Solid-State Redox Reaction of Oxide Ions for Rechargeable Batteries

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The use of anion redox, especially oxide ions, is a crucial strategy to design and develop new electrode materials with high gravimetric/volumetric energy density for rechargeable lithium batteries. Reversible capacity of electrode materials is potentially further increased by the enrichment of lithium contents with less transition metals in the close-packed structure of oxide ions. Our group has reported that $Li_3Nb^{5+}O_4$[1] and $Li_4Mo^{6+}O_5$[2], which have higher lithium contents than that of Li_2MnO_3, are potentially utilized as host structures for a new series of high-capacity electrode materials. Recently, $Li_2Ti^{4+}O_3$ is also proposed as the host structure for high-capacity electrode materials with redox reaction of oxide ions.[3] Mn^{3+}-substituted sample, $0.5Li_2TiO_3 - 0.5LiMnO_2$ ($Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$), delivers large reversible capacity of 300 mAh g^{-1} as shown in Figure 1a. Available energy density of $Li_{1.2-x}Ti_{0.4}Mn_{0.4}O_2$ exceeds 1,000 mWh g^{-1} as a positive electrode material. Moreover, charge compensation is realized by oxidation of oxide ions as evidenced by O K-edge X-ray absorption spectroscopy (Figure 1b) as a reversible process.

From these results, we will further discuss the possibility of high-capacity positive electrode materials, which effectively use the solid-state redox of oxide ions for the charge compensation, consisting of only 3d-transtion metals.

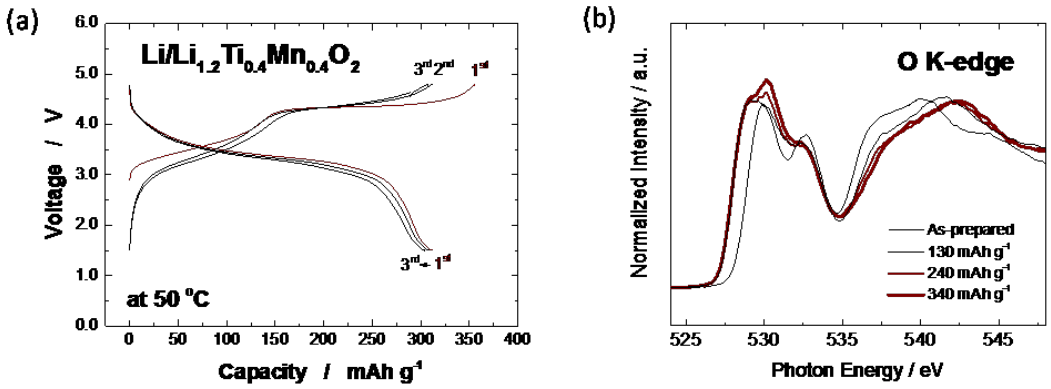

Figure 1. (a) Charge/discharge curves of ball-milled $Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$ in the voltage range of 1.5 – 4.8 V at a rate of 5.0 mA g^{-1} at 50 °C, and (b) changes in O K-edge XAS spectra on charge for $Li_{1.2-x}Ti_{0.4}Mn_{0.4}O_2$.

References

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