Short communication

Mesoporous α-MnO₂/Pd catalyst air electrode for rechargeable lithium–air battery

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ABSTRACT

Rechargeable lithium–air battery is studied using Pd/mesoporous α-MnO₂ air composite electrode. In the present work, we have studied the preparation and electrochemical performance of ordered mesoporous α-MnO₂ as a cathode catalyst for rechargeable Li–air batteries. α-MnO₂ was prepared by reduction of $KMnO_4$ solution in acidic aqueous solution followed by successive proton and alkali-ion exchange method. α-MnO₂ with high surface area of 33–133.0 $m^2\,g^{-1}$ was successively synthesized and used as an electrode catalyst for Li–air battery. It was found that the mixture of Pd and mesoporous α-MnO₂ electrode shows the high activity to oxidation and reduction of Li to form Li_2O_2 or Li_2O. Application of Pd/mesoporous α-MnO₂, which is mixed with teflonized acetylene binder (TAB), for air electrode is effective for decreasing the charge potential and also improved the energy efficiency as well as cyclability.

1. Introduction

Recently, metal/air batteries have been attracting much attention because of its extremely high specific capacity. The reason for such high specific capacity is that the cell consists of metal for an anode electrode and a cathodic reactant of O_2 from air, and hence these batteries are unique in structure and works as a half cell. Among the various metal/air battery systems, lithium–air battery is the most attractive one since the cell discharge reaction between Li and oxygen to yield Li_2O_2 ($2Li + O_2 \rightarrow Li_2O_2$) has a theoretical discharge voltage of 3.10 V and a theoretical specific energy of 5200 Wh kg_{-Li}. In practice, oxygen is not needed to be stored in the battery and the theoretical specific energy excluding oxygen is as high as 11,140 Wh kg_{-Li}, which is much higher capacity than that of any advanced batteries and even higher than that of fuel cells. Abraham and Jiang reported a Li–air battery using non-aqueous electrolyte [1]. They suggested that during discharge, Li reacts with O_2 to form Li_2O_2. In addition to this, Read [2] suggested that there was another reaction occurred based on oxygen consumption measurement i.e. $4Li + O_2 \rightarrow 2Li_2O$, has an open circuit voltage of 2.91 V. However, due to low oxygen solubility in non-aqueous electrolyte, the power density of Li–air battery using non-aqueous electrolyte is low [2,3]. In the lithium–air batteries, the non-aqueous electrolyte at the anode side is used in order to eliminate the dangerous

reaction between metallic lithium and water. Dobley et al. [4] and Kuboki et al. [5] had employed liquid aprotic organic solvents for the electrolyte solution. By applying an organic based [3] or ionic liquid based electrolyte solution [5], the products of the cell reactions involve the insoluble Li_2O and Li_2O_2 product. Both Li_2O and Li_2O_2 are not soluble in an organic electrolyte solution and these oxides will precipitate in the pores of the carbon based cathode which blocks further intake of oxygen and thus abruptly ends cell life. Recently, lithium–air rechargeable battery was reported using MnO_2 for air electrode [6,7]. In the previous work [8], it was found that the higher charging potential above 4.2 V leads to the decomposition of Li_2CO_3 into Li^+, CO_2, and O_2. At the charging potential above 4.2 V, oxidation of carbon binder leads to the formation of CO_2, which further reacts with Li resulting in the formation Li_2CO_3. In this study, we have synthesized the mesoporous α-MnO₂ as a catalyst cathode electrode for Li–air battery by alkali-ion exchange method. We have investigated the charge and discharge property of this cell and the electrode reaction was analyzed. During discharge, the first initial product Li_2O_2 was observed and then the final product after discharge was Li_2O. However during the charge process, decomposition of Li_2O_2 to Li and O_2 takes place.

2. Experimental

2.1. Synthesis of the materials

Synthesis of mesoporous α-MnO₂ was performed by reduction of $KMnO_4$ solution in acidic aqueous solution at 333 K for 10 h. The products were then washed with distilled water until free from the

resulting KCl. Some products were then further stirred with HNO_3 solution for 10 h, and finally washed with distilled water and dried in air.

