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 $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiM}_2\text{O}_2\ (M = \text{Mn, Ni, Co, etc.})$ during 1\textsuperscript{st} 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 1\textsuperscript{st} 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 $\text{Mn}^{4+}$ to $\text{Mn}^{3+}$.

Furthermore, the anode oxide $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) shows little volume change during charging/discharging cycles with potential for high rate applications. However, as-received $\text{Li}_4\text{Ti}_5\text{O}_{12}$ 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\textsubscript{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\textsubscript{2} environment. In other words, lattice oxygen near surface of LTO tends to be removed under very low pO\textsubscript{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 $\text{Ti}^{3+}$ and $\text{Ti}^{4+}$ 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.

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.pdf}
\caption{1\textsuperscript{st} Charge/Discharge Curves for (a) Li\textsubscript{1.2}Mn\textsubscript{0.54}Co\textsubscript{0.13}Ni\textsubscript{0.13}O\textsubscript{2} at 0.05 C; (b) Undoped and doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ tested at 1C}
\end{figure}