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**In-situ** neutron diffraction study of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($x = 0, 0.5; M = \text{Ni, Mn, Co}$) layered oxide compounds during electrochemical cycling

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**HIGHLIGHTS**
- Pouch cells have been built for *in-situ* neutron diffraction study.
- *In-situ* neutron diffraction was performed on layered oxide compounds.
- *Ex-situ* neutron powder diffraction was performed on Li-excess layered compounds.
- The dynamic changes in both cathode and anode have been observed simultaneously.

**ABSTRACT**

The layered oxide compounds $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (M = Ni, Mn, Co) are of great interest as positive electrode materials for high energy density lithium-ion batteries. *In-situ* neutron diffraction was carried out to compare the structural changes between the classical layered compound $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}O_2]$ ($x = 0$) and lithium-excess layered compound $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Mn}_{0.53}\text{Co}_{0.1}O_2]$ ($x = 0.5$) during electrochemical cycling. In this work, lab made pouch cells were built for the *in-situ* study and graphite was used as the anode material. Irreversible structural change of $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.18}\text{Mn}_{0.53}\text{Co}_{0.1}O_2]$ during first charge (4.7 V) indicated by dynamic changes in lattice d-spacing, while the $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]O_2$ showed completely reversible structural evolution between 4.4 V and 2.5 V. *Ex-situ* neutron powder diffraction performed on Li-excess layered compounds better understand the irreversible structure change.

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1. Introduction

Rechargeable lithium-ion batteries play a significant role in many portable devices such as laptops and cell phones. They are emerging as the energy storage systems for electric vehicles because of high energy density and long cycle life. The layered oxide compounds $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (M = Ni, Mn, Co) are of great interest as a new generation of positive electrode materials for high energy density layered-oxide batteries because of their high energy density at lower costs. The currently commercialized $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}O_2$ (x = 0) cathode material, has, firstly been reported to have a capacity of 150 mAh g$^{-1}$ in the voltage window of 2.5–4.2 V by Ohzuku et al., [1] and 200 mAh g$^{-1}$ in the voltage window of 2.5–4.6 V. [2] S.C. Yin et al. suggests an upper cutoff voltage of 4.3–4.4 V for good cycling retention, as their observation shows that in this voltage window, lithium de/re-intercalation is reversible. [3] Recently, there is an intense research effort focused on the Lithium excess material $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (in LiMO$_2$, M = Ni, Mn, Co) where x > 0, which has excess Li in the transition metal layer. The X-ray diffraction pattern of the layered oxides can be refined with the z-NaFeO$_2$ structure (R-3m) [1–3]. Superlattice peaks exist in the X-ray diffraction pattern between 20 and 25° (2θ), which are associated with a honeycomb ordering of Li$^{+}$, Ni$^{2+}$, Mn$^{4+}$, and Co$^{3+}$ in the transition metal layer [4,5]. The Lithium-excess materials can deliver reversible capacities in excess of 250 mAh g$^{-1}$ when the x is close to 0.5 [6–8], but large irreversible capacity up to ~100 mAh g$^{-1}$ exists in the first charge and discharge between 2 V and 4.8 V, several groups have proposed detailed mechanisms for this large irreversible capacity [9,10].
During the initial charging region in first cycle, as lithium is removed from the layered structure the capacity originates from the oxidation of $\text{Ni}^{2+}$ to $\text{Ni}^{3+}$ and $\text{Co}^{3+}$ to $\text{Co}^{4+}$ up to 4.4 V. A high voltage plateau region around 4.5 V appears after the slope region. The large first cycle irreversible capacity has been mainly attributed to an irreversible loss of oxygen from the lattice during the first charge accompanied by Li removal. It is also a result of side reactions with the electrolyte on the electrode surface [7,9,11]. However, it is still up to debate where the anomalous high reversible capacity comes from in the lithium excess layered oxides. In order to gain more in-depth insights about the differences in classical layered oxide ($x = 0$) and lithium excess layered oxide ($x = 0.5$), in-situ neutron diffraction experiments were designed to observe the structural and compositional changes in these oxides during electrochemical process.