2.2. Characterization of the samples

The mesoporous α-MnO$_2$ compound was characterized by a combination of techniques including X-ray diffraction (XRD, Rigaku Rint 2500), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and BET surface area measurements (Nippon Bell. BELSORP 18PLUS-FS).

Powder X-ray diffraction (XRD) was carried out using a Rigaku Rint 2500HLR diffractometer with Cu Kα radiation at the low angle scanning range of 0.5–5° and the wide angle range of 10–80° (2θ). Nitrogen adsorption–desorption isotherm was measured using a Bell Japan (Bell Mini) instrument and the specific surface area was calculated by the Brunauer, Emmett and Teller (BET) method. The particle morphologies of the resulting mesoporous α-MnO$_2$ compound were observed using a scanning electron microscope (SEM, Keyence VE-7800). TEM observation was performed using a JEOL JEM-2010 electron microscope.

2.3. Electrochemical measurements

The electrochemical characterizations were carried out using Swagelok type cell. The cathode was prepared using a mixture of α-MnO$_2$, Pd, and teflonized acetylene black (TAB-2) as a binder (mol ratio of 75:15:10) and then mixture was pressed onto a stainless steel mesh and lithium foil was used as an anode electrode separated by a porous polypropylene film (Celgard 3401). The cell was gas tightness excepting for the stainless steel mesh window that is exposed the porous cathode to O_2 atmosphere. The electrolyte used was 1 M LiTFSI-EC:DEC (3:7 by volume) lithium bis (trifluoromethanesulfonyl) imide-ethylene carbonate:diethyl carbonate supplied by Ube Chemical Co. Ltd., Japan. Charge–discharge performance was carried out at the voltage range of 4.0–2.0 V at a constant current of 0.025 mA cm^{-2}. A practical lithium/air battery should be tested on air operational environment. Since the moisture content in the air will react with lithium negative electrode and CO_2 will consume all lithium salt in the electrolyte. To avoid such negative effect, the cell was tested in a dry pure oxygen atmosphere.

Examination of the discharged electrode involves first disassemble of the cell in the glove box, rinsing the cathode electrode with diethyl carbonate, removing the solvent under vacuum, and then the electrode was introduced to air tight holder.

It is observed that the discharge capacity increases with increasing the amount of air electrode because of the enlarged catalytic activity and also storage capacity for the resulting lithium oxides. Therefore, in the conventional metal–air battery, the discharge capacity was generally normalized by the amount of carbon used for air electrode. In this study, composite with metal or metal oxide was used for air electrode and the capacity of charge and discharge was expressed by total weight basis of air electrode.

3. Results and discussion

Low angle XRD data for α-MnO$_2$ prepared was shown in Fig. 1(a). The characteristic sharp diffraction peak at 1.02° indicates that the mesoporous α-MnO$_2$ was successfully synthesized. Wide angle XRD pattern of as-synthesized mesoporous α-MnO$_2$ is shown in Fig. 1(b). Peaks at 13°, 18°, 29°, 38°, 42°, 50°, 57° and 61° are characteristic ones for the α-MnO$_2$ phase [9], except for some Mn$_2$O$_3$ impurities peak was also observed at 22° and 34.9°. The transformation of KMnO$_4$ compounds that the cation/proton exchange leads to the formation of α-MnO$_2$ is in good agreement with the literatures [10–12].
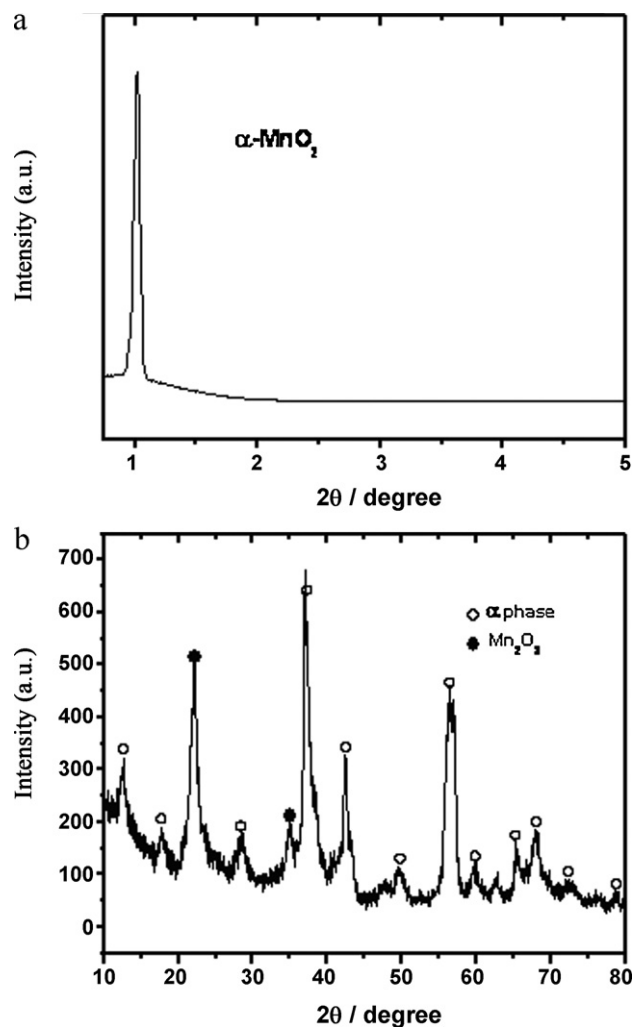

