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The Influence of Heat-Treatment Temperature on the Cation Distribution of LiNi0.5Mn0.5O2 and Its Rate Capability in Lithium Rechargeable Batteries

Naoaki Yabuuchi, Yi-Chun Lu, Azzam N. Mansour, Shuo Chen, and Yang Shao-Horn

LiNi0.5Mn0.5O2 samples were prepared from NiMnO2 and Li2CO3 in a range of temperatures from 900 to 1050°C. Synchrotron X-ray diffraction analysis combined with X-ray absorption spectroscopy showed that LiNi0.5Mn0.5O2 segregated into one major Ni4+O-enriched phase and one minor Li2Mn4+O3-enriched phase, where the extent of segregation decreased with increasing synthesis temperature from 900 to 1050°C. Scanning and transmission electron microscopy combined with energy dispersive X-ray spectroscopy revealed that the segregated domains exist in individual particles. Although all of the LiNi0.5Mn0.5O2 samples showed comparable specific capacity (~200 mAh/g) and capacity retention at low current densities, the rate capability of LiNi0.5Mn0.5O2 of 900°C is lower than that of LiNi0.5Mn0.5O2 of 1000°C. As X-ray photoelectron spectroscopy analysis showed that all of the LiNi0.5Mn0.5O2 samples had comparable surface chemistry, the higher rate capability of LiNi0.5Mn0.5O2 of 1000°C can be attributed to reduced cation segregation of Ni4+O-enriched domains in the layered structure of the major phase, having potentially faster lithium diffusion than that of LiNi0.5Mn0.5O2 of 900°C.© 2010 The Electrochemical Society.

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Experimental

Preparation of NiMnO2.—Because LiNi0.5Mn0.5O2 prepared from NiMnO2 shows the highest reversible capacities reported, NiMnO2 was chosen as the starting material. NiMnO2 is known to crystallize into ilmenite-type structure with the space group R3̅m which consists of octahedrally coordinated divalent nickel and tetravalent manganese ions, and ~10% of Ni and Li ions displaced in the lithium and transition metal layers. Displaced Li ions (0.71 Å) in the transition metal layer induces in-plane cation ordering of 3ahex × 3ahex-type, where the stacking sequence of the ordered layers can vary from “abab” to “abcabc.” LiNi0.5Mn0.5O2 can deliver ~200 mAh/g of rechargeable discharge capacity at low rates with voltage cutoff limits of 2.5 and 4.5 V, where Ni2+ to Ni4+ via Ni3+ is the active redox couple upon lithium deintercalation from LiNi0.5Mn0.5O2 while Mn4+ ions remain inactive.

Considerable research efforts have been focused on developing LiNi0.5Mn0.5O2 as the positive electrode materials in large-scale lithium rechargeable batteries. LiNi0.5Mn0.5O2 has the O3 layered structure (space group R3̅m), which consists of octahedrally coordinated divalent nickel and tetravalent manganese ions, and ~10% of Ni and Li ions displaced in the lithium and transition metal layers. Displaced Li ions (0.71 Å) in the transition metal layer induces in-plane cation ordering of 3ahex × 3ahex-type, where the stacking sequence of the ordered layers can vary from “abab” to “abcabc.” LiNi0.5Mn0.5O2 can deliver ~200 mAh/g of rechargeable discharge capacity at low rates with voltage cutoff limits of 2.5 and 4.5 V, where Ni2+ to Ni4+ via Ni3+ is the active redox couple upon lithium deintercalation from LiNi0.5Mn0.5O2 while Mn4+ ions remain inactive.

Decreasing the interlayer mixing is shown to increase the rate capability of LiNi0.5Mn0.5O2, which is attributed to faster Li diffusion with increasing layered character of LiNi0.5Mn0.5O2. In this study, NiMnO2 was chosen as the starting material. NiMnO2 is known to crystallize into ilmenite-type structure with the space group R3̅m which consists of a slightly distorted hexagonal close-packed oxygen array having octahedral Ni2+ and Mn4+ ions. In this study, NiMnO2 was prepared by a coprecipitation method. 1 mol/l of the Ni(NO3)2 and Mn(NO3)2 solution (1:1 in molar ratio) was added slowly using a burette into 1 mol/l of tetramethyl ammonium hydroxide solution (20% excess amount in volume) containing 3 mol/l of NH4OH as a chelating agent at room temperature. Argon gas was purged into tetramethyl ammonium hydroxide solution for 30 min before the titration process and was continued until the completion of the titration process. The resulting yellowish green (before exposing into air) Ni and Mn hydroxide was filtered and washed by deionized water to remove undesirable impurities, i.e., NO3− (CH3)4N+, and NH4+. The precipitates were dried at 200°C and then calcined in air at 680°C for 12 h.

Preparation of LiNi0.5Mn0.5O2 powder samples.—LiNi0.5Mn0.5O2 samples were prepared by heating the mixture of NiMnO2 and Li2CO3 at 900, 950, 1000, and 1050°C for 30 min. NiMnO2 and Li2CO3 were mixed with a mortar and pestle and pressed into a pellet. The pellet was heated in a tube furnace under a flow of dry air at a heating rate of 10°C/min. After holding at each targeted temperature for 30 min, the power supply to the furnace was turned off to allow the pellets to cool to room temperature. Three percent of excess Li in molar ratio was used to compensate for the volatilization of Li during synthesis, and the reaction with the crucible.

