Rechargeable Lithium-Air Battery Using Mesoporous Co_3O_4 Modified with Pd for Air Electrode

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ABSTRACT

Mesoporous cobalt oxide (Co_3O_4) was studied for air electrode of Li-air rechargeable battery. In this study, mesoporous Co_3O_4 with an average pore radius of 3.09 nm and BET surface area of $99 \text{ m}^2/\text{g}$ was successfully prepared by using mesoporous SiO_2 for template. Prepared mesoporous Co_3O_4 was applied for air electrode of Li-air battery after mixing with Pd and it was found that the cell showed a reasonably large discharge capacity of $481 \text{ mAh/g}_{\text{cat}}$ at 0.1 mA/cm^2 at the initial cycle. Energy efficiency for charge and discharge was estimated to be ca. 75%. Raman spectroscopy suggests that the main product during discharge was Li_2O_2 and formation of Li_2CO_3 was hardly observed.

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1. Introduction

Rapid growth of a portable electronic device for various applications requires batteries with high energy-density. Recently, lithium-air batteries have been attracting much attention because of its extremely large specific capacity.^{1,2} The high specific capacity results from the high energy density of Li metal and simple structure of battery. Namely, this battery consists of a lithium sheet as an anode electrode and cathodic reactant of O_2 , which is obtained from air and no necessary to contain in battery. Among the various metal air battery system, Li-air battery is the most attractive since the cell discharge reaction between Li and oxygen to yield Li_2O or Li_2O_2 , according to $4\text{Li} + \text{O}_2 = 2\text{Li}_2\text{O}$ or $2\text{Li} + \text{O}_2 = \text{Li}_2\text{O}_2$, has an open circuit voltage of 2.91 or 2.95 V, respectively and the theoretical specific energy of 5200 Wh/kg , and the theoretical specific energy excluding oxygen is as high as 11140 Wh/kg , which is much higher than not only that of any advanced batteries but also fuel cells. Abraham and Jiang reported first time a Li-air battery by using nonaqueous electrolyte.³ Bruce et al. reported application of MnO_2 -acetylene black carbon is useful for improved reversibility of electrode reaction and reasonably large capacity was sustained over 50 cycles of charge and discharge.^{4,5}

Mizuno et al. also reported that the rechargeable Li- O_2 battery using propylene carbonate electrolyte containing ketjen black (EC600JD) carbon with MnO_2 catalyst had initial discharge capacity of 820 mAh/g and 60% of capacity retention after 100 cycles, which is the longest cycle life reported for a rechargeable Li- O_2 at present.⁶ However, decrease in charge potential is required because of low energy efficiency (60% of the reported cell) and for this purpose, further improvement in catalytic activity for air electrode is requested. MnO_2 with nanorod shape can be used as an alternative and low cost electrocatalyst for oxygen reduction/evolution reactions (ORRs/OERs).⁷ However, MnO_2 prepared by traditional ceramic route have limited electrocatalytic activity due to their large particle size and low specific surface areas.

In our previous study, it was found that mesoporous oxide is active for air electrode of Li-air battery, in particular, $\beta\text{-MnO}_2$ shows a reasonable capacity like $800 \text{ mAh/g}_{\text{cat}}$ and cycle stability over 100 cycles.^{8–10} However, because of high charge potential, improvement in energy efficiency for charge and discharge is

requested in particular, decrease in charge potential. It is reported that Co_3O_4 nano particles deposited on carbon nanotube shows low overpotential for air electrode of Li-air battery, however, cycle stability is not high.¹¹ Since mesopore is an important role for improved cycle stability, we have synthesized mesoporous Co_3O_4 by using mesoporous silica so-called KIT-6 as a template in this study and applied for a cathode catalyst of Li-air battery. It was found that mixture of Pd and mesoporous Co_3O_4 shows the high activity to air electrode reaction.

2. Experimental

Mesoporous Co_3O_4 was prepared by using mesoporous silica (KIT-6) as a template. Mesoporous silica KIT-6 template was prepared with the same procedure reported in the literature.^{12,13} $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in ethanol (15 ml) and then the mesoporous silica KIT-6 template was added in a beaker. The mixture was stirred continuously at room temperature till all solution was adsorbed. The solid product was then heated slowly to 300°C for 3 h and allowed to cool slowly. The product was reheated to 350°C at the rate of $1^\circ\text{C}/\text{min}$ for 5 h. Mesoporous Co_3O_4 was treated with hot 2 M NaOH solution to remove the silica KIT-6 template and then washed with distilled water and ethanol several times. The product was then kept at 60°C for 12 h for removing water.