Fig. 1. (a) Low-angle and (b) wide-angle XRD pattern of mesoporous α-MnO$_2$.

Fig. 2(a) shows the scanning electron microscope image of the mesoporous α-MnO$_2$ powder. It shows that small round microparticles were aggregated with each other to form mesopore with a hollow structure. Fig. 2(b) shows the TEM image of the mesoporous α-MnO$_2$ having a hollow tube like structure with 10–20 nm in diameter. Analysis of the transmission electron microscopy image revealed that the rod axis of the α-MnO$_2$ crystal coincident with the c-axis of the unit cell, which is in the direction of (2×2) tunnels.

Fig. 3 shows the nitrogen adsorption–desorption isotherms of mesoporous α-MnO$_2$. The isotherms of mesoporous α-MnO$_2$ are typical IV type isotherms with H$_1$-type hysteresis loop, which is characteristic one for mesoporous materials. The mesoporous α-MnO$_2$ has a surface area of 33.0 m^2 g^{-1} with a pore diameter of 4.05 nm.

We investigated the charge–discharge measurement of lithium/air battery using α-MnO$_2$/TAB(90/10) air electrode as shown in Fig. 4(a). Charge–discharge measurement was carried out in the potential window of 4.0–2.0 V versus Li/Li$^+$, at the current density of 0.025 mA cm^{-2}. An initial discharge capacity of 365 mAh g$_{-catalyst}$$^{-1}$ (corresponded to 3650 mAh g$_{-carbon}$$^{-1}$) with high reversible capacity was exhibited. The discharge plateau was large in capacity and flat at 2.9–2.7 V. However, the charge potential was flat at 3.6 V with high reversible capacity. Further charge–discharge measurement shows the stable discharge capacity of 350 mAh g$_{-catalyst}$$^{-1}$ after 7 cycles. The capacity retention rate was only 96% after 7 cycles. By removing high surface area carbon binder for lithium–air battery, α-MnO$_2$ electrode can

