ESRF	**Experiment title:** **Operando Characterization of Lithium Metal Polymer Battery by Wide Angle X-ray Scattering.**	**Experiment number**: MA-3966
Beamline: ID31	**Date of experiment**: from: June 13, 2018 to: June 19, 2018	**Date of report**: October 2, 2018 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Maria Blanco	

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Report:

Objective & expected results

We have developed a single-ion conductor solid polymer electrolyte (SPE), in contrast to conventional binary conductor SPE, stable up to 5 V that showed excellent performances between 60 and 80 °C when used as separator and positive electrode binder in lithium (Li) metal batteries comprising $LiFePO_4$ (LFP) as active material. LFP, a reference material, operates at about 3.4 V for a specific capacity of 170 mAh.g^{-1}. Replacing LFP by a higher voltage material such as $LiMn_{0.6}Fe_{0.4}PO_4$ (LMFP) in which Li^+ is inserted/de-inserted at 3.4 V (Fe^{2+}/Fe^{3+}) and at 4.1 V (Mn^{2+}/Mn^{3+}) is a way to increase the energy density.

The main goal of the MA-3966 proposal is to finely study the behavior of the LMFP material in an all-solid-state Li/LMFP battery comprising a single-ion or binary conductor SPE at a temperature of 80 °C. To follow LMFP structural changes (electrochemical process, reversibility) wide-angle X-ray scattering (WAXS) is performed during battery cycling (*operando* characterization). This technique permits to observe and quantify the evolution of the material structure during each charge/discharge cycle. In addition, the kinetic of the electrochemical reactions will be followed along the positive electrode thickness (from its current collector to the SPE layer) by WAXS analysis. The secondary goal of the proposal is to design new small-size electrochemical cells specifically adapted to the ID31 beamline with cycling signature similar to regular lab-scale cells (coin and pouch cells). This versatile cell should ultimately allow to perform both X-ray diffraction (SAXS, WAXS...) and tomography (absorption, diffraction...) experiments.

Experimental work

Prior beamtime two types of electrochemical cells were designed, assembled in argon filled glove box, tested, and optimized through a collaboration between LEPMI, ID31, and Sample Environment Support Laboratory (SESL, Yves Watier). These air-tight cells have a casing made of plastic (polytetrafluoroethylene, PTFE) or glass with stainless steel pistons for electrical contact. Both are able to cycle small-size battery (3 mm active diameter) up to 80 °C with electrochemical signature similar to that of coin or pouch cells.

During beamtime, the experiments were carried out at ID31 in its WAXS configuration using a Pilatus 2M CdTe detector coupled to an incident X-ray beam of 70 keV in transmission mode. The PTFE and glass cells were held at 80°C using gas blowers and a specifically home-made heating element by SESL, respectively. **Figure 1** are pictures of the cells when connected to a potentiostat and ready to be cycled while being X-ray illuminated. For each battery, the experimental setup consists in cycling at a low regime (~ 10 h per charge or discharge) while collecting WAXS patterns of the entire cell by a z-scan from one electrode to the other in 5 μm slice step.

Results and the conclusions of the study

1. Comparison of PTFE and glass cell

The two electrochemical cells made of PTFE and glass were cycled at 80°C while analyzed by WAXS. **Figure 2** represents the potential as a function of the capacity of batteries comprising a Li negative electrode, a binary conductor SPE and a $LiFePO_4$ based positive electrodes during a charge step. The cycling profiles are similar with a plateau at about 3.55 V corresponding to the oxidation of $LiFePO_4$ in $FePO_4$. The inset of **Figure 2** shows the WAXS profile, relative intensity versus the Bragg 2θ angle, of both cells at a capacity of 0.6 $mAh.cm^{-2,}$ (about at the half of the LFP plateau). The peak positions are similar for both cells whereas peaks are much better defined (intensity relative to the background, full width at half maximum) for the glass rather than the PTFE cell. In addition, initial analysis of the electrochemical process is consistent with literature data in which the transition of $LiFePO_4$ into $FePO_4$ is driven by a non-ideal biphasic mechanism. Furthermore, we are still processing the data to follow the reaction kinetic through the positive electrode thickness. Preliminary results show that LFP is reacting from the SPE side to the positive electrode current collector.

