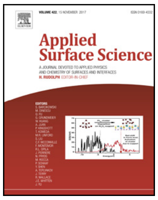
Applied Surface Science 422 (2017) 406–412

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc



Full Length Article

Shield effect of polyaniline between zinc active material and aqueous electrolyte in zinc-air batteries

Yong Nam Jo[a], Suk Hyun Kang[a], K. Prasanna[a], Seung Wook Eom[b], Chang Woo Lee[a,*]

[a] Department of Chemical Engineering, College of Engineering, Kyung Hee University, 1732 Deogyeong-daero, Gihung, Yongin, Gyeonggi, 17104, Republic of Korea

[b] Battery Research Center, Korea Electrotechnology Research Institute (KERI), 12 Bulmosan-ro 10 Beon-gil, Seongsan-gu, Changwon 642-120, Republic of Korea

ARTICLE INFO

Article history:
Received 24 January 2017
Received in revised form 17 May 2017
Accepted 4 June 2017
Available online 6 June 2017

Keywords:
Zinc-air
Polyaniline-coated zinc
Self-discharge
Hydrogen evolution reaction

ABSTRACT

The self-discharge behavior of zinc-air batteries is a critical issue that is induced by corrosion and hydrogen evolution reaction (HER) of zinc anodes. Polyaniline (PANI) coatings help control the HER and the corrosion reaction. Herein, PANI is synthesized with different amounts of HCl (20, 50, 100 ml). Among these, the PANI synthesized using 20 ml of HCl (20PANI@Zn) is the most effective for reducing the self-discharge behavior because it provides more amount of coating layer on the surfaces of the zinc particles compared to other prepared materials. This layer prevents direct contact between zinc and the aqueous electrolyte and minimize HER. The 20PANI@Zn shows 85% corrosion inhibition efficiency against pure zinc and results in 97.81% capacity retention after 24 h storage against no-storage condition at ambient temperature.

1. Introduction

Global warming and the growing demand for energy in modern society have motivated researchers to study energy conversion and storage systems. Among the different types of energy storage systems, Li-ion batteries (LIBs) are most widely used because they have a high specific energy density, high voltage, and long cycle life [1–3]. Nevertheless, LIBs also have some limitations, such as high cost, toxicity, and use of organic solvents, which can cause safety concerns [4]. Although LIBs deliver higher specific energy density compared with other commercialized secondary batteries, the current LIB technology is still insufficient for use in electric vehicles. Metal-air batteries have received much attention as an alternative to LIBs because they have a higher specific energy density than most energy storage systems because oxygen gas in ambient air (the quantity of which is essentially unlimited) is used as a cathode material [5–11].

Zinc is one of the most widely used electrodes and has various advantages. Namely, it is environmentally benign, abundant, cheap, easy to handle, stable in aqueous solution, and has a good electrochemical equivalence of 820 Ah/kg [12–15]. In addition, zinc is safer than lithium and can be fully recycled [6]. Zinc-air batteries deliver higher specific energy density compared with other energy storage systems due to the configuration of the metal-air batteries. The theoretical specific energy density of zinc-air batteries is 1086 Wh/kg [13]. The discharge reactions of the zinc-air battery are summarized below: [16–18]

$$\text{Anode}: \mathrm{Zn} + 4\mathrm{OH}^- \rightarrow \mathrm{Zn(OH)_4}^{2-} + 2e^- \quad (1)$$

$$\mathrm{Zn(OH)_4}^{2-} \rightarrow \mathrm{ZnO} + \mathrm{H_2O} + 2\mathrm{OH}^- \quad (2)$$

$$\text{Cathode}: \mathrm{O_2} + 4e^- + 2\mathrm{H_2O} \rightarrow 4\mathrm{OH}^- \quad (3)$$

$$\text{Overall}: 2\mathrm{Zn} + \mathrm{O_2} \rightarrow 2\mathrm{ZnO} \quad (4)$$

Zinc-air secondary batteries can be classified into two categories: electrically rechargeable and mechanically rechargeable systems. Electrically rechargeable zinc-air batteries have disadvantages including dendrite formation during the recharging process, a limited cycle life, and the hydrogen evolution reaction (HER), which is due to the more negative reduction potential of zinc than of hydrogen. The HER leads to self-discharge of zinc-air batteries.

