

# Model-Based Development of Advanced Aqueous Electrolytes for Zinc-Air Batteries

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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 widely-available materials, and have superior operational safety characteristics. But over time, the performance of the cell is significantly degraded due to a parasitic reaction between the alkaline electrolyte (KOH) and  $\text{CO}_2$  (1). Furthermore, local depletion of electrolyte species at the electrolyte-electrode interface can contribute to the irreversible passivation of zinc when discharged and the development of zinc dendrites when charged.

To better understand and solve these challenges, we have developed continuum models based on the principles of electrochemical thermodynamics and kinetics to simulate the performance of metal-air batteries (2, 3). Using this approach, we are able to investigate transient and spatially resolved changes in cell potential, electrolyte concentrations, and multi-phase volume fractions. Our investigation begins by analyzing the performance of ZABs with traditional KOH electrolytes to show how the electrolyte and cell design influence overall performance. We then expand our analysis to include new aqueous electrolytes, such as near-neutral  $\text{ZnCl}_2\text{-NH}_4\text{Cl}$ .

Our simulations show that in alkaline KOH electrolytes, inhomogeneous Zn dissolution and ZnO precipitation cause the electrode to change shape upon cycling and affect the discharge voltage. When operated at high current densities, significant concentration gradients are induced in the cell, which causes ZnO type II (irreversible) passivation. Furthermore, the dissolution of  $\text{CO}_2$  in the electrolyte leads to a steady drop in cell voltage and limits the operational lifetime of the battery to just a few months (1).

The near-neutral  $\text{ZnCl}_2\text{-NH}_4\text{Cl}$  electrolyte helps address some of these challenges. This electrolyte is not susceptible to the same parasitic reactions as the KOH electrolyte and could potentially extend the lifetime of the battery (4-6). However, in the near-neutral pH regime the stability of aqueous zinc-ligand complexes shifts significantly with even small changes in pH. This affects the composition of the final discharge product and the overall energy density of the battery. Our simulations show that under experimental conditions reported in the literature (5), strong pH gradients develop across the cell, which may accelerate the degradation of the bifunctional air catalyst (6, 7). We show 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 coupled effects between electrolyte composition and ZAB performance, and discuss how these processes can be managed to develop a rechargeable battery. This work is supported by the European Commission Horizon 2020 project ZAS! (Zinc Air Secondary Batteries Based on Innovative Nanotechnology for Efficient Energy Storage).

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