
**Structural Studies of New Cathode and Anode
Materials for Lithium Batteries Using *In Situ*
XRD and x-ray Absorption Spectroscopy**

Dr. X.-Q. Yang

(Brookhaven National Lab. USA)

Structural Studies of New Cathode and Anode Materials for Lithium Batteries Using *In Situ* XRD and x-ray Absorption Spectroscopy

X. Q. Yang, J. McBreen, and M. Balasubramanian
Brookhaven National Lab. Upton, NY11973, USA
W-S. Yoon and C. P. Grey, SUNY Stony Brook, Stony Brook NY11794, USA
M. Yoshio, Saga University, Saga, 840-8502, Japan
X. Huang, L. Chen, and L. Liu, Institute of Physics, Chinese Academy of Sciences

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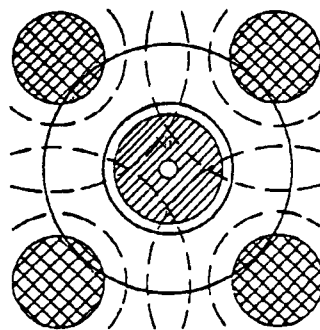
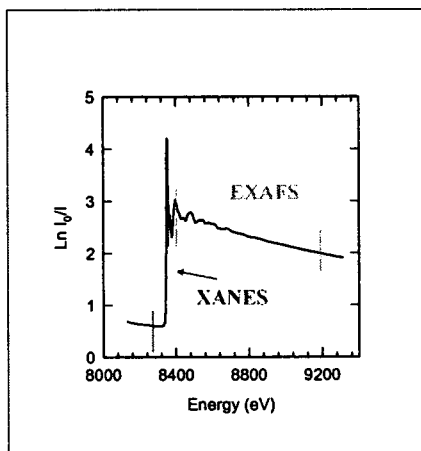
Acknowledgment

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Outlines

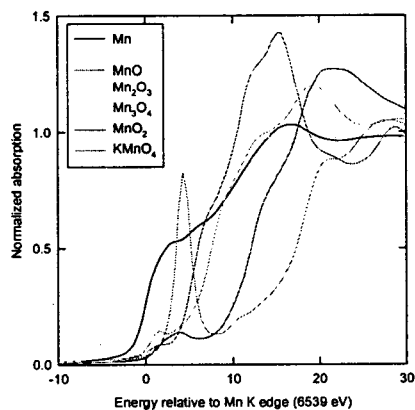
- The structure studies of the new carbon coated silicon anode materials using *in situ* XRD
- The long-range and local structure changes of the $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cathode material during electrochemical cycling using *in situ* XRD, *in situ* x-ray absorption and NMR spectroscopy
- The surface damages of cathode materials caused by interaction with electrolytes and the effects of surface coating

