Ni-rich layered transition metal oxide are one of the most promising positive electrode materials for lithium ion batteries. Many derivatives of LiNiO2, such as LiNi1-yMnymO2 (NMC) and LiNi1-yCoyAlyO2 (NCA) have been of great interest in both industry and academia. As the trend continues to reduce the Co, Mn and Al content in these materials, a careful, modern study of LiNiO2, the end member of the NMC and NCA series when x = y = 0, is required as a solid reference for workers in the field.

For Ni-rich NMC and NCA materials, although Ni is partially substituted by other transition metal atoms such as Co, Mn and Al to improve structural and electrochemical stability, the substituted materials still have many properties that originate from LiNiO2. Without an in-depth understanding of the structural and electrochemical behavior of LiNiO2, it is hard to effectively solve existing problems.

T. Ohzuku et al. reported several methods to synthesize LiNiO2 in 1993 and found that LiNiO2 with a reversible specific capacity of 200 mAh/g could be made. In the same year, W. Li et al. studied LiNiO2 with in-situ X-ray diffraction, and multiple phase transitions during Li intercalation and deintercalation were found. Twenty years later, with modern synthesis methods, LiNiO2 with superior quality can be made. Figure 1 shows a comparison of voltage (vs. Li/Li+) versus x in Li1-xNiO2 for a sample made in 1993 by W. Li et al. and modern LiNiO2, made by the authors. Black lines and red lines show the cell voltage as a function of x in Li1-xNiO2 of the old and modern LiNiO2 materials respectively. The value of x is calculated assuming LiNiO2 has a theoretical first charge capacity of 274 mAh/g. The old LiNiO2 was made by lithiating Ni(OH)2 at 700 °C for 2 hours, and then at 700 °C for 20 hours. A heating rate of 10 °C/min was used to increase the temperature to the set point. The preheated powders were taken out of the furnace and ground again by hand milling to minimize areas of local LiOH excess. The ground powders were then heated in oxygen in the tube furnace at 485 °C for 3 hours. A heating rate of 10 °C/min was used to increase the temperature to the set point. The preheated powders were taken out of the furnace and ground again by hand milling to minimize areas of local LiOH excess.

Scanning electron microscopy imaging (SEM).—SEM imaging was conducted using a Nano Science Phenom Pro G2 Desktop Scanning Electron Microscope with a backscattered electron detector.

Figure 1. A comparison between old and modern LiNiO2. Black lines and red lines are the cell voltage as a function of x in Li1-xNiO2 of old and modern LiNiO2 materials respectively. The data was collected both at room temperature. The data for old LiNiO2 was taken from Reference 9.
Figure 2. SEM images of synthesized LiNiO$_2$ (A),(B); XRD patterns of LiNiO$_2$ (C1), expanded view of the (104) Bragg peak of LiNiO$_2$ (C2), expanded view of (108)/(110) Bragg peaks of LiNiO$_2$ (C3), impurity regions in the XRD patterns of LiNiO$_2$ where Li$_2$CO$_3$, if present, can be observed (C4). Black circles are experimental XRD data, solid red lines are calculated patterns from Rietveld refinement, green lines show the differences between the measured and calculated patterns.

Samples were prepared by mounting the powders onto adhesive carbon tape. The images of samples were taken with an accelerating voltage of 5 kV and a current of 0.6 nA.

Powder X-ray diffraction (XRD) and In-situ XRD.—Powder X-ray diffraction (XRD) was conducted to study the structure of materials using a Siemens D5000 diffractometer equipped with a Cu target X-ray tube and a diffracted beam monochromator. Diffraction patterns were collected in the scattering angle ($2\theta$) range of 15–70$^\circ$ at 0.02$^\circ$ intervals with a dwell time of 3 s. A 1$^\circ$ divergence slit, 1$^\circ$ anti-scattering slit and 0.2 mm receiving slit were used for the measurements. The collected XRD patterns were refined (Rietveld method) using “Rietica”.10

