Inhibiting the Formation of Zinc Hydroxy Sulfate for High-Performance Aqueous Zn Batteries by Stabilizing the pH of Electrolyte

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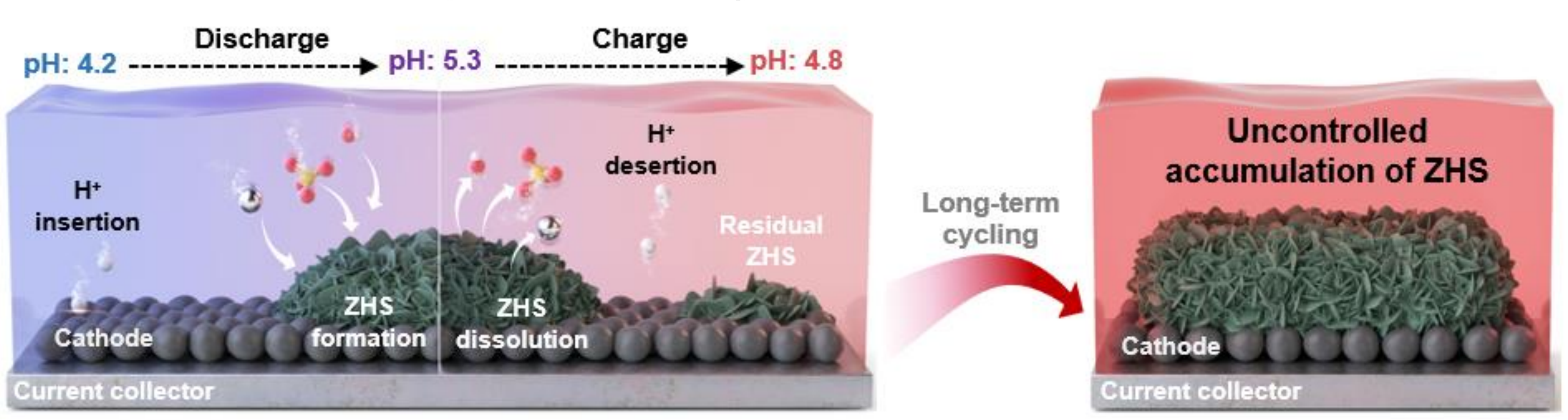
Won-Gwang Lim[1], Zane M.A Grady[1], Matthew Fayette[1], Xiaolin Li[1], and David Reed[1]
[1]Battery Development and Reliability Group, Pacific Northwest National Laboratory (PNNL), Richland, Washington, USA

Introduction: Aqueous Zn batteries (AZBs), particularly the systems with mildly acidic conditions have attracted tremendous attention because of the integrated merits of Zn anode (*i.e.*, low redox potential, high theoretical capacity, and resource abundance) and the improved reversibility in mildly acidic aqueous electrolyte.[1,2]

