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Zn-ion Capacitors

Long-lifespan Zinc-ion Capacitors Enabled by Anodes Integrated with Interconnected Mesoporous Chitosan Membranes through Electrophoresis-driven Phase Separation

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Abstract: The advancement of highly secure and inexpensive aqueous zinc ion energy storage devices is impeded by issues, including dendrite growth, hydrogen evolution and corrosion of zinc anodes. It is essential to modify the interface of zinc anodes that homogenizes ion flux and facilitates highly reversible zinc planarized deposition and stripping. Herein, by coupling zinc ion coordination with acid-base neutralization under the driving of electrophoresis, manageable mesoscopic phase separation for constructing chitosan frameworks was achieved, thereby fabricating interconnected mesoporous chitosan membranes based heterogeneous quasi-solid-state electrolytes integrated with anodes. The framework is constructed by twisted chitosan nanofiber bundles, forming a three-dimensional continuous spindle-shaped pore structure. With this framework, the electrolyte provides exceptional ion conductivity of 25.1 $mS\,cm^{-1}$, with a puncture resistance strength of 2.3 GPa. In addition, the amino groups of chitosan molecule can make the surface of the framework positively charged. Thus, reversible zinc planarized deposition is successfully induced by the synergistic effect of stress constraint and electrostatic modulation. As a result, as-assembled zinc ion capacitor has an excellent cycle life and sustains the capacity by over 95% after 20000 cycles at a current density of 5 $A\,g^{-1}$. This research presents a constructive strategy for stable electrolytes-integrated zinc anodes.

Introduction

The objectives of "emission peak" and "carbon neutrality" necessitate clean energy resources to replace fossil fuels, and advanced energy storage devices are indispensable to attain efficient energy storage and utilization.[1] Aqueous zinc ion capacitors and batteries excel in various power supply systems thanks to their high safety, low cost, and high energy density.[2] However, zinc dendrites resulting from the irregular deposition, hydrogen evolution, and corrosion of zinc anodes significantly reduce the lifespan of devices and restrict their application. Hence, enhancing the stability of zinc anodes is imminent.[3]

So far, enhancing the stability of zinc anodes has concentrated primarily on the zinc anode itself and its interface environment. Strategies focusing on the zinc anode itself such as altering the crystal structure and morphology of zinc metal[4] and preparing zinc alloys,[5] are not easily scalable nor widely applicable because of the complicated processing technology. In contrast, quasi-solid-state electrolytes (QSSEs), an entity with interaction of polymer matrices and salt solution, can effectively regulate the interface environment to induce zinc uniform deposition and inhibit dendrite growth in a more manageable approach.[6] Structurally, QSSEs are classified into heterogeneous ones (*he*-QSSEs) with solid–liquid phase separation and homogeneous ones (*ho*-QSSEs) with uniformly mixed solid and liquid phases. Compared to *ho*-QSSEs, *he*-QSSEs introduce the polymer morphology as a new adjustable dimension, regulating ion conductivity and mechanical properties. Unfortunately, the incompatible solid-solid interface between *he*-QSSE and anode causes a performance bottleneck for this system. Therefore, an integrated structure of anodes anchored with *he*-QSSE is proposed, which can reduce interfacial charge transfer resistance, decreasing overpotential.[7] Consequently, the strategy of constructing *he*-QSSEs integrated with zinc anodes is worth investigating.

Recently, chitosan, a biocompatible and biodegradable polysaccharide with abundant amino and hydroxyl groups, has been found to be capable of stabilizing zinc anodes as polymer matrices in *he*-QSSEs, thus attracts wide attention.[8] However, all of preparation methods for chitosan-based *he*-QSSEs reported in current researches are casting and spin-coating, which fail to achieve integration with zinc anodes and result in unregulated pore structure, leading to unsatisfactory electrochemical and mechanical properties. Therefore, it is worth exploring the accurate regulation of chitosan matrix, which will take full advantages of chitosan based *he*-QSSEs in stabilizing zinc anodes. Notably, the phase separation method offers optimal controllability and convenience in preparing chitosan matrix because the solubility of chitosan is highly dependent on pH. The phase separation method can be accomplished

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