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To cite this article: S.-H. Kang *et al* 2003 *Electrochem. Solid-State Lett.* **6** A183

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Electrochemical and *Ex Situ* X-Ray Study of Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O₂ Cathode Material for Li Secondary Batteries

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Electrochemical properties of Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O₂, synthesized by a sol-gel method, were studied by galvanostatic cycling. When the Li/Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O₂ cell was cycled at 2.0-4.6 V, the material showed a long, irreversible plateau at 4.5-4.6 V and exhibited very high initial charge capacity of 240 mAh/g, which is much larger than a theoretical value for the reaction of Li(Li⁺_{0.2}Ni²⁺_{0.2}Mn⁴⁺_{0.6})O₂ → Li_{0.6}(Li⁺_{0.2}Ni⁴⁺_{0.2}Mn⁴⁺_{0.6})O₂ + 0.4Li (126 mAh/g). Discharge capacity of the material gradually increased from 155 at the first cycle to 205 mAh/g at the tenth cycle and was stabilized afterward. From the *ex situ* X-ray study, we found that Li ions in the transition metal layer were irreversibly extracted during charging at a voltage higher than 4.5 V; the diffraction peaks corresponding to Li in the transition metal layer were hardly observed in the cathode material after extended cycling. The Li/Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O₂ cell that was cycled at 2.0-4.3 V showed stable but very small capacity (69 mAh/g) and Li in the transition metal layer remained almost intact. When the cell was initially charged to 4.6 V and then cycled at 2.0-4.3 V, the cathode material showed higher capacity (114 mAh/g) than the one cycled at 2.0-4.3 V.

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Manuscript submitted March 18, 2003; revised manuscript received May 8, 2003. Available electronically June 30, 2003.

Due to their low cost and improved thermal stability, Li(Ni_{0.5}Mn_{0.5})O₂-based materials are considered possible alternatives to LiCoO₂- and LiNiO₂-based cathode materials for rechargeable lithium batteries. Of these, a solid mixture of Li(Ni_{0.5}Mn_{0.5})O₂ and Li₂MnO₃ is attractive because of its high usable capacity (>200 mAh/g) and stability at high voltage (>4.5 V),^{1,2} although it is not clear whether the two end members make a solid solution or a composite.^{1,3} The most interesting feature of the solid mixture, or Li(Li_{1/3-2x/3}Ni_xMn_{2/3-x/3})O₂, is its discharge capacity, which is higher than theoretical value. For example, according to Lu *et al.*,¹ Li(Li_{0.113}Ni_{0.33}Mn_{0.556})O₂ exhibited an initial charge capacity of ~280 mAh/g and a subsequent stable discharge capacity of ~225 mAh/g between 2.0 and 4.8 V. However, the theoretical capacity of the material for the Ni²⁺/Ni⁴⁺ redox couple is only 200 mAh/g. It is curious where the extra capacity originates, especially during the first charging process. Lu and Dahn⁴ explained that during the first charge the material first reached the stoichiometry of Li_{0.33}(Li⁺_{0.113}Ni⁴⁺_{0.33}Mn⁴⁺_{0.556})O₂ at 4.45 V, which corresponds to the theoretical capacity of 200 mAh/g, and then further Li extraction from the Li layer was compensated by oxygen loss so that the final composition at 4.8 V was (Li⁺_{0.113}Ni⁴⁺_{0.33}Mn⁴⁺_{0.556})O_{1.833}. Another possible explanation of the extra capacity is participation of oxygen ions in the redox reactions. Recently, we reported that oxygen ions also contributed to the charge compensation during delithiation of Li(Li_{0.15}Ni_{0.275-x}Mg_xMn_{0.575})O₂.² Contribution of oxygen to the charge compensation has also been reported in other cathode materials such as LiCo_{0.5}Ni_{0.5}O₂,^{5,6} and LiAl_yCo_{1-y}O₂ (0 ≤ y ≤ 0.25).^{7,8}

In this work, Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O₂ was prepared by a sol-gel method; electrochemical cycling and an *ex situ* X-ray study were performed to enhance understanding of the electrochemistry of the material.