Previous literature has focused heavily on the use of X-ray scattering to understand the structural evolution of these materials. Recently, an in-situ XRD study has been done on the Li [$\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_{2}$] to investigate the structural change and microstrain during the first electrochemical cycle [12]. In addition, an in-situ XAS experiment was performed on the Li[$\text{Li}_{0.17}\text{Li}_{0.2}\text{Co}_{0.07}\text{Mn}_{0.56}\text{O}_{2}$] to study the charge–discharge reaction mechanism in the first 2 cycles [13]. However, X-ray scattering is limited in that it interacts with the electrons surrounding the atoms making it difficult for Li-ion battery compounds, whereas neutron interacts with the atomic nuclei of materials. Neutron scattering has several distinct advantages over X-ray scattering for in-situ battery studies [14]: 1) Deep penetration that allows simultaneous observation of the cathode and anode; 2) Larger scattering contrast between neighboring elements in the periodic table specifically the scattering lengths, e.g. for transition metals in this case: Ni, 10.3 fm; Mn, $-3.73$ fm; Co, 2.49 fm; [3] and 3) The sensitivity to light elements such as Li is significant in order to estimate their position in the crystal structure. However, due to the large incoherent neutron-scattering cross-section of hydrogen, the existence of hydrogen is detrimental to the signal-to-noise ratio of neutron diffraction pattern. Separators (polyethylene based porous membrane) and poly carbonate based electrolyte solutions contain large amount of hydrogen. This poses a significant challenge to in-situ neutron diffraction for lithium ion battery research although it is such a powerful technique.

The number of in-situ ND studies are limited and have focused on traditional materials such as LiCoO$_2$ [14,15], LiMn$_2$O$_4$ [16,17], Li$_4$Ti$_5$O$_12$ [18] and graphite [19]. In order to avoid large absorption from the presence of hydrogen in the separator and electrolyte, most studies use a special designed electrochemical cell [14–16,18,19]. In this work, lab made pouch cell were designed for in-situ ND study. Both LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and Li [$\text{Li}_{0.2}\text{Ni}_{0.18}\text{Mn}_{0.53}\text{Co}_{0.1}\text{O}_{2}$] materials are studied by in-situ neutron diffraction during electrochemical cycling on the engineering materials diffractometer VULCAN (see the references), at Spallation Neutron Source, Oak Ridge National Laboratory. The structural transition behaviors of the two cathode compounds during the first few cycles are presented. Structure change and phase transition of anode graphite is also discussed briefly in this article.

2. Experimental methods

2.1. Synthesis

A coprecipitation followed by two steps calcination was used for the synthesis of the materials [20]. Transition metal (TM) nitrates, Ni(NO$_3$)$_2$·6H$_2$O (ARCROS, 99%), Co(NO$_3$)$_2$·6H$_2$O (ARCOS, 99%), and Mn(NO$_3$)$_2$·4H$_2$O (Alfa Aesar, 98%) were dissolved into deionized water then titrated into LiOH·H$_2$O (Fisher) solution. The coprecipitated TM hydroxides were then filtered using vacuum filtration 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 then mixed with a stoichiometric amount of LiOH·H$_2$O (Fisher) 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 then calcinated at 900 °C for 12 h in air.

Chemical delithiations were performed in a glovebox (argon atmosphere) with <1 ppm moisture, Li$_{1.2}$Ni$_{0.2}$Mn$_{0.6}$O$_2$ was mixed with the designed amount of NO$_2$BF$_4$ (ARCOS, 97%) in acetonitrile (Alfa Aesar, 99.8%) and stirred for 24 h, then filtered.

![Fig. 1.](image-url) (a): Simple schematic of lab made pouch cell for in-situ neutron diffraction study; (b): Pouch cell installed on VULCAN beamline.
2.2. Cell design

Fig. 1a is a simple schematic of our pouch cell, which includes a dual sided graphite anode (the anode is based on standard graphite material) and two pieces of single side cathode. The electrode loading for the anode and Li[Li0.2Ni0.18Mn0.53Co0.1]O2 cathode is around 8 mg cm\(^{-2}\), while the loading for LiNi\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\) cathode is around 12 mg cm\(^{-2}\). This cell configuration design aimed at increasing the loading of active materials in our pouch cells to increase neutron diffraction pattern statistics. Cells were all assembled in a glovebox under argon atmosphere. A Celgard separator is used to cover the anode with a piece of single side cathode on each side of the anode. The electrolyte solution composed of 1 M LiPF\(_6\) in a 1:1 ethylene carbonate (EC):dimethyl carbonate (DMC). The cathode is composed of 90% active material, 5% PVDF and 5% carbon black on an aluminum collector. In order to ensure the full charge performance of the cathode materials, about 25% excess anode material was used in the pouch cell.

