Design and Advanced Characterization of Aqueous Na- and Zn-Ion Battery Materials

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Aqueous insertion batteries offer a safe, sustainable, and low-cost alternative to conventional Li-ion systems for large-scale stationary energy storage. However, practical scale-up is hindered by narrow electrochemical stability windows and severe electrode degradation driven by the complex acid-base chemistry of aqueous mediums. To address these challenges, this work utilizes a comprehensive multi-technique synthesis and characterization approach to investigate framework-structured NASICON and Prussian Blue Analogue (PBA) materials. For the negative electrode, NASICON-type $NaTi_2(PO_4)_3$ (NTP) suffers from parasitic reactions causing self-discharge and degradation. Through operando local pH monitoring combined with solid-state NMR, XRD, and EDX, we demonstrated that both hydrogen evolution (HER) and oxygen reduction (ORR) drive a pH increase during cycling. While HER is negligible under mildly alkaline conditions, chemical ORR, driven by O_2 reacting with Ti(III), dominates. Crucially, capacity fade stems primarily from electronic contact failure caused by the growth of amorphous $TiO(OH)(H_2PO_4)\cdot nH_2O$ interphase layers, rather than bulk NTP decomposition. Managing local oxygen concentration and pH enables highly stable NTP operation in low-concentration aqueous electrolytes. For the positive electrode, Zn-rich PBAs like $Zn_2[Fe(CN)_6]$ were studied for zero-excess-metal-free (anode-free) aqueous Zn-ion batteries. We elucidated synthesis–structure–property relationships by focusing on phase formation, Fe(II/III) oxidation states, and structural hydration, with operando XRD revealing previously unreported phase evolution during synthesis and cycling. Together, these findings provide critical insights into degradation mechanisms and mitigation strategies, unlocking the potential of stable, high-efficiency aqueous battery systems.

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