Journal of Power Sources 242 (2013) 216–221

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

Discharge/charge characteristic of Li-air cells using carbon-supported $LaMn_{0.6}Fe_{0.4}O_3$ as an electrocatalyst

Masayoshi Yuasa [a,*], Tsubasa Matsuyoshi [b], Tetsuya Kida [a], Kengo Shimanoe [a]

[a] Department of Energy and Material Sciences, Faculty of Engineering Sciences, Kyushu University, 6-1 Kasuga-koen, Kasuga-shi, Fukuoka 816-8580, Japan
[b] Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koen, Kasuga-shi, Fukuoka 816-8580, Japan

HIGHLIGHTS

- A carbon-supported $LaMn_{0.6}Fe_{0.4}O_3$ nanoparticle was synthesized.
- $LaMn_{0.6}Fe_{0.4}O_3$ exhibited the oxygen reduction activity for Li-air cell.
- $LaMn_{0.6}Fe_{0.4}O_3$ also exhibited the oxygen evolution activity for Li-air cell.
- Discharge capacity of Li-air cell depended on the structure of air electrode.
- Oxygen diffusion into air electrode is important for the excellent Li-air cells.

ARTICLE INFO

Article history:
Received 10 April 2013
Received in revised form
17 May 2013
Accepted 18 May 2013
Available online 29 May 2013

Keywords:
Li-air cell
Oxygen reduction
Oxygen evolution
Perovskite-type oxide
Gas diffusion

ABSTRACT

The discharge/charge performance of Li-air cell using the carbon-supported $LaMn_{0.6}Fe_{0.4}O_3$ nanoparticle as a cathode catalyst was investigated in this study. The carbon-supported $LaMn_{0.6}Fe_{0.4}O_3$ nanoparticle was prepared via a reverse homogeneous precipitation method, and fabricated to air electrode. Li-air cell was constructed using air electrode, Li metal foil and 1.0 M $LiPF_6$ in propylene carbonate as a cathode, anode and electrolyte, respectively. As the result, the carbon-supported $LaMn_{0.6}Fe_{0.4}O_3$ nanoparticle exhibited both the oxygen evolution activity and the oxygen reduction activity in the non-aqueous electrolyte. The investigation about the presence and absence of the catalytic layer and the gas diffusion layer revealed that each layer is indispensable for the excellent electrode performance, and that the catalytic layer and the gas diffusion layer has a important role to supply the electrolyte and the oxygen gas, respectively. The investigation about the amount of the catalytic layer and the effect of the oxygen concentration revealed that the oxygen diffusability into the air electrode strongly affects to the discharge capacity of Li-air cells.

1. Introduction

Metal-air batteries utilize non-noble metals (Fe [1] , Zn [2], Al [3], Mg [4], Li [5]) and an atmospheric oxygen as an anode and a cathode materials, respectively. Therefore, metal-air batteries can be attractive power sources of electric vehicles and storages of renewable energies such as wind-powered electricity and photovoltaic power generation because of its high energy density. Especially, Li-air cells have largest theoretical energy density of 13,000 Wh kg^{-1} [6] because the lithium has the lowest equilibrium electrode potential (−3.05 V vs. NHE) and the lowest density among all metals (0.534 g cm^{-3}). A typical Li-air cell is composed of a lithium metal, an electrolyte and a porous-structured air electrode. The electrolyte is organic solvents or ionic liquids with lithium salts such as $LiPF_6$ and $LiOCl_4$ [7,8]. Usually, the air electrode is composed of a catalytic layer and a gas diffusion layer. During the discharge reaction, the atmospheric oxygen diffuses into the catalytic layer through the gas diffusion layer and reduced to oxide ions (O_2^{2-} or O^{2-}). The oxide ions react with lithium ions in the electrolyte, and then lithium oxides (Li_2O) or lithium peroxides (Li_2O_2) are produced in the pores of the air electrode [9]. The electrochemical equation and equilibrium electrode potential for the formation of Li_2O and Li_2O_2 during discharge reaction are the followings [10–12];

$$2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2 \; E^0 = 2.959 \text{ V vs. Li/Li}^+ \quad (1)$$

$$4Li^+ + O_2 + 4e^- \leftrightarrow Li_2O \; E^0 = 2.913 \text{ V vs. Li/Li}^+ \quad (2)$$

