

Understanding of Ion Diffusion for Non-Spillable Zn|MnO₂ Rechargeable Batteries Allowing for the 2nd Electron MnO₂ Cycling in Hydrogel Electrolytes

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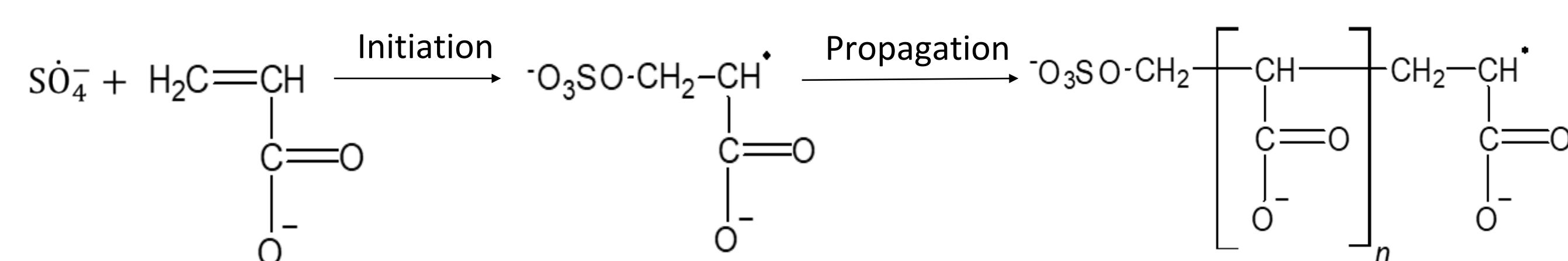
Motivation

A gel electrolyte have drawn research interest as an alternative to a traditional liquid electrolyte, such as potassium hydroxide, for Zn-MnO₂ rechargeable alkaline batteries. Not only because of the safety issue from the spill, but also it was reported that using a gel electrolyte mitigated short circuiting from Zn dendrite formation and Zn ion crossover to MnO₂ cathodes that causes the loss of active Mn³⁺ ions due to the inactive spinel formation, hetaerolite (ZnMn₂O₄). With this in mind, we tried to use a gel electrolyte for Zn-MnO₂ rechargeable batteries allowing for the 2nd electron reaction of MnO₂. Here we report the development of a gel electrolyte that successfully creates leak-free Zn-MnO₂ rechargeable alkaline batteries. In addition, we report EIS measurement data for Zn foil symmetric cell and galvanostatic/potentiostatic data assuming that a gel electrolyte could help stabilize [(Cu-Bi)MnO₂] complex by limiting Cu ion diffusion while cycling.

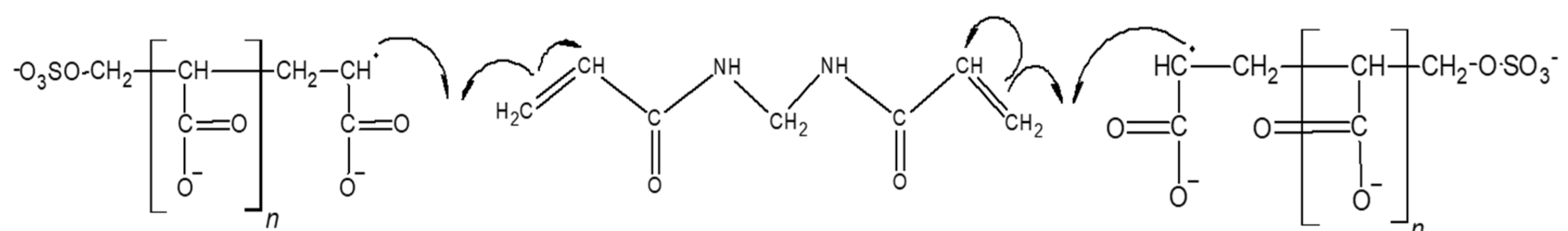
Optimizing the Gel Electrolyte Formulation

- 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 (K₂S₂O₈, initiator), Potassium hydroxide (KOH), Acrylic acid (C₂H₃COOH, monomer), N,N'-Methylenebisacrylamide (cross-linker)
- Reaction mechanism: Free radical polymerization.