Experimental

Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O₂ powder was prepared by a sol-gel method using glycolic acid as a chelating agent. Li(CH₃COO) · 2H₂O (Kanto Chemical Co.), Ni(CH₃COO)₂ · 4H₂O (Aldrich Chemical Co.), and Mn(CH₃COO)₂ · 4H₂O (Acros Organics) were dissolved

in distilled water, and added dropwise to a continuously stirred aqueous solution of glycolic acid; solution pH was adjusted to 8-8.5 using ammonium hydroxide. The resultant solution was evaporated at 70-80°C until a transparent sol and gel were obtained. The resulting gel precursors were decomposed at 450°C for 10 h in air and then thoroughly ground using a mortar and pestle. The obtained powder was pressed into pellets, heated at 900°C for 3 h in air, and then quenched to room temperature. Crystallographic structure of the synthesized material was examined by a powder X-ray diffractometer using Cu Kα radiation.

Galvanostatic charge/discharge cycling was conducted with coin cells. The positive electrode consisted of 80 wt % oxide powder, 10 wt % carbon, and 10 wt % polyvinylidene difluoride (PVDF) binder on aluminum foil. The negative electrode was metallic lithium. The electrolyte was 1 M LiPF₆ in a 1:1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC); the separator was Celgard 2500. The coin cells were galvanostatically cycled between 2.0-4.6 V and 2.0-4.3 V at 0.1 mA/cm² (10 mA/g).

Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) pattern of the synthesized Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O₂. Most peaks in the XRD pattern of the sample could be indexed based on the α-NaFeO₂ structure (*R* $\bar{3}m$) with small extra peaks between 20 and 25° marked with arrows. Lu *et al.*¹ attributed the small, extra peaks that appeared near 21° in the XRD patterns of Li[Ni_xLi_{1/3-2x/3}Mn_{2/3-x/3}]O₂ (0 < x < 1/2) to the superlattice ordering of Li and Mn in the transition-metal layers; Kim *et al.*³ proposed another possibility, *i.e.*, the presence of discrete domains of Li₂M'O₃ and LiMO₂ (or MO) components within a common closed-packed oxygen array. Recently, Ohzuku *et al.*⁹ reported an electron diffraction pattern of Li(Ni_{0.5}Mn_{0.5})O₂ with *ca.* 9% displacement between Ni²⁺ at the 3a site and Li⁺ at the 3b site that showed extra spots corresponding to a [$\sqrt{3} \times \sqrt{3}$]R30° superlattice in addition to fundamental spots based on an α-NaFeO₂-type structure. More extensive studies such as transmission electron microscopy (TEM) and local structure refinement are necessary to interpret the crystal structure conclusively.

Galvanostatic charge/discharge curves of the Li/Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O₂ cell cycled between 2.0 and 4.6 V at 0.1 mA/cm² are shown in Fig. 2a; the corresponding capacity is given in Fig. 2b. During the initial charge to 4.6 V, a long, irreversible plateau appeared at 4.5-4.6 V, which is consistent with Lu *et al.*'s report,¹ and the initial charge capacity of 240 mAh/g was