X-RAY ABSORPTION SPECTRUM FOR $\text{Ni}(\text{OH})_2$ AT Ni K EDGE



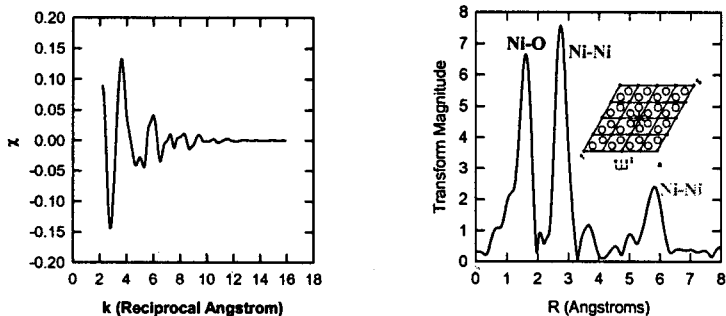
XANES GIVES INFORMATION ON OXIDATION STATE AND COORDINATION

Effect of oxidation state on Mn XANES



EXAFS AND FOURIER TRANSFORM OF

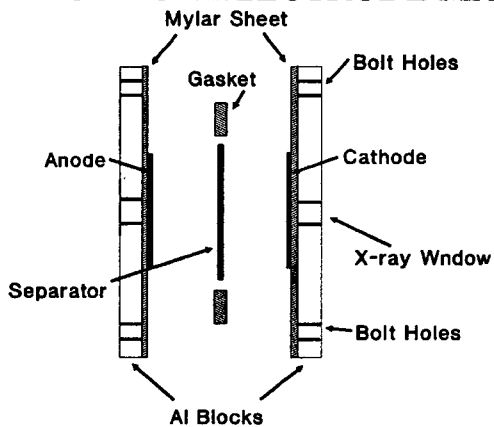
II



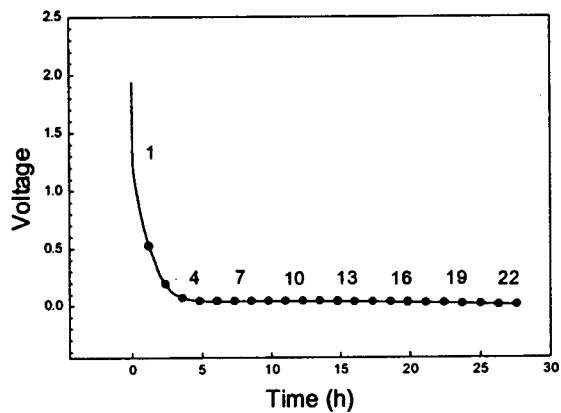
EXAFS data can be fitted in k and R space to derive bond distances and coordination numbers

EXAFS gives structural information

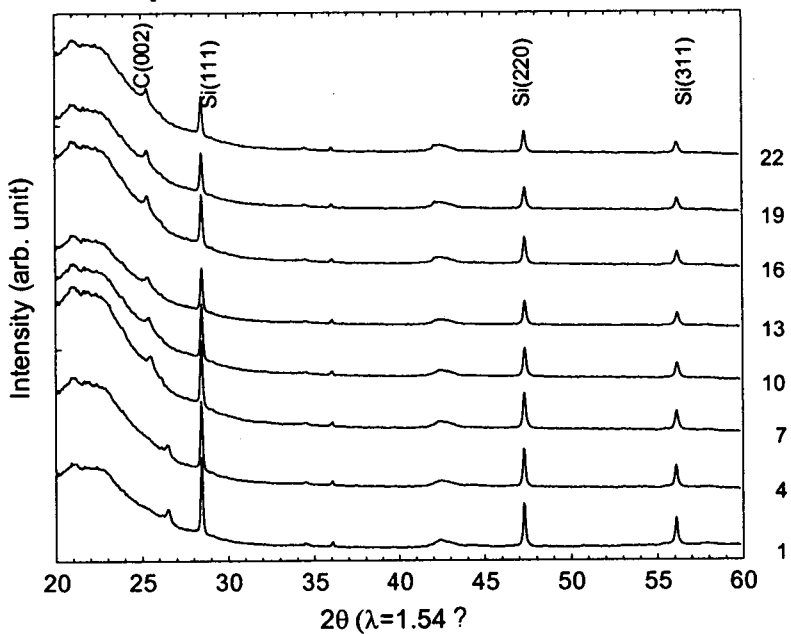
CELL FOR IN SITU XAS AND XRD STUDIES OF LITHIUM-ION ELECTRODE MATERIALS



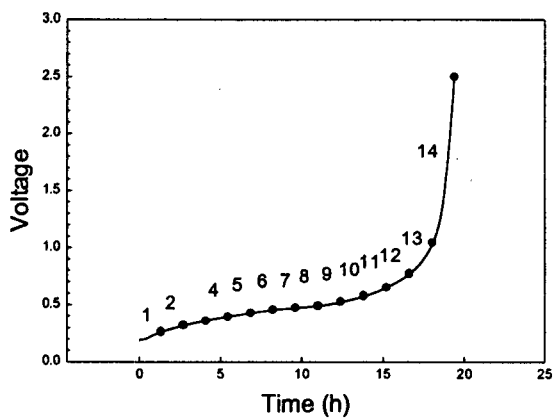
First discharge (Li intercalation) of carbon coated, graphite mixed Si



