# Mn K-, L-, and O K-edge XANES Spectra of Sol-Gel Derived $Li_2MnSiO_4$ for Cathode Material of Lithium-Ion Batteries

**Kazuo Kojima[1], Kosuke Tsuji[1], Chihiro Yogi[2], Misaki Katayama[1], Yasuhiro Inada[1], Daiki Fujioka[2], Toshiaki Ohta[2]**

*1) Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan*

*2) SR Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan*

$Li_2MnSiO_4$ has been investigated as one of the high-capacity, promising cathode materials for rechargeable Li-ion batteries. Recently, Kristiansen *et al*. have confirmed the presence of $Mn^{4+}$ ions upon charging of this $Li_2MnSiO_4$ material from their somewhat noisy data of X-ray absorption spectroscopy (XAS) [1]. In the present paper, we report Mn and O XANES spectra of $Li_2MnSiO_4$ prepared by a sol-gel method.

We obtained samples 1 and 2 of orthorhombic $Li_2MnSiO_4$. XANES spectra were measured at BL-3 for Mn-K edge of sample 1 and BL-2 for Mn-L and O-K edges of sample 2, at the SR Center of Ritsumeikan University.

Fig. 1 shows that $Mn^{2+}$ ions in sample 1 were oxidized and reduced during the first charge and discharge, respectively. However, it is not clear whether $Mn^{4+}$ ions are present or not after the first charge.

Fig. 2 indicates the points where *ex-situ* Mn-L edge (Fig. 3) and *ex-situ* O-K edge (Figs. 4 and 5) XANES spectra of sample 2 were measured.

Spectra of (d), (e), and (k) in Fig. 3 show the presence of $Mn^{4+}$ ions as well as $Mn^{3+}$ ions, which implies charge compensation for lithium delithiation in $Li_2MnSiO_4$.

Figs. 4 and 5 show opposite spectral changes each other. Fig. 4 shows that a pre-edge peak around 530 eV strengthens and a pre-edge peak around 534 eV weakens during the first charge, and that a broad, main band ranging from about 536 to 548 eV has three features before the first charge and these features become featureless during the first charge.

Kristiansen *et al*. [1] have observed similar spectral changes and assigned these peaks and band as follows: the 530-eV peak is assigned to empty O 2p-orbitals that are hybridized with Mn 3d-states, the 534-eV peak to empty O 2p-orbitals hybridized with Si 2p-states, and the band of 536-548 eV to O 2p-states hybridized with delocalized s- and p-states of Mn and Si.

The spectral changes in Fig. 4 is therefore considered to imply that the intensity growth in the 530-eV peak is caused by the decrease in the electron density of Mn due to oxidation of Mn, and the intensity decrease in the 534-eV peak by the electron- density increase of Si due to its reduction. Oxide ions probably do not contribute to charge compensation for lithium delithiation in $Li_2MnSiO_4$.

## Reference

[1] P. T. Kristiansen, M. Dahbi, T. Gustafsson, K. Edstrom, D. Newby, K. E. Smith, and L. -C. Duda, *Phys*. *Chem*. *Chem*. *Phys*., 2014, **16**, 3846-3852.