The dendrite formation and limited cycle life issues can be solved by employing a mechanically rechargeable zinc-air battery. However, HER cannot be reduced merely by changing the system. During the HER, the metal undergoes anodic dissolution, with cathodic evolution of hydrogen in an aqueous solution. The corrosion potential of the metal in an aqueous solution is a mixed potential that includes the partial oxidation reaction. In other

---

[*] Corresponding author.
E-mail address: cwlee@khu.ac.kr (C.W. Lee).

http://dx.doi.org/10.1016/j.apsusc.2017.06.033
0169-4332/© 2017 Elsevier B.V. All rights reserved.

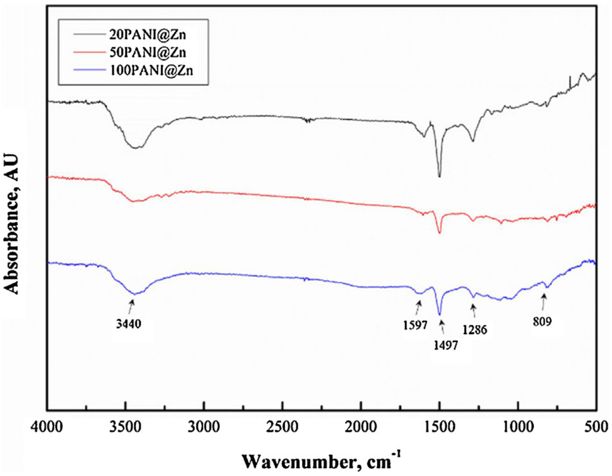


Fig. 1. The FTIR spectra of PANI@Zn materials prepared with three different amount of HCl.

words, in the anodic direction, anodic dissolution occurs according to the reaction shown below: [19,20]

$$Zn + 4OH^- \rightarrow Zn(OH)_4{}^{2-} + 2e^- \quad (5)$$

The partial reduction reaction can also occur, which is the HER in an alkaline solution:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (6)$$

The HER in the zinc-air battery is given as: [8,16,17]

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2\uparrow \quad (7)$$

In order to overcome the corrosion of zinc anodes and suppress the HER, Lee et al. introduced zinc alloys and acid additives to reduce dendrite formation and raise the hydrogen overpotential of zinc-air batteries [14,21]. Zhang et al. reported that introducing Bi and Ca into a pasted zinc electrode improved the discharge behavior [22]. Ein-Eli et al. introduced polyethylene glycol (PEG) as an electrolyte additive for corrosion inhibition [23]. Kim et al. reported that suppression of ZnO formation is advantageous, decreasing both resistance and hydrogen evolution in zinc-air secondary batteries [24].

Among the intrinsically conducting polymers, polyaniline (PANI) was found to be most interesting because of its wide range of conductivity, high stability, tunable property, low cost, and ease of synthesis [25,26]. In general, PANI is synthesized by chemical or electrochemical oxidative polymerization of monomers. In addition, plasma, electroless, and solid-state polymerization methods have also been reported [27–29]. Conventionally, irregular PANI is synthesized by dropwise addition of ammonium persulfate (APS) into aniline while stirring. The sonochemical process is similar to the conventional process, initiated with dropwise addition of an APS solution to an aniline solution. The quality and uniformity of synthesized PANI are affected by the acid concentration during synthesis. Lower concentrations of acid result in lower yields of final product [30,31].

In this paper, we synthesized PANI using the sonochemical method with different amounts of HCl. We also synthesized PANI-coated zinc to suppress the self-discharge behavior, inhibit corrosion reactions and the HER in zinc-air batteries.