Initiator: S₂O₈²⁻ → 2SO₄⁻



Acrylic Acid (AA)



N,N'-methylene bisacrylamide (MBA, cross-linker)

Mole fraction MBA:H ₂ O	Flow from ~2.4 mm gap	Flow from ~75 mm gap
2.61E-5	Flow	Flow
3.4E-5		
3.92E-5	No Flow	
4.7E-5		
5.2E-5		
6E-5		
6.5E-5		
7.3E-5		
7.8E-5		No flow

Table 1. The amount of crosslinker varied for hydrogel synthesis. The 3.92E-5 mole fraction of MBA was chosen for the optimized hydrogel electrolytes

- 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 but to prevent leaks
- By keeping the reaction temperature constant at 0 °C, the reaction kinetics was retarded to have enough soaking time for porous Zn and MnO₂ electrodes

EIS Measurement for Zn Foil Symmetric Cell



Figure 1. Experiment setup for Zn foil EIS measurement. The gel electrolyte was put into the square area from the top of the rubber gasket. Then, each Zn foil was assembled

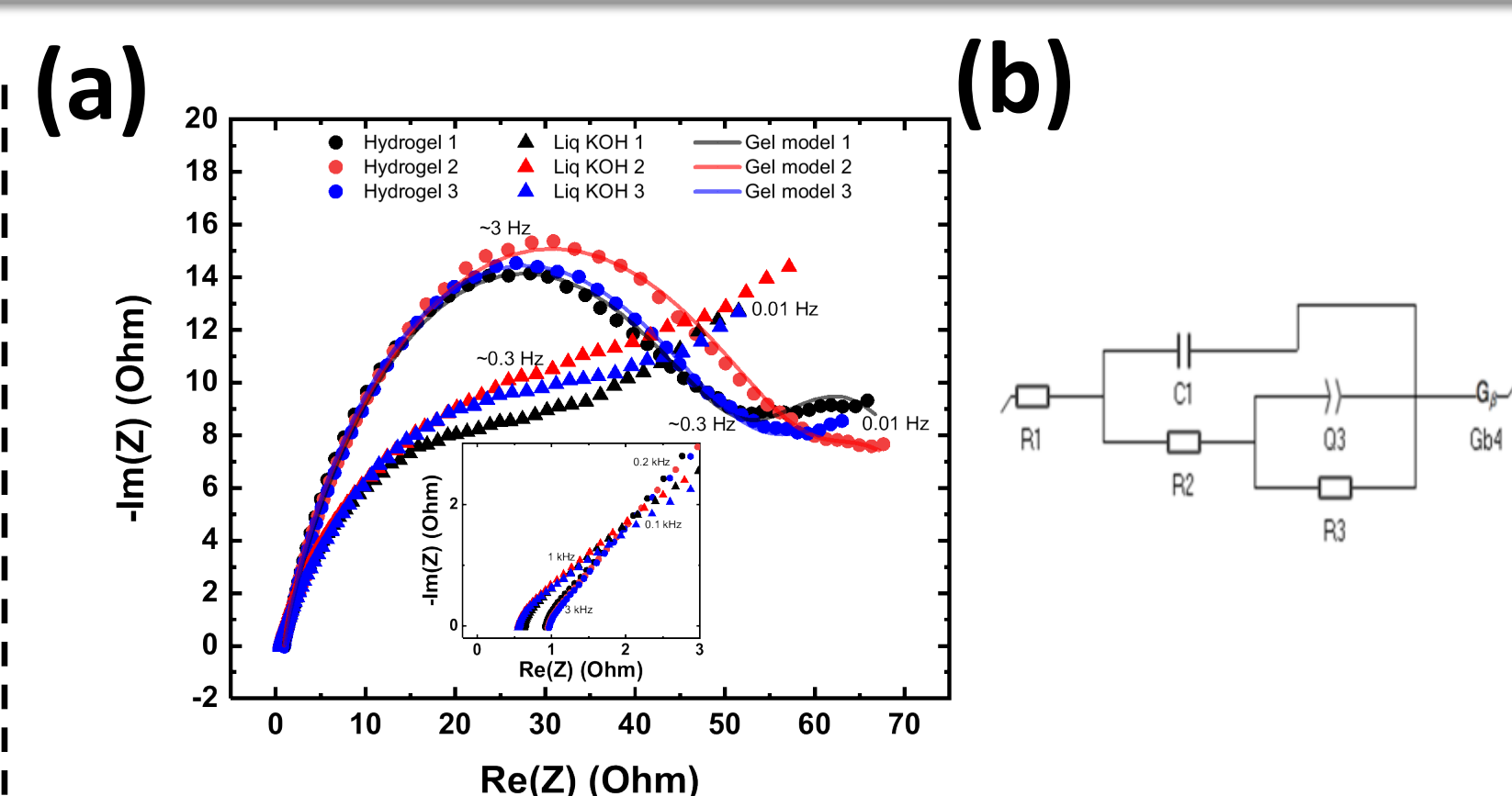


Figure 2 (a) EIS measurement data for Zn foil symmetric cell with the gel electrolyte (circle) and a liquid KOH electrolyte (triangle). The solid lines represent the fit. The numbers in the legend corresponds to the number of repeats (b) The equivalent circuit model is described