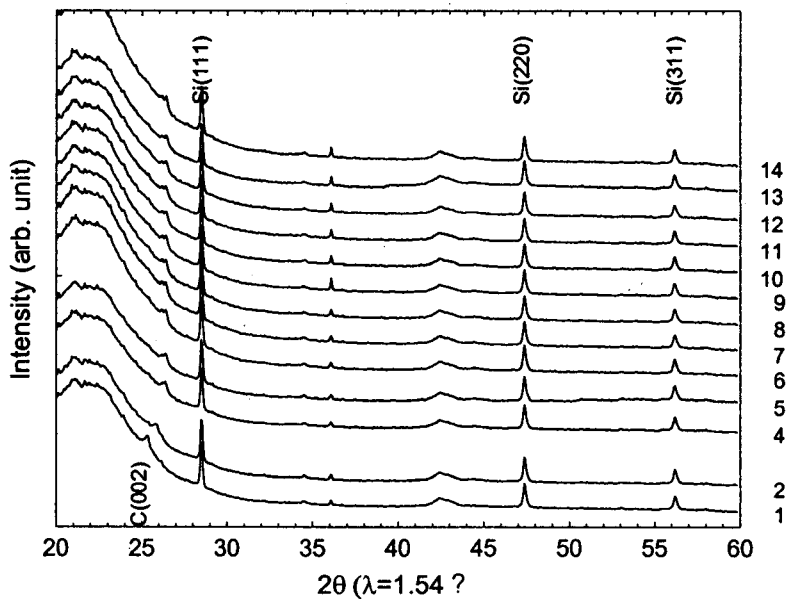
In situ XRD spectra of carbon coated, graphite mixed Si during 1st discharge



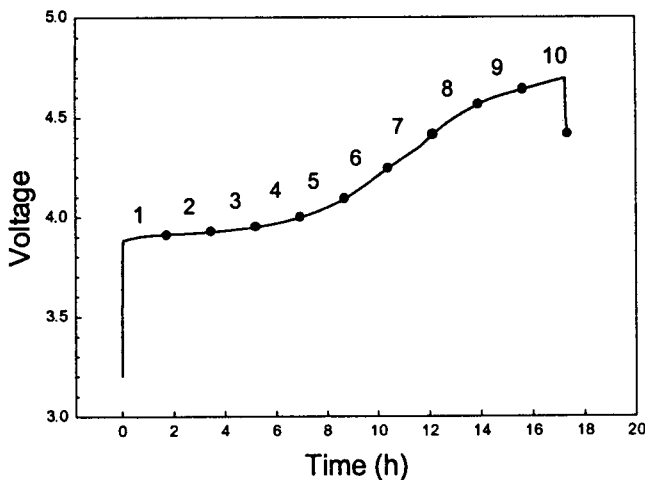
First charge (Li de-intercalation) of carbon coated, graphite mixed Si



