The design and improvement of the cathode materials for Li-ion batteries requires detailed knowledge on the crystal structure at different charge/discharge states and comprehensive understanding of the processes occurring at the atomic scale level. Cathode materials are the challenging objects for both powder X-ray and neutron diffraction because of small quantity of the material available from the electrochemical cells, large fraction of amorphous component (carbon black and organic binders), small crystallite size due to electrochemical milling and often multiphase nature of the samples. These complications are not the obstacles for electron diffraction tomography, which provides quantitative diffraction data enabling reliable structure solution and refinement from extremely small crystallites, typically smaller than 1 cubic micron. Electron diffraction data can be acquired at very low electron dose, enabling investigation of the materials sensitive to the electron beam irradiation damage, such as polyanion and mixed-anion Li-ion battery cathodes, particularly in their charged state with large excess of energy. Moreover, the requirement of high specific capacity restricts the composition of the cathode materials to relatively "light" elements that naturally diminishes the dynamical effects usually deteriorating electron diffraction data. The capabilities of quantitative electron diffraction in locating Li atoms and refining the occupancy of the Li positions will be demonstrated using the (Li,K)VPO4F [1], Li2FePO4F [2] and LiMn1-xFexPO4 [3] materials. The quality of the structure solution and refinement even in a kinematic approximation is comparable to that of the Rietveld refinement from laboratory powder X-ray diffraction data. Finally, approaches to collecting electron diffraction data in situ in the electrochemical TEM cells will be demonstrated.

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