Electrochemical and in situ XANES studies of a LiNi_{0.8}Co_{0.17}Al_{0.03}O_{2} cathode material

A.A.M. Prince\textsuperscript{a}, S. Mylswamy\textsuperscript{a}, C.Y. Wang\textsuperscript{a}, S.C. Chang\textsuperscript{a}, R.S. Liu\textsuperscript{a,\*}, C.H. Lin\textsuperscript{b}, Y.K. Lin\textsuperscript{b}, C.H. Shen\textsuperscript{b}, S.M. Huang\textsuperscript{b}, J.F. Lee\textsuperscript{c}

\textsuperscript{a}Department of Chemistry, National Taiwan University, Roosevelt Road, Section 4, Taipei 106, Taiwan, ROC
\textsuperscript{b}SYNergy Scien Tech Corporation, Science-based Industrial Park, Hsinchu 300, Taiwan, ROC
\textsuperscript{c}National Synchrotron Radiation Research Centre, Hsinchu 300, Taiwan, ROC

Received 23 June 2004; accepted 13 July 2004 by C.N.R. Rao
Available online 3 August 2004

Abstract

Structural and electrochemical studies have been carried out on LiNi_{0.8}Co_{0.17}Al_{0.03}O_{2} cathode material. X-ray diffraction refinement results confirmed that the material is in a pure phase having a layered structure. The electrochemical study on LiNi_{0.8}Co_{0.17}Al_{0.03}O_{2} shows high specific discharge capacity with good cycle life upon different charge-discharge. In situ X-ray absorption near edge structure analysis confirmed the transformation of Ni state from Ni\textsuperscript{3+} to Ni\textsuperscript{4+} during the delithiation process without affecting the valency of Co. The electrochemical results revealed that the doping of Co\textsuperscript{3+} and Al\textsuperscript{3+} stabilized the layered structure considerably during delithiation process.

PACS: 61.10.Ht; 82.45.Fk; 82.47.Aa

Keywords: B. Lithium ion batteries; C. Cathode material; E. Electric charge and discharge; X. XANES

1. Introduction

Rechargeable lithium ion batteries are well-accepted power source for a wide range of electronic devices. In lithium ion batteries different kinds of cathode materials such as LiCoO\textsubscript{2}, LiNiO\textsubscript{2}, LiMnO\textsubscript{2}, LiMn\textsubscript{2}O\textsubscript{4}, LiFePO\textsubscript{4} and their derivatives have been studied [1,2]. Among these compounds LiCoO\textsubscript{2} is commercially used as cathode material in rechargeable batteries [3]. Due to its high cost, limited capacity and environmental toxic nature, cobalt promotes exploration of a suitable alternative. In this aspect, LiNiO\textsubscript{2} has been proposed as an alternative cathode material for LiCoO\textsubscript{2} due to its structural similarity, higher capacity and low cost [4]. However, there are some difficulties in using LiNiO\textsubscript{2} as cathode material due to the following facts: (i) difficulty involved in the synthesis of stoichiometry LiNiO\textsubscript{2}, (ii) safety problems associated with the instability of delithiated form of LiNiO\textsubscript{2} (oxygen evolution occurs at elevated temperatures) and (iii) poor cyclic performance due to its structural instability upon electrochemical studies [5].

Some groups investigated the effect of other metal ion substitution on LiNi_{1-x}M_{x}O\textsubscript{2} (M = Mg, Mn, Co, Al or combination of two metal ions) in order to improve the electrochemical properties [6–9].

Among various metal ions doping, Co substitution (LiNi_{1-x}Co_{x}O\textsubscript{2}) showed a promising candidate for lithium ion batteries. This is due to the significant improvement in the thermal stability of delithiated phase of LiNiO\textsubscript{2}, thereby reducing the safety problems associated with it [10]. A small amount of doping of cost effective metal ion like Al\textsuperscript{3+} has profound effect on the structure and electrochemical
behavior of LiNi$_{1-x}$Co$_x$O$_2$. Based on the investigation of Ohzuku et al. [11], it is understood that the Al$^{3+}$ doping retains Ni in 3+ state and enhances the stabilization of layered structure. In addition, the doping of Al$^{3+}$ for Ni prevents the cell from over charging and hence improves the cell safety [12].

X-ray absorption spectroscopy with synchrotron radiation is a power technique, give information about the local structure and electronic state of absorbing atoms. In particular, the in situ X-ray absorption near-edge structure (XANES), a more effective tool has been used for different cathode materials such as LiNiO$_2$, Li(Mn$_{2-x}$Co$_x$)O$_4$ and Li$_{0.85}$Co$_{0.15}$O$_2$ to probe the change in oxidation state of metal ions during charge and discharge process [13–15].

