Experimental report – Experiment MA-5637

High Entropy Nasicon materials $NaMNb(PO_4)_3$ as anodes for sodium ion batteries: in situ diffraction analysis to track the electrode reaction

Original proposal

The proposal was centered on the acquisition of operando XRD data for selected composition of NASICON compounds $NaMNb(PO_4)_3$ with M = Fe, Al, Mn, V, Ti, W. The original idea of the proposal was to study these materials under working conditions during the charge and discharge of the cell vs Na as this approach allow for the i) identification of the eventual phase(s) evolution, ii) assessment of the Nasicon structural evolution and location of the Na sites upon insertion and deinsertion, iii) characterization of the electrode reactions of the two compounds, showing different electrochemical profiles despite the same crystallographic structure. Globally, it is expected that the experiment can help in gaining insight into the correlation of the structural aspects - functional properties on the present materials and possibly to the identification of guidelines to produce new compositions with improved properties.

Considering both the complexity of the system and the best electrochemical performance, we focus our attention on the $NaFeNb(PO_4)_3$ composition vs Na. The operando diffraction analysis has been performed considering the use of a LeRiche optical cell (Figure 1) in transmission mode equipped with beryllium windows, the main one exploited as current collector. Self-standing electrodes were prepared by grounding NFNP together with Super P conductive carbon in a mortar and mixing the obtained powder with a suspension of PTFE in water (Sigma- Aldrich, 60 wt%) to obtain a homogenous dough. The amount of suspension was calculated in order to achieve a ratio of active material/binder of 8:1. The dough was then calendered several times reducing the thickness up to obtain a flexible film with final thickness of 180 µm and around 12 mg cm2 of active mass loading; the cell has been assemmbled using Na vs counter electrode.

Figure 1 – Optical cell used for the operando XRD experiment (left) and experimental configuration at the beamline (right).

The diffraction and electrochemical measurements have been coupled as following:

- Loop acquisition for XRD data using 0.5 Å wavelength, data acquisition ~15 minutes per scan;
- The active material was reduced/oxidised through constant current cycling (gravimetric current: 15 mA g-1) between 0.75 and 3 V vs metallic sodium.

This enables for a realistic charge/discharge rate of the cell and thus to monitor the electrode reaction under real working conditions and to obtain XRD data in continuum with sufficient S/N for qualitative and quantitative analysis. The overall charge/discharge experiments lasted ~28 h.

The collected data are reported in Figure 2; the cell successfully cycled, and the profiles are characteristic of the material, already tested in traditional coin cells. After the collection of the first sodiation and desodiation cycle, the cell has been cycled offline on a second potentiostat; selected XRD patterns have been collected after 10, 20, and 30 cycles to follow the eventual structural evolution; results are reported in Figure 3.

