

Synthesis of $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ solid solution with enhanced thermal stability

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Introduction

Lithium nickelate and lithium cobaltate lacks the thermal stability especially when charged. Several researchers worked on enhancing thermal stability by the addition of substitutional dopants for nickel (cobalt) or lithium. Nevertheless, especially for lithium nickelate, the thermal stability was not improved greatly. Most of the previous works were based upon using nickel source which valence of 2. Practically the stoichiometric lithium nickelate was impossible to synthesize due to the ease of changing valence of nickel. To produce near stoichiometric lithium nickelate, sustaining nickel valence to 3 is important.

Results and discussion

In this work, applying nickel source of 3 valencies, near stoichiometric lithium nickelate was manufactured. Nickel source of 3 valencies was induced from the oxidation of nickel hydroxide via 2 ways. The one is using oxidizer such as sodium persulfate and the other is firing at oxygen environment. In case of firing, slight over-firing results to NiO not $\beta\text{-NiOOH}$. (Fig. 1)

From the precursor of 3 valencies, near stoichiometric lithium nickelate was synthesized using ion exchange method. Ion exchange was performed via hydrothermal way and co-precipitation. Hydrothermally treated and co-precipitated powders were further calcined without oxygen flowing, even though the hydrothermally treated powder showed the crystallinity. After the calcination, the powder was fully crystallized and showed no difference between solid-state reacted powders with oxygen flowing. (Fig. 2)

Prepared powder was pure lithium nickelate, and to test thermal stability above ambient temperature, electrochemically de-lithiated. For $\text{Li}_{0.2}\text{NiO}_2$, hexagonal structure (R3m) was sustained over 200°C, and after further firing at 250°C, the structure was converted to spinel structure (Fd3m). Even more firing over 300°C, then the transformation to rock salt structure (Fm3m), which is electrochemically non-active, was occurred. From this point of view, using the precursor of 3 valencies, the highly de-lithiated lithium nickelate was stabilized above ambient temperature. To enhance thermal stability further, the addition of cobalt, magnesium, and gallium will be reviewed.

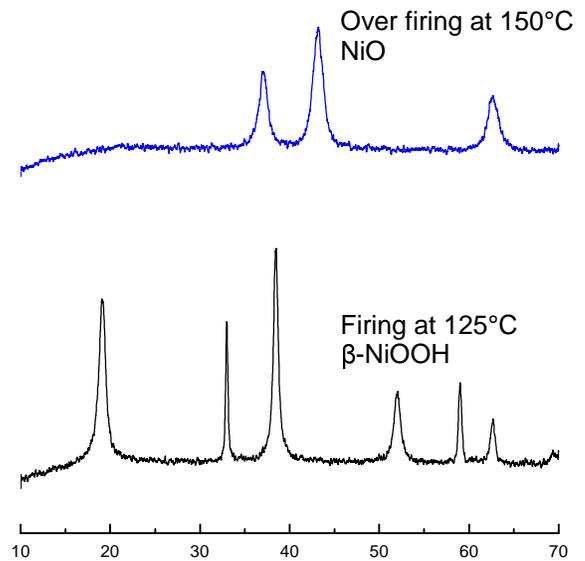


Fig. 1. XRD patterns of precursor powders.

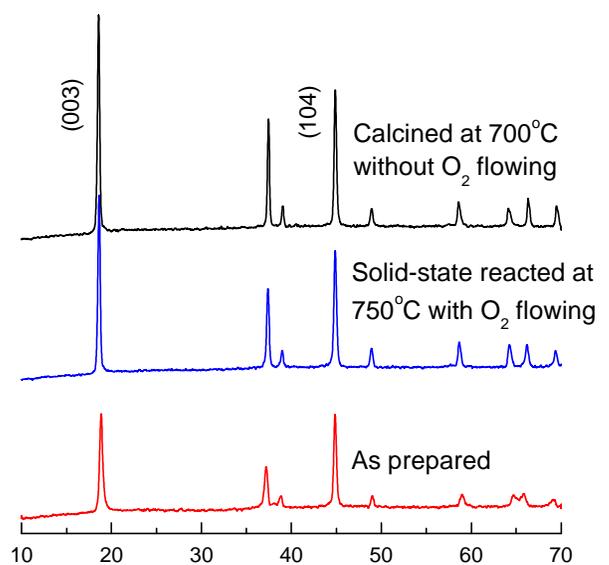


Fig. 2. XRD patterns of calcined, solid-state reacted, and as prepared powders.