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

Naoaki YABUUCHI*
Department of Chemistry and Life Science,
Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan

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, their 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-3m) is known to be electrochemical inactive, associated with phase transition during charge. Nevertheless, our group has reported Li-excess Li$_3$NbO$_4$–LiVO$_2$ binary oxides, and Li$_{1.28}$Nb$_{0.26}$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$_3$NbO$_4$, Li$_2$TiO$_3$–LiVO$_2$ binary oxides are targeted as potential high capacity positive electrode materials.

Li$_2$TiO$_3$–LiVO$_2$ binary oxides were prepared by conventional calcination method from stoichiometric amounts of Li$_2$CO$_3$, anatase type TiO$_2$, and V$_2$O$_3$ 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$_2$TiO$_3$–(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]

References

* yabuuchi-naoaki-pw@ynu.ac.jp