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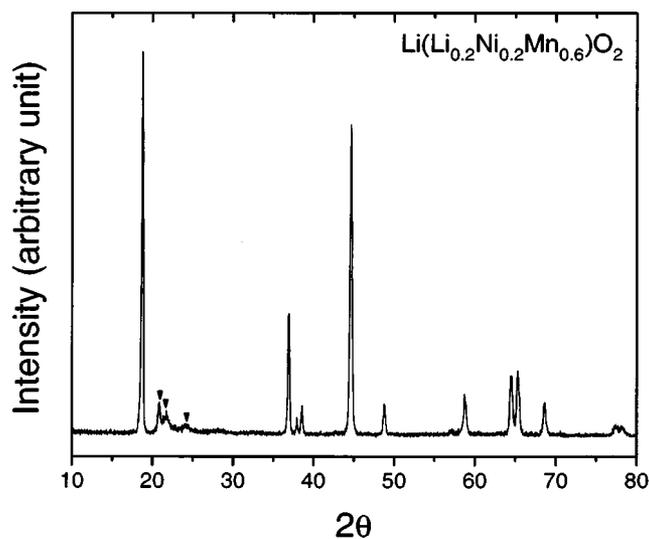


Figure 1. XRD pattern of $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ calcined at 900°C for 3 h in air.

observed, which is much larger than a theoretical value for the reaction of $\text{Li}(\text{Li}^+_{0.2}\text{Ni}^{2+}_{0.2}\text{Mn}^{4+}_{0.6})\text{O}_2 \rightarrow \text{Li}_{0.6}(\text{Li}^+_{0.2}\text{Ni}^{4+}_{0.2}\text{Mn}^{4+}_{0.6})\text{O}_2 + 0.4\text{Li}$ (126 mAh/g). At the first discharge to 2.0 V, however, the cells exhibited large irreversible loss and the first discharge capacity was only 155 mAh/g; by the repeated cycling between 2.0 and 4.6 V, the discharge capacity increased slowly and was stabilized at ca. 205 mAh/g after 10 cycles.

Figure 3 shows the differential capacity vs. voltage obtained from the charge/discharge curves given in Fig. 2a. The sharp peak at 4.5 V corresponds to the long plateau that appeared in the first charge curve in Fig. 2a. Unlike Lu *et al.*'s

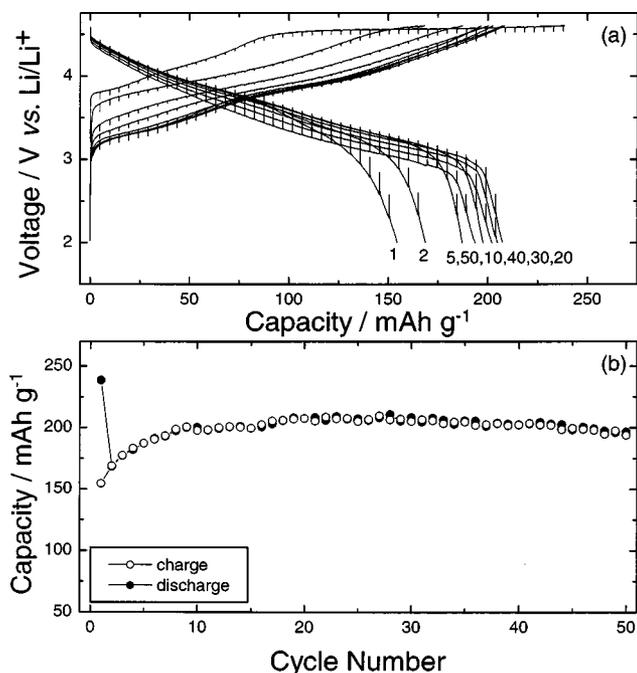


Figure 2. Galvanostatic charge/discharge curves of $\text{Li}/\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ cell in the voltage range 2.0-4.6 V at a current density of $0.1 \text{ mA}/\text{cm}^2$ (a) and (b) the corresponding capacity with cycling.

