

In Situ Electrochemical Doping for Mn-Rich Layered Oxide Cathode Materials in Lithium-Ion Batteries

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Lithium ion batteries are considered one of the most promising energy storage devices for large-scale energy storage systems (ESS) and electric vehicles (EVs). The energy density of current lithium-ion batteries is, however, insufficient to meet the demands of ESS and EVs.[1] In this connection, various layered transition metal oxides such as Ni-rich $\text{Li}(\text{Ni}_x\text{Co}_y\text{Mn}_z)\text{O}_2$ ($x+y+z=1$, denoted as NCM xyz) and Mn-rich $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (denoted as over-lithiated layered oxide, OLO) have been examined because their reversible capacities are higher than that of currently commercialized cathodes such as LiCoO_2 . However, Ni-rich NCM and OLO materials show poor electrochemical performance because of structural degradation during cycling and storage.[2] Their structural stability is known to be improved though the doping of electrochemically inactive elements such as Mg^{2+} and Al^{3+} . [3] Most doped-materials are obtained through solid state methods such as heating at high temperature.

In this presentation, we introduce in situ electrochemical doping to selectively substitutes Li^+ at Li sites in Mn-rich layered oxides with Mg^{2+} . [4] We demonstrate that Mg^{2+} cations are electrochemically intercalated into Li sites in delithiated Mn-rich layered oxides. As a result, $[\text{Li}_{1-x}\text{Mg}_y][\text{Mn}_{1-z}\text{M}_z]\text{O}_2$ ($\text{M} = \text{Co}$ and Ni) are formed during discharging. Interestingly, this Mg^{2+} intercalation into $[\text{Li}_{1-x}\text{Mg}_y][\text{Mn}_{1-z}\text{M}_z]\text{O}_2$ is irreversible, and thus, Mg^{2+} is not deintercalated during cycling. This results in the favorable doping of Mg^{2+} at the Li sites in $[\text{Li}_{1-x}\text{Mg}_y][\text{Mn}_{1-z}\text{M}_z]\text{O}_2$. Moreover, we show that the amount of Mg^{2+} intercalation into $\text{Li}_{1-x}[\text{Mn}_{1-z}\text{M}_z]\text{O}_2$ is linearly proportional to the amount of Mn in $\text{Li}_{1-x}[\text{Mn}_{1-z}\text{M}_z]\text{O}_2$. In addition, Mg^{2+} at the Li sites in $[\text{Li}_{1-x}\text{Mg}_y][\text{Mn}_{1-z}\text{M}_z]\text{O}_2$ suppresses cation mixing between Li^+ and transition metal cation during cycling, leading to the improved cycle retention over 200 cycles.

We believe our new concept of in situ electrochemical doping provides a new avenue for the development of various cathode materials in lithium-ion batteries.

References:

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