Study of Reaction Mechanisms of Li-Co-Nb Oxides for Rechargeable Li Batteries

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The demand of rechargeable Li batteries with high-energy density is continuously growing with expanding the market of electric vehicles in world wide. To increase the energy density of Li batteries, the development of positive electrode materials with high energy density is needed. Recently, the use of anionic redox is proposed as new chemistry to realize high-reversible capacity as electrode materials. Nevertheless, its origin of stabilization/destabilization mechanisms for the anionic redox is still unclear. In this study, Reaction mechanisms for a binary system of Li_3NbO_4-CoO as a model material is examined by X-ray absorption spectroscopy (XAS). Figure 1 shows Co *L*-edge and O *K*-edge XAS spectra of $Li_{4/3-y}Co_{2/9}Nb_{2/9}O_2$ upon charge (electrochemical oxidation coupled with Li extraction from the host structure). On early charge, partial oxidation of Co is noted from Co *L*-edge spectra, and this fact also changes the profile of O *K*-edge spectra as shown in Fig. 1. During further charge, intensity at *ca.* 531 eV increases for the O *K*-edge spectra. A similar change is noted for $Li_{1.2-y}Mn_{0.4}Ti_{0.4}O_2$.(1) This fact suggests that ligand holes are created for $Li_{4/3-y}Co_{2/9}Nb_{2/9}O_2$, and ligand holes are probably stabilized through π-type bond formation with Co t_{2g} orbital. However, this process is also found as the mainly irreversible process. Energy of Co *L*-edge XAS spectrum shift toward the lower energy region by further charge, indicating that reduction of Co on charge, probably associated with irreversible oxygen loss. A similar trend is also noted for O *K*-edge XAS spectra. Such oxygen loss triggers conversion reaction on a subsequent discharge process, leading to large electrochemical polarization. These observations probably originate from the competition of anionic/cationic redox for Li-excess system. Co with high oxidation states is not energetically stable, which is stabilized through electron donation from oxygen, leading to reduction of Co and irreversible oxygen loss. These findings will contribute further development of the positive electrode materials with high-energy density based on the ligand hole formation in the future.

Reference

(1) N. Yabuuchi, M. Nakayama, M. Takeuchi, S. Komaba, Y. Hashimoto, T. Mukai, H. Shiiba, K. Sato, Y. Kobayashi, A. Nakao, M. Yonemura, K. Yamanaka, K. Mitsuhara, and T. Ohta, *Nature Commun.*, **2016**, *7*, 13814.

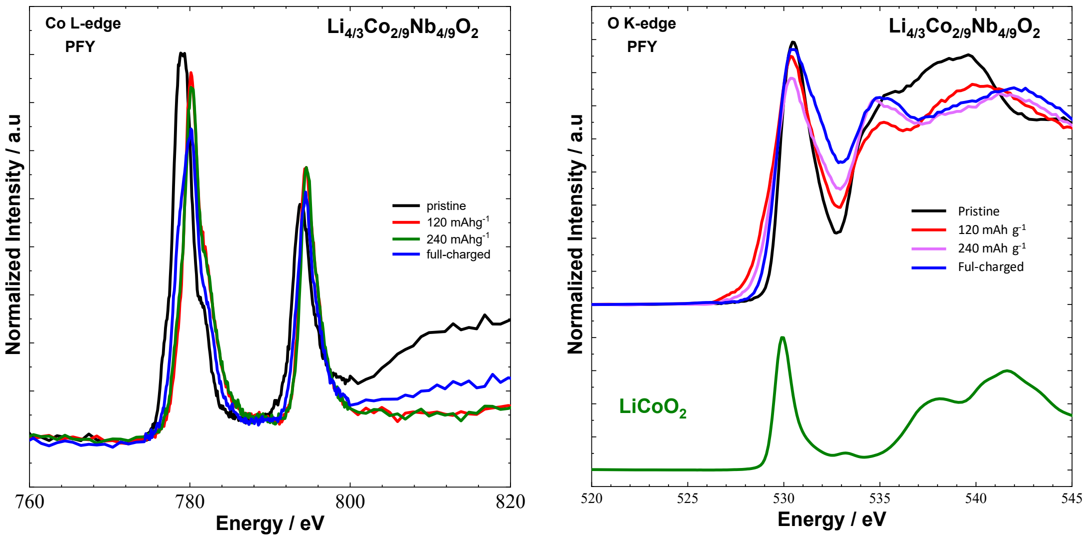

Fig. 1 Co *L*-edge and O *K*-edge XAS spectra of $Li_{4/3-y}Co_{2/9}Nb_{2/9}O_2$ on initial charge. Some extent of changes in oxidation state of Co ions is evidenced for $Li_{4/3-y}Co_{2/9}Nb_{2/9}O_2$ from Co *L*-edge while clear changes are noted for O *K*-edge.