Improved electrochemical properties by lithium insertion into Co$_3$O$_4$ in aqueous LiOH solution

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Abstract Co$_3$O$_4$ microspheres were synthesized by a simple hydrothermal treatment. The first-cycle charge–discharge tests were carried out between −0.6 and 0.6 V vs. SCE. The pristine, discharged and recharged specimens were characterized by X-ray power diffraction and scanning electron microscopy. Cyclic voltammetry (CV) curves of Co$_3$O$_4$ at various concentrations in LiOH solution were investigated. The appearance of the two pairs of redox peaks indicated that two sets of faradaic reactions were involved in the redox reactions of Co$_3$O$_4$ to LiCoO$_2$ and LiHCoO$_2$.

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1. Introduction

Micro-sized transition-metal oxides, such as cobalt oxide, iron oxide, manganese oxide and nickel oxide have attracted considerable attention owing to their potential as the promising potential electrode materials for lithium-ion batteries [1–7]. In particular, cobalt oxide, with excellent cycle reversibility and high specific capacity, has received a considerable amount of attention over the last few years. Extensive research works [8–14] have been carried out on lithium insertion into Co$_3$O$_4$ in non-aqueous cells. Intercalation of Li$^+$ ions into the host Co$_3$O$_4$ structures is widely reported in non-aqueous batteries [15,16]. They reported the electrochemical behaviors in a Co$_3$O$_4$ electrode, which produced nano-sized metallic cobalt and Li$_2$O in the first discharge process. At initial charging, the metallic cobalt which was embedded in Li$_2$O matrix generated CoO instead of Co$_3$O$_4$ due to the similarity of oxygen lattices in Li$_2$O and CoO. After the first cycle, the subsequent steps were reversible reactions involving the oxidation and reduction between nano-sized Co and CoO.

However, there is very limited information on the electrochemical characteristics and the discharge mechanism of Co$_3$O$_4$ material in aqueous media. In the present work, we have investigated the electrochemical behaviors of Co$_3$O$_4$ in lithium hydroxide (LiOH) solution. The electrochemical characterization of Co$_3$O$_4$ was studied by focusing on the initial reduction/oxidation behaviors of Co$_3$O$_4$ in LiOH solution as well as the pristine, discharged and recharged properties. The main objective is to investigate whether intercalation of Li$^+$ into the host structure of Co$_3$O$_4$ occurs.
2. Experimental

Co$_3$O$_4$ microspheres were prepared according to the procedure by our group [17]. The product was characterized by X-ray power diffraction (XRD Bruker D8 advance, Germany) with Cu Kα radiation ($\lambda$=0.1518 nm), employing a scanning rate of 10° min$^{-1}$ in 2θ ranging from 10° to 70°. The scanning electron microscopy (SEM) images were obtained using a Leo 1430 VP microscope.

The electrochemical properties of the powders were examined using a standard three-electrode cell. The reference electrode and counter electrode were used as saturated calomel electrode and platinum gauze, respectively. The working electrodes were prepared by a slurry coating procedure. The slurry consisted of 80 wt % active material, 15 wt% acetylene black and 5 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidinone (NMP), spread uniformly on a Pt disk, and then dried in a vacuum oven for 12 h at 100 °C. The electrolyte was LiOH solution, which was thoroughly deaerated with high-purified argon for at least 10 min. The frequency of EIS ranged from 0.01 to 100 kHz at the open-circuit potential. All electrochemical measurements were performed on a CHI 660 B electrochemical workstation and equilibrated for about 1 h prior to measurement. The potentials of the electrode were cycled between −0.6 and 0.6 V vs. SCE. On each occasion, the potential scans started at the open-circuit voltage, moving initially in the cathodic direction.

3. Results and discussion

Fig. 1(a)–(c) shows the XRD patterns of the Co$_3$O$_4$ microspheres powder heated at 200 °C, after being fully discharged to −0.6 V, and fully recharged to 0.6 V. All the reflections in Fig. 1(a) are comparable with standard crystallographic data (JCPDS card no. 78-1970) and show the typical Co$_3$O$_4$ phase. No peaks for impurities are discerned. The pattern has three main diffraction peaks at 36.9°, 65.2°, and 31.2° ((311), (440), and (220) reflections, respectively). XRD measurements were conducted on Co$_3$O$_4$ electrodes in the fully lithiated and the delithiated states, correspondingly. The diffraction peaks of Co$_3$O$_4$ disappeared, as shown in Fig. 1(b) and (c).

