

# Dynamic Analysis for Electrode Reaction of Lithium Manganese Oxide Cathode Using Vertically Dispersive XAFS Instrument

Hirona Yamagishi, Ryota Miyahara, Misaki Katayama, Yasuhiro Inada\*  
Graduate School of Life Sciences, Ritsumeikan University,  
1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan

## 1 Introduction

Lithium ion secondary batteries (LIBs) are widely used as energy storage devices, and the effective electrode reaction related to lithiation/delithiation of the active material is a key objective for the lifetime improvement the safety utilization. The XAFS technique is one of the powerful tools for such the observation, because it is enable to measure inside of LIBs non-destructively and is sensitive to the valence state of metal species. In order to detect the reaction distribution in the electrode plate, the 2D imaging XAFS technique was developed [1], and the in-plane inhomogeneous distribution was revealed for the LIB cathodes composed of lithium iron phosphate (LFP). The heterogeneity has been ascribed by the electrochemical conductivity in the cathode plate [2]. On the other hand, the lithium manganese oxide (LMO) cathode has not showed such the heterogeneity during the charge/discharge processes. To achieve the dynamic observation for the cathode reaction, the vertically dispersive XAFS (VDXAFS) instrument has been developed [3]. The purpose of this study is to measure dynamically the electrode reaction in the LMO cathode after a potential jump as the trigger of the reaction.

## 2 Experiment

The LIB cell for the VDXAFS measurement was composed of an LMO sheet, two separator sheets, Li anode plate, and 1 mol dm<sup>-3</sup> LiPF<sub>6</sub> solution as the electrolyte dissolved in ethylene carbonate and ethyl methyl carbonate with the volume ratio of 3:7 enclosing in the Al-laminated films. The cathode material was the mixture of LMO, acetylene black, and polyvinylidene difluoride with the mass ratio of 14:3:3.

The VDXAFS measurements at the Mn K-edge were performed at NW2A of PF-AR (KEK, Japan) and BL-5 of SR Center (Ritsumeikan University, Japan). The electrode potential was jumped to 4.5 V as the charging process, and the measurements were continued until the electrode current became less than 0.1 C.

## 3 Results and Discussion

Figure 1 shows the time-course change of the electrode current and the dynamic changeover of the chemical state of LMO as a typical example of the VDXAFS measurement. The time of applying voltage is indicated at 0 s. The chemical state was judged by the XANES spectrum of LMO. The blue and red pixels indicate LiMn<sub>2</sub>O<sub>4</sub> and Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub> ( $x < 1$ ) before and after the charging process, respectively.

The time-course change of chemical state map showed that the delithiation was ahead at the both edges of the

cathode and that there was an additional reaction channel at the position of *ca.* 5.0 mm. The charging reaction was almost finished at 750 s, at which the electrode current reached to less than 1 C. The dynamic measurement presented in this study detected the inhomogeneous distribution in the LMO cathode, although such the distribution was not observed for the 2D XAFS imaging, for which the conventional step scanning of the monochromator is necessary, during the 0.5 C constant-current charging process. The present results indicates that the electrode reaction of LMO proceeds heterogeneously when the electrode current is larger than 1 C. The VDXAFS measurements were conducted for the LFP cathode under the same charging conditions [3], and the heterogeneous distribution was also observed for the high current condition after the potential jump similar to the 2D imaging under 0.5 C [2]. The disappearance of its heterogeneity for LMO under the low current condition indicates the fast relaxation of the instantaneous heterogeneity.

This study showed the appearance of inhomogeneous distribution on the LMO cathode for the first time and suggested the difference of the relaxation property between LMO and LFP. The detail analysis of the reaction propagation will lead the real image of the electrode reaction in the composite electrode.

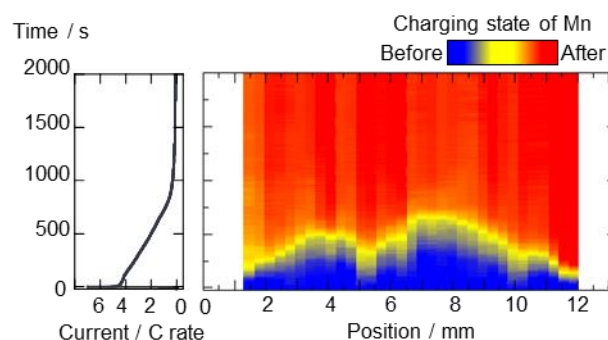


Figure 1: The time-course change of the current change (left) and the chemical state map (right) of lithium manganese oxide cathode.

## References

- [1] M. Katayama *et al.*, *J. Synchrotron Rad.*, **19**, 717 (2012).
- [2] M. Katayama *et al.*, *J. Power Sourc.*, **269**, 994 (2014).
- [3] M. Katayama *et al.*, *J. Synchrotron Rad.*, **22**, 1227 (2015).

\* yinada@fc.ritsumei.ac.jp