Iron Migration and Oxygen Redox in Layered O3 type $Na_xFe_yMn_{1-y}O_2$ Cathodes for Na-ion Batteries

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Most Li-ion batteries rely on chemistries including toxic and scarce elements such as Co, Ni, and Li. Thus, developing novel and sustainable alternative technologies based on abundant elements such as Na, Mn and Fe is of high priority [1, 2]. In recent years, Na-ion batteries have advanced significantly and have become a promising alternative to Li-ion technology. Herein, layered transition metal oxides are a promising class of electrode materials owing to their high capacity. However, we still need to identify materials with truly sustainable elemental compositions that maintain stable capacities during repeated battery discharges and charges. Materials based on iron and manganese, $NaFe_yMn_{1-y}O_2$, are of high interest due to the high abundance of these elements, and reports have shown capacities exceeding 160 mAh/g [3–5]. The layered transition metal oxides are typically obtained in one of two polymorphs, denoted as the P2- or O3-phase described by space groups $P6_3/mmc$ and $R\text{-}3m$, respectively. The O3-phase is notable for its higher initial sodium loading (i.e., higher capacity) than P2-analogues.

In this study, we investigate how structural transformations correlate with Fe migration and oxygen redox as the Fe:Mn ratio is varied in O3-$NaFe_yMn_{1-y}O_2$ (y = 0.5, 0.6, 0.7, and 0.8). High Fe-containing materials, $NaFe_{0.7}Mn_{0.3}O_2$ and $NaFe_{0.8}Mn_{0.2}O_2$, rearrange into a disordered O3-like structure upon Na extraction, while the materials with lower Fe content, $NaFe_{0.5}Mn_{0.5}O_2$ and $NaFe_{0.6}Mn_{0.4}O_2$, undergo multiple phase transitions including P3 (space group $R3m$), OP2 (space group $P3m$), and X-phases. Based on the description of the severely stacking faulted “X-phase” by Drejer et al. [6], we have described the stacking faulted $O3_{\Delta p}$ phase occurring at high voltages (>3.5 V) in the materials with high Fe content. Our study reveals that, due to Fe^{3+} migration, the O-to-P-type layer gliding is “pinned,” locking the structure in an $O3_{\Delta p}$ state. Higher Fe content increases the covalency of the Fe-O bond, activating oxygen redox. This suggests a direct correlation between Fe^{3+} migration, which locks Fe in a trivalent state, and the preference for anion redox over transition-metal redox.

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