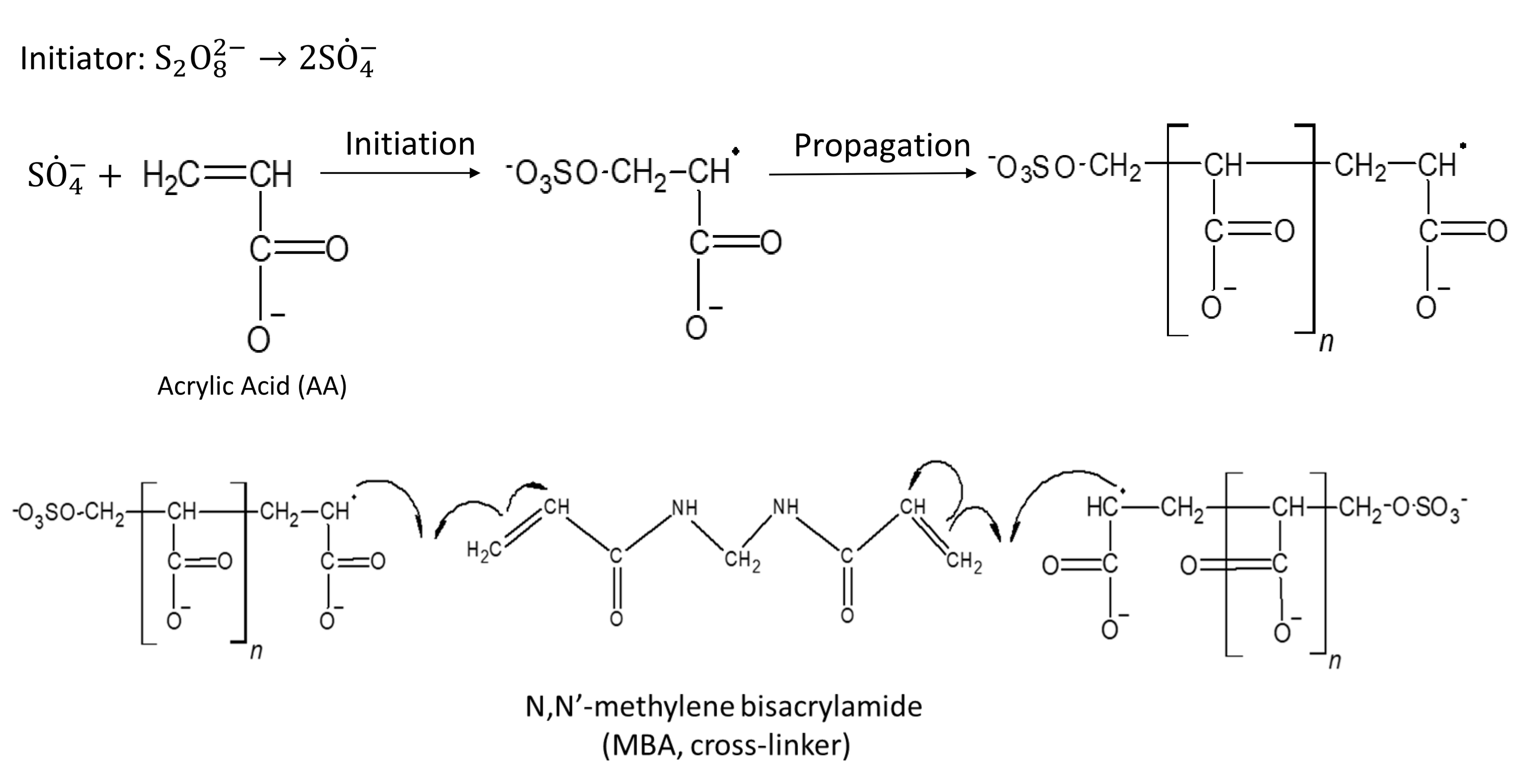
[1.] CUNY Energy Institute, [2.] Urban Electric Power Inc., [3.] Department of Photovoltaics and Materials Technology, Sandia National Laboratories, [4.] Center of Integrated Nanotechnologies, Sandia National Laboratories

Motivation

A gel electrolyte is essential for maintenance free and portable (leakproof) alkaline Zn-MnO_2 battery. Traditionally, liquid potassium hydroxide is used as an electrolyte for Zn-MnO_2 batteries. However, the use of liquid electrolytes has the potential to lead to shorts between anodes and cathodes in cells due to diffusion of metallic ions. Moreover, liquid electrolytes used for alkaline Zn-MnO_2 batteries generally have high pH ≥ 12, suggesting the safety issue matters once leaked. We reported that using gel electrolytes mitigated Zn growth and anode shape change and reduced manganese dissolution, leading to longer battery cycle life in the 1e$^-$ cycling region. Also, we showed hydrogel-containing cells were non-spillable and low-maintenance, which is in compliance with U.S. Department of Transportation regulations. In our work in the 2nd electron reaction region, cell dissection indicated Cu ions diffused from the cathode, which contains Cu as an additives, and deposited onto separators, which may have caused cell shorting in liquid electrolyte. Here we report the mitigation of Cu diffusion and a way of quantifying Cu diffusion in gel electrolyte. Further tests are underway with our gel electrolyte to determine if failure mechanisms are mitigated in Zn-MnO_2 batteries.