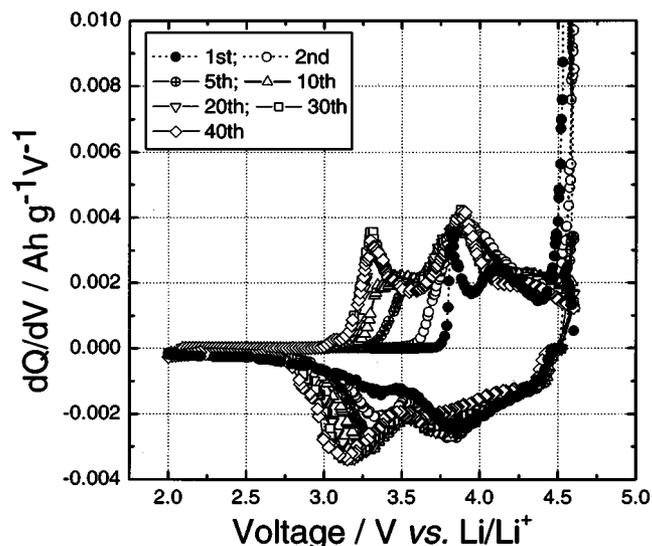


Figure 3. Differential capacity vs. voltage of the cell $\text{Li}/\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ cycled at 2.0-4.6 V.

$\text{Li}(\text{Ni}_x\text{Li}_{1/3-2x/3}\text{Mn}_{2/3-x/3})\text{O}_2$ ($1/6 \leq x < 1/2$), which showed the sharp peak at 4.5 V only at the first charge,¹ the sharp 4.5 V peaks in the differential capacity plot were observed up to the ninth cycle in our material; the 4.5 V peak intensity decreased with cycling to disappear almost completely after the tenth cycle. Note that the capacity was also stabilized after the tenth cycle. Lu *et al.*¹ attributed the sharp 4.5 V peak (or 4.5 V plateau) to the irreversible oxygen loss; they proposed that $\text{Li}(\text{Ni}^{2+}_x\text{Li}^{1/3-2x/3}\text{Mn}^{4+}_{2/3-x/3})\text{O}_2$ reached $\text{Li}_{1-2x}(\text{Ni}^{4+}_x\text{Li}^{1/3-2x/3}\text{Mn}^{4+}_{2/3-x/3})\text{O}_2$ upon charging at 4.45 V and further charging removed all the lithium from the lithium layer and induced oxygen loss so that the final stoichiometry at the top of charge (4.8 V in their cycling procedure) was $(\text{Ni}^{4+}_x\text{Li}^{1/3-2x/3}\text{Mn}^{4+}_{2/3-x/3})\text{O}_{1.5+x}$ based on simple calculation and *in situ* X-ray study. Another possibility for the charge compensation at voltage higher than 4.5 V is participation of oxygen ions in the redox reactions. Recently, it was reported that oxidation of oxygen was partially responsible for charge compensation in $\text{Li}(\text{Li}_{0.15}\text{Ni}_{0.275-x}\text{Mg}_x\text{Mn}_{0.575})\text{O}_2$,² $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$,^{5,6} and $\text{LiAl}_y\text{Co}_{1-y}\text{O}_2$ ($0 \leq y \leq 0.25$).^{7,8} One can see in Fig. 3 that new differential capacity peaks emerge below 3.5 V (3.30 V on charging and 3.15 V on discharging). Because the redox reaction between Ni^{2+} and Ni^{4+} occurs above 3.5 V, only the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple explains the differential peaks below 3.5 V in Fig. 3, as discussed by Lu and Dahn.⁴ In a similar layered structure, $\text{Li}_{2/3}(\text{Ni}_{1/3}\text{Mn}_{2/3})\text{O}_2$, $\text{Mn}^{3+}/\text{Mn}^{4+}$ a redox reaction was reported to occur at about 2.9 V.¹⁰ It is presumed that a different oxygen environment (either due to a reduced number of surrounding oxygen by oxygen loss or due to the higher valence of oxidized oxygen, *i.e.*, $\text{O}^{(2-\delta)-}$, $\delta > 0$) resulted in a higher redox potential of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couple. More careful studies are needed to explore the charge compensation mechanism at high voltage range and the oxidation state of transition metal at the discharged state.