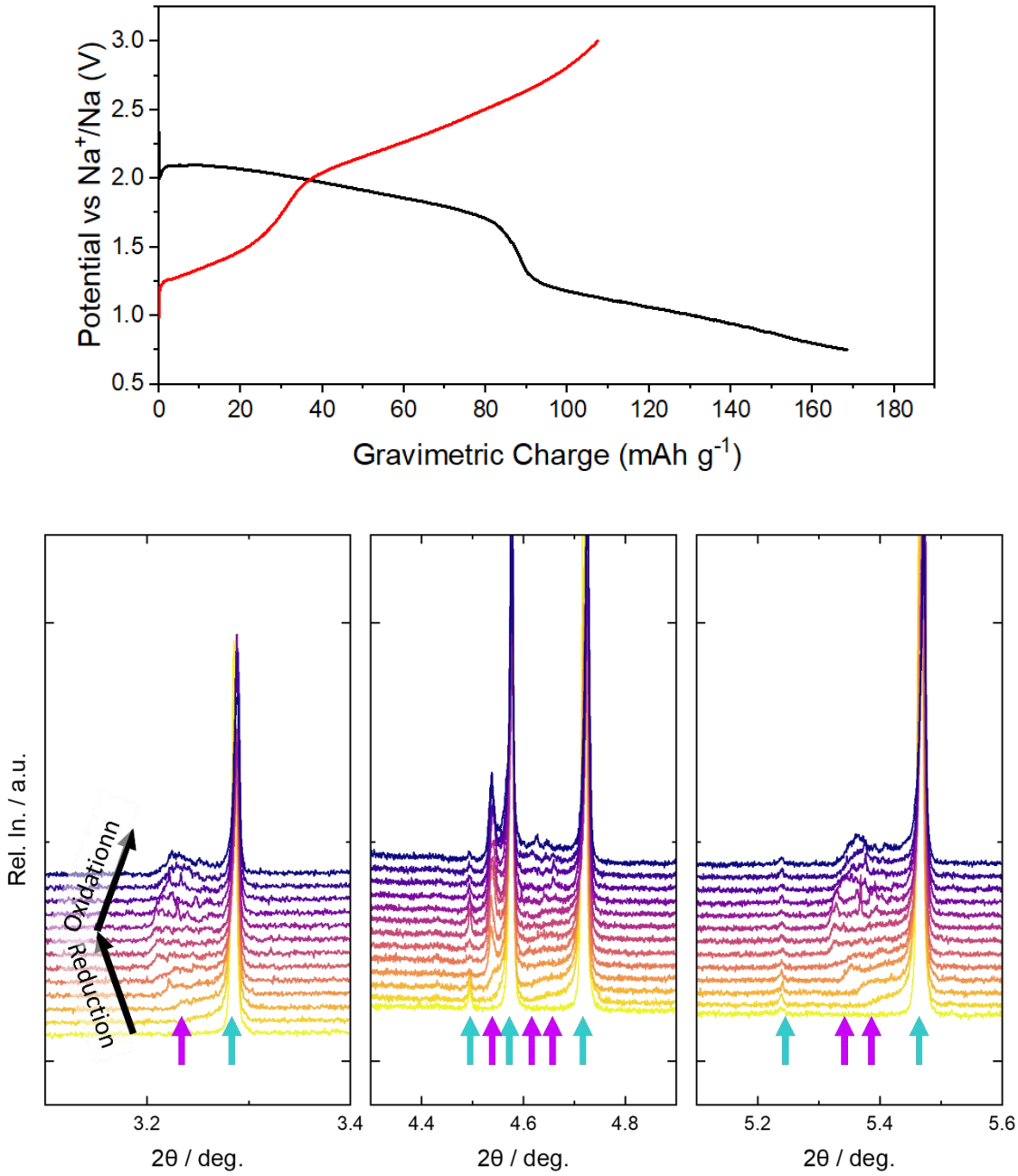

Figure 2 – Charge/discharge profile acquired during the operando XRD analysis (upper panel) Plot of selected XRD patterns (1 over 10, for a total of 118 patterns) during the first reduction/oxidation cycle. The main peaks are associated with the $NaFeNb(PO_4)_3$ structure (azure arrows, ICPDS 98-026-2812); extra peaks appearing upon cycling are indicated by purple arrows (lower panel).

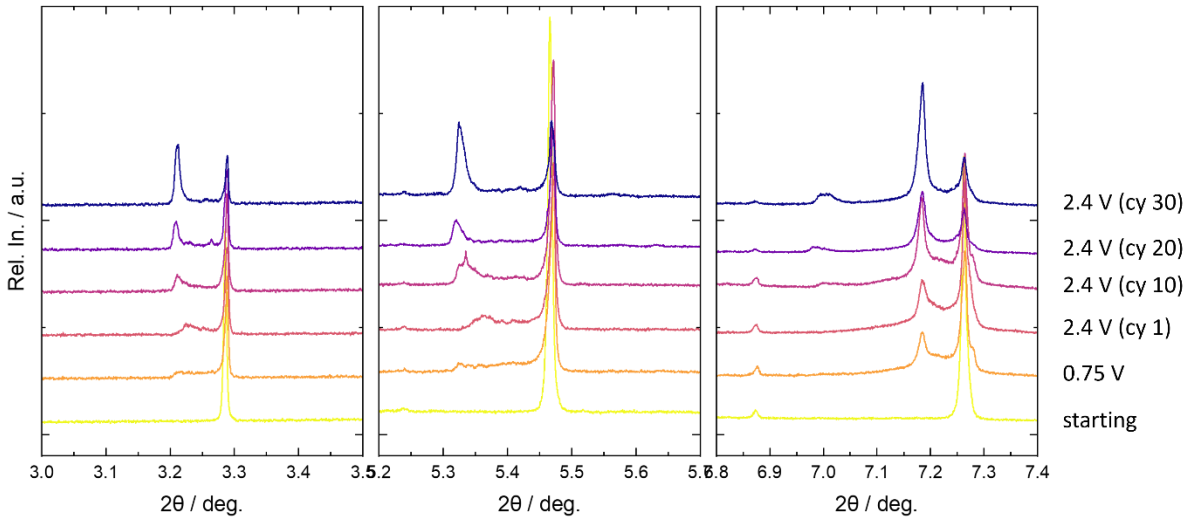

Figure 3 – Plot of selected XRD patterns collected for the cell at the OCV, after the first reduction, first oxidation (1' cycle), 10, 20, and 30 cycles. The incremental formation of new phase(s) is evenident from the change in the relative intensity of the different peaks.

The main results of this experiment are:

- The proposed experimental setup, here tested from our group for the first time, has been successfully exploited. The use of the LeRiche cell in transmission mode allows for acquisition of fast and high S/N XRD data and at the same time provide the same electrochemical profiles as a traditional coin cell. This is considered as a first results as it opens us the way for the design of new experiments and proposals.

