EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

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://wwws.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.

ESRF	**Experiment title:** Electrospun hybrid electrolytic membranes for energy devices	**Experiment number**: 02-01-860
Beamline:	**Date of experiment**: from: 11/06/2015 to: 14/06/2015	**Date of report**: 14/02/2017
Shifts:	**Local contact(s)**: Cyrille Rochas	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
*__Manuel Maréchal (SyMMES)__
*Natacha Krins (LCMCP)
*Christel Laberty-Robert (LCMCP)

Report:

Paper submitted to Langmuir:

Hybrid Li-ion Conducting Membrane as Protection of Li-anode in aqueous Li-air Battery: Coupling Sol-gel Chemistry and Electrospinning

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KEYWORDS. Aqueous Li-air battery, Hybrid membrane, LATP, electrospinning, sol-gel

ABSTRACT
Aqueous lithium–air batteries have theoretical energy densities which potentially makes this technology very interesting for energy storage in electric mobility application. However, performance still needs to be improved by diminishing the ohmic resistance due to thick NaSiCON–like electrolyte. This paper deals with the replacement of this ceramic electrolyte by a hybrid organic–inorganic membrane. This new membrane combines a $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) inorganic phase for Li-ion transport and poly(vinylidene fluoride–co–hexafluoropropylene (PVDF–HFP) polymer for water-tightness. The Li–ion transport through the membrane is ensured by an interconnected 3D network of crystalline LATP fibers obtained by combining an electrospinning process coupled with the sol-gel synthesis. After an impregnation step with PVDF–HFP, hybrid membranes with different volume fractions of PVDF–HFP have been synthesized. These membranes are water tightness and have Li–ion conductivities ranging from 10^{-5} to 10^{-3} mS/cm. The conductivity depends on the alignment of the fibers in the membrane thickness, the relative humidity in the electrospinning chamber and the PVDF–HFP volume fraction. Taking into account the porosity of the LATP fiber mat, a conductivity value of 10^{-1} mS/cm is calculated, comparable to dense LATP fibers, confirming the excellent nature of the 3D LATP network.

Experimental

The incident photon energy was tuned to 11 keV which corresponds to a wavelength of λ= 1.12 Å. A two-dimensional detector, a CDD camera developed by Princeton, presently Ropper Scientific, was used. The

magnitude of the scattering vector is defined as $q=(4\pi/\lambda)\sin\theta$, where θ is half of the scattering angle and λ is the wave length. The distance from the sample to the detector was 164cm, which covers the q range from 0.06 to 1.56 nm^{-1}. The corrections of primary data were carried out using the software Bm2Img available on the beamline: (i) the dark current (i.e. non-illuminated camera), (ii) the flat field response (i.e. homogeneously illuminated camera), and (iii) the tapper distortion. The standard silver behenate was used for the q-range calibration. 2D images were converted into radial averages over the image center to yield the scattered intensity I vs. the scattering vector q.

Results

A SAXS analysis, showing the homogeneity of the fiber mat before and after impregnation is presented in Figure 1. The fiber mats (b, c) before impregnation give a featureless SAXS intensity, regardless of the humidity used during the electrospinning process. After impregnation (d), the spectrum exhibits, at high q, a broad correlation peak (around q = 0.85 nm^{-1}) related to the organization of the PVDF-HFP crystalline domains. This correlation length is attributed to the distance between the crystallites of the semi-crystalline polymer phase considering a sufficient electronic contrast between the amorphous and the crystalline phases.[28] The semi-crystalline polymer phase can be treated as lamellar systems. The lamellar period is the sum of the average widths of the lamellae and amorphous layers. In the present case this value is 7.4 nm. The spectrum of pure PVDF-HFD fibers without LATP (a) is also represented as a reference. In the unsintered fiber mat (d), the peak is broader than the pure PVDF-HFP fibers (a), which would suggest a higher dispersion of the characteristic correlation lengths of PVDF-HFP crystallite domains. In all cases, at low q, the graphs (log(abs. int.) vs. log(q)) show a straight line, which corresponds to a q^{-x} evolution (where x is about 4). This behavior tends to highlight, according to Porod's law, the existence of a sharp and smooth interface between air and the material at a nanoscale. Please note that the evolution is not modified after impregnation of the membrane, which suggests that the nanostructure is intact after calcination and impregnation.

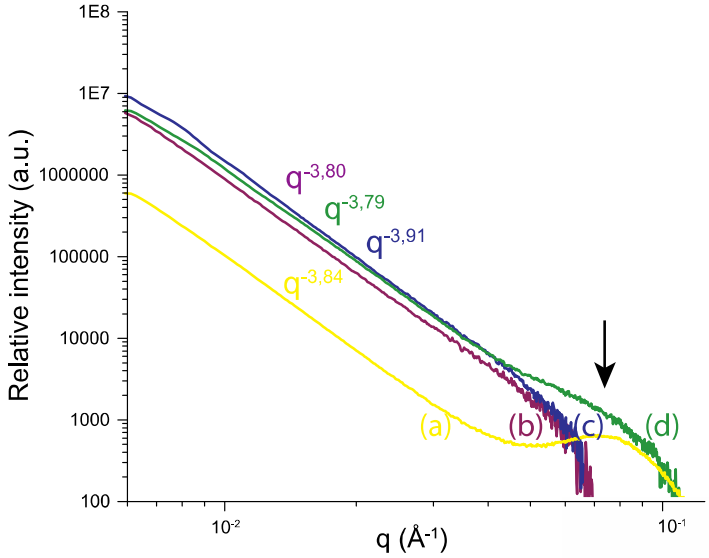

Figure 1. SAXS absolute intensity as a function of the scattering-vector modulus on fiber mats of (a) pure PVDF-HFP; (b, c) LATP (before calcination) obtained at high RH (b) at low RH (c); (d) LATP-PVDF-HFP from low RH conditions after impregnation.