The In-situ X-ray diffraction experiment was carried out with a Bruker D8 diffractometer equipped with a Cu target X ray source and a diffracted beam monochromator. Measurements were conducted with a step size of 0.05$^\circ$ and a 10 second dwell time per step. The scattering angle ($2\theta$) range was 17.5–68$^\circ$. Each scan took 2.808 hours, and the corresponding change of x value in Li$_{1-x}$NiO$_2$ is about 0.025. A 1 mm divergence slit, 1 mm anti-scattering slit and 0.2 mm receiving slit were used for the measurements. Diffraction patterns were refined (LeBail method) using “Rietica”.

Coin cells and in-situ coin cells.—Synthesized LiNiO$_2$ positive electrode materials were mixed with polyvinylidene difluoride (PVDF) and Super-S carbon black having a mass ratio of 92:4:4 in N-methyl-2-pyrrolidone (NMP) to make a slurry. Single side coated electrodes were made by casting the slurry onto aluminum foil with a 150 μm notch bar spreader. The electrodes were dried in an oven at 120°C for 3 hours. Dried electrodes were then calendared at a pressure of 2000 atm. The loading of electrode material was 10.51mg/cm$^2$. Coin cell electrodes were punched (1.2 cm in diameter) and further dried under vacuum at 120°C for 14 hours before coin cell fabrication. The electrode fabrication procedure closely followed that described by Marks et al.11

Electrolyte used for coin cell testing was 1.0 M LiPF$_6$ in EC:DEC (1:2 v/v). Standard 2325 coin cells were assembled in an argon-filled glovebox. Each coin cell had a positive electrode and a Li foil negative electrode with two layers of separators (Celgard #2300) in between. Galvanostatic charge/discharge cycling was conducted with E-one Moli Energy Canada battery testing systems.

The coin cell used for in-situ XRD used a beryllium x-ray window as the positive electrode current collector. The LiNiO$_2$ slurry was made as described above but less NMP was used to increase the slurry viscosity. The slurry was coated onto a 2 cm diameter beryllium disc with a 660 μm notch bar spreader and dried at 120°C for 2 hours. The coated beryllium disc was pressed at a pressure of 2000 kPa, and further dried under vacuum at 120°C for 14 hours before coin cell fabrication. The loading of electrode material was 24.01 mg/cm$^2$. The coated beryllium disc was attached using Roscobond pressure sensitive adhesive to the positive electrode side of the cell case that had a pre-cut 1.5 cm diameter hole. After this, the remaining steps of in-situ coin cell fabrication were the same as described above for regular coin cells. The cell was cycled at a rate of ~C/100 between

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10. Rietica, a software tool for powder diffraction data analysis and refinement.

11. Marks et al., [Reference number](https://doi.org/10.1021/acs.jpccl.8b08809)
Figure 3 shows the crystal structure of LiNiO₂. Blue balls are Li, red balls are oxygen, and black balls are Ni. In this figure, two choices of unit cell are shown. The unit cell drawn with solid black lines is the conventional choice of unit cell for hexagonal structured LiNiO₂. Vector \( \mathbf{a}_h \) is equal to vector \( \mathbf{b}_m \) in magnitude and the angle between them is 120°. Vector \( \mathbf{c}_h \) is perpendicular to both \( \mathbf{a}_h \) and \( \mathbf{b}_m \). The dashed lines depict a monoclinic unit cell, in which vector \( \mathbf{b}_h \) is perpendicular to \( \mathbf{a}_m \) and \( \mathbf{c}_m \), and the angle between \( \mathbf{a}_m \) and \( \mathbf{c}_m \) is \( \beta \) (≠ 90°). When there is no distortion in crystal structure, the transformation between the hexagonal unit cell vectors and the monoclinic unit cell vectors can be described by:

\[
\begin{bmatrix}
\mathbf{a}_m \\
\mathbf{b}_m \\
\mathbf{c}_m
\end{bmatrix} = \begin{bmatrix}
-1 & 1 & 0 \\
1 & 1 & 0 \\
1/3 & -1/3 & -1/3
\end{bmatrix}
\begin{bmatrix}
\mathbf{a}_h \\
\mathbf{b}_h \\
\mathbf{c}_h
\end{bmatrix}.
\]

