

Effect of molar ratios of Ni, Mn, and Fe on structural stability and electrochemical performance of layered cathode materials for sodium-ion batteries

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The increasing adoption of renewable energy necessitates the increase in the development of efficient and affordable energy storage technologies. Since intermittent renewable energy sources such as wave, solar, and wind need to turn into dominant and integrated into the power grid, there is a demand for large-scale energy storage solutions [1]. Modern market is dominated by lithium-ion batteries. The dominance of LIBs can be attributed to low self-discharge rates, high coulombic efficiency, high energy density, and a spectrum of chemical potentials available with various electrode designs [2]. Even though LIB technology is well-established, there are still issues regarding its cost-effectiveness, lifetime, safety, and performance at low temperatures [2]. Additionally, since there is high demand for lithium, which is not considered abundant in the Earth's crust, its feasibility for large-scale utilization has begun being questioned. Ongoing research on cathode materials is aiming to replace the most expensive and important part with more affordable and superior replacement. Sodium-ion batteries (SIBs) have a slight disadvantage over LIBs such as low electrochemical potential of -2.71 V compared to the standard hydrogen electrode (SHE) which is only slightly higher than that of LIBs (330 mV), however much more abundant, thus enabling SIBs meet requirements of large-scale electrical energy storage [1]. Polyanionic compounds, layered oxides, Prussian blue analogs, and organic compounds are the materials that have been extensively investigated as potential positive electrodes for SIBs. Layered transition metal oxides (TMO) are a type of cathode material with greater capabilities regarding up-scalability, energy density and stability [3]. Among TMOs NaMnO₂ based cathode materials are competitive as low-cost and high-power cathode material. However, the complex phase transitions with large volume changes during cycling leads to rapid degradation of the crystal structure and as a result capacity. Recent investigation suggests that undesirable phase transformation can be dampened via doping additional transitional TMs into the structure [3].

O3-NaNi_{0.5}Mn_{0.5}O₂ transition metal oxide, as reported by Komaba et al., is one of the most promising cathode materials for SIBs because of its good cycling performance with capacity retention of 81% after 20 cycles and capacity of 120 mAh g⁻¹ [4]. Following this, they substituted Ni_{0.5}Mn_{0.5} with Fe in O3-NaFeO₂ to create O3-Na(Ni_{0.5}Mn_{0.5})_{1-x}Fe_xO₂ and proposed NaNi_{1/3}Mn_{1/3}Fe_{1/3} as the optimum material due to a balance between capacity, cycling, and cost [5]. Currently, the full extent of effects of different concentrations of Fe and Ni as well as of Na on electrochemical performance and structural changes of NaNiFeMnO have not been fully studied.

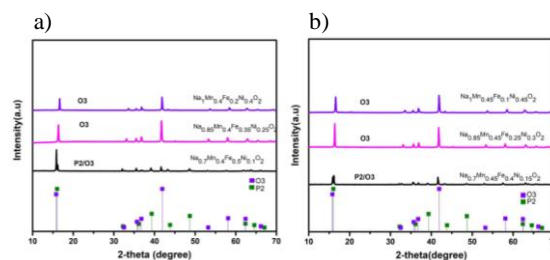


Figure 1. a) XRD data for Na_xMn_{0.4}Fe_yNi_{0.6-y} cathode materials. b) XRD data for Na_xMn_{0.45}Fe_yNi_{0.55-y} cathode materials.

In this research, we studied the combination of different ratios of Ni, Mn, and Fe in O3 and P2 type NaNi_xMn_yFe_{1-(x+y)}O₂ cathode material. NaNi_xMn_yFe_{1-(x+y)}O₂ has been synthesized via solid-state method in open air. During experiments, the correlation between the characteristics of the material (both morphological and electrochemical) and concentrations of the elements has been investigated. Na_{0.7}Mn_{0.4}Fe_{0.5}Ni_{0.1}O₂ and Na_{0.7}Mn_{0.45}Fe_{0.4}Ni_{0.15}O₂ cathode materials exhibited biphasic P2/O3 structure while Na_{0.85}Mn_{0.4}Fe_{0.35}Ni_{0.25}O₂ and Na_{0.85}Mn_{0.45}Fe_{0.25}Ni_{0.3}O₂, Na_{0.95}Mn_{0.4}Fe_{0.25}Ni_{0.35}O₂ and Na_{0.95}Mn_{0.45}Fe_{0.15}Ni_{0.4}O₂, Na₁Mn_{0.4}Fe_{0.2}Ni_{0.4}O₂ and Na₁Mn_{0.45}Fe_{0.1}Ni_{0.45} corresponded to O3 structure. Further XPS, SEM-EDS, ICP-OES, and electrochemical studies were done to investigate the link between the structure and electrochemical performance.

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