The Synthesis of the Gel Electrolyte Formulation

- A poly(acrylic acid)-potassium hydroxide (PAA-KOH) hydrogel was investigated and optimized as the electrolyte due to its high hydrophilicity and high ionic conductivity
- Chemicals: Potassium persulfate ($K_2S_2O_8$, initiator), Potassium hydroxide (KOH), Acrylic acid (C_2H_3COOH, monomer), N,N'-Methylenebisacrylamide (cross-linker)
- Reaction mechanism: Free radical polymerization.



- The amount of crosslinker added determines the degree of polymer crosslinking. If it is high, the ion diffusion is affected, leading to poor battery cycling performance
- By varying the amount of crosslinker, the hydrogel properties were optimized to allow ion diffusion while preventing leaks
- Cells were filled with gel electrolytes and polymerized in situ by keeping the reaction temperature constant at 0 ^oC. This slows down the reaction kinetics sufficiently to allow the electrodes pours to be filled

Cyclic Voltammetry Results with Liquid and Gel Electrolytes

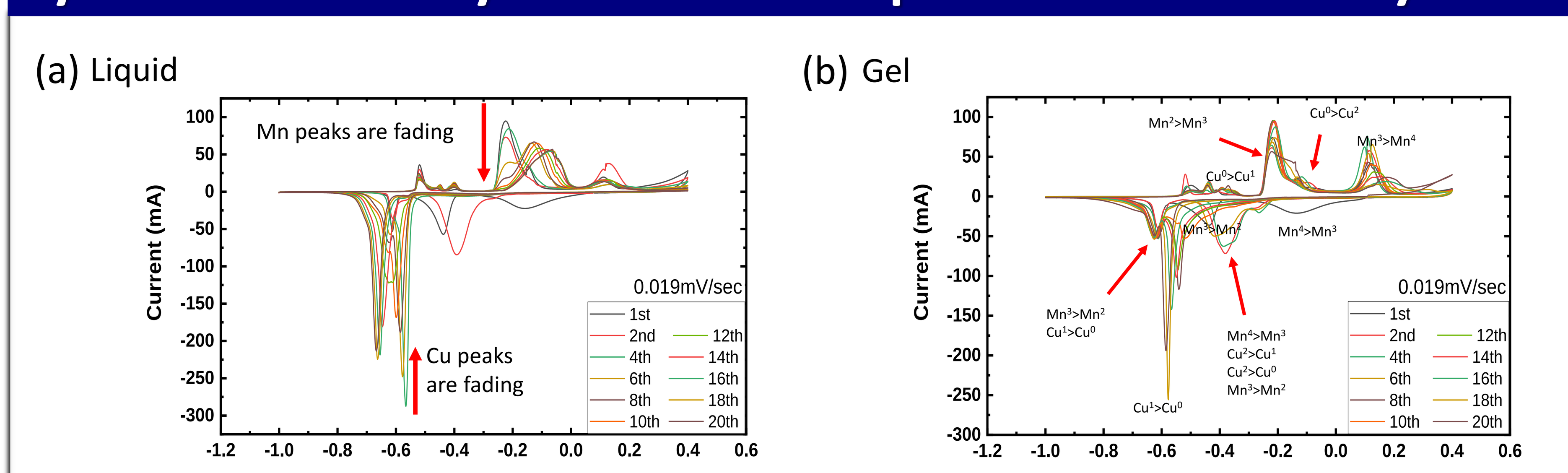


Figure 1. Cyclic voltammetry performances of MnO_2 cathode vs NiOOH anode, with a Hg|HgO reference electrode. (a) liquid electrolyte and (b) gel electrolyte at 0.019 mV/sec, which means it takes 20 hours for charge and discharge. All cell construction seen in Figure 1 is identical except for the type of electrolytes

- The cell with liquid KOH electrolyte showed fading peaks at -0.25 V and -0.6 V vs Hg|HgO, whereas the gel-containing cell maintain all peaks through 20 cycles
- It is hypothesized that using gel electrolytes helps localize active materials and limit Cu diffusion, and therefore it makes possible the reversible formation of the [(Cu-Bi)Mn] complex
- In this way, the cell with gel electrolyte could lead to a stable long cycle life under the 2nd electron reaction region