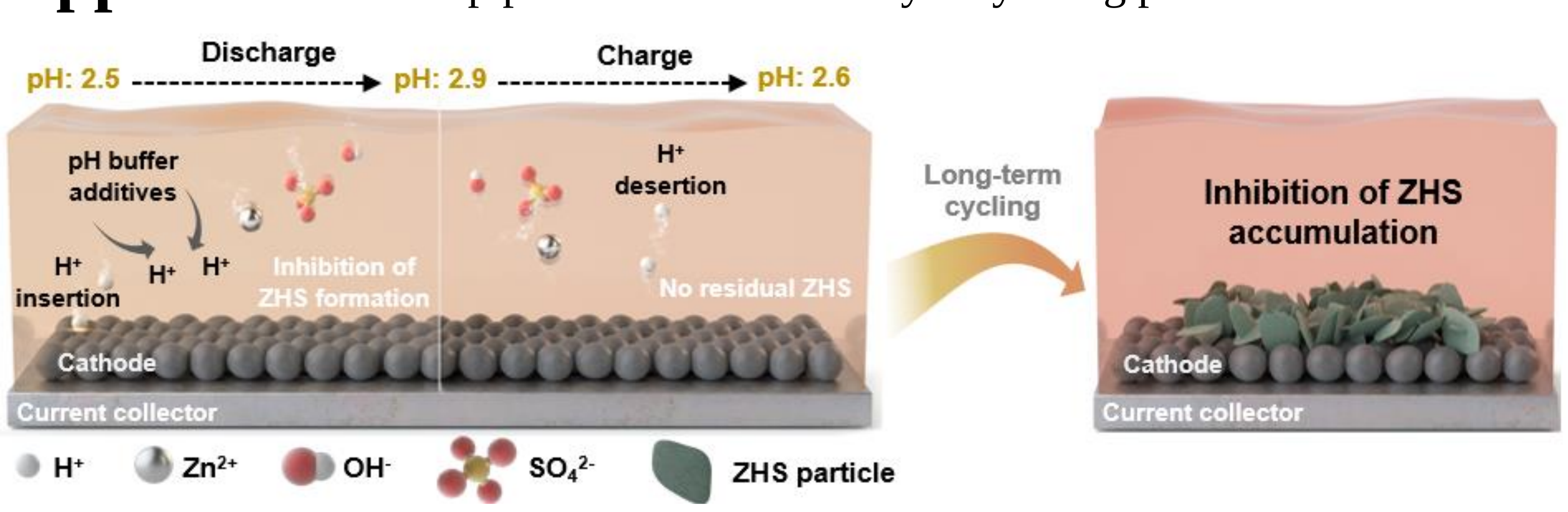
MnO_2-Zn battery is of particularly interest because it uses no critical raw materials and the cathode has high theoretical capacity of ~616 mA h g^{-1} based on two-electron redox reaction. However, despite these advantages, MnO_2-Zn battery grapples with several challenges stemming from the undesirable behavior of aqueous electrolyte. One of the most remarkable phenomena of MnO_2-Zn battery is the unavoidable electrochemical reactions involving H^+ and a dynamic change of the H^+ concentration in electrolyte during cycling, which causes the irreversible precipitation of non-conductive zinc hydroxy sulfate (ZHS) byproducts at the interface of electrode/electrolyte.[3,4]

Objective: Achieve high cycle stability of MnO_2-Zn battery by inhibiting the irreversible formation of ZHS byproducts at the interface of electrode/electrolyte

Conventional electrolyte (1M $ZnSO_4$)



Approach: Develop pH-stabilized electrolyte by using pH buffer additives



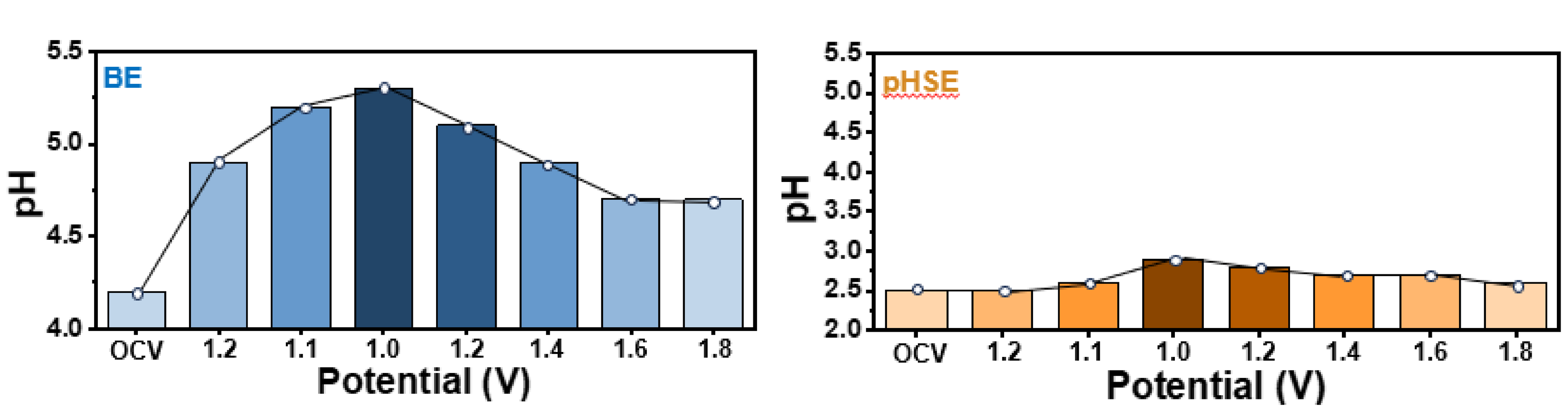
- pH buffer additives can stabilize the pH of electrolyte at ~2.5 throughout the H^+ insertion/desertion of MnO_2 cathode. This stabilization of H^+ concentration in electrolyte inhibits the chemical formation reaction of ZHS solid byproducts.

