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Oxygen reduction on Ag–MnO_2/SWNT and Ag–MnO_2/AB electrodes

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Abstract

Bifunctional catalysts (Ag–MnO_2)/SWNT were prepared by using a simple chemical reduction route on single-walled carbon nanotubes (SWNT). Five weight percentage of Ag–MnO_2 on SWNT was found to be the best loading in terms of current density. The (Ag–MnO_2)/SWNT catalyst was characterized and the kinetics towards oxygen reduction reaction (ORR) was determined and compared with that of Ag–MnO_2 on acetylene black (AB) catalyst. The number of exchanged electrons for the ORR was found to be close to four on both (Ag–MnO_2)/SWNT and (Ag–MnO_2)/AB. The kinetic rate constant of catalytic reaction for the two catalysts was of the same order. The zinc–air batteries with both catalysts were fabricated and examined. A stable discharge potential plateau appeared at approximately 1.2 and 1.1 V with discharge capacities 261 and 190 mAh/g, respectively.

Keywords: Catalyst; ORR; SWNT; Acetylene black (AB)

1. Introduction

The wide application of metal–air batteries, especially zinc–air batteries [1,2] have promoted the development of air electrode on the mechanism of catalytic reduction of oxygen and optimizing of new catalyst. Numerous less expensive materials of carbon, manganese oxides [3–5] and composite materials [6–8] are successfully used to replace expensive metal materials in alkaline medium for air electrodes. Molecular oxygen takes electrons from the counter metal electrode to complete the electrochemical reaction generating electrical energy at air electrode. The mechanism and kinetics of the oxygen reduction reaction rely greatly on the choice of active materials. The composition and structure of active material and even the form of presentation of substrate are key factor for successful development of air electrode for ORR [9]. The surface-catalyzed reactions are relative to the atomic-level details of the catalysts surface. The macrostructure of the electrode provides the skeleton to contain the electrolyte and ensure ionic transport and determines the mechanical strength; the microstructure ensures gas transport. The electrochemical processes take place at the boundary where the three-zone interface is created between the micro- and macrostructure. The nanostructured catalysts could lead to new electronic and catalytic properties due to their large BET surface area and homogeneous size distribution [10,11]. The CNTs, as a new form of carbon [12–14], it has been suggested that carbon nanotubes (CNTs) are suitable catalyst supports [15–18] in air electrode due to their highly accessible surface area, low resistance and high stability. In our previous reports [19,20], different forms of carbon as catalyst supports

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were successfully prepared and characterized. These composite materials have shown good catalytic activity and high catalytic efficiency compared with other common active materials. The kinetics and mechanisms [21–23] of oxygen reduction reaction have been widely studied. The direct four-electron pathway ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$) or the peroxide pathway ($O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$; $2HO_2^- \rightarrow O_2 + 2OH^-$) were supposed in alkaline electrolytes. The method of rotating disk electrode (RDE) [24,25] is a powerful tool to study the kinetics of oxygen reduction. The kinetic rate constants of catalytic oxygen reduction can be evaluated through a Koutecky–Levich plot and Levich formation. In the present paper, the RDE method was used to study the kinetics of air electrode reactions, using Ag–MnO_2/SWNT and Ag–MnO_2/AB as the catalysts. The number of exchanged electrons for the ORR was found to be close to four. The kinetic rate constant of catalytic reaction for two catalysts were of the same order. Furthermore, we examined the properties of zinc–air batteries by the discharge technique, and obtained the discharge capacities of 261 and 190 mAh/g, respectively.

2. Experimental

2.1. Preparation of catalysts and air electrodes

SWNT was produced via the chemical vapor deposition (CVD) method [26]. 13.05 mg of silver permanganate from Aldrich was dissolved in 50 ml distilled water at 25 °C to produce a deep purple solution. After the silver permanganate was dissolved, 100 mg of as-prepared carbon nanotubes were placed into the silver permanganate aqueous solution. The solution was stirred at 50 °C for 24 h until the supernatant liquid was colorless. The supernatant liquid was then decanted. The remaining mixture was poured into a stainless steel pan, placed in a furnace and heated at 70 °C for 8 h. The resulting carbon cake was pulverized and the (Ag–MnO_2)/SWNT catalyst was obtained. The final catalyst MnO_2 is 5% by weight based on carbon nanotubes. As comparison, 100 mg acetylene black was used as a substrate by the same method.

A rotating disc electrode (RDE) with a glassy carbon (GC) electrode (6 mm diameter) was used; the electrode was pretreated as follows [27]. (Ag–MnO_2)/SWNT catalyst and (Ag–MnO_2)/AB were dispersed in 0.05 wt.% Nafion solution from Aldrich and the resultant suspension was agitated in an ultrasonic bath for 10 min. The suspension was coated on the GC electrodes, which were air-dried for 30 min to evaporate the solvent; the (Ag–MnO_2)/SWNT/Nafion- or (Ag–MnO_2)/AB/Nafion-modified GC electrodes were thus obtained. The air electrode was prepared according to the steps detailed in [19].

2.2. Instruments and measurements

The morphology of the (Ag–MnO_2)/SWNT and the (Ag–MnO_2)/AB catalysts was investigated using a scanning electron microscope (SEM) (Leo1430VP). Cyclic voltammetry measurements were performed in N_2-saturated or O_2-saturated 1 M KOH solution in a three-electrode cell with (Ag–MnO_2)/SWNT/Nafion- or (Ag–MnO_2)/AB/Nafion-modified glassy carbon (GC) electrodes as the working electrode, Ag/AgCl electrode (KCl-saturated) as the reference electrode, and platinum spiral wire as the auxiliary electrode. A CHI 660A electrochemical workstation system (CH Instrument, Cordova TN) was used. RDE voltammetry was performed by the CHI 660A in O_2-saturated 1 M KOH solution and the rotation rates were controlled by 636 motor speed controller (EG&G, USA). The discharge characteristic of the cell was characterized at a constant current of 94.2 mA in a galvanostatic charge–discharge unit (Arbins AT2042, USA), using the 0.5 g zinc powder as anode material.

3. Results and discussion

3.1. Morphology and composition analysis

The SEM images of the as-prepared (Ag–MnO_2)/SWNT catalyst and (Ag–MnO_2)/AB catalyst are shown in Fig. 1. From Fig. 1(a), we can see that catalyst powders, i.e., silver and MnO_2 powder particles, obtained with about 50–60 nm of diameter, are dispersed onto and between SWNT. In contrast, catalyst particles and acetylene black formed uniformly clusters with particles about 150–250 nm as shown in Fig. 1(b). The performance of the electrode depends on the activity of porous material, agglomerate size internal porosity real surface area and binder content etc. Apparently, the structure of (Ag–MnO_2)/SWNT catalyst in the air electrode, would increase the gas/liquid interfacial area and provide an easier path for oxygen transport; this results in the materials having a high density of active sites and a relatively easy path for percolation of the reactive fluid or gas through the catalyst. Thus, the electrochemical processes should occur more effectively on (Ag–MnO_2)/SWNT than on (Ag–MnO_2)/AB.

In order to investigate the composition of the (Ag–MnO_2)/SWNT and (Ag–MnO_2)/AB catalysts, EDS analysis were carried out. The EDS results confirmed the existence of silver and manganese dioxide supported on the SWNT and AB with 5 wt.%.

3.2. Cyclic voltammetric study

The electrocatalytic properties of the (Ag–MnO_2)/SWNT and (Ag–MnO_2)/AB catalysts have been tested