- R₁ is the solution resistance; R₂ is the charge transfer resistance between Zn foil and the gel electrolyte; C₁ is the capacitance from the gel electrolyte; R₃ is the resistance resulting from hydroxyl ion transport; Q₃ is the constant phase element for non-faradaic charging of the double layer; Gb₄ is the resistance from the chemical reaction between Zn and OH⁻

Cycle Performance of Gel Electrolyte Cells

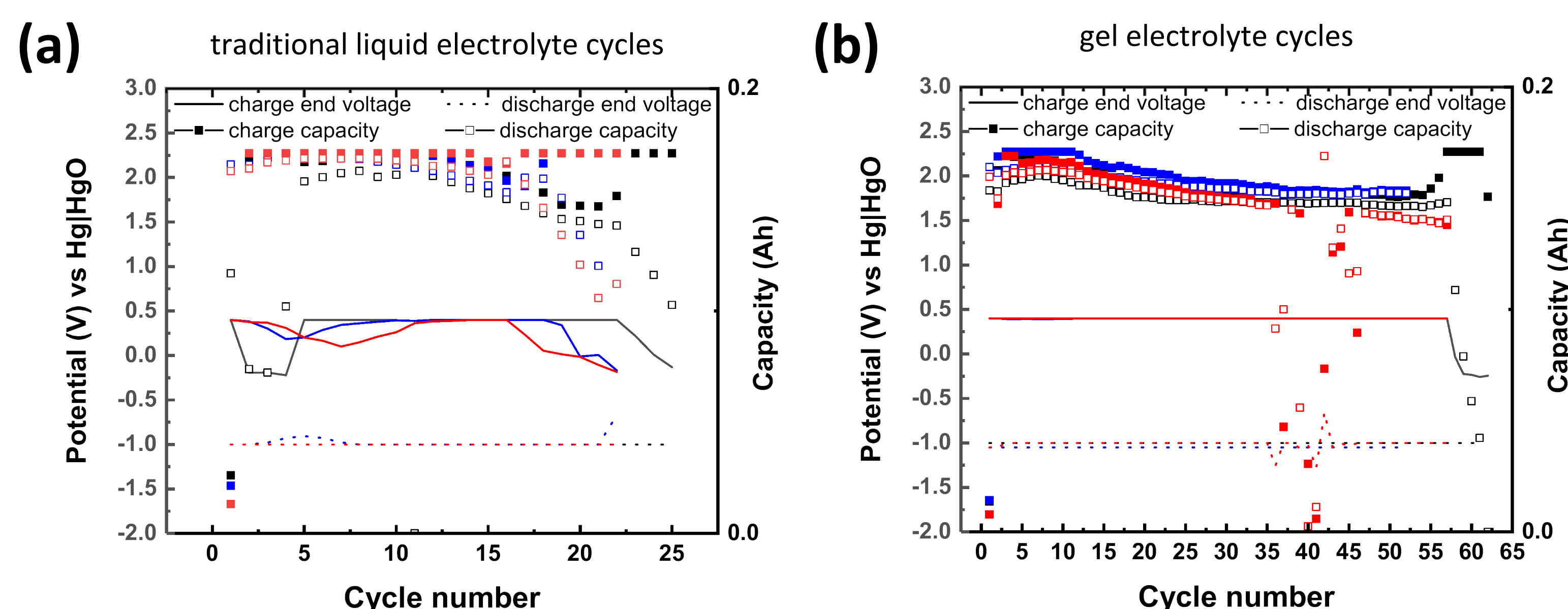


Figure 3. Cycling performances of MnO₂ cathode vs NiOOH anode, with a Hg|HgO reference electrode. (a) liquid electrolyte and (b) gel electrolyte at C/20 Charge and discharge (C is based on the 2nd electron capacity of MnO₂). All cell construction seen in figure 3 is identical except for the type of electrolytes. The theoretical capacity of the used cathode is 0.169 Ah. Gel electrolyte cells are ongoing and outperforming the liquid electrolyte cells. The unstable voltage and capacity achievement at 40th cycle was due to the reference electrode, and they fell into place after being replaced with a new reference electrode.