In situ XRD spectra of carbon coated, graphite mixed Si during 1st charge

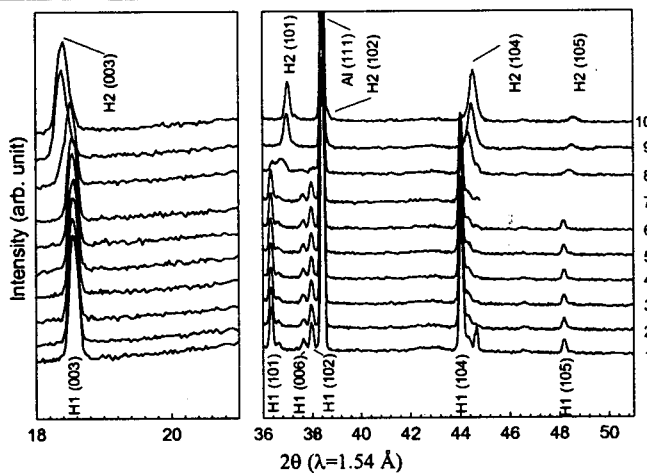


First charge curve of $\text{LiMn}_{0.5}\text{Ni}_{0.5}$ for *in situ* XRD



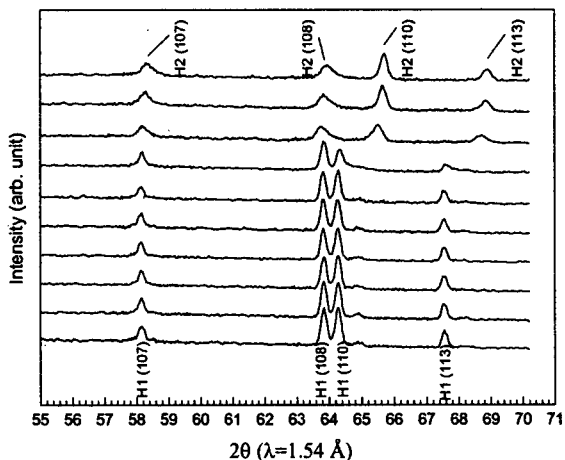
The cell was charged at a constant current of 0.3 mA for 17 hours to reach the 4.7 V cut-off limit with a specific charge capacity about 175 mAh/g.

In-situ XRD patterns of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$



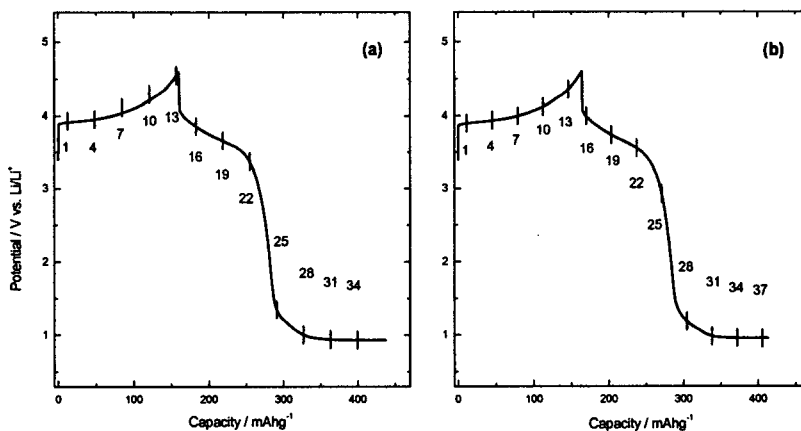
Two hexagonal phases (H1, H2) are identified and the Bragg peaks related to each of them are indexed. H3 phase formation suppressed (at least up to 4.6V).

In-situ XRD patterns of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$



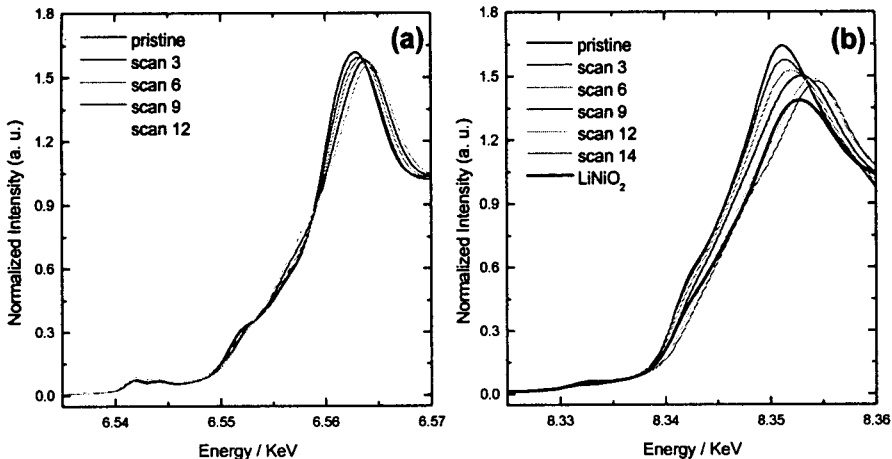
The changes in lattice parameters from H1 ($a=2.895 \text{ \AA}$ and $c=14.311 \text{ \AA}$ from scan 1) to H2 ($a=2.839 \text{ \AA}$ and $c=14.428 \text{ \AA}$ from scan 10) are significantly smaller than those in the LiNiO_2 system

