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Development of flexible zinc–air battery with nanocomposite electrodes and a novel separator

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A B S T R A C T

In this paper, we present the development of flexible zinc–air battery. Multiwalled carbon nanotubes (MWCNTs) were added into electrodes to improve their performance. It was found that MWCNTs were effective conductive additive in anode as they bridged the zinc particles. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was applied as a co-binder to enhance both the conductivity and flexibility. A poly (acrylic acid) (PAA) and polyvinyl alcohol (PVA) coated paper separator was used to enhance the battery performance where the PVP–PAA layer facilitated electrolyte storage. The batteries remained functional under bending conditions and after bending. Multiple design optimizations were also carried out for storage and performance purposes.

1. Introduction

The development of flexible electronic devices such as flexible circuits, displays, and wearable electronics requires the development of flexible power supplies [1–5]. Efforts are underway to develop different flexible power sources including batteries [6–11] and super capacitors [12–15]. There have been several reported studies on the development of flexible versions of conventional batteries including zinc–carbon, alkaline, and lithium-ion. Researchers have used novel nanoparticles, polymeric materials, have utilized techniques such as screen and 3D printing [16,17]; to make batteries on substrates such as fabrics and paper [7,12,15,18–20].

Aqueous electrolyte based batteries offer several advantages. These include safety, lower costs and the ease of fabrication. Zinc based flexible batteries are the most widely used aqueous battery systems for their lower costs [8,10]. However, most of the zinc batteries have low energy/capacity densities, where MnO_2 serves as the cathode active material along with zinc anode. For commercially available Zn–MnO_2 batteries, the typical energy density was 85 Wh/kg (zinc–carbon) or 105 Wh/kg (alkaline) [21]. As alternatives, zinc–air batteries utilizing the O_2 from the air have been developed, which feature lightweight, higher energy and capacity, and are suitable for lower power continuous discharges. The common zinc–air cells have energy densities of around 350 Wh/kg [22]. Limited reports on flexible zinc–air batteries [23,24] including cable batteries [25,26] are available, and there is need to explore novel designs for composite electrodes, separators as well as fabrication techniques. The objective of this paper is to develop a flexible primary zinc–air battery with carbon nanotube enhanced composite electrodes using a low-cost metal oxide catalyst and novel separator with high electrolyte storage capacity.

2. Experimental

2.1. Preparation of electrodes

The standard cathode paste was prepared by mixing electrolytic manganese dioxide powder (EMD, TRONOX, ≥ 92%, AB Grade), binder, and multiwalled carbon nanotubes (MWCNTs). Before electrode preparation, MWCNTs (purity 95%, diameter 20–30 nm, length 10–30 µm, Cheap Tubes Inc. Brattleboro, VT, USA) were purified in a Microwave Accelerated Reaction System (Mode: CEM Mars) using previously reported method [27,28]. Polymers such as polyethylene oxide (PEO, Sigma Aldrich, Mv~400,000) and polyvinylpyrrolidone (PVP, Sigma Aldrich, average mol wt 10,000) were purchased and used without further treatment. The powders added into the solvent, mixed for 30 min to form homogeneous slurry, and then sonicated for 30 min using OMNI SONIC RUPTOR 250 ultrasonic homogenizer. The dry formulation for the cathode comprised of MWCNTs (6%, wt%) and binder (10%, wt%) and the rest was EMD (84%, wt%). The anode paste was prepared by mixing zinc, polymer binder, Bismuth (III) oxide (Sigma Aldrich, 90–210 nm particle size, ≥ 99.8%) and purified MWCNTs. Both chemical grade zinc (Sigma Aldrich, ≤10 µm, ≥ 98%) and industrial battery grade zinc (Umicore, BIA 100 200 65 d140, ≤425 µm) were