SEM morphologies of the obtained Co$_3$O$_4$ were presented in Fig. 2. The Co$_3$O$_4$ microspheres were relatively monodisperse, as shown in Fig. 2(a). To further examine the electrochemical processes of Co$_3$O$_4$ in the first cycling, the lithiated and delithiated electrodes were observed as shown in Fig. 2(b) and (c), respectively. After being fully discharged to −0.6 V, the Co$_3$O$_4$ microspheres disappeared. From Fig. 2(c), it is obvious that the microspheres formed again when Co$_3$O$_4$ material was recharged to 0.6 V. However, some unformed particles existed among the microspheres, which were in good agreement with the results of XRD in Fig. 1(b) and (c).

Fig. 3 gives the first-cycle charge–discharge test of Co$_3$O$_4$ electrode at the current density of 50 mA/g in 2 M LiOH solution.
From the first discharge curve, we can see that the potential rapidly drops to reach a slope at about $-0.4$ V, followed by a decrease in the cut-off voltage to $-0.6$ V. In the subsequent charge segment, there were three inflexions at about 0, 0.2, and 0.3 V, corresponding to two oxidation processes.

To understand the charge–discharge behavior in 2 M LiOH solution, the electrochemical impedance spectroscopy (EIS) tests before and after the first-cycle charge–discharge measurements were carried out using the cells. From the Nyquist impedance plots presented in Fig. 4, three well-differentiated regions are presented in the fresh curve. However, in the high region frequency it is more difficult to distinguish the two arcs due to the cycled curve. Generally, the depressed high-frequency semicircle was related to the Li-ion migration resistance through the SEI film formed on the anode surface and film capacitance. The semicircle in the medium-frequency region was attributed to the Li$^+$ charge-transfer impedance and interfacial capacitance between the electrode and electrolyte. An intercept on the $Z_{\text{real}}$ axis in the high frequency corresponded to the ohmic resistance, which represented the combined series resistance of electrodes, electrolyte, current collectors, and the contact resistance between electrodes and current collectors. The slope line in the lower frequency represented the Warburg impedance, which was associated with lithium-ion diffusion in the solid state electrodes [18–20]. It is obvious from the spectra in Fig. 4 that the high- and medium-frequency semicircles for the cycled electrode are a little smaller than those of the fresh electrode, otherwise than those of the intercept on the $Z_{\text{real}}$ axis in the high frequency. The larger ohmic resistance represented that the resistance between the electrolyte and electrode increased after the first charge–discharge experiments.

Cyclic voltammetry measurements were performed to examine the electrochemical properties of the Co$_3$O$_4$ powders. To investigate the redox behaviors of electrodes in LiOH solution at room temperature, their CV curves at the scan rate of 0.3 mV/s between $-0.6$ and 0.6 V were recorded in Fig. 5. Two pairs of the anodic and cathodic peaks appeared due to the redox activity of cobalt species in Co$_3$O$_4$. In the reduction scan, the reduction peaks were composed of main peaks at around 0.013 V (P1) and $-0.285$ V (P3). In the oxidation scan, the two oxidation peaks were composed of a main peak at around 0.084 V (P2) and a low shoulder peak near $-0.128$ V (P4). Especially it should be noted that these two oxidation peaks in Fig. 5 were consistent with the charge slopes in Fig. 3.

In order to verify whether the redox processes were interdependent or independent of each other, cyclic voltammograms in the two redox couple regions between the potential limits of
–0.660 V and 0 to 0.6 V were shown in Fig. 6, respectively. In Fig. 6(a), there was a single oxidation peak (P4) in the forward scan and a reduction peak (P3) in the reverse scan, same as the couple of peaks (P2 and P1) in Fig. 6(b). This result indicated that P3 and P1 peaks in the reduction scan formed as a result of the subsequent oxidation of the resultant products at P4 and P2 peaks, respectively. These two couples of redox processes became independent of each other. The appearance of the two pairs of redox peaks indicated that there were two sets of faradaic reactions involved.

For further clarification of each pair of redox peak, cyclic voltammetry measurements of Co3O4 electrode in LiOH solution at the scan rate of 0.3 mV/s with various concentrations were performed and the formal potentials of Co3O4 were shown in Table 1. According to the Raman spectra, if we suppose that the intercalating cation is H+ in P1, then the equation representing the redox reaction (between P1 and P2) may be written as follows:

\[ \text{Co3O4} + 3\text{Li}^+ + 4\text{OH}^- \xrightarrow{\text{charge}} 3\text{LiCoO2} + 2\text{H}_2\text{O} + e^- \] (1)

In accordance with the Nernst law, reaction (1) should observe the linear relation of \( E_{1f} \) to \( \log C_{\text{LiOH}} \). The linear relation of the formal potentials of Co3O4 was obtained, see Fig. 7(a). The formal potentials enhanced with the increase in concentrations of the LiOH solution. These results indicated that Li+ intercalated in Co3O4, which were in agreement with the Raman spectra results.