Comparison of Fig. 2a and Fig. 3 suggests that the existence and disappearance of the 4.5 V peak in the differential capacity plot are related with gradual increase and saturation of capacity, respectively. To examine the structural change in $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ during cycling, *ex situ* X-ray study of the cathode material was carried out during the first charge and discharge; Fig. 4 shows the XRD patterns of the cathode materials at various states of charge. When the cathode was charged to a voltage lower than 4.5 V, the small peaks near 21° of 2θ remained almost intact. When the charging voltage was higher than 4.5 V, however, they started to diminish; at the top of

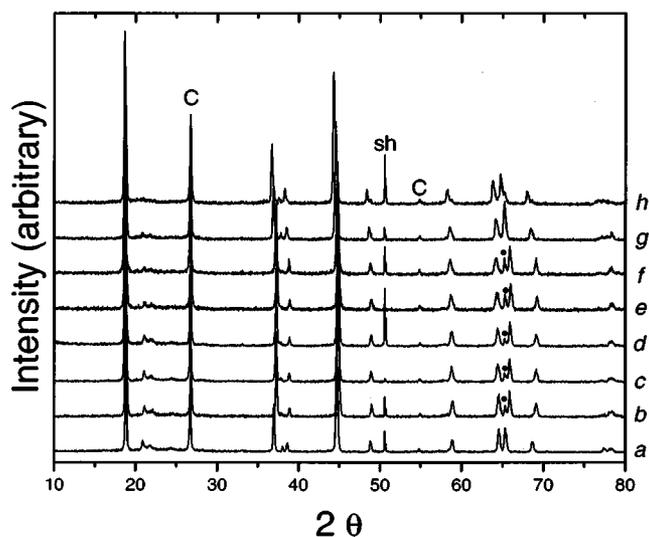


Figure 4. *Ex situ* XRD patterns of the $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ cathode at various states of charge. (a) Fresh cathode; (b) 4.2 V (58 mAh/g); (c) 4.3 V (74 mAh/g); (d) 4.45 V (88 mAh/g); (e) 4.57 V (194 mAh/g); (f) 4.6 V (240 mAh/g); (g) discharged to 2.0 V; (h) cycled 50 times at 2.0-4.6 V and discharged to 2.0 V. All the diffraction patterns except h were taken during the first cycling. C and sh denote carbon and X-ray sample holder, respectively. The diffraction peaks marked with a dot at $\sim 65^\circ$ are from an aluminum current collector.

charging (4.6 V), there existed only a trace of the peaks near 21° . After discharging the cathode to 2.0 V, those peaks were not recovered; they completely disappeared after the extended cycling between 2.0 and 4.6 V. Because the small peaks near 21° are indicative of the presence of Li in the transition metal layers, the XRD patterns shown in Fig. 4 suggest that Li is extracted from the Li layer at voltages lower than 4.5 V and from the transition metal layer at voltages higher than 4.5 V, which is contrary to Lu and Dahn's speculation that Li was extracted only from the Li layer.⁴ Since the amount of Li in the transition metal layer corresponds to 63 mAh/g of capacity and the length of the 4.5 V plateau in Fig. 2 is 130 mAh/g, Li seems to be extracted also from the Li layer at 4.5-4.6 V. Recently, Yoon *et al.*¹¹ detected the presence of Li in the transition metal layer even in $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ by Li^6 magic-angle spinning (MAS) NMR spectroscopy; their NMR spectrum of $\text{Li}_{1-x}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ indicated that Li ions were removed from both transition metal and Li layers. The XRD patterns f and g in Fig. 4 also suggest that Li ions in the transition metal layer were not removed completely during the first charge nor reinserted reversibly. During subsequent cycling, Li ions in the transition metal layer seem to be gradually removed further during the first ten cycles where the capacity also increased gradually. Our speculation is that Li is inserted/extracted only to/from the Li layer so that capacity becomes stable when Li in the transition metal layer is removed completely or no further extraction of Li from the transition metal layer is possible. In summary, (i) Li is extracted mostly from the Li layer below 4.5 V and simultaneous removal of Li from Li and transition metal layers occurs above 4.5 V; (ii) the long plateau at 4.5-4.6 V observed during the first charge is closely related to the extraction of Li from the transition metal layer; and (iii) Li is not reinserted into the transition metal layer reversibly.

