Journal of Power Sources 203 (2012) 159–164

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

Manganese oxide with a card-house-like structure reassembled from nanosheets for rechargeable Li-air battery

Shintaro Ida*, Arjun Kumar Thapa, Yuiko Hidaka, Yohei Okamoto, Maki Matsuka, Hidehisa Hagiwara, Tatsumi Ishihara**

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

ARTICLE INFO

Article history:
Received 25 August 2011
Received in revised form 3 November 2011
Accepted 15 November 2011
Available online 23 November 2011

Keywords:
Nanosheets
Manganese oxide
Catalyst
Li-air battery

ABSTRACT

Li-air batteries have attracted attention as a next generation secondary battery because of their potentials such as a high theoretical specific energy density. One of the main issues for the Li-air batteries is the development of a cathode oxygen electrode with high capacity and charge–discharge cycle stability. Here we report a manganese oxide with a card-house-like structure for the cathode oxygen electrode. The manganese oxide was synthesized by reassembling two-dimensional manganese oxide nanosheets. The cathode electrode containing the manganese oxide exhibited high catalytic activity for Li^+/Li_2O_x ($x = 1, 2$) redox reactions, and its discharge capacity was 1300–1500 mAh g^{-1} catalyst, which was higher than that of Li-air batteries using electrolytic MnO_2 as catalysts.

1. Introduction

Rechargeable Li-air batteries have attracted considerable attention as high capacity electrical storage devices for the use in electric and hybrid vehicles [1–3]. Among the various known metal-air battery systems, Li-air battery is the most attractive one as it has the highest energy density per unit weight. Its discharge reaction occurs between Li and oxygen to yield Li_2O or Li_2O_2, and a theoretical specific energy density of 5200 Wh kg^{-1}. In practice, the storage of oxygen is not required, since air can be used directly in the battery. Therefore, the theoretical specific energy density (excluding oxygen) is 11,140 Wh kg^{-1}, which is much higher than that of other advanced batteries [4]. In general, a Li-air battery consists of a lithium anode, an air cathode that supplies oxygen, and an electrolyte. Abraham and Jiang reported a Li-air battery using a nonaqueous electrolyte [1]. However, due to the low oxygen solubility in the nonaqueous electrolyte, the reported power density of the Li-air battery was much lower than the theoretical value [5,6]. During the discharge reactions, oxygen is reduced by lithium ions to form lithium peroxide or oxide 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):

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

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

Anode (discharge reaction):

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

Rechargeable Li-air batteries require reversible cathode electrode reactions between the Li_2O_x ($x = 1, 2$) deposition reaction (discharge reaction, reaction of Eqs. (1) and (2)) and the Li_2O_x decomposition reaction (charge reaction) at the cathode (these reactions are complex reactions, and have not been fully understood). However, discharge and charge reactions are still relatively slow for practical applications. Therefore, one of the main issues for the improvement of Li-air batteries is the development of effective catalysts for the both reactions. Recently, MnO_2 [7,8], MnO_2/Pd [9,10], and Pt–Au nanoparticle [11] have been reported as the effective catalysts for this purpose. Another issue is the control of pore size in the cathode electrodes. Lithium oxides and peroxides generated during the discharge reactions precipitate in the pores of the air cathode electrodes, and interfere with further intake of oxygen, which can abruptly terminate the discharge reactions. Thus, the catalytic materials with relatively large pore sizes and surface area are essential to obtain high capacity and charge–discharge cycle stability.

In this study, we report manganese oxide with a card-house-like structure for the cathode oxygen electrode, which was prepared by reassembling manganese oxide nanosheets. This uniquely

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* Corresponding author. Fax: +81 928022870.
** Corresponding author. Fax: +81 928022871.
E-mail addresses: s-ida@cstf.kyushu-u.ac.jp (S. Ida), ishihara@cstf.kyushu-u.ac.jp (T. Ishihara).

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doi:10.1016/j.jpowsour.2011.11.042

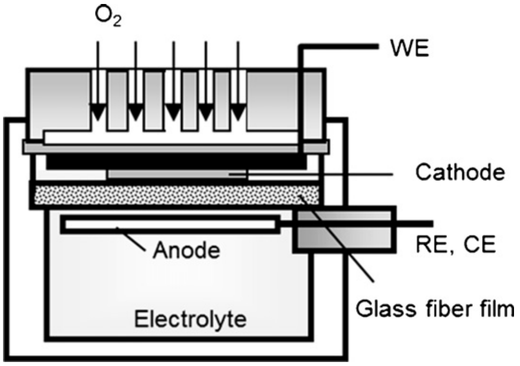

Fig. 1. Structural model of cell.

structured manganese oxide exhibited high catalytic activities for the Li^+/Li_2O_x redox reactions, and the consumption and release of oxygen were confirmed during the Li^+/Li_2O_x redox reactions.

