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Zinc electrode with anion conducting polyvinyl alcohol/poly (diallyldimethylammonium chloride) film coated ZnO for secondary zinc air batteries

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ABSTRACT

Zinc electrode with polyvinyl alcohol(PVA)/poly(diallyldimethylammonium chloride) (PDDA) film coated ZnO was prepared by a chemical cross-linking method. The PVA/PDDA polymer film has an interpenetrating network structure where PVA works as polymer matrix and PDDA as anion charge carriers. Fourier transform infrared spectra (FT-IR), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies reveal that a polymer film with well-connected three dimensional network structure is formed around ZnO nanoparticles. Linear sweep voltammetry, cyclic voltammetry (CV) and charge/discharge cycling tests were carried out on the ZnO/PVA/PDDA composite electrode, which exhibits higher electrochemical activity and dramatically superior cycle stability than the bare ZnO electrode without polymer films. The ZnO/PVA/PDDA electrode showed remarkably lower solubility during cycling.

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1. Introduction

As one of the most promising candidate for energy storage, zinc–air batteries posses cost, safety, environment and technology advantages over lithium-air batteries, magnesium–air batteries and aluminum–air batteries [1]. Currently, the range of applications include hearing aids, navigation lights and railway signals and military uses [2–4]. However, extensive commercialization of zinc secondary systems is hampered by the short cycle life and discharge capacity fading of the zinc anode due to the dendritic growth of zinc electrodepostion and morphology shape change of zinc electrode [5], especially at high charge–discharge rate. In the past years, many attempts have been made to solve these problems including the use of additives either to the electrode or to the electrolyte, current pulses, hydrodynamic conditions, zinc alloys, and surface modification technique to improve the electrochemical performance of ZnO [6–17], among which surface modification technique is considered to be a promising way.

Polymer coating of zinc electrode has been investigated. Zhu et al. [18] and Miyazakiet al. [19] reported that coating zinc anodes with ionomer films was effective in impeding the dissolution of zinc discharge products into electrolyte, thus restricting zinc dendrite formation and shape change of zinc electrodes.

In the present work, we design a new type of alkaline polymer film, based on PVA and poly(diallyldimethylammonium chloride) (PDDA) blends, to uniformly coat ZnO particles. PVA is a polyhydroxy polymer, it has film forming capacity, hydrophilic properties, and a high density of reactive chemical functions that are favorable for cross-linking by chemical or thermal treatments [20,21]. PDDA, a quaterized water soluble copolymer, can offer conductive anions (OH^-) as charge carriers. Along with the cross-linked PVA, it is expected to improve the film's chemical stability [22,23]. The cross-linked structure of PVA hydrogel was obtained through the reaction of the hydroxyl groups (—OH) of PVA with the aldehyde groups (—CHO) of glutaraldehyde in the presence of a strong acid. This hydrogel possesses ionic permeability, alkaline stability and well mechanical property [24,25], providing fast ionic transfer channels, as well as free space for zinc volume changes during repeated cycles, which make it an appropriate solution for the drawback of secondary zinc anodes. Compared with bare ZnO electrode using traditional PVA as binder, zinc electrode with PVA/PDDA polymer film exhibits much better cycle stability, owing to the retainment of zinc active material and reduction of zinc dendrite formation.

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2. Experimental

2.1. Material preparation

All chemicals were of analytical grade, and doubly distilled water was used for preparing all solutions. A stock 10 wt% PVA (99% hydrolyzed, average molecular weight: 86,000–89,000, Aldrich) aqueous solution was prepared by dissolving PVA in distilled water at 90 °C with continuous stirring until a transparent solution was obtained. Appropriate amounts of PDDA (20% water solution) and glutaraldehyde (GA, 25% water solution, Sinopharm Chemical Reagent Co., Ltd) were then mixed with the above PVA solution. The resulting mixture took on a homogeneous and transparent appearance, labeled as solution A. The mass ratio of PDDA, GA and PVA could affect OH^- conductivity and alkaline stability of the polymer film. Improvement in OH^- conductivity benefits the utilization of active material, while higher alkali resistance is in favor of the stability of zinc electrode. A series of experiments have been conducted to evaluate the cycle performance of zinc electrodes and the final mass ratio of PDDA, GA and PVA was set as 3:1:6.

