

実験報告書様式(一般利用課題・成果公開利用)

(※本報告書は英語で記述してください。ただし、産業利用課題として採択されている方は日本語で記述していただいても結構です。)

 <b>MLF Experimental Report</b>	提出日 Date of Report 2015/5/5
課題番号 Project No. 2014B0067 実験課題名 Title of experiment Crystal structure change of reduced $\text{Li}(\text{Mn,Ni,Co,Li})\text{O}_{2-d}$ during charge process at high rate 実験責任者名 Name of principal investigator Yasushi Idemoto 所属 Affiliation Tokyo University of Science	装置責任者 Name of responsible person Toru Ishigaki 装置名 Name of Instrument/(BL No.) iMATERIA/BL20 実施日 Date of Experiment 2014/12/15 - 2014/12/16 2015/3/21 - 2015/3/22 2015/3/27 - 2015/3/28

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)  
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

<p>1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.</p> <p>Compositions: <math>\text{Li}(\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Li}_{0.2})\text{O}_{2-d}</math> (Pristine and samples after several charge voltages) Physical form: Powder or film(electrode)</p>
--

<p>2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。) Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.</p> <p><b>Experimental method</b></p> <p><math>\text{Li}(\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{Li}_{0.2})\text{O}_{2-\delta}</math> were synthesized by a co-precipitation and solid-state reaction method using Mn-, Ni- and Co- nitrates and LiOH as starting materials. First, the lattice parameters of these samples were estimated by powder X-ray diffraction measurements, and the metal compositions were confirmed by inductively-coupled plasma (ICP) technique.</p> <p>In order to clarify crystal-structure changes of the samples during the charge process, cathodes after the several voltages with 1C and 3C rates were prepared. Neutron diffraction measurements of the powders and cathodes after charge were performed by iMATERIA installed at J-PARC. Each powder and cathode with a weight of 0.5 g and 10 mg was loaded in a vanadium can, and then mounted in a sample holder. The measurements were conducted at room temperature with a SF mode, and the measurement times for powder and cathode were ca. 15 min and 4 h, respectively. Crystal structures of the samples were refined by the Rietveld technique using the Z-Rietveld program.</p>
--

## 2. 実験方法及び結果(つづき) Experimental method and results (continued)

### Results

Figure 1 shows Rietveld refinement patterns of  $\text{Li}(\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Li}_{0.2})\text{O}_2$  during charge process at (a) 4.5 V with 3C rate, (b) 4.8 V with 3C, (c) 4.5 V with 1C and (d) 4.8 V with 1C rate, assuming the crystal structure as the  $\text{Li}_2\text{MnO}_3$ -type structure (S. G.:  $C2/m$ ). Site occupancies of metals were refined under constraints of chemical analysis by ICP-AES. It was demonstrated that the samples after charge at 4.8 V with 1C and 3C rates had a single phase as well as pristine sample although the lattice parameter,  $c$  became longer than that of pristine due to a decrease in the bond strength from lithium layers to oxygen layers.

From the results of Rietveld analysis, the mixing of Ni to Li sites was significantly increased with charge depths at 3C rate in contrast to 1C charge rate. The delithiation from 4h site was difficult in 3C charge process to indicate the difference of diffusivity in the lithium sites, i.e. 2c and 4h sites. Although the Mn-ordering increased at 2b site after charge at 4.8 V with 3C rate, the occupancies of Mn at 4g and 2b showed about constant value during charge process with 1C rate. The occupancy of Co localized from 4g and 2b sites to only 4g site after charged at 4.8 V with 3C rate, while the Co occupation were uniformly distributed at 4g and 2b sites after charge with 1C rate. The occupancy of oxygen significantly decreased with charge depth at 1C rate. Therefore, the displacements of constituent atoms during charge process at 1C and 3C exhibited different behavior due to the diffusivities of Li, Mn, Co and Ni. We further continue the analysis for the reduced samples.