[1]

and the transformation of the Miller indices of the Bragg peaks can be described by:

\[
\begin{bmatrix}
\mathbf{k}_m \\
\mathbf{l}_m \\
\mathbf{m}_m
\end{bmatrix} = \begin{bmatrix}
-1 & 1 & 0 \\
1 & 1 & 0 \\
1/3 & -1/3 & -1/3
\end{bmatrix}
\begin{bmatrix}
\mathbf{k}_h \\
\mathbf{l}_h \\
\mathbf{m}_h
\end{bmatrix}.
\]

[2]

Figure 4 shows the in-situ X ray diffraction patterns, with a sequential offset in intensity for clarity, accompanied by the in-situ coin cell cycling profile in which voltage was plotted as a function of cell running time. Figure 4a shows that during the first charge, the (003) peak shifted continuously until two peaks coexisted at high state of charge. Figures 4c and 4d show that for the (101) and (104) peaks, clear peak splitting was observed at certain states of charge. This observed peak coexistence and peak splitting were reported by W. Li et al., and are caused by a two-phase region at the top of charge and a monoclinic distortion, respectively. The in-situ XRD patterns were analyzed using the LeBail refinement method with Rietica. For refinements, a hexagonal R-3m space group was assumed in the single or two hexagonal phase regions, and a monoclinic c2/m space group was assumed in the single monoclinic phase region, and a mixture of the two space groups was assumed in the hexagonal-monoclinic two-phase regions.

Results and Discussion

Figures 2A and 2B show SEM images of the synthesized LiNiO₂ materials. The synthesized materials have \( \sim 18 \mu \text{m} \) diameter spherical secondary particles and each secondary particle consists of dense small-size (about 200 nm) primary particles. Figures 2C1, 2C2 and 2C3 show the full X-ray diffraction patterns and two expanded views of the (104) and (108)/(110) Bragg peaks of the synthesized LiNiO₂. The black dots are the measured diffraction data, and the solid red lines show the calculated pattern from Rietveld refinement. The green lines show the differences between the measured and calculated patterns. Rietveld refinements were performed on the full XRD data (15–70°) assuming a hexagonal layered phase in the R-3m space group (\( \alpha \)-NaFeO₂-type structure) to obtain the structural information. Li ions were assumed to be on the 3a sites (lithium layer), Ni ions were on the 3b sites (transition metal layer), and oxygen ions were on the 6c sites. The exchange of Ni and Li atoms between 3a and 3b sites was allowed with constraints such that the stoichiometry of the phase was fixed to the values assumed from the target composition. Figure 2C4 shows that the synthesized LiNiO₂ has no appreciable impurity phase. The refinement results show that cation mixing between Li ions and Ni ions is 1.81(4)%; lattice constants \( a \) and \( c \) are 2.8751(1) Å and 14.2000(3) Å, respectively, and the \( z \) value of oxygen atomic fractional coordinate is 0.2424(1). The refinement has a Bragg R factor (\( R_{\text{Bragg}} \)) of the refinement was 1.87. An estimate for the lithium fractional coordinate is 0.2424(1). The refinement has a Bragg R factor (\( R_{\text{Bragg}} \)) of the refinement was 1.87. An estimate for the lithium fractional coordinate is 0.2424(1).
Figure 4. Diffraction patterns from the in-situ XRD experiment. Cell voltage as a function of time, which is aligned with the diffraction patterns (a). In-situ XRD patterns of selected scattering angle regions: 18–21° (b), 36–40° (c), 43–51° (d), 58–68° (d). The cell was charged and discharged between 3.0–4.3 V at a rate of ∼C/100 for 1 cycle, and charged to 4.6 V at a rate of ∼C/100.

