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Synthesis–Structure–Property Relations in Layered, "Li-excess" Oxides Electrode Materials Li[$Li_{1/3-2x/3}Ni_xMn_{2/3-x/3}$]O₂ (x = 1/3, 1/4, and 1/5)

Christopher R. Fell,^{a,*} Kyler J. Carroll,^{b,d} Miaofang Chi,^c and Ying Shirley Meng^{a,d,**,z}

^aDepartment of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, USA ^bDepartment of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284, USA ^cMaterials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

^dDepartment of NanoEngineering, University of California, San Diego, La Jolla, California 90393, USA

Relations between synthesis conditions, detailed crystal structures, and electrochemical properties of the Li-excess layered oxides $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2(0 < x < 1/2)$ are studied by X-ray diffraction, scanning electron microscopy (EELS), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and electron energy-loss spectrometry, combined with electrochemical property measurements including potentiostatic intermittent titration technique (PITT). Optimal synthesis conditions are obtained for stoichiometric samples sintered at 1000°C in air followed by furnace cooling. The materials exhibit capacities of ~250, 230, and 200 mAh/g within a voltage range of 2–4.8 V on discharge for x = 1/5, 1/4 and 1/3, respectively. Diffraction data of electrochemically cycled electrode materials show an expanded *c/a* lattice ratio and changing Li/Ni interlayer mixing indicating peculiar cation migration in the structures. High resolution TEM images and XPS spectra show obvious differences in the surface characteristics of the samples synthesized with stoichiometric and excess amount of LiOH, suggesting that surface characteristics is one of the contributing factors to the difference in electrochemical properties. Our results suggest that the first cycle irreversible capacity is affected by both the bulk and surface characteristics of pristine materials, which is strongly influenced by precursor chemistry. The PITT results suggest that cation rearrangement during the charge/discharge has a significant impact on the lithium chemical diffusivity.

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The lithium-excess layered oxide compounds Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ (0 < x < 1/2) are of great interests as a new generation of positive electrode materials for high energy density lithium-ion batteries. This series of layered lithium transition-metal (TM) oxides is attractive because of higher energy density and lower costs then other layered oxides such as LiCoO₂. $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$ compounds were first reported by Lu et al. in 2001.^{1,2} This material family can be viewed as a solid solution between the two end members, Li₂MnO₃ and Li[Ni_{1/2}Mn_{1/2}]O₂, though alternatively it can be expressed as a composite xLi[Li_{1/3}Mn_{2/3}]O₂ · (1 – x)LiNi_{1/2}Mn_{1/2}O₂.³ The structure of these compounds differs from conventional layered oxides such as LiCoO₂ because additional Li is present in the TM layer inducing cation ordering in the TM layers.⁴ The lithium present in the layer arranges to form a partially disordered honeycomb structure as seen in the end member Li₂MnO₃, resulting in superlattice peaks between 20 and 35° 2 Θ (Cu K α_1) in X-ray diffraction (XRD) patterns.⁵ Previous X-ray absorption spectroscopy data showed that the average valences for Ni and Mn ions in these pristine compounds are +2and +4, respectively, and upon lithium extraction, the nickel is oxidized to Ni⁴⁺ up to 4.4 V. Lithium may continue to be extracted from these materials although all the manganese and nickel ions are in their fully charged (+4) oxidation state, which is associated with a plateau region at 4.4 V.^{2,6,7} The high charge voltage (4.6 or 4.8 V) is above the stable window of common alkyl carbonate electrolytes used.^{8,9} Significant efforts have been devoted to reduce first cycle irreversible capacity with ionic substitutions, preconditioning with acidic solutions, and surface modifications. Improvements on cycling were shown by Kang and Thackeray following treatment of electrodes with mildly acidic, fluorinated solutions.¹⁰ The reasons for the improved cycling performance through the use of substitutions and acid conditions are complex and not well understood. Surface modifications can also improve cell polarization and rate capa-

** Electrochemical Society Active Member.

^z E-mail: shirleymeng@ucsd.edu

bility, as shown by previous work exploring the effect of different coatings including Al(OH)₃,¹¹ AlF₃,¹² ZrO₂,¹³ carbon coating,¹⁴ Al₂O₃,¹⁵ AlPO₄,¹⁵ as well as LiNiPO₄.¹⁶ The electrochemical properties of the lithium-excess layered compounds are also influenced by the synthesis temperatures. As the firing temperature increases from 800 to 1000 °C, the lattice parameters and the *c/a* ratio increase and the amount of cation disorder decreases, resulting in an improved reversible discharge capacity.¹⁷

To systematically study the remarkable synthesis–structure– property relations of Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂, we investigated the compounds synthesized with different precursor stoichiometries, nickel content (x = 1/3, 1/4, and 1/5), synthesis temperature, atmosphere, and cooling rates. XRD, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and electron energy-loss spectrometry (EELS), combined with electrochemical property measurements including potentiostatic intermittent titration technique (PITT) were carried out to study the structural differences associated with various synthesis conditions before, during, and after electrochemical processes.

