



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.



	Experiment title: Polymer-sulphur composites as cathodes in Li-S batteries	Experiment number: 28-01 1122
Beamline: BM28	Date of experiment: from: 29/1/2016 to: 2/2/2016	Date of report:
Shifts: 9	Local contact(s): Paul Thompson (email: pthomps@esrf.fr)	<i>Received at ESRF:</i>

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Report:

Conventional lithium-sulphur batteries consist of a lithium metal anode, a sulphur cathode, and an organic liquid electrolyte. As the battery is discharged the lithium metal is oxidized, generating electrons and lithium ions. Instead sulphur is reduced by accepting the lithium ions and electrons (see **Figure 1**). In the initial reduction step S_8 rings are opened, yielding high-order lithium polysulfides Li_2S_x ($6 < x \leq 8$). However, as the discharge progress, low-order lithium polysulfides, Li_2S_x ($2 < x \leq 6$), are formed, where Li_2S is the final product.

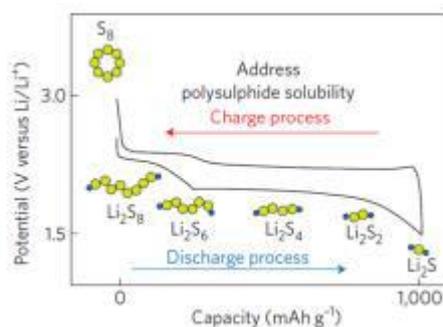


Figure 1 Ideal cycling performance of Li-S battery showing lithium sulphide products formed during discharge.¹

Despite much research Li-S batteries still suffer from poor life time and charge efficiency. One explanation to these shortcomings are the solubility of the high-order lithium polysulphides, Li_2S_x ($6 < x \leq 8$), in the liquid electrolytes used in the batteries. Dissolved in the electrolyte they can travel between the cathode and anode. As Li_2S_x ($6 < x \leq 8$) species are formed, they migrate to the anode, where they are reduced to Li_2S_x ($2 < x \leq 6$). In a similar fashion the low-order polysulphides instead travel back to the cathode, where they again form high-order polysulphides, as so on. This phenomenon is referred to as the “shuttle mechanism”.

One method attempting to control the shuttle mechanism is by using carbon-sulphur composite cathode materials.¹ Work at the University of Kent instead explores the route to use polymer-sulphur composite materials, where the polymer is a mixed electronic and ionic conducting material with the aim to reduce the dissolution mechanism and shuttle mechanism of the polysulphides. Our work includes coating sulphur

nanomaterials with sulphur-based conducting polymers, including PEDOT and poly-thiophene (PTh). For comparison we also studied a nitrogen-base polymer, poly-aniline (PANI). We have found that the capacity of the batteries are decreasing in the order of PEDOT > PTh > PANI. In agreement with a similar study on long-term stability and capacity on polymer-sulphur composites.²

Method

Measurements were obtained by collecting XAFS spectrum from '2025' coin cells with 2mm hole. This hole was covered with 3.4 μ m mylar film and the cathode material was detected directly through this window. A 2mm hole was also drilled through aluminium current collector and faced to the top cap of the coin cell. The active cathode materials were spin-coated, covering the hole, on the aluminium current collector (see **Figure 2**). The coin cell holders was glued onto the sample holder used in the XAFS chamber and connected to a Maccor battery cyler. During the measurement the XAFS chamber was filled with helium air. The VORTEX detector was assembled and focused to the cathode through mylar window. A nickel grid was used for normalisation of collected data. Instead the KEYTEK detector was used for the standards and $\text{Li}_x\text{FeSO}_4\text{F}$ compounds. All measurement was conducted in fluorescence mode.

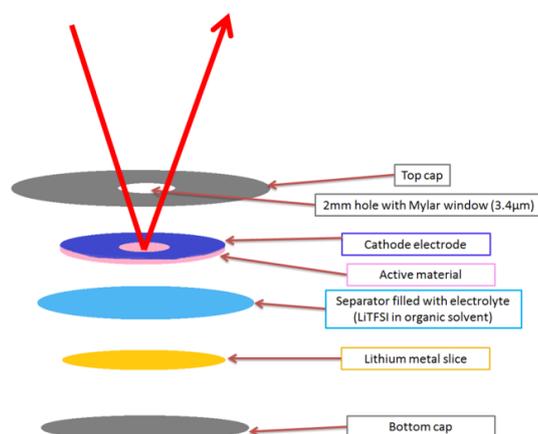


Figure 2
Schematic of '2025' coin cell construction.

