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Charge Compensation Mechanisms of High-Capacity Li-excess V/Ti Oxides

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Further demand for higher energy density of lithium-ion batteries is growing, especially for the development of electric vehicles to reduce dependence on fossil fuel. Although Co/Ni ions are used as positive electrode materials, its depletion of material resources is an emerging problem. Among electrode materials with 3d transition metal ions, $LiVO_2$ with a layered rocksalt structure (s.g. *R*-3*m*) is known to be electrochemical inactive, associated with phase transition during charge. Nevertheless, our group has reported Li-excess Li_3NbO_4–$LiVO_2$ binary oxides, and $Li_{1.25}Nb_{0.25}V_{0.5}O_2$ on this binary system with a cation disordered rocksalt structure delivers a large reversible capacity of 250 mA h g^{-1} with two-electron redox of V^{3+}/V^{5+} at room temperature.[1] In this study, instead of Li_3NbO_4, Li_2TiO_3–$LiVO_2$ binary oxides are targeted as potential high capacity positive electrode materials.

Li_2TiO_3–$LiVO_2$ binary oxides were prepared by conventional calcination method from stoichiometric amounts of Li_2CO_3, anatase type TiO_2, and V_2O_3 at 900 °C for 12 h in argon atmosphere. Electrode performance of the oxides was examined after reducing particle sizes by ball milling with 10 wt% acetylene black. Electrochemical properties of the oxides were studied by galvanostatic charge/discharge measurement in two-electrode cells. Among the tested samples, $Li_{8/7}Ti_{2/7}V_{4/7}O_2$, which corresponds to the sample with x = 0.33 in x Li_2TiO_3– (1–x) $LiVO_2$ binary system, delivers a large reversible capacity of 270 mA h g^{-1} as shown in Figure 1. V ions in the as-prepared sample has the similar electronic configuration with V^{3+} in $LiVO_2$ as shown in Figure 2. Energy of the XANES spectrum shifts toward a higher energy region and a pre-edge peak at 5468 eV is intensified after charge. The clear pre-edge peak is a specific feature of V^{5+} without d-electrons. V ions are reduced back to the trivalent state after lithiation. XAS study reveals that reversible two-electron vanadium redox reaction (V^{3+}/V^{5+}) is activated for $Li_{8/7}Ti_{2/7}V_{4/7}O_2$.

From these results, it is concluded Li-excess V/Ti oxides are used as potential high-capacity and long-cycle-life electrode materials with highly reversible V^{3+}/V^{5+} two-electron redox in the future.[2]

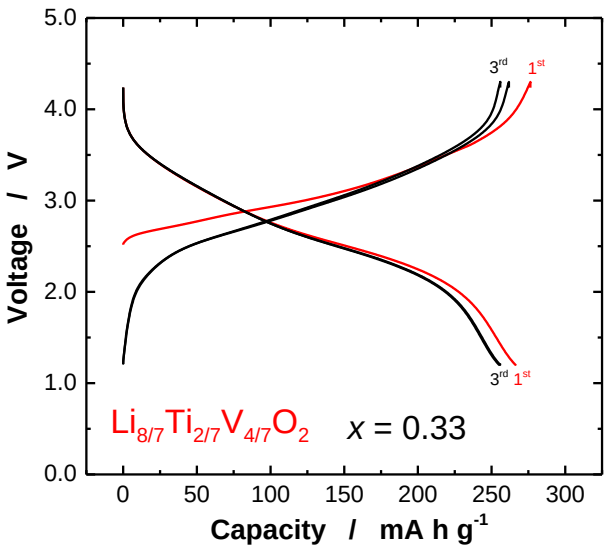

Fig. 1: Galvanostatic charge/discharge curves of $Li_{8/7}Ti_{2/7}V_{4/7}O_2$ in a Li cells at a rate of 10 mA g^{-1}.

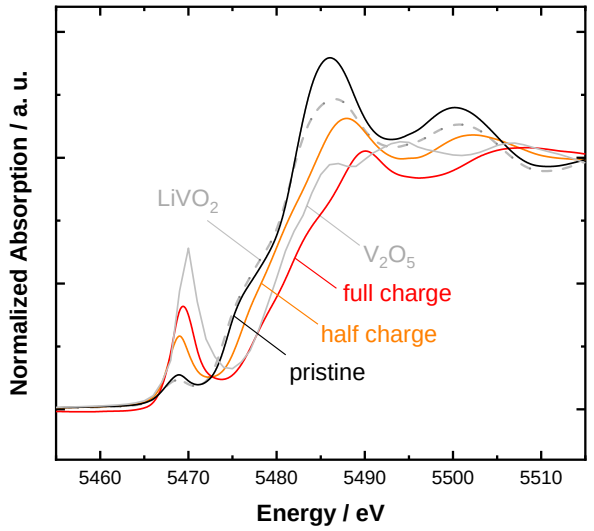

Fig. 2: V K-edge XAS spectra of $Li_{8/7-y}Ti_{2/7}V_{4/7}O_2$ on the charged process. The data of $LiVO_2$ used as a dereference material is also shown for comparison.

References
[1] N. Nakajima and N. Yabuuchi, *Chem. Mater.*, **29**, 6927 (2017).
[2] I. Konuma *et al.*, and N. Yabuuchi, submitted

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