Figure 5 shows the charge/discharge curves of the $\text{Li}/\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ cell cycled between 2.0 and 4.3 V at $0.1 \text{ mA}/\text{cm}^2$ and corresponding discharge capacity as a function of cycle number. When the cell was cycled only at 2.0-4.3 V, it exhibited a very small discharge capacity of 69 mAh/g, and no significant change in the differential capacity curves was observed throughout the whole cycling as shown in Fig. 6a. However, when the cell was

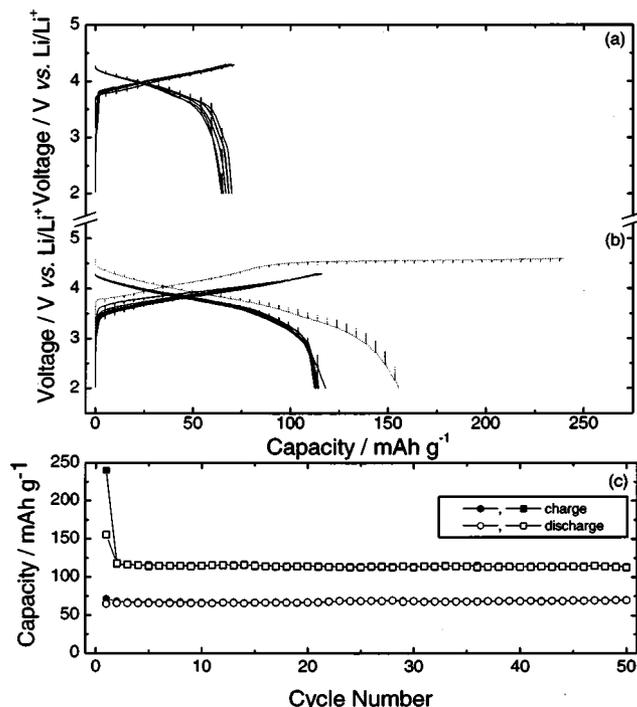


Figure 5. Charge/discharge curves of $\text{Li}/\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ cells (a) cycled in the voltage range 2.0-4.3, (b) charged to 4.6 V and then cycled in the voltage range 2.0-4.3, and (c) the corresponding capacity with cycling.

first charged to 4.6 V and then cycled at 2.0-4.3 V, it delivered a discharge capacity of 114 mAh/g and showed different differential capacity curves from the cell cycled only at 2.0-4.3 V.

The XRD patterns of the two cycled cathodes are shown in Fig. 7. The cathode cycled only at 2.0-4.3 V exhibited almost the same diffraction pattern as the fresh one; the small peaks near 21° remained almost intact. The diffraction pattern of the cathode charged to 4.6 V and then cycled at 2.0-4.3 V is similar to diffraction pattern g in Fig. 4, which indicates that no further Li removal occurred during the subsequent cycling at 2.0-4.3 V.

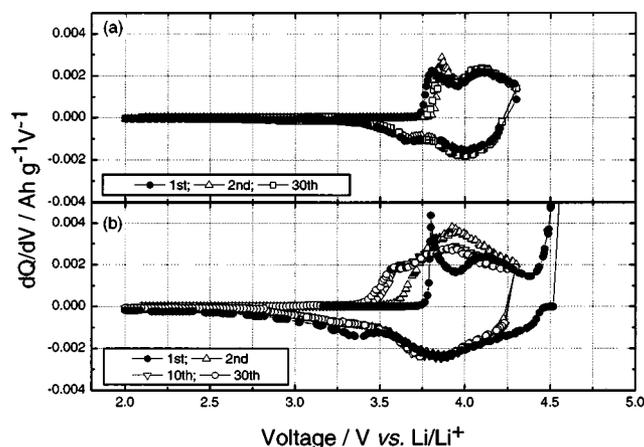


Figure 6. Differential capacity vs. voltage of the cell $\text{Li}/\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ (a) cycled at 2.0-4.3 V, (b) charged to 4.6 V and then cycled at 2.0-4.3 V.