it disappeared, and two peaks close to the initial (101)H1 peak started to emerge. In a hexagonal structure, the (101)H1 peak has a multiplicity of 12 including the ±(01±1)H1, ±(10±1)H1 and ±(1−1±1)H1 peaks. In the case of the R-3m space group only 6 of these peaks have non-zero geometrical structure factor. Table I shows the six peaks with non-zero structure factor and the corresponding monoclinic Miller indices calculated using Eq. 2. When the structure is not distorted, the (110)M and (201)M planes have the same plane spacing as the (101)H planes, and a single diffraction peak appears at a certain scattering angle. When the basal plane distortion occurs and the monoclinic phase forms, the inter-plane distance of the (110)M planes is no longer equal to that of (201)M planes, thus two corresponding diffraction peaks will emerge. Table I also shows that in the monoclinic phase, the (110)M peak has a multiplicity of four, while the (201)M has a multiplicity of two. Due to the factor of two difference in multiplicity, the intensity of the (201)M peak is expected to be half of the intensity of the (110)M peak as observed in Figure 5b. As the charge continued, the (110)M peak and the (201)M peak shifted smoothly until they merged forming a single peak at higher state of charge, and the distorted monoclinic phase transformed back to the hexagonal, H2 phase. The mechanism of the monoclinic phase formation was proposed by H. Arai et al.13 It is potentially driven by an ordering of lithium in alternating rows of

Figure 5. In-situ coin cell cycling profile in which voltage was plotted as a function of cell running time (i). In-situ XRD scans during 1st charge of selected scattering angle regions. 18–21° (a), 36–40° (b), 43–47° (c). Miller indices of the diffraction peaks are labeled according to XRD profile refinement. Voltages are labeled according to the cell voltage profile.
mostly full and mostly empty sites in the lithium layer which breaks the hexagonal symmetry. An analogous ordering was also observed in Li$_2$Co$_2$O$_4$ when x is near 0.5 and can be explained by a lattice gas model.\textsuperscript{13} Driven by further de-intercalation of Li, a transition from the H2 phase to the H3 phase started near the end of the 1st charge, which can be clearly observed in Figure 5a.

Table I lists the transformations of the Miller indices of selected diffraction peaks of the hexagonal phase and monoclinic phase. Using Table I the Miller indices of the other peaks shown in Figures 5b and 5c can be determined and they are labeled in the Figures. The (006)$_{H1}$ peak did not split, as expected in the monoclinic phase region, while the (012)$_{H1}$ and (104)$_{H1}$ peaks split into two peaks when the distorted monoclinic phase formed. The observed intensity ratios of the split peaks agree well with calculated diffraction multiplicity listed in Table I.

Table 1. Hexagonal-Monoclinic plane indices transformation list.

| Hexagonal Indices | Monoclinic Indices |
|------------------|--------------------|
| 003              | 00-1               |
| 00-3             | 001                |
| 101              | $-110$             |
| 01-1             | 110                |
| $-10$-1          | 1-10               |
| 0-11             | $-1-10$            |
| $-111$           | 20-1               |
| 1-1-1            | $-201$             |
| 006              | 00-2               |
| 00-6             | 002                |
| 012              | 11-1               |
| 1-12             | $-200$             |
| 10-2             | $-111$             |
| $-1-2$           | 200                |
| $-102$           | 1-1-1              |
| 0-1-2            | $-1-11$            |
| 104              | $-111$             |
| $-10$-4          | 1-11               |
| 01-4             | 111                |
| 0-14             | $-1-1-1$           |
| $-114$           | 20-2               |
| 1-1-4            | $-202$             |

