Manganese dioxide nanotube and nitrogen-doped carbon nanotube based composite bifunctional catalyst for rechargeable zinc-air battery

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ABSTRACT

A composite bifunctional catalyst (MnO_2–NCNT) was prepared from manganese dioxide (MnO_2) nanotubes and nitrogen-doped carbon nanotubes (NCNT) for the purpose of oxygen reduction (ORR) and evolution (OER) catalysis in the rechargeable zinc-air battery. From the half cell test, the MnO_2–NCNT composite illustrated excellent activities towards ORR and OER in alkaline conditions. Based on the battery test, the composite catalyst displayed outstanding discharge and charge performance while maintaining good stability. In both cases, the marked performance improvements from MnO_2–NCNT compared favourably to the NCNT and MnO_2, which are the constituents of the composite. In particular, MnO_2–NCNT exhibited improved half wave potential by 220 mV compared to MnO_2 and much superior OER stability compared to NCNT based on the rotating ring disk voltammetry results. According to battery test, MnO_2–NCNT decrease the battery resistance by 34% and concurrently improved the durability, discharge and charge performance in comparison to the MnO_2 nanotubes.

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1. Introduction

Electrochemical devices such as fuel cell, battery and supercapacitors are potential alternatives for energy conversion and storage apart from the burning of fossil fuels. Among the different energy storage systems, the rechargeable zinc-air battery displays great promise due to many attractive features; for example, high energy density, cost-effective and environmentally friendly design, as well as low operating risks [1]. The excellent properties of rechargeable zinc-air batteries lead to potential applications in areas, such as stationary and portable power applications including electric vehicles [2,3]. In a rechargeable zinc-air battery, oxygen evolution (OER) and oxygen reduction (ORR) reactions occur on the air electrode during battery charge and discharge, respectively. The sluggish reaction kinetics and large overpotential associated with OER and ORR greatly limit the performance of rechargeable zinc-air batteries [2,4]. Bifunctional catalysts can greatly improve the kinetics of OER and ORR making it the most critical determining factor to the performance and lifetime of the battery [2]. As a result, an affordable, active and stable bifunctional catalyst is in great demands to improve to the performance of rechargeable zinc-air batteries.

Currently, the most effective bifunctional catalysts are based on precious metals, for example, Pt-IrO_2 and PtIrRu [5,6]. However, the high cost and scarcity of the precious metals greatly hinder the large scale implementation. Non-precious metal catalysts including mixed metal oxides with perovskite [7], or spinel [8] structures have been studied extensively, however further improvements to the performance are required before successful commercialization. Recently, perovskite oxide has been combined with nitrogen doped carbon nanotube (NCNT) in a core-corona fashion to produce bifunctional catalyst with excellent activity and stability [9]. In this paper, similar idea is explored where transition metal oxides and NCNT will be integrated. Transition metal oxides, in particular, the manganese oxide, has demonstrated great potential due to high ORR activity [10,11] and low cost. Furthermore, manganese oxide is an appealing candidate of bifunctional catalyst for air electrode based on previously documented OER activity [12]. Nevertheless, the poor electrical conductivity of manganese oxide greatly inhibits the catalyst performance in term of high electrical resistance. This problem can be mitigated through the use of different catalyst supports such as graphene and carbon nanotubes [13,14]. Using catalyst supports, increase performance and stability of MnO_2 could be achieved similar to the commercial carbon supported platinum catalyst in polymer electrolyte membrane (PEM) fuel cell [15,16]. Recently, NCNT has been used as catalyst support which enhanced the performance of the cathode catalyst in PEM fuel cell [17–19]. Similar to many other non-precious metal catalysts [20–22], NCNT has shown ORR activity comparable to that of Pt/C in alkaline conditions [19–25], which leads to recent applications in the air cathode

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of zinc air battery [26]. As a result, combining NCNT and MnO_2 could be beneficial in two-folds, where improvements to the electrical conductivity and the overall activity of the manganese oxide are expected. In this paper, we report the preparation of a composite bifunctional catalyst—MnO_2–NCNT by simple mixing of MnO_2 nanotube and NCNT. The catalytic performance towards ORR and OER was evaluated in a home-made zinc-air battery under alkaline conditions. The contribution of NCNT catalyst towards the performance of the composite was evaluated, and it is compared to that of pure MnO_2 to assess the potential use of MnO_2–NCNT as the air electrode catalyst for rechargeable zinc-air batteries.

2. Experimental methods

MnO_2 nanotubes were synthesized by a hydrothermal treatment at 140 °C for 12 h. The sample was washed with de-ionized water and dried overnight before use. NCNT was prepared by chemical vapour deposition of a precursor admixture containing ethylenediamine (99%, Aldrich) and ferrocene (98%, Aldrich), at 700 °C under N_2 protection in a horizontal tube furnace. The MnO_2–NCNT was prepared by mixing the MnO_2 nanotube and NCNT in 1:1 weight ratio in ethanol followed by drying in oven.

To characterize the pure MnO_2 and MnO_2–NCNT composite, scanning electron microscopy (SEM) (JEOL, Leo 1530) was used to examine the morphology of the catalysts. X-ray diffraction (XRD) (Bruker AXS D8 Advance) was used to study the crystallography structure of the MnO_2 nanotubes and X-ray photoelectron spectroscopy (XPS) was used to investigate the surface elemental composition of the NCNTs. The electrocatalytic activity and stability of the catalyst were measured using rotating ring disk electrode (RRDE) voltammetry, which employed a bipotentiostat (Pine Instrument Co., AFCBP1) and a rotation speed controller (Pine Instrument Co., AFMSRCE). Battery test was conducted using a multichannel potentiostat (Princeton Applied Research, VersaSTAT MC) and a home-made zinc-air battery.