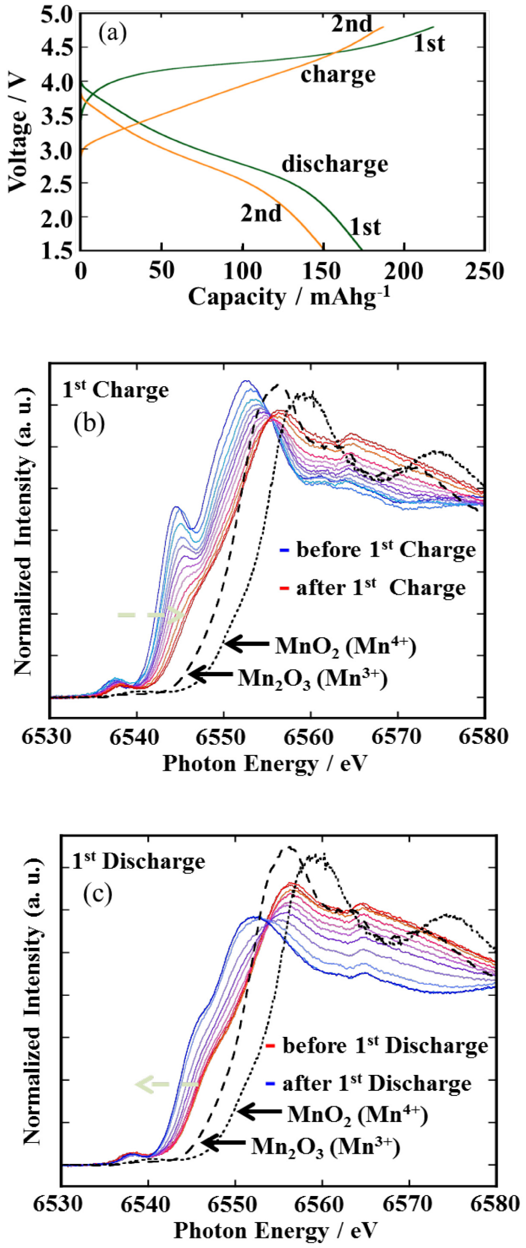

Fig. 1. Charge and discharge curves of sample 1 of $Li_2MnSiO_4$ (a), and *in-situ* Mn-K edge XANES spectra (transmission mode) of sample 1 during the first charge (b) and discharge (c) as shown in (a).

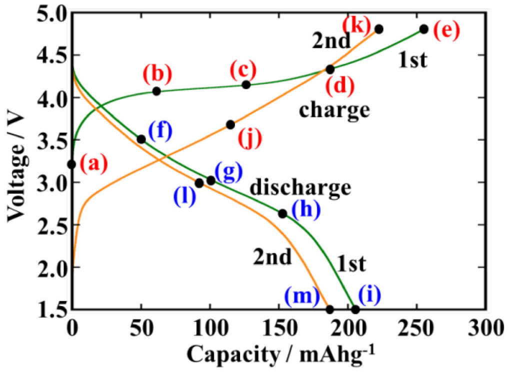

Fig. 2. Charge and discharge curves of sample 2 of $Li_2MnSiO_4$.

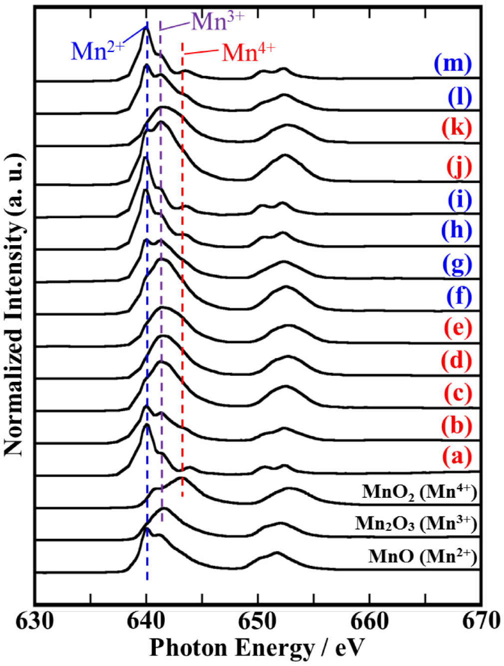

Fig. 3. *Ex-situ* Mn-L edge XANES spectra (TEY mode) of sample 2 measured at the points shown in Fig. 2.

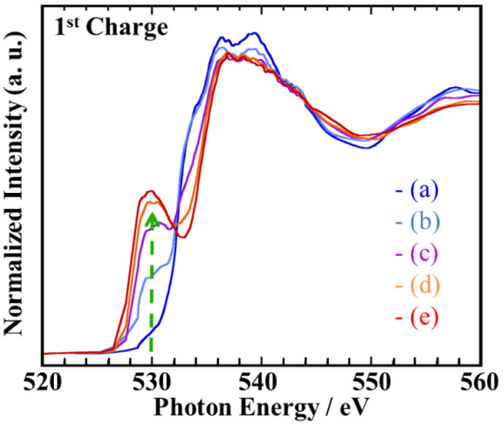

Fig. 4. *Ex-situ* O-K edge XANES spectra (FY mode) of sample 2 measured at the first-charge points shown in Fig. 2.

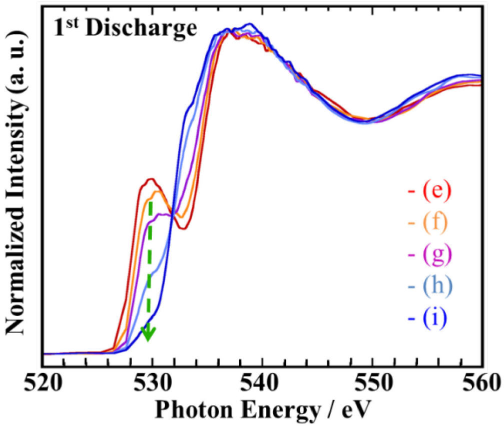

Fig. 5. *Ex-situ* O-K edge XANES spectra (FY mode) of sample 2 measured at the first-discharge points shown in Fig. 2.