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Nano-Scale Lamellar Monoclinic Li2MnO3 Phase with Stacking Disordering in Lithium-Rich and Oxygen-Deficient Li-Mn-O Cathode Materials

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The cubic spinel $LiMn_2O_4$ is considered as one of the most promising cathode materials for secondary lithium batteries with many excellent properties such as less cost and environmental friendliness, but its fast capacity fading during cycling prevents it from commercial use. The study of the lithium-rich and oxygen-deficient $Li_{1.07}Mn_{1.93}O_{4-\delta}$ through systematic synchrotron radiation X-ray power diffraction (XRD) and differential scanning calorimetry indicates the cubic-tetragonal phase transition with different oxygen vacancy δ, which may be a key factor for the structural transition and electric capacity fading [1]. However, more detailed study is required to clarify the remained inconsistency in structural and magnetic transitions in the literature and the degradation of electro-chemical performance.

The serial $Li_{1.07}Mn_{1.93}O_{4-\delta}$ samples with different oxygen vacancy δ have been studied by the combined TEM, XRD and DIFFaX simulation [2] techniques. Besides the predominant cubic spinel phase of $LiMn_2O_4$ (SG: *Fd-3m*) or its slightly distorted tetragonal counterpart, the monoclinic Li_2MnO_3 (SG: *C2/m*) [3] which exists as nano-scale lamellar variants with 120^o rotational twinning stacked randomly along pseudo-three-fold axis $[111]_c//[103]_m$, has been identified using SAED, dark field (DF) imaging (Fig. 1) and HRTEM analysis. The XRD result confirms the existence of the monoclinic Li_2MnO_3 and reveals that its content is increasing with the oxygen vacancy δ. The determination of the monoclinic Li_2MnO_3 phase with poor electro-chemical performance and different magnetic transition behavior enables better understanding of the inconsistency in phase transition in the literature and electric capacity fading.

DF imaging (Fig. 1b) has clearly shown the nano-scale domain structures with three Li_2MnO_3 variants rather than the homogeneous hexagonal phase with superstructure [4]. The composite SAED patterns (Fig. 2a), simulated with three rotational twinning variants of monoclinic Li_2MnO_3 phase, are consistent with all the experimental SAED results (eg. Fig. 1a) including superstructure reflections reported in the literature [4]. XRD simulation (Fig. 2b) with DIFFaX [2] considering the stacking disordering shows that the characteristic reflections with 2θ between 20^o and 35^o in the XRD spectrum (CuKα) will become more and more broadened and weakened with the increasing interlayer disordering, indicating the difficulty in the XRD detecting the monoclinic Li_2MnO_3 phase with stacking disordering. Moreover, the extremely disordered stacking sequence may lead to the selective peak asymmetry (Fig. 2b). The analysis elucidates all the experimental observations by us and others and further SAED and neutron diffraction calculation analysis can clarify the similar ambiguity among other structurally related cathode materials.

