Experimental report

17/08/2022

Proposal: 5-23-759 **Council:** 10/2020

Title: Li-Fe-M-O (M = Sb, Te) oxides as Li-ion cathode materials

Research area: Chemistry

This proposal is a new proposal

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Samples: Li2FeSbO5
LiFe2SbO6
FeSbO5
Fe3Te2O12
Li3Fe3Te2O12
FeSb2O6

Instrument	Requested days	Allocated days	From	To
D2B	2	2	04/06/2021	06/06/2021

Abstract:

We propose to collect high-resolution neutron powder diffraction data from three novel Fe-based Li-ion cathode materials, Li2FeSbO5, LiFe2SbO6 and Li3Fe3Te2O12, to determine their crystal structures, with a particular emphasis on locating the exact position of the lithium ions (information not available in X-ray diffraction data).
In addition, by reaction with NO2BF4, these samples can be delithiated to form materials of composition LixFeSbO5, LixFe2SbO6 and LixFe3Te2O12, and we propose to also collect NPD data from these materials to better understand the structural consequences of the battery charging process in parallel with electrochemical cycling data.

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Li-Fe-M-O (M = Sb, Te) Oxides as Li-Ion Cathode Materials

1. Background

As part of the UK Faraday Institute FutureCat project we are investigating a range of new lithium-ion battery cathode materials. We are focusing on materials containing earth-abundant elements, with a particular emphasis on iron-based materials. Most of the iron cathode materials, in particular Fe^{3+} materials, that have been investigated to-date suffer from a capacity loss after long term cycling, although a good performance can be achieved for the first cycle. This capacity loss is generally attributed to the easy migration of Fe^{3+} between different coordination sites in cathode materials and the electronic instabilities associated to Fe^{4+}. To get more insight into these issues, we are currently investigating three novel Fe-based oxides, Li_2FeSbO_5, $LiFe_2SbO_6$ and $Li_3Fe_3Te_2O_{12}$, to evaluate and optimize their performance as Li-ion cathodes.

These three oxides crystallize with $LiSbO_3$ related structures, but to clarify the actual cation distribution and ordering NPD data essential. Cyclic voltammetry (CV) measurements indicate that these materials are working in the range between 2 and 3 V which suggests the $Fe^{2+/3+}$ redox couple and further suggests that both Fe^{3+}-containing compositions stated represent the charged state of the cathode. However, we also observe irreversible peaks in CV data at high voltages (while deintercalating Li) for $Li_3Fe3Te_2O_{12}$ which can be attributed to the $Fe^{3+/4+}$ couple, with the irreversibility presumably being due to oxygen loss.

We are able to vary the Li content in these materials by chemical routes, both chemically deintercalating Li and chemically intercalating extra Li into the material. The location of Li by NPD of the 'as made', Li-intercalated and Li-deintercalated materials has helped us to understand the electrochemical processes occurring in the materials, and thus better enable us to optimise both the capacity and cycling stability of these materials.

2. Results

The aim of the proposal 5-23-759 was to get a comprehensive structural analysis of Li_2FeSbO_5, $LiFe_2SbO_6$ and $Li_3Fe_3Te_2O_{12}$ oxides, in particular, to obtain an accurate location and amount of the lithium cations within the channels and to determine cation orderings. The NPD data collected in the framework of the present experiment allowed to fully understand the structure of these three oxides (see Figure 1). Structural variations and Li location were also addressed by NPD experiments from the intercalated $Li_xFe_2SbO_6$ and the deintercalated and intercalated $Li_xFe3Te_2O_{12}$ oxides (see Figure 2).

Results associated with Li_2FeSbO_5 have been published in one paper, Chem. Mater. 2022, 34, 5, 2468-2475 (https://doi.org/10.1021/acs.chemmater.2c00156). The remaining data, corresponding to $LiFe_2SbO_6$ and $Li_3Fe_3Te_2O_{12}$ systems, will be published in other two papers in the coming months.