Prior to the RRDE voltammetry, 0.5 wt.% Nafion solution was prepared by dilution of 15 wt.% Nafion stock solution from Ion Power Inc. (Liquion Solution LQ-1115 1100EW 15 wt.%). This solution was used to prepare the catalyst ink by adding to it 4 mg of catalyst and sonicating to homogenous dispersion. The working electrode was deposited with 20 μL of catalyst ink, and once dried, immersed into a glass cell containing 0.1 M KOH electrolyte. A double junction Ag/AgCl reference and a platinum wire were employed as the reference and counter electrodes, respectively. ORR experiments were carried out in O_2 saturated electrolyte with different electrode rotation speeds, and the background measurements were performed in N_2 saturated electrolyte solution without electrode rotation. The potential range of ORR and background measurements was from −1 to 0.2 V vs. Ag/AgCl at a scan rate of 10 mV/s. The capacitive current was measured by the cyclic voltammetry (CV) method in N_2 saturated electrolyte solution and the potential was swept from −1 to 0.2 V at 50 mV/s. The evaluation of OER catalysis was performed in N_2 saturated electrolyte and the working electrode potential was swept from 0 to 1 V at 50 mV/s. In addition, the electrode was rotated at 900 rpm to remove the evolved O_2 from surface of the electrode during the OER test.

Prior to the battery test, the air electrode was prepared by spraying the catalyst on to a gas diffusion layer (Ion Power Inc., SGL Carbon 10 BB, 2.5 cm × 2.5 cm) to achieve catalyst loading of 0.5 $mg_{catalyst}$/cm^2. The electrolyte used in the zinc-air battery was 6 M KOH, and a polished zinc plate was used as the anode. Galvanodynamic method was used to discharge or charge the battery from 0 to 200 mA. Battery cycling experiments were performed using the recurrent galvanic pulse method, where one cycle consisted of a discharge step at 50 mA for 300 s followed by a charging step

of the same current and duration. Impedance measurements were carried out from 100 kHz to 0.1 Hz while applying an AC potential of 20 mV.

3. Results and discussion

SEM and TEM techniques were used to investigate the morphology of the MnO_2 nanotubes and NCNT. The tubular structures of MnO_2 and the bamboo compartments of NCNT are clearly shown in Fig. 1. Based on the SEM image, the diameter of MnO_2 nanotube is estimated to be approximately 100 nm and the diameter of the NCNT is about 20-50 nm. XRD pattern of MnO_2 nanotubes (Fig. 1c) confirms the alpha-MnO_2 structure (JCPDS: 44-0141), which has been proposed to be favourable for ORR in the past [10]. The surface nitrogen content of NCNT is approximately 4 at.% according to the XPS analysis (Fig. 1d). The nitrogen content and the surface morphology of the NCNT have been reported to correlate with ORR activity and stability in alkaline conditions [27,28].

The electrochemical behaviours of the catalysts towards ORR and OER in half cell setup were evaluated using RRDE voltammetry (Fig. 2). Based on the voltammetry results, a significant positive shift (+0.22 V) in the half wave potential and a doubled limiting current density are observed for the MnO_2–NCNT in comparison to the pure MnO_2 (Fig. 2a). The marked enhancements in the half cell performance observed for the MnO_2–NCNT composite can be attributed to the higher electrical conductivity as a consequence of NCNT addition. The effect of support on the performance of MnO_2 catalyst has been investigated where the addition of carbon support drastically improves the performance of the catalyst [11,29]. Furthermore, NCNT has been reported to be an efficient ORR catalyst via the four electron transfer reaction pathway [30]. The incorporation of NCNT in the composite catalyst not only improves the electrical conductivity, but also the overall activity for ORR catalysis. Besides the ORR activity, excellent OER activity and stability are particularly critical for bifunctional catalysts. Poor OER performance of NCNT is immediately apparent in Fig. 2b, where 94% decrease in current density at 1 V is observed after 50 cycles. The fast degradation associated with NCNT is in sharp contrast to the stable OER behaviour of pure MnO_2 nanotube, where only 3% decrease in current density is observed (Fig. 2b). However, the obvious disadvantage of pure MnO_2 is the low current density obtained at 1 V. In order to simultaneously achieve high electrical conductivity and OER stability, NCNT was added to the MnO_2 nanotubes to obtain the MnO_2–NCNT composite material, and the advantage is evident through Fig. 2. The MnO_2–NCNT composite has retained 96% of the OER current density at 1 V after 50 cycles, which is drastically higher compared to NCNT (only 4% remained) indicating excellent OER stability of the composite material (Fig. 2b). Additionally, the MnO_2–NCNT compared demonstrates 7.4 times higher OER current density in comparison to the pure MnO_2. Excellent OER stability and current density have been exhibited by the MnO_2–NCNT composite, which suggest high catalyst activity and stability during charge operation of the battery.

The Koutecky–Levich (K–L) plots were constructed for potentials from −0.5 V to −0.65 V (Fig. 3b and d) using the following equation,

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\sqrt{\omega}} \tag{1}$$

where j_k is the kinetic current density, B is the Levich slope, ω is the rotation speed and j is the observed current density. The Levich slope can be further defined as:

$$B = 0.62nFC_{O_2}D_{O_2}^{2/3}\upsilon^{-1/6} \tag{2}$$