Study on Charge Compensation Mechanisms of Ni-based Positive Electrode Materials for Li-ion Batteries

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Recently, Mn-based Li-excess oxides have been studied as high-capacity positive electrode materials for advanced Li-ion batteries. The Mn-based Li-excess oxides deliver large reversible capacities associated with relatively stable oxygen redox reaction without significant oxygen loss.[1] In this study, Ni-based Li-excess oxides are target as potential high-capacity positive electrode materials, and reaction mechanisms have been studied by soft X-ray absorption spectroscopy.

Figure 1a shows changes in Ni L-edge XAS spectra of a Ni-based Li-excess oxide, $Li_{4/3}Ni_{2/9}Nb_{4/9}O_2$ and Ni-based stoichiometric oxide, $LiNi_{2/3}Nb_{1/3}O_2$, on electrochemical charge processes. Clear shift for Ni L-edge spectra is noted for $Li_{4/3-y}Ni_{2/9}Nb_{4/9}O_2$, indicating that Ni ions are oxidized upon charge. Note that similar trend is noted for layered $Li_{1-y}Ni_{1/2}Mn_{1/2}O_2$ as shown in Figure 1b, and cationic Ni redox (Ni^{2+}/Ni^{4+}) proceeds for both materials. Nevertheless, electrochemical and structural data clearly suggests that oxygen loss is the dominative process for $Li_{4/3-y}Ni_{2/9}Nb_{4/9}O_2$, and anionic redox reaction is not stable for the Ni-based Li-excess oxides.[2]

In contrast, for the stoichiometric sample, $Li_{1-y}Ni_{2/3}Nb_{1/3}O_2$, an anomalously small contribution of Ni ions on charge is evidenced in Ni L-edge XAS spectra while a relatively large contribution of O ions is noted in O K-edge XAS spectra.[2] Theoretical study reveals that local structures of O for $LiNi_{2/3}Nb_{1/3}O_2$ are clearly different from that of $LiNi_{1/2}Mn_{1/2}O_2$ because of structural disordering triggered by the presence of Nb ions in the structure. Anionic redox is promoted for the disordered and stoichiometric Ni-based compounds coupled with minor contribution of Ni cationic redox. Moreover, high reversibility of anionic redox is evidenced with small polarization on charge/discharge processes.[2] This finding opens new ways to design high-capacity positive electrode materials with highly reversible anionic redox, leading to the development of advanced Li-ion batteries in the future.

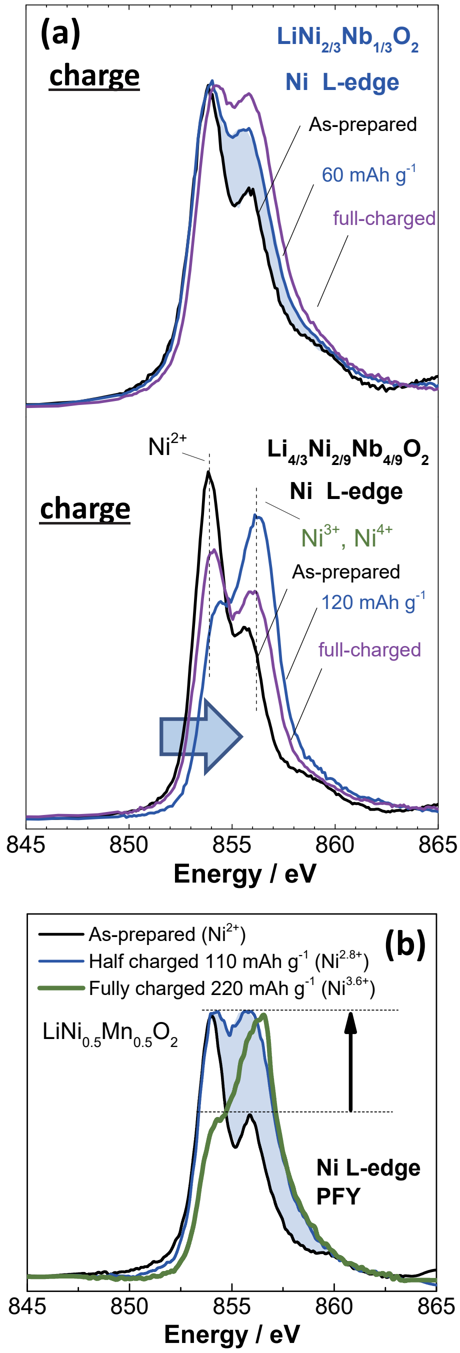

Fig. 1. Variations of electronic structures of Ni on electrochemical charge/discharge processes; (a) $Li_{1-y}Ni_{2/3}Nb_{1/3}O_2$ and $Li_{4/3-y}Ni_{2/9}Nb_{4/9}O_2$ with the disordered structure, and (b) $Li_{1-y}Ni_{1/2}Mn_{1/2}O_2$ with the layered structure.

References

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