2.3. In-situ neutron diffraction

A Bio-Logic SP-300 potentiostat was used to electrochemically cycle the cell under constant charge and discharge currents. The Li[Li0.2Ni0.18Mn0.53Co0.1]O2/C pouch cell was charged at 32 mA (~C/15) to 4.7 V then discharged at ~27 mA (~C/15) to 2 V while the LiNi\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\)/C pouch cell was charged at 43.2 mA (~C/5) to 4.4 V then discharged at ~43.2 mA (~C/5) to 2.5 V. In order to observe more cycles within the limited beam time, the following cycles between a voltage range of 2.5–4.4 V were used: 84 mA (~C/2) to charge and discharge. Fig. 1b is the cell setup at the VULCAN beamline. An incident beam (5 mm × 12 mm) of 0.5–3.5 Å bandwidth allowing 0.5–2.5 Å d-space in diffracted pattern in the \(\theta \pm 90^\circ\) detector bank was selected using the double-disk choppers at 30 Hz speed. The SNS was at nominal 800 KW. Time stamped neutron event data were collected while the cells were under continuous cycling [21]. Neutron diffraction data were sliced (every 3600 s) and reduced by the VDRIVE software [22]. Single peak refinements were carried out using the GSAS [23] program.

2.4. Ex-situ neutron powder diffraction

Neutron powder diffraction patterns were collected for the lithium excess materials Li[Li0.2Ni0.18Mn0.53Co0.1]O2 and chemically delithiated lithium excess sample using beamline HB2A [24] at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory. Samples were loaded in a hermetically sealed holder to prevent air exposure. A monochromatic incident wavelength of 1.54 Å was chosen. Full pattern Rietveld refinement was performed using the GSAS [23] programs with the EXPGUI [25] interface.

3. Results and discussion

3.1. Cathode in Li[Ni\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)]O\(_2\)/C pouch cell

Fig. 2(a)−(c) shows the charge/discharge curve with surface contour plots of Li[Ni\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)]O\(_2\) (102), (108) and (110) ND peaks evolution as a function of time. The hydrogen atoms due to the presence of a large volume of electrolyte and separator materials contribute to the large fraction of the background, which reduces the signal-to-noise ratio. Other components in the pouch cell, such as the Al and Cu current collectors have crystalline features and cause ND peak overlap. These factors forced the use of single peak refinement to prevent erroneous full profile fitting results. Since both the cathode and anode material have a hexagonal lattice, \(d_{hkl}\) can be calculated by using the equation below:

\[
1/d_{hkl} = \left\{ 4/3*\left[ (h^2 + hk + k^2) / a^2 + l^2 / c^2 \right] \right\}^{1/2}
\]

Fig. 4a is \(a\)- and \(c\)-lattice parameters evolution during cycling. During charging, Li\(^+\) is extracted from the layered structure, at the same time Ni\(^{2+}\) is oxidized to Ni\(^{3+}\) which leads to ionic radii decreasing (e.g. r Ni\(^{3+}\) = 0.60 Å, r Ni\(^{4+}\) = 0.48 Å), as a consequence \(a\)-lattice parameter contracted monotonously. The removal of Li\(^+\) introduces a concentration gradient and electrostatic repulsion from adjacent oxygen layers accounting for the increased \(c\)-lattice parameter [26]. The (108) peak remains unchanged while (110) decreased rapidly when Li ions are extracted, and at the end of charge (110) planes have the shortest distance. The (108) plane corresponds to the out-of-plane periodicity, which intersects 1 in
every 8 transition metal (TM) or Li⁺ layers (along the c-axis). The out-of-plane lattice spacing changes correspond strongly to the c-lattice parameter. As I increases in the (10f) family of peaks, the d₁₀₂ shift decreases in magnitude. Since f here equals to 8 the change of c only brings negligible change of d₁₀₂. The (110) plane depends strongly on a-lattice parameter, illustrating strong anisotropy in the material during electrochemical cycling. At the beginning of the charge a = 2.852 ± 0.001Å c = 14.173 ± 0.0008Å which are close to the reported results, [3] and the trends upon charge are consistent with previous work [27]. The discharge is a process of Li⁺ reinserting into the layered structure. After discharge, a- and c-parameter return to a = 2.851 ± 0.001Å c = 14.179 ± 0.0006Å illustrating a completely reversible intercalation mechanism. Fig. 2(e) and (f) show the (102), (110) and (108) peaks in the following cycles, only 5–7th cycles data were collected due to beam off during 2nd–4th cycles. But we can clearly see the (108) remains unchanged, while (102) and (110) repeatedly decrease during charge and increase during discharge.

