Electrochimica Acta 127 (2014) 410–415

Contents lists available at ScienceDirect

Electrochimica Acta

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

Polythiophene Mesoporous Birnessite-MnO_2/Pd Cathode Air Electrode for Rechargeable Li-Air Battery

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ARTICLE INFO

Article history:
Received 26 November 2013
Received in revised form 27 January 2014
Accepted 11 February 2014
Available online 26 February 2014

Keywords:
Mesoporous
Birnessite-MnO_2
Ex-situ XRD
Raman spectroscopy
Li-Air battery

ABSTRACT

Mesoporous birnessite-manganese oxide (b-MnO_2) was studied for air electrode for Li-air rechargeable battery. In this study, mesoporous b-MnO_2 with an average pore size of 3.52 nm and BET surface area of 237 m^2 g^{-1} was successfully prepared using inorganic/organic phase. Prepared mesoporous b-MnO_2 was applied for air electrode for Li-air battery and discharge capacity of 345 mAh g^{-1} was observed at a current of 0.13 mA cm^{-2}. With the dispersion of small amount of Pd to mesoporous b-MnO_2, it was found that the Li-air cell showed a reasonably large discharge capacity of 487 mAh g^{-1} at 0.13 mA cm^{-2} at the initial cycle. The first discharge plateau around 2.71 V vs. Li/Li^+ and charge plateau at 3.58 V vs. Li/Li^+ with highly reversible capacity were observed. The energy efficiency for the charge and discharge was estimated to be ca. 76.4%. The *ex-situ* XRD result of the mesoporous b-MnO_2/Pd/TAB-2 (85/5/10) air electrode suggested that the observed capacity mainly came from Li^+ and O_2 to form Li_2O_2 after discharge to 2.0 V. Formation of Li_2CO_3 was hardly observed.

1. Introduction

Rechargeable Li-air batteries have attracted considerable attention as high capacity electrical storage devices for the use in electric and hybrid vehicles. Currently, efforts in battery research and development are devoted to energy storage and conversion with high energy density, high power density, and reliable safety [1–3]. Metal-air batteries have attracted considerable attention, due to their extremely large specific capacity. The reason for such large specific capacity is that the cell consists of lithium metal as an anode and air electrode for activation of oxygen in air; and hence these metal-air batteries are of simple structure. Among the various metal-air battery systems, lithium-air battery is the most attractive because it has the highest energy density per unit weight. During discharge the reaction between Li and oxygen yields Li_2O_2 or Li_2O, and a theoretical specific energy density of Li-Air battery is around 5200 Wh Kg^{-1}. Abraham and Jiang reported a Li-air battery using non-aqueous electrolyte [4]. They suggested that lithium-peroxide is a discharge product, based on $2Li + O_2 \rightarrow Li_2O_2$, which resulted in a theoretical voltage of 3.10 V. However, due to low oxygen solubility in non-aqueous electrolyte, the reported power density of Li-air battery was much lower than the theoretical value[5,6]. During discharge reaction, oxygen is reduced by lithium ions to form Li_2O_2 or Li_2O at the air cathode, while lithium-ions dissolve into the electrolyte from the lithium metal anode, as shown in the following reactions.

Cathode (discharge reaction):

$$2Li^+ + O_2 + 2e^- \rightarrow Li_2O_2 \qquad (1)$$

$$4Li^+ + O_2 + 4e^- \rightarrow Li_2O \qquad (2)$$

Anode (discharge reaction):

$$Li \rightarrow Li^+ + e^- \qquad (3)$$

Rechargeable Li-Air batteries require reversible cathode electrode reaction between Li_2O_2 or Li_2O deposition reaction products (discharge reaction) and Li_2O_2 or Li_2O decomposition reaction (charge reaction) at the cathode, which are complex reactions and have not fully been understood. However, discharge and charge reactions are still relatively slow for practical application of Li-air

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http://dx.doi.org/10.1016/j.electacta.2014.02.071
0013-4686/

battery. Therefore, one of the main issues for the improvement of Li-air battery is the development of effective cathode electrode for both oxygen reduction/oxygen evolution reactions (ORR/OERs). Recently, MnO_2 [7,8], MnO_2/Pd [9–11], MnO_2 nanosheet [12], Co_3O_4/Pd [13], and Au-Pd/β-MnO_2 [14] have been reported as effective catalysts for oxygen reduction/oxygen evolution reactions (ORR/OER) for rechargeable Li-air battery. Another issue is the control of pore size in cathode electrodes. Lithium oxides and peroxides generated during discharge reactions precipitated in the pores of the air cathode electrodes and interfered with further intake of oxygen, which can abruptly terminate the discharge reaction. Thus, the catalytic materials with relatively large pore sizes and high surface area are essential to obtain high capacity and charge–discharge cycle stability.

Previously, we studied various MnO_2/Pd [9–11], MnO_2 nanosheet [12], Au-Pd/β-MnO_2[13], and Co_3O_4/Pd [14] cathode air electrode for a rechargeable Li-air battery, which showed higher reversible capacity as well as higher current density than the standard Li-air battery. In this study, we report a facile one-pot synthesis of polythiophene mesoporous birnessite MnO_2 nanocomposite with a submicron-sphere/nanosheet hierarchical structure via a modified inorganic/organic interfacial route [15,16]. The mesoporous b-MnO_2 was used as a cathode air electrode for Li-air battery which also shows a high capacity as well as stable cycleability due to the electrocatalytic activity of the air electrode.