a

b
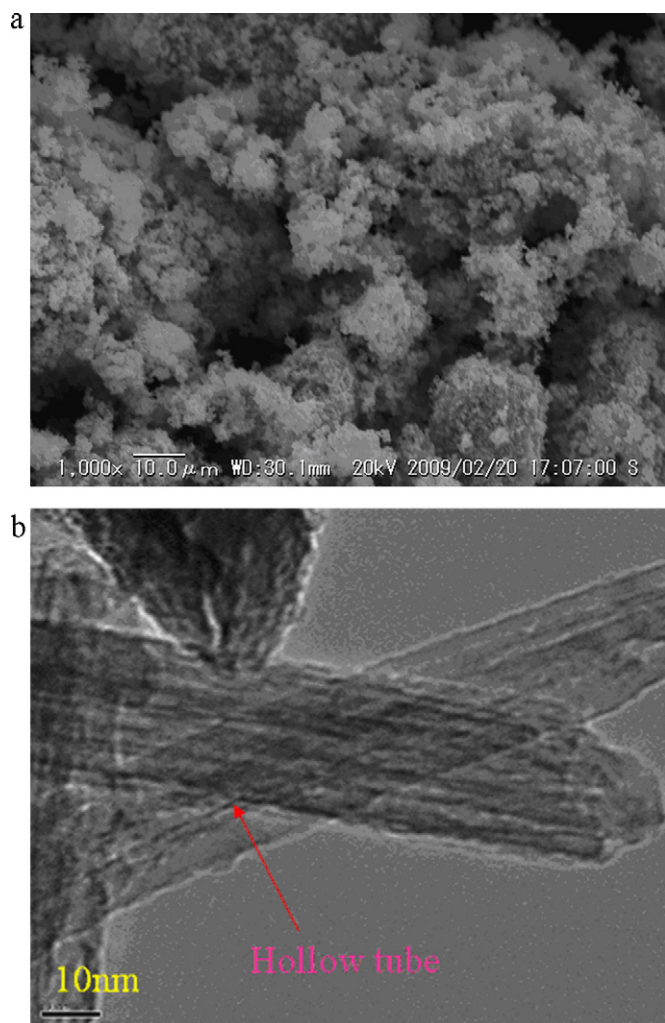

Fig. 2. (a) SEM image and (b) TEM image of mesoporous α-MnO$_2$.

enable to charge the cell below 4.0 V and it was found that the charging potential plateau was reduced drastically using α-MnO$_2$ for electrode. The difference between the charge and discharge voltage was $\Delta V = 0.8$ V, demonstrating that the battery had become more reversible (energy efficiency ca. 78%).
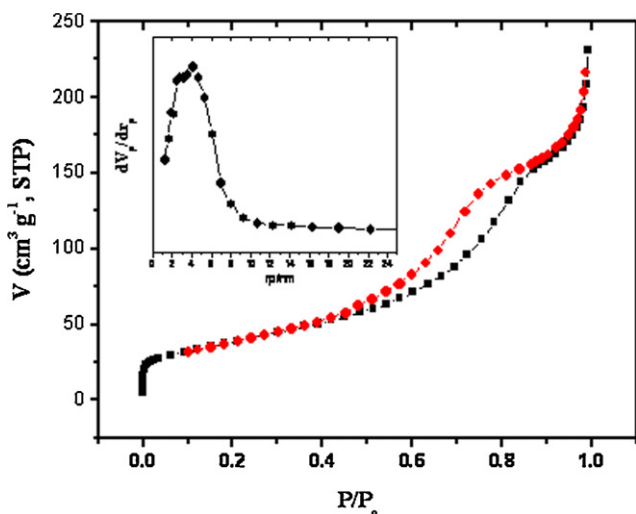

Fig. 3. Nitrogen adsorption–desorption isotherms of mesoporous α-MnO$_2$. The inset is the pore size distribution of mesoporous of α-MnO$_2$.
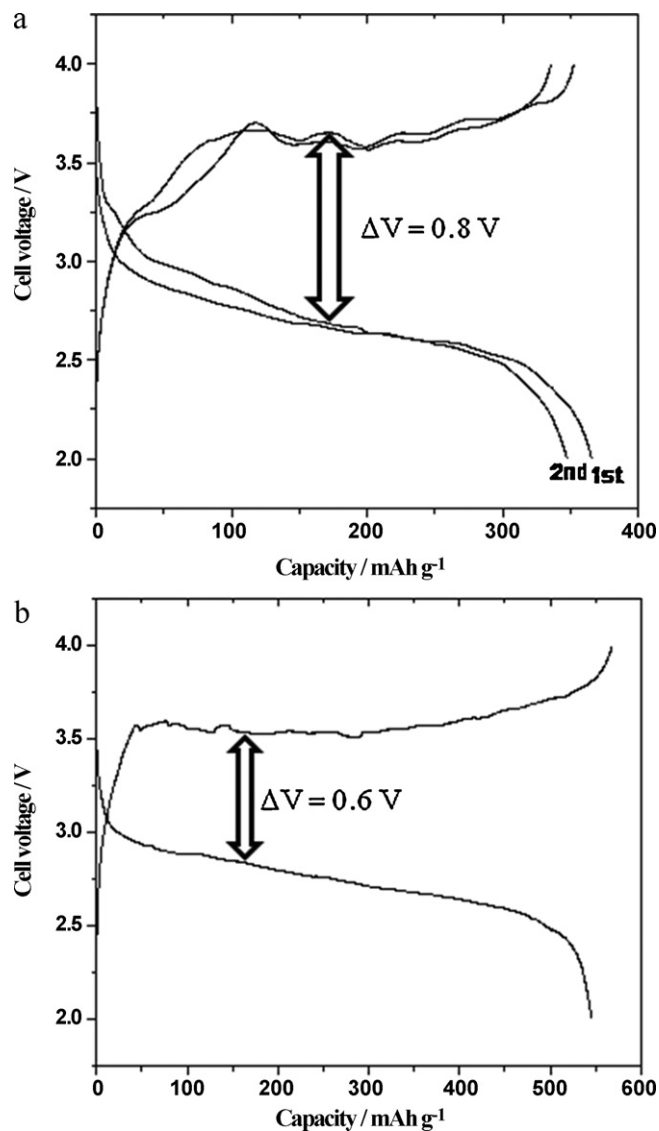
a