Experimental

Sample preparation. TM nitrates, Ni(NO₃)₂ 6H₂O, and Mn(NO₃)₂ 4H₂O (Fisher), were dissolved into 50 mL of deionized water then titrated into a 400 mL LiOH · H₂O solution for a duration of 2 h. Both the stoichiometric and excess amounts of LiOH · H₂O solution were used for the coprecipitation step. The reason for the excess amount of the LiOH \cdot H₂O solution was used to ensure complete precipitation of the TM double hydroxide, $(Ni_xMn_{2/3-x/3})(OH_2)$. The coprecipitated TM hydroxides were then filtered using a vacuum filter and washed three times with deionized water. The collected TM hydroxides were dried in an oven at 180°C. for 10 h in air. The dried TM precursors were mixed with a stoichiometric amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ corresponding to the amount of $M(OH)_2$ from the coprecipitation step. This mixture was ground for 30 min to ensure adequate mixing and then placed into a furnace at 480°C for 12 h. The precalcinated powders were prepared as a pellet or in powder form for high temperature sintering. These samples

^{*} Electrochemical Society Student Member.

Sample	Ni:Mn ratio experimental (ICP-OES)	Theoretical	Li:(Ni + Mn) experimental (ICP-OES)	Theoretical
		ICP LiOH excess ma	terials	
Ni1/3	1.59	1.66	1.30	1.25
Ni1/4	2.27	2.33	1.56	1.40
Ni1/5	2.89	3.00	1.62	1.50
		ICP stoichiometric m	aterials	
Ni1/3	1.58	1.66	1.27	1.25
Ni1/4	2.28	2.33	1.43	1.40
Ni1/5	2.85	3.00	1.54	1.50

Table I. Li/[Mn + Ni] and Mn:Ni ratios of the pristine Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ materials where x = 1/5, 1/4, and 1/3 with excess and stoichiometric amounts of LiOH as measured by ICP-OES.

were then calcinated at 900 or 1000°C for 12 h in air or in oxygen. Samples were brought back to room temperature by quenching with metal plates or furnace cooling.

XRD.— Powder diffractions of all samples were taken using a laboratory X-ray diffractometer equipped with a curved position sensitive detector (CPS120, Inel, detection range $0-120^{\circ}$), a Cu X-ray tube source, and a Göbel mirror on the incident beam. XRD data analysis was carried out by Rietveld refinement method using FullProf software.¹⁸ The Inel detector had an issue with Mn fluorescence radiation, which was believed to be the reason for the poor $R_{\rm B}$ factor (even though $R_{\rm wp}$ is excellent). We checked the reliability of the refinement result: For the Ni1/5 sample, we also performed the XRD using an X'Pert PRO Materials Research diffractometer. A comparison is shown in the Supplement Materials S0.¹⁹

ICP optical emission spectra.— The lithium, nickel, and manganese contents in the pristine samples were determined by optical emission spectroscopy using a Perkin-Elmer Plasma 3200 inductively coupled plasma (ICP) spectroscopy system. The instrument was equipped with two monochromators covering the spectral range of 165–785 nm with a grated ruling of 3600 lines/mm. The system was capable of analyzing materials in both the organic and aqueous matrices with a detection limit range of less than 1 ppm. The instrument was initially calibrated using commercial LiCoO₂ and LiFePO₄ powders.

SEM.— The particle morphology and size of the powders were determined using a JEOL 6320FV field-emission high resolution scanning electron microscope (SEM). Images were collected with an accelerating voltage of 15 kV.

TEM.— TEM images were collected from both the pristine sample powders and the powders discharged to 2.0 V after being charged to 4.8 V. To minimize the exposure to air for the electrochemically charged/discharged samples, the samples were prepared in an Ar environment. The powders were suspended on a copper grid with lacey carbon and investigated by using a JEOL 2010F microscope with an accelerating voltage of 200 kV and a fieldemission gun. The samples were briefly exposed to air (<1 min) when loaded on to the TEM grid, before they were transferred into the microscope ultrahigh vacuum column.

EELS.— The EELS spectra presented in this work was carried out in an aberration corrected Titan 80/30 microscope equipped with a Gatan imaging filter 2002F. Each spectrum was acquired from a square area of $\sim 1 \times 1$ nm with an acquisition time of 2 s and a collection angle of ~ 10 mrad. To minimize possible electron-beam irradiation effects on EELS fine structures, all EELS spectra presented here are acquired from areas without prebeam irradiation.

XPS.— The powdered samples were pressed onto a strip of indium foil and mounted onto a sample holder using double-sided adhesive tape. XPS was performed on a Thermo Scientific ES-CALAB 250 microprobe with a focused monochromatic Al K α X-ray (1486.6 eV) source. A 180° hemispherical analyzer with a 16-element multichannel detector was used. The incident X-ray beam was 45° off normal to the sample while the X-ray photoelectron detector was normal to the sample. Charge compensation was employed during data collection by using an internal flood gun (1 eV, 20 μ A electrons) and a low energy Ar⁺ external flood gun. Binding energies of the photoelectron were correlated with the aliphatic hydrocarbon C 1s peak at 284.6 eV. A large area XL magnetic lens with a 500 μ m spot size in constant analyzer energy mode was utilized with a pass energy of 20 eV. 30 scans per region were taken with a step size of 0.100 eV.