3.2. Li[Li₀.₂Ni₀.₁₈Mn₀.₅₃Co₀.₁]O₂/C pouch cell

As a comparison study, the structural changes of the Li [Li₀.₂Ni₀.₁₈Mn₀.₅₃Co₀.₁]O₂ cathode and graphite anode during first electrochemical cycle were observed. The pouch cell has a characteristic sloping region up to 4.3 V and a plateau region at 4.4 V. The charge capacity is more than 250 mAh g⁻¹, discharge capacity is more than 200 mAh g⁻¹ due to irreversible capacity loss in the first cycle. The capacity before 4.3 V is more than 90 mAh g⁻¹, suggesting that most of the Co³⁺ has been oxidized to Co⁴⁺.

Fig. 3(a)–(e) shows the charge/discharge curve with several selected ND peaks visually depicted as surface contour plots to show the peak evolution as a function time. Due to the limited amount of active materials in the beam, only the evolution of (102) peak of Li[Li₀.₂Ni₀.₁₈Mn₀.₅₃Co₀.₁]O₂ has been observed. Fig. 4b is the single peak refinement results for d₁₀₂ change during the first electrochemical cycle. In the slope region before 4.3 V, d₁₀₂ decreased rapidly from 2.326 ± 0.0005Å to 2.318 ± 0.0006Å, corresponding to the Ni²⁺/Ni⁴⁺ and Co³⁺/Co⁴⁺ redox reaction. As aforementioned, when Li⁺ is extracted from the layered structure, Ni²⁺ is oxidized to Ni⁴⁺ and Co³⁺ is oxidized to Co⁴⁺ which results in a decrease in the ionic radii of these ions and a larger repulsion from the adjacent oxygen layers. After the slope region a plateau is observed, in this region the d₁₀₂ spacing decreased slightly by 0.002 ± 0.0005Å. During discharge, Li⁺ is reinserted into the structure, subsequently the d₁₀₂ spacing increases monotonically. At the end of first cycle, d₁₀₂ is 2.338 ± 0.0006Å which is larger than the pristine value. Although it is hard to distinguish how the a- and c-lattice parameters have changed after the first electrochemical cycle, it is obvious that the volume of the lattice has increased, which is consistent with previous reports [7,12].

Compared to the cathode, the graphite anode shows stronger peaks such as the (112), (110), (004) and (006). Fig. 3(c)–(e) only shows the Li₃C₆ (004) and (110) peak. Since several in-situ ND studies have previously reported the structural changes seen with the graphite anode [15,28], it will not be discussed in detail here. By looking at Fig. 3(c)–(e), at the end of charge, the Li₃C₆ (004) peak becomes weak while LiC₆ (002) peak starts to appear, indicating a phase transformation process. The phase change process is also indicated by Li₃C₆ (110) peak, at the middle stage of charge LiC₁₂ phase formed, then gradually transforms to LiC₆ phase as more Li⁺ inserted into the anode. In the current cell design there is 25% excess graphite anode, so at the end of charge we should have a mixed phase between Li₃C₆ and LiC₆. Neeraj Sharma [15] also observed a two phase system at end of charge for their in-situ ND study on the LiCoO₂/C system. Fig. 4c shows the calculated graphite lattice parameters during the first charge/discharge process. At the beginning of the 1st charge, the a-parameter of the graphite anode is 2.458 ± 0.0017Å and the c-parameter is 6.776 ± 0.0004Å (distance between carbon layers equals c/2), while at the end of charge it undergoes a phase change to LiC₁₂ phase coupled with a large increase in the a-parameter of 4.304 ± 0.0003Å and the c-parameter of 3.666 ± 0.0003Å (distance between carbon layers equals c/2), which is consistent with previous work [29,30]. During discharge, as Li⁺ is extracted from the graphite layer the LiC₆ phase disappeared. At the end of the discharge the a-parameter of the LiC₆ phase goes back to 2.462 ± 0.0024Å slightly larger than the pristine which is 2.458 ± 0.0017Å, possibly because of the irreversible Li⁺ in the graphite. In another word, the structure of anode
as reversible during electrochemical cycle. The ability of monitoring the dynamic structural changes in cathode and anode simultaneously is another strong merit of neutron scattering technique.

