

Synthesis and characterization of Li excess layered material synthesized under high oxygen pressure

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Lithium rich layered materials hold great promise as a next generation cathode material for lithium ion batteries. They promise high capacities of around 200-250 mAh•g⁻¹ compared to 150 mAh•g⁻¹ over conventional LiCoO₂ cathode materials. However, this material has yet to be fully investigated and has been plagued with problems such as an oxygen generation during the initial charge process and poor cycle stability [1]. Especially promising has been a material that combines the elements of Mn, Co, and Ni as opposed to the single use of Co. This high capacity phase has been proposed to be the result of a structure rearrangement due to the oxygen evolution. In our previous study we tried to directly synthesize this phase in a high-pressure environment [2]. In this study we synthesized Li rich layered phase with the Mn, Co, Ni compositions using a high-pressure synthesis technique under high oxygen pressure. A range of Li content in these compositions was investigated ranging from normal to extremely Li rich in order to investigate the Li content limits of these new materials. The effects of the high oxygen pressure on the structure and charge discharge capacity were also investigated

Layered Li_{1+x}[Li_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.4}]O₂ was synthesized using a high pressure technique under high oxygen pressure. The oxygen source was introduced by means of KClO₄ as oxygen generator and separated from the reaction materials by a layer of ZrO₂. The materials were characterized using synchrotron radiation and neutron radiation diffraction techniques and analyzed using Rietveld refinement. ICP measurements were taken to confirm composition, and electrochemical properties were investigated to check capacity and cycle stability.

All starting materials were prepared in an argon-filled glove box. The starting materials were then ball milled to attain a uniform mixture of ingredients. Synthesis was performed using a cubic anvil type high-pressure apparatus. The samples were sealed in either gold or platinum, heated and pressurized in a range from 800-1200 °C and 1-4 GPa.

Samples were extracted and handled in an argon-filled glove box. KClO₄ was separated from active material by a layer of ZrO₂. Structure analysis was performed using XRD powder diffraction with Cu K α radiation and Neutron diffraction experiments were carried out at the BL20 iMateria facility at J-PARC. Electrochemical properties were investigated using a CR-2032 type coin cell. Cathodes were prepared at 80% active material, 10% acetylene black, and 10% PVdF binder. Charge and discharge tests were carried out from 2.0-4.8 V vs. Li/Li⁺ at 5.5-13.75 mAh/g.

Synthesis at 1 GPa and 950 °C successfully resulted in a layered structure, which could be categorized with a R-3m or C2/m space group depending on Li content. XRD Rietveld analysis revealed a decrease in the lattice parameter as the value of x increased from x=0.2 to x=0.6. Refinement results showed that samples moved from an R-3m phase to a C2/m phase as the amount of Li was increased with no indication of a cubic phase. Electrochemical performance was evaluated and revealed that a plateau around 4.4 V occurred which can be associated with an oxygen-generation. A capacity around 220 mAh•g⁻¹ for a KClO₄ assisted sample was observed with good cycle retention after 10 cycles. ICP data was also taken and confirmed that there was some Li loss however the overall compositions remained lithium rich. The relationship between the composition synthesized under high oxygen pressure and normal oxygen pressure will be discussed.

References

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