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

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$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples were prepared from NiMnO_3 and Li_2CO_3 in a range of temperatures from 900 to 1050°C. Synchrotron X-ray diffraction analysis combined with X-ray absorption spectroscopy showed that $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ segregated into one major Ni^{2+}O -enriched phase and one minor $\text{Li}_2\text{Mn}^{4+}\text{O}_3$ -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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples showed comparable specific capacity (~ 200 mAh/g) and capacity retention at low current densities, the rate capability of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ of 900°C is lower than that of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ of 1000°C. As X-ray photoelectron spectroscopy analysis showed that all of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples had comparable surface chemistry, the higher rate capability of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ of 900°C.

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Considerable research efforts¹⁻²⁰ have been focused on developing $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ as the positive electrode materials in large-scale lithium rechargeable batteries. $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ has the O3 layered structure (space group $R\bar{3}m$), which consists of octahedrally coordinated divalent nickel and tetravalent manganese ions,^{3,6-8,15} and $\sim 10\%$ of Ni and Li ions displaced in the lithium and transition metal layers.^{3,21-23} Displaced Li ions (0.71 Å) in the transition metal layer induces in-plane cation ordering of $\sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$ -type, where the stacking sequence of the ordered layers can vary from “abab” to “abcabc.”^{12,16,17} $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ can deliver ~ 200 mAh/g of rechargeable discharge capacity at low rates with voltage cutoff limits of 2.5 and 4.5 V,^{2,20} where Ni^{2+} to Ni^{4+} via Ni^{3+} is the active redox couple upon lithium deintercalation from $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ while Mn^{4+} ions remain inactive.^{7,9,15,24}

Decreasing the interlayer mixing is shown to increase the rate capability of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$,^{25,26} which is attributed to faster Li diffusion with increasing layered character of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$. In addition, researchers have recently shown that the rate capability of $\text{Li/LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cells can be improved greatly by modifying the surface chemistry of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ via surface coating^{27,28} or varying heat-treatment conditions.²⁹ Although Lu et al.³⁰ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in lithium cells. The heat-treatment temperature may influence the extent of cation ordering in the transition metal layers of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ as suggested previously.³¹ Although density functional theory studies have suggested ordering of Ni and Mn in a zigzag arrangement without the cation displacement^{3,10} and a flower-type arrangement with some displaced cations,^{10,11} experimental findings of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ show no evidence of Ni and Mn ordering, but suggest some evidence of Ni and Mn segregation⁷ to form Li_2MnO_3 -like domains with a $\sqrt{3} \times \sqrt{3}$ -type cation ordering. Such segregation of transition metal ions in the layered structure has been observed in a number of materials such as $\text{Li}[\text{Li}_{0.2}\text{Cr}_{0.4}\text{Mn}_{0.4}]\text{O}_2$,^{23,32} $\text{LiNi}_{1-y}\text{Al}_y\text{O}_2$ ³³ and

$\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$.³⁴⁻³⁶ Here, we investigate the influence of the synthesis temperature on the structure of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ by synchrotron X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), and scanning and transmission electron microscopy (STEM). The structural analyses on the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples synthesized at different temperatures reveal phase segregation into a mixture of NiO-enriched major and Li_2MnO_3 -enriched minor layered phases. The extent of phase segregation will be related to the rate capability of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in lithium cells at 30 and 55°C.

Experimental

Preparation of NiMnO_3 .— Because $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ prepared from NiMnO_3 shows the highest reversible capacities reported,³⁷ NiMnO_3 was chosen as the starting material. NiMnO_3 is known to crystallize into ilmenite-type structure with the space group $R\bar{3}$,³⁸ 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 NiNO_3 and MnNO_3 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_4OH 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^- , $(\text{CH}_4)_4\text{N}^+$, and NH_4^+ . The precipitates were dried at 200°C and then calcined in air at 680°C for 12 h.

Preparation of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ powder samples.— $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples were prepared by heating the mixture of NiMnO_3 and Li_2CO_3 at 900, 950, 1000, and 1050°C for 30 min. NiMnO_3 and Li_2CO_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 synthesis¹⁸ 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–Scherrer camera,³⁹ 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 ($a = 5.4111(1)$ 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 FULLPROF⁴⁰ with a two-phase model.

XAS experiments.— XAS experiments of LiNi_{0.5}Mn_{0.5}O₂ 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, 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-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.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. The extended X-ray absorption fine structure (EXAFS) data, $\chi(k)$, were extracted using multinode cubic spline procedures applied to k^3 -weighted EXAFS spectra over the k -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.^{42,43} The data analysis up to this point was carried out using the WINXAS software package (version 3.1).^{44,45} Details of quantitative analysis of Mn and Ni 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 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 LiNi_{0.5}Mn_{0.5}O₂ samples were investigated by XPS using a Kratos Axis Ultra spectrometer (Manchester, U.K.)