2. Experimenal

2.1. Synthesis of materials

In a typical synthesis of mesoporous polythiophene MnO_2, 0.5 g of $KMnO_4$ was dissolved in 100 ml of distilled water. The pH value of the solution was adjusted at 2 by slowly adding drops of 0.02 M dilute HCl solution. The organic phase was formed by adding 2 mL of thiophene in 100 mL of dichloromethane solution. Both solutions were cooled to 4 °C before the reaction. Finally, a $KMnO_4$ solution having pH value of 2 was poured into a beaker with the organic solution of dichloromethane and thiophene. The two-phase layer was clearly observed in a beaker. The mixed solution was kept at 4 °C for 16 h. After 16 h of reaction, a dark purple-brown powder was collected by centrifugation from the upper aqueous suspensions and then washed 5 times with distilled water and once with ethanol before vacuum drying at room temperature.

2.2. Characterization of samples

Powder X-ray diffraction (XRD, Rigaku Rint 2500) of polythiophene coated MnO_2 was carried out with CuKα ($\lambda \equiv 1.541$ Å) at a low-angle scanning range of 0.5–10° and a wide-angle range of 10 – 80° (2θ) with a scan speed of 0.02° sec^{-1}. Thermal behaviors of samples were examined by thermogravimetric analysis (TGA, Shimadzu DTG-60) from room temperature up to 600 °C at a heating rate of 5 °C min^{-1} in air. The bonding properties of the samples were characterized with attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR Perkin-Elmer, Spectrum series 100 spectroscopy). Powdered sample was placed above ZnSe crystal and pressed with a pressure of 80 psi. Each FTIR spectrum was collected after 50 scans at a resolution of 2 cm^{-1} from 500 to 4000 cm^{-1}. Morphologies of samples were examined with field-emission scanning electron microscopy (FESEM; Hitachi, S-8000) and transmission electron microscope (TEM, JEOL JEM 2100, 200 kV) imaging. The Brunauer-Emmett-Teller (BET) specific surface area was determined from (N_2) nitrogen adsorption-desorption isotherm using Nippon Bell, BELSORP 18PLUS-FS, Japan. The pore-size distribution was calculated using adsorption curve by the Barrett-Joyner-Halenda (BJH) method. Raman spectroscopy was carried out using a Horiba Jobin Yvon HR800 with 744 nm initial excitation laser.

2.3. Electrochemical measurements

The electrochemical characterizations were carried out using a Swagelok-type cell. The cathode electrode was formed by casting a mixture of polythiophene mesoporous (birnessite) b-MnO_2 poly tetrafluroethylene (PTFE) coated teflonized acetylene black (TAB-2) (mol ratio of 90:10), mesoporous b-MnO_2, palladium, and TAB-2 (mol ratio of 85:5:10) and then pressing the mixture onto a stainless steel mesh. A lithium foil with diameter of 1.2 cm^2 was used as an anode and was separated by porous polypropylene glass fiber filter (ADVANTEC, GB-100R) from Toyo Rishi Co., Ltd., Japan. The cell was gas tight, except for the stainless steel mesh window exposing the porous cathode electrode to 1 atm pressure of oxygen atmosphere. The electrolyte was lithium bis(trifluoromethanesulfonyl)imide-ethylene carbonate (EC)-diethyl carbonate (DEC) [1 M LiTFSI-EC:DEC (3:7) by vlume] supplied by Ube Chemical Co., Ltd., Japan. The charge-discharge performance was carried out in the voltage range of 4.0–2.0 V at a constant current of 0.13 mA cm^{-2} and the cell was maintained in an O_2 atmosphere to avoid any negative effects of humidity and CO_2. In this study, we have normalized the observed capacity by the total weight of air electrode, but not with the weight of carbon, for capacity comparison.

The examination of the discharge electrode involves disassembly of the cell in a glove box, rinsing the cathode electrode thrice with diethyl carbonate, removing the solvent under vacuum, and then placing the electrode in an airtight holder.

3. Results and discussion

A low angle XRD pattern of the as-prepared mesoporous MnO_2 is shown in Fig. 1a. A sharp diffraction intensity peak was observed at 1.0°, suggesting the formation of mesoporous structure. Wide angle XRD pattern of as–synthesized meoporous b-MnO_2 is shown in Fig. 1b. The relatively large and increased intensity peak located at 37.2° may be related to the scattering from polymer. The relatively low-intensity and broad peaks observed in the XRD pattern are the low crystalline state of the sample and the existence of amorphous polymer. Birnessite-type MnO_2 has a 2-dimensional lamellar structure with an interlayer gap of 0.73 nm [17]. The pattern can be indexed to the layered birnessite-type MnO_2 (JCPDS No. 80-1098, monoclinic, C2/m, $a = 5.15$ Å, b = 2.84 Å, c = 7.17 Å).

The existence of polymer in the prepared MnO_2 sample was confirmed by ATR-FTIR, as shown in the Fig. 2. The bands from 500–600 cm^{-1} can be assigned to Mn – O stretching vibrations. The large characteristic band appearing at 3390 cm^{-1} is attributed to O – H stretching vibration; while the other band at 1625 cm^{-1} is ascribed to the O – H bending vibration from crystal or adsorbed water molecules [18]. Vibration bands between 950 cm^{-1} and 1450 cm^{-1} originated from stretching or bending bands of polythiophene, suggesting the presence of polythiophene in the sample [18,19].

The TGA curve of the prepared sample powder is shown in Fig. 3. The weight loss from room temperature to 200 °C can be attributed to the dehydrating of physically adsorbed and chemically bonded hydrates. The weight loss between 200 °C and 490 °C is assigned to the pyrolysis of polymer. Another weight loss between 490 °C and 600 °C is derived from the self-decomposition from MnO_2 to Mn_2O_3[20,21]. The weight fraction of polythiophene in the prepared MnO_2 composite is about 4.72 wt% based on TGA result.