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As Published
http://dx.doi.org/10.1149/1.3526309

Publisher
Electrochemical Society

Version
Final published version

Accessed
Tue Dec 18 15:17:10 EST 2018

Citable Link
http://hdl.handle.net/1721.1/82513

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Detailed Terms
The Influence of Heat-Treatment Temperature on the Cation Distribution of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ and Its Rate Capability in Lithium Rechargeable Batteries

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Abstract—X-ray diffraction analysis combined with X-ray absorption spectroscopy showed that LiNi$_{0.5}$Mn$_{0.5}$O$_2$ segregated into one major Ni$^{2+}$O-enriched phase and one minor Li$_2$Mn$^{4+}$O$_3$-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 LiNi$_{0.5}$Mn$_{0.5}$O$_2$ samples showed comparable specific capacity (≈200 mAh/g) and capacity retention at low current densities, the rate capability of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ of 1000°C can be attributed to reduced cation segregation of Ni$^{2+}$O-enriched domains in the layered structure of the major phase, having potentially faster lithium diffusion than that of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ of 900°C.

1. Introduction

2. Experimental

3. Results and Discussion

4. Conclusions

5. References

Manuscript submitted August 17, 2010; revised manuscript received November 15, 2010. Published December 23, 2010.

Considerable research efforts have been focused on developing LiNi$_{0.5}$Mn$_{0.5}$O$_2$ as the positive electrode materials in large-scale lithium rechargeable batteries. LiNi$_{0.5}$Mn$_{0.5}$O$_2$ has the O3 layered structure (space group R3m), 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 $2\sqrt{3}a_{BCC} \times 3a_{BCC}$-type, where the stacking sequence of the ordered layers can vary from “abab” to “abcabc.” LiNi$_{0.5}$Mn$_{0.5}$O$_2$ can deliver 200 mAh/g of rechargeable discharge capacity at low rates with voltage cutoff limits of 2.5 and 4.5 V, which Ni$^{2+}$ to Ni$^{3+}$ via Ni$^{3+}$ is the active redox couple upon lithium intercalation from LiNi$_{0.5}$Mn$_{0.5}$O$_2$ while Mn$^{4+}$ ions remain inactive.

Decreasing the interlayer mixing is shown to increase the rate capability of LiNi$_{0.5}$Mn$_{0.5}$O$_2$; which is attributed to faster Li diffusion with increasing layered character of LiNi$_{0.5}$Mn$_{0.5}$O$_2$. In addition, researchers have recently shown that the rate capability of Li/LiNi$_{0.5}$Mn$_{0.5}$O$_2$ cells can be improved greatly by modifying the surface chemistry of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ via surface coating or varying heat-treatment conditions. Although Lu et al. have shown that increasing the synthesis temperature from 900 to 1000°C can reduce the voltage polarization on discharge and charge at low rates, the influence of heat-treatment temperature of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ on its rate capability is not examined in detail.

In this study, we examined the influence of heat-treatment temperature on the rate capability of LiNi$_{0.5}$Mn$_{0.5}$O$_2$. The heat-treatment temperature may influence the extent of cation ordering in the transition metal layers of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ from Ni$_2$MnO$_3$ to a layered structure consisting 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 $2\sqrt{3}a_{BCC} \times 3a_{BCC}$-type, where the stacking sequence of the ordered layers can vary from “abab” to “abcabc.” LiNi$_{0.5}$Mn$_{0.5}$O$_2$ can deliver 200 mAh/g of rechargeable discharge capacity at low rates with voltage cutoff limits of 2.5 and 4.5 V, which Ni$^{2+}$ to Ni$^{3+}$ via Ni$^{3+}$ is the active redox couple upon lithium intercalation from LiNi$_{0.5}$Mn$_{0.5}$O$_2$ while Mn$^{4+}$ ions remain inactive.

Experimental

Preparation of NiMnO$_3$—Because LiNi$_{0.5}$Mn$_{0.5}$O$_2$ prepared from NiMnO$_3$ shows the highest reversible capacities reported which consists of a slightly distorted hexagonal close-packed oxygen array having octahedral Ni$^{2+}$ and Mn$^{4+}$ ions. In this study, NiMnO$_3$ was prepared by a coprecipitation method. 1 mol/l of the Ni(NO$_3$)$_2$ and Mn(NO$_3$)$_2$ 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 NH$_4$OH 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., NO$_3^-$, (CH$_3$)$_2$N$^+$, and NH$_4^+$. The precipitates were dried at 200°C and then calcined in air at 680°C for 12 h.