2. LMFP battery comprising a single-ion conductor polymer electrolyte

Figure 3 shows a representative cycling profile of a battery in a PTFE cell comprising a single-ion conductor SPE in between a Li metal and a LMFP based positive electrode. We successfully cycled three times this battery at the beamline. Two plateaus per charge or discharge steps are distinguishable with a battery performance similar to that obtained at the LEPMI laboratory. **Figure 4** shows the WAXS profile recorded at one of the potential vs. time data point in **Figure 3,** in which all the battery layers are clearly resolved from the Li part to the positive current collector. Analyses are under ways to track the LMFP phase transition all along the electrode thickness and along the different cycling steps. Data has also been recorded on battery replicates as well as for Li/LMFP battery comprising a binary conductor SPE for comparison.

Publications are in preparation

Figures

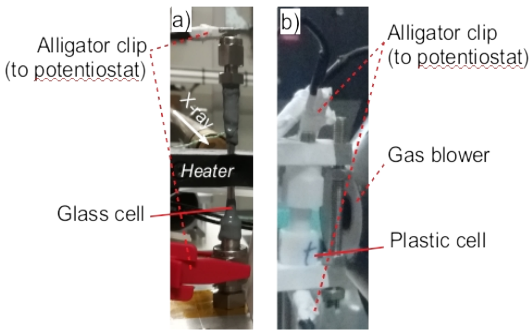

Figure 1. Pictures of the electrochemical cells connected to a potentiostat at the beamline with casing made of a) glass and b) PTFE.

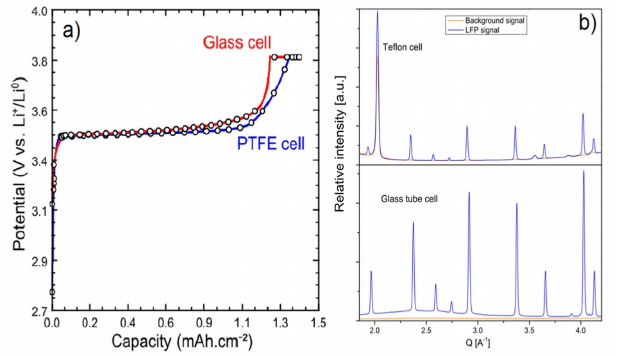

Figure 2. a) Potential vs. capacity of Li/LFP batteries, the open symbols are the X-ray illumination. b) WAXS profiles of the LFP in the middle of the electrodes.

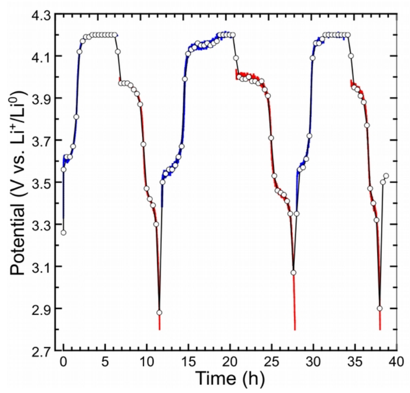

Figure 3. Potential vs. capacity of a Li/LMFP battery with a single-ion conductor SPE. (blue) charge step, (red) discharge step, and the open symbols are the X-ray illumination.

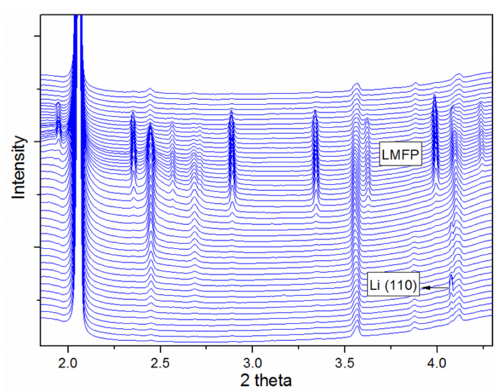

Figure 4. WAXS profile at a cycling data point of the Li/LMFP battery (see Fig. 3) all along the different battery layers