Mind the miscibility gap: Cationic disorder drives non-equilibrium phase transformations during electrochemical cycling of LiNi_{0.5}Mn_{1.5}O_{4}

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LiNi_{0.5}Mn_{1.5}O_{4} (LNMO) is a promising high voltage positive electrode material for lithium ion batteries which unfortunately suffers from cycle life and stability issues. These shortcomings are intricately linked to the subtle structural configurations the material can adopt. LNMO is a spinel structure which can be derived from rock-salt with anions forming a cubic close packed array within which the cations sit in the octahedral or tetrahedral interstitial sites. However, like all rock-salt derived electrode materials, the cations can be organized in different ways over the interstitial sites forming different structural configurations, e.g., the ordered (P4_32) and disordered (Fd3m) forms. In the ordered form Ni and Mn occupy crystallographically distinct sites (4a and 12d positions respectively) whereas in the disordered they are mixed. This subtle difference in cationic ordering can have a profound effect on the electrochemical performance. In the case of LNMO the degree of ordering dictates the nature of the phase transition occurring during Li\(^{+}\) extraction and insertion. Electrode materials that exhibit phase transitions with large structural rearrangements during electrochemical cycling are disadvantageous. Structural mismatches lead to a buildup of strain and particle cracking, accelerating the surface driven aging processes occurring in batteries. For disordered Li_{1-x}Ni_{0.5}Mn_{1.5}O_{4} a solid solution is observed up to x=0.5 followed by a phase conversion between the x=0.5 and x=0 phases with no compositions in between. Whereas the ordered form exhibits two discontinuous phase transitions between x=1, 0.5 and 0 [1]. In the presented work operando X-ray diffraction was utilized together with detailed peak profile analysis to elucidate the phase transition mechanism dependency on transition metal cation order and current density.

Figure 1. Miscibility gap narrowing in “less-ordered” and “ordered” spinel at high current densities represented by a distribution of cell parameters between the main phases. The distribution of cell parameters is interpreted as a widening of the coherent interphase (right).

When fully disordered, LNMO undergoes a bulk single-phase solid solution reaction between the intermediate phases LiNi_{0.44}Mn_{1.56}O_{4} and Li_{0.5}Ni_{0.44}Mn_{1.56}O_{4} followed by a first order phase transition with a coherent interphase between the intermediates Li_{0.5}Ni_{0.44}Mn_{1.56}O_{4} and Ni_{0.44}Mn_{1.6}O_{4}. When fully ordered and slightly less ordered, two separate first order phase transitions with a coherent interphase between the same intermediate phases were observed. By using a custom high rate electrochemical cell for operando diffraction [2] and discharging the battery over 6 minutes, the miscibility gap between the intermediate phases narrowed, extending the solid solution domain formed at the coherent interphase (Figure 1). This effect was found to be stronger in samples exhibiting a higher degree of disorder [3]. The results reveal that the presence of cation disorder in the material is an important parameter for the rational design of materials that favor solid solution processes.

[2] Gustafsson, O.; Batteries & Supercaps 2021, 4 (10), 1599