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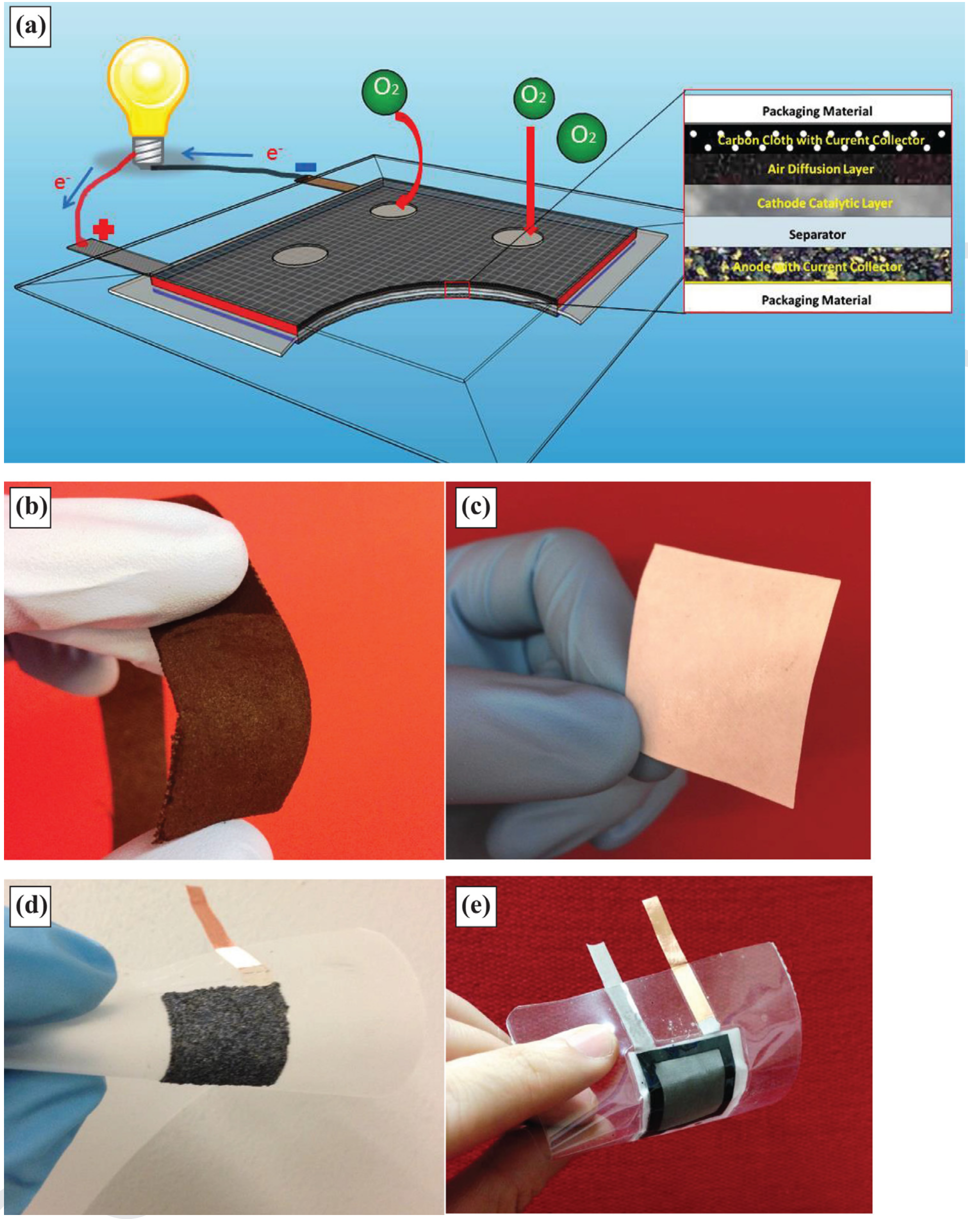

Fig. 1. Fabrication of flexible zinc–air battery: (a) Structure and design of a flexible zinc–air battery; (b) catalytic layer coated on flexible carbon cloth as cathode; (c) polymer enhanced paper separator/substrate; (d) zinc anode; (e) assembled flexible zinc–air cell.

tried. The powders were mixed in the presence of DI water or PEDOT:PSS and stirred to form a homogeneous anode paste.

After applying the electrode slurry onto the current collector, the electrodes were allowed to dry at ~60 °C for 30 min with the last 5 min under vacuum (9.893 kPa) to completely remove any residual water.

2.2. Preparation of separator

A poly (acrylic acid) (PAA, Sigma Aldrich, Mv~*450,000*) and polyvinyl alcohol (PVA, Mowiol 18-88, Sigma Aldrich, Mv~130,000) enhanced filter paper (Whatman, 5 qualitative) was used as the separator in the flexible battery. 0.45 g PAA was first added into 20 mL DI water, partially neutralized with LiOH (sigma, powder, reagent grade, ≥ 98%), stirred until dissolved, before 0.4 g PVA was added. Such polymer solution was added onto each side of the filter paper (0.2 ml per cm^2). The paper was then dried and heated at 150 °C for 50 min. A small piece (1×1 cm^2) of separator was cut and then weighed before and after soaking into the electrolyte.

2.3. Cell optimization and fabrication

The electrochemical performances of different formulations were optimized in fixed cells with Swagelok fittings. In this case, the electrode paste was cast directly onto the current collectors (graphite rods, 12.5 mm diameter) and dried. Typical weight of the cathode and anode pastes after drying were 0.065 g and 0.02 g respectively. Glass microfiber filters (Grade GF/A: 1.6 µm, Whatman) were used as separators in fixed Swagelok-type cells unless other mentioned.

The flexible anodes were prepared by casting the slurries onto the current collector made of silver ink (CAIG Laboratories Inc.) and pasted directly onto the polyethylene terephthalate (PET) substrate. Cathode catalytic ink was applied onto carbon foam (MTI, EQ-bcgdl-1400S-LD). For flexible cells, the typical weight of the cathode and anode after drying were 0.07 g and 0.1 g respectively. The flexible batteries were fabricated and encapsulated. The typical active area of zinc electrode was 2×2 cm^2; separator area was 3×3 cm^2; carbon foam size was 2.6×2.6 cm^2. The opening