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The Influence of Surface Chemistry on the Rate Capability of LiNi0.5Mn0.5O2 for Lithium Rechargeable Batteries

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Subsequent annealing at 700°C enhances the rate capability of LiNi0.5Mn0.5O2, delivering 180 mA/h at 55°C and 8C rate compared to 50 mA/h of LiNi0.5Mn0.5O2 quenched from 1000°C. Although Rietveld refinement analyses of X-ray diffraction (XRD) data showed that there were no significant changes in the lattice parameters and cation distributions of the layered structure before and after annealing, XRD and X-ray photoelectron spectroscopy revealed that annealing significantly reduced surface impurity phases such as lithium carbonate and Mn4+ containing species. The influence of surface chemistry changes on the rate capability of LiNi0.5Mn0.5O2 was discussed.

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LiNi0.5Mn0.5O2 is one of the promising positive electrode materials for large-scale lithium-ion batteries because of its high specific capacity (up to ~200 mA/h/g),1,2 thermal stability associated with redox-active Ni2+ and inactive Mn4+,3,4 and low material cost. LiNi0.5Mn0.5O2 crystallizes in the O3 layered structure (space group R3m), having typically ~10% interlayer mixing of Ni and Li ions (i.e., ~10% Ni in the Li layer and ~10% Li in the Ni layer), which is much greater than that of LiCoO2 and LiCo0.15Ni0.85O2. Previous studies have shown that decreasing the interlayer mixing can increase the rate capability of LiNi0.5Mn0.5O2, which is attributed to faster Li diffusion with increasing layered character of LiNi0.5Mn0.5O2. More recently, researchers have shown that the rate capability of Li/LiNi0.5Mn0.5O2 cells can be improved greatly by applying surface coatings such as AlF3. Although the physical origin is not understood fully, the coating influence has been attributed to the suppression of transition-metal dissolution and the reduction in the charge-transfer resistance of lithium cells. In this article, we show that annealing of LiNi0.5Mn0.5O2 at 700°C can significantly increase the rate capability of LiNi0.5Mn0.5O2 at room and elevated temperatures. The influence of annealing on the bulk crystal structure and surface chemistry of LiNi0.5Mn0.5O2 quenched from 1000°C is examined by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively, which is related to the difference in the rate capability of quenched and annealed LiNi0.5Mn0.5O2.

Experimental

A quenched LiNi0.5Mn0.5O2 sample was prepared by heating a stoichiometric mixture of Li2CO3 and NiMnO2 in air at 1000°C for 30 min, which was quenched to room temperature by pressing between two copper plates. An annealed sample was obtained by heating the quenched sample at 700°C in air for 12 h and then cooling slowly to room temperature. The as-prepared quenched and annealed LiNi0.5Mn0.5O2 samples were examined by XRD using a Rigaku diffractometer equipped with a high power rotating copper anode. The Rietveld analysis was conducted using FullProf,11 where the nominal stoichiometry was constrained and the detailed constraints used were described elsewhere.12

The surface chemical compositions of the LiNi0.5Mn0.5O2 samples were investigated by XPS using a Physical Electronics model 5400 spectrometer. The data were collected using monochromatic Mg Kα (1253.6 eV) X-ray source operating at 350 W (15 kV and 23 mA). The analyzed area was set to 1 × 3.5 mm. The C 1s, O 1s, and Li 1s lines were deconvoluted using a Shirley-type background and a combined Gaussian-Lorentzian line shape, whereas the Mn and Ni 2p lines were deconvoluted using an asymmetric line shape. Other analysis details were described elsewhere.

LiNi0.5Mn0.5O2 composite electrodes with 10 wt % poly(vinylidene fluoride) and 10 wt % Super P carbon black were prepared for electrochemical measurements and details can be found in our previous work.13 A two-electrode cell (Tomcell Co. Ltd., Type TJ-AC), having a lithium metal foil and a LiNi0.5Mn0.5O2 composite electrode separated by two pieces of Celgard 2500, was assembled in an argon-filled glove box (oxygen and water levels less than 2.0 and 1.5 ppm, respectively). 1 M LiPF6 dissolved in ethylene carbonate/dimethyl carbonate (3/7 by volume) (Kishida Chem. Co., Ltd.) was used as the electrolyte. Electrochemical measurements were carried out by using a Solartron 1470 battery testing unit at 30 and 55°C. The rate-capability data for the quenched and annealed samples were collected first from 1/25C (11.2 mA/g or ~0.04 mA/cm²) and then to 8C (2240 mA/g or ~8.3 mA/cm²), which were reproduced in multiple cells.

