

Investigation of Electrochemical properties and Phase Stability of Li_2NiO_2 with the Immm structure

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Motivation

In materials such as $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, $\text{Li}_{0.9}\text{Ni}_{0.45}\text{Ti}_{0.55}\text{O}_2$, and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox couple exchanges two electrons per Ni ion in a narrow voltage window [1-6]. Such a redox couple with multiple oxidation states opens up the potential for a significant increase in specific capacity. Theoretically, if the electrochemically inactive Mn or Ti can be removed from the structure, and Ni is the only transition metal in the structure, the specific capacity can be almost doubled. A composition such as Li_2NiO_2 has a theoretical specific capacity of 513 mAh/g. We have performed both first principles computations and experiments to test the performance of Li_2NiO_2 compounds.

Li_2NiO_2 can be obtained by overlithiating LiNiO_2 to form the layered 1T structure (Fig. 1(a)). The groundstate of Li_2NiO_2 is not this layered structure, but an orthorhombic form with Immm space group (Fig. 1(b)). Indeed, upon heating 1T- Li_2NiO_2 it converts to the Immm structure [7]. In this work we synthesize the Immm form directly (Fig. 2) and investigate its electrochemical activity.

Results

The electrochemical properties and phase stability of the orthorhombic Immm structure of composition Li_2NiO_2 are studied experimentally and with first principles calculations. The material shows a high specific charge capacity of about 320 mAh/g and discharge capacity of about 240 mAh/g at the first cycle. The experimental results and first principles calculations all indicate that the orthorhombic Immm structure is rather prone to phase transformation to a close-packed layered structure during the electrochemical cycling.

The possibility of stabilizing the orthorhombic Immm structure during the electrochemical cycling by partial substitution of Ni is also evaluated. A detailed analysis of the crystal field energy difference between octahedral and square-planar coordinated Ni^{+2} indicates that crystal field effects may not be large enough to stabilize Ni^{+2} in a square planar environment when the cost of electron pairing is taken into account. Rather, we attribute the stability of Li_2NiO_2 in the Immm structure to the more favorable Li arrangement possible as compared to a possible Li_2NiO_2 structure with octahedral Ni.

References

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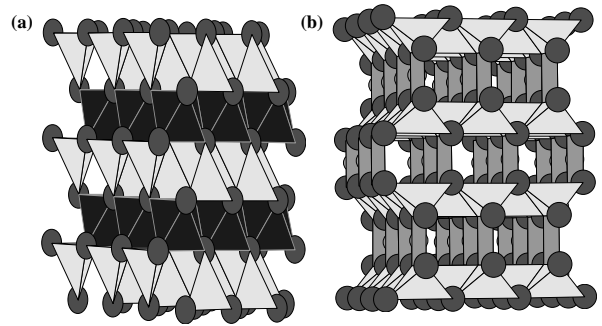


Figure 1. Crystal structure of (a) 1T- Li_2NiO_2 (Ni occupies the center of the octahedron (dark shaded) and Li occupies the center of a tetrahedron (light shaded)); (b) Immm- Li_2NiO_2 (Ni occupies the center of the rectangle (dark shaded) and Li occupies the center of a tetrahedron (light shaded).)

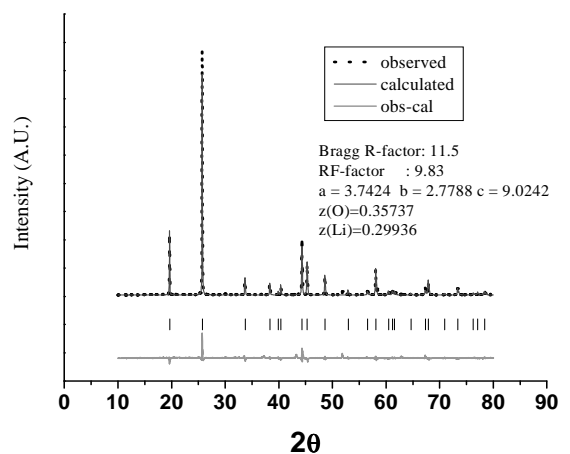


Figure 2. XRD pattern and Rietveld refinement of Li_2NiO_2 (a, b and c are the lattice parameters and z the atomic position of oxygen or Li along the c axis.) [8]