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Durable rechargeable zinc-air batteries with neutral electrolyte and manganese oxide catalyst

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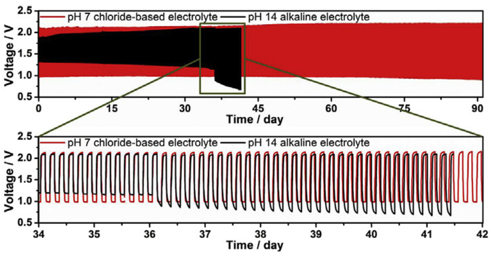
HIGHLIGHTS

- ORR and OER of MnO_x bifunctional catalyst in chloride-based electrolyte.
- pH-dependent electrocatalytic activity of MnO_x.
- Rechargeable Zn-air battery was stable during three-months of cycling test.
- Method to eliminate carbon corrosion in air cathode and carbonation in electrolyte.

GRAPHICAL ABSTRACT



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ABSTRACT

Neutral chloride-based electrolyte and directly grown manganese oxide on carbon paper are used as the electrolyte and air cathode respectively for rechargeable Zn-air batteries. Oxygen reduction and oxygen evolution reactions on manganese oxide show dependence of activities on the pH of the electrolyte. Zn-air batteries with chloride-based electrolyte and manganese oxide catalyst exhibit satisfactory voltage profile (discharge and charge voltage of 1 and 2 V at 1 mA cm^{-2}) and excellent cycling stability (≈90 days of continuous cycle test), which is attributed to the reduced carbon corrosion on the air cathode and decreased carbonation in neutral electrolyte. This work describes a robust electrolyte system that improves the cycle life of rechargeable Zn-air batteries.

1. Introduction

Battery is one of the key enablers in large-scale adoption of renewable energy resources. Metal-air batteries, in particular Zn-air batteries are promising candidate for large-scale energy storage as they offer higher energy density, better safety, and lower cost than most of the currently available battery technologies [1,2]. Although primary Zn-air batteries have been well developed, successful applications of secondary Zn-air batteries are hindered by the various technical hurdles. The most notable challenge in advancing rechargeable Zn-air batteries is to improve their cycle life, which can be affected by the choice of air cathode, Zn anode, and electrolyte [3,4]. Researches on Zn-air batteries have been

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focused on synthesizing efficient bifunctional catalysts for air-cathode and stable zinc for anode [5–8]. Limited attention was paid to the electrolyte, which has a significant impact on the cycle life of the batteries. Potassium hydroxide (KOH) has been primarily used as the electrolyte for Zn-air batteries due to its excellent ionic conductivity, high oxygen diffusion coefficient, low viscosity, as well as good activity for both Zn anode and air cathode [3,9]. Despite its desirable properties, the usage of KOH in Zn-air batteries raises several technical problems [3,4,10,11]. The first problem is associated with the corrosion of carbon-based air cathode in concentrated alkaline electrolyte which may proceed via following reaction [12,13]:

$$C + 6OH^- \rightarrow CO_3^{2-} + 3H_2O + 4e^-$$

Carbon in the air cathode is oxidized to carbonate ions and dissolves into the electrolyte. Continuous oxidation of carbon in alkaline electrolyte also results in brown colored electrolyte due to the formation of carboxylic acids, such as mellitic acid and humic acid [14,15]. Therefore, it is desirable to reduce the pH of the electrolyte to improve the long-term stability of Zn-air batteries with carbon-based air cathode. Another problem is related to the formation of insoluble K_2CO_3 arising from the reaction of aerial CO_2 with KOH. The carbonate will eventually precipitate out, resulting in electrolyte consumption and reduction in electrolyte conductivity. Precipitates may also block the pores within the air cathode, causing gradual passivation of the air cathode, and degrading the long-term performance of the batteries [2,10,11].

Neutral electrolytes are environmentally friendly and able to remediate the corrosion problem related to the use of alkaline or acidic electrolytes. They are also attractive for biofuel and biosensor applications, which are sensitive to extreme pH environments [16]. Despite these advantages, metal-air batteries with aqueous neutral electrolyte have been rarely reported. Amendola et al. [17] demonstrated that Zn-air batteries with near-neutral electrolyte showed discharge and charge voltage of 0.9 and 2.1 V. Goh et al. [11] studied the reaction mechanism of Zn and air cathode in chloride-based electrolyte, revealing that oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in air cathode are more sluggish than Zn dissolution/deposition in anode.

