

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>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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: Elucidating the Structure of Lithium Polysulfides by Total Scattering	Experiment number: P84608
Beamline: ID15A	Date of experiment: from: 11 th October 2020 to: 12 th October 2020	Date of report: 20 th January 2019
Shifts: 3	Local contact(s): Gavin Vaughan (vaughan@esrf.fr)	<i>Received at ESRF:</i> 15 th October 2022
Names and affiliations of applicants (* indicates experimentalists): Dr. Alex Rettie (University College London) – a.rettie@ucl.ac.uk *Michael Johnson (University College London) – michael.johnson.19@ucl.ac.uk		

Report:

Abstract:

Lithium-sulfur (Li-S) batteries are an emerging class of rechargeable electrochemical cells with applications in specialty electric vehicles, including aviation, and grid-scale energy storage. In-situ X-ray computed tomography and diffraction have provided a wealth of information on crystalline transformations during cell cycling, but are unable to probe the solution-based processes thought to be responsible for capacity fade. These conversions between lithium polysulfide intermediates (Li_2S_n , where $n = 2-8$) underpin Li-S battery operation but are poorly understood. To date, these species have not been unambiguously observed by X-ray scattering techniques, obscuring their local structure and behaviour *in situ*. Progress has been inhibited by the lack of “standard” solutions and the typically low concentrations of these species present in in-situ cells. Recent work has established methods to produce concentrated solutions (>1 M) with quantified compositions and phase diagrams in commercially-relevant electrolyte systems. We will build on these results to report the first X-ray pair-distribution-function (PDF) analysis of these species, shedding light on their structure, interactions with different electrolyte systems and paving the way to track these species *in situ*, enabling long-life Li-S batteries.

Experimental Details:

All sample preparation were prepared at University College London (UCL). The desired stoichiometric amounts of dry S_8 and Li_2S powders were dissolved in various solvent systems (tetrahydrofuran (THF) and dioxolane (DOL):dimethoxyethane (DME), at 80 °C in sealed vials for 72 hours with constant stirring, to yield standard solutions of varying concentrations (10 M in terms of sulfur) of the desired Li_2S_n (Figure 1). All handling took place under inert atmosphere in an Ar-filled glovebox, and glass capillaries were flame-sealed under Ar (Figure 1). Four additional capillaries will contain only solvent mixtures, which were used for subtraction of the electrolyte and container contributions in differential PDF analysis. These samples were critical as the solvent and container comprise a large proportion of material in the X-ray beam and thus were significant in the raw scattering data collected. All scattering data was taken at room temperature.

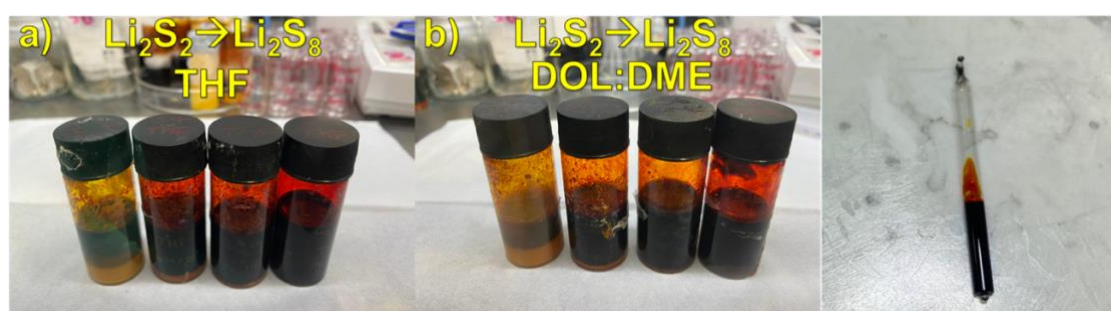


Figure 1. Saturated solutions of lithium polysulfides (Li_2S_n , $n = 2,4,6,8$) in THF and DOL:DME. Borosilicate capillary filled with lithium polysulfide solution and flame-sealed under an Ar atmosphere.

Results:

Figure 2 shows the $G(r)$ functions for the THF and DOL:DME solutions. As can be seen from Figure 2a, at least two distinct peaks can be identified from the scattering data of the Li_2S_n solutions that are distinct from the neat solvent. The first of which, at ~ 2.1 Å, corresponds to the nearest neighbour (NN) S-S correlation from the dissolved Li_2S_n species. This is followed by the next (NNN) S-S correlation at ~ 3.3 Å. The other two distinct peaks at ~ 1.7 and ~ 2.3 Å, present in both the solvent sample and Li_2S_n solutions, are consistent with contributions from the C-C and C-O bond lengths of the solvent. In Figure 2b we can see each of the functions overlaid and here it is observed that the solvent signatures (C-C and C-O) have a shift to smaller bond lengths in the Li_2S_n solutions. This made the background subtraction of the solvent non-trivial as the shift in bond length suggests that the solvent molecules strongly interact with the Li_2S_n species.