Rao et al. [21] found that proton inserted upon the reduction of Co3+ to Co2+ in LiCoO2 material in LiOH solution. If we suppose that the intercalating cation is H+ in P3, then the equation representing the redox reaction (between P3 and P4) may be written as follows:

\[ \text{LiCoO2} + \text{H}^+ + e^- \xrightarrow{\text{charge}} \text{LiHCoO2} \] (2)

According to the Nernst law, reaction (2) should observe the following dependence of the formal potentials on the activity of H+:

\[ E_{2f} = E^0 + 0.059 \log a^0 \text{H} = E^0 - 0.059 \log a_{\text{LiOH}} \]

From Table 1, the formal potentials \( E_{2f} \) decreased with the increase in concentration of the LiOH solution and the linear relation of \( E_{2f} \) to \( \log C_{\text{LiOH}} \) was observed as shown in Fig. 7(b). In this case, the slope of the plot was negative, which indicated that \( E_{2f} \) should be proportional to the logarithm of the proton activity in LiOH solution. The result was in good agreement with the idea of redox reaction (2).

### Table 1: The formal potentials of Co3O4 in LiOH solution with various concentrations.

<table>
<thead>
<tr>
<th>( C_{\text{LiOH}} ) (mol/l)</th>
<th>( \log C_{\text{LiOH}} )</th>
<th>( E_{1a,p} ) (mV)</th>
<th>( E_{1c,p} ) (mV)</th>
<th>( E_{1f} ) (mV)</th>
<th>( E_{2a,p} ) (mV)</th>
<th>( E_{2c,p} ) (mV)</th>
<th>( E_{2f} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>−0.3</td>
<td>84</td>
<td>13</td>
<td>48.5</td>
<td>−128</td>
<td>−285</td>
<td>−206.5</td>
</tr>
<tr>
<td>1.6</td>
<td>−0.2</td>
<td>204</td>
<td>25</td>
<td>114.5</td>
<td>−167</td>
<td>−316</td>
<td>−241.5</td>
</tr>
<tr>
<td>1.2</td>
<td>−0.08</td>
<td>267</td>
<td>31</td>
<td>149</td>
<td>−185</td>
<td>−350</td>
<td>−267.5</td>
</tr>
<tr>
<td>0.8</td>
<td>0.1</td>
<td>397</td>
<td>48</td>
<td>222.5</td>
<td>−211</td>
<td>−405</td>
<td>−308</td>
</tr>
<tr>
<td>0.4</td>
<td>0.4</td>
<td>545</td>
<td>86</td>
<td>315.5</td>
<td>−246</td>
<td>−503</td>
<td>−374.5</td>
</tr>
</tbody>
</table>

Therefore, the overall electrochemical processes can be expressed as follows:

\[ \text{Co3O4} + 3\text{Li}^+ + 4\text{OH}^- \xrightarrow{\text{charge}} 3\text{LiCoO2} + 2\text{H}_2\text{O} \]

\[ + e^- \xrightarrow{\text{charge}} \text{LiHCoO2 (P3} \leftrightarrow \text{P4)} \]

In the reduction scan, the reduction peaks corresponded to the initial reduction of Co3O4 to LiCoO2 and LiHCoO2. These corresponded to the reverse processes in the oxidation scan where LiCoO2 and LiHCoO2 were reoxidized to Co3O4. These processes are different to the reactions in non-aqueous electrolyte in which the well-known mechanisms for these reactions are the reversible reactions between Co3O4 and Co/Li2O, and the partial electrolytical composition/decomposition coating on the surface of Co3O4 [14,22,23].

### 4. Conclusions

Co3O4 microspheres were synthesized by a simple hydrothermal reaction. The appearance of the two pairs of redox peaks indicated that two sets of faradaic reactions were involved in the redox reactions of Co3O4 to LiCoO2 and LiHCoO2. These processes are different to the reactions in non-aqueous electrolyte, which are the reversible reactions between Co3O4 and Co/Li2O, and the partial electrolytical composition/decomposition coating on the surface of Co3O4. It is found that the ohmic resistance became larger than that of the fresh electrode after charge–discharge experiments.
Acknowledgments

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References