MS15-P13 Effect of pristine nanostructure on first cycle electrochemical characteristics in Lithium-excess cathode ceramics

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The rechargeable Lithium ion battery is a very important energy storage technology today. Layered transition metal oxides that are mainly based on $LiCoO_2$ or $LiNiO_2$ are currently used as cathode ceramic due to their high operating voltage and high specific capacity of 140-160 mAh/g.In order to obtain even higher energy densities, materials such as the "Li-excess" layered oxides, a composite structure of $Li[Li_{1/3}Mn_{2/3}]O_2$ (LIR) and $LiMO_2$ (M = Ni, Co, Mn) (NCM) are promising candidates, because of their high specific capacity (> 250 mAh/g), higher safety and reduced cost [1-4]. Conventional NCM layered oxides with alternating Li- and TM-layers exhibit R-3m space group symmetry, while the honey comb like ordering of Li and Mn ions within the transition metal (TM) layer of LIR and their characteristic stacking sequences reduce space group symmetry to C2/m. In Li-excess layered materials, NCM and LIR form a nanocomposite embedded in a coherent cubic closed packed oxygen lattice. Concerning application as cathode material, size and distribution of domains with C2/m like cation ordering in the composite structure are of great importance. Cathode materials with a certain ratio of LIR:NCM have been prepared by different synthesis routes as well as two other ratios of composition. The complex nano structures of the pristine material has been extensively characterized by detailed (HR)TEM investigations and a profound evaluation of the synchrotron XRD patterns by conventional Rietveld refinement and by DIFFaX simulations to estimate C2/m domain sizes by modelling the Warren shaped C2/m superstructure reflections. The nanocomposite structure is correlated with first electrochemical cycle characteristics including a complex activation process, initial irreversible capacity loss, anomalous capacity etc.

References:

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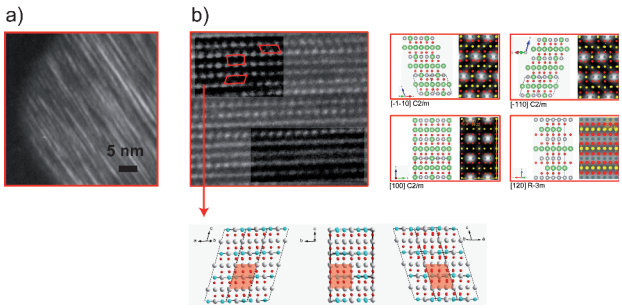

Figure 1. a) TEM dark-field image using C2/m related reflections. The bright regions correspond to C2/m 'domains' in agreement with results from XRD data analysis. b) HRTEM image showing individual 'double TM metal' columns of C2/m 'domains' with high density of different crystallographic orientations.

Keywords: HRTEM, synchrotron XRD, DIFFaX, Lithium Ion Battery, Li-rich layered structures