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Synchrotron XRD experiments.— Synchrotron radiation in BL02B2 station at SPring-8 (Sayo-gun, Hyogo, Japan), which was equipped with a large Debye–Scherer camera, was used to collect the X-ray diffraction data. The incident beam was adjusted to a wavelength of 0.5 Å by a Si(111) monochromator to minimize the absorption by the samples. The wavelength was calibrated to be 0.5027 Å using a CeO2 standard (a = 5.41111(1) Å). The diffraction patterns were collected in the 2θ-range of 0–75°. A few milligrams of each sample was placed in a Lindeman capillary (0.5 mm diameter and approximately 2 cm height) for the XRD measurements. The XRD patterns were recorded on an imaging plate for 20 min. Phase analysis was performed using FULLPROF, with a two-phase model.

XPS experiments.— XPS experiments of LiNi0.5Mn0.5O2 samples synthesized at different temperatures were performed at the BL-12C beam line of the Photon Factory Synchrotron Source in Japan, operating at electron energy of 2.5 GeV and a stored current in the range of 300 to 450 mA. XPS experiments of NiO, NiMnO3, and Li2MnO3 reference samples were conducted at the X11A beam line of the National Synchrotron Light Source with the electron storage ring operating at electron energy of 2.8 GeV and a stored current in the range of 200–300 mA. The Ni K-edge (8333.0 eV) and the Mn K-edge (6539.0 eV) X-ray absorption fine structure (XAFS) spectra were collected in a transmission mode at 298 K using a Si(111) double crystal monochromator. Intensities of the incident and transmitted X rays were measured using ionization chambers filled with appropriate gases. Powders of various materials were mixed with BN and pressed into self-supporting pellets. The weight fraction for the oxide in the mixture was adjusted to yield an absorption edge jump suitable for the XAFS measurements.

The Ni K- and Mn K-edge spectra were calibrated by setting the first inflection point energy for elemental Ni and Mn to 8333.0 eV.41 The K-edge absorption was isolated by fitting the pre-edge region (−300 to −100 eV relative to the edge energy) with a second order polynomial, extrapolating over the entire range of the spectrum, and subtracting the pre-edge background from the entire spectrum. Energy dependent normalization was applied using the atomic absorption, which was determined by fitting the post edge region to a fourth order polynomial. The photoelectron wave number was derived by setting the inner potential to the first inflection point energy for elemental Ni and Mn to 8333.0 eV.41 Details of quantitative analysis of Ni and Mn EXAFS and Fourier transforms are included in the supplementary information section.46

Scanning and transmission electron microscopy and energy dispersive X-ray spectroscopy experiments.— Compositional studies were performed by X-ray energy dispersive spectroscopy (EDS) with the same transmission electron microscopy (TEM) in both STEM and TEM modes. The EDS results were collected by INCA software (version 4.08, Oxford Instruments Analytical Ltd., Abingdon, UK). Averaged compositional results of many particles were collected in STEM mode with a typical acquisition time of 300 s. Individual particles were studied in STEM mode with an electron beam diameter of 0.5 nm. In the STEM mode, elemental maps were generated to study the elemental distribution. In addition, a number of spot captures (2 nm in diameter) were taken within the individual particle, where the local composition at the nanoscale can be quantified from Mn K series and Ni K series.

X-ray photoelectron spectroscopy experiments.— Surface chemical compositions of LiNi0.5Mn0.5O2 samples were investigated by XPS using a Kratos Axis Ultra spectrometer (Manchester, U.K.) with a monochromatized aluminum X-ray source (Al Kα). The analyzed area was set to a minimum size of 1.1 mm diameter spot. Multiplex spectra of various photoemission lines were collected using analyzer pass energy of 20.0 eV. All samples were analyzed at an electron takeoff angle of 90° relative to the sample plane. The C 1s and O 1s lines were deconvoluted using a Shirley-type background and a combined Gaussian–Lorentzian line shape. All spectra were calibrated with the C 1s photoelectron spectrum for adventitious hydrocarbons at 285.0 eV.

Results and Discussion

Synchrotron X-ray powder diffraction analysis.— Synchrotron X-ray diffraction data (Fig. 1) showed that the NiMnO3 sample used to synthesize LiNi0.5Mn0.5O2 was nearly single phase having an illuiminate-type structure (R3). A minute amount of Ni5MnO8 (space group Fm3m) impurity less than 3% by volume was detected. Interestingly, Rietveld analysis (Table I) revealed that not only Ni and Mn ions were ordered on two different 6c sites in the structure as evidenced by the presence of (101)hex reflection (Fig. 1 inset) but also Ni ions were primarily divalent and Mn ions were primarily tetravalent as evidenced by interatomic distances for Mn4+–O (1.91 Å) and Ni2+–O (2.05 Å). In addition, the Ni6MnO8 crystals were found by TEM to have a plate-like morphology with relatively uniform sizes in the range of 50–100 nm.