Figure 1. (Color online) Synchrotron X-ray diffraction pattern of NiMnO₃. Inset shows superlattice reflections indicative of ordering of Ni and Mn and a small amount of the impurity phase, Ni₆MnO₈ (<3% by volume fraction).

with a monochromatized aluminum X-ray source (Al K α). 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.

Electrochemical measurements for LiNi_{0.5}Mn_{0.5}O₂.— Electrode slurry was prepared by mixing the LiNi_{0.5}Mn_{0.5}O₂ 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 12 h, and then electrodes in disk form (1.77 cm²) were punched out. A two-electrode cell (Tomcell Co. Ltd., Type TJ-AC, Osaka, Japan) was assembled in an argon filled glove box (oxygen level less than 2 ppm and water level less than 1.5 ppm). The cells consisted of the LiNi_{0.5}Mn_{0.5}O₂ 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 NiMnO₃ sample used to synthesize LiNi_{0.5}Mn_{0.5}O₂ was nearly single phase having a illumenite-type structure ($R\bar{3}$). A minute amount of Ni₆MnO₈ (space group $Fm\bar{3}m$) 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 the (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 NiMnO₃ 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 LiNi_{0.5}Mn_{0.5}O₂ 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 NiMnO₃ analyzed by the Rietveld refinement. Ni₆MnO₈ was found as a minor phase. Reliable parameters were obtained by using a two-phase model.

Phase	NiMnO ₃						Ni ₆ MnO ₈						
Space group	<i>R</i> $\bar{3}$						<i>Fm</i> $\bar{3}m$						
Lattice constants	<i>a</i> _{hex.} = 4.90388(9) Å			<i>c</i> _{hex.} = 13.5867(3) Å			<i>a</i> = 8.3168(1) Å						
	Wyckoff site	<i>g</i> ^a	<i>x</i>	<i>y</i>	<i>z</i>	B (Å ²) ^a	Wyckoff site	<i>g</i> ^a	<i>x</i>	<i>y</i>	<i>z</i>	B (Å ²) ^a	
Ni	6 <i>c</i>	1.00	0.00	0.00	0.1446(1)	0.20	Ni	24 <i>d</i>	1.00	0.00	0.25	0.25	0.20
Mn	6 <i>c</i>	1.00	0.00	0.00	0.3439(1)	0.20	Mn	4 <i>a</i>	1.00	0.00	0.00	0.00	0.20
O	18 <i>f</i>	1.00	0.296(1)	−0.019(1)	0.2545(6)	0.50	O1	8 <i>c</i>	1.00	0.25	0.25	0.25	0.50
							O2	24 <i>e</i>	1.00	0.255(8)	0.00	0.00	0.50
Interatomic distances	Ni–O = 2.052 Å			Mn–O = 1.908 Å			Ni–O = 2.09 Å			Mn–O = 1.87 Å			
R _B (%)	4.76						11.2						
R _{wp} (%)	10.8												

^a Not refined.

$R\bar{3}m$. 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}O₂ 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}O₂ samples, the shoulder is most pronounced for the $(110)_{\text{hex.}}$ peak of LiNi_{0.5}Mn_{0.5}O₂-900C (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}O₂-900C and the uniformity increases with increasing synthesis temperature. It should be mentioned that the impurity phase (Ni₆MnO₈) in the NiMnO₃ precursor was not detected in the LiNi_{0.5}Mn_{0.5}O₂ 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 Li₂CO₃ completely reacts with NiMnO₃ 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 K α 1 and K α 2 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}O₂ samples, a detailed phase analysis was performed. We found that two rhombohedral phases with space group $R\bar{3}m$ 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}O₂-900C 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 $a_{\text{hex.}} = 2.874 \text{ \AA}$, $c_{\text{hex.}} = 14.291 \text{ \AA}$ (in addition to a major phase with $a_{\text{hex.}} = 2.891 \text{ \AA}$, $c_{\text{hex.}} = 14.295 \text{ \AA}$).

Figure 2. Synchrotron XRD patterns of LiNi_{0.5}Mn_{0.5}O₂ synthesized from NiMnO₃ and Li₂CO₃ at different temperatures (900–1050°C) with holding time for 30 min at each temperature (a). The distinct intensities of the $\sqrt{3}a_{\text{hex.}} \times \sqrt{3}a_{\text{hex.}}$ -type cation ordering were noted, as shown in the inset. Highlighted XRD patterns of $(104)_{\text{hex.}}$, $(108)_{\text{hex.}}$, and $(110)_{\text{hex.}}$ Bragg reflection lines are shown in parts (b) and (c).