First Cycle Curve for *in-situ* XAS results



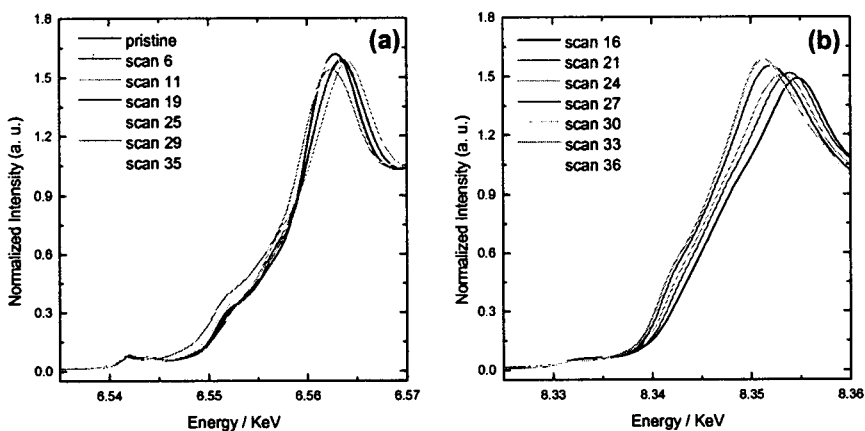
Voltage profiles during the first charge and discharge; (a) cell for the Mn XAS (b) cell for the Ni XAS. Every third XAS scan was marked on the curves.

In-Situ XANES during charge



Normalized (a) Mn K-edge and (b) Ni K-edge XANES spectra of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ during charge. The spectrum of LiNiO_2 is included as a standard in (b).

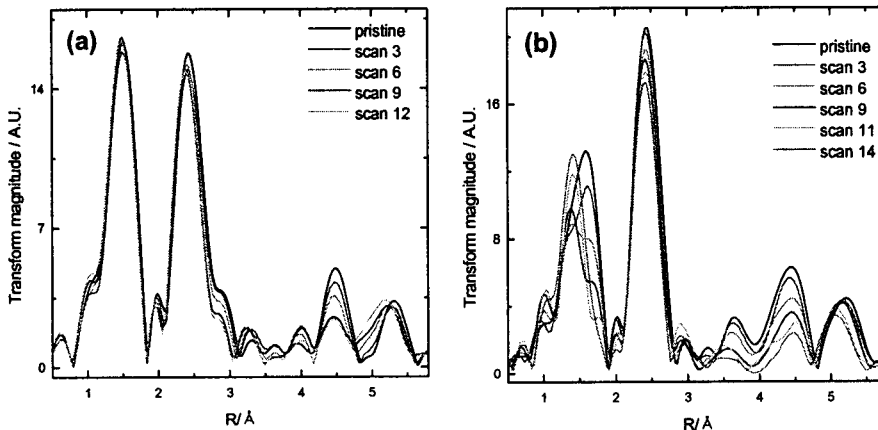
In-Situ XANES during discharge



Normalized (a) Mn K-edge and (b) Ni K-edge XANES spectra of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ during discharge.

In-Situ EXAFS during charge

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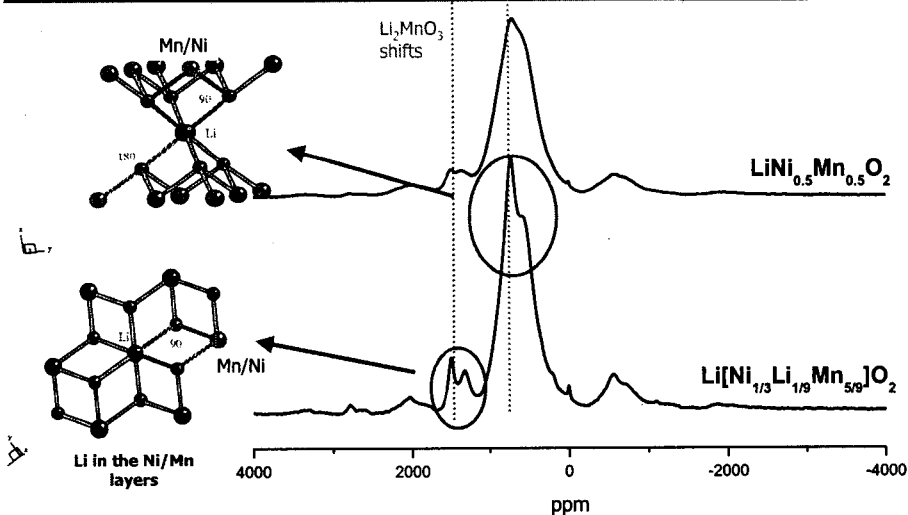