Chloride-based electrolyte is preferred due to its sufficiently high buffering capacity, good conductivity, and absence of electrolyte carbonation [10,18]. It has been widely used in electroplating of Zn to replace the toxic cyanide bath [19]. Furthermore, instead of using conventional method of physical mixing and coating of powder-based catalyst on air cathode, we grow amorphous MnO_x catalyst directly on carbon paper air cathode. This method effectively reduces contact resistance, improves discharge/charge profile, and enhances the cycle life of Zn-air batteries [20]. MnO_x is an attractive catalyst in neutral chloride-based electrolyte due to its abundance and environmental friendliness. It has high selectivity towards oxygen evolution instead of chlorine evolution reaction, and hence effectively prevented the generation of chlorine gas [17,21,22]. Although its catalytic activity has been widely investigated in alkaline medium [23,24], limited studies have been carried out in neutral pH and they were mainly reported for microbial fuel cell application [25,26]. Combining the advantage of directly grown MnO_x catalyst, neutral pH electrolyte is expected to enhance the cycle life of Zn-air batteries. Rechargeable Zn-air batteries with directly grown MnO_x catalyst and chloride-based electrolyte show excellent stability for up to 90 days, far exceeding the stability of the same batteries tested in alkaline electrolyte ($\approx$41 days). Electrochemical studies were performed to investigate the electrochemistry of oxygen in chloride-based and alkaline electrolytes. Material characterizations suggest the failure of Zn-air batteries with alkaline electrolyte is associated with the corrosion of carbon-based air cathode and carbonation of alkaline electrolyte.

2. Experimental

MnO_x grown on carbon paper was synthesized according to our previous report [20]. In brief, carbon paper (10 BN SGL Carbon, size 2×2 cm^2) was immersed into the solution containing 0.5 mmol of $Mn(NO_3)_2$in 10 ml ethanol for 15 min, and was left partially dried in the air for 60 s. It was then immersed into a mixture of 10 ml 0.1 M $KMnO_4$ and 10 ml 0.1 M H_2SO_4 for 30 min while stirring at room temperature. The sample was rinsed with DI water and baked at 180 °C over 24 h in an oven.

Rotating disc electrode (RDE) in three-electrode set-up was used to investigate catalytic activity of directly grown MnO_x on carbon in different type of electrolytes (i.e. 0.1 M NH_4Cl, 0.1 M NH_4Cl pH 7, or 0.1 M KOH). NH_4OH was used to adjust the pH of NH_4Cl to 7. Working electrode was prepared by casting MnO_x catalyst ink onto 5 mm diameter RDE tip (Metrohm). The ink was prepared by crushing directly grown MnO_x on carbon paper into powder. The powder (9 mg) and carbon black (2.25 mg) were ultrasonically dispersed into 2.4 ml of H_2O:IPA:Nafion solution (ratio: 2.5:1:0.094) to form catalyst ink. Appropriate amount of the ink was dripped onto RDE tip to achieve loading of 0.1 mg cm^{-2}. RDE, platinum counter electrode, and Ag/AgCl (3 M KCl) reference electrode were connected to potentiostat (Autolab PGSTAT302N) and immersed into electrolytes that were purged by O_2 or N_2 gas. Electrochemical activity of the catalyst was studied via cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) with sweeping rates of 5 mV s^{-1} at various rotating speeds. Potential scale was calibrated to reversible hydrogen electrode (RHE). $E_{RHE} = E_{Ag/AgCl(3M\ KCl)} + 0.209\ V + 0.059\ V \times pH$.

Battery tests were performed in Zn-air cell using directly grown MnO_x on carbon paper air cathode and polished Zn plate anode. Ti mesh and hydrophobic carbon paper were placed next to air cathode as current collector and waterproof backing layer. Area of air cathode exposed to electrolyte and air is $\approx$0.79 cm^2. Electrolyte was injected into the cell after the assembly. Conductivity and pH of electrolytes was measured by a conductivity and pH meter (Horiba Scientific). Chloride-based electrolyte consisted of 5 M NH_4Cl, 35 g L^{-1} $ZnCl_2$, and 1000 ppm thiourea. Conductivity and pH of as-prepared chloride-based electrolyte was about 37.1 S m^{-1} and 4.9, respectively. NH_4OH was used to adjust the pH of electrolyte to 7. Upon pH adjustment, chloride-based electrolyte maintained similar conductivity ($\approx$37.5 S m^{-1}) which is smaller than pH 14 alkaline electrolyte ($\approx$51.5 S m^{-1}). Alkaline electrolyte comprised of 5 M KOH, 35 g L^{-1} $ZnCl_2$, and 1000 ppm thiourea. Thiourea was added as brightening agent to produce fine zinc deposits during charging which can mitigate the growth of Zn dendrite [11,27]. Polarization curves and Nyquist plots were obtained from galvanodynamic and electrochemical impedance spectroscopy (EIS) measurements (potentiostat, Autolab PGSTAT302N). Cycling test was performed using recurrent galvanostatic test (battery tester, Maccor 4300).

Morphology and elemental analysis of the samples was investigated by scanning electron microscopy and energy dispersive X-ray spectroscopy (FESEM, JEOL JSM-6700F). Crystal structure of the samples was studied by X-ray diffractrometer (Bruker D8 Advance). Gas identification during charging of Zn-air batteries was carried out by gas chromatography mass spectrometry (GC-MS, Varian GC3800 and MS4000). The battery was subjected to constant voltage of 2.2 V for 48 h in a closed container that had been purged by Ar gas. The collected gas in the container was then introduced to the head of GC-MS column.