Figure 3. (Color online) Experimentally observed and simulated patterns of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized at 900°C for 30 min ($\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2\text{-900C}$). Two-phase analysis allows better fit including systematic peak broadening. Superlattice reflections from the in-plane cation ordering and the peak positions estimated from the a_{hex} lattice parameters of the two phases are shown in part (a) inset. Experimentally observed and simulated $(104)_{\text{hex}}$ peaks for the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2\text{-900C}$ and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2\text{-1000C}$ are shown in parts (b) and (c), respectively.

The difference in a_{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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2\text{-1000C}$ is much smaller relative to that for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2\text{-900C}$, as shown in Figs. 3b and 3c. This detailed phase analysis also revealed that the diffraction lines indicative of in-plane ordering of the $\sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$ -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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ unlike that suggested in an earlier study.²⁰

The lattice parameters, unit cell volume and phase fractions of the major and minor phases in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ reported previously.^{1,2,5,15,20,22,28,30} The a_{hex} lattice parameter of the major phase decreased while the c_{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 $900\text{--}1050^\circ\text{C}$. Of significance to note is that the fraction of the minor phase was reduced from ~ 17 to $\sim 6\%$ 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

Figure 4. The variation in the lattice parameters of two rhombohedral phases (a) and unit cell volume per 1 mol of LiMeO_2 (b), in which the unit volumes of NiO and Li_2MnO_3 per mole are also shown for comparison. The unit cell volume of the main phase shrinks as the synthesis temperature increases. The scaling factor ratio between the main and minor phases (c) decreases as the synthesis temperature increases.

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 ($Fm\bar{3}m$) domains in the matrix of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($R\bar{3}m$) while the minor phase has Li_2MnO_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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples in this study was nearly phase pure having primarily ordered Ni^{2+} and Mn^{4+} ions (Table I and Fig. 1). With

Figure 5. (Color online) Normalized Ni K-edge (a) and Mn K-edge (b) XANES spectra for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples synthesized at 900 and 1000°C. An expanded view of the Mn pre-edge region is shown as an inset in part (b). Fourier transforms of k^3 -weighted EXAFS spectra for Ni K-edge (c) and Mn K-edge (d). The corresponding data for NiO, NiMnO_3 , and Li_2MnO_3 were also included for comparison purposes. The Fourier transforms of Mn and Ni were generated from k^3 -weighted EXAFS spectra over the k -range of 3.0–13.0 $\text{\AA}^{-1}$.

increasing synthesis temperature, the fraction of the minor phase decreases, which can be explained by the hypothesis that Li_2MnO_3 -rich and NiO-rich regions can react to form $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (one limiting case, $0.5\text{Li}_2\text{MnO}_3 + 0.5\text{NiO} \rightarrow \text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$). 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_2MnO_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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ is analogous to that reported for $\text{LiNi}_{1-x}\text{Al}_x\text{O}_2$ (Ref. 33) but is dissimilar to that in $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Fe}_{0.4}\text{O}_2$ ³⁵ which segregates into one major disordered rock-salt ($Fm\bar{3}m$) phase and one minor (layered structure; $R\bar{3}m$) phase.

Synchrotron X-ray absorption spectroscopy analysis.—Normalized Ni and Mn x-ray absorption near-edge structure (XANES) spectra of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized at 900 and 1000°C are shown

in Figs. 5a and 5b. Clearly, the Ni and Mn XANES data for the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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.^{9,10} Using XANES spectra of NiO, NiMnO_3 and Li_2MnO_3 as standards for Ni^{2+} and Mn^{4+} , we confirm that Ni and Mn in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized at 900 and 1000°C with those of NiMnO_3 and Li_2MnO_3 , where the intensity of the A1 peak (the transition to t_{2g} orbitals) is greater than that of the A2 peak (the transition to e_g orbitals⁴⁷), as shown in Fig. 5b inset. If some Ni^{2+} ions replace some Li^+ ions in the minor Li_2MnO_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_2MnO_3 are shown in Figs. 5c and 5d. Similar to the XANES spectra, the Fourier transforms of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ are comparable to those of the reference materials (2.09 Å for Ni^{2+}O ; 2.05 Å for $\text{Ni}^{2+}\text{MnO}_3$; 1.91 Å for $\text{Li}_2\text{Mn}^{4+}\text{O}_3$ and $\text{NiMn}^{4+}\text{O}_3$). They are also in good agreement with those reported previously⁹ for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (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 represents 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_2MnO_3 -enriched regions (having in-plane second-shell distance of 2.847 Å for Li_2MnO_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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C can be somewhat lower than that of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C, 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ particles.—Low magnification TEM images shown in Figs. 6a and 6b reveal that the sizes of the primary particles for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C 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