2. Experimental

The coating material PANI was synthesized using a sonochemical method. First, acidic aniline solution was prepared by adding 1.86 g of aniline to a beaker containing 20, 50, and 100 ml of 1 M hydrochloric acid (HCl), respectively. This solution was sonicated in an ultrasonic bath at 50 kHz using a power of 100 W. Then, 1.14 g of APS was separately dissolved in 20, 50, and 100 ml of 1 M HCl solution, and this was added dropwise to the 20, 50, 100 ml of acidic aniline solution, respectively, during this reaction temperature was maintained at 2 °C. After the addition of the acidic APS solution, 20 g of zinc was added, and the mixture was kept in an ultrasonic bath for 30 min. After sonication, the powder was collected in a Büchner funnel using a water aspirator. The precipitate cake was filtered and washed with deionized water and ethanol until the filtrate became colorless. In addition, washed materials were dried at 60 °C under vacuum overnight. The synthesized PANI-coated zinc materials with 20, 50, and 100 ml of acidic aniline and acidic APS solution were designated as 20PANI@Zn, 50PANI@Zn, and 100PANI@Zn, respectively.

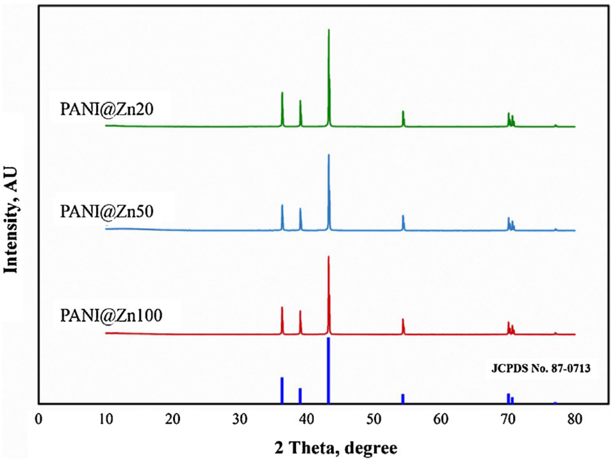


Fig. 2. XRD patterns of the PANI coated on zinc materials.

Table 1
Corrosion parameters.

Materials	E_{corr} (V)	I_{corr} (mA/cm^2)	η (%)
Zn	−1.399	3.836	–
20PANI@Zn	−1.395	0.591	85
50PANI@Zn	−1.403	1.115	71
100PANI@Zn	−1.397	1.267	67

The zinc-air battery consisted of a top cover with holes, an air cathode (ADE-75, MEET), a separator (Celgard 3401), an electrode container, a Cu current collector, and a bottom cover. To fabricate the gel electrolyte, a 7 M aqueous solution of KOH was mixed with 2 wt% polyacrylic acid (PAA). Then, 0.6 ml of the gel electrolyte was mixed with 0.6 g of the synthesized material, which was located in an electrode container having length, width, and height dimensions of 2.5, 2, and 0.1 cm, respectively. The electrochemical discharge behaviors were characterized at room temperature using a battery cycler (BaTester 05001, HTC) at a 100 mA current and a 0.2 V cut-off voltage. A 60-min rest time allowed the gelled electrolyte to soak in the active materials. To characterize the self-discharge behavior, the materials were analyzed immediately after cell fabrication and after being stored at room temperature for 24 h without any treatment. Tafel extrapolation was performed using an electrochemical analyzer (COMPACTSTAT, IVIUM technologies), and the electrochemical cell was composed of an Hg/HgO reference electrode, a platinum wire as a counter electrode, and the working electrode. The crystallinity of the coated materials was characterized using an X-ray diffractometer (XRD, D8 Advance, Bruker) using Cu Kα radiation over a scattering angle range of 10° to 80°. The morphology was determined using a field emission scanning electron microscope (FE-SEM, LEO SUPRA 55, Carl Zeiss) and a transmission