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Cation distribution and mixing thermodynamics in Li(Mn_{1-x}Ni_x)O₄ spinel via tuning of the Ni concentration

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Spinel LiMn₂O₄ is a promising cathode material for secondary lithium-ion batteries which, despite its high average voltage of lithium intercalation, suffers crystal symmetry lowering due to the Jahn-Teller active six-fold Mn₃₊ cations. LiMn₂ O₄ is a low-cost, environmentally friendly, and highly abundant material used as a cathode in Li-ion batteries. Although Ni has been proposed as a suitable substitutional dopant to improve the structural and mechanical stability of LiMn₂O₄ and enhance the average lithium intercalation voltage, the thermodynamics of the Ni incorporation and its effect on the electrochemical properties of spinel LiMn₂O₄ is not known yet. In this paper we have implemented two approaches; the cluster expansion which determined stable multi-component crystal structures and ranks metastable structures by the enthalpy of formation, while maintaining the accuracy of first-principles density functional methods. In the second approach we employed density functional theory calculations with a Hubbard Hamiltonian (DFT+U) to investigate the thermodynamics of mixing of the Li(Mn_{1-x}Ni_x)O₄ solid solution. The results suggest that LiMn_{1.5}Ni_{0.5} O₄ is the most stable composition at temperatures ranging from room temperature to 1000K. The configurational entropy is much lower at low temperatures. It was also found that the mechanical properties of Ni-doped LiMn₂O₄ are stable at 0K. The calculated maximum average lithium intercalation voltage was found to be 4.8 V for LiMn1.5Ni0.5O4 composition and is in agreement with the experimental value of 4.7 V. The temperature was found to have a negligible effect on the Li intercalation voltage of the most stable composition.

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