

Structure–Electrochemical Evolution of a Mn-Rich P2 $\text{Na}_{2/3}\text{Fe}_{0.2}\text{Mn}_{0.8}\text{O}_2$ Na-Ion Battery Cathode

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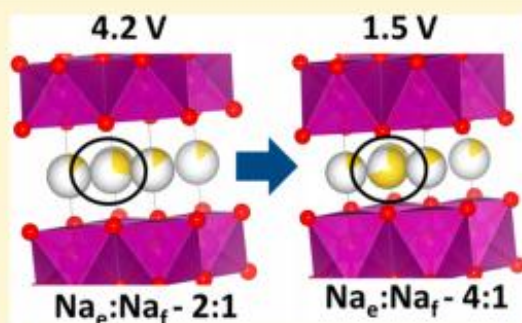
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Supporting Information

ABSTRACT: The structural evolution of electrode materials directly influences the performance of sodium-ion batteries. In this work, in situ synchrotron X-ray diffraction is used to investigate the evolution of the crystal structure of a Mn-rich P2-phase $\text{Na}_{2/3}\text{Fe}_{0.2}\text{Mn}_{0.8}\text{O}_2$ cathode. A single-phase reaction takes place for the majority of the discharge–charge cycle at $\sim C/10$, with only a short, subtle hexagonal P2 to hexagonal P2 two-phase region early in the first charge. Thus, a higher fraction of Mn compared to previous studies is demonstrated to stabilize the P2 structure at high and low potentials, with neither “Z”/OP4 phases in the charged state nor significant quantities of the P’2 phase in the discharged state between 1.5 and 4.2 V. Notably, sodium ions inserted during discharge are located on both available crystallographic sites, albeit with a preference for the site sharing edges with the MO_6 octahedral unit. The composition $\text{Na}_{\sim 0.70}\text{Fe}_{0.2}\text{Mn}_{0.8}\text{O}_2$ prompts a reversible single-phase sodium redistribution between the two sites. Sodium ions vacate the site sharing faces (Na_f), favoring the site sharing edges (Na_e) to give a Na_e/Na_f site occupation of 4:1 in the discharged state. This site preference could be an intermediate state prior to the formation of the P’2 phase. Thus, this work shows how the Mn-rich $\text{Na}_{2/3}\text{Fe}_{0.2}\text{Mn}_{0.8}\text{O}_2$ composition and its sodium-ion distribution can minimize phase transitions during battery function, especially in the discharged state.



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