- The acquired data reveal the complex electrode mechanism. Indeed, as the materials belong to the class of Nasicon compounds, we expected an intercalation like-behavior. Nevertheless, from the analysis of the operando XRD it is possible to infer a different mechanism, with the formation of new phase(s). We are currently testing two different hypotheses:
  - Phase transition between two Nasicon polymorphs. Indeed the $NaFeNb(PO_4)_3$ structure can be described by the R-3c space group (the most common structure reported for Nasicon material) but several polymorphs have been previously reported with the monoclinic (C2/c space group) as the most diffuse. The transition between the two is often leaded by the Na content within the cell.
  - Phase evolution with Nasicon structure decomposing into two products; $Na_2Nb_2(P_2O_7)_6$ and FeO. The former is electrochemically active while the latter remain unaltered during the cycling of the cell. To test this model, we are currently trying to synthesize the $Na_2Nb_2(P_2O_7)_6$ composition to check its electrochemical activity and behavior.

Overall, the obtained results provide us unique information about the evolution of the material upon sodiation and desociation; we expect to be able to fully analyze the collected data from the qualitative and quantitative point of view and, combining the information from XRD and electrochemical profiles and capacity values, to finally determine the electrode reaction and mechanism.

One scientific publication is expected from this part of the work; the XRD results will be couples with operando XAS analysis and full electrochemical characterization.

Extra measurements

During the beamtime (cell preparation and fast charge/discharge) we had the chance to measure another sample in a second LeRiche cell; the material considered is the oxidized $Ti_3Sn_{07}Al_{03}C_2$ MAX phase composition. The material is a complex nanostructure composite of the original pristine $Ti_3Sn_{07}Al_{03}C_2$ phase that during the oxidation at 700°C in air lead to the formation of surface $(Ti/Sn)O_2$ and Al_2O_3 nanoparticles. The electrochemical behavior and performance of such nanocomposite overcome those of the two materials (the MAX phase and the oxides). The goal of this part of the experiment was to track the electrode reaction and identify the phase evolution during cycling of the cell vs Li. The same LeRich cell and setup exploited for the Nasicon case and presented in Figure 1 have been considered. The results are reported in Figure 4.

We expected the $(Ti/Sn)O_2$ and Al_2O_3 nanoparticles to be electrochemically active and to provide the observed capacity values. The operando experiment was successfully conducted; the results are unexpected. Indeed, no clear evolution of the phases is observed (no peaks shift).

This result are still informative as they suggest that the $(Ti/Sn)O_2$ and Al_2O_3 nanoparticles are maintained during the cycling of the cell. To go further and get insight into the electrode reaction we are currently collecting operando XAS data (at the Sn edge, to track the change in the oxidation state) and XPS analysis on selected cycled electrodes.

We expect one scientific publication from these results, combined with the operando HRTEM analysis performed on the same materials.

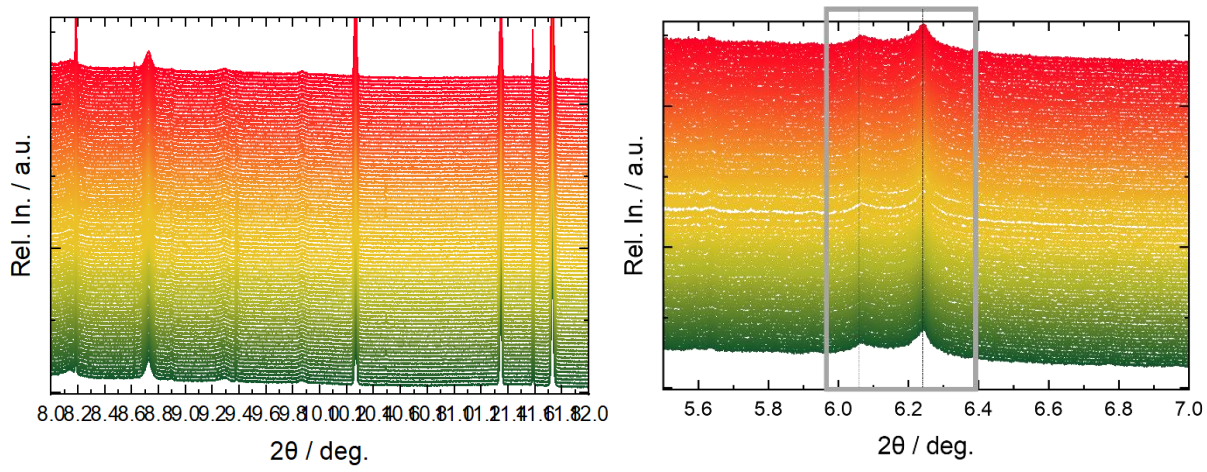

Figure 4 – XRD patterns collected for the oxidazed MAX phase composition during the first cycle (reduction and oxidation) vs Li (left); highlight on the peaks related to the $(Ti/Sn)O_2$ phase the one expected to be the one providing the observed capacity, showing no evident evolution of the peaks.

Comments

We consider the experiment as completely successful as the first test of the LeRiche cell from our group lead to the acquisition of two distinct operando XRD dataset for two materials of interest. We are currently analyzed the data trough phase identification and then we will proceed with Rietveld refinements for quantitative phase analysis.