Experimental report

03/04/2024

Proposal:	**5-24-713**	**Council:**	4/2023

Title: More insights into Wadsley-Roth phases FeNb11O29 obtained by ultrafast solid-state micro-wave synthesis as Li-ion batteries anode materials

Research area: Materials

This proposal is a new proposal

Main proposer: **Romain BERTHELOT**

Experimental team: Romain BERTHELOT

Local contacts: Emmanuelle SUARD

Samples: FeNb11O29, 4 samples
LixFeNb11O29, 12 samples

Instrument	Requested days	Allocated days	From	To
D20	4	3	17/11/2023	20/11/2023
D2B	3	3	17/11/2023	20/11/2023

Abstract:

Next generation of electrode materials for batteries will need to exhibit high performance at important current rate. In this context, the Wadsley-Roth family recently attracted the attention, for example composition FeNb11O29 existing in monoclinic and orthorhombic forms, for which a high capacity of 400 mAh/g has been achieved. In the search for faster and cost-effective synthesis protocols, we recently discovered that microwave-assisted heating offers the two polymorphs in few minutes. XPS analysis revealed the presence of additional Nb4+ cations, and consequently the possibility of having oxygen vacancies, which can be directly quantified by ND. Besides, we want to better characterize the materials during electrochemical lithiation. Operando ND can give the exact localization of lithium ions at different states of charge and dynamical information on the diffusion of Li+. Ex situ and operando ND can help to answer some questions: does monoclinic/orthorhombic difference remain upon electrochemical lithiation, is there a preferential Li+ distribution in the intermediate compositions, is there some crystallographic limitation that could explain capacity fading at high current?

Ex situ and *operando* neutron diffraction studies of anode material $FeNb_{11}O_{29}$ for Li-ion battery

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During our D20 beamtime in November 2023, *operando* neutron diffraction (ND) was carried out for monoclinic $FeNb_{11}O_{29}$ inside an electrochemical Swagelok-type cell designed by ILL (Bianchini's cell). A high mass of active material (around 500 mg) was used, which enabled us to obtain strong diffraction peaks with better signal-to-noise ratio in 15 mins, but at a consequence of more potential polarization. Clear shifts of peak position in the contour plot (Figure 1) indicates the evolution of the unit cell, while the emergence of new peaks may suggest a new phase. Generally, the evolution of ND during charge step is not completely reversible due to some side reactions observed in the charge-discharge curve.

ND patterns of eight e*x situ* samples of compositions $Li_xFeNb_{11}O_{29}$ (x = 1; 2; 3; 4; 6; 7; 11; 15), which were obtained by electrochemical lithiation of $FeNb_{11}O_{29}$ inside Swagelok cell, each weighed around 450 mg, were measured at D2B with better signal-to-noise and higher resolution than the patterns obtained by *operando* experiment. Data analysis of this experiment is still ongoing, which promises to give information on the changes in unit cell parameters and lithium position during cycling.

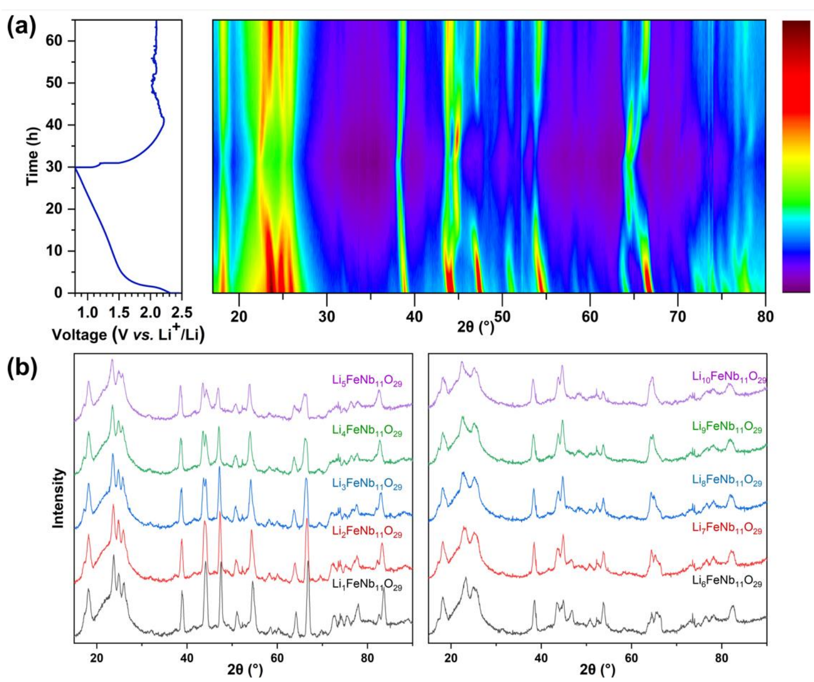

Figure 1. Discharge-charge profile and the 2-dimensional contour plot of *operando* ND experiment for monoclinic $FeNb_{11}O_{29}$ at D20 diffractometer in November 2023 (a), and the evolution of ND patterns of lithiated $Li_xFeNb_{11}O_{29}$ obtained in 30 minutes (b)