---

* Corresponding author. Tel.: +81 92 583 7539; fax: +81 92 583 7538.
E-mail address: yuasa@mm.kyushu-u.ac.jp (M. Yuasa).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.05.076

Recently, it has been reported that discharge reaction in Li-air cells also produces lithium carbonate (Li_2CO_3) [13] or lithium carboxides (HCO_2Li, CH_3CO_2Li and $C_3H_6(OCO_2Li)_2$) [14]. As the discharge reaction proceeds, discharge products are formed in the pores of the air electrode one after another. Finally, when discharge products fill up the all of the pores, the discharge reaction is finished because the oxygen cannot diffuse into the catalytic layer any more. During the charge reaction, lithium oxides in the pores are reversibly oxidized to Li^+ and O_2, and thus the air electrode is restored for next discharge reactions.

In order to improve the discharge/charge voltage and the discharge capacity of Li-air cells, investigations about the air electrode have been numerously carried out. It has been reported that loading of an electrocatalyst is effective to improve the discharge/charge voltage and the discharge capacity. For the electrocatalyst, metals [15–17], metal oxides [18–22], composites of oxide and noble metal [23], graphene [24] and CF_x [20] have been reported. Moreover, it has been reported that a control of electrode structures is effective to improve the discharge capacity. Zheng et al. have theoretically elucidated that the discharge capacity of Li-air cell increases with an increase in a porosity of air electrodes [25].

In this work, we focused on the La-Mn-based perovskite-type oxide as an oxygen reduction catalsyt for Li-air cells using the non-aqueous electrolyte. Perovskite-type oxides have widely been investigated as an oxygen reduction catalyst in the alkaline aqueous solution [26–28] since Meadowcroft first pointed out the potentiality of it [29]. In particular, we tried to disperse nanoparticles of La-Mn-based perovskite-type oxides on the carbon-support in order to increase the catalytic reaction site for oxygen reduction. This attempt achieved the highly active oxygen reduction electrode for the metal-air battery using aqueous alkaline electrolyte as compared with the electrode using a carbon-supported Pt nanoparticle [30,31]. Therefore, in this work, we attempt to apply the La-Mn-based perovskite-type oxide as an oxygen reduction catalyst of the Li-air cell using the non-aqueous electrolyte. As a La-Mn-based perovskite-type oxide, $LaMn_{0.6}Fe_{0.4}O_3$ was chosen due to its stability against cathodic polarization as reported in our previous report [32]. In addition, we investigated a structure of air electrode in order to improve the discharge capacity of Li-air cell. The order of the catalytic layer and the gas diffusion layer, the amount of the catalytic layer per unit area, and the effect of oxygen concentration on the discharge capacity were investigated in order to elucidate the correlation between the structure of air electrode and the oxygen diffusion into air electrode.

2. Experimental

2.1. Chemicals

$La(NO_3)_3 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, 10% solution of tetramethylammonium hydroxide (TMAH) and tetrapropylammonium bromide (TPAB) were purchased from Kishida chemical Co., Ltd. (Osaka, Japan) and used for the synthesis of $LaMn_{0.6}Fe_{0.4}O_3$. Ketjen Black (EC600JD, specific surface area: 1280 $m^2\ g^{-1}$) was kindly provided by LION Co., Ltd. (Tokyo, Japan) and used as a material for the catalytic layer. Acetylene black (AB-7, specific surface area: 47 $m^2\ g^{-1}$) was kindly provided by DENKI KAGAKU KOGYO KABUSHIKI KAISHA (Tokyo, Japan) and used as a material for the gas diffusion layer. Polytetrafluoroethylene (PTFE) dispersion (Polyflon TFE Series D-1) was purchased from DAIKIN INDUSTRIES, Ltd. (Osaka, Japan) and used as a binder of electrode materials. Li metal foil was purchased from Honjo Metal Co., Ltd. (Higashiosaka, Japan). 1.0 M $LiPF_6$ in propylene carbonate was purchased from Kishida Chemical Co., Ltd. and used as an electrolyte. All chemicals were used as received without further purifications.