Figure 5. Figure 4a shows that during the first charging process, the peaks appear to be much sharper compared with the same peaks shown in Figure 5. However, during the second charge, the phase transition from the H1 phase to M phase occurred more quickly than the same transition during the first charge. Figure 6b shows that in the monoclinic phase region, the (110)$_M$ peaks and (201)$_M$ peaks appear to be much sharper compared with the same peaks shown in Figure 5. Figure 4a shows that during the first charging process, the phase transition from the H1 phase to M phase was accompanied by a sloping voltage region from about 3.65–3.8 V. By comparison, during the second charge (see Figure 4a), the voltage plateau at 3.65 V was flat and short, indicating a rapid phase transition from H1 phase to M phase. A similar phenomenon was also observed during the first discharge. After the first charge, apparently the transition between the H1 phase and the M phase became kinetically easier, and there was a smaller Li concentration gradient in the LiNiO$_2$ particles. As a result, diffraction peaks were sharper and the voltage plateau was flatter.

Figure 7 shows refinement results of the in-situ XRD patterns accompanied by cell charge and discharge profiles. Figure 7A1 shows the in-situ cell voltage as a function of specific capacity during the first charge; Figure 7A2 shows the unit cell constants $a_H$, $b_M$, and $3c_M\sin\beta$ as a function of specific capacity during the first charge; Figure 7A3 shows the unit cell constants $c_H$ and $3c_M\sin\beta$ as a function of specific capacity during the first charge and Figure 7A4 shows the angle $\beta$ as a function of specific capacity during the first charge. Figures 7B1–7B4 and Figures 7C1–7C4 show the same parameters as a function of specific capacity during first discharge and second charge, respectively.

Figures 7A2, 7B2 and 7C2 show that $a_H$, $b_M$ and $a_M/\sqrt{3}$ generally decrease as Li is extracted from Li$_x$Ni$_2$O$_4$. In the figures, $a_M/\sqrt{3}$ and $b_M$ were plotted in order to show the magnitude of the distortion. Figure 3 shows that in the undistorted monoclinic cell, $a_M/\sqrt{3}$ is equal to $b_M$. Figure 7 clearly shows that in the hexagonal-monoclinic phase transition region and in the monoclinic single phase region, a distortion in the basal plane exists.

In Figures 7A3, 7B3, and 7C3, $3c_M\sin\beta$ was plotted in order to show the changes along the $c_H$ axis in a consistent way. In an undistorted monoclinic cell, $3c_M\sin\beta$ is equal to $c_H$. Figures 7A3, 7B3, and 7C3 show that unit cell expanded along $c_H$ axis initially as Li ions get extracted until the H3 phase with small $c_H$ forms. Figures 7A4, 7B4, and 7C4 show that after the first charge, the angle $\beta$ in the monoclinic cell changed in a more reversible manner during the following discharge and charge.

Figure 6 shows the in-situ XRD patterns measured during the 2nd charge accompanied by the corresponding in-situ coin cell cycling profile. All the peaks changed in a similar manner as during the 1st charge shown in Figure 5. In-situ XRD scans during 2nd charge of selected scattering angle regions. 18–21° (a), 36–40° (b), 43–47° (c). Miller indices of the diffraction peaks are labeled according to XRD profile refinement. Voltages are labeled according to the cell voltage profile.
Figure 7. Cell voltage as a function of specific capacity during the 1st charge (A(1)), 1st discharge (B(1)), and 2nd charge (C(1)). Lattice parameters and $\beta$ values as a function of specific capacity during 1st charge (A(2)-A(4)), 1st discharge (B(2)-B(4)), and 2nd charge (C(2)-C(4)).

