

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Operando PXD of novel cathode materials for Mg-ion batteries	<b>Experiment number:</b> MA 3213
<b>Beamline:</b> BM01	<b>Date of experiment:</b> from: 16/02/17 to: 21/02/17	<b>Date of report:</b>
<b>Shifts:</b> 15	<b>Local contact(s):</b> Vadim Diadkin	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>Daniel Risskov Sørensen<sup>1*</sup>, Christian Henriksen<sup>1*</sup>, Martin Aaskov Karlsen<sup>1*</sup></b> (1) Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense, Denmark.		

## Report:

### Purpose:

In rechargeable batteries based on intercalation-type cathodes, the atomic structure of the cathode material is one of the governing factors for the battery performance. During insertion and extraction of the active ion, any phase transformation or structural change will largely determine the features observed in the galvanostatic charge/discharge curves. Operando synchrotron powder X-ray diffraction (PXD) is ideal for observing these structural changes while they occur during charging or discharging of the battery.

Rechargeable magnesium-ion batteries is a relatively new type of battery, based on multivalent Mg-ion as the active intercalation ion. The Mg-ion possesses a number of properties which might serve a niche market for batteries: (i) higher volumetric capacity than Li-ion batteries due to Mg being a divalent ion, (ii) non-dendritic Mg-metal anodes, (iii) low cost, as Mg is very abundant in the Earth's crust<sup>1</sup>. Efficient Mg-ion intercalation cathodes are very important for a commercialization of this battery type.

Our objectives in this experiment was to determine the structural changes in selected Mg-intercalation cathodes in-situ to explain the electrochemical features observed in the galvanostatic charge/discharge curves.

### Materials:

The main material selected as a Mg-ion cathode in this experiment consists of vanadium oxide nanotubes (VONT) stabilized by linear amines. The nanotubes consist of sheets of

vanadium oxide curled up into rolls with amines in-between the layers<sup>2</sup>, and by using amines with different chain length the inter layer spacing can be tuned. This is expected to affect the electrochemically induced transformations.

During this beam time, we also found time for a few preliminary measurements on two selected Li-ion cathode materials. These were the vanadium fluorides,  $\text{LiVPO}_4\text{F}$  and  $\text{VO}_2\text{F}$ . Fluoride anion substitution is known to increase the redox potential and the thermal stability of the material.  $\text{LiVPO}_4\text{F}$  has the triclinic Tavorite structure, but transforms to a monoclinic structure,  $\text{VPO}_4\text{F}$ , during lithium extraction. Interestingly, it was found that  $\text{LiVPO}_4\text{F}$  can intercalate an extra Li-ion at low potential to form monoclinic  $\text{Li}_2\text{VPO}_4\text{F}$ <sup>3</sup>.

$\text{VO}_2\text{F}$  is a novel Li-ion battery cathode material with a very high theoretical capacity, 526 mAh/g. This material has been reported to transform from its initial hexagonal structure to a cubic structure upon insertion of lithium<sup>4</sup>. This phase transformation is irreversible when cycling the battery. We hoped to monitor the structural changes in  $\text{LiVPO}_4\text{F}$  and  $\text{VO}_2\text{F}$  in-situ.

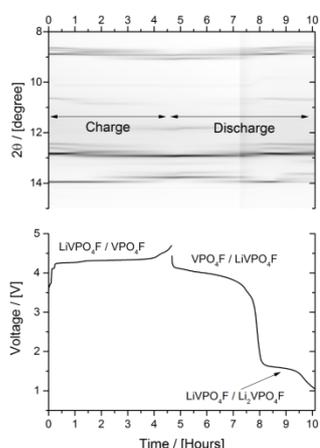


Figure 1: Charge and discharge of a Li-ion battery with a  $\text{LiVPO}_4\text{F}$  cathode. Top: Overview-plot of the in-situ diffractograms as a function of time. Bottom: Potential as a function of time during charge and discharge.

### Methods:

The cathode materials were mixed with conductive carbon and a binder material, and then mounted in special PXD operando cells with the appropriate electrolyte and anode. Six cells were measured in parallel while the batteries were charged/discharged, usually during 20 hours. The 2D-detector at BM01 allowed for a fast X-ray exposure time of 30 seconds, and a measurement cycle on all six cells took around six minutes.

### Results:

The diffractograms of the VONT reveals an expansion of the interlayer distance upon discharge and subsequent contraction upon charging, while the underlying  $\text{VO}_x$ -frameworks of the walls are affected only to a minor degree by the intercalation. More structural detail and trends regarding inter layer spacing and electrochemical properties will be extracted as we progress with data analysis (Beamtime ended just one week ago). These results clearly demonstrate Mg-intercalation and extraction, and we hope to publish soon.

Figure 1 shows an overview PXD plot of the charging and discharging of  $\text{LiVPO}_4\text{F}$ . The voltage vs. time plot clearly shows three plateaus, indicative of three two-phase systems. From the diffractograms it will be possible to estimate the percentage of each phase present, and correlate it with the charge/discharge curves. This result, as well as the result obtained for  $\text{VO}_2\text{F}$ , is very interesting, and will be the basis for another beamtime application in the near future.

### References:

1. Rana Mohtadi and Fuminori Mizuno, *Beilstein J. Nanotechnol.*, **2014**, 5, 1291-1311.
2. Reinoso, J. M. et al., *Helvetica Chimica Acta*, 2000, 83, 1724-1733.
3. Peng Li et al., *Ceramics International* 41, **2015**, 10766-10774.
4. Ruiyong Chen et al., *RSC Adv.*, **2016**, 6, 65112-65118.