The electrochemical characterizations were carried out using a Swagelok-type cell. Details was reported in our previous report.⁸ The cathode was formed by casting a mixture of mesoporous Co_3O_4 , PdO, and PTFE-coated teflonized acetylene black (TAB-2) as a conducting binder (mol ratio of 75:15:10). The resulting mixture was pressed onto a stainless steel mesh and the cathode was dried at 160°C for 12 h under vacuum. Li-air cell measurements were carried out at room temperature. The Li-air battery configuration used in this study consists of a lithium foil (12 mm in diameter) as an anode electrode separated by glass separator. The cell was gas tight excepting for the stainless steel mesh window that exposes the porous cathode to O_2 atmosphere. The electrolyte used was 1 M lithium bis(trifluoromethanesulfonyl)imide-ethylene carbonate:diethyl carbonate (LiTFSI-EC:DEC, 3:7 by volume) supplied by Ube Chemical Co. Ltd., Japan. Charge-discharge performance was carried out in a voltage range of 4.0–2.0 V at current densities of 0.1 mA cm^{-2} .

Figure 1. XRD patterns of the prepared Co_3O_4 (a) wide scan (b) lower angle scan.

Figure 2. (Color online) N_2 gas adsorption isotherms at 77 K (a) and pore size distribution (b).

Powder X-ray diffraction (XRD) analysis of mesoporous Co_3O_4 was carried out with $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$, Rigaku Rint 2500) at the low-angle scanning range of $0.5\text{--}10^\circ$ and a wide-angle range of $10\text{--}80^\circ$ (2θ) with a scan speed of $0.02^\circ/\text{s}$. Specific surface area (S_{BET}) was determined with nitrogen adsorption-desorption isotherm using BELSORP 18PLUS-FS (Nippon Bell, Japan).

3. Results and Discussion

Figure 1 shows XRD patterns of the prepared Co_3O_4 in this study at lower and wide angle scan. Typical diffraction peaks from Co_3O_4 were observed in wider angle scan and all diffraction peaks were assigned to Co_3O_4 phase in Joint Committee for Powder Diffraction Standards (JCPDS) data (No. 76-1802). Since there are no diffraction peaks from impurity phase, Co_3O_4 with single phase seems to be successfully prepared in this study. In addition, as shown in Fig. 1(b), strong diffraction peak was observed at $2\theta = 1.02^\circ$, which suggests formation of a mesoporous structure. The estimated diameter of mesopore in prepared Co_3O_4 is 8.71 nm. From JCPDS data base, the prepared sample could be assigned to a cubic lattice of Co_3O_4 [space group $\text{Fd-}3\text{m}(227)$], where the lattice parameter values are $a = 807.2 \text{ pm}$.

Figure 2 shows N_2 gas adsorption isotherms. The observed isotherm of the prepared Co_3O_4 is a typical type IV adsorption one and large hysteresis in N_2 adsorption was observed in a relative pressure range from $P/P_0 = 0.6$ to 0.8 , which suggests that mesopore is contained in the sample. Figure 2(b) is the pore size distribution estimated by N_2 adsorption isotherms. Evidently, single and narrow pore distribution was observed at 3.09 nm for pore radius and so the prepared Co_3O_4 has mesoporous structure with a relatively narrow distribution. Outer and inner diameter can be estimated from XRD and N_2 adsorption, respectively and the wall thickness could be estimated from the difference in outer and inner diameter, that is ca. 1.26 nm. BET surface area of the sample is $99 \text{ m}^2/\text{g}$, which is reasonably large for air electrode of Li-air battery. Considering XRD and N_2 adsorption, the sample obtained by using KIT-6 mesoporous SiO_2 as a template is mesoporous Co_3O_4 with ca. 1.3 nm wall thickness.

Figure 3. Charge-discharge curve of the Li-air cell using Pd/mesoporous Co_3O_4 for air electrode.