Electrochemistry.— Cathodes were prepared by mixing Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ with 10 wt % Super P carbon (Timcal) and 10 wt % poly(vinylidene fluoride) in N-methyl pyrrolidone solution. The slurry was cast onto an Al foil using a doctor blade and dried in a vacuum oven at 80°C. The electrode disks were punched and dried again at 80°C for 6 h before storing them in an argonfilled glove box (H₂O level of < 2 ppm). 2016 type coin cells were used to study the electrochemical behavior of the compounds and cycled samples for XRD and TEM. Lithium metal ribbon and 1 M LiPF₆ in a 1:1 ethylene carbonate:dimethyl carbonate solution (Ferro) were used as the counter electrode and electrolyte, respectively. A Celgard model C480 separator (Celgard Inc.) was used as the separator. The coin cells were assembled in an argon-filled glove box and tested on an Arbin battery cycler in galvanostatic mode. The tests were conducted between 2.0 and 4.8 V at a constant current rate of C/50 (0.016 mA/cm²) or C/20 (0.04 mA/cm²), unless otherwise mentioned. The samples for XRD and TEM were recovered by disassembling cycled batteries in an argon-filled glove box, and the powder mixture was scraped from the aluminum disks. The PITT experiment was carried out by applying potential steps of 10 mV and measuring the current as a function of time. The potential step was stepped to the next level when the measured current fell below the threshold limit of 10 μ A, corresponding to a C/200 rate. The voltage window was set at 4.8-3.0 V.

Results

Composition analysis.— Table I lists the atomic compositions of $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]O_2$ electrode materials synthesized for this study obtained from ICP-optical emission spectra (OES) analysis. For LiOH excess samples, the Ni/Mn ratios for x = 1/3, 1/4, and 1/5 agree with the target stoichiometry; however, the lithium values were, on average, approximately 5–10% higher than anticipated values based on the ICP-OES analysis. For the stoichiometric samples, where no excess LiOH was used, the experimental Li/Ni/Mn ratios agree well with the target stoichiometry.

XRD.— XRD spectra for the LiOH excess Li[Ni_xLi_{1/3-2x/3} $Mn_{2/3-x/3}$]O₂ samples synthesized at 1000°C are depicted in Fig. 1. Table II lists the results of the Rietveld refinement for the XRD spectra shown in Fig. 1. The major diffraction peaks of the Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ material are indexed according to the parent hexagonal structure with space group $R\overline{3}m$. The patterns in-



Figure 1. XRD patterns of pristine $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}\text{O}_2$ where x = (a) 1/5, (b) 1/4, and (c) 1/3. The samples were synthesized with an excess amount of LiOH precursor at 1000°C with furnace cooling to room temperature.

dicate that although excess lithium is present, the sample adopts a well-layered structure with little Li/Ni interlayer mixing evidenced by the existence of doublets at (006)/(102) and (108)/(110). The superlattice peaks between 20–30° 2 Θ can be clearly seen, and their intensity increases with increasing amounts of Li in the TM layers. Such superstructure peaks are associated with a honeycomb ordering of Li, Ni, and Mn in the TM layers.

XRD data for the stoichiometric Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ samples where x = 1/5, 1/4, and 1/3 are seen in Fig. 2a-c, respectively. The superlattice peaks at 20–30° 2 Θ are distinct. Table II lists the results of the Rietveld refinement for the XRD spectra shown in Fig. 2. Consistent with what is observed in the LiOH excess samples, the lattice parameters and the amount of interlayer Li/Ni mixing increases as the value of *x* increases in Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂. In addition, the *c/a* ratio decreases for increasing values of *x*, which supports the work of Lu et al. who similarly found that as the value of *x* increases. ¹⁷ Stoichiometric



Figure 2. XRD patterns of pristine $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]\text{O}_2$ where x = (a) 1/5, (b) 1/4, and (c) 1/3. The samples were synthesized with a stoichiometric amount of LiOH precursor at 1000°C with furnace cooling to room temperature.

Ni1/5 samples were also synthesized under a range of conditions to determine the effect of sintering temperature, cooling rate, and synthesis atmosphere. XRD patterns of pellet samples synthesized at differing temperatures and cooling rates can be seen in Fig. 3a-d. As shown in Fig. 3a and b, heating the stoichiometric Ni1/5 samples at 900°C requires a fast cooling rate to obtain a phase pure compound. If furnace cooled, the stoichiometric Ni1/5 sample consists of a second phase indicated by shoulders next to the (003), (101), and (104) peaks. For the stoichiometric samples sintered at 1000°C, however, samples that were furnace cooled, as illustrated in Fig. 3c, showed a lower Li/Ni interlayer mixing on the 3a sites vs that of quenched samples (Fig. 3d), see Table III.

For the LiOH excess samples, the sample synthesized at 1000°C shows an increased c/a ratio and a decreased interlayer Li/Ni mixing, compared to that synthesized at 900°C. In addition, more distinct superlattice peaks are evident in the sample synthesized at 1000°C and only a broad peak is observed in the 20–30° range for the 900°C sample (see details in Supplement Materials S1¹⁹). The

Table II. Rietveld fitting results of pristine Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ where x = 1/5, 1/4, and 1/3 synthesized at 1000 °C with excess and stoichiometric amounts of LiOH precursor.

