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学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Suppressing Dendrites Growth of Zinc Metal Anodes by Modulating Electrode-Electrolyte Interfaces for the Development of High-Performance Zinc-ion Batteries

（高性能亜鉛イオン電池開発のための電極-電解質界面制御による亜鉛金属負極の デンドライト成長の抑制）

Rechargeable aqueous zinc-ion batteries (RAZIBs) are emerging as promising energy storage devices due to their high energy density, environmental friendliness, safety, and cost-effectiveness. However, the utilization of zinc (Zn) metal anodes in RAZIBs faces significant challenges, including the growth of Zn dendrites, electrolyte-induced corrosion, and undesirable side reactions, which hinder the real-world application of current RAZIBs. This study aims to contribute to the development of RAZIBs for real-world applications. This thesis comprises six chapters. Chapter 1 provides an overview of the significance and research status of RAZIBs. Chapter 2 reveals the reasons for the growth of Zn dendrites in mildly acidic electrolytes and the main factors affecting the electrochemical reversibility of Zn anodes. Then, building on this understanding, Chapters 3 to 5 propose novel approaches for optimizing Zn metal anodes by modulating the electrode-electrolyte interface to suppress Zn dendrite growth and improve the cyclic stability of Zn anodes.

The growth of Zn dendrites in mildly acidic electrolytes, e.g., $ZnSO_4$ aqueous solution, has been thought to originate from the high local current density and the uneven distribution of Zn ion fluxes on the electrode surface. Moreover, the hydrogen evolution reaction (HER) on the electrode surface and the accompanying by-product zinc hydroxide sulfate (ZHS) have been considered only to exacerbate the inhomogeneous electric field distribution rather than being the direct cause of Zn dendrites growth. However, in Chapter 2, a co-growth pattern of Zn metal and ZHS is demonstrated, and the co-growth of both results in the generation of Zn dendrites in the mildly acidic electrolytes. In addition, the electrochemical reversibility of Zn metal anodes can be enhanced by reducing the proportion of HER, such as using substrates with lower HER catalytic activity, or by reducing the production of ZHS, such as increasing the current density of Zn deposition. This insight provides a vital understanding of the fundamental processes occurring at the Zn anode surface and suggests potential strategies for dendrite suppression.

Then, some novel approaches are proposed for optimizing Zn metal anodes by modulating the electrode-electrolyte interface to suppress Zn dendrites growth and improve the cyclic stability of Zn anodes. In Chapter 3, the Al-Nb foil is fabricated by magnetron sputtering a layer of niobium (Nb) on top of the aluminum (Al) foil as a current collector for Zn metal anodes. Thanks to the excellent anti-corrosion and anti-HER properties of Nb metal, Zn can be electrodeposited onto the Al-Nb foil with almost no ZHS formation, thus exhibiting a plating/stripping Coulombic efficiency of over 99% and can be stably cycled for 300 cycles under a current

density of 25 mA cm^{-2} and a deposition capacity of 6.25 mAh cm^{-2}. Additionally, the Al foil with Nb coating can be used directly as a current collector for a MnO_2 cathode, resulting in a stable cycle for 120 cycles with 90% capacity retention.

In Chapter 4, to further adjust the deposition behavior of Zn on the anode surface, a non-toxic and non-corrosive diethylene glycol (DEG) solution is employed as an electrolyte to electropolish the surface of Zn metal electrodes. The electropolishing treatment effectively refines the anode surface, thus promoting uniform Zn deposition and limiting the formation of dendrites. Furthermore, the electropolished Zn metal can maintain its homogeneous surface nature in the mildly acidic electrolyte, thereby governing a stable Zn plating/stripping cycle for more than 6000 times at a current density of 40 mA cm^{-2} and an areal capacity of 2 mAh cm^{-2}. The polished Zn metal also exhibits better cyclic performance when charging/discharging Zn-MnO_2 cells with an areal capacity of more than 20 mAh cm^{-2}. Moreover, electropolishing of Zn metal is a treatment that can be combined with the most currently reported anode protection strategies to form a composite strategy.

In Chapter 5, to eliminate Zn dendrites growth caused by drastic changes in the surface morphology of Zn during long-time Zn plating/stripping cycles, semi-solid hydrogel electrolytes based on poly (2-acrylamide-2-methyl-propane sulfonic acid)-polyacrylamide (PAMPS-PAM) are prepared. The hydrogel electrolytes can reduce the tendency of Zn metal to grow upward by a modified mechanical suppression effect, thus forcing the Zn deposition to become uniform and flat. In this way, even with surface property changes of Zn metal during cycling, Zn deposition is always influenced by the separator from above. Zn electrodeposition under the protection from the hydrogel electrolytes exhibits a slight increase in overpotential while the stable Zn plating/stripping cycle can be maintained more than 1000 times under a current of 5 mA cm^{-2} and a capacity of 2.5 mAh cm^{-2}. The Zn-MnO_2 cells with the hydrogel electrolytes can be stably charged/discharged more than 500 times at a capacity of 4.5 mAh cm^{-2} with capacity retention close to 50%.

Chapter 6 is general conclusions, and the future prospects of RAZIBs are briefly described. This thesis demonstrates a promising avenue for suppressing Zn dendrites growth and enhancing the overall performance of RAZIBs. Through a detailed understanding of Zn dendrites formation and the application of several electrode-electrolyte interface engineering techniques, this work provides new insights into the protection of Zn anodes in RAZIBs and promotes the development of practically applicable aqueous rechargeable batteries.