Preparation of LiNi$_{0.5}$Mn$_{0.5}$O$_2$ powder samples—LiNi$_{0.5}$Mn$_{0.5}$O$_2$ samples were prepared by heating the mixture of NiMnO$_3$ and Li$_2$CO$_3$ at 900, 950, 1000, and 1050°C for 30 min. NiMnO$_3$ and Li$_2$CO$_3$ 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 (α = 5.4111(1) Å). The diffraction patterns were collected in the 2θ-range of 0–75°. A few milligrams of each sample was placed in a Linderman 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.

XAS experiments.—XAS 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. XAS experiments of NiO, NiMnO₂, 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 (8933.0 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-edge and Mn K-edge spectra were calibrated by setting the first inflection point energy for elemental Ni and Mn to 8333.0 and 6539.0 eV. 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. The extended X-ray absorption fine structure (EXAFS) data, χ(κ), were extracted using multinode cubic spline procedures applied to k³-weighted EXAFS spectra over the κ-range of 2.0–16.0 Å⁻¹. The postedge background was optimized by minimizing the amplitude of nonphysical peaks in the 0–0.9 Å region of the Fourier transform. The data analysis up to this point was carried out using the wixas software package (version 3.1). Details of quantitative analysis of Mn and Ni EXAFS and Fourier transforms are included in the supplementary information section.

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 TEM and STEM 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 TEM 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 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.

Electrochemical measurements for LiNi₀.₅Mn₀.₅O₂.—Electrode slurry was prepared by mixing the LiNi₀.₅Mn₀.₅O₂ powders with 10 wt % Super P carbon (TIMCAL Inc.) and 10 wt % poly(vinylidene fluoride) dissolved in N-methyl pyrrolidone. The slurry was cast onto a sheet of Al foil and dried in a vacuum oven at 120°C for 20 min. The cells consisted of the LiNi₀.₅Mn₀.₅O₂ composites as the positive electrode and lithium foil as the negative electrode, which were separated by two pieces of polypropylene micro-porous membrane (Celgard 2500). 1 mol/L LiPF₆ dissolved in ethylene carbonate/dimethyl carbonate (3.7 by volume) solvent (Kishida Chem. Co., Ltd) was used as the electrolyte solution. Electrochemical testing was conducted at 30 or 55°C using a Solartron Analytical Ltd., UK, 1470 battery testing unit.

Results and Discussion

Synchrotron X-ray powder diffraction analysis.—Synchrotron X-ray diffraction data (Fig. 1) showed that the NiMnO₂ sample used to synthesize LiNi₀.₅Mn₀.₅O₂ was nearly single phase having a illmenite-type structure (R3). A two-electrode cell was assembled in an argon filled glove box. 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.
Table I. Crystallographic parameters of NiMnO$_3$ analyzed by the Rietveld refinement. Ni$_6$MnO$_8$ 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$_6$MnO$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$R3$</td>
<td>$Pm\bar{3}m$</td>
</tr>
<tr>
<td>Lattice constants</td>
<td>$a_{\text{hex}}$ = 4.90388(9) Å</td>
<td>$a$ = 8.3168(1) Å</td>
</tr>
<tr>
<td>Wyckoff site</td>
<td>$g^2$</td>
<td>$g^2$</td>
</tr>
<tr>
<td>Ni</td>
<td>6c</td>
<td>0.00</td>
</tr>
<tr>
<td>Mn</td>
<td>6c</td>
<td>0.00</td>
</tr>
<tr>
<td>O</td>
<td>18f</td>
<td>0.10</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></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$_6$MnO$_8$) 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 Kα1 and Kα2 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, $c_{\text{hex}} = 14.291$ Å (in addition to a major phase with $a_{\text{hex}} = 2.891$ Å, $c_{\text{hex}} = 14.295$ Å).
The difference in $a_{\text{hex}}$ 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 $\text{3a}_{\text{hex}} \times \text{3a}_{\text{hex}}$ 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 0)$_{\text{hex}}$ 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 $a_{\text{hex}}$ 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)$_{\text{hex}}$ lines. To determine the integrated intensities of the diffraction lines for the main phase, the minor phase contribution was excluded by a curve fitting procedure. 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
were generated from k also included for comparison purposes. The Fourier transforms of Mn and Ni LiNi0.5Mn0.5O2 900 to 1000°C while that of the Li2MnO3-rich minor phase remains the unit cell volume of the Ni-rich major phase decreases from 3.0–13.0 Å. An expanded view of the Mn pre-edge region is shown as an inset in part (b). Fourier transforms of k3-weighted EXAFS spectra for Ni K-edge (c) and Mn K-edge (d). The corresponding data for NiO, NiMnO3, and Li2MnO3 were also included for comparison purposes. The Fourier transforms of Mn and Ni were generated from k-weighted EXAFS spectra over the k-range of 0.0–13.0 Å.