The electrocatalytic activity of mesoporous $\text{Co}_3\text{O}_4/\text{Pd}/\text{TAB-2}$ (75/15/10) air electrode in the Li-air battery were measured. Figure 3 shows the charge-discharge curve of the Li-air cell. Mesoporous Co_3O_4 showed an initial discharge capacity of $481 \text{ mAh/g}_{\text{cat}}$ during the first cycle (Fig. 3). Comparing with α or β - MnO_2 air electrode in our previous study,^{9,10} the observed capacity is slightly lower, however, reasonable large discharge capacity was achieved on mesoporous Co_3O_4 . Since surface area of Co_3O_4 is larger than that of MnO_2 , discharge capacity seems not be simply determined by surface area but by activity to Li^+ oxidation. The discharge potential plateau was flat at 2.8–2.75 V, which is comparable with that of β - MnO_2 .¹⁴ However, although capacity is not large, it is also observed the potential plateau around 3.0 V, which may reflect Li intercalation into Co_3O_4 or formation of LiOH on air electrode by reaction with humidity in air. However, at present, detail reason for this high potential plateau in discharge curve is not clear. After few cycles, discharge capacity around 3.0 V was disappeared. As shown in Fig. 3, the charge potential plateau curve was observed at 3.75 V, which is higher than the theoretical value of 2.95 V vs. Li/Li^+ but almost compatible with that of Pd/β - MnO_2 . In our previous study, we found that Pd was highly active for Li^+ oxidation and decomposition of Li_2O_2 or Li_2O .⁸ Loading Pd on Co_3O_4 is also effective for decreasing charge potential (from 4.0 to 3.75 V) and energy efficiency for charge and discharge was also improved by loading Pd. Since the organic EC-DEC electrolyte was significantly decomposed at potential higher than 4 V, decrease in charge potential is strongly requested for stable cycle performance of Li-air rechargeable battery and so, addition of Pd is effective for improved reversibility of air electrode reaction. The estimated efficiency of charge and discharge was 74.7% which is slightly lower than that of β - MnO_2 .¹⁰ Therefore, from viewpoint of energy efficiency, β - MnO_2 shows better performance than that of Co_3O_4 which shows better cycle stability.

Figure 4 shows the cycle stability of Li-air battery using Pd/mesoporous Co_3O_4 . The discharge capacity decreased with increasing cycle number. However, stable cycle performance was observed for Li-air battery using mesoporous Co_3O_4 for air electrode. Coulomb efficiency is always close to 100% at each cycle and the discharge capacity of $321 \text{ mAh/g}_{\text{cat}}$, which is 67% of initial discharge, was sustained after 23 cycles. Therefore, it can be said that cycle stability of this Li-air battery with Pd/mesoporous Co_3O_4 was reasonably high and this could be assigned to the low discharge potential. This is because degradation in capacitance was mainly caused by formation of Li_2CO_3 as a result of electrolyte decomposition during charge process at the potential higher than 4 V.

Analysis of discharge product is an important subject for improving the cycle stability. It is reported that Li_2O_2 is the main product in Li-air battery for discharge,^{1,2} however, formation of

Figure 4. (Color online) Cycle stability of Li-air battery using Pd/mesoporous Co_3O_4 .

Figure 5. (Color online) Raman spectra before measurement and after discharge at 23rd cycles. (○) Co_3O_4 , (△) LiTFSI, (●) Carbon.

Li_2CO_3 is also observed as a result of electrolyte decomposition. Since the discharge potential of 4 V used in this study is insufficient for decomposition of Li_2CO_3 , discharge capacity will decrease if Li_2CO_3 is formed. Figure 5 shows Raman spectra before measurement and after discharge at 23rd cycles. Although air electrode was washed with propylene carbonate (PC) before Raman measurement, strong absorption peaks from TFSI were observed suggesting that removing the electrolyte was not sufficient. Except for peaks from LiTFSI, there is no strong new peaks observed after discharge. However, weak and broader absorption peaks for Li_2O_2 or Li_2O were recognized around 300 and 750 cm^{-1} . In particular, absorption peak at 750 cm^{-1} , which is assigned to Li_2O_2 , is more obvious. Therefore, main discharge product on mesoporous Co_3O_4 modified with Pd could be Li_2O_2 . In contrast, no clear peak was significant

around 1150 cm^{-1} , which is characteristic Raman peak for Li_2CO_3 . As a result, formation of Li_2CO_3 seems not to be detected on mesoporous Co_3O_4 modified with Pd. Consequently, reasonable cycle stability could be explained by no formation of Li_2CO_3 during discharge.

4. Conclusion

Mesoporous Co_3O_4 was successfully prepared in this study by using mesoporous SiO_2 (KIT-6) as a template. After removing SiO_2 by alkaline treatment, obtained Co_3O_4 has a mesoporous structure with 3.09 nm average pore radius and BET surface area of 99 m^2/g . Application of mesoporous Co_3O_4 modified with Pd for air electrode of Li-air battery shows high discharge potential (2.8 V) and charge potential (3.7 V). Furthermore, it was found that reasonably large capacity of 481 $\text{mAh/g}_{\text{cat}}$ at initial discharge and cycle stability were exhibited on Li-air battery using Pd/mesoporous Co_3O_4 for air electrode. Raman spectroscopy analysis suggests that the main product during discharge is Li_2O_2 and negligible amount of Li_2CO_3 was formed. This study reveals that mesoporous Co_3O_4 modified with Pd is active as air electrode for Li-air battery.

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