Anionic and Cationic Redox Reaction for Rechargeable Li/Na Batteries

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In the past decade, lithium-enriched compounds, Li_2MeO_3 (Me = Mn^{4+}, Ru^{4+} etc.), have been extensively studied for high-capacity positive electrode materials of lithium batteries. Although the origin of high reversible capacities was a debatable subject for a long time, recently it has been evidenced that charge compensation is partly achieved by solid-state redox of non-metal anions, *i.e.*, oxide ions (anionic redox),[1] coupled with conventional redox of transition metal ions (cationic redox). Recently, we reported that $Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$ delivers a reversible capacity of 300 mA h g^{-1} with a large contribution of anionic redox reaction (Fig. 1 left). Competition between cationic and anionic redox reactions is often evidenced for the lithium-enriched materials because the energy level of oxygen 2p band is lowered by the presence of excess lithium ions with high ionic characters in the crystal lattice. Reversibility of anionic redox reactions is also influenced by ionic and covalent characters for chemical bonds of transition metal ions.[2, 3] In contrast, when the energy of metal 3d band is low enough than that of oxygen 2p, pure cationic redox is realized for the lithium-excess system (*e.g.*, $Li_{1.25}Nb_{0.25}V_{0.5}O_2$, Fig. 1 right).[4, 5] Moreover, this concept is further extended to sodium battery applications.[6] From these findings, we discuss the stabilization and destabilization mechanisms and material design strategy with the concept of cationic and anionic redox reactions to develop new high-capacity lithium/sodium insertion materials for battery applications.
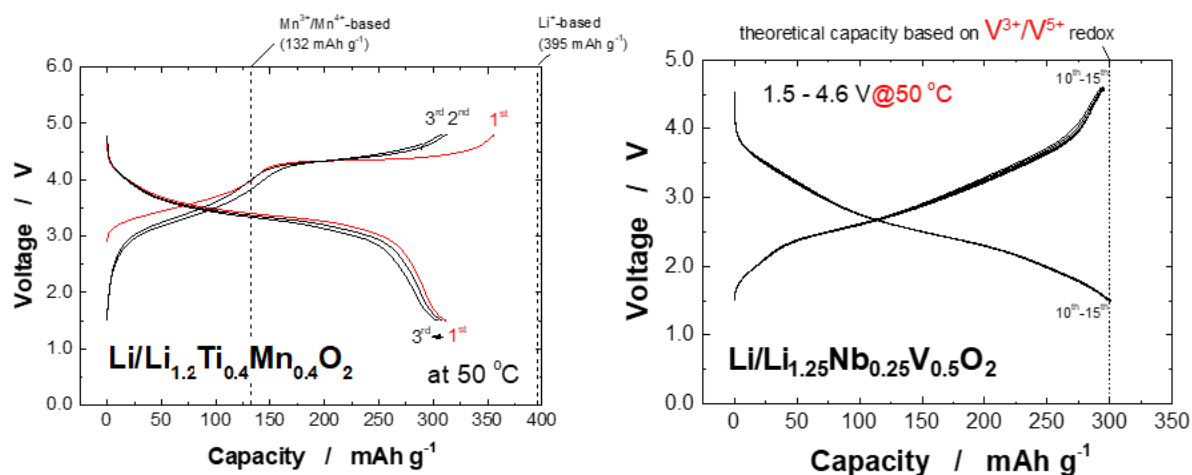

Figure 1. Charge/discharge curves of $Li_{1.2}Ti_{0.4}Mn_{0.4}O_2$ (left) and $Li_{1.25}Nb_{0.25}V_{0.5}O_2$ (right) in Li cells at 10 mA g^{-1} at 50 °C.

References:

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