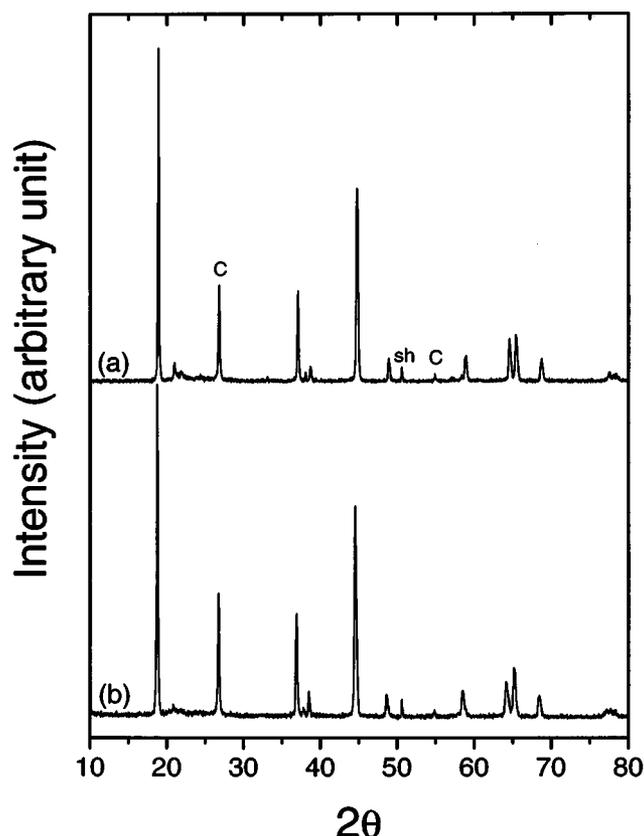


Figure 7. XRD patterns of the $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ cathode (a) cycled at 2.0-4.3 V, (b) charged to 4.6 V and then cycled at 2.0-4.3. C and sh denote carbon and X-ray sample holder, respectively.

Conclusions

Layered $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6})\text{O}_2$ was prepared by a sol-gel method and galvanostatically cycled between 2.0 and 4.6 V with different cycling procedures. The first charge capacity of the material cycled

at 2.0-4.6 V was 240 mAh/g, which is much higher than the theoretical value; the discharge capacity was only 155 mAh/g at the first cycling and increased gradually to 205 mAh/g. When the material was cycled only at 2.0-4.3 V, it delivered only 69 mAh/g of capacity. When the material was charged to 4.6 V initially and then cycled at 2.0-4.3 V, the discharge capacity was 114 mAh/g. From the variation of capacity with cycling, differential capacity curves, and *ex situ* X-ray studies, we concluded that Li was extracted from the Li layer below 4.5 V and from both the Li and the transition metal layers above 4.5 V; the removed Li was not reinserted reversibly into the transition metal layer. The results of this work suggest that all the Li ions must be extracted from the transition metal layer to obtain high capacity from $\text{Li}(\text{Li}_{1/3-2x/3}\text{Ni}_x\text{Mn}_{2/3-x/3})\text{O}_2$.

Acknowledgments

This work was supported by the U.S. Department of Energy, Office of Advanced Automotive Technologies, under contract no. W-31-109-ENG-38. Argonne National Laboratory is managed by the University of Chicago for the U.S. Department of Energy under this contract.

Argonne National Laboratory assisted in meeting the publication costs of this article.

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