k^3 -weighted Fourier transform magnitudes of the (a) Mn and (b) Ni K-edge EXAFS spectra of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ during charge.

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^6Li MAS NMR

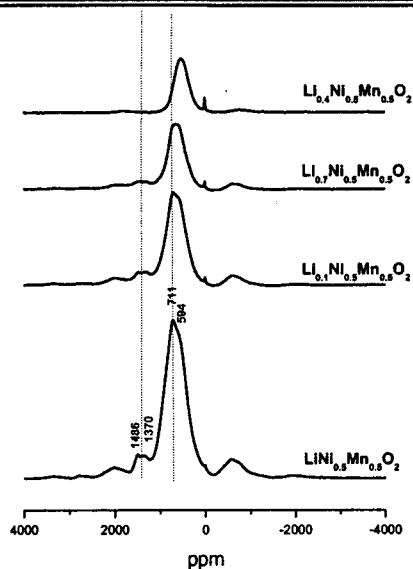
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The ^6Li MAS NMR of $\text{Li}_{1-x}\text{Mn}_x\text{Ni}_{0.5}\text{O}_2$. All spectra were acquired with spinning speeds of 38 kHz. Dashed lines indicating the approximate shift positions of the ^6Li resonances of Li_2MnO_3 have been added for comparison.

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${}^6\text{Li}$ MAS NMR of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$



• On charging, Li ions in both the $\text{Mn}^{4+}/\text{Ni}^{2+}$ and lithium layers are removed and no new resonances are observed.

• Only the resonance due to Li in the lithium layers at ~ 600 ppm is observed for the $\text{Li}_{0.4}\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ sample.

• Li NMR results as a function of state of charge indicate that, in contrast to $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2]$, the Li is removed from the Ni/Mn layers

• The lithium that remains in the lattice at higher potentials appears to be predominantly nearby nickel.

Summaries

- The charge process above 2 V is accompanied by a reversible phase transition between H1 to H2, similar to the LiNiO_2 system.
- From the Mn and Ni K-edge XANES results of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, we conclude that the charge compensation, when charging between 2 and 4.6 V, is achieved mainly by the oxidation of Ni^{2+} to Ni^{4+} ions, while the manganese ions remain mostly unchanged in the Mn^{4+} state.
- When discharging $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ at low voltage plateau (~ 1 V), however, the charge compensation for the Li-ion intercalation process is achieved via reduction of Mn^{4+} .
- The ${}^6\text{Li}$ MAS NMR results of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ at different charge states reveal that Li is found not only in the Li layer but also in the $\text{Ni}^{2+}/\text{Mn}^{4+}$ layers, primarily in an environment surrounded by 6 Mn^{4+} as in Li_2MnO_3 .
- All the Li^+ in the $\text{Ni}^{2+}/\text{Mn}^{4+}$ layers are removed on charging to form $\text{Li}_{0.4}\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, the residual Li^+ occupying sites near nickel in the lithium layers.
- The ${}^6\text{Li}$ MAS NMR results of $\text{Li}[\text{Li}_{1/9}\text{Mn}_{5/9}\text{Ni}_{3/9}\text{O}_2]$ after first cycle reveal that Li ions re-intercalated not only into the Li layer but also into the $\text{Ni}^{2+}/\text{Mn}^{4+}$ layers.