	Stoichiometric	LiOH excess
x = 1/3	$a = 2.8748 \pm 0.001$	$a = 2.8766 \pm 0.001$
	$c = 14.2988 \pm 0.005$	$c = 14.2995 \pm 0.006$
	c/a = 4.974	c/a = 4.971
	$z(O) = 0.2528 \pm 0.0004$	$z(O) = 0.2545 \pm 0.0004$
	n_Ni (in Li layer) = 0.081 ± 0.002	n_Ni (in Li layer) = 0.063 ± 0.002
	$R_{\rm wp} = 1.53 R_{\rm B} = 15.5$	$R_{\rm wp} = 1.78 R_{\rm B} = 13.8$
x = 1/4	$a = 2.8713 \pm 0.001$	$a = 2.8699 \pm 0.001$
	$c = 14.2958 \pm 0.005$	$c = 14.2967 \pm 0.005$
	c/a = 4.979	c/a = 4.982
	$z(O) = 0.2533 \pm 0.0004$	$z(O) = 0.2548 \pm 0.0004$
	n_Ni (in Li layer) = 0.060 ± 0.002	n_Ni (in Li layer) = 0.045 ± 0.002
	$R_{\rm wp} = 1.49 \ R_{\rm B} = 14.9$	$R_{\rm wp} = 1.71 \ R_{\rm B} = 15.3$
x = 1/5	$a = 2.8668 \pm 0.001$	$a = 2.8664 \pm 0.001$
	$c = 14.2873 \pm 0.006$	$c = 14.2927 \pm 0.006$
	c/a = 4.984	c/a = 4.986
	$z(O) = 0.2531 \pm 0.0004$	$z(O) = 0.2559 \pm 0.0003$
	n_Ni (in Li layer) = 0.041 ± 0.003	n_Ni (in Li layer) = 0.028 ± 0.002
	$R_{\rm wp} = 1.73 R_{\rm B} = 15.4$	$R_{\rm wp} = 1.75 R_{\rm B} = 16.5$



Figure 3. XRD patterns of pristine $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$ with a stoichiometric amount of LiOH precursor. Samples were synthesized at 900 or 1000°C and furnace cooled (a) and (c) or quenched between stainless steel plates (b) and (d) to room temperature.

effect of cooling rate was also studied for the LiOH excess samples. Our results show that quenching or furnace cooling does not have a critical effect on the structural and electrochemical properties of LiOH excess samples (see details in Supplement Materials S2¹⁹). An oxygen environment or an ambient atmosphere has little effect on the structural and electrochemical properties (see Supplement Materials S3).¹⁹

The XRD spectra of the cycled stoichiometric $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$ (x = 1/5) samples are depicted in Fig. 4. The samples that were charged and discharged (between 4.8-2.0 V) for 1 (Fig. 4b) and 10 cycles (Fig. 4c) remain phase pure without XRD peaks from secondary phases. The inserts in Fig. 4 show that the superstructure peaks weaken their intensities following the first cycle and become undetectable after 10 cycles, consistent with what has been previously observed for a Ni1/3 compound.⁸ The Rietveld refinement (Table IV) of the XRD spectra of the cycled samples reveals an overall lattice expansion and a significantly increased c/aratio compared with the pristine materials, assuming a single phase layered structure.

Table III. Rietveld fitting results for pristine stoichiometric LiOH samples of Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ where x = 1/5 comparing the effects of synthesis temperature and cooling rate.

900°C quenched (b)	$a = 2.8664 \pm 0.001$
· · ·	$c = 14.2793 \pm 0.005$
	c/a = 4.982
	$z(O) = 0.2544 \pm 0.0004$
	n_Ni (in Li layer) = 0.063 ± 0.002
	$R_{\rm wp} = 1.77 \ R_{\rm B} = 16.0$
1000°C furnace cooled (c)	$a = 2.8668 \pm 0.001$
	$c = 14.2873 \pm 0.006$
	c/a = 4.984
	$z(O) = 0.2531 \pm 0.0004$
	n_Ni (in Li layer) = 0.041 ± 0.003
	$R_{\rm wp} = 1.73 \ R_{\rm B} = 15.4$
1000°C quenched (d)	$a = 2.8690 \pm 0.001$
	$c = 14.2949 \pm 0.005$
	c/a = 4.982
	$z(O) = 0.2545 \pm 0.0004$
	n_Ni (in Li layer) = 0.055 ± 0.002
	$R_{\rm wp} = 1.62 \ R_{\rm B} = 14.7$
	-



Figure 4. XRD patterns of (a) pristine stoichiometric LiOH samples where x = 1/5 synthesized at 1000°C, discharged samples after (b) 1 and (c) 10 cycles. Discharged samples were electrochemically cycled with a cutoff voltage window of 4.8–2.0 V.

The XRD patterns of cycled LiOH excess Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O₂ samples are compared in Fig. 5. Similar to the stoichiometric compounds, the intensity of the superlattice peaks of the sample significantly decreased after the first cycle and disappeared after 10 cycles. Different from the stoichiometric compounds, the intensity ratio of (003)/(104) becomes much less than unity and the (110) peak intensity increases dramatically in the sample after 10 cycles (Fig. 5a), indicating the loss of layeredness in the material. The Rietveld refinement results of the cycled LiOH excess materials can be seen in Table IV, and the results show that the amount of Li/Ni mixing increases after the first cycle. The c/a ratio increases after the 1st and 10th cycles indicating an expanded structure.