Results

During this experiment, three different types of cathode were analysed during battery cycling. One cathode was composed of pure sulphur and carbon and assembled into a coin cell. This battery was used as a reference cell to confirm the set up of the in-situ XAFS measurement during battery cycling. In the other two batteries, PANI and PEDOT:PSS binders were added to the sulphur-carbon composition cathode. Spectra were obtained directly from the cathode material. Two different types of sulphur were observed in all of the pristine samples at 2473 eV and 2480 eV which contribute to sulphur from cathode composite and sulphate from the electrolyte. Sulphate in electrolyte was expected because LiTFSI salt was employed in electrolyte. In all of three batteries, formation of polysulphide was confirmed by growth of a third peak at 2471 eV during the discharge of the batteries. First discharge profile and XAFS of Li-S batteries with PANI and PEDOT:PSS binders are shown in **Figure 3**. Intensity of polysulphide peak was the highest at the end of the lower voltage plateau in both reference and PEDOT:PSS binder batteries (**Figure 3a**) whereas the most intense peak was at the start of the lower voltage plateau in the PANI-binded battery (**Figure 3b**). Polysulphide peaks were then decreased after experiencing the highest intensity in all of the cells. In the reference and PANI-binded cell, polysulphide peaks were no longer detected at the end of discharge. This suggests either all of the polysulphide was reacted and reduced back to lithium sulphide or that the polysulphide formed at the cathode travelled to the Li anode side where it got trapped. However, in PEDOT:PSS-binder cell the polysulphide peak was still detected at the end of discharge. This suggests that polysulphide was dissolved in the electrolyte and became unreactive, which disabled the reduction of soluble polysulphide to insoluble lithium sulphide.

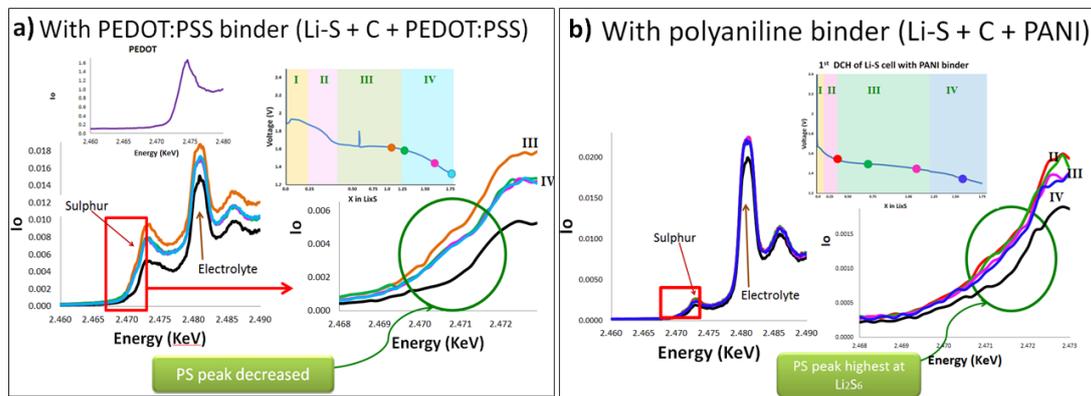


Figure 3 1st discharge profile and XAFS spectrum of Li-S battery with (a) PEDOT:PSS binder and (b) PANI binder.

Also $\text{Li}_x\text{FeSO}_4\text{F}$ battery samples were analysed using the KEYTEK detector, allowing us to study both the Fe K-edge as well as the S K-edge. These measurements showed that the Fe valence state is oxidised from Fe^{2+} , in the $\text{Li}_x\text{FeSO}_4\text{F}$, compound, to Fe^{3+} , in $\text{Fe}_x\text{SO}_4\text{F}$, as Li-ions are extracted from the structure during battery charging (**Figure 4a**). The novelty of this experiment was the observation of additional activity of the S K-edge (**Figure 4b**), implying that the ‘extra’ capacity of this cathode material is associated with the sulphate group in the structure.

$\text{Li}_x\text{FeSO}_4\text{F}$ as cathode in Li-ion battery

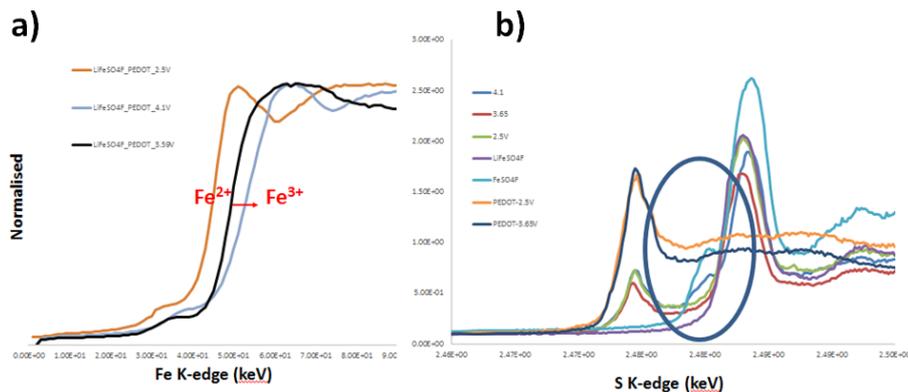
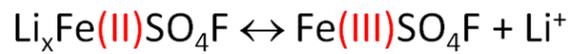


Figure 4 XAFS spectrum of $\text{Fe}_x\text{SO}_4\text{F}$ shows (a) Fe valence state oxidised from Fe^{2+} to Fe^{3+} (b) S K-edge showing extra capacity of cathode material associating to sulphate group in $\text{Li}_x\text{FeSO}_4\text{F}$ structure.