

## Local structure analysis of Li-rich Li-Mn-O materials at various states of charge by soft X-ray absorption fine structure

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$\text{Li}_2\text{MnO}_3$  is expected as a positive electrode material for next-generation lithium-ion batteries because a quite high capacity of  $460 \text{ mAh g}^{-1}$  as the theoretical capacity can be obtained if all contained lithium can be used. Recently, it has been found that by milling treatment to  $\text{Li}_2\text{MnO}_3$ , the electrode performances are improved [1]. Furthermore, by simultaneously adding  $\text{LiMn}_2\text{O}_4$  at the time of milling, both reversible capacity and cycle characteristics are greatly improved [2]. In this study, we measured O K-edge and Mn L-edge XANES spectra of the NaCl type  $\text{Li}_2\text{MnO}_3$ , and  $\text{Li}_2\text{MnO}_3$ - $\text{LiMn}_2\text{O}_4$  composite after charging and discharging, and then discussed the factors for improving the electrode characteristics.

$\text{Li}_2\text{MnO}_3$  or  $\text{Li}_2\text{MnO}_3$ - $\text{LiMn}_2\text{O}_4$  (2: 1 molar ratio) was mechanically ball milled using  $\text{ZrO}_2$  pot and ball at 500 rpm for 20 hours. The obtained powder was mixed with Ketjen Black (KB) and PTFE at a weight ratio of 84: 8: 8 for the preparation of electrode. Two electrode cell was assembled using Li foil as a counter electrode and 1 M  $\text{LiPF}_6$  EC-DEC as an electrolyte. Galvanostatic charge and discharge measurements at the current density of  $10 \text{ mA g}^{-1}$  were performed to the various charge and discharge states. X-ray absorption measurements at Mn L-edge and O K-edge were performed at BL-11 in SR Center, Ritsumeikan University.

The change of the O K-edge XANES in the NaCl type  $\text{Li}_2\text{MnO}_3$  and the  $\text{Li}_2\text{MnO}_3$ - $\text{LiMn}_2\text{O}_4$  composite in various states of charge show the characteristic change during charge-discharge. For both the NaCl type  $\text{Li}_2\text{MnO}_3$  and the  $\text{Li}_2\text{MnO}_3$ - $\text{LiMn}_2\text{O}_4$  composite, after the initial charge, the peak intensity near 530 eV corresponding to the peak of peroxide ion was increased, suggesting that peroxide was contained in the sample after charging. In the subsequent discharge, the peak corresponding to lithium carbonate is observed. Though it is difficult to distinguish the peak from the peroxide, the peak intensity might be decreased, suggesting the reduction of the peroxide. O K-edge XANES of NaCl type  $\text{Li}_2\text{MnO}_3$  charged at 4.2 V is almost similar to that charged at 4.8 V. On the other hand,

for the  $\text{Li}_2\text{MnO}_3$ - $\text{LiMn}_2\text{O}_4$  composite, the difference of the peak intensity at 530 eV between 4.2 V and 4.8 V is observed. From Mn L-edge XANES, it is found that Mn is oxidized and reduced between trivalence and tetravalence during the first cycle and the second charge. On the other hand, the divalent component is confirmed with the charge-discharge cycle. The peak intensity of the divalent component in XANES of the  $\text{Li}_2\text{MnO}_3$ - $\text{LiMn}_2\text{O}_4$  composite is smaller than that of the NaCl type  $\text{Li}_2\text{MnO}_3$ .

By mixing between  $\text{LiMn}_2\text{O}_4$  and  $\text{Li}_2\text{MnO}_3$ , the structural stability during charging and discharging is improved. As a result, the release of oxygen from the  $\text{Li}_2\text{MnO}_3$  structure is suppressed, and the redox contribution and reversibility of oxygen are improved. Formation of Mn divalent component is suppressed, which improve cycle characteristics.

### References

- (1) Riki Kataoka *et al.*, *J. Electrochem. Soc.*, **2018**, 165, A291-296.
- (2) Riki Kataoka *et al.*, The 58th Battery Symposium in Japan, **2017**, 2A02.