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

Sample	Shell number	X–Y pair	S_0^2	N	R (Å)	σ^2 ($10^{-3} \text{ \AA}^2$)	E_0 (eV)	R -factor for k^3 , k^2
$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C	1st	Mn–O	0.74(3)	6	1.915(4)	4.4(4)	6.2(6)	0.0146, 0.0180
	2nd	Mn–Ni/Mn	0.74(3)	6.1(6)	2.901(4)	6.1(6)	6.2(6)	
	1st	Ni–O	0.92(4)	6	2.052(5)	5.9(7)	6.6(6)	0.0136, 0.0122
	2nd	Ni–Mn/Ni	0.92(4)	6.9(7)	2.923(4)	5.9(6)	6.6(6)	
$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C	1st	Mn–O	0.74(3)	6	1.912(4)	3.8(4)	5.9(6)	0.0089, 0.0143
	2nd	Mn–Ni/Mn	0.74(3)	6.0(6)	2.898(4)	5.4(6)	5.9(6)	
	1st	Ni–O	0.92(4)	6	2.054(4)	5.1(5)	6.5(4)	0.0135, 0.0124
	2nd	Ni–Mn/Ni	0.92(4)	7.4(6)	2.924(3)	6.4(5)	6.5(4)

Figure 6. TEM/STEM/EDS analysis on the single particles of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C, (a)–(c), and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C, (b)–(d). The atomic ratio of Ni/Mn averaged from the entire particle is close to unity (within $\sim 3\%$) for both samples. However, the elemental spot capture analyses show a relatively uniform cation distribution for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C, whereas some Mn rich domains are found for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C.

in the cation distribution within individual particles of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C, as shown in Figs. 6c and 6d. In contrast, the atomic ratios of Ni to Mn for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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/C–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 (CO_3^{2-}) 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 atoms⁴⁹ and oxygen atoms doubly bound to carbon atoms in Li_2CO_3 [~ 532.0 eV (Ref. 50)] to lattice oxygen (529.8 eV) among these three samples.

The Mn 2p and Ni 2p lines of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples prepared at 900, 950, and 1000°C are shown in Fig. 8. Mn^{4+} was found primarily for the surfaces of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -950C, $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C, and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C. The Mn 2p_{3/2} and Mn 2p_{1/2} binding energies (BEs) for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C (642.4, 654.1 eV) and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C and -950C (642.7, 654.3 eV) are close to those reported for MnO_2 (642.8, 654.4 eV) measured in this study and those reported previously.⁵¹ The existence of Mn^{3+} on the surface cannot be excluded completely as the binding energy of Mn 2p_{3/2} for Mn_2O_3 (642.2 eV) is very close to the observed values of MnO_2 and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples. On the other hand, the Ni 2p_{3/2} (Fig. 8b) binding energy values for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C (855.1 eV), $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -950C

Figure 7. (Color online) X-ray photoelectron spectra of (a) C 1s and (b) O 1s photoemission lines for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized at 900, 950, and 1000°C.

(855.2 eV), and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C (854.9 eV) are close to those reported for NiO (855.0 eV) (Ref. 52) and are much lower than those for LiNiO_2 (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 Ni^{2+} . Although the surface atomic Ni/Mn ratios of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ could undergo partial surface decomposition [one limiting reaction can be $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2 \rightarrow 0.5\text{Li}_2\text{O} + 0.25\text{NiO} + 0.25\text{NiMn}_2\text{O}_4 + 0.125\text{O}_2$, which yields only Mn^{3+} (Ref. 55)] and yield Ni enrichment (NiO-like phase) and Mn^{3+} phase, where Li_2O can react with CO_2 upon cooling to produce lithium carbonate.

Rate capability of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in lithium cells.— $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples upon discharge, which is consistent with the results reported previously.^{2,20,28,30} One additional process at 3.3 V was noted for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C and was more pronounced at 55°C than at 30°C. This 3.3 V peak has been observed in the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ - Li_2MnO_3 system such as $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]\text{O}_2$ (Ref. 5) and $0.3\text{Li}_2\text{MnO}_3 \cdot 0.7\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$.³⁶ The 3.3 V peak has been attributed to the redox of $\text{Mn}^{3+}/\text{Mn}^{4+}$ in the Li_2MnO_3 -enriched domains of $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples synthesized at 900, 950, and 1000 °C.