Results and Discussion

Although quenched and annealed LiNi0.5Mn0.5O2 were found to have comparable specific discharge capacities at low rates, annealed LiNi0.5Mn0.5O2 exhibited considerably higher specific capacities than quenched LiNi0.5Mn0.5O2, as shown in Fig. 1. In particular, annealed LiNi0.5Mn0.5O2 was shown to deliver ~120 mA/h/g on discharge at 8C, which is much higher than quenched LiNi0.5Mn0.5O2 having ~50 mA/h/g at 30°C. Although it is very difficult to compare the rate capability data with those of the previous work in detail due to different C rate definitions, electrode thicknesses, electrode packing densities, etc., the rate capability of annealed LiNi0.5Mn0.5O2 is higher than that of the quenched samples reported previously, whereas the rate capability of annealed LiNi0.5Mn0.5O2 generally compares well with that of state-of-the-art high rate LiNi0.5Mn0.5O2.9,3,4,15 The rate capability of annealed LiNi0.5Mn0.5O2 was further increased significantly at 55°C, delivering ~180 mA/h/g on discharge at 8C. In contrast, there was no significant increase in the rate capability of the quenched sample at 55°C. Moreover, annealed LiNi0.5Mn0.5O2 showed an enhanced capacity retention upon cycling compared to quenched LiNi0.5Mn0.5O2, as shown in Fig. 2. The discharge capacities of annealed LiNi0.5Mn0.5O2 reached a steady-state value of ~190 mA/h/g on discharge after 20 cycles to 4.6 V, which is comparable to the highest value reported previously.10,11,12 To understand the origin of the difference in the electrochemical performance characteristics of quenched and annealed LiNi0.5Mn0.5O2, XRD and XPS data are discussed below.

XRD analysis confirmed that both quenched and annealed LiNi0.5Mn0.5O2 had rhombohedral symmetry (space group R3m), as

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shown in Fig. 3a. The lattice parameters in the hexagonal setting for quenched LiNi$_{0.5}$Mn$_{0.5}$O$_2$ [$a_{\text{hex}} = 2.88982(6)$ Å and $c_{\text{hex}} = 14.2940(3)$ Å] are very comparable to those of annealed LiNi$_{0.5}$Mn$_{0.5}$O$_2$ [$a_{\text{hex}} = 2.88916(6)$ Å and $c_{\text{hex}} = 14.2940(3)$ Å]. In addition, the intensity ratios between the (003)$_{\text{hex}}$ and (104)$_{\text{hex}}$ peaks are very similar before and after annealing (Fig. 1b), which indicates that there is no significant change in the cation distribution during annealing. This is further confirmed by the Rietveld refinement analysis showing 11 and 9% Ni in the lithium layer per formula unit before and after annealing, which is very comparable to those reported previously for LiNi$_{0.5}$Mn$_{0.5}$O$_2$ synthesized from solid-state routes. The minor differences in the structural parameters of quenched and annealed LiNi$_{0.5}$Mn$_{0.5}$O$_2$ are very unlikely to give rise to the apparent different rate capability measured in this study.

The XPS analysis of the C 1s and O 1s regions indicated that the amount of surface carbonate species for annealed LiNi$_{0.5}$Mn$_{0.5}$O$_2$ was significantly lower than that of quenched LiNi$_{0.5}$Mn$_{0.5}$O$_2$, as shown in Fig. 4. The C 1s line was deconvoluted into four components: (i) adventitious hydrocarbon at 285.0 eV; (ii) carbon in C—O (286.5 eV) and (O—C—O/C=O) (~288/287.5 eV); (iii) carbon in the carboxylic groups (O—C=O) at 289 eV; and (iv) carbon in the carbonate (CO$_3^{2−}$) form (near 290.6 eV). Of significance, the surface carbonate contribution to C 1s for quenched LiNi$_{0.5}$Mn$_{0.5}$O$_2$ is considerably larger than that for annealed LiNi$_{0.5}$Mn$_{0.5}$O$_2$, as shown in Table I. Correspondingly, in the O 1s region, the relative intensity of surface oxygen species such as surface terminated oxy-
gen atoms\(^{21}\) and oxygen atoms doubly bound to carbon atoms in 
Li\(_2\)CO\(_3\) (~532.0 eV)\(^{25}\) to lattice oxygen (529.9 eV) is greater for quenched than annealed LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\). This result agrees well with the observation that a small amount of Li\(_2\)CO\(_3\) was detected in the XRD data of quenched but not of annealed LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\), as shown in Fig. 3b.