2.2. Preparation of zinc anode and air cathode

The zinc anode was prepared by mixing 0.30 g ZnO (Tianjin Kemiou Chemical Reagent Co.), 0.03 g carbon fiber and 0.10 solution A together, then casting the slurry onto a copper mesh substrate (current collector, 2 cm × 2 cm in size). The electrode was dried at room temperature and pressed into a tablet through a rotating roller with a gap of 0.3 mm. Then the electrode was soaked in initiator consisting of hydrochloric acid (0.2%) in acetone for chemical cross-linking for 3 h. The cross-link reaction took place between the PVA hydroxyl and the GA aldehyde groups due to the catalysis of H^+. At last, the electrode was immersed in 2.0 M KOH solution for 12 h, then washed with sufficient distilled water and dried in air. The ZnO/PVA/PDDA composite obtained was identified by Fourier transform infrared (FT-IR) spectroscopy (Nicolet 6700 FT-IR spectrometer as KBr discs). The surface morphology of ZnO/PVA/PDDA composite electrode was recorded by scanning electronmicroscope (SEM, Nova NanoSEM230) with an accelerating voltage of 10 kV (SE mode). ZnO/PVA/PDDA composite was ground via conventional means to obtain powders, then the ZnO/PVA/PDDA powders were dispersed in ethanol under sonication. A drop of above dispersion solution was added on Carbon Support Film. The Carbon Support Film was finally inserted into the TEM after drying. The microstucture of ZnO/PVA/PDDA powders was observed by transmission electron microscope (TEM, JEM-2100F) with an accelerating voltage of 200 kV (TEM mode). A model of the inner structure of ZnO/PVA/PDDA composite electrode is given in Fig. 1. For comparison, the bare ZnO electrode was fabricated by casting slurry containing 0.3 g ZnO, 0.03 g carbon fiber, 0.06 g PVA solution onto the current collector, then dried at room temperature and pressed into a tablet.

A home made air electrode was served as the cathode (2 cm × 2 cm in size). The air electrode was made of sandwich structure with a catalyst layer on one side and a gas-diffusion layer on the other side. Nickel foam was embedded between two layers for effective current collection. To prepare the catalyst layer, Co–Fe/C, PTFE and Vulcan XC72Carbon were uniformly mixed in excess ethanol. Thereafter, the mixture was re-roll pressed to form a catalyst film. Gas-diffusion layer containing acetylene black (AB50) and PTFE was fabricated by the same way [26]. An aqueous solution of 33% KOH was used as the electrolyte. The distance between zinc anode and air cathode is about 2.5 mm.

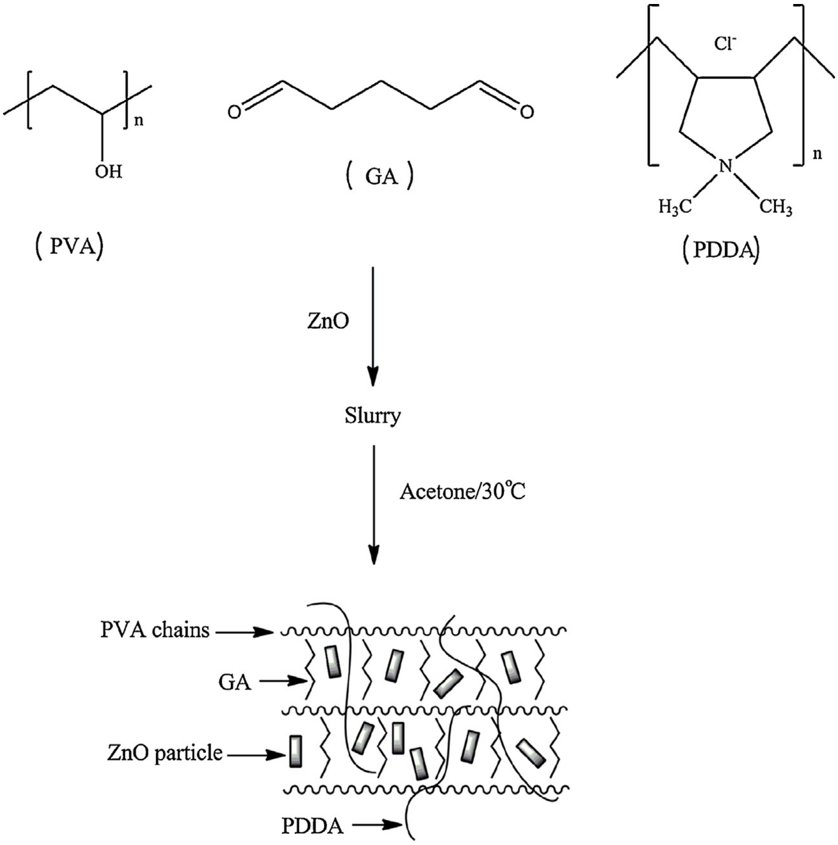

Fig. 1. Structures of PVA, PDDA and ZnO/PVA/PDDA composite.

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