3.3. Ex-situ neutron diffraction on Li[Li0.2Ni0.2Mn0.6]O2

As a complementary experiment of in-situ neutron study of lithium-excess layered oxide material, ex-situ neutron diffractions were carried out on lithium-excess material Li[Li0.2Ni0.2Mn0.6]O2. Chemical delithiation was designed to simulate the charge process where a large amount of Li is extracted from the structure. Chemical delithiation was designed to remove 0.8 mol of Li+ from Li[Li0.2Ni0.2Mn0.6]O2 by using NO2BF4. After 0.4 mol of Li+ removed from the structure, all the Ni2+ were oxidized to Ni4+. The rest 0.4 mol Li+ were assumed to be removed in the form of Li2O. Neutron diffraction patterns of the pristine sample and chemically delithiated sample are shown in Fig. 5 and refined using a single R-3m phase [4,5]. The superlattice peaks can be seen more clearly in the chemically delithiated sample. It is possible that the irreversible loss of oxygen increased the contrast between the superlattice peaks and main peaks. These peaks cannot be fitted by using R-3m space group. According to previous study of layered oxides [31], we used C2/m and P3112 space groups to do the pattern matching (see support information Figure S1–S4). By applying C2/m and P3112 space group, not only these superlattice peaks, but also other peaks can be fitted, e.g. the peak at 4.2 Å. Although these peaks can be fitted using the C2/m or P3112 space groups, refinement of the structural model is lacking due to large amounts of defects originating from chemical delithiation oxygen vacancies. We propose that chemical delithiation creates large amounts of site disorder as well as structural defects within the lithium-excess material that prohibit simple structural refinement using a single R-3m, C2/m or P3112 space group. In order to refine the pattern quantitatively, more work has to be done to identify the suitable structure model.

Rietveld refinement of the chemically delithiated structure used a single R-3m space group excluding the superlattice range and was based on 0.4 mol Li+ in the structure (Li0.8Ni0.2Mn0.6O1.8). After delithiation, the lattice parameter a decreased 0.008 Å, while the lattice parameter c increased 0.0141 Å due to Ni oxidation from Ni2+.
the layered oxides family: classical layered oxide LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and lithium excess layered oxide Li[Li$_{0.2}$Ni$_{0.18}$Mn$_{0.53}$Co$_{0.1}$]O$_2$. By using a single peak refinement technique, structural changes of these two materials are observed quantitatively. Li excess layered oxide Li[Li$_{0.2}$Ni$_{0.18}$Mn$_{0.53}$Co$_{0.1}$]O$_2$ shows an irreversible volume expansion after the first cycle which is most likely caused by oxygen loss from the structure, while classical layered oxide LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ retains the reversible structure in the electrochemical voltage window. Anisotropy in the a- and c-lattice directions are observed. Ex-situ neutron diffraction experiments on lithium-excess material also reveal irreversible changes of structure after chemical delithiation. Major efforts are currently underway to improve the in-situ neutron scattering data quality to enable full Rietveld refinement of atomic positions. In addition to having the ability to monitor the dynamic changes in the cathode, our setup allows for the simultaneous observation of the anode material. Our observation shows a phase transformation in the anode at end of charge and start of discharge. The reversible change of structure and phase transformation shows good reversibility performance of the graphite anode.

4. Conclusion

In this work, a lab pouch cell was designed for in-situ Neutron diffraction in order to study two high capacity cathode materials in the layered oxides family: classical layered oxide LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and lithium excess layered oxide Li[Li$_{0.2}$Ni$_{0.18}$Mn$_{0.53}$Co$_{0.1}$]O$_2$. By using a single peak refinement technique, structural changes of these two materials are observed quantitatively. Li excess layered oxide Li[Li$_{0.2}$Ni$_{0.18}$Mn$_{0.53}$Co$_{0.1}$]O$_2$ shows an irreversible volume expansion after the first cycle which is most likely caused by oxygen loss from the structure, while classical layered oxide LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ retains the reversible structure in the electrochemical voltage window. Anisotropy in the a- and c-lattice directions are observed. Ex-situ neutron diffraction experiments on lithium-excess material also reveal irreversible changes of structure after chemical delithiation. Major efforts are currently underway to improve the in-situ neutron scattering data quality to enable full Rietveld refinement of atomic positions. In addition to having the ability to monitor the dynamic changes in the cathode, our setup allows for the simultaneous observation of the anode material. Our observation shows a phase transformation in the anode at end of charge and start of discharge. The reversible change of structure and phase transformation shows good reversibility performance of the graphite anode.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2013.04.149.

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