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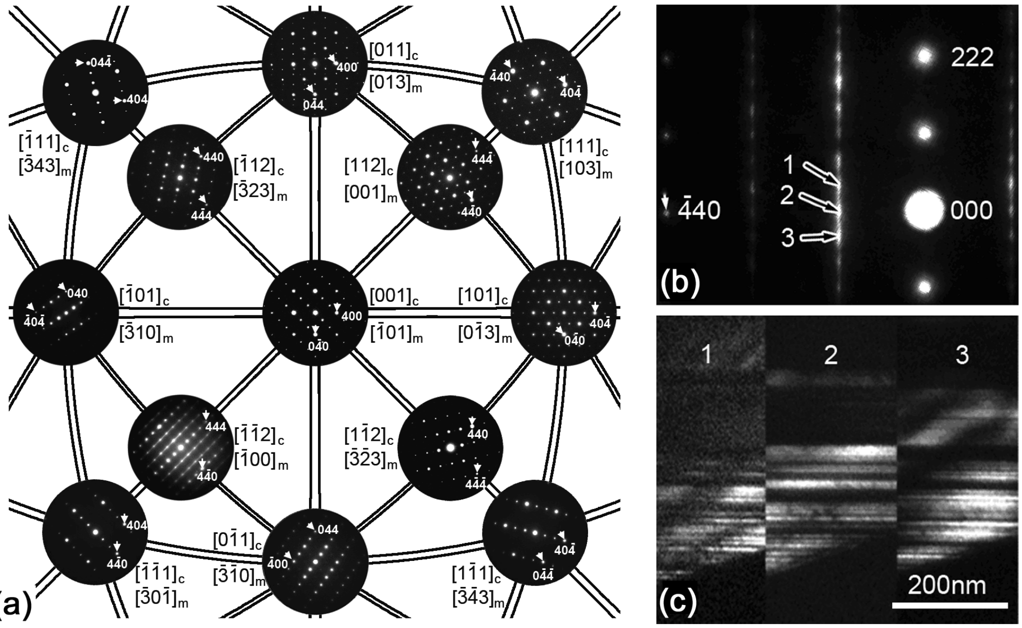

FIG. 1. (a) Experimental SAED patterns of monoclinic Li_2MnO_3, (b) zoomed-in SAED pattern along $[-1-12]_c$ with pseudo-cubic indexes and (c) the corresponding DF images, which clearly illustrate the presence of three twinning variants.

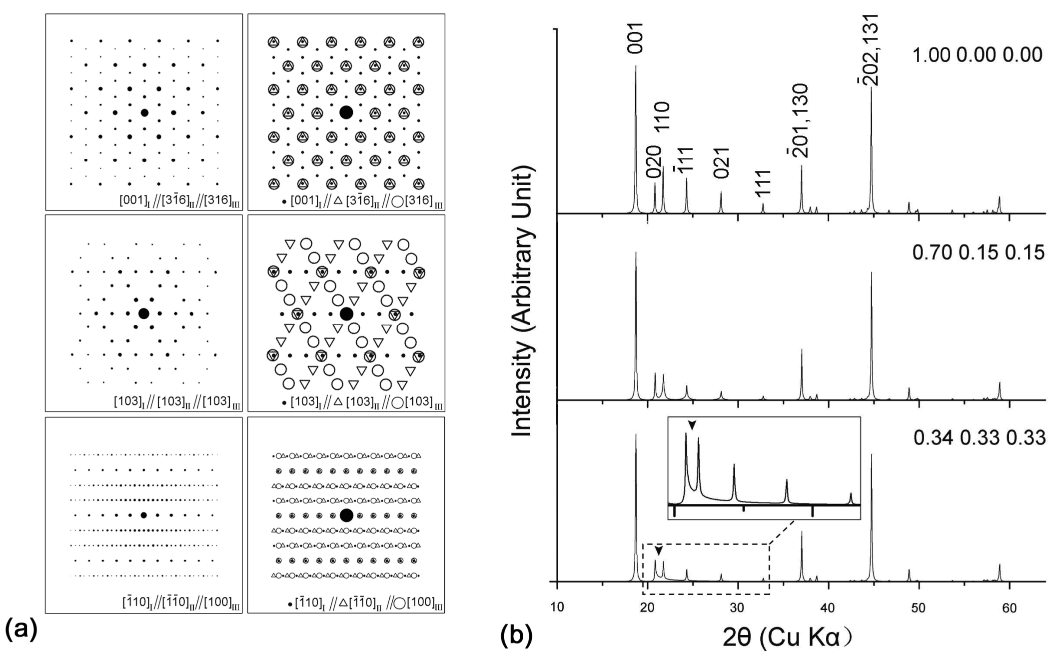

FIG. 2. (a) Composite SAED patterns of Li_2MnO_3 simulated with three twinning variants, (b) simulated XRD patterns of Li_2MnO_3 with increasing stacking disordering from above to bottom.