In the present study, structural and electrochemical studies have been carried out on the LiNi$_{0.8}$Co$_{0.17}$Al$_{0.03}$O$_2$ sample. A detailed in situ XANES investigation has been carried out during the charging of electrodes to understand the real time change in the oxidation states of Ni and Co.

2. Experimental

The LiNi$_{0.8}$Co$_{0.17}$Al$_{0.03}$O$_2$ sample was obtained from Lithium Ion Business Unit, Rechargeable Battery Company, Matsushita Battery Industrial Co., Ltd, Japan. The sample was characterized by X-ray diffraction (XRD) using SCITAG (X1) diffractometer with Cu K$_\alpha$ radiation. The diffraction intensity was measured from 20 to 120° ($2\theta$) in a step size of 0.02° with a count time of 10 s per step. Rietveld refinement was performed using GSAS program to obtain the crystal structure parameters [16].

Scanning electron micrographs (SEM) were recorded to understand the surface morphology of LiNi$_{0.8}$Co$_{0.17}$Al$_{0.03}$O$_2$ using Hitachi S-2400.

Electrochemical studies were performed by assembling coin cells using Li metal as anode. Cathode films were prepared by mixing 94 wt% active material, 2.5 wt% S-P carbon, 2.25 wt% KS-6 carbon and 3 wt% KF 1300 binder (consists of N-methyl-2-pyrrolidone (NMP) and polyvinylidene difluoride in the ratio of 9:1). All ingredients were thoroughly mixed in a mechanical stirrer at ~3000 rpm for 1 h. The resultant slurry was coated uniformly onto an aluminum foil (used as current collector) which was dried at 75 °C for 1 h in a vacuum oven and further dried at 110 °C for 1 h. The cathode film was subjected to roll press and discs of size 1.3 cm diameter were punched out. The average active material present in each disc was ca. 23 mg/cm$^2$. The electrolyte consists of 1 M LiPF$_6$ (Merck) in EC (ethylene carbonate) and DMC (dimethyl carbonate) in a 1:1 volume ratio. A polymer membrane was used as separator. The coin-cells were assembled in an argon filled glove box. The cells were galvanostatically cycled at room temperature (MACCOR 4000) in the range of 3–4.25 V using current densities between 0.15 and 3 mA/cm$^2$.

Fort the in situ XANES measurement, 5 mm holes were made on both stainless steel cover plates of coin cell and Kapton film was pasted on the holes so as to allow X-ray to pass through the cell. The cell was hermetically sealed with O-ring. The whole cell was assembled in glove box with controlled levels of oxygen and moisture. In situ X-ray absorption experiments were carried out at the Wiggler beam line BL 17C of National Synchrotron Radiation Research Centre with an electron beam energy of 1.5 GeV and a beam current of 200 mA. A Si(111) double-crystal monochromator was employed for energy scanning. The XANES measurements at Co and Ni K-edges were performed at room temperature during charging in a transmission mode using ionization chambers to measure the intensities of the incident and transmitted X-ray beams. The XANES spectra were normalized with respect to the edge jump after completing the background subtraction using the code AUTOBK.

3. Results and discussion

The XRD refinement was carried out on the LiNi$_{0.8}$Co$_{0.17}$Al$_{0.03}$O$_2$ sample using GSAS (General Structure Analysis System) program and the XRD pattern is presented in Fig. 1. The refinement was performed by assuming the structure is similar to LiNiO$_2$ with a space group of R-3m. Refinement results show there is a good agreement between the experimental and calculated intensities. The crystal parameter values, atomic positions, isotropic thermal factors, occupancy and the reliability factors for the refinement are listed in Table. 1.

SEM micrographs of LiNi$_{0.8}$Co$_{0.17}$Al$_{0.03}$O$_2$ sample is shown in Fig. 2(a) and (b). Typical SEM images were captured under a magnification of 5K at different locations on the sample. As depicted in Fig. 2(a) and (b) the primary
particles are found to have similar particle size (1 \mu m), consists of well-defined crystallites, which agglomerates around 1 \mu m level.

The electrochemical property of LiNi_{0.8}Co_{0.17}Al_{0.03}O_2 was investigated at room temperature. Charge/discharge study has been performed using coin cells, which were cycled between 3.0 and 4.25 V vs. Li/Li^+. Fig. 3 shows the discharge curves for LiNi_{0.8}Co_{0.17}Al_{0.03}O_2 at different discharge rates. During the first discharge (0.1 C rate) a capacity value of 183 mA h g^{-1} is observed. The capacity gradually decreased as the discharge rate is increased. The observed capacities for the discharge rates 0.2, 0.5 and 1 C are 174, 165 and 158 mA h g^{-1}, respectively. Fig. 4 shows the cyclability of the cell up to 21 cycles. It is interesting to note that the capacity is retained up to first four cycles with a capacity fade of about 10% at the end of 21 cycles. In addition, the doping of Al^{3+} lowers the capacity fading to a larger extent [17]. A similar trend was observed by Kalyani et al. [12].