Cycling Performance of Gel Electrolyte Cells

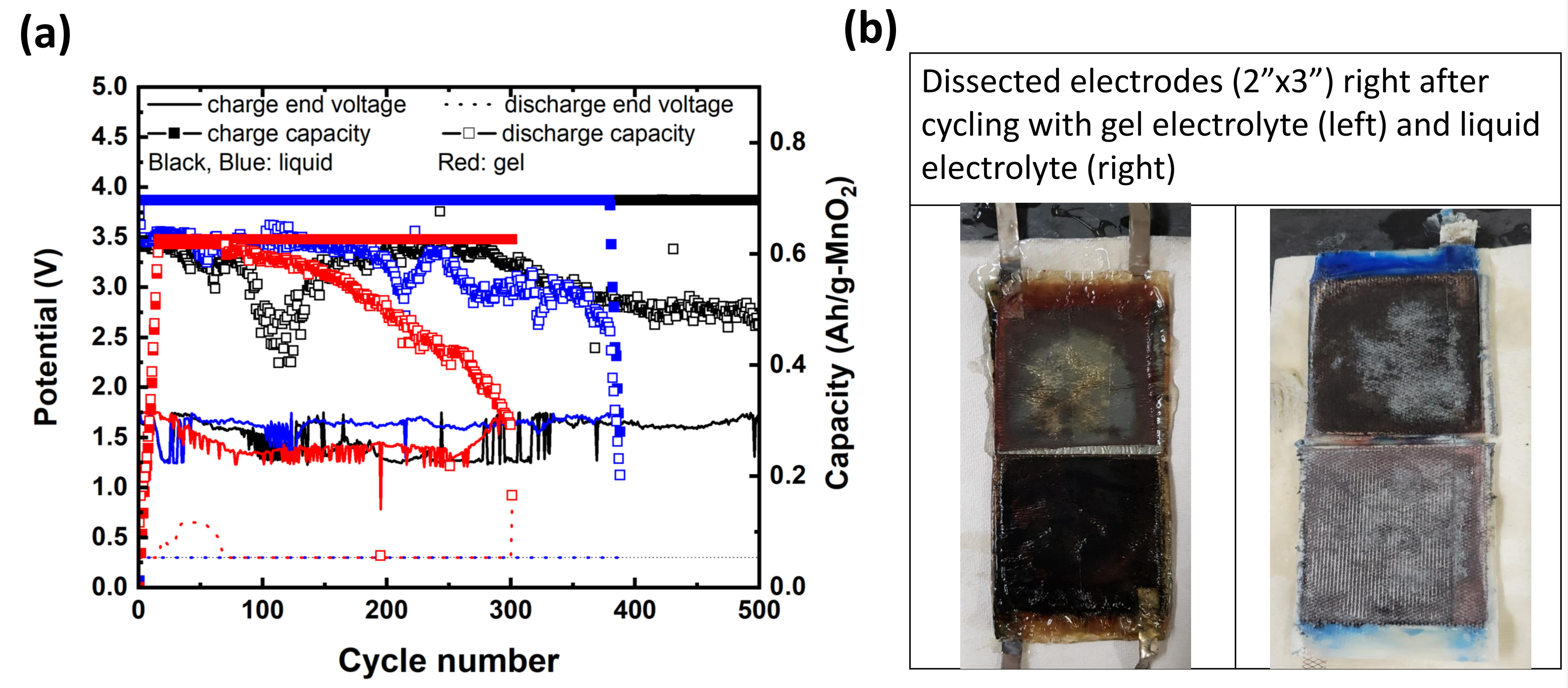
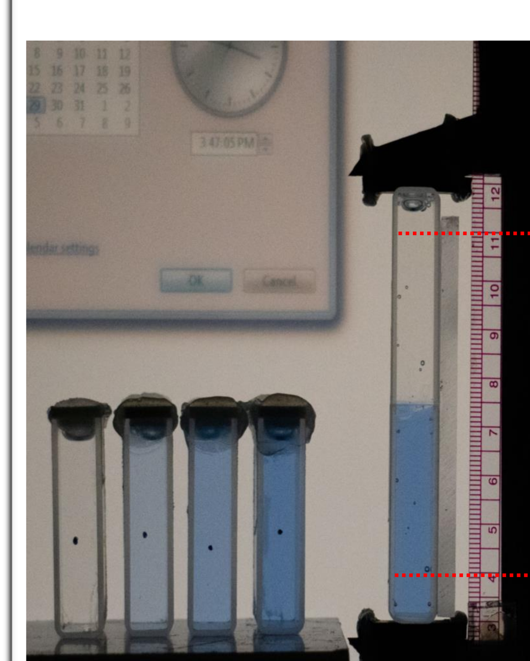