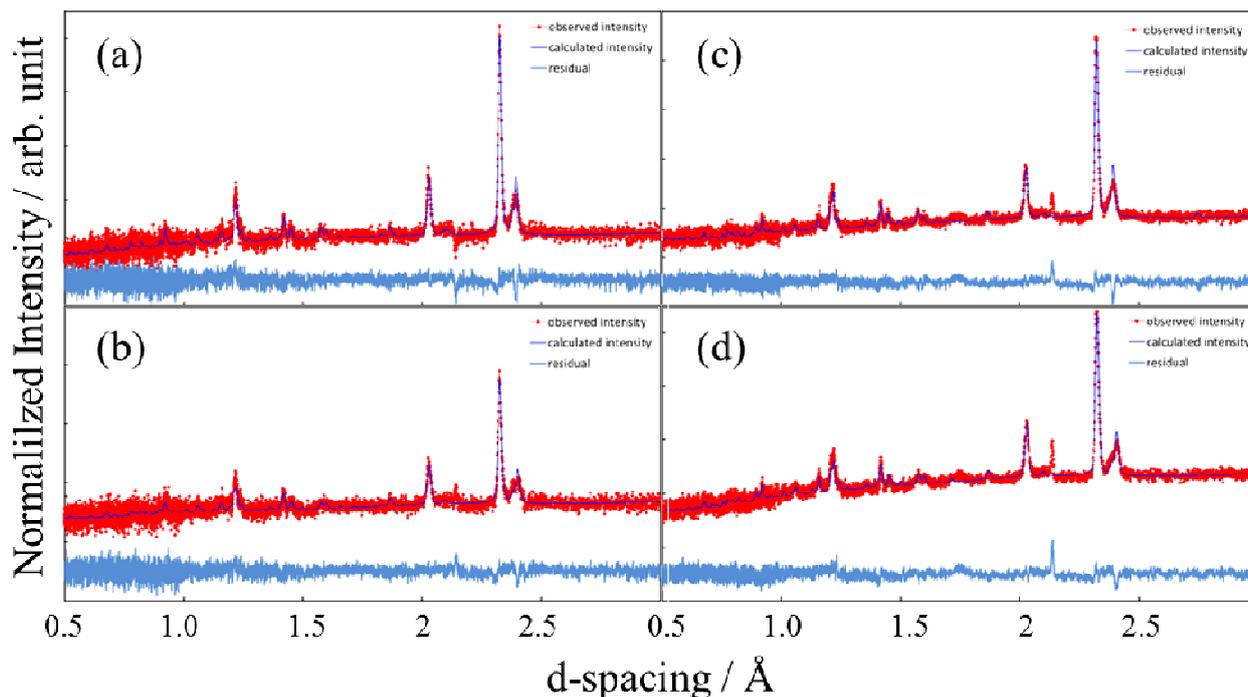


Fig. 1 Rietveld refinement patterns of  $\text{Li}(\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Li}_{0.2})\text{O}_2$  electrodes after charging at (a) 4.5 V with 3C rate, (b) 4.8 V with 3C rate, (c) 4.5 V with 1C rate and (d) 4.8 V with 1C rate. Red marks show observed neutron diffraction intensities [iMATERIA] and a solid blue line represents calculated intensities. The curve at the bottom is a difference between the observed and calculated intensities in the same scale.

以下は、MLFで内部資料として使用します。(日本語可)

The following sheet is for internal use only. Description in Japanese is acceptable.

○論文等による成果発表の予定 (Your publication plan)

a) 発表形式 <sup>(*1)</sup> Publication style <sup>(*1)</sup>	b) 発表先(誌名、講演先) <sup>(*2)</sup> Publication/Meeting information <sup>(*2)</sup> (Name of journal/book or meeting)	c) 投稿/発表時期 <sup>(*3)</sup> Date of paper submission or presentation <sup>(*3)</sup>
口頭発表	電気化学会第 82 回大会 電気化学会秋季大会	2015年3月 2015年9月
原著論文	Journal of Power Sources	2年以内

【記入要領】(Instructions)

- (\*1) 原著論文、総説、プロシーディングス、単行本、特許、招待講演(国際会議)、その他口頭発表等、具体的な発表方法を示して下さい。  
Please describe planned publication and/or presentation style; *ex.* refereed journal, review article, conference proceedings, book, patent, invited talk, oral presentation *etc.*
- (\*2) 成果を発表する誌名、講演先を示して下さい。  
Please describe the name of journal or book you are planning to submit, or name of meeting you will make a presentation.
- (\*3) およその発表予定時期を示して下さい。(3月以内、6月以内、1年以内、2年以内、2年以上先、等)  
Please describe the estimated date of paper submission or presentation; *ex.* within 3 months, within 6 months, within 1 year, within 2 years, beyond 2 years, *etc.*

○成果になる予定が立たない場合の理由と今後の計画を記述してください。

In case you can not publish your results, please describe reasons and future plan.

(例:「論文になる十分な結果が得られなかった」、「複数回の実験が必要で次回の課題終了後に発表予定」、等)