Synchrotron X-ray diffraction patterns of LiNi0.5Mn0.5O2 samples, whose intensities were normalized based on the (003)hex Bragg diffraction line, are shown in Fig. 2. All samples can be indexed into the α-NaFeO2-type layered structure with space group
Table I. Crystallographic parameters of NiMnO$_3$ analyzed by the Rietveld refinement. Ni$_x$MnO$_x$ was found as a minor phase. Reliable parameters were obtained by using a two-phase model.

<table>
<thead>
<tr>
<th>Phase</th>
<th>NiMnO$_3$</th>
<th>Ni$_x$MnO$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$R3\bar{m}$</td>
<td>$Fm\bar{3}m$</td>
</tr>
<tr>
<td>Lattice constants</td>
<td>$\alpha_{\text{hex}} = 4.90388(9)$ Å</td>
<td>$a = 8.3168(1)$ Å</td>
</tr>
<tr>
<td>Wyckoff site</td>
<td>$g^a$</td>
<td>$y$</td>
</tr>
<tr>
<td>Ni</td>
<td>6c</td>
<td>1.00</td>
</tr>
<tr>
<td>Mn</td>
<td>6c</td>
<td>1.00</td>
</tr>
<tr>
<td>O</td>
<td>18f</td>
<td>1.00</td>
</tr>
<tr>
<td>Interatomic distances</td>
<td>Ni–O = 2.052 Å</td>
<td>Mn–O = 1.908 Å</td>
</tr>
<tr>
<td>$R_B$ (%)</td>
<td>4.76</td>
<td>10.8</td>
</tr>
<tr>
<td>$R_{wp}$ (%)</td>
<td>11.2</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Not refined.

$R3m$. Three important findings are noted. First, the intensities of diffraction lines associated with the $\sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$-type ordering decreased (indicating reduced in-plane cation ordering) as the synthesis temperature increased, as shown in Fig. 2a inset. Second, the full-width at half-maximum (fwhm) of all diffraction lines decreased with increasing synthesis temperature indicating increased crystallinity and/or increased cation uniformity in the structure. Third, high-angle peak shoulders were noted for some diffraction lines and their intensities were reduced with increasing synthesis temperature, as shown by the $(104)_{\text{hex}}$, $(108)_{\text{hex}}$, and $(110)_{\text{hex}}$ reflections enlarged in Figs. 2b and 2c. The presence and changes in the intensity of these high-angle peak shoulders for LiNi$_0.5$Mn$_0.5$O$_2$ samples as a function of synthesis temperature were revealed for the first time, to the authors’ knowledge, presumably due to the high-resolution of the monochromatized synchrotron X-rays. Among all of the diffraction lines and the LiNi$_0.5$Mn$_0.5$O$_2$ samples, the shoulder is most pronounced for the $(110)_{\text{hex}}$ peak of LiNi$_0.5$Mn$_0.5$O$_2$-900C (Fig. 2c), whose peak position is most sensitive to in-plane cation–cation distances. This observation suggests that distributions of Ni and Mn ions are not uniform, particularly in the case of LiNi$_0.5$Mn$_0.5$O$_2$-900C and the uniformity increases with increasing synthesis temperature. It should be mentioned that the impurity phase (Ni$_x$MnO$_x$) in the NiMnO$_3$ precursor was not detected in the LiNi$_0.5$Mn$_0.5$O$_2$ samples.

Further experiments show that the presence of the minor impurity phase cannot result from the short heat-treatment time of 30 min used in this study as Li$_2$CO$_3$ completely reacts with NiMnO$_3$ to form the major phase and the minor phase within 30 min at synthesis temperatures of 900–1000°C. This is supported by the following observations. First, increasing heat-treatment time at 900°C to 18 h did not improve the uniformity of Ni and Mn distributions (no change in the intensity of the $(110)_{\text{hex}}$ peak shoulder on the right) but led to increased crystallinity of the major phase (clearer peak splitting between the Cu Ko1 and Ko2 diffraction peaks). Second, although increasing temperature to 1000°C led to a more uniform cation distribution, increasing heat-treatment time from 30 min to 8 h did not further improve the cation distribution but increased crystallinity (including growth of particle sizes) of the major phase.

To provide insights into the nonuniformity of Ni and Mn distributions in LiNi$_0.5$Mn$_0.5$O$_2$ samples, a detailed phase analysis was performed. We found that two rhombohedral phases with space group $R3m$ but having slightly different lattice parameters are required to satisfactorily generate the experimental data. Experimental and calculated patterns based on the two-phase model for LiNi$_0.5$Mn$_0.5$O$_2$-900C are compared in Fig. 3, which shows that the high diffraction angle shoulder can be explained satisfactorily by the presence of a minor phase with $a_{\text{hex}} = 2.874$ Å, $\epsilon_{\text{hex}} = 14.291$ Å (in addition to a major phase with $a_{\text{hex}} = 2.891$ Å, $\epsilon_{\text{hex}} = 14.295$ Å).
The difference in $d_{\text{hex}}$ between these two phases leads to the peak asymmetry of each Bragg diffraction line, especially for the (110)$_{\text{hex}}$ (Fig. 2c). The contribution of the minor phase in LiNi$_{0.5}$Mn$_{0.5}$O$_2$-1000°C is much smaller relative to that for LiNi$_{0.5}$Mn$_{0.5}$O$_2$-900°C, as shown in Figs. 3b and 3c. This detailed phase analysis also revealed that the diffraction lines indicative of in-plane ordering of the 3$a_{\text{hex}}$ × 3$a_{\text{hex}}$-type belong to the minor phase and not the major phase, where the angles for (1/3 1/3 1/3)$_{\text{hex}}$ calculated from the fundamental diffractions (1 1/1)$_{\text{hex}}$ of the major phase clearly deviate from the observed positions shown in Fig. 3a inset. This is consistent with the reduced intensities of these diffraction lines as the synthesis temperature increased (Fig. 2a inset). It is interesting to note that there is no XRD evidence for cation ordering (no superlattice reflections) in the major layered phase of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ unlike that suggested in an earlier study.20