SEM.— Scanning electron microscopy was performed to study the morphology and particle size of Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ obtained under different synthesis conditions. Figure 6 compares Ni1/5 samples synthesized with stoichiometric vs excess LiOH during the coprecipitation stage. Figure 6a and b illustrate stoichiometric samples after 1000°C firing with average particle sizes of 100–300 nm. Samples synthesized with excess LiOH in Fig. 6c and d show a particle size distribution ranging from 200 to 600nm. Consistent trends were observed for Ni1/3 and Ni1/4 samples.

TEM/EELS.— Figures 7 and 8 are TEM micrographs and EELS spectra of the oxygen K-edge of the as-synthesized stoichiometric and LiOH excess Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O₂ samples, respectively. The data from various grains were very similar; therefore, only representative data is presented. Figure 7a is a TEM bright-field image showing that the stoichiometric particle has a clean and well-defined surface with excellent crystallinity. On the contrary, the LiOH excess sample shows poor crystallinity at the surface. The preliminary EELS data we collected confirm that the bulk vs surface uniformity is excellent in the stoichiometry sample, as depicted in Fig. 8a. The O-EELS spectra of the surface and the bulk are identical. On the contrary, the O-EELS spectra from the LiOH excess sample (Fig. 8b) show significant difference in the local environment of the oxygen: The pre-edge peak intensity decreases considerably at the surface and the profile of the EELS spectra changes at the surface. The quantitative analysis of TEM and EELS results will be reported elsewhere.

XPS.— XPS measurements were taken on as-synthesized stoichiometric and LiOH excess Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O₂ samples. The multiplet data of the Mn, Ni $2p_{3/2}$, and O 1s peaks can be seen in Fig.

	Stoichiometric	LiOH excess
Pristine	$a = 2.8668 \pm 0.001$	$a = 2.8664 \pm 0.001$
	$c = 14.2873 \pm 0.006$	$c = 14.2927 \pm 0.006$
	c/a = 4.984	c/a = 4.986
	$z(O) = 0.2531 \pm 0.0004$	$z(O) = 0.2559 \pm 0.0003$
	n_Ni (in Li layer) = 0.041 \pm 0.003	n_Ni (in Li layer) = 0.028 ± 0.002
	$R_{\rm wp} = 1.73 R_{\rm B} = 15.4$	$R_{\rm wp} = 1.75 R_{\rm B} = 16.5$
1 cycle	$a = 2.8745 \pm 0.001$	$a = 2.86954 \pm 0.002$
	$c = 14.3560 \pm 0.008$	$c = 14.3352 \pm 0.01$
	c/a = 4.994	c/a = 4.995
	$z(O) = 0.2562 \pm 0.0006$	$z(O) = 0.2533 \pm 0.0006$
	n_Ni (in Li layer) = 0.040 \pm 0.003	n_Ni (in Li layer) = 0.044 \pm 0.004
	$R_{wp} = 2.01 R_{\rm B} = 15.6$	$R_{\rm wp} = 2.00 R_{\rm B} = 15.7$
10 cycles	$a = 2.8873 \pm 0.002$	$a = 2.8736 \pm 0.001$
-	$c = 14.4073 \pm 0.011$	$c = 14.3807 \pm 0.006$
	c/a = 4.990	c/a = 5.005
	$z(O) = 0.2526 \pm 0.0004$	$z(O) = 0.260 \pm 0.0005$
	n_Ni (in Li layer) = 0.069 ± 0.003	n_Ni (in Li layer) = 0.040 \pm 0.003
	$R_{\rm wp} = 1.61 \ R_{\rm B} = 15.0$	$R_{\rm wp} = 1.54 \ R_{\rm B} = 16.7$
	*	*

Table IV. Comparison of Rietveld fitting results for stoichiometric and LiOH excess discharged samples and the pristine material where x = 1/5 synthesized at 1000 °C.

9a-c respectively. The binding energies from the XPS measurements are found in Table V. The Mn $2p_{3/2}$ binding energies observed for the stoichiometric and LiOH excess materials were 642.45 and 642.29 eV, respectively, and the binding energy values agree with the standard for Mn^{4+} ,²¹ though there is a trace amount of Mn^{3+} indicated by the broadening of the peaks. The fraction of Mn³⁺ is higher in a LiOH excess sample than in a stoichiometric sample as the average Mn $2p_{3/2}$ binding energy for the LiOH excess sample is slightly lower than that of the stoichiometric sample. This implies the presence of a trace amount of Ni³⁺ on the surfaces, and the fraction of Ni³⁺ is higher in the LiOH excess sample. A Ni $2p_{3/2}$ satellite peak at 861 eV was observed in both samples indicating splitting in the energy levels.²² The Ni 2p spectra in Fig. 9b show a mixed valence state material with Ni²⁺ and Ni³⁺. A slight shift in the binding energies for both materials can be seen, which equates to different fractions of Ni²⁺ and Ni³⁺. The Ni 2p_{3/2} peak for the LiOH excess sample shows a larger high binding energy shoulder with respect to the stoichiometric sample indicating an increased presence of Ni³⁺ at the surface. The O 1s XPS spectra in Fig. 9c show



Figure 5. XRD patterns of (a) pristine LiOH excess samples where x = 1/5 synthesized at 1000°C, and discharged samples after (b) 1 and (c) 10 cycles. Discharged samples were electrochemically cycled with a cutoff voltage window of 4.8–2.0 V.

two peaks located at ~532 and ~529 eV that correlate to OH⁻ and O²⁻ environments, respectively. An increase in the 532 eV peak for the LiOH excess sample indicates that OH ions are possibly adsorbed onto the surface of the sample.