In terms of differentiating each chain length Li_2S_n it is difficult to judge from these results whether X-ray scattering can reliably distinguish between the species. It is possible that the magnitude of the NN S-S correlation could be used as an indication of sulfur content. In Figure 2b we can see that the longest chain length Li_2S_n (Li_2S_8) has the highest intensity for this peak. This is understandable as this species has the highest sulfur loading. This trend continues in the other samples as the intensity of this peak decreases with decreasing chain length, until it disappears in the solvent sample. This correlation can also be observed in the NNN S-S peak, which shows a decrease in intensity for Li_2S_2 in comparison to Li_2S_4 and Li_2S_8 . However, Li_2S_4 shows little difference in intensity for this peak compared to Li_2S_8 , which is likely due to the disproportionation reactions that can occur in these solutions.

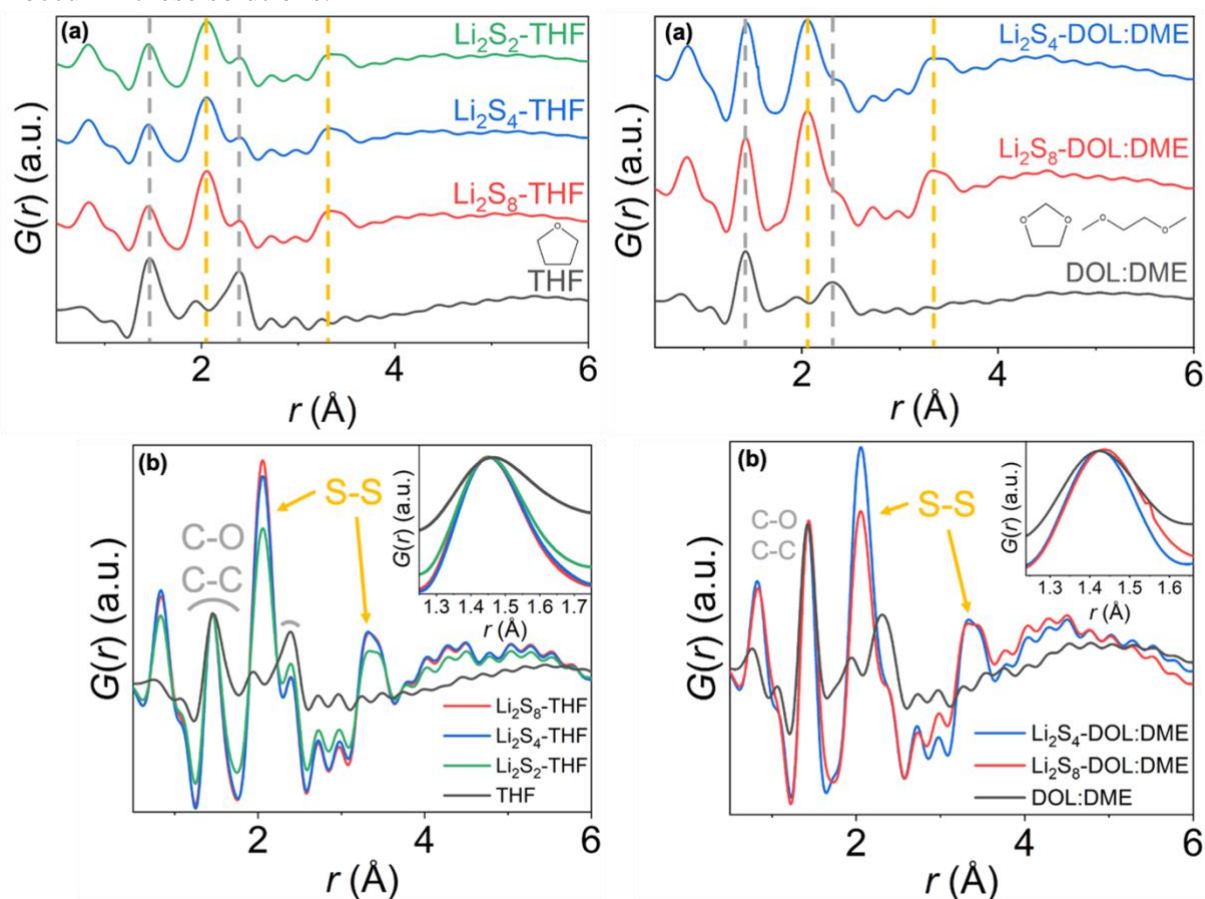


Figure 2. Stacked $G(r)$ plots for solutions of lithium polysulfides (Li_2S_n , $n = 2, 4, 8$) in THF compared to neat THF. Stacked and overlapped $G(r)$ plots for solutions of lithium polysulfides (Li_2S_n , $n = 4, 8$) in a mixture of DOL and DME compared to neat DOL:DME.

Conclusions:

This work investigated the structures of the species by total X-ray scattering with PDF analysis, which revealed signatures of the dissolved species. Furthermore, the data highlighted the importance of the solvent interactions to understanding the structures of the Li_2S_n species, which has inspired further neutron studies of the solvent systems.