

Development of Zinc-Air Batteries with Advanced Aqueous Electrolytes: A Model-Based Approach

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Zinc-air batteries (ZABs) are promising candidates for next-generation electrochemical energy storage. They offer a high theoretical specific energy ($1086 \text{ Wh}\cdot\text{kg}^{-1}$) and energy density ($6093 \text{ Wh}\cdot\text{l}^{-1}$), are based on cheap and non-hazardous materials, and have superior operational safety characteristics. In fact, primary alkaline ZABs already have a long history in low-current industrial applications like hearing aids (1). But over time, the alkaline electrolyte reacts with CO_2 to form carbonates, which reduces the ionic conductivity of the electrolyte and degrades the performance of the battery (2). Furthermore, metallic zinc can irreversibly passivate when discharged and may build dendrites when charged.

We have developed continuum models based on principles of electrochemical thermodynamics and kinetics to simulate the performance of metal-air batteries (3, 4). Our models for ZABs introduce a new method for considering the thermodynamic stability of aqueous species in continuum simulations. By combining this approach with the basic aspects of electrochemical cell modeling (like mass transport in concentrated electrolytes, multi-phase flow in porous media, and concentration-dependent electrochemical reaction kinetics), we are able to investigate transient and spatially resolved changes in cell potential, electrolyte concentrations, and multi-phase volume fractions. Our investigation specifically considers ZABs with two different types of aqueous electrolytes: alkaline KOH and neutral $\text{ZnCl}_2\text{-NH}_4\text{Cl}$.

For ZABs with alkaline KOH electrolytes, our simulations show that inhomogeneous Zn dissolution and ZnO precipitation cause the zinc electrode to change shape when cycled and lead to the local depletion of KOH, which induces type II (irreversible) ZnO passivation. Furthermore, the dissolution of CO_2 in the electrolyte leads to a steady drop in cell potential over months of operation (2).

In the neutral $\text{ZnCl}_2\text{-NH}_4\text{Cl}$ electrolyte, the low OH^- concentration limits the formation of carbonates, potentially extending the lifetime of the battery (5-7). However, in the near-neutral pH regime the stability of the aqueous zinc-ligand complexes shifts significantly with even small changes in concentration. This affects the ionic conductivity of the electrolyte, the composition of the final discharge product, and the pH stability. Our simulations show that under conditions reported in the literature, the pH may become strongly acidic, which affects the performance and stability of the bifunctional air catalyst (6-8). We investigate how the composition of the electrolyte and the architecture of the cell can be adjusted to maintain a stable, neutral pH over cycling.

In this contribution, we highlight the physical and electrochemical processes which govern ZAB performance, and discuss how these processes can be managed to develop a rechargeable battery. This work is supported by the European Union Horizon 2020 project ZAS! (Zinc Air Secondary Batteries Based on Innovative Nanotechnology for Efficient Energy Storage).

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