

Development of Energy Storage Materials for Rechargeable Aqueous Zinc-Ion Batteries

Abstract

Rechargeable aqueous zinc-ion batteries (ZIBs) have attracted significant attention as next-generation energy storage systems for large-scale energy storage applications, owing to their low cost, enhanced safety, and promising electrochemical properties. However, the advancement of ZIB technology toward practical applications is hindered by several critical challenges, including the formation and growth of zinc (Zn) dendrites, short cycle life, limited operating voltage, reduced energy density, and complex charge storage mechanisms. The present work proposes a strategic approach focused on the development of stable electrodes by integrating sustainable material design and interface engineering to overcome key issues, such as dendrite formation, poor cycling stability, and sluggish ion kinetics. To suppress dendritic growth and enhance anode performance, activated carbon (AC) derived from corn husk biomass is incorporated into the Zn anode. At an optimal loading of 15 wt.% AC, the modified anode achieves a high initial discharge capacity of 211.67 mAh.g⁻¹ and retains 86.42% of its capacity after 125 galvanostatic charge-discharge (GCD) cycles, indicating improved electrochemical reversibility and cycling stability. Further enhancement is realized through surface engineering of the Zn anode using a metal-organic framework (MOF), specifically zeolitic imidazolate framework-8 (ZIF-8), electrodeposited onto a zinc-copper (Zn-Cu) structure. This interface-engineered structure promotes uniform Zn nucleation, minimizes dendritic growth, and enables stable plating/stripping of Zn²⁺ for 1000 hours in symmetrical cells. Post-cycling characterization confirms that the ZIF-8 layer effectively mitigates morphological degradation, contributing to extended anode lifespan in ZIBs. To gain quantitative insights into dendritic growth minimization, a mathematical model is developed that incorporates ion transport and electrochemical kinetics. The ZIF-8-modified electrode exhibits the highest Zn²⁺ transference number (t_+), the lowest dendritic current density, and a favorable steady-state Zn²⁺ concentration profile near the electrode surface. The developed mathematical model suggests that while increasing the t_+ significantly reduce dendritic growth, it cannot be eliminated completely. Enhanced Zn²⁺ transport also reduces the charge transfer resistance, promoting more stable and uniform Zn deposition at the anode surface. On the cathode side, two multivalent transition metal oxide systems are studied: ZIF-67-derived Co₃O₄/α-MnO₂ composite and mixed-valence spinel-type NiMn₂O₄. Zn//Co₃O₄/α-MnO₂ delivers a discharge capacity of 243.51 mAh.g⁻¹ at 0.4 C and 140.2 mAh.g⁻¹ at 4 C, retaining 90.59% of its capacity after 2000 GCD cycles at 4 C, while maintaining high Coulombic efficiency and redox reversibility. Zn//NiMn₂O₄ delivers a discharge capacity of 146.4 mAh.g⁻¹ at 1 C, with 88.5% capacity retention after 2050 GCD cycles with stable Coulombic efficiency. The findings of this work demonstrate that the use of biomass-derived porous AC and ZIF-based interface engineering effectively enhanced anode stability by minimizing Zn dendrite growth, while the development of mixed-valence spinel-type and tunnel-structured cathode materials improved capacity and cycling performance in ZIBs. The coupling of experimental validation with mathematical modeling provides a robust approach for the rational design of high-performance, sustainable, and safe energy storage systems.

Keywords: Zinc-ion battery, aqueous battery, zinc dendrite, metal-organic framework, spinel cathode, zinc dendrite modelling