

MS14-2-2 Influence of Li and Mg substitution on structural properties and electrochemical performance of Na_xMnO_2 -based cathode material for Na-ion batteries
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Abstract

In the continuous search for high energy density post-lithium batteries, one should not forget the fundamental reasons for such research: providing earth-abundant, safe for the environment, and inexpensive materials [1]. At the same time, ensuring the high capacity and long cycle life of Na-ion battery is crucial. In this regard, agents activating oxygen redox seem to be especially promising. Here we present a complex investigation of Li and Mg substitutions in the Mn sublattice that affect crystal structure in layered $\text{Na}_{0.67}\text{MnO}_2$.

The samples were synthesized via sol-gel method using acetates and sucrose as a fuel. Crystal structure was determined using X-ray diffractometry, and transport properties were investigated by impedance spectroscopy. The most promising compositions were used as an active materials and mixed with carbon black and PVDF to prepare cathode layers. Then, the CR2032-type coin cells were assembled in an argon-filled glovebox with high purity, using metallic sodium as an anode and 1M NaPF_6 in EC:DEC as an electrolyte. Electrochemical performance was tested using cyclic voltammetry and cyclic charge/discharge techniques. Changes of the crystal structure in selected samples during cell performance were inspected via ex-situ and in situ XRD measurements. X-ray absorption spectroscopy allowed to determine oxidation states of transition metal in selected samples and investigate the changes in sodium and oxygen behaviour during cycling.

All investigated materials crystallize in P2-type layered structure, described as $P6_3/mmc$ or $P6_3/mcm$ space group. X-ray diffraction measurements of cathode materials in the batteries showed that Mg substitution stabilises the crystal structure and prevents phase transition during cycling. Mg substitution enhances the capacity, reaching 112% of theoretical capacity for $\text{Na}/\text{Na}^+/\text{Na}_x\text{Mg}_{0.25}\text{Mn}_{0.75}\text{O}_2$ cell in the first discharge, followed by 105% in the next one. The characteristic plateau on the first charge on charge/discharge plots can be associated with the activation of oxygen-related electrochemical processes. The first charge suggests the irreversible character of anionic redox process, which is confirmed by the cyclic voltammetry. This behaviour applies to the whole $\text{Na}_x\text{Mg}_y\text{Mn}_{1-y}\text{O}_2$ system with various amounts of Mg. On the contrary, the mechanism is different for Li-substituted Na_xMnO_2 . It is because alkali metal in transition metal sublattice affects the electronic structure in a different way [2]. To some extent, this phenomenon is visible in cyclic voltammetry and cyclic charge/discharge plots: CV shows plenty irregular peaks, which reflect in irregular charge/discharge curves.

A complex analysis of Mg- and Li-substituted Na_xMnO_2 system properties gives a huge insight into the work mechanisms induced by such different elements. This approach can have a great impact on designing and understanding advanced cathode materials for Na-ion batteries.

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References

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