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 Li(Ni\textsubscript{x}Co\textsubscript{y}Mn\textsubscript{z})O\textsubscript{2} (x+y+z=1, denoted as NCM xyz) and Mn-rich xLi\textsubscript{2}MnO\textsubscript{3}•(1-x)LiMO\textsubscript{2} (denoted as overlithiated layered oxide, OLO) have been examined because their reversible capacities are higher than that of currently commercialized cathodes such as LiCoO\textsubscript{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\textsuperscript{2+} and Al\textsuperscript{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\textsuperscript{+} at Li sites in Mn-rich layered oxides with Mg\textsuperscript{2+}.[4] We demonstrate that Mg\textsuperscript{2+} cations are electrochemically intercalated into Li sites in delithiated Mn-rich layered oxides. As a result, [Li\textsubscript{1-x}Mg\textsubscript{x}][Mn\textsubscript{1-z}M\textsubscript{z}]O\textsubscript{2} (M = Co and Ni) are formed during discharging. Interestingly, this Mg\textsuperscript{2+} intercalation into [Li\textsubscript{1-x}Mg\textsubscript{x}][Mn\textsubscript{1-z}M\textsubscript{z}]O\textsubscript{2} is irreversible, and thus, Mg\textsuperscript{2+} is not deintercalated during cycling. This results in the favorable doping of Mg\textsuperscript{2+} at the Li sites in [Li\textsubscript{1-x}Mg\textsubscript{x}][Mn\textsubscript{1-z}M\textsubscript{z}]O\textsubscript{2}. Moreover, we show that the amount of Mg\textsuperscript{2+} intercalation into Li\textsubscript{1-x}[Mn\textsubscript{1-z}M\textsubscript{z}]O\textsubscript{2} is linearly proportional to the amount of Mn in Li\textsubscript{1-x}[Mn\textsubscript{1-z}M\textsubscript{z}]O\textsubscript{2}. In addition, Mg\textsuperscript{2+} at the Li sites in [Li\textsubscript{1-x}Mg\textsubscript{x}][Mn\textsubscript{1-z}M\textsubscript{z}]O\textsubscript{2} suppresses cation mixing between Li\textsuperscript{+} 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: