Novel Complex Stacking of Fully-Ordered Transition Metal Layers in \( \text{Li}_4\text{FeSbO}_6 \) Materials

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Supporting Information

ABSTRACT: As part of a broad project to explore \( \text{Li}_4\text{MM'}\text{O}_6 \) materials (with \( \text{M} \) and \( \text{M}' \) being selected from a wide variety of metals) as positive electrode materials for Li-ion batteries, the structures of \( \text{Li}_4\text{FeSbO}_6 \) materials with both stoichiometric and slightly deficient lithium contents are studied here. For lithium content varying from 3.8 to 4.0, the color changes from yellow to black and extra superstructure peaks are seen in the XRD patterns. These extra peaks appear as satellites around the four superstructure peaks affected by the stacking of the transition metal atoms. Refinements of both XRD and neutron scattering patterns show a nearly perfect ordering of Li, Fe, and Sb in the transition metal layers of all samples, although these refinements must take the stacking faults into account in order to extract information about the structure of the TM layers. The structure of the most lithium rich sample, where the satellite superstructure peaks are seen, was determined with the help of HRTEM, XRD, and neutron scattering. The satellites arise due to a new stacking sequence where not all transition metal layers are identical but instead two slightly different compositions stack in an AABB sequence giving a unit cell that is four times larger than normal for such monoclinic layered materials. The more lithium deficient samples are found to contain metal site vacancies based on elemental analysis and Mössbauer spectroscopy results. The significant changes in physical properties are attributed to the presence of these vacancies. This study illustrates the great importance of carefully determining the final compositions in these materials, as very small differences in compositions may have large impacts on structures and properties.

Received: December 8, 2014
Revised: February 11, 2015
Published: February 12, 2015

DOI: 10.1021/cm504500a
Chem. Mater. 2015, 27, 1699–1708