Figure 8 shows the volumes of the hexagonal unit cells and $3/2$ the volume of the monoclinic unit cell accompanied by the in-situ cell voltage profiles. Figure 8A1, shows the in-situ cell voltage as a function of specific capacity during the first charge, and Figure 8A2 shows the corresponding unit cell volumes during the first charge. The volume of monolithic unit cell is multiplied by $3/2$ and shown in the figure to observe the unit cell volume changes in a consistent way. Figure 2 shows that the unit cell volume of the undistorted monoclinic phase is equal to $2/3$ of the hexagonal unit cell volume. Figures 8B1–8B2 and Figures 8C1 and 8C2 show the same parameters as a function of specific capacity during first discharge and second charge, respectively. Figures 8A2, 8B2 and 8C2 show that as Li was de-intercalated, the unit cell volume decreased continuously until the H3 phase formed. From the H2 phase to the H3 phase, the unit cell volume decreases dramatically. The volume contraction at high states of charge observed is consistent with many studies on LiNiO$_2$ derivatives such as NMC and NCA positive electrode materials. However the NMC and NCA samples do not show a two-phase region at top of charge; instead the materials contract as a single phase.

In order to assist possible theoretical efforts on Li$_x$NiO$_2$, Table II lists the structural parameters versus x in Li$_{1-x}$NiO$_2$ as determined during the second charge of the in-situ cell. Based on the work of Mueller-Neuhaus et al. and M. Winter et al., it is assumed that all the Li atoms did not re-insert into the material at the bottom of the first discharge, i.e. the measured irreversible capacity represents Li that cannot be re-inserted at the applied specific current. The values of x in Table II have been derived based on this assumption.

Figure 9 shows the differential capacity as a function of cell voltage (dQ/dV vs. V) of the in-situ cell (black solid lines) and of a regular coin cell (red dotted lines). Figure 9a shows dQ/dV vs. V during the first charge and Figure 9b shows dQ/dV vs. V during the following discharge and charge. The regular coin cell was tested with a specific current of 10 mA/g ($\sim$C/20) at 30°C and the in-situ cell was tested with a specific current of 2 mA/g($\sim$C/100) at room temperature ($\sim$25°C). The good match between in-situ cell data and the coin cell data indicates the exceptional quality of the in-situ cell. Figures 9a and 9b show the phase evolution labeled according to the in-situ XRD refinements and analysis. Figure 9a shows that starting from a fresh cell, LiNiO$_2$ had a relatively large H1-M phase transition peak, which overlaps with the H1 single phase capacity. This is consistent with the previous discussions of the in-situ XRD refinement results, which showed that during the first charge, the H1-M phase transition was much slower. However during the following discharge and charge, the H1-M phase transition peak was sharp and narrow. This also agrees well with the in-situ XRD refinement results, which show that after the first charge, LiNiO$_2$ had a more rapid H1-M phase transition. Figure 9c shows the dQ/dV vs. V between 3.45 V to 3.75 V during the 1st charge (black line) and 2nd charge (blue line). It is likely that during the 1st charge, because of slow kinetics, the two peaks that appeared in the 2nd charge were shifted to higher potential and overlapped with each other.

Figure 9b shows that after the first charge, there was a new peak at $\sim$3.5 V in the H1 phase region. Figure 4 clearly shows that there is no two phase co-existence in the region between 3–3.6 V at least at the resolution of the x-ray diffractometer used. It may be that this peak is related to a transition between states where Li ions are ordered and disordered, respectively, and that the lattice constants of the two phases are very similar. The significant “step” in the voltage curve near 3.6 V and the corresponding minimum in dQ/dV vs. V is a strong signature of a composition where Li atoms are ordered. If there is an ordered state at x = 1/4 or x = 1/7 in Li$_{1-x}$NiO$_2$ on the triangular lattice of sites within each Li layer then unoccupied sites will have no unoccupied neighboring sites and diffusion will be very slow according to the work of A. Ven der Ven et al. They reported that lithium ions diffuse from one octahedral site to an adjacent octahedral vacant
Figure 8. Cell voltage as a function of specific capacity during the 1st charge (A(1)), 1st discharge (B(1)), and 2nd charge (C(1)). Unit cell volumes as a function of specific capacity during 1st charge (A(2)), 1st discharge (B(2)), and 2nd charge (C(2)).