Peak	Assignment	$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C			$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -950C			$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C		
		BE (eV)	fwhm (eV)	Atom %	BE (eV)	fwhm (eV)	Atom %	BE (eV)	fwhm (eV)	Atom %
C 1s	Hydro carbon (285.0 eV)	285.0	1.30	14.6	285.0	1.26	11.4	285.0	1.26	12.2
	C-O (~286.5 eV)/O-C-O/C=O (~287.5 eV)	286.3	1.59	4.3	286.2	1.80	3.2	286.4	1.70	2.8
	O-C=O (~289 eV)	288.6	1.52	1.6	288.5	1.39	1.7	288.4	0.99	1.2
	CO_3 (~290.3 eV)	289.8	1.79	2.1	289.9	1.22	1.7	289.8	1.46	2.4
Total C				22.6			18.1			18.5
O 1s	Lattice oxygen in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (~529.8 eV)	529.9	1.49	23.6	529.7	1.42	22.7	529.7	1.12	25.0
	Surface oxygen in $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (~531.7 eV)	531.5	2.10	14.1	531.5	2.00	17.8	531.6	1.86	16.0
	& Carbonates (CO_3) (~532.1 eV) O-C=O (~533.3 eV)	533.3	1.81	3.3	533.2	1.80	2.2			
Total O				41.0			42.7			40.9
Mn 2p3/2	Mn_2O_3 (642.2 eV)/ MnO_2 (642.8 eV)	642.7	2.65	7.6	642.7	2.62	7.6	642.4	2.41	7.5
Mn 2p1/2	MnO_2 (654.0 eV)	654.1	2.60		654.3	2.52		654.3	2.31	
Ni 2p3/2	NiO (855.0 eV)	855.1	2.13	10.2	855.2	2.18	10.4	854.9	1.87	10.1
Ni 2p3/2 sat.		861.5	4.00		861.6	4.00		861.3	4.00	
Li 1s	$\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (~54.4 eV)	54.6	1.70	18.7	54.4	1.69	21.2	54.5	1.73	22.9
	Ni/Mn		1.34			1.37			1.35	

peak is less visible for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C with a smaller fraction of this minor phase. In addition, all $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples exhibited comparable cycling performance at low current densities and capacity loss within the first 20 cycles was minimal, as shown in supporting Fig. S1.⁴⁶

The rate capability data of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C at 30 and 55 °C are shown in supporting Fig. S2.⁴⁶ It should be noted that both samples exhibit rate capability higher than $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ quenched from 1000 °C but lower than quenched and subsequently annealed $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ at 700 °C, which we reported very recently.²⁹ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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

Figure 8. (Color online) X-ray photoelectron spectra of (a) Mn 2p and (b) Ni 2p photoemission lines for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ synthesized at 900, 950, and 1000 °C.

Figure 9. (Color online) (a) First discharge curves of $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cells at a rate of 1/50 C (5.6 mA/g) at 30 °C. (b) First discharge curves of $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cells at a rate of 1/25 C at 55 °C. The 1 C rate is based on the theoretical capacity of the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (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) Differential dQ/dV plots on the discharge curves of the $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cells shown in Fig S2 of Ref. 46: $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C [(a), (b)] and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C [(c), (d)] at 30 °C [(a), (c)] and 55 °C [(b), (d)].

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 $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in this region is limited by its electronic resistance,⁵⁸⁻⁶⁰ but not by Li diffusion in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$.²⁰ On the other hand, the 3.75 V process, which contributed $\sim 70\%$ 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 $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$, 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C is greater than that for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C, 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ particle sizes as thinner electrodes were used and smaller particle sizes were found for $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C compared to $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C. Although recent studies²⁹ have shown that the surface chemistry of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ can greatly influence its rate capability, XPS analysis of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -900C, -950C, and -1000C show that they have comparable surface chemistry. Therefore, the increased rate capability of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -1000C 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 NiMnO_3 precursor that is nearly phase pure, having primarily ordered Ni^{2+} and Mn^{4+} ions, high-quality synchrotron X-ray powder diffraction data show that $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ segregates into two phases: a NiO-enriched major phase and a Li_2MnO_3 -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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ decreases to $\sim 7\%$ 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 NiMnO_3 as the precursor leads to $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples prepared from other precursors such as Ni/Mn hydroxides used previously.^{5,30} At low rates, $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ 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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