b

Fig. 4. Charge–discharge curves for a lithium/air battery using mesoporous α-MnO$_2$ supported palladium electrode in an O$_2$ atmosphere between 4.0 and 2.0 V at a current density of 0.025 mA cm^{-2}. (a) Mesoporous α-MnO$_2$/TAB (90/10) electrode, and (b) mesoporous α-MnO$_2$/Pd/TAB (75/15/10) electrode.

In our previous report [8] we found that the addition of Pd is effective for enlarging discharge capacity and effects of Pd on α-MnO$_2$ was also studied. By addition of small amount of Pd to mesoporous α-MnO$_2$ air electrode, the initial discharge capacity of Pd/α-MnO$_2$/TAB (15/75/10) electrode can be increased to 545 mAh g$_{-catalyst}^{-1}$, which is corresponded to 5450 mAh g$_{-carbon}^{-1}$ as shown in Fig. 4(b). The charge–discharge voltage difference (ΔV) on Pd/α-MnO$_2$/TAB (15/75/10) air electrode was $\sim$0.6 V. Based on the charge discharge capacity potential plateaus of Pd/mesoporous α-MnO$_2$/TAB (15/75/10) air electrode, the specific energy efficiency of $\sim$82% was observed for Pd/mesoporous α-MnO$_2$/TAB (15/75/10) air electrode. Therefore, the combination of palladium with mesoporous α-MnO$_2$ seems to be highly effective for decreasing the charging potential close to the theoretical value. Therefore, Pd/mesoporous α-MnO$_2$ electrode was highly active to air electrode of lithium–air battery.

Decrease in capacity with increasing the current density is another serious issue for the present Li–air battery. Therefore, charge–discharge property was studied at various current densities for the Li–air cell using Pd/α-MnO$_2$ air electrode. Although
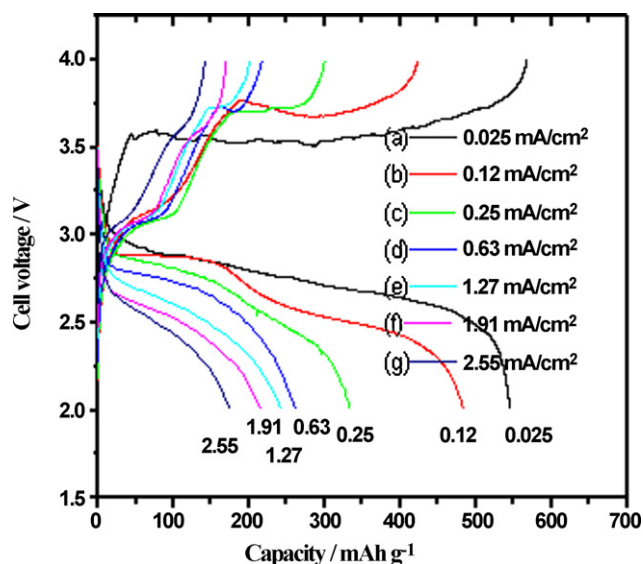
Fig. 5. First charge–discharge curves of (a) mesoporous α-MnO_2/Pd/TAB (75/15/10) electrode at a current rate of 0.025, (b) 0.13, (c) 0.25, (d) 0.65, (e) 1.27, (f) 1.91, and (g) 2.55 mA cm^{-2}.