increasing synthesis temperature, the fraction of the minor phase decreases, which can be explained by the hypothesis that Li2MnO3-rich and NiO-rich regions can react to form LiNi0.5Mn0.5O2 (one limiting case, 0.5Li1.5MnO + 0.5NiO → LiNi0.5Mn0.5O2). 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)hex line to that of the (104)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,Mn-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 LiNi0.5Mn0.5O2 is analogous to that reported for LiNi1/3Al2O (Ref. 33) but is dissimilar to that in Li1.2Mn0.8Fe0.2O3, 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 LiNi0.5Mn0.5O2 synthesized at 900 and 1000°C are shown in Figs. 5a and 5b. Clearly, the Ni and Mn XANES data for the LiNi0.5Mn0.5O2 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.8,10 Using XANES spectra of NiO, NiMnO3 and Li2MnO3 as standards for Ni2+ and Mn4+, we confirm that Ni and Mn in LiNi0.5Mn0.5O2 are present primarily as Ni2+ and Mn4+. Some evidence of minority Mn5+ species was noted by comparing the pre-edge peaks of Mn K-edge of LiNi0.5Mn0.5O2 synthesized at 900 and 1000°C with those of NiMnO3 and Li2MnO3, where the intensity of the A1 peak (the transition to t2g orbitals) is greater than that of the A2 peak (the transition to eg orbitals), as shown in Fig. 5b inset. If some Ni2+ ions replace some Li+ ions in the minor LiMnO3-enriched phase, this can result in the formation of some Mn5+.

Fourier transforms of Ni and Mn k3-weighted EXAFS spectra of these samples along with those for NiO, NiMnO3, and Li2MnO3 are shown in Figs. 5c and 5d. Similar to the XANES spectra, the Fourier transforms of the LiNi0.5Mn0.5O2 samples are also quite similar regardless of the synthesis temperature. Aside from differences in the amplitudes of various peaks, the Fourier transforms of Ni in LiNi0.5Mn0.5O2 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 LiNi0.5Mn0.5O2 are comparable to those of the reference materials (2.09 Å for Ni2+O2−: 2.05 Å for Ni3+Mn3+O2−: 1.91 Å for Li2Mn4+O3+ and NiMn4+O4+). They are also in good agreement with those reported previously for LiNi0.5Mn0.5O2 (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 consistent with the average of the Ni–O and Mn–O distances. Interestingly, the EXAFS-determined Ni–Mn/Ni distance (2.92 Å) 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), larger than the EXAFS-determined Mn–Ni/Mn distance (2.90 Å). This result is consistent with cation segregation into Li2MnO3-enriched regions (having in-plane second-shell distance of 2.847 Å for Li2MnO3) 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 LiNi0.5Mn0.5O2–1000°C can be somewhat lower than that of LiNi0.5Mn0.5O2–900°C, possibly indicating a lower degree of cation interlayer mixing at 1000°C, which is consistent with XRD findings discussed previously.

