Abstract

The thesis entitled "*Defect-Engineered Electrode Materials for High-Performance Aqueous Zinc-Based Energy Storage Devices*" presents the rational design and synthesis of advanced electrode materials for aqueous zinc-ion batteries (AZIBs) and aqueous zinc-ion hybrid capacitors (AZIHCs). The charge-storage performance of electrochemical energy storage devices is strongly governed by the nature of electrode materials. Vanadium-based oxides are considered promising cathodes for AZIBs due to their rich multivalent redox chemistry and high theoretical capacity. However, their practical performance is limited by sluggish Zn^{2+} diffusion, electronic conductivity, and structural instability during prolonged cycling. To overcome these limitations, this thesis demonstrates defect-engineering strategies, including oxygen-vacancy creation, cation-vacancy regulation, and heteroatom incorporation, to enhance charge-storage performance and cycling durability. The defect engineering of ZnV_2O_4 and $Na_2V_6O_{16}\cdot 3H_2O$ by carbothermal, chemical, and electrochemical strategies improves the charge storage performance (*Chapters 3-5*). Carbothermal reduction of ZnV_2O_4 generates oxygen vacancies and electrochemical amorphization, which enhances the diffusion kinetics of charge carriers. Doping of Mn^{2+} into the ZnV_2O_4 lattice introduces both oxygen and vanadium vacancies and significantly improves the cycling stability of the device. Charge storage in defect-engineered cathodes follows the reversible Zn^{2+}/H^+ co-intercalation/deintercalation mechanism, facilitated by the formation of vacancies and potential cycling-induced structural evolution. The electrochemical generation of Na^+ vacancies in $Na_2V_6O_{16}\cdot 3H_2O$ facilitates fast ion transport, delivering an ultrahigh capacity and exceptional cycling stability exceeding 75,000 cycles. Notably, the contribution of H^+ to charge storage is quantitatively established, revealing its dominant role in enabling fast-charging behavior. High-performance AZIHC is developed using the heteroatom (N, P)-doped highly porous carbon (*Chapter 6*). It delivers a high power density and an ultra-long cycling life of over 100,000 cycles. Overall, this work establishes defect engineering as an effective strategy for advancing high-performance aqueous zinc-based energy storage systems.

Keywords: Zinc-ion batteries, zinc-ion hybrid capacitors, defect engineering, fast-charging, co-intercalation