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Direct Observation of Transition-Metal-Cation and Oxygen-Anion Redox Reaction in Mn-Based Li-Rich Positive Electrode Material

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For the next-generation lithium-ion batteries, lithium-rich layered oxides (LLOs), which exhibit high capacity owing to the contribution of redox reaction by oxygen anions in addition to metal cations as charge compensation during lithium desorption and insertion, have been expected as one of the high-capacity cathode materials [1,2]. The redox reaction of oxygen anions should be considered regarding the electronic state of metal cations that form mixed electron orbitals [3,4]. Therefore, soft X-ray absorption spectroscopy (SXAS) is appropriate as it proves both the electronic states of cation and anion electron orbitals at the Fermi level. In this study, Mn-based LLO positive electrode was evaluated in a highly concentrated electrolyte [5]. Mn-based LLO material $0.3Li_2MnO_3$-$0.7LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was prepared by the solid phase reaction method. A cell is composed of a composite cathode, a lithium-metal anode, and a separator. The electrolyte is 5.5 mol/L LiFSA: DMC (1:1.1 molar ratio). Battery tests were performed at 50°C with a cutoff potential of 2.0~4.8 V. The cells were disassembled in an argon-filled glovebox to remove the cathodes. The *Me* (Me=Mn, Co, and Ni) L- and O K-edge XAS spectra were collected at the soft X-ray beam line, BL-11, at the SR Center, Ritsumeikan University. To avoid exposure of the samples to air, the electrode samples were transferred to a high vacuum sample chamber via a transfer vessel filled with argon gas [6].

In the 1st cycle samples, the Ni and Co L-edge XAS spectra shifted to the higher photon energy at the charged state and to the lower photon energy in the discharged state, indicating a charge compensation by the redox reaction of Ni and Co cations. Figure 1(a) shows the Mn-L edge spectrum in TEY mode, which shifted to lower photon energy in the 52-cycle discharged sample, suggesting the formation of oxygen defects after the cycles. Figure 1(b) shows the O K-edge XAS spectra in PFY mode. The O K-edge spectrum consists of a pre-edge peak and a broad band starting at 534 eV. The broadband above 534 eV shifted to higher energies by delithiation. This shift to higher energies is associated with a shortening of the *Me*-O bond distance, reflecting charge compensation by redox of Ni and Co cations. The pre-edge structure corresponds to the transition to the hybridized state of Mn 3d and O 2p orbitals, which increased at the 1st charged state, and decreased at the 1st discharged state, which suggested the contribution of O anions in the charge compensation. The O K-edge XAS spectrum of the 52-cycle discharged state is different compared to that of the pristine, suggesting that the electrode surface is covered with an oxide different from the active material.

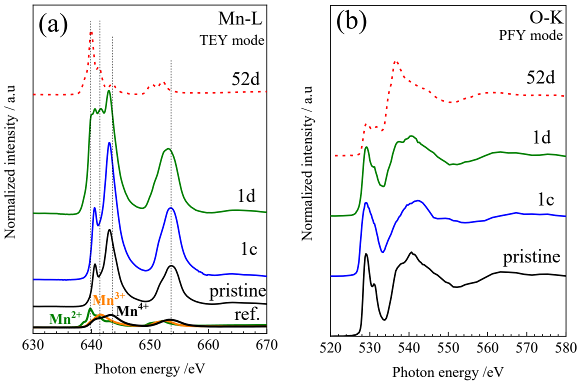

Fig. 1 XAS spectra of (a) Mn L-edge TEY mode, and (b) O K-edge PFY mode.

References

[1] J. B. Goodenough and Y. Kim, *Chem. Mater.*, **2010**, 22, 587.

[2] N. Yabuuchi, K. Yoshii, S.-T. Myung, I. Nakai and S. Komaba, *J. Am. Chem. Soc.*, **2011**, 133. 4404.

[3] M. Oishi, K. Yamanaka, I. Watanabe, K. Shimoda, T. Matsunaga, H. Arai, Y. Ukyo, Y. Uchimoto, Z. Ogumi and T. Ohta, *J. Mater. Chem. A*. **2016**, 4, 9293.

[4] M. Oishi, K. Shimoda, S. Okada, R. Imura, K. Yamanaka, H. Yamashige, H. Mizuguchi, I. Watanabe, Y. Uchimoto, T. Ohta, *Mater. Today Commu.* **2020**, 25, 101673.

[5] J. Wang, Y. Yamada, K. Sodeyama, C. H. Chiang, Y. Tateyama, A. Yamada, *Nat. Commun.* **2016**, 7, 12032.

[6] K. Nakanishi and T. Ohta, Advanced Topics in Measurements, ed. Z. Zahurul Haq, InTech, Croatia, **2012**, 43-60.

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