Table II. Summary of quantitative analysis of the Mn and Ni K-edge XAS spectra for LiNi0.5Mn0.5O2 samples synthesized at 900 and 1000°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shell number</th>
<th>X–Y pair</th>
<th>S02</th>
<th>N</th>
<th>R (Å)</th>
<th>σ2 (10−4 Å2)</th>
<th>E0 (eV)</th>
<th>R-factor for k3</th>
<th>k3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi0.5Mn0.5O2–1000C</td>
<td>1st</td>
<td>Mn–O</td>
<td>0.74(3)</td>
<td>6</td>
<td>1.91(4)</td>
<td>4.4(4)</td>
<td>6.2(6)</td>
<td>0.0146, 0.0180</td>
<td></td>
</tr>
<tr>
<td>2nd</td>
<td>Mn–Ni/Mn</td>
<td>0.74(3)</td>
<td>6.1(6)</td>
<td>2.90(4)</td>
<td>6.1(6)</td>
<td>6.2(6)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st</td>
<td>Ni–O</td>
<td>0.92(4)</td>
<td>6</td>
<td>2.05(2)</td>
<td>5.9(7)</td>
<td>6.6(6)</td>
<td></td>
<td>0.0136, 0.0122</td>
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<tr>
<td>2nd</td>
<td>Ni–Mn/Ni</td>
<td>0.92(4)</td>
<td>6.9(7)</td>
<td>2.92(3)</td>
<td>5.9(6)</td>
<td>6.6(6)</td>
<td></td>
<td>0.0089, 0.0143</td>
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<tr>
<td>LiNi0.5Mn0.5O2–900C</td>
<td>1st</td>
<td>Mn–O</td>
<td>0.74(3)</td>
<td>6</td>
<td>1.91(4)</td>
<td>3.8(4)</td>
<td>5.9(6)</td>
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<tr>
<td>2nd</td>
<td>Mn–Ni/Mn</td>
<td>0.74(3)</td>
<td>6.0(6)</td>
<td>2.89(4)</td>
<td>5.4(6)</td>
<td>5.9(6)</td>
<td></td>
<td>0.0135, 0.0124</td>
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<tr>
<td>1st</td>
<td>Ni–O</td>
<td>0.92(4)</td>
<td>6</td>
<td>2.05(4)</td>
<td>5.1(5)</td>
<td>6.5(4)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2nd</td>
<td>Ni–Mn/Ni</td>
<td>0.92(4)</td>
<td>7.4(6)</td>
<td>2.92(3)</td>
<td>6.4(5)</td>
<td>6.5(4)</td>
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</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 LiNi0.5Mn0.5O2-950°C, as shown in Figs. 6c and 6d. In contrast, the atomic ratios of Ni to Mn for LiNi0.5Mn0.5O2-1000°C 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) or 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 (CO3−) form (near 290 eV). As shown in Fig. 7a and Table III, it is clear that the amount 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 atoms85 and oxygen atoms doubly bound to carbon atoms in Li2CO3 [-352.0 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. Mn16 was found primarily for the surfaces of LiNi0.5Mn0.5O2-950°C, LiNi0.5Mn0.5O2-900°C, and LiNi0.5Mn0.5O2-1000°C. The Mn 2p3/2 and Mn 2p1/2 binding energies (BES) for LiNi0.5Mn0.5O2-1000°C (642.4, 654.1 eV) and LiNi0.5Mn0.5O2-900°C and -950°C (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 Mn16 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 LiNi0.5Mn0.5O2-900°C (855.1 eV), LiNi0.5Mn0.5O2-950°C (855.2 eV), and LiNi0.5Mn0.5O2-1000°C (854.9 eV) are close to those reported for NiO (855.0 eV) (Ref. 52) and are much lower than those for Li2NiO3 (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).54 Therefore, it is concluded that surface Ni is present as Ni2+. 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 → 0.5Li2O + 0.25NiO + 0.25MnO2 + 0.125O2, which yields only Mn16 (Ref. 51)] and yield Ni enrichment (NiO-like phase) and Mn3+ phase, where Li2O can react with CO2 upon cooling to produce lithium carbonate.

Rate capability of LiNi0.5Mn0.5O2 in lithium cells.—LiNi0.5Mn0.5O2 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.2,28 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.2,28,29 One additional process at 3.3 V was noted for LiNi0.5Mn0.5O2-900°C 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[LiNi1/3Li2/3Mn2O4] (Ref. 5) and 0.3Li2MnO3·0.7LiNi0.5Mn0.5O2.36 The 3.3 V peak has been attributed to the reduction of Mn16/Mn4+ in the Li1MnO2-enriched domains of Li[LiNi1/3Li2/3Mn2O4] synthesized at 900°C as it grows as a function of x.37 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
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$<em>{0.5}$Mn$</em>{0.5}$O$_2$–900C</th>
<th>LiNi$<em>{0.5}$Mn$</em>{0.5}$O$_2$–950C</th>
<th>LiNi$<em>{0.5}$Mn$</em>{0.5}$O$_2$–1000C</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)/C–O/C = O (~287.5 eV)</td>
<td>286.3</td>
<td>1.59</td>
<td>4.3</td>
<td>286.2</td>
</tr>
<tr>
<td>O–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$_2$ (~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></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>Surface oxygen in LiNi$<em>{0.5}$Mn$</em>{0.5}$O$_2$ (~531.7 eV)</td>
<td>531.5</td>
<td>2.10</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td>O–C (~532.1 eV) &amp; Carbonates (CO$_2$)</td>
<td>533.3</td>
<td>1.81</td>
<td>3.3</td>
</tr>
<tr>
<td>Total O</td>
<td></td>
<td>41.0</td>
<td>42.7</td>
<td>10.9</td>
</tr>
<tr>
<td>Mn 2p/2</td>
<td>Mn$_2$O$_4$ (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 2p/1</td>
<td>MnO$_2$ (654.0 eV)</td>
<td>654.1</td>
<td>2.60</td>
<td>10.2</td>
</tr>
<tr>
<td>Ni 2p/3/2</td>
<td>NiO (855.0 eV)</td>
<td>855.1</td>
<td>2.13</td>
<td>10.4</td>
</tr>
<tr>
<td>Ni 2p/3/2 sat.</td>
<td></td>
<td>861.5</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td>Li 1s</td>
<td>LiNi$<em>{0.5}$Mn$</em>{0.5}$O$_2$ (~54.4 eV)</td>
<td>54.6</td>
<td>1.70</td>
<td>18.7</td>
</tr>
<tr>
<td></td>
<td>Ni/Li</td>
<td>1.34</td>
<td>1.37</td>
<td></td>
</tr>
</tbody>
</table>