Table II. Structural parameters versus \( x \) in Li\(_{1-x}\)NiO\(_2\) as determined during the second charge of the in-situ cell.

| Phase | \( x \) | \( a/b \) (Å) | \( c \) (Å) | Volume(Å\(^3\)) | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) | \( \beta \) (°) | Volume(Å\(^3\)) | \( a/b \) (Å) | \( c \) (Å) | Volume(Å\(^3\)) |
|-------|--------|-------------|--------|----------------|--------|--------|--------|--------|----------------|--------|--------|----------------|
| H1    | 0.0636 | 2.8734      | 14.211 | 101.6126       | 4.9948 | 2.8357 | 5.0655 | 109.87 | 101.2127       |
|       | 0.0900 | 2.8714      | 14.218 | 101.5212       | 4.9965 | 2.8341 | 5.0635 | 109.98 | 101.0797       |
|       | 0.1166 | 2.8696      | 14.224 | 101.4367       | 4.9972 | 2.8312 | 5.0639 | 109.98 | 100.9984       |
|       | 0.1433 | 2.8678      | 14.233 | 101.3736       | 4.9999 | 2.8281 | 5.0623 | 109.99 | 100.9041       |
|       | 0.1694 | 2.8659      | 14.243 | 101.3104       | 4.9997 | 2.8263 | 5.0672 | 109.99 | 100.8789       |
|       | 0.1910 | 2.8639      | 14.245 | 101.1833       | 4.9991 | 2.8234 | 5.0698 | 109.94 | 100.8207       |
| H1-M  | 0.2158 | 2.8637      | 14.243 | 101.1550       | 4.99   | 2.8218 | 5.0722 | 109.84 | 100.7720       |
|       | 0.2453 | 2.8628      | 14.241 | 101.0772       | 4.9804 | 2.8211 | 5.0767 | 109.76 | 100.6930       |
|       | 0.2631 | 2.8613      | 14.257 | 101.0847       | 4.9712 | 2.82   | 5.0801 | 109.65 | 100.6042       |
|       | 0.2897 | 2.8638      | 14.264 | 101.3112       | 4.9611 | 2.8199 | 5.0833 | 109.56 | 100.5157       |
| M     | 0.3140 | 2.8637      | 14.243 | 101.1550       | 4.9512 | 2.82   | 5.0846 | 109.48 | 100.3940       |
|       | 0.3412 | 2.8637      | 14.243 | 101.1550       | 4.9457 | 2.8187 | 5.0872 | 109.43 | 100.3184       |
|       | 0.3780 | 2.8613      | 14.257 | 101.0847       | 4.9432 | 2.8154 | 5.0911 | 109.37 | 100.2641       |
|       | 0.4149 | 2.8613      | 14.257 | 101.0847       | 4.9407 | 2.8104 | 5.0997 | 109.32 | 100.2351       |
|       | 0.4518 | 2.8613      | 14.257 | 101.0847       | 4.9416 | 2.8035 | 5.1045 | 109.24 | 100.2038       |
|       | 0.4869 | 2.8613      | 14.257 | 101.0847       | 4.9414 | 2.8047 | 5.1022 | 109.18 | 100.1805       |
| M-H2  | 0.6144 | 2.8201      | 14.473 | 99.6823       | 4.9328 | 2.8059 | 5.0994 | 109.15 | 100.0122       |
|       | 0.6407 | 2.821      | 14.455 | 99.6219       | 4.9315 | 2.8071 | 5.0926 | 109.05 | 99.9556        |
|       | 0.6674 | 2.8212     | 14.447 | 99.5809       | 4.927 | 2.8099 | 5.0868 | 109.02 | 99.8682        |
|       | 0.6940 | 2.8197     | 14.447 | 99.4750       | 4.8894 | 2.8334 | 5.062 | 108.9 | 99.5193        |
| H2    | 0.7126 | 2.8183     | 14.399 | 99.0461       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |
|       | 0.7374 | 2.8168     | 14.399 | 98.9407       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |
| H2-H3 | 0.7652 | 2.8167     | 14.38  | 98.8031       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |
|       | 0.7911 | 2.8162     | 14.383 | 98.7887       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |
|       | 0.8178 | 2.8159     | 14.387 | 98.7951       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |
|       | 0.8444 | 2.8142     | 14.399 | 98.7581       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |
|       | 0.8622 | 2.8138     | 14.398 | 98.7232       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |
|       | 0.8889 | 2.8137     | 14.398 | 98.7162       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |
|       | 0.9150 | 2.8157     | 14.379 | 98.7261       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |
| H3    | 0.9369 | 2.8168     | 14.399 | 98.9407       | 4.8794 | 2.8334 | 5.062 | 108.9 | 99.5193        |