The XPS analysis of the Mn 2p3/2 region showed that Mn was present as a mixture of Mn\(^{3+}\) and Mn\(^{4+}\) for quenched LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\), and having Mn/Ni ratios greater than 1 and mixed Mn\(^{3+}\)-containing phases.

We showed that an additional annealing step can significantly enhance the rate capability of LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) relative to quenched LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\). The enhanced rate capability can be attributed to making surface chemistry more stoichiometric having Li\(_{2+}\)Mn\(_{0.5}\)O\(_{4}\) during annealing by reducing surface Li\(_2\)CO\(_3\) and Mn\(^{3+}\)-containing phases.

**Conclusions**

We showed that an additional annealing step can significantly enhance the rate capability of LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) relative to quenched LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\). This hypothesis agrees with the fact that the difference in the rate capability of quenched and annealed LiNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) is greater at 55°C than at room temperature as the Mn dissolution\(^{29}\) and growth of impeding films are expected to increase at higher testing temperatures.

**Acknowledgments**

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**References**


**Table I. Summary of XPS results including BE in eV, fwhm, and atomic percents.**

<table>
<thead>
<tr>
<th>Peak</th>
<th>Assignment</th>
<th>Quenched</th>
<th>Annealed</th>
</tr>
</thead>
<tbody>
<tr>
<td>C Is</td>
<td>Hydrocarbon (285.0 eV)</td>
<td>285.0, 2.25, 5.0</td>
<td>285.0, 2.35, 14.6</td>
</tr>
<tr>
<td>C—O (~286.1 eV)</td>
<td>287.0, 1.6, 0.8</td>
<td>287.3, 1.34, 0.4</td>
<td></td>
</tr>
<tr>
<td>O—C=O (~289 eV)</td>
<td>288.7, 1.67, 1.3</td>
<td>288.7, 2.00, 1.2</td>
<td></td>
</tr>
<tr>
<td>CO(_{2}) (~290.3 eV)</td>
<td>290.4, 1.88, 3.1</td>
<td>290.7, 2.00, 1.3</td>
<td></td>
</tr>
<tr>
<td>Total C</td>
<td></td>
<td>10.2</td>
<td>5.9</td>
</tr>
<tr>
<td>O Is</td>
<td>Surface oxygen in LiNi(<em>{0.5})Mn(</em>{0.5})O(<em>2) (~531.7 eV) and carbonates CO(</em>{2}) (~532.1 eV)</td>
<td>532.0, 2.11, 18.8</td>
<td>532.3, 2.27, 10.6</td>
</tr>
<tr>
<td>Total O</td>
<td></td>
<td>59.7</td>
<td>53.6</td>
</tr>
<tr>
<td>Mn 2p3/2</td>
<td>LiNi(<em>{0.5})Mn(</em>{0.5})O(_2) (~642.5 eV)</td>
<td>642.4, 2.69, 12.5</td>
<td>642.7, 2.74, 12.8</td>
</tr>
<tr>
<td>Ni 2p3/2</td>
<td>LiNi(<em>{0.5})Mn(</em>{0.5})O(_2) (854.2-854.9 eV)</td>
<td>855.2, 2.35, 10.5</td>
<td>855.3, 2.31, 10.3</td>
</tr>
<tr>
<td>Ni 2p3/2 sat.</td>
<td>Li(_{2})CO(_3) (~532.0 eV)</td>
<td>861.7, 3.87, 7.2</td>
<td>861.8, 3.66, 5.8</td>
</tr>
</tbody>
</table>

BE = binding energy, fwhm = full width at half-maximum.

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