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锌铋合金电极在强碱电解液中的电化学行为研究

Study on the Electrochemical Behaviors of Zinc-Bismuth Alloy Electrode in Alkaline Electrolyte

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**Study on the Electrochemical Behaviors of Zinc-Bismuth
Alloy Electrode in Alkaline Electrolyte**



A Dissertation Submitted for the Degree of

Master of Science

By

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At

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摘 要

锌是一种重要的金属能源材料，由于其具有储量丰富、电极平衡电位负、比能量高、可逆性好、成本低、无环境污染等优点，已被广泛用作碱性一次和二次电池的负极材料。随着全球对能源和环境问题的高度关注，锌作为能源材料的重要地位日益突显。由于锌电极在浓的碱性溶液中存在着自腐蚀、自钝化、形变和枝晶等问题，使二次锌电池的性能变差，如自放电严重，循环容量迅速降低，严重缩短了电池的寿命，甚至存在安全隐患，从而使锌系列二次电池的大规模开发和应用受到极大的限制。目前有关电极的合金化、电解液中 Carbopol 树脂的添加量以及工作电极与对电极的距离等电池体系因素对锌电极在强碱性溶液中的电化学反应的影响仍缺乏系统和深入的研究。

本工作针对碱性锌锰电池的研究热点，围绕碱性锌锰电池体系中的核心课题——锌阳极电化学反应行为，包括开路电位下的锌腐蚀速度，持续放电下的阳极溶解速度和出现钝化的电流密度等进行研究。应用多种电化学技术，结合其他表面微观表征技术，研究了合金电极中 Bi 的添加、电解液中 Carbopol 树脂的添加量以及电极间距离等电池体系参数对锌阳极电化学反应行为的影响，主要的研究工作和结果如下：

1. 锌电极中添加Bi对合金电极电化学反应行为的影响研究

考察了电极中Bi的添加对合金电极的电化学反应行为的影响，包括：合金电极的自腐蚀、阳极溶解峰电流和溶解电位以及致钝时间，并对合金电极浸蚀及溶解致钝后的表面形貌进行了表征。结果表明，合金电极中添加一定量的Bi可明显减小合金的晶粒尺寸，增大界相长度，降低晶界杂质的浓度，从而有效抑制电极的自腐蚀，在开路电位附近极化电阻增大；同时可改善电极表面氧化物的沉积形貌和结晶取向，提高了电极活性。在连续溶解条件下，Bi的添加对电极溶解电位及阳极过电位影响程度较小；在大电流溶解致钝过程中，Bi的添加不同程度地促进了电极的钝化过程。

2. 电解液中添加Carbopol树脂对合金电极电化学反应行为的影响研究

考察了电解液中添加 Carbopol 树脂对电化学反应行为的影响，包括：合金电极的自腐蚀、阳极溶解峰电流和溶解电位以及电极达到钝化的时间等。结果表明，电解液中添加 Carbopol 树脂可提高电解液粘性，增大了扩散层厚度，进而显著

提高了电极极化电阻，有效降低了电极的自腐蚀速率。在连续溶解条件下，Carbopol 树脂的添加使电极阳极的溶解电位出现不同程度的正移，阳极极化过电位明显增大；大电流放电致钝过程中，Carbopol 树脂的添加较明显地促进了电极的致钝过程。

3. 电解池中工作电极与对电极距离对合金电极电化学行为的影响研究

通过精确调节对电极 (MnO_2) 与工作电极 (Zn-Bi 合金) 的距离，较系统地研究了不同电极间距离对锌合金电极的电化学行为的影响。结果表明，电极间距离的缩短使电极溶解电位出现不同程度的正移，溶解电位的波动程度明显加剧，电极表面的双电层电容和电荷传递电阻增大，电极表面反应产物的吸附作用增强，电极的溶解活性受到一定程度地抑制。

关键词： 锌铋合金，Carbopol 树脂，电极间距离，阳极行为，EIS

Abstract

Zinc is one of the most important energy materials, and it is widely used as an anode in alkaline primary and secondary battery due to its various advantages including rich resource, negative equilibrium potential, high specific energy, good reversible, low cost, no environmental pollution, etc. With the increasing attention to the energy and environment problems, the importance of zinc as energy materials is increasingly risen. However, some technical problems of zinc alloy electrodes in alkaline solution remain, including self-corrosion, self-passivation, deformation and dendrite, which result in the performance of alkaline secondary batteries becomes worse, that is, self discharge is serious, cycling capacity rapidly and battery life decrease. At present, there are still lack of systematic and in-depth study on the effects of alloying of the electrode, the addition of Carbopol resin into electrolyte and the distance between working electrode and counter electrode on the electrochemical behaviors of zinc alloy electrode in strong alkali solution.