The peak is less visible for LiNi$_{0.5}$Mn$_{0.5}$O$_2$–1000C with a smaller fraction of this minor phase. In addition, all LiNi$_{0.5}$Mn$_{0.5}$O$_2$ samples exhibited comparable cycling performance at low current densities and capacity loss within the first 20 cycles was minimal, as shown in supporting Fig. S1. The rate capability data of LiNi$_{0.5}$Mn$_{0.5}$O$_2$–900C and LiNi$_{0.5}$Mn$_{0.5}$O$_2$–1000C at 30 and 55 °C are shown in supporting Fig. S2. 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. 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 specific 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.

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.
lower voltages with increasing current density from 1/25 to 1 C without apparent loss in capacity. This response indicates that the rate capability of LiNi0.5Mn0.5O2 in this region is limited by its electronic resistance, but not by Li diffusion in LiNi0.5Mn0.5O2.20 On the other hand, the 3.75 V process, which contributed ~70% of the discharge capacity, was found to exhibit negligible voltage shifts with increasing current densities at rates lower than 1 C but suffer considerable capacity loss with increasing rates. This suggests that the rate capability of this process is limited by slow Li diffusion in LiNi0.5Mn0.5O2, but not the electronic resistance, which is consistent with the minimum in lithium diffusivity at ~3.75 V, which was reported previously.20 Interestingly the rate capability of the 3.75 V process for LiNi0.5Mn0.5O2-1000°C is greater than that for LiNi0.5Mn0.5O2-900°C, while the rate capability of the 4.35 V process is very comparable for these two samples at 30 and 55°C (Fig. 10). This difference cannot result from different electrode thicknesses nor from LiNi0.5Mn0.5O2 particle size as thinner electrodes were used and smaller particle sizes were found for LiNi0.5Mn0.5O2-900°C compared to LiNi0.5Mn0.5O2-1000°C. Although recent studies24 have shown that the surface chemistry of LiNi0.5Mn0.5O2 can greatly influence its rate capability, XPS analysis of LiNi0.5Mn0.5O2-900°C, -950°C, and -1000°C show that they have comparable surface chemistry. Therefore, the increased rate capability of LiNi0.5Mn0.5O2-1000°C at 3.75 V process can be attributed to changes in the cation distribution of the major phase, specifically lower Li/Ni interlayer mixing having fewer NiO-enriched domains, which can allow faster lithium-ion diffusion in the bulk of the particles.25,26

Conclusions

Using a NiMnO4 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 Li2MnO4-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 nonuniformity (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

Acknowledgments

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the DOE (DE-AC03-76SF00098 with LBNL). The synchrotron X-ray diffraction experiments were made possible through the support of the Japanese Ministry of Education, Science, Sports and Culture, Nanotechnology Support Project (Proposal no. 2009A1074/BL02B2) with the approval of Japan Synchrotron Radiation Research Institute (JASRI). The XAS experiments were conducted at the Advanced Photon Factory in Japan and the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory in the USA. NSLS is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract no. DE-AC02-98CH10886. The authors are grateful to Professor Komaba (Tokyo University of Science, Japan) for granting access to the synchrotron equipment for XAS and fruitful discussions.

Massachusetts Institute of Technology assisted in meeting the publication costs of this article.

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A200

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