Table II. Structural parameters versus \( x \) in Li\(_{1-x}\)NiO\(_2\) as determined during the second charge of the in-situ cell.
site by passing through a tetragonal site. Based on their calculation, the diffusivity of lithium ion is dependent on the number of nearest vacancies in the Li layer. When a di-vacancy, exists the energy barrier to pass through the tetragonal site is much lower.

Figure 10a shows the specific capacity versus cycle number of Li/LiNiO₂ coin cells made with the same LiNiO₂ studied in the in-situ XRD studies. Coin cells were first cycled at 30°C between 3.0 and 4.3 V with a specific current of 10 mA/g (∼C/20) for two cycles, and then were cycled with a specific current of 40 mA/g (∼C/5) for 20 cycles. After the cycling, coin cells were cycled with a specific current of 10 mA/g (∼C/20) for one more cycle. Figure 10b shows dQ/dV vs. V of the C/20 cycle (black curves) of the fresh cell and the 1st C/5 cycle (blue curves). Figure 10c shows the 20th C/5 cycle (green curves) and the C/20 cycle (red curves) after the cycling tests. The 1st C/5 cycle dQ/dV vs. V is also shown in Figure 10c for comparison. Figure 10b shows that compared with the C/20 cycle, the C/5 cycle has the same peak shape as the preceding C/20 cycle except for the peak at ∼3.5 V, which diminished with the increase in rate. Figure 10c shows that after the 20 C/5 cycles, the 3.5 V peak shrank dramatically while other peaks in dQ/dV were virtually the same. The post cycling C/20 cycle shows that with a relatively low rate, the diminished 3.5 V peak can be partially recovered. The origin of the increased kinetic hindrance is still unclear although there are some works about lithium kinetics in literature. C. Delmas et al.²³ shows that for lithium deficient Li₁₋ₓNiₓO₂, there were more Ni atoms in the Li layer, and cells showed huge polarization and irreversible capacity, which can be attributed to a poorer lithium diffusion.¹⁷ It is believed that the Ni atoms between the transition metal oxide slabs can hinder the lithium diffusion by reducing the number of divacancies, and also increase the local lithium diffusion activation energy by decreasing inter slab distance in the vicinity of cationic mixing Ni atoms.²³ This region of kinetic hindrance near 3.5 V was recently highlighted in a study of NCA by J. Li. et al.²⁴ It may be that developing a complete understanding of the kinetic hindrance region in the model system LiNiO₂ will enable greater understanding of the commercially relevant NCA materials as well.

Conclusions

With commercial Ni(OH)₂ precursors and an improved synthesis method, modern LiNiO₂ with high capacity and low irreversible
capacity was made. Using this high quality LiNiO₂, this work systematically measured the electrochemical and structural properties of LiNiO₂ with in-situ XRD and careful electrochemical measurements. Multiple phase transitions during charge and discharge were carefully observed and analyzed. A distinct slow H₁-M phase transition behavior during first charge and the development of kinetic hindrance, most likely due to slow Li diffusion, in the H₁ phase region during extended charge-discharge cycling was observed. For LiNiO₂ and other high Ni content positive electrode materials like NCA, an understanding of the kinetic hindrance is essential in order to eliminate it.

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