Fig. 6. Charge–discharge capacities versus cycle performance of mesoporous α-MnO_2/Pd/TAB (75/15/10) electrode at a current rate of 0. 25, and 1.91 mA cm^{-2}.

Li–air battery is always considered for its poor rate property and shows only large capacity at low current density, this study reveals that reasonably high capacity is exhibited at high current density on the cell using Pd/mesoporous α-MnO_2 as shown in Fig. 5. Pd/mesoporous α-MnO_2 air electrode shows the first charge–discharge profile at different rates, 0.023, 0.12, 0.25, 0.63, 1.27, 1.91, and 2.55 mA cm^{-2}. The capacity of the Pd/mesoporous α-MnO_2 air electrode at 0.025 mA cm^{-2} is 545 mAh g$_{-catalyst}$$^{-1}$, while at 0.12, 0.25, 0.63, 1.27, 1.91, and 2.55 mA cm^{-1}, it was 483, 334, 261, 242, 215, and 175 mAh g$_{-catalyst}$$^{-1}$, respectively. That means that at 0.12, 0.25, 0.63, 1.27, 1.91, and 2.55 mA cm^{-2}, the capacity retention rates are 88.6%, 61.3%, 47.9%, 44.4%, 39.5%, and 32.1%, respectively. Pd/α-MnO_2/TAB(15/75/10) electrode shows high capacity retention with increasing current density, and 32.1% to its initial capacity was still exhibited from 0.025 to 2.55 mA cm^{-2}, which is much higher than that of the lithium–air batteries reported. That means that the rate property of the Pd/mesoporous α-MnO_2 air electrode for Li–air battery is acceptably high and this could be assigned to the high activity of air electrode.

Fig. 6 shows the capacity as a function of cycle number of the cell using Pd/α-MnO_2 air cathode electrode at low and high current densities. Pd/mesoporous α-MnO_2 electrode shows the initial discharge capacity of 334 mAh g$_{-catalyst}$$^{-1}$ during the first initial cycle at the current density of 0.25 mA cm^{-1}. After 15 cycles, the capacity of 261 mAh g$_{-catalyst}$$^{-1}$ is still retained. While applying a high current density of 1.91 mA cm^{-2}, it shows the initial discharge capacity of 215 mAh g$_{-catalyst}$$^{-1}$ and 121 mAh g$_{-catalyst}$$^{-1}$ after 15 cycles. The capacity retention rate was 78.1% and 56.3% at 0.25 and 1.91 mA cm^{-2}, respectively. Therefore, increase in current density decreases the cycle stability of the cell and this could be explained by the unusual deposition of Li_2O_2 or Li_2O because of excessively fast deposition rate. In any case, it can be said that the lithium–air battery using Pd/mesoporous α-MnO_2 electrode shows the superior cycle stability for charge and discharge even at high current densities.