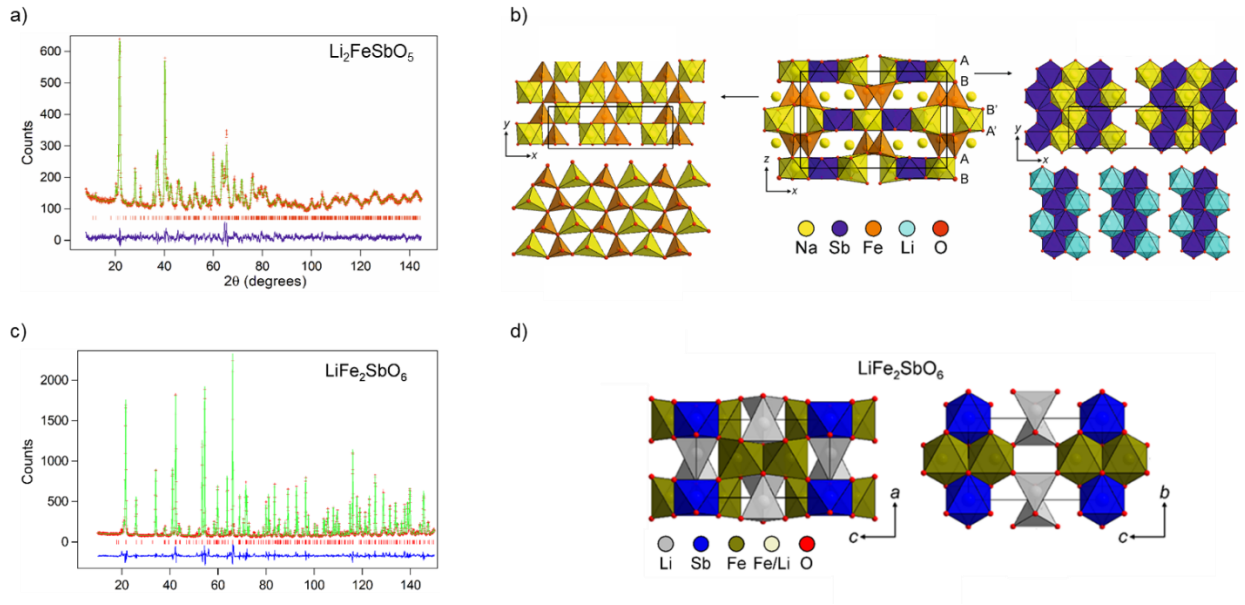

Figure 1. Observed, calculated and difference plots from the structural and magnetic refinement of Li_2FeSbO_5 (a) and $LiFe_2SbO_6$ (c) against NPD data collected at room temperature. Crystal structure of b) Li_2FeSbO_5 and d) $LiFe_2SbO_6$.

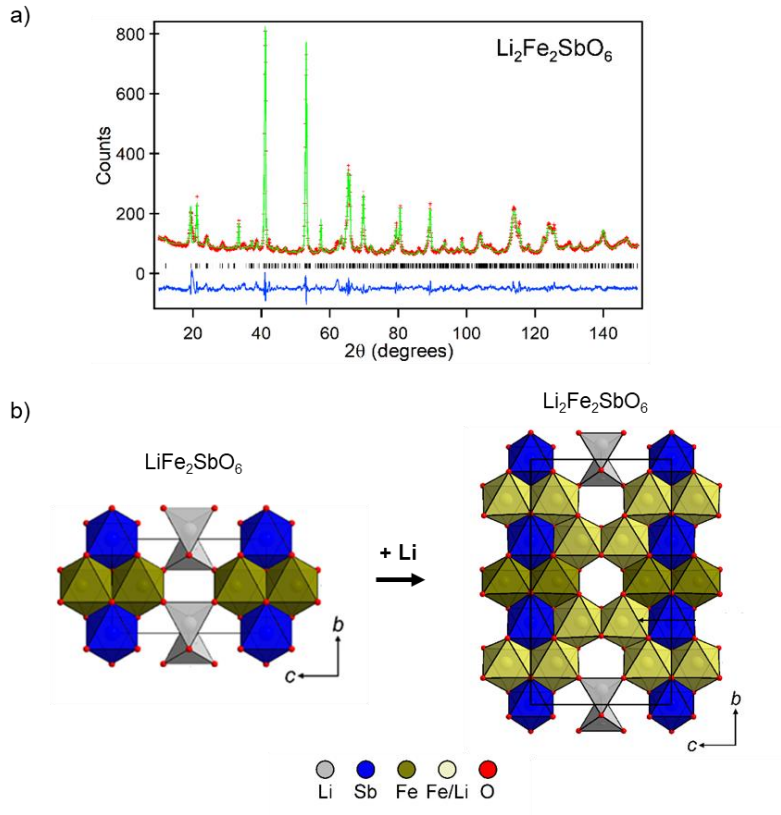

Figure 2. a) Observed, calculated and difference plots from the structural and magnetic refinement of $Li_2Fe_2SbO_6$ against NPD data collected at room temperature. b) Crystal structure modification while Li deintercalation in $Li_xFe_2SbO_6$.