Results and Discussion:

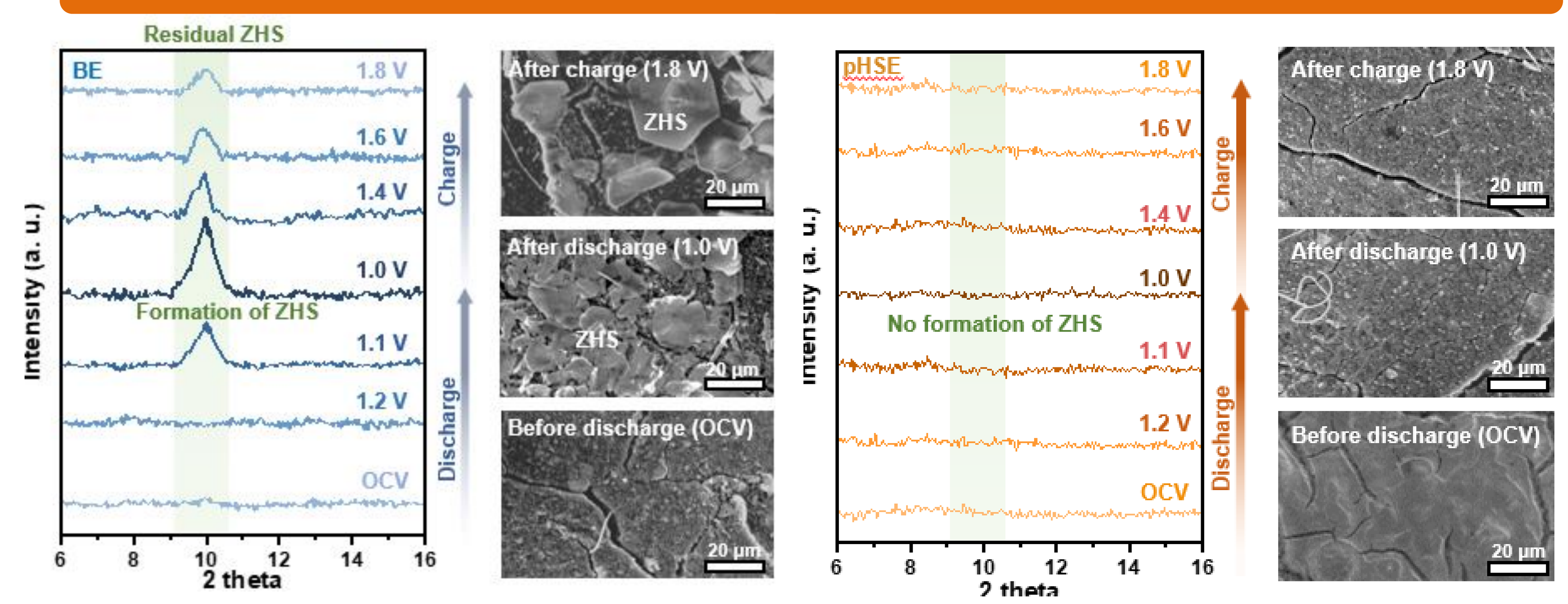
Ex-situ pH measurement results

BE: baseline electrolyte (1M $ZnSO_4$)
pHSE: pH stabilized electrolyte (1M $ZnSO_4$ with pH buffer additives)

