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MS-14-P-2519 Electrochemical investigation and microstructural characterization of $Li_{1.07}Mn_{1.93}O_{4-\delta}$ cathode materials

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Developing advanced cathode materials with superior energy density, power density, and cycle stability has long been an engineering pursuit, since the energy and power density in lithium-ion batteries (LIBs) is largely determined by the cathode materials, which store Li by incorporation into their crystal structure.[1] Li-rich and O-deficient $Li_{1+\alpha}Mn_{2-\alpha}O_{4-\delta}$ is considered as one of the most promising cathode material for secondary lithium batteries with less cost and environmental friendliness. However, it is speculated that oxygen vacancies that induce phase transitions during cycling are harmful for its cycling performance. Thus, a thorough knowledge of the structural characteristics in these materials is of wide technological relevance, which unfortunately remains unclear.

Herein, the serial $Li_{1.07}Mn_{1.93}O_{4-\delta}$ samples with different oxygen vacancy δ have been investigated. With the combination of transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and DIFFaX simulation techniques, it is shown that besides the predominant occurrence of cubic spinel $LiMn_2O_4$ (SG: Fd-3m), there exist two other phases: (1) the monoclinic Li_2MnO_3 (SG: C2/m) which exists as nano-scale lamellar variants with 120° rotational twinning stacked randomly along pseudo-three-fold axis $[111]_c//[103]_m$, has been identified using selected-area electron diffraction (SAED) and dark field (DF) imaging (Fig. 1).[2] XRD simulation (Fig. 2) with DIFFaX considering the stacking disordering shows that the characteristic reflections with 2θ between 20° and 35° in the XRD pattern (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.[3] Moreover, the extremely disordered stacking sequence may lead to the selective peak asymmetry (Fig. 2c). (2) Secondary tetragonal phases (SG: $I4_1$/amd) with different lattice parameters, whereas twinning and defects are commonly observed. The existence of both monoclinic and tetragonal phases will have negative effects on the electrochemical performance of the annealed materials (Fig. 3).[4] Our results provide the detailed structural information about the $Li_{1.07}Mn_{1.93}O_{4-\delta}$ samples and advance the understanding of corresponding electrochemical properties of this material as well as other layer structured cathode materials for LIBs.

1. Z. Xu, et al. Power Sources 248, 180 (2014).
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3. H. Zheng, et al. in revision, J. Appl. Cryst. (2014).
4. Z. Xu, et al. J. Power Sources 248, 1201 (2014).

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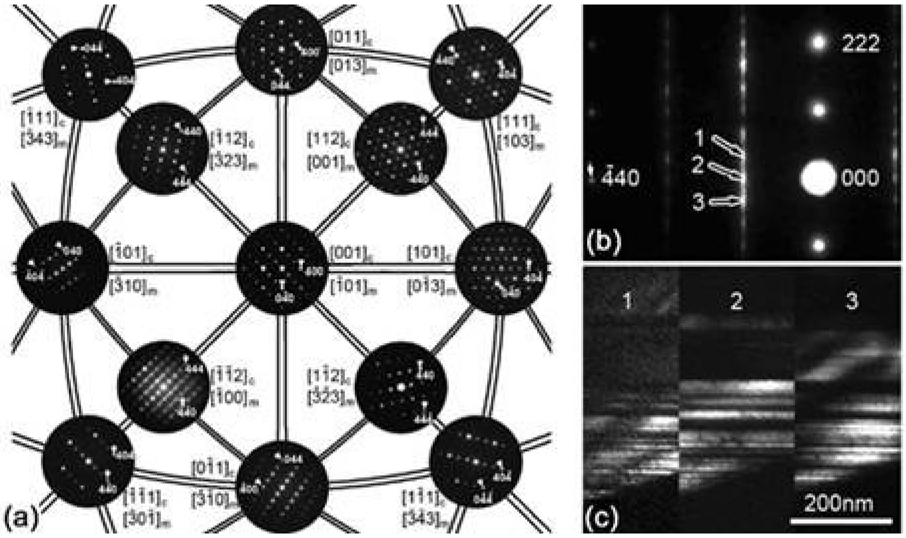

Fig. 1: (a) Experimental SAED patterns of monoclinic Li_2MnO_3, (b) zoomed-in SAED pattern along the $[-1-12]_c$ with pseudo-cubic indexes and (c) the corresponding DF images, which clearly illustrate the presence of three twinning variants.

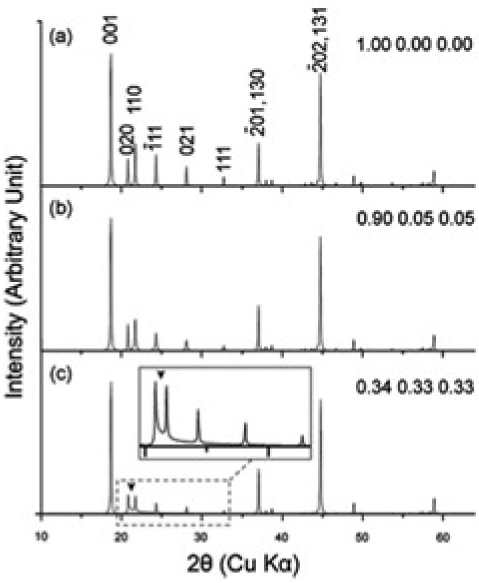

Fig. 2: (a-c) Simulated XRD patterns with the increasing degree of stacking disordering using DIFFaX program.

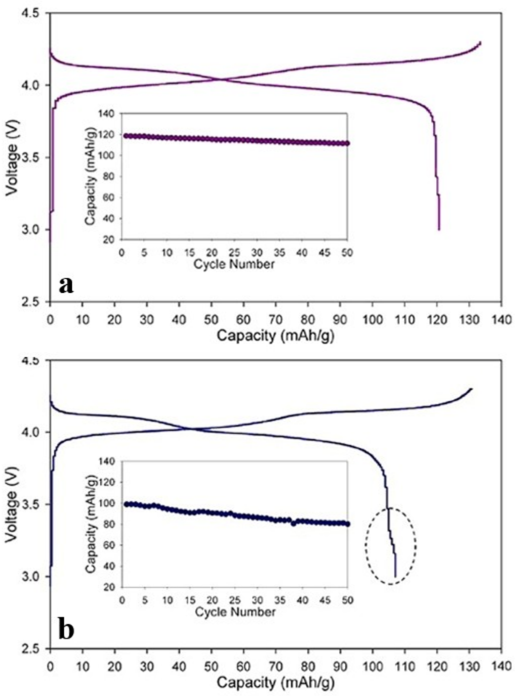

Fig. 3: Charge/discharge voltage profiles for the initial (0.1 C) cycles and cycling performance at 1 C rate of discharge (insets) in $Li_{1.07}Mn_{1.93}O_{4-\delta}$ with δ values of 0 (a) and 0.299 (b) at room temperature.