2. Experimental

Manganese oxide nanosheets were prepared by exfoliating layered $K_{0.45}MnO_2$ according to a procedure given in the literature [12]. $K_{0.45}MnO_2$ was prepared by reacting stoichiometric amounts of intimately mixed K_2CO_3 (Wako Pure Chemical Co., Japan; 99.9%) and Mn_2O_3 (Wako Pure Chemical Co., Japan; 99.9%) at 750 °C for 30 h in O_2 gas. Proton exchange reaction of K^+ in the layered manganese oxide was carried out by stirring 1.0 g of $K_{0.45}MnO_2$ powder in 100 mL of 1 M aqueous HCl solution for 7 days at room temperature. Finally, the protonated form (0.4 g) was mixed with 100 mL of 0.05 M tetrabutylammonium hydroxide aqueous solution to exfoliate the host layers, and the resulting suspension was stirred at room temperature for 10 days. The suspension was then centrifuged for 30 min to remove the unexfoliated layered manganese oxide, and the supernatant was used as the nanosheet suspension. Manganese oxide with a card-house-like structure was prepared by drying the suspension of the manganese oxide nanosheets. 50 mL of the nanosheet suspension was placed into an agate mortar, and then heated under an incandescent lamp until reduced by quarter in volume (surface temperature: 80–85 °C). The nanosheets gradually reassembled into mesoporous manganese oxides during the heat treatment, as the concentration of the electrolyte (tetrabutylammonium hydroxide) increased with evaporating the solvent. 35 mL of ethanol was then added to the suspension, and left until the manganese oxide precipitated to the bottom of the mortar. Subsequently, approximately 35 mL of the solvent was absorbed. This process was repeated 5 times to remove the tetrabutylammonium hydroxide. Finally, the solvent was evaporated under an incandescent lamp, and the manganese oxide powder obtained was dried in a vacuum drier at 150 °C.

Two types of manganese oxides with non-card-house like structure were prepared from the manganese oxide nanosheets for comparison. One was prepared by naturally drying of sediment obtained by centrifugation (12,000 rpm, 60 h) of 50 mL of manganese oxide nanosheet suspension. The other one was prepared as follows. The sediment prepared obtained by centrifugation (12,000 rpm, 60 h) of 50 mL of manganese oxide nanosheet suspension was dispersed into water by ultrasonic agitation, and the suspension was freeze-dried. Finally, these manganese oxide powders obtained were dried in a vacuum drier at 150 °C.

The cathode for the Li-air battery was prepared by casting a mixture of the manganese oxide powder, PTFE-coated acetylene black (PTFE: acetylene black = 1:3, Hirota) as the conducting binder, and Ketjenblack (EC600JD) as a conducting material with a total weight ratio of 42:56:2. The resulting mixture was pressed onto a stainless steel mesh, and dried at 160 °C for 12 h in vacuum. Fig. 1 shows the structural model of the cell. A piece of lithium foil (thickness: 0.1 mm) was used as the anode, and was separated by a porous polypropylene film (Mitsubishi Chemical, Celgard 3401). The cell was gas-tight except for the stainless steel mesh windows to expose the porous cathode to the O_2 atmosphere. A mixed solution of 1 M lithium bis-(trifluoromethanesulfonyl) imide, ethylene carbonate (EC), and diethyl carbonate (DEC) (Ube Chemical Co., Ltd., Japan) with a volume ratio (EC:DEC) of 3:7 was used as the electrolyte. It has been widely accepted that carbonate electrolyte, especially propylene carbonate, is decomposed easily. However, we have confirmed that the EC/DEC electrolyte is unlikely to decomposed under less than 4.0 V [9,10]. Therefore, in this present study, the charge–discharge curves were measured in the voltage range of 4.0–2.0 V (current density of 0.05 mA cm^{-2}) to avoid the decomposition of the electrolyte.

X-ray diffraction (XRD) analysis was undertaken with Cu Kα radiation (λ = 1.541 Å, Rigaku Rint 2500). TEM observation was performed using a JEOL 2100 electron microscope operating at an accelerating voltage of 200 kV. Scanning electron micrographs (SEM) were obtained using a Hitachi SU-8000 and Keyence VE-7800 electron microscopes. Specific surface area was determined from nitrogen adsorption–desorption isotherm using Nippon Bell, BELSORP 18PLUS-FS, Japan. Atomic force microscopy (AFM) image was obtained using a SII Nano navi 2.

3. Results and discussion

The cathode electrode of Li-air batteries requires catalytic activities for redox reaction of the Li_2O_x (x = 1, 2) and mesoporous structure with relatively large pore size for the Li_2O_x depositions and continuous diffusion of oxygen. A card-house structure is one of the ideal catalyst structures for the Li^+/Li_2O_x redox reactions, since it has large pore size and surface area. Fig. 2 shows a schematic illustration of the preparation for a manganese oxide with card-house structure from manganese oxide nanosheets. In general, the

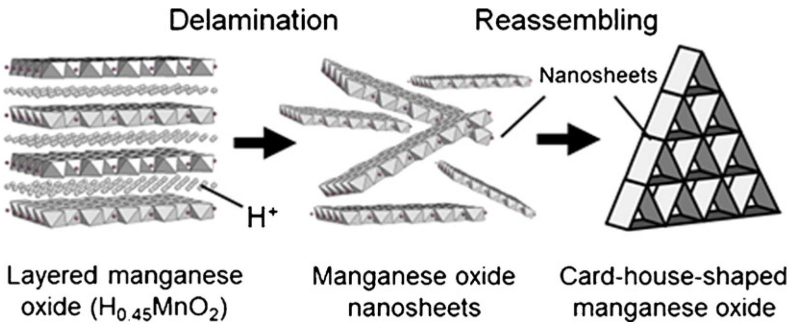

Fig. 2. Schematic illustration of the preparation of a card-house-shaped manganese oxide from manganese oxide nanosheets.