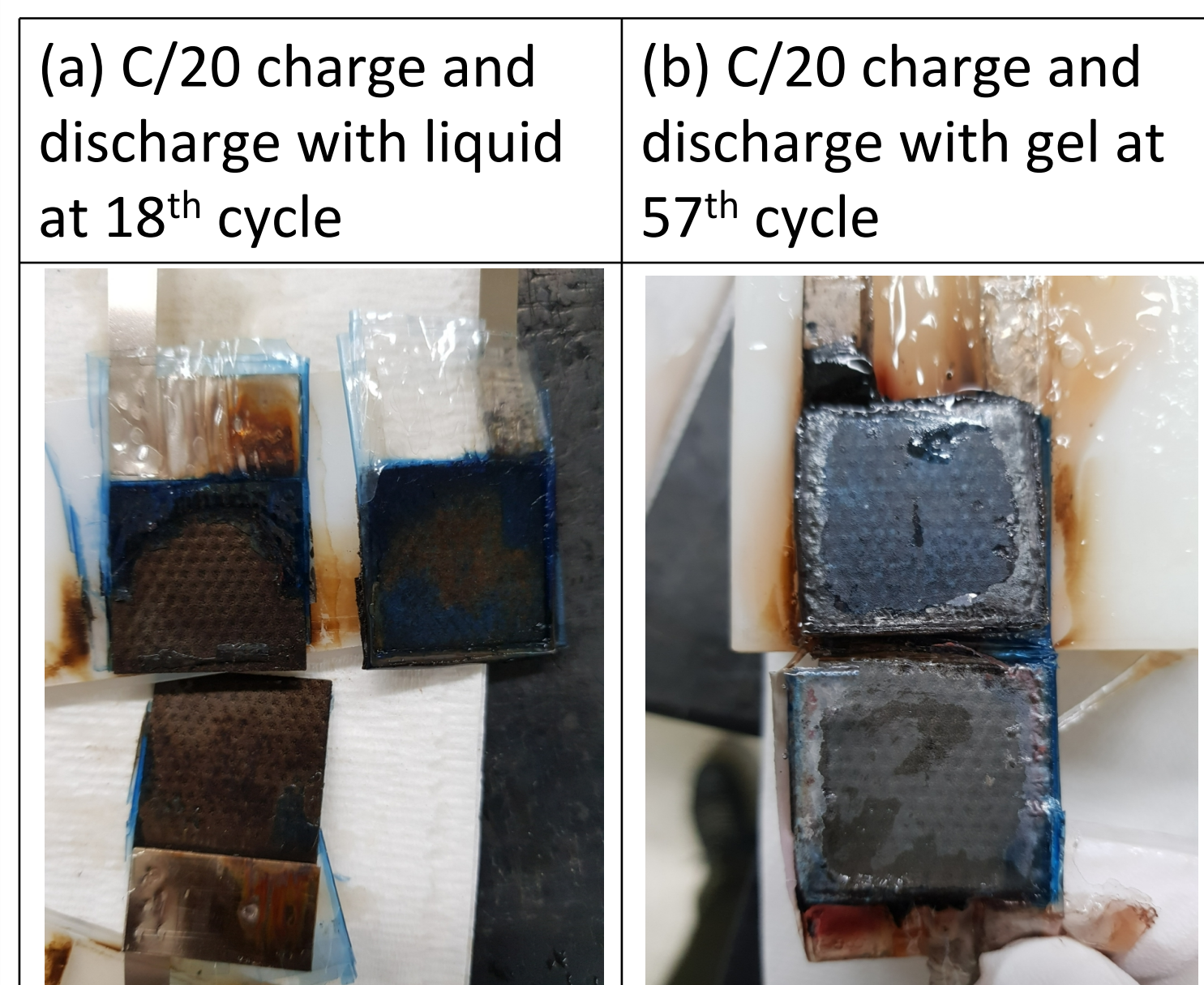


Figure 4: The pictures of the dissected cells after cycling: (a) liquid electrolyte and (b) gel electrolyte.

- Cycle life tests of MnO₂ cathodes cells filled with gel electrolyte and liquid KOH solution with the same effective hydroxide concentration were carried out
- The gel electrolyte cells provided more stable performance than the liquid electrolyte cells and achieved longer cycle life (Figure 3).
- The failure mechanism for the liquid electrolyte cell was due to short circuit caused by Cu deposition all around the separator, while Cu is limitedly diffused in the gel cell (Figure 4).