Electrochemistry.— Electrochemical measurements of Li $[Ni_x Li_{1/3-2x/3} Mn_{2/3-x/3}]O_2$ electrodes were performed in lithium half-cells cycled between 2.0 to 4.8 V. Figure 10 shows the chargedischarge electrochemical data from stoichiometric samples of Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ where x = 1/3, 1/4, and 1/5. During the first charge cycle, the voltage increases monotonically until $\sim\!4.4\,$ V, which can be attributed to the redox reaction of Ni^{2+} to $Ni^{4+,\,8}$ A plateaulike region can be observed between 4.4 and 4.6 V upon first charge. As the amount of nickel increases, the discharge capacity and length of the plateau region decreases, consistent with the previous papers on this family of materials. A summary of the theoretical capacity based on the Ni redox, the theoretical capacity based on total amount of Li, and the actual discharge capacity are depicted in Table VI. The Mn oxidation state was considered 4+ for capacity calculations. The comparison clearly shows that when x < 1/3, much more discharge capacity than Ni redox capacity can be obtained. Figure 11 compares the charge-discharge curves from a



Figure 6. SEM pictures of Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O₂ synthesized at 1000°C with [(a) and (b)] stoichiometric and [(c) and (d)] excess LiOH.





Figure 7. TEM images of (a) stoichiometric and (b) LiOH excess Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2 synthesized at 1000°C with furnace cooling.

LiOH excess Ni1/5 (x = 1/5) sample to a stoichiometric Ni1/5 sample. During the first charge cycle, the voltage in both cells increases monotonically until 4.4 V and reach a plateau region between 4.4 and 4.6 V. However, for the LiOH excess sample, a second plateau appears at the end of charging, and the discharge capacity is 20% less than that of the stoichiometric sample. We observe this phenomenon consistently for all cells we made and also in Ni1/4 (x = 1/4) cells.

The capacity vs cycle number of Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O₂ electrodes cycled between 2.0 and 4.8 V are compared in Fig. 12 for stoichiometric and LiOH excess samples. The data suggests that the cycling stability is not affected by the presence of excess lithium in LiOH excess samples. For the LiOH excess Ni1/5 sample, the re-



Figure 8. (Color online) EELS spectra of (a) stoichiometric and (b) LiOH excess $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$ synthesized at 1000°C with furnace cooling.

versible capacity decreases from ~ 185 to 155 mAh/g at C/50 and C/20 respectively. For the stoichiometric sample, the reversible discharge capacity exceeds 200 mAh/g at C/20. The differences in the stoichiometric and LiOH excess samples are discussed in details in a later section.

The effects of temperature and cooling rate on the electrochemistry properties of the stoichiometric sample, where x = 1/5, were also investigated. Quenched samples synthesized at 900 and 1000°C were tested, and the results are illustrated in Fig. 13. The charging capacities of the materials are similar for both quenched samples; however, the discharging capacity for the 900°C material decreased to 210 mAh/g and the discharge voltage is lower and unstable compared to that of 1000°C sample. A comparison of a pellet sample furnace cooled (shown in Fig. 10) vs quenched from 1000°C (shown in Fig. 13) suggests that furnace cooling leads to better overall electrochemical properties of the $Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O_2$ when x < 1/2.

PITT .-- PITT experiments were performed to identify the lithium diffusion coefficient associated with the high voltage plateau observed in the first charging cycle of the electrochemical curve (Fig. 10). Figure 14a shows the PITT profile for the stoichiometric Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O₂ sample between 3.85 and 4.40 V. Within this region, the current exhibits cottrellian $(1/t^{1/2})$ dependence. This is indicative of a solid-solution insertion reaction.²³ The PITT profile between 4.45 and 4.63 V in Fig. 14b shows a change in behavior consistent with the plateau region observed in the electrochemical curve. Within this region, the current decays very quickly then takes a long time to reach the limit value. If we wait for the current to reach the limit value of 10 $\,\mu A$ (takes more than 96 h), the current strays from logarithmic decay and behaves erratically in the range of 4.50-4.60 V. Therefore, we chose this set of data where the linearity of $\ln(I)$ vs t is good enough for the analysis shown below. A semilogarithmic plot of the current vs time was extracted based on the



Figure 9. (Color online) XPS data from stoichiometric and LiOH excess samples of Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂, where x = 1/5. The Mn 2p_{3/2} spectrum is seen in a, Ni 2p_{3/2} spectrum is seen in b, and O 1s is seen in c.

long-time dependence, $\tau \gg L^2 \widetilde{D}_{\text{Li}}$. The Li diffusion can be solved using Fick's law for a semi-infinite system with a perturbation of the surface concentration in Eq. 1^{24,25}

$$I(t) = \frac{2Fa(C_{\rm s} - C_0)\tilde{D}}{L} \exp\left(-\frac{\pi^2 \tilde{D}t}{4L^2}\right)$$
[1]

The lithium chemical diffusion coefficient was obtained from the slope of the ln(I) vs *t* in Eq. 2

$$\tilde{D} = -\frac{d \ln(l)}{dt} \frac{4L^2}{\pi^2}$$
[2]

Figure 14c plots the lithium chemical diffusion coefficient (\tilde{D}_{Li}) vs the state of charge. The values range from 5.6×10^{-14} to 2.5×10^{-13} cm² s⁻¹ between 3.85 and 4.80 V. Starting at 4.45 V, the lithium chemical diffusion coefficient begins to rapidly decrease until 4.60 V. The PITT results obtained for stoichiometric x = 1/4 and 1/3 samples show similar trends.

