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Understanding the transition metal order in spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by electron microscopy

Gozde ONEY^{1,2}, François WEILL¹, Jacob OLCHOWKA¹, Chunyang ZHANG³, Muriel VÉRON³, Christian MASQUELIER⁴, Arnaud DEMORTIÈRE², Laurence CROGUENNE¹

¹Institut de Chimie de la Matière Condensée de Bordeaux, France,

²Laboratoire de Réactivité et Chimie des Solides, France,

³Laboratoire de Science et Ingénierie des Matériaux et Procédés, France,

⁴Université de Picardie Jules Verne, France,

The spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) is one of the most promising candidates as a cobalt-free positive electrode material. Its theoretical capacity of 147 mAh.g^{-1} obtained by oxidation of Ni^{2+} to Ni^{4+} at an average potential of approximately 4.7 V vs. Li/Li^+ leads to a high energy density of 650 Wh/kg. However, several characteristics affect this material's performance and stability, such as the stoichiometry and the morphology of the primary particles. Additionally, Ni and Mn can occupy either a single crystallographic site or two different ones, forming two polymorphs with cubic symmetry called disordered and ordered structures, respectively. Even though averaged information can be obtained about the extent of the transition metal order by diffraction or spectroscopy techniques, the local information on the process of ordering within the crystal and its homogeneity at the particle scale are still unknown. In our study, we used molten salt synthesis to control LNMO particles' morphology (platelets versus octahedra) and thickness by changing the annealing conditions while keeping the transition metal disorder in the crystal structure. Moreover, a post-annealing step allowed us to tailor the extent of ordering between Ni and Mn while maintaining the thin platelet morphology. Indeed, various Li environments were observed by neutron powder diffraction and spectroscopies (Raman and nuclear magnetic resonance (NMR)), whereas a single Li site is expected for a fully ordered LNMO structure. These samples being transparent to electrons due to their morphology were analyzed by scanning transmission electron microscopy coupled with precession (ASTAR System - Nanomegas). We collected electron diffraction data for each pixel of the acquired images (4D-STEM). This technique

gave in-depth information on the homogeneity of the transition metal order at the particle scale, with a spatial resolution of 10 nm, and allowed to propose the mechanism involved throughout the post-annealing process.

Keywords: high-voltage spinel, transition metal order, 4D-STEM