The lattice parameters, unit cell volume and phase fractions of the major and minor phases in LiNi$_{0.5}$Mn$_{0.5}$O$_2$ were compared as a function of synthesis temperature in Fig. 4. The lattice parameters of the major phase in this study are comparable to those of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ reported previously.1,2,5,15,20,22,28,30 The $d_{\text{hex}}$ lattice parameter of the major phase decreased while the $c_{\text{hex}}$-axis parameter remained nearly constant as the synthesis temperature increased (Fig. 4a), leading to smaller unit cell volume of the main phase at higher synthesis temperature (Fig. 4b). On the other hand, the unit cell volume of the minor phase remained constant in the temperature range of 900–1050°C. Of significance to note is that the fraction of the minor phase was reduced from ~17 to ~6% by increasing synthesis temperature from 900 to 1050°C, as shown in Fig. 4c. In addition to reduced unit cell volume, detailed phase analysis with the two-phase model revealed that the degree of cation interlayer mixing (between the 3a and 3b sites) was reduced for the main phase at higher temperatures as evidenced by the increased ratio of the integrated area of the (003)$_{\text{hex}}$ and (104)$_{\text{hex}}$ peaks. This indicates that the cation distributions of Ni and Mn became more uniform within and across different particles with increasing synthesis temperature.

From these XRD findings, it is hypothesized that the major phase has Ni$^{2+}$O-rich ($Fm\overline{3}m$) domains in the matrix of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ ($R\overline{3}m$) while the minor phase has Li$_2$MnO$_3$-rich regions. This phase segregation cannot be explained by poor mixing of Ni and Mn during synthesis as the NiMnO$_3$ precursor used to make the LiNi$_{0.5}$Mn$_{0.5}$O$_2$ samples in this study was nearly phase pure having primarily ordered Ni$^{2+}$ and Mn$^{4+}$ ions (Table I and Fig. 1). With
increasing synthesis temperature, the fraction of the minor phase decreases, which can be explained by the hypothesis that Li$_2$MnO$_3$-rich and NiO-rich regions can react to form LiNi$_{0.5}$Mn$_{0.5}$O$_2$ (one limiting case, 0.5Li$_2$MnO$_3$ + 0.5NiO $\rightarrow$ LiNi$_{0.5}$Mn$_{0.5}$O$_2$). In addition, NiO-rich domains introduce Ni ions into the lithium layer and interlayer mixing, and the degree of interlayer mixing decreases with increasing temperature from 900 to 1000°C, which is supported by the lower integrated intensity ratio of the (003)$_{\text{hex}}$ line to that of the (104)$_{\text{hex}}$ line. Moreover, as the unit cell volume of the Ni-rich major phase decreases from 900 to 1000°C while that of the Li$_2$MnO$_3$-rich minor phase remains constant (Fig. 4b), it is proposed that the chemical composition of the minor Mn-rich phase is unchanged but the phase fraction decreases with increasing synthesis temperature. Lastly, it is interesting to note that cation segregation into two layered phases (with cation interlayer mixing) in LiNi$_{0.5}$Mn$_{0.5}$O$_2$ is analogous to that reported for LiNi$_{1/3}$Al$_{2/3}$O$_2$ (Ref. 33) but is dissimilar to that in Li$_{1-x}$Mn$_x$Fe$_2$O$_4$ which segregates into one major disordered rock-salt (Fm3m) phase and one minor (layered structure; R3m) phase.

**Synchrotron X-ray absorption spectroscopy analysis.**— Normalized Ni and Mn x-ray absorption near-edge structure (XANES) spectra of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ synthesized at 900 and 1000°C are shown in Figs. 5a and 5b. Clearly, the Ni and Mn XANES data for the LiNi$_{0.5}$Mn$_{0.5}$O$_2$ samples are very similar regardless of synthesis temperatures in the range of 900–1000°C. The XANES spectra are comparable to those reported previously for samples with similar composition.$^6,10$ Using XANES spectra of NiO, NiMnO$_3$ and Li$_2$MnO$_3$ as standards for Ni$^{2+}$ and Mn$^{4+}$, we confirm that Ni and Mn in LiNi$_{0.5}$Mn$_{0.5}$O$_2$ are present primarily as Ni$^{2+}$ and Mn$^{4+}$. Some evidence of minority Mn$^{3+}$ species was noted by comparing the pre-edge peaks of Mn K-edge of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ synthesized at 900 and 1000°C with those of NiMnO$_3$ and Li$_2$MnO$_3$, where the intensity of the A1 peak (the transition to $t_2$ orbitals) is greater than that of the A2 peak (the transition to $e_g$ orbitals$^{47}$), as shown in Fig. 5b inset. If some Ni$^{3+}$ ions replace some Li$^+$ ions in the minor Li$_2$MnO$_3$-enriched phase, this can result in the formation of some Mn$^{3+}$.