Discussion

Effect of LiOH in the co-precipitation precursor.— The results obtained from XRD refinement, XPS, SEM, TEM, and electrochemical testing show that the electrochemical properties of $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]O_2$ are significantly influenced by synthesis conditions, particularly the amount of LiOH in the precursor. During the coprecipitation, an excess amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ solution was used to ensure complete precipitation of the TM double hydroxide, $(\text{Ni}_x\text{Mn}_{2/3-x/3})(\text{OH}_2)$. In principle, all excess LiOH are

washed away with deionized water, as shown in the Experimental section. Nevertheless, several major differences are observed compared to the stoichiometric samples:

1. The ICP-OES data (Table I) shows a significant amount of excess Li (5-10%) deviation from the designated lithium concentration in the materials. The XRD refinement shows little evidence of the excess Li in terms of structural characteristics (Table II).

2. The XRD results indicate that a pure layered phase can be obtained at 900 and 1000° C by furnace cooling or quenching with excess LiOH. However, phase separation is seen if the stoichiometric Ni1/5 sample is synthesized at 900°C without quenching (Fig. 3).

3. The average particle size of LiOH excess materials is larger than that of the stoichiometric materials.

4. The LiOH excess materials exhibit consistently inferior electrochemical properties compared with stoichiometric samples. A stable capacity of less than 200 mAh/g is usually obtained when cycled at C/50 between 2.0-4.8 V. The capacity drops to about 150 mAh/g when the rate is increased to C/20.

5. After electrochemical cycling, the stoichiometric Ni1/5 sample retains the $R\bar{3}m$ parent layer structure, while the LiOH excess sample has significant structural changes, indicated by the disappearance of the (006) peak intensity and increasing peak intensities of (104) and (110).

Our high resolution TEM, EELS, and XPS studies reveal that the difference lies in the surface layer characteristics that are most probably caused by the presence of excess LiOH during coprecipitation.

Table V. XPS binding energies for Mn $2p_{3/2}$, Ni $2p_{3/2}$, and O 1s for as-synthesized samples of stoichiometric and LiOH excess $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$.

Material	$\begin{array}{cc} Mn & 2p_{3/2} & binding \ energy \\ (eV) \end{array}$	Ni 2p _{3/2} binding energy (eV)	O 1s binding energy (eV)
$Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2 \ stoichiometric$	642.45	854.72 (Ni ²⁺) 855.48 (Ni ³⁺)	531.73 529.90
$Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2 \ LiOH \ excess$	642.29	854.51 (Ni ²⁺) 855.75 (Ni ³⁺)	531.91 529.68



Figure 10. (Color online) Electrochemical profiles of Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ where x = 1/5, 1/4, and 1/3 synthesized at 1000 °C with a C/50 rate (0.016 mA/cm²). Voltage windows of 4.8–2.0 V were used.

The excess LiOH might have led to the formation of a nickel-rich Ni³⁺ compound with increased Ni concentration at the surface of the particles due to the increased alkalinity in the precipitating solution. Subsequent washing and high temperature synthesis cannot completely remove the surface layer, which resulted in a larger polarization and a more irreversible first cycle capacity due to the side reaction with the electrolyte. It has been shown by a previous work that intentional surface modifications of $xLi_2MnO_3 \cdot (1 - x)LiMO_2$ (M = Mn, Ni, and/or Co) can significantly improve the electrochemical performance compared to bare-surface materials. The stoichiometric materials had well-defined clean crystalline surfaces, as shown in Fig. 7a, while the LiOH excess materials showed different surface characteristics from the bulk (Fig. 7b). EELS data reveals that the local environments of oxygen are identical at the surface and in the bulk for stochiometric sample and different for the LiOH excess sample. This distinct surface layer in the LiOH excess material is believed to be the contributing factor for the observed secondary plateau around 4.60-4.70 V and the inferior reversible capacity.

Effect of synthesis temperature and cooling rate.— Based on our results, it is optimal to synthesize the Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ material with a stoichiometric amount of LiOH precursor during the coprecipitation step, fire at 1000°C, and allow the sample to furnace cool. A previous work by Lu et al. determined that increasing the sintering temperature improved the layered structure as well as the electrochemical performance of Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ (0 < x < 0.5).¹⁷ The XRD patterns (Fig. 3) of the samples sintered at 1000°C have increased the superlattice peak intensity as well as decreased the amounts of the Li/Ni 3a site mixing compared to that sintered at 900°C, indicating improved cation ordering for samples made at high temperature. The



Figure 11. (Color online) Comparison of the electrochemical profiles of $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$ for stoichiometric and excess LiOH samples synthesized at 1000°C with furnace cooling to room temperature. Voltage windows of 4.8–2.0 V were used.

electrochemical performance of the material sintered at 1000°C shows a consistently better reversible capacity compared to that synthesized at 900°C. Samples sintered at 1000°C show increased *c* and *a* lattice parameters, and less Li/Ni interlayer mixing. The lattice expansion and improved cation ordering may improve Li mobility leading to the improved electrochemical performance.

