

Tailoring the Electrochemical Performance of P2- $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ as High Voltage or High Capacity Cathode Material for Sodium-Ion Batteries

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Sodium-Ion batteries are currently discussed to be an interesting alternative to the commonly used lithium-ion battery technology because of a lithium shortage possibly occurring if lithium-ion batteries are used for large scale applications like e.g. electric vehicles or plug-in hybrids. In contrast to lithium, sodium-based raw materials are abundant and easily available. The low cost advantage thereby is not only interconnected with the lower price of sodium but rather more with the feasible use of aluminum as anode current collector since sodium is not alloying with it. The avoidance of copper thus results not only in a cheaper but also in a lighter battery with increased energy density. [1-3]

Currently, especially layered oxides are discussed to be promising cathode material for sodium-ion batteries. Generally, superior electrochemical performances compared to other secondary battery systems, except for the lithium-ion technology, have been demonstrated for the sodium-based systems. [4-6]

In analogy to the famous and commercially available $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) cathode material we have developed the synthesis of layered $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ cathode material with decreased nickel and cobalt content resulting in lower cost. [7,8] The material is synthesized by firing a mixture of a transition metal hydroxide precursor, obtained via co-precipitation method, and sodium hydroxide in a simple two step solid state annealing process in air, followed by a water (rinsing) treatment.

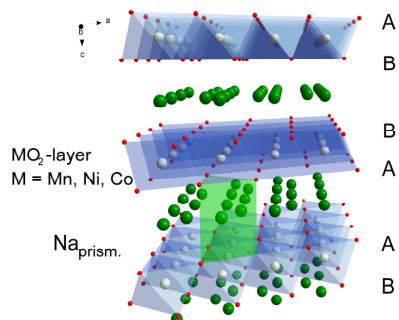


Figure 1: Schematic illustration of layered P2- $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ [7]

The simultaneous presence of nickel, cobalt and manganese is beneficial for the overall electrochemical performance. In fact, while the Ni^{2+} to Ni^{4+} redox reaction is increasing the capacity of the material, cobalt is improving the ionic and electronic conductivity and manganese, in its highest oxidation state of Mn^{4+} , is stabilizing the transition metal layer.

In the past we have demonstrated and reported the extraordinary good cycling performance of $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ in a sodium half cell system containing in 0.5M NaPF_6 in PC.

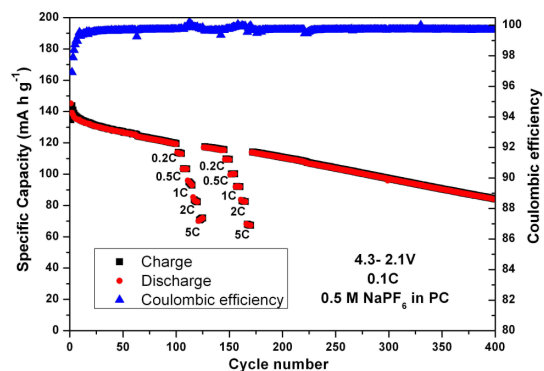


Figure 2: Electrochemical performance of layered P2- $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ during galvanostatic cycling at 0.1C (12 mA g^{-1}) and a C-rate test from 0.2C to 5C.

Herein, we will demonstrate how the performance of layered P2- $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ can be tailored by changing the potential range of use. In addition, we will show how the electrochemical performance can be interconnected and explained with the structural phenomena occurring at different potentials for $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$.

In dependence of the upper and lower cut-off potentials, $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ can work as high potential or high capacity cathode material. In this way average capacities of 90 mAh g^{-1} , 125 mAh g^{-1} and 210 mAh g^{-1} with the corresponding average potentials (vs. Na/Na^+) of 3.7 V, 3.35 V and 2.7 V can be achieved.

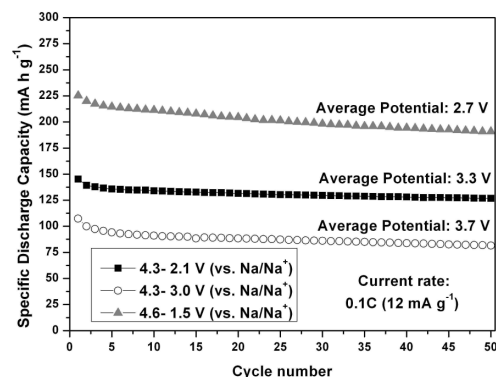


Figure 3: Electrochemical performance of layered P2- $\text{Na}_{0.45}\text{Ni}_{0.22}\text{Co}_{0.11}\text{Mn}_{0.66}\text{O}_2$ in dependence of the potential range of use during the galvanostatic cycling at 0.1C (12 mA g^{-1}).

To the best of our knowledge such high capacities in combination with a stable cycling behavior have not been reported so far for similar layered sodium based cathode materials.

References

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