

Investigating Doping and Calcination Effects on Nickel-Rich Layered Oxide Positive Electrode Material Enhancing the Lithium-Ion Batteries Performance

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Global energy storage capacity is likely to fall behind global energy demand soon, and therefore, additional energy storage solutions are needed. Lithium-ion batteries are dominating the electrochemical energy storage market and they need to be improved to address this challenge. The energy sector is currently focused on developing new positive electrode materials for Li-ion batteries with high energy density, longer life durability, and meeting ecological and ethical standards. Nickel-rich layered oxides, such as $\text{Li}(\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1})\text{O}_2$ (i.e., NMC811) are the type of positive electrode materials which possess excellent performance, high specific capacity (up to 200 mAh g^{-1}) and energy density, good stability. Reducing cobalt content, as seen in NMC811, addresses ethical concerns associated with cobalt mining. However, challenges like rapid capacity decline, potential structural disorder, and side reactions hinder their performance, leading to reduced specific capacity and preventing Li-ion transport. Doping elements into a crystalline structure, a common strategy, aims to stabilize the crystal structure of materials like NMC811 during Li-ion intercalation/deintercalation, thereby enhancing cycling properties. Incorporating electrochemically inactive substituents like magnesium aids in stabilizing the layered structure and suppressing nickel ion migration into the lithium layer. The calcination condition during the lithiation of NMC811 is another point that plays a crucial role in determining several key properties. Optimal calcination temperature is vital for controlling morphology, doping effectiveness, and crystal structure, which in turn determines the electrochemical performance of the final electrode material. This work focuses on understanding the effects of calcination conditions on the electrochemical performance of NMC811 doped with magnesium.

In this work, three types of NMC811 precursors with 0 at.%, 0.25 at.%, and 0.50 at.% of Mg content were used. Additionally, during the lithiation step, 0.75 at.% of Mg was added to each sample. The lithiation temperatures of 650, 700, 750, 800, 850, and 900 °C were chosen to investigate the effect of calcination conditions on the morphology and crystal structure. By investigating phase changes through in-situ high-temperature X-ray diffraction under the synthesis conditions, as well as primary particle growth via scanning electron microscopy at various calcination temperatures, this research aims to provide insights into the relationship between the structural features and electrochemical performance. It is shown that only beyond 750 °C the primary particles completely turn to spherical shapes, while at the 900 °C calcination temperature, the primary particles grow so fast that the single-crystal particles are formed. The cation mixing and layered structure formation for all obtained materials were investigated by powder X-ray diffraction. The electrochemical behaviour is tested in Li half-cells. The combination of two types of doping leads to better electrochemical performance and cycling stability even at high potentials (3.0 – 4.6 V vs. $\text{Li}|\text{Li}^+$) beyond the stable potential window for NMC811. The increasing calcination temperature leads to the increase of the specific capacity and capacity retention after 100 cycles with the increasing amount of Mg in the structure.