2.2. Material synthesis

The carbon-supported $LaMn_{0.6}Fe_{0.4}O_3$ was prepared by a reverse homogeneous precipitation (RHP) method as reported in elsewhere [33,34]. At first, an aqueous solution of $La(NO_3)_3$, $Mn(NO_3)_2$ and $Fe(NO_3)_3$ was placed in a burette and titrated against a 1% TMAH solution containing dissolved TPAB under vigorous stirring. The concentration of metal ions in the solution was fixed at 0.2 M. The amount of TBAH was equimolar to the metal ions in the solution. After mixing, a brown-colored precipitate was obtained immediately. The precipitate obtained was collected by filtration and re-dispersed into 2-propanol. Then, Ketjen Black EC600JD was added to the solution and dispersed under ultrasonic agitation (45 kHz) for 30 min. After the filtration and drying at 120 °C for more than 12 h, the powder obtained was calcined at 650 °C for 5 h in N_2 flow (100 ml min^{-1}) to produce the carbon-supported $LaMn_{0.6}Fe_{0.4}O_3$. The content of $LaMn_{0.6}Fe_{0.4}O_3$ was fixed at 30 wt.%. The carbon-supported $LaMn_{0.6}Fe_{0.4}O_3$ obtained, a PTFE dispersion and 1-buthanol were added to de-ionized water and mixed for 1 h. The content of PTFE in the carbon-supported $LaMn_{0.6}Fe_{0.4}O_3$ was fixed at 15 wt.%. After the filtration and drying at 120 °C, a powder for the catalytic layer was finally obtained. The crystalline phase and the particle size of $LaMn_{0.6}Fe_{0.4}O_3$ on the carbon-support were analyzed by means of a X-ray diffractmetry with Cu Kα radiation ($\lambda = 1.54056$ Å) (XRD; RINT 2100, Rigaku, Tokyo, Japan) and a transmission electron microscopy (TEM; JEM-2000EX, JEOL, Tokyo, Japan), respectively. Separately, a powder for the gas diffusion layer was fabricated by mixing an acetylene black (AB-7) and PTFE. The content of PTFE in the powder was fixed at 30 wt.%. The specific surface area of the powder for the catalytic layer and the gas diffusion layer were evaluated by means of a nitrogen adsorption/desorption apparatus (BELSORP-mini, BEL JAPAN, Inc., Osaka, Japan).

2.3. Electrode fabrication and cell measurements

Powders for the catalytic layer and the gas diffusion layer were stacked on the Ni mesh (100 mesh) and pressed into sheets under the pressure of 2.0 MPa. Then the stacked sheets were bound together by hot-pressing under the pressure of 5.2 MPa at 365 °C to produce air electrodes of 16 mm in diameter. The pore size distribution and pore volume of the catalytic layer and the gas diffusion layer were measured by means of a mercury porosimetry (Pore Sizer 9320, Shimadzu, Kyoto, Japan). The air electrode obtained, Li foil and electrolyte (1.0 M $LiPF_6$ in propylene carbonate) were fabricated to Li-air cells. Fig. 1 shows the schematic cell

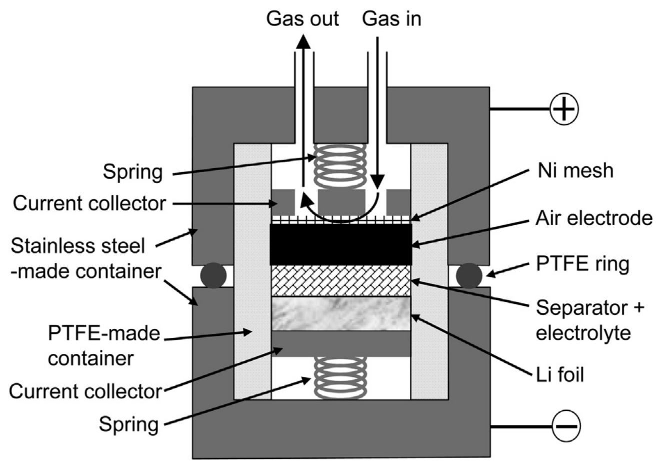

Fig. 1. Schematic cell configuration of Li-air batteries.