For samples synthesized at 1000°C, cooling rate plays a role in the electrochemical performance. Opposite as what is previously observed in $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$,²⁷ quenching leads to higher first cycle irreversible capacity and less discharge capacity in lithium excess layered oxides. The furnace cooled sample shows a less first cycle irreversible capacity and a better reversible discharge capacity exceeding 250 mAh/g. This could be because the furnace cooled sample exhibits improved layeredness, less Li/Ni mixing, and better crystallinity at the surface.

Effect of cation migration lithium chemical on diffusivity.- Rietveld refinement of the XRD patterns following electrochemical cycling indicates that although the stoichiometric material remains layered after electrochemical cycling between 2.0-4.8 V, significant cation rearrangement has occurred. The major changes in the XRD patterns of the cycled stoichiometric samples are the disappearance of the superlattice peaks and expanding c and a lattice parameters. Previous experiments that examined the structure of $\text{Li}[\text{Ni}_{1/3}\text{Li}_{1/9}\text{Mn}_{5/9}]O_2$ (x = 1/3) following 1, 5, and 10 cycles reported similar trends and concluded that the TM ordering disappears following 10 cycles; in addition, a second phase following the first cycle was observed with synchrotron XRD.⁸ The disappearance of the superlattice peaks is consistent with this work and our preliminary synchrotron data also suggests the formation of a second phase. The details will be reported in a separate publication. The Ni content in Li layers decreased after the first cycle and in-

Table VI. Comparison of the theoretical capacities of $\text{Li}[\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3}]O_2$ based on the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple and full Li extraction vs the observed first cycle discharge capacity.

Material	Nickel redox capacity (mAh/g)	Theoretical Li capacity (mAh/g)	First cycle actual discharge capacity (mAh/g)
$ \begin{array}{l} \text{Li}[\text{Ni}_{1/5}\text{Li}_{1/5}\text{Mn}_{3/5}]\text{O}_2 \ x = 1/5 \\ \text{Li}[\text{Ni}_{1/4}\text{Li}_{2/12}\text{Mn}_{7/12}]\text{O}_2 \ x = 1/4 \\ \text{Li}[\text{Ni}_{1/3}\text{Li}_{1/9}\text{Mn}_{5/9}]\text{O}_2 \ x = 1/3 \end{array} $	126	378	255
	154	360	237
	199	331	197



Figure 12. (Color online) Comparison of the cyclability of $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$ with stoichiometric and excess amounts of LiOH. The first five cycles correspond to a C/50 rate (0.016 mA/cm²) and cycles 6–10 correspond to a C/20 rate (0.04 mA/cm²).



Figure 13. (Color online) Comparison of the electrochemical profiles of $Li[Ni_{1/5}Li_{1/5}Mn_{3/5}]O_2$ for samples with stoichiometric amounts of LiOH synthesized at 900 and 1000°C.

creased to a higher value after 10 cycles. Such trend is somewhat consistent with Jiang et al.'s early work on a Ni1/3 material. It suggests that not only the Li ions but also the TM ions dynamically moves during the electrochemical charging/discharging process. The exact mechanisms of such cation migration is unclear at the moment; however, our PITT data (Fig. 14c) clearly show that the lithium chemical diffusion coefficient drops significantly in the voltage range 4.45–4.65 V. This is the voltage range where TM ion migration occurs and impedes the lithium ion transport.

Conclusions

The relations between synthesis conditions, detailed crystal structures, and electrochemical properties of Li-excess layered oxides have been studied. The data provides evidence that optimal synthesis conditions of the Li-excess layered oxide Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ (0 < x < 1/2) are obtained for stoichiometric samples sintered at 1000°C in air followed by furnace cooling.

The XRD data of the electrochemically cycled electrode materials show an expanded c/a lattice ratio and a changing Li/Ni interlayer mixing indicating peculiar cation migration. PITT measurements indicate a decrease in the Li chemical diffusion coefficient during the initial charging process from 4.45 to 4.65V suggesting that during this region not only the Li ions but the TM ions dynamically migrate during electrochemical processes.

Samples synthesized with stoichiometric and excess amounts of LiOH show obvious differences in surface characteristics. The electrochemical results obtained from these materials favor the well-defined clean crystalline surfaces of the stoichiometric materials. The results indicated the formation of a compound with increased Ni³⁺ concentrations accumulated at the surface of the LiOH excess particles due to the increased alkalinity in the precipitating solution. Our data illustrates that the first cycle irreversible capacity is affected by both the bulk and surface characteristics of the pristine materials, which are strongly influenced by precursor chemistry.

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Figure 14. (Color online) Results of PITT acquired with a step size of 10 mV and current limit corresponding to a C/200 rate. The two plots show the different voltage windows, (a) 3.85–4.40 V and (b) 4.40–4.80 V, for the first charge cycle. (c) Plot of the calculated Li chemical diffusion coefficient vs voltage on the first charging cycle.

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