In situ XANES spectra were recorded for LiNi_{0.8}Co_{0.17}Al_{0.03}O_2 cathode material during charging of coin cell at Ni and Co K-edges. Fig. 5(a) and (b) show XANES spectra of Ni and Co K-edges during charging the battery at different
In the present study, many spectra were recorded throughout the charging process. Selected six scans were presented in the figures for both Ni and Co edges during delithiation process (charging) from 3 to 4.25 V.

From the XANES spectra at Ni and Co K-edges (Fig. 5(a) and (b)) it is observed that a weak absorption (labeled as 'A') around 8333 eV for Ni and 7709 eV for Co is due to a dipole forbidden transition for the electrons from 1s orbital to 3d orbital. A shoulder B with relatively low intensity is due to a 1s to 4p transition followed by a ligand to metal charge transfer process and the main peak C is due to 1s to 4p transition without the shake down process [15].

In the charging process Ni edge position (8350 eV shown as peak C) clearly shifted to higher energy values. This positive energy shift indicates that upon delithiation the average valence of Ni slowly shifted from 3$^+$ to 4$^+$. Upon careful examination of Fig. 5(a) it is also observed that there is no considerable change occurred in energy position from 3.0 to 3.15 V. At 3.74 V a drastic energy shift has been observed. This may be due to charge inefficiency caused by the growth of surface electrolyte interphase up to 3.15 V. After occurrence of drastic shift in energy position at 3.74 V, again there is no considerable energy shift observed from 3.74 to 4.25 V. Based on the above observations it is concluded that at initial stages of charging (delithiation process) Ni oxidizes to higher state. Similar kinds of result were reported by Naki et al. [18] and Balasubramanian et al. [19].

As far as cobalt K-edge is concerned no chemical shift is observed when compared to Ni K-edge. Reported data [19] reveal that on cathode delithiation charge compensation occurred first on Ni and then on the Co atom. There is no shift was observed in Co K-edge position up to 4.5 V, indicating that none of the cobalt was oxidized to Co$^{4+}$ since XANES was recorded only up to 4.25 V in the present study, it is understood that no shift appeared in Co K-edge.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Uiso (Å$^2$)</th>
<th>Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>0.0043 (12)</td>
<td>1.0000</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0266 (7)</td>
<td>0.8000</td>
</tr>
<tr>
<td>Co</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0266 (7)</td>
<td>0.1700</td>
</tr>
<tr>
<td>Al</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0266 (7)</td>
<td>0.0300</td>
</tr>
<tr>
<td>O</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.2586</td>
<td>0.0235 (11)</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crystal parameters</th>
<th>Reliability factors</th>
<th>Inter atomic distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group: R-3m</td>
<td>Rp = 1.66%</td>
<td>Li–O 2.1058 (7)</td>
</tr>
<tr>
<td>a=b=2.8654 (13) Å, c=14. 1699 (7) Å</td>
<td>Rwp = 2.09%</td>
<td>Ni–O 1.9641 (7)</td>
</tr>
<tr>
<td>α=90°, β=90° and γ = 120°</td>
<td>$\chi^2=0.75$</td>
<td>Co–O 1.9641 (7)</td>
</tr>
<tr>
<td>Cell volume = 100.757(8) Å$^3$</td>
<td></td>
<td>Al–O 1.9641 (7)</td>
</tr>
</tbody>
</table>

![Figure 5](image_url)

Fig. 5. (a). Ni K-edge XANES spectra of LiNi$_{0.8}$Co$_{0.17}$Al$_{0.03}$O$_2$ (b) Co K-edge XANES spectra of LiNi$_{0.8}$Co$_{0.17}$Al$_{0.03}$O$_2$ during charging.
4. Conclusions

The XRD refinement shows that the sample is in a single phase. Based on the charge-discharge cycling study on LiNi0.8Co0.17Al0.03O2 coin cells, it is inferred that it has higher specific discharge capacity of 183 mA h g⁻¹ at 0.1 C. The discharge capacity is gradually decreased to 158 mA h g⁻¹ at a discharge rate of 1 C. The in situ XANES study revealed that the Ni K-edge spectra are shifted to a higher energy value during charging of the cell. However, there is no significant shift observed at the Co K-edge spectra even up a potential of 4.25 V. This result confirmed that the charge compensation occurs only on Ni ions during delithiation process.

Acknowledgements

This work was supported by National Science Council (NSC) under the grant number NSC 93-2113-M-002-006, Taiwan, ROC. The authors acknowledge with gratitude the financial support extended by NSC.

References