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Comparing Charge Compensation Mechanisms of $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Fe}_{0.4}\text{O}_2$ As Novel Cathode Material

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Abstract

Li-rich oxides have generated widespread interest for their use as next generation high energy density Li-ion battery cathodes. Among Li-rich candidates, cation disordered phases are novel lithium intercalation compounds that warrant further fundamental characterization. Here, we compare $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ and $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Fe}_{0.4}\text{O}_2$ system to explore differences in charge compensation and electrochemical performance. Using Operando XANES/EXAFS measurements examine how the Mn/Fe/Nb local environments and oxidation states change and their effect on electrochemistry. $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Mn}_{0.4}\text{O}_2$ displays capacities beyond the traditional transition metal redox ($\text{Mn}^{3+/4+}$), which is considered accessible through oxygen redox. $\text{Li}_{1.3}\text{Nb}_{0.3}\text{Fe}_{0.4}\text{O}_2$ exhibits charge capacities at similar potentials to that of anionic redox but our investigations suggest the charge compensation mechanism displays more $\text{Fe}^{3+/4+}$ redox in origin. By using a suite of characterization techniques, we explore the capacity contributions of cation and anionic components in these systems.