Based on the research hotspot of alkaline zinc manganese battery, this work focuses on the electrochemical behaviors of zinc alloy anode in alkaline electrolyte, including the zinc corrosion rate at open circuit potential, the anodic dissolution rate under continuous discharge and the dissolution peak current density. The electrochemical behaviors were studied by various electrochemical techniques, combined with other surface characterization techniques. The effects of the addition of bismuth into zinc electrode, the addition of Carbopol resin into electrolyte and the distance between working electrode and counter electrode were studied, the main research work and results are as follows:

1. The influence of the addition of bismuth into zinc electrode on the electrochemical behavior of zinc-bismuth alloy electrodes

The influence of the addition of bismuth on the electrochemical behavior of zinc alloy electrode was investigated, including the self-corrosion of zinc alloy electrode, the anodic dissolution peak current density, the dissolution potential and passivation time. The surface morphologies of zinc alloy electrodes after etched and passivated

were characterized. The results showed that the appropriate addition of bismuth to Zn decreased the grain size, increased the length of the boundary phase, reduced the concentration of impurities in the grain boundary. So it is possible to inhibit the self-corrosion of alloy electrode, improve the morphology and crystal orientation of oxides on the electrode surface, and increase the dissolution activity of zinc alloy electrodes. Under the continuous dissolution condition, the addition of bismuth had little influence on the anodic dissolution potential and the anodic overpotential. Under the relatively large dissolution current condition, the addition of bismuth promoted the passivation process to a different extent.

2. The influence of the addition of Carbopol resin in electrolyte on the electrochemical behavior of zinc-bismuth alloy electrodes

The influences of the addition of Carbopol resin into electrolyte on the electrochemical behavior of zinc alloy electrode were studied, including the self-corrosion of zinc alloy electrode, the anodic dissolution peak current density, the dissolution potential and passivation time. The results showed that the appropriate addition of Carbopol resin increased electrolyte viscous and the diffusion layer thickness, which significantly enhanced the polarization resistance, restrained the self-corrosion. Under the continuous dissolution condition, the anodic dissolution potential shift positively with the addition of Carbopol resin. Under the relatively large dissolution current condition, the addition of Carbopol resin promote the passivation process.

3. The influence of the distance between working electrode and counter electrode (d_{w-c}) on the electrochemical behavior of zinc-bismuth alloy electrodes

The electrochemical behavior of zinc-bismuth alloy electrodes at different d_{w-c} were systematically studied by accurately modulating the d_{w-c} . The results indicated that the shortening of the d_{w-c} led to the positive shift of anodic dissolution potential and increased the potential fluctuation, which was attributed to the increasing of the double-layer capacitance and the charge transfer resistance of the electrodes surface, which was possible to enhance the adsorption of reactants and productions, and inhibit the dissolution activity of zinc alloy electrode.

Keywords: Zinc-Bismuth Alloy Electrode, Carbopol Resin, Distance Parameter,
Anodic Behavior, EIS

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第一章 绪论

1.1 碱性锌锰电池发展简史

锌/二氧化锰电池是以 Zn 为负极、 MnO_2 为正极的一个电池系列。电解液可采用中性的 NH_4Cl 、 ZnCl_2 水溶液或碱性的 KOH 水溶液，简称锌锰电池。

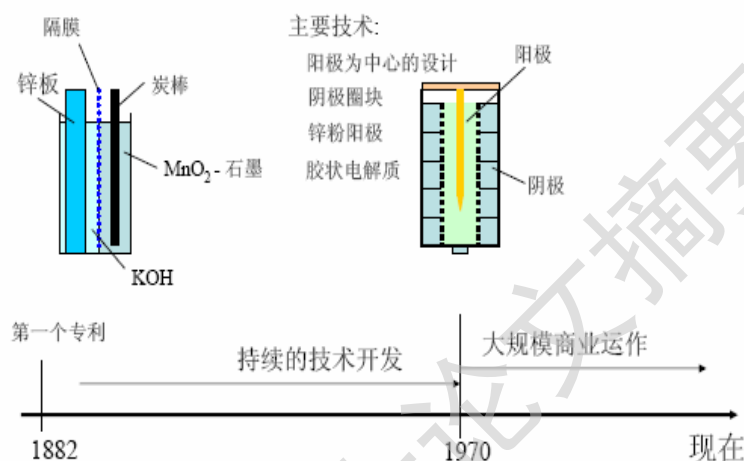


图 1.1 碱电池技术的发展过程示意图^[1]

Fig. 1.1 The schematic diagram of the development process for alkaline battery technology

碱性锌锰电池技术的发展大致经历了如图 1.1 所示的几个过程^[1]，碱性锌锰电池始于 1882 年，Leuchs G 研制成了以 MnO_2 碳极板为正极，氢氧化钠或氢氧化钾溶液为电解液，锌极板为负极的碱锰电池。此后，电极与电解液得到更新取代，以 MnO_2 和石墨的混合物作为阴极，碳棒作集流体，氢氧化钾为电解质，氧化锌包裹的锌作阳极，并使用了一种多孔隔膜。但是，这些早期的电池都没有商业上的应用价值。到 20 世纪 50 年代中期，商业碱性锌锰电池逐渐出现，同时其它系列碱性一次电池也得以发展和使用，从而促进了锌锰电池的研究。20 世纪 50 年代末的深入研究发现，碱性锌锰电池能够提供比勒克朗谢电池及其它电池高得多的电流和容量，使得碱性锌锰电池的前景大大改观^[2]，20 世纪 60 至 70 年代形成了碱性锌锰电池的新时代^[3]。20 世纪 70 年代至今则是碱性锌锰电池的发展及完善阶段，碱锰电池的许多关键技术障碍得到了突破性解决，其性能得到了显著提高。第一，用锌粉取代了锌筒，用电解二氧化锰取代了天然二氧化锰，用再生纤维和烯烃聚合物取代了浆糊隔离层和纸板隔膜，用铜钉和钢壳取代了碳棒和锌筒作为集流体，正是由于这些取代，促进了原材料和工艺的发展；第二，解决了因使用

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