Fourier transforms of Ni and Mn k$^3$-weighted EXAFS spectra of these samples along with those for NiO, NiMnO$_3$, and Li$_2$MnO$_3$ are shown in Figs. 5c and 5d. Similar to the XANES spectra, the Fourier transforms of Ni in LiNi$_{0.5}$Mn$_{0.5}$O$_2$ are qualitatively similar to those of NiO. Local structure parameters for the first and second coordination shells of Mn and Ni derived from quantitative analysis of Fourier transforms are summarized in Table II. The Ni–O (2.05 Å) and Mn–O (1.91 Å) distances in LiNi$_{0.5}$Mn$_{0.5}$O$_2$ are comparable to those of the reference materials (2.09 Å for Ni$^{2+}$; 2.05 Å for Ni$^{3+}$Mn$_{0.5}$O$_2$; 1.91 Å for Li$_2$MnO$_4$ and NiMnO$_4$). They are also in good agreement with those reported previously$^9$ for LiNi$_{0.5}$Mn$_{0.5}$O$_2$ (2.06 and 1.92 Å). In addition, the average of the Ni–O and Mn–O distances of 1.98 Å is consistent with that estimated by synchrotron XRD (1.98 Å), which is different from the average of the Ni–O and Mn–O distances. Interestingly, the EXAFS-determined Ni–Mn/Ni distance (2.92 Å), which is intermediate to that of Ni–Ni for reference NiO (2.95 Å) and the in-plane lattice parameter of the main phase (2.89 Å), is larger than the EXAFS-determined Mn–Ni/Mn distance (2.90 Å). This result is consistent with cation segregation into Li$_2$MnO$_3$-enriched regions (having in-plane second-shell distance of 2.847 Å for Li$_2$MnO$_3$) and the presence of Ni in the Li layer. This hypothesis is further supported by the fact that the coordination number for the second-shell of Ni is higher than the nominal value of 6 for an ideal layered structure without cation interlayer mixing, as shown in Table II. Moreover, the coordination number of the second-shell of Ni for LiNi$_{0.5}$Mn$_{0.5}$O$_2$-1000°C can be somewhat lower than that of LiNi$_{0.5}$Mn$_{0.5}$O$_2$-900°C, possibly indicating a lower degree of cation interlayer mixing at 1000°C, which is consistent with XRD findings discussed previously.

**TEM and STEM EDS analysis of cation distributions within individual LiNi$_{0.5}$Mn$_{0.5}$O$_2$ particles.**— Low magnification TEM images shown in Figs. 6a and 6b reveal that the sizes of the primary particles for LiNi$_{0.5}$Mn$_{0.5}$O$_2$-900°C and LiNi$_{0.5}$Mn$_{0.5}$O$_2$-1000°C are comparable in the range from 100 to 300 nm. X-ray EDS maps of Ni and Mn collected in the STEM mode further confirm variations

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**Table II. Summary of quantitative analysis of the Mn and Ni K-edge XAS spectra for LiNi$_{0.5}$Mn$_{0.5}$O$_2$ samples synthesized at 900 and 1000°C.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell number</th>
<th>X–Y pair</th>
<th>$S^2_0$</th>
<th>N</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ $(10^{-3}$ Å$^2)$</th>
<th>$E_0$ (eV)</th>
<th>R-factor for $k^3$, $k^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi$<em>{0.5}$Mn$</em>{0.5}$O$_2$–1000°C</td>
<td>1st</td>
<td>Mn–O</td>
<td>0.74(3)</td>
<td>6</td>
<td>1.915(4)</td>
<td>4.4(4)</td>
<td>6.2(6)</td>
<td>0.0146, 0.0180</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>Mn–Ni/Mn</td>
<td>0.74(3)</td>
<td>6</td>
<td>6.1(6)</td>
<td>2.901(4)</td>
<td>6.1(6)</td>
<td>6.2(6)</td>
</tr>
<tr>
<td>LiNi$<em>{0.5}$Mn$</em>{0.5}$O$_2$–900°C</td>
<td>1st</td>
<td>Mn–O</td>
<td>0.74(3)</td>
<td>6</td>
<td>1.912(4)</td>
<td>3.8(4)</td>
<td>5.9(6)</td>
<td>0.0089, 0.0143</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>Mn–Ni/Mn</td>
<td>0.74(3)</td>
<td>6</td>
<td>6.0(6)</td>
<td>2.898(4)</td>
<td>5.4(6)</td>
<td>5.9(6)</td>
</tr>
<tr>
<td>LiNi$<em>{0.5}$Mn$</em>{0.5}$O$_2$–900°C</td>
<td>1st</td>
<td>Ni–O</td>
<td>0.92(4)</td>
<td>6</td>
<td>2.054(4)</td>
<td>5.1(5)</td>
<td>6.5(4)</td>
<td>0.0135, 0.0124</td>
</tr>
<tr>
<td></td>
<td>2nd</td>
<td>Ni–Mn/Ni</td>
<td>0.92(4)</td>
<td>7.4(6)</td>
<td>2.924(3)</td>
<td>6.4(5)</td>
<td>6.5(4)</td>
<td>0.0146, 0.0180</td>
</tr>
</tbody>
</table>
in the cation distribution within individual particles of LiNi0.5Mn0.5O2 synthesized at 900 and 1000°C. Although the atomic ratios of Ni to Mn averaged from individual particles were found to be close to unity (expected for the nominal composition), many regions (analyzed with an electron beam of 2 nm in diameter) within an individual particle have considerably different Ni/Mn ratios (i.e., Mn 62%: Ni 38%) in LiNi0.5Mn0.5O2-900C, as shown in Figs. 6c and 6d. In contrast, the atomic ratios of Ni to Mn for LiNi0.5Mn0.5O2-1000C is much more uniform within individual particles, which is in good agreement with a smaller fraction of the minor phase as revealed from synchrotron X-ray diffraction (Figs. 3 and 4).