Fig. 7 shows the *ex situ* XRD of Pd/α-MnO_2 electrodes before charge and those after discharge to 200, 400 mAh g$_{-catalyst}$$^{-1}$, and 2.0 V, respectively. Since two potential plateaus were observed for discharge in Li–air battery, we measured XRD to know what kind of reactions mainly occurs during discharge process. Before charge, *ex situ* XRD pattern of Pd/mesoporous α-MnO_2 electrode shows the diffraction peaks from each component except for new
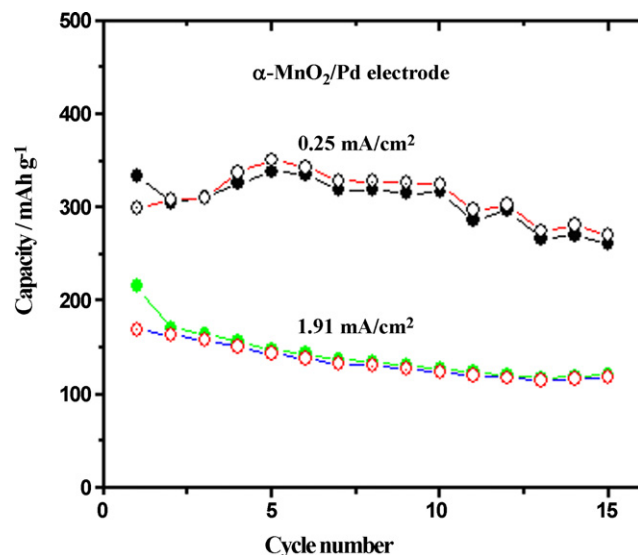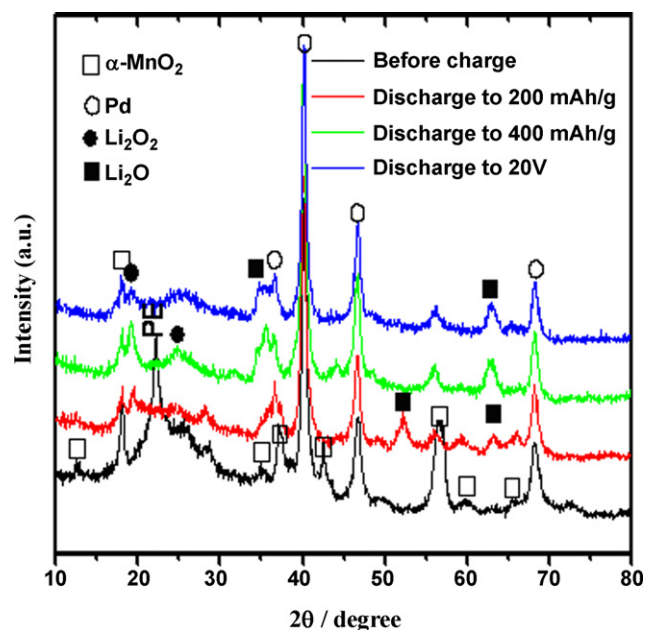

Fig. 7. *Ex situ* XRD of mesoporous α-MnO_2/Pd/TAB (75/15/10) electrode before charge and after discharge to 200, 400 mAh g$_{-catalyst}$$^{-1}$, and 2.0 V.

peak at 23° which is assigned to a polythene bag. After discharge to 200 mAh g$_{-catalyst}$$^{-1}$, Pd/$\alpha$-$MnO_2$ electrode shows new peaks at 19.3° and 52° corresponds to the formation of Li_2O_2. After discharge to 400 mAh g$_{-catalyst}$$^{-1}$, *ex situ* XRD of Pd/$\alpha$-$MnO_2$ electrode shows the new peaks at 25.4° and 62° corresponds to the formation of Li_2O. While after discharge to 2.0 V, the peaks at 34.8° and 56° become sharper and increased intensity due to increased amount of Li_2O, while the peak at 19.3° with reduced intensity. These results suggest that the formation of Li_2O_2 at initial high potential range and then Li_2O was mainly formed in low potential range to 2.0 V.

4. Conclusions

This study revealed that Pd/mesoporous α-MnO_2 electrode is highly active as air electrode of lithium/air battery. Using Pd/mesoporous α-MnO_2/TAB, charging potential can

be suppressed to 3.6 V and high reversible capacity of ca. 545 mAh $g_{-catalyst}^{-1}$ was observed at 0.025 mA cm^{-2}. Applying high current densities of 0.25 and 1.91 mA cm^{-2}, Pd/mesoporous α-MnO$_2$ electrode shows the stable capacity of 261 and 212 mAh $g_{-catalyst}^{-1}$, respectively after 15 cycles. These results suggest that lithium–air battery can be reversibly used even at high current densities. Using Pd/mesoporous α-MnO$_2$ electrode, *ex situ* XRD result shows the formation of Li$_2$O$_2$ followed by Li$_2$O after discharge to 2.0 V but no Li$_2$CO$_3$ formation is observed. Consequently, energy efficiency for charge and discharge in this study can be achieved to be 82%, which is much higher than that of the reported value (ca. 65%).

Acknowledgement

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