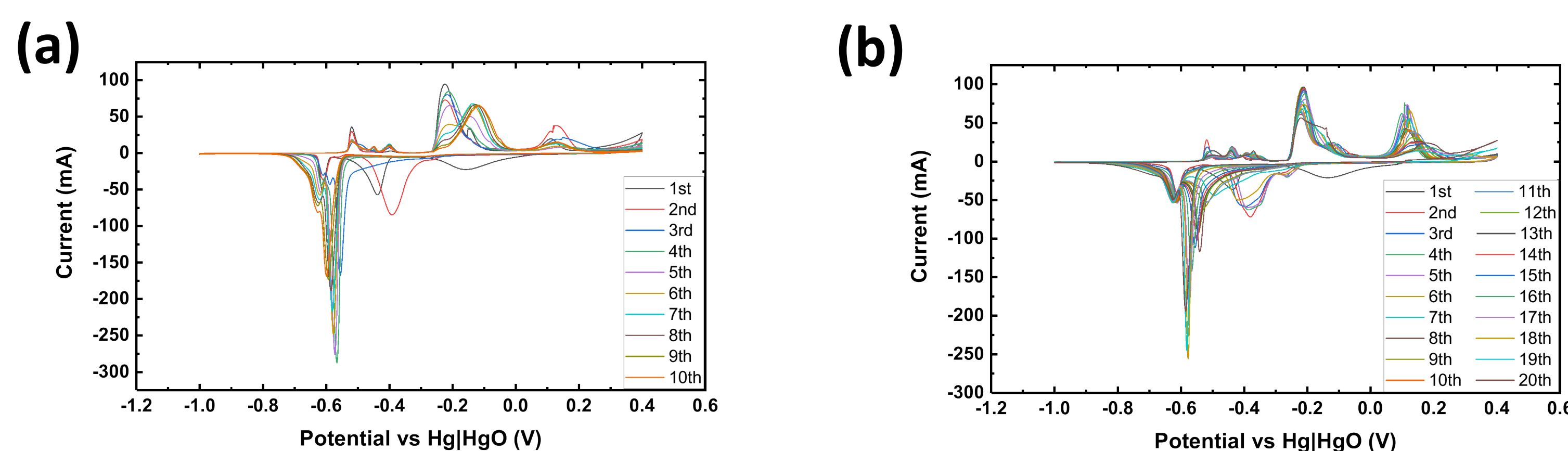


Figure 5. Cyclic voltammetry data of MnO₂ cathode* against NiOOH monitored by Hg|HgO electrodes with a liquid KOH electrolyte (left) and the optimized gel electrolyte (right). It ran at 0.019 mV/sec, which is approximately 20 hours charge and discharge

* Yadav et al, Nature Communication

- The data with the liquid electrolyte shows the peak (Mn⁺⁴ to Mn⁺²) at -0.4 V vs Hg|HgO is fading from the 3rd cycle and the peak (Cu⁺¹ to Cu⁰) at -0.6 V vs Hg|HgO is getting stronger from the 3rd cycle
- The gel electrolyte cell shows the peak (Mn⁺⁴ to Mn⁺²) at -0.4 V vs Hg|HgO during the first few cycles and the peak (Cu⁺¹ to Cu⁰) at -0.6 V vs Hg|HgO is shown from the 8th cycle. All reduction curves show stable Mn reduction (Mn⁺³ to Mn⁺²) peaks at -0.65 V vs Hg|HgO
- The liquid electrolyte cell shows that the peak (Mn⁺² to Mn⁺³) at -0.25V vs Hg|HgO is fading but the peak (Cu⁰ to Cu⁺²) at -0.15V vs Hg|HgO is getting stronger
- The peaks at -0.25V and -0.15V vs Hg|HgO of the gel electrolyte cell are showing stable Mn and Cu electrochemical reaction performance
- Using the gel electrolyte is assumed to limit Cu diffusion so that it could make (Cu-Bi)Mn complex formation reversible, leading stable performance

Conclusions

- A poly(acrylic acid)-potassium hydroxide (PAA-KOH) hydrogel electrolyte was developed and incorporated into non-spillable rechargeable alkaline Zn-MnO₂ batteries.
- The gel electrolyte was tested for Zn ion diffusion via EIS measurement
- Galvanostatic/Potentiostatic results suggested that using the gel electrolyte helped Cu diffusion and was assumed to stable [Cu-Bi(MnO₂)] complex, leading stable performance compared to the data with a liquid electrolyte

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