X-ray photoelectron spectroscopy analysis.—The C 1s and O 1s lines of LiNi0.5Mn0.5O2 samples prepared at 900, 950, and 1000°C are shown in Fig. 7. The C 1s can be deconvoluted into four components: (1) adventitious hydrocarbon at 285.0 eV; (2) carbon in C–O (286.5 eV) and (O–C–O — O) [—288/287.5 eV (Ref. 48)]; (3) carbon in the carboxylic groups (O–C — O) at 289 eV; and (4) carbon in the carbonate (CO32−) form (near 290.3 eV). As shown in Fig. 7a and Table III, it is clear that the amounts of oxidized surface carbonate species are comparable for all samples regardless of the synthesis temperature. Similarly, the O 1s region (Fig. 7b and Table III) shows no significant difference in the relative intensities of surface oxygen species such as surface terminated oxygen atoms and oxygen atoms doubly bound to carbon atoms in Li2CO3 [-512.0 eV (Ref. 50)] to lattice oxygen (529.8 eV) among these three samples.

The Mn 2p and Ni 2p lines of LiNi0.5Mn0.5O2 samples prepared at 900, 950, and 1000°C are shown in Fig. 8. Mn38 was found primarily for the surfaces of LiNi0.5Mn0.5O2-950C, LiNi0.5Mn0.5O2-900C, and LiNi0.5Mn0.5O2-1000C. The Mn 2p3/2 and Mn 2p1/2 binding energies (BEs) for LiNi0.5Mn0.5O2-1000C (642.4, 654.1 eV) and LiNi0.5Mn0.5O2-900C and -950C (642.7, 654.3 eV) are close to those reported for MnO2 (642.8, 654.4 eV) measured in this study and those reported previously.51 The existence of Mn38 on the surface cannot be excluded completely as the binding energy of Mn 2p3/2 for MnO2 (642.2 eV) is very close to the observed values of MnO2 and LiNi0.5Mn0.5O2 samples. On the other hand, the Ni 2p3/2 (Fig. 8b) binding energy values for LiNi0.5Mn0.5O2-900C (855.1 eV), LiNi0.5Mn0.5O2-950C (855.2 eV), and LiNi0.5Mn0.5O2-1000C (854.9 eV) are close to those reported for NiO (855.0 eV) (Ref. 52) and are much lower than those for LiNiO2 (856.0 eV),53 after adjusting spectrometer calibration to our scale. Furthermore, the Ni binding energies are close to the weighted average of the NiO double peak structure (855.4 eV).53 Therefore, it is concluded that surface Ni is present as Ni38. Although the surface atomic Ni/Mn ratios of LiNi0.5Mn0.5O2 synthesized at 900°C (1.34), 950°C (1.37), and 1000°C (1.35) are much greater than the stoichiometric value of 1, they are comparable among these three samples, as shown in Table III. Such a surface composition may result from a process that LiNi0.5Mn0.5O2 could undergo partial surface decomposition [one limiting reaction can be LiNi0.5Mn0.5O2 Æ 0.5Li2O + 0.25NiO + 0.25NiMnO2 + 0.125O2, which yields only Mn38 (Ref. 55)] and yield Ni enrichment (NiO-like phase) and Mn38 phase, where Li2O can react with CO2 upon cooling to produce lithium carbonate.

Rate capability of LiNi0.5Mn0.5O2 in lithium cells.—LiNi0.5Mn0.5 O2 samples obtained at different temperatures were found to provide very comparable discharge capacities of ~200 and ~220 mAh/g under low rates at 30 and 55°C, as shown in Figs. 9a and 9b, respectively. These specific capacities of LiNi0.5Mn0.5O2 samples are comparable to the highest values reported previously for samples prepared by the solid-state method.26,28 Two steps of lithium intercalation at 4.35 and 3.75 V were observed for all LiNi0.5Mn0.5O2 samples upon discharge, which is consistent with the results reported previously.2,27,28,9 One additional process at 3.3 V was noted for LiNi0.5Mn0.5O2-900C and was more pronounced at 55°C than at 30°C. This 3.3 V peak has been observed in the LiNi0.5Mn0.5O2–Li2MnO3 system such as Li[LiNi0.5Mn0.5O2–Li2MnO3] (Ref. 5) and 0.3Li2MnO3–0.7LiNi0.5Mn0.5O2.36 The 3.3 V peak has been attributed to the redox of Mn4+/Mn3+ in the Li2MnO3-enriched domains of Li[LiNi0.5Mn0.5O2–Li2MnO3] synthesized at 900°C as it grows as a function of x.5 Therefore, it is proposed that the 3.3 V peak is associated with lithium intercalation into the minor phase found in the LiNi0.5Mn0.5O2 samples, which is in agreement with the fact that the
LiNi_{0.5}Mn_{0.5}O_2-1000°C at 30 and 55°C are shown in supporting Fig. S1. 46 and capacity loss within the first 20 cycles was minimal, as shown in Fig. 8. 46