- Potential range: 1.0-1.8 V (*vs* Zn/Zn^{2+})

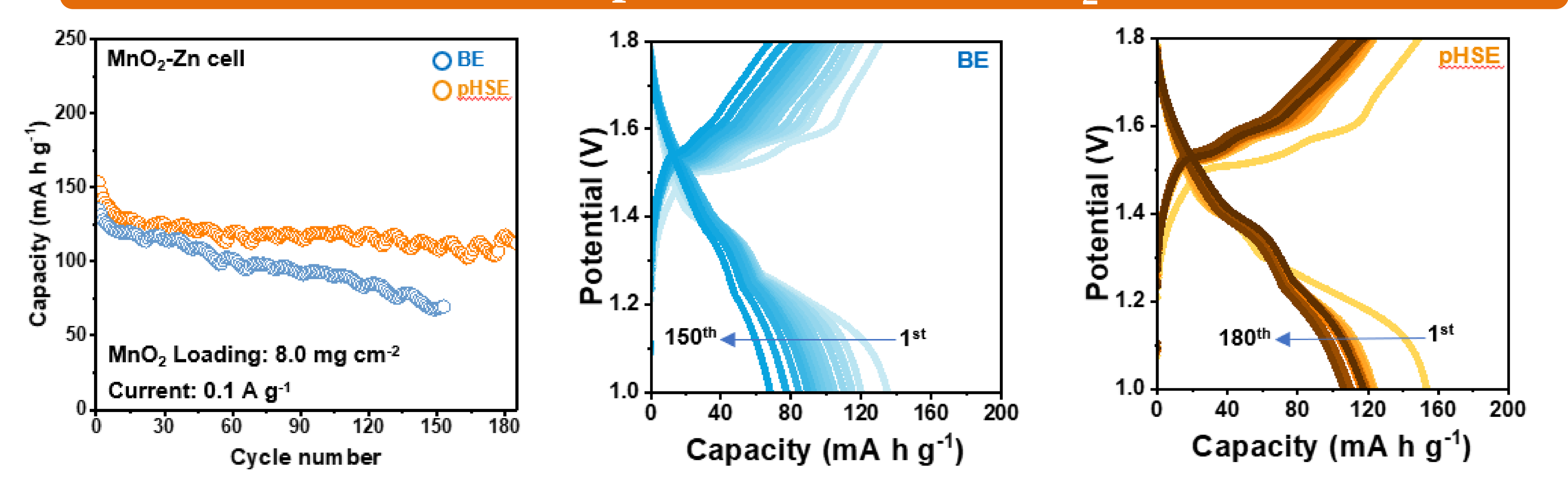


Difference in ZHS formation/dissolution reaction



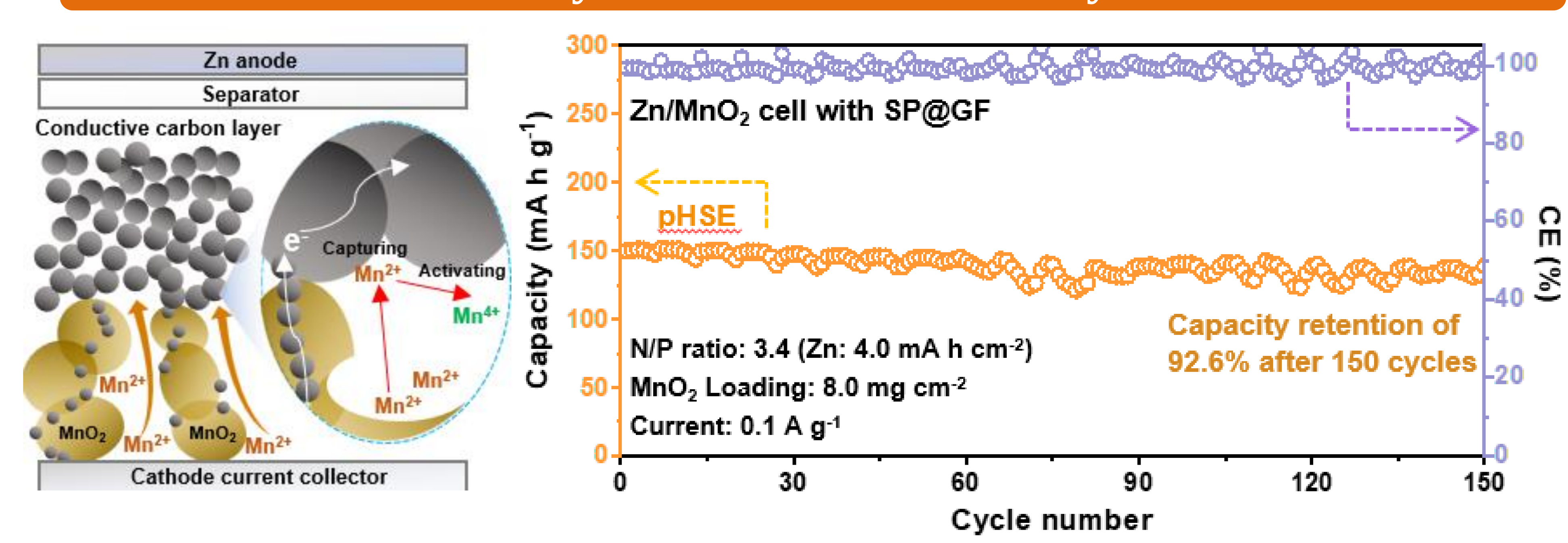
- In the case of using BE, ZHS was formed during discharge process and residual ZHS was observed even after charge process.
- In the case of using pHSE, ZHS was not formed during discharge process

Electrochemical performance of MnO_2-Zn batteries



- MnO_2-Zn cell with BE showed the capacity retention ratio of 50.4% (68.1 mA h g^{-1}) after 150 cycles, whereas MnO_2-Zn cell with pHSE showed the capacity retention ratio of 70.7% (108.4 mA h g^{-1}) after 150 cycles.
- MnO_2-Zn cell with BE showed the remarkable increase of overpotential, whereas redox overpotential was well-maintained in the case of using pHSE.
- Irreversible accumulation of ZHS on the surface of electrode during cycling impedes charge transfer behavior and causes the continuous chemical decomposition of electrolyte.

Conductive layer at electrode/electrolyte interface



- Incorporation of conductive layer on the surface of cathode can suppress the Mn^{2+} dissolution and reactivate the Mn^{2+}/Mn^{4+} electrochemistry.
- Under N/P ratio of 3.4, MnO_2-Zn cell showed capacity retention ratio of 92.6% after 150 cycles.

Summary and Perspective

- Stabilization of the H^+ concentration of electrolyte by pH buffer additives in response to the unbalanced H^+ insertion/desertion electrochemistry in MnO_2 cathode can inhibit the irreversible formation of ZHS solid products on the surface of electrode, which resultingly improved cycle stability of MnO_2-Zn aqueous batteries.

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Contact: Won-Gwang Lim
Battery Development & Reliability Group
Energy & Environmental Directorate
Pacific Northwest National Laboratory
Email: wonkwang.lim@pnnl.gov
Tel: (509) 518-7311

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