Behavior/Properties of Electrode Materials for Li Batteries viewing from Defect Considerations

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In lithium batteries, functional oxides with desired defect structures may show interesting electrochemical properties. For examples, Li-rich layer-structured cathode formulated as xLi_2MnO_3-$(1-x)LiMO_2$(M = Mn, Ni, Co, etc.) during 1st charging process was found to exhibit oxygen oxidation, vacancy formation. In the following discharging, the manganese reduction (or activation) occurred. As a result, a reversible capacity as high as 250 mAh/g was observed (Fig. 1(a)). Such redox reactions may be illustrated by defect chemistry. In other words, during 1st charging, electrons and oxygen was extracted from lattice oxygen with the formation of oxygen vacancies. In the next discharging process, electrons was accepted by cathode oxides accompanied by valence changing of Mn^{+4} to Mn^{+3}.

Furthermore, the anode oxide $Li_4Ti_5O_{12}$ (LTO) shows little volume change during charging/discharging cycles with potential for high rate applications. However, as-received $Li_4Ti_5O_{12}$ shows conductivity as low as 10^{-9} S/cm and then causes high interface polarization and low rate capability. With proper processing under low pO_2, the electron conduction and electrochemical properties of LTO was significantly improved as seen in Fig 1(b). Such property enhancement may be well illustrated by defect reaction under low pO_2 environment. In other words, lattice oxygen near surface of LTO tends to be removed under very low pO_2. Consequently, positively charged oxygen vacancy is formed and then charge-compensated by the creation of two negatively charged electrons. These electrons are eventually associated with tetravalent Ti ions. The fast electron pathway is established by the coexistence of Ti^{+3} and Ti^{+4} in Ti cation sublattice.

It is known that typical electrochemical reactions are highly dependent up movement of electrons and ions. With understanding of defect reaction during materials processing and charging/discharging, advanced electrode materials with much improved electrochemical and/or stability may be developed.

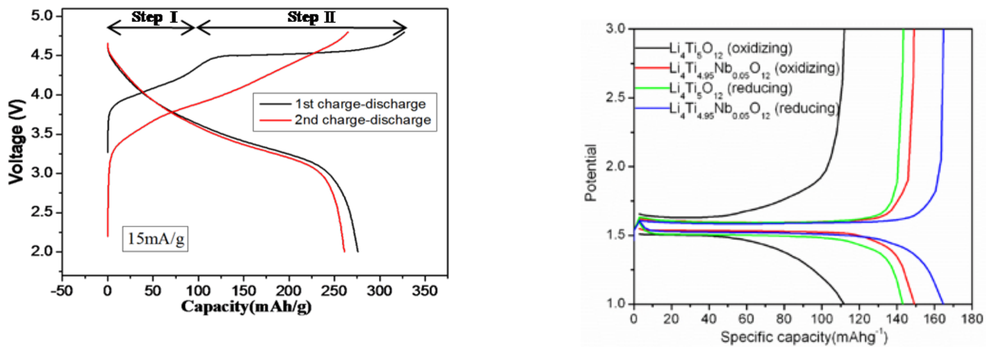

Figure 1. 1st Charge/Discharge Curves for (a) $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ at 0.05 C; (b) Undoped and doped $Li_4Ti_5O_{12}$ tested at 1C