It should be noted that both samples exhibit rate capability higher than LiNi_{0.5}Mn_{0.5}O_2 quenched from 1000°C but lower than LiNi_{0.5}Mn_{0.5}O_2 synthesized at 900, 950, and 1000°C. However, the rate capability of these samples generally compares well with state-of-the-art high-rate LiNi_{0.5}Mn_{0.5}O_2 reported previously. 2,26,28,57

Table III. Summary of XPS results including BE in electronvolts, fwhm, and atomic percents for LiNi_{0.5}Mn_{0.5}O_2 samples synthesized at 900, 950, and 1000°C.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Assignment</th>
<th>LiNi_{0.5}Mn_{0.5}O_2-900°C</th>
<th>LiNi_{0.5}Mn_{0.5}O_2-950°C</th>
<th>LiNi_{0.5}Mn_{0.5}O_2-1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BE (eV)</td>
<td>fwhm (eV)</td>
<td>Atom %</td>
</tr>
<tr>
<td>C 1s</td>
<td>Hydro carbon (285.0 eV)</td>
<td>285.0</td>
<td>1.30</td>
<td>14.6</td>
</tr>
<tr>
<td>C-O (~286.5 eV)/O-C/ C=O (~285.7 eV)</td>
<td>286.3</td>
<td>1.59</td>
<td>4.3</td>
<td>286.2</td>
</tr>
<tr>
<td>O-C/ C=O (~289 eV)</td>
<td>288.6</td>
<td>1.52</td>
<td>1.6</td>
<td>288.5</td>
</tr>
<tr>
<td>CO_3 (~290.3 eV)</td>
<td>289.8</td>
<td>1.79</td>
<td>2.1</td>
<td>289.9</td>
</tr>
<tr>
<td>Total C</td>
<td>22.6</td>
<td>18.1</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>Lattice oxygen in LiNi_{0.5}Mn_{0.5}O_2 (~529.8 eV)</td>
<td>529.9</td>
<td>1.49</td>
<td>23.6</td>
</tr>
<tr>
<td>Surface oxygen in LiNi_{0.5}Mn_{0.5}O_2 (~531.7 eV)</td>
<td>531.5</td>
<td>2.10</td>
<td>14.1</td>
<td>531.5</td>
</tr>
<tr>
<td>O-C (~532.1 eV)</td>
<td>533.3</td>
<td>1.81</td>
<td>3.3</td>
<td>533.2</td>
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<tr>
<td>Total O</td>
<td>41.0</td>
<td>42.7</td>
<td>40.9</td>
<td></td>
</tr>
<tr>
<td>Mn 2p3/2</td>
<td>MnO_2 (642.2 eV)/MnO_2 (642.8 eV)</td>
<td>642.7</td>
<td>2.65</td>
<td>7.6</td>
</tr>
<tr>
<td>Mn 2p1/2</td>
<td>MnO_2 (654.0 eV)</td>
<td>654.1</td>
<td>2.60</td>
<td>7.6</td>
</tr>
<tr>
<td>Ni 2p3/2</td>
<td>NiO (855.0 eV)</td>
<td>855.1</td>
<td>2.13</td>
<td>10.2</td>
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<tr>
<td>Ni 2p3/2 sat.</td>
<td>861.5</td>
<td>4.00</td>
<td>64.2</td>
<td>861.6</td>
</tr>
<tr>
<td>Li 1s</td>
<td>LiNi_{0.5}Mn_{0.5}O_2 (~54.4 eV)</td>
<td>54.6</td>
<td>1.70</td>
<td>18.7</td>
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<tr>
<td>Ni/Mn</td>
<td>1.34</td>
<td>1.37</td>
<td>1.35</td>
<td></td>
</tr>
</tbody>
</table>

The rate capability data of LiNi_{0.5}Mn_{0.5}O_2-900°C and LiNi_{0.5}Mn_{0.5}O_2-1000°C at 30 and 55°C are shown in supporting Fig. S2. 46 It should be noted that both samples exhibit rate capability higher than LiNi_{0.5}Mn_{0.5}O_2 quenched from 1000°C but lower than quenched and subsequently annealed LiNi_{0.5}Mn_{0.5}O_2 at 700°C, which we reported very recently. 46 Although it is very difficult to compare rate capability data with previous work in detail due to different C rate definitions (1 C rate can be defined as a mass-normalized current to obtain the charge associated with the highest experimentally obtainable specific capacity or the theoretical special capacity of LiNi_{0.5}Mn_{0.5}O_2 upon complete lithium removal in 1 h, and using the mass-normalized current to obtain charge based on the theoretical capacity in 1 h was used a 1 C in this study), electrode thicknesses, electrode packing densities, etc., the rate capability of these samples generally compares well with state-of-the-art high-rate LiNi_{0.5}Mn_{0.5}O_2 reported previously. 2,26,28,57

Differential capacity plots in Fig. 10 clearly show how different intercalation processes change as a function of current density. The 4.35 V process, which contributed ~30% of the discharge capacity, was found to be very sensitive to current density and rapidly shift to a lower BE (~2.5 V) at rates prior to the discharge at the indicated rates. Differential dQ/dV curves of the cells are shown in the insets.