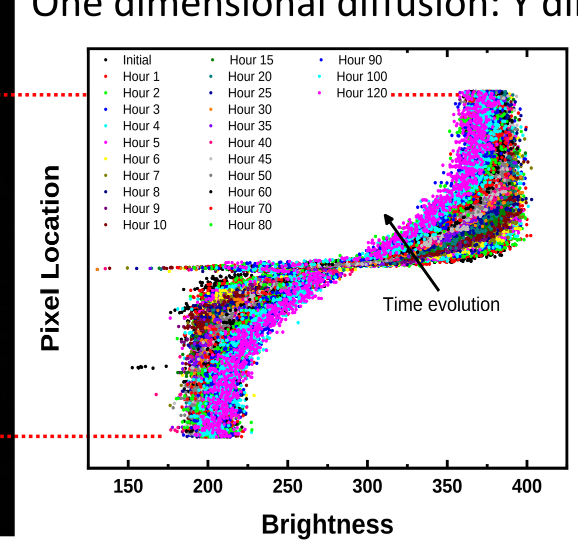
Figure 2. Cycling performances of Zn-MnO_2 full cells with liquid and gel electrolyte, and the picture of dissected electrodes after cycling. (a) The cycling experiments were performed at C/20 (C is based on the 2nd electron capacity of MnO_2). (b) The pictures describe dissected electrodes with liquid and gel electrolyte

- Cycle life tests of MnO_2 cathodes cells filled with gel electrolyte and liquid KOH solution with the same effective hydroxide concentration were carried out
- The gel electrolyte cell showed 50% capacity fade at 300th cycle. This cell is cycling at the time of this writing, and the post-mortem analysis will be performed
- During the 2nd electron reaction, it is assumed that Cu ions help the reversibility of the complex. It was observed that Cu ions of the cell with liquid electrolyte spread all over the electrode and deposited onto the top part of the separator, while the cell with gel electrolyte helped localize Cu ions



No chemical reaction at the interface
Constant temperature at all times
One dimensional diffusion: Y direction

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial y^2}$$



C: concentration as a function of C(y,t)
D: diffusion coefficient

$$\lambda_n = \sqrt{D}\frac{n\pi}{7}$$

$$C(y,t) = \frac{1}{2} + \sum_{n=1}^{\infty}\frac{2}{n\pi}\sin\frac{n\pi}{2}\cos\frac{n\pi y}{7}e^{-\lambda_n^2 t}$$

Figure 3. The experimental setup for the diffusion measurement. Two cuvettes were used, and each cuvette was filled with a gel electrolyte with/without $Cu(OH)_2$. All images were taken automatically on an hourly basis. The four cuvettes beside the setup are the reference cuvettes, each of which has a gel electrolyte with known $Cu(OH)_2$ concentration.

- The gap of the brightness value at the top and at the bottom is narrowing and the plot keeps symmetric, which means that $Cu(OH)_2$ evenly diffuses in the Y direction
- Assuming the diffusion is one dimensional in the Y direction, the governing equation can be solved through Fourier transform, and the particular solution is shown above
- The experimental data and the theoretical data will be compared to determine the diffusion coefficient of $Cu(OH)_2$ in the gel electrolyte

Conclusions

- A poly(acrylic acid)-potassium hydroxide (PAA-KOH) hydrogel electrolyte was developed and incorporated into the rechargeable alkaline Zn-MnO_2 batteries.
- The gel electrolyte was optimized to balance the ionic conductivity, chemical/mechanical stability, polymerization kinetics and electrochemical properties.
- Using gel electrolytes helps the reversible formation of the [(Cu-Bi)Mn] complex, leading to a stable cycle life performance
- The diffusion coefficient of $Cu(OH)_2$ in the gel electrolyte can be quantified from the governing equation, and the diffusion coefficient of that in a liquid electrolyte will be quantified

Acknowledgements

This work was supported by the U.S. Department of Energy Office of Electricity. Dr. Imre Gyuk, Director of Energy Storage Research at the U.S. Department of Energy Office of Electricity, is thanked for his financial support of this project. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. The views expressed in this article do not necessarily represent the views of the U.S. Department of Energy or the United States Government. This article has been authored by an employee of National Technology & Engineering Solutions of Sandia, LLC under Contract No. DE-NA0003525 with the U.S. Department of Energy (DOE). The National Technology & Engineering Solutions of Sandia, LLC employee owns all right, title and interest to their contribution to the article and is responsible for its contents. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this article or allow others to do so, for United States Government purposes. The DOE will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan https://www.energy.gov/downloads/doe-public-access-plan