Figure 8. (Color online) X-ray photoelectron spectra of (a) Mn 2p and (b) Ni 2p photoemission lines for LiNi_{0.5}Mn_{0.5}O_2 synthesized at 900, 950, and 1000°C.

Figure 9. (Color online) (a) First discharge curves of Li/LiNi_{0.5}Mn_{0.5}O_2 cells at a rate of 1/50 C (5.6 mA/g) at 30°C. (b) First discharge curves of Li/LiNi_{0.5}Mn_{0.5}O_2 cells at a rate of 1/25 C at 55°C. The 1 C rate is based on the theoretical capacity of the LiNi_{0.5}Mn_{0.5}O_2 (280 mAh/g). The cells were charged to 4.6 V at 1/50 C (a) and 1/25 C (b) rates prior to the discharge at the indicated rates. Differential dQ/dV curves of the cells are shown in the insets.

Figure 10. (Color online) Temperature dependence of the first discharge curves of Li/LiNi_{0.5}Mn_{0.5}O_2 cells at fixed current rates of (a) 1/50 C and (b) 1/25 C at rates prior to the discharge at the indicated rates. Differential dQ/dV curves of the cells are shown in the insets.
LiNi0.5Mn0.5O2-1000°C at 3.75 V process can be attributed to -950°C, and -1000°C show that they have comparable surface chemistry. While the rate capability of the 4.35 V process is very comparable to that of LiNi0.5Mn0.5O2-1000°C, and LiNi0.5Mn0.5O2-900°C samples prepared from other precursors such as Ni/Mn hydroxides used previously. At low rates, LiNi0.5Mn0.5O2 samples are shown to have three distinct lithium intercalation processes at (1) 3.3 V corresponding to the minor phase, (2) 3.75 V, and (3) 4.35 V coming from the major phase, and comparable capacity retention during cycling to 4.6 V vs Li. Interestingly we note that the 3.75 V process, responsible for the majority of the discharge capacity is highly dependent on rate and its rate capability is higher for LiNi0.5Mn0.5O2 synthesized at higher temperatures, where the major phase has fewer NiO-enriched domains and lower interlayer mixing of Li/Ni. These findings show that the synthesis conditions of LiNi0.5Mn0.5O2 are critical to obtain the cation uniformity and reduce interlayer mixing of Li/Ni, which can greatly influence the rate capability of this electrode material in lithium batteries.

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Conclusions

Using a NiMnO3 precursor that is nearly phase pure, having primarily ordered Ni2+ and Mn4+ ions, high-quality synchrotron X-ray powder diffraction data show that LiNi0.5Mn0.5O2 segregates into two phases: a NiO-enriched major phase and a Li2MnO3-enriched minor phase, which is difficult to detect using conventional X-ray diffraction due to the close proximity of lattice parameters for these two phases. Such phase separation is further confirmed by STEM-EDS analysis, which reveals that cation non-uniformity (Ni-enriched and Mn-enriched regions) exists within individual particles. Local structural parameters for Ni and Mn as determined by XANES and EXAFS are also consistent with the proposed phase segregation. Two-phase model analysis of synchrotron X-ray diffraction data shows that the volume fraction of the minor phase in LiNi0.5Mn0.5O2 decreases to ~7% and shows some evidence for the reduction of the Li/Ni interlayer mixing in the major phase with increasing synthesis temperature from 900 to 1000°C. It is believed that using NiMnO3 as the precursor leads to LiNi0.5Mn0.5O2 having minimum phase segregation and impure phases. The XRD peak asymmetry due to phase segregation reported in this work is also evident in the XRD of LiNi0.5Mn0.5O2 samples prepared from other precursors such as Ni/Mn hydroxides used previously. At low rates, LiNi0.5Mn0.5O2 samples are shown to have three distinct lithium intercalation processes at (1) 3.3 V corresponding to the minor phase, (2) 3.75 V, and (3) 4.35 V coming from the major phase, and comparable capacity retention during cycling to 4.6 V vs Li. Interestingly we note that the 3.75 V process, responsible for the majority of the discharge capacity is highly dependent on rate and its rate capability is higher for LiNi0.5Mn0.5O2 synthesized at higher temperatures, where the major phase has fewer NiO-enriched domains and lower interlayer mixing of Li/Ni. These findings show that the synthesis conditions of LiNi0.5Mn0.5O2 are critical to obtain the cation uniformity and reduce interlayer mixing of Li/Ni, which can greatly influence the rate capability of this electrode material in lithium batteries.

References

46. See supplementary material at http://dx.doi.org/10.1149/1.3526309-E-JESOAN-158-094102 for additional information.

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