

	<b>Experiment title: Study of Li-S batteries by RIXS spectroscopy at the S K edge</b>	<b>Experiment number:</b> CH-4422
<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 1. 7. 2015 to: 7. 7. 2015	<b>Date of report:</b> 10. 9. 2015
<b>Shifts: 18</b>	<b>Local contact(s):</b> P. Glatzel	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants (* indicates experimentalists):</b> *M. Kavčič, *M. Žitnik, *K. Bučar, *M. Petric, *I. Arčon <i>J. Stefan Institute, Ljubljana, Slovenia</i> *R. Dominko, *A. Vižintin <i>National Institute of Chemistry, Ljubljana Slovenia</i>		

### Report:

We have successfully performed sulfur K-edge resonant X-ray emission measurements on the lithium sulfur (Li-S) battery in operando mode using the high resolution Johansson type x-ray emission spectrometer of J. Stefan Institute, Ljubljana. The main motivation was to characterize sulfur and study the mechanism of polysulfide (PS) formation and the interaction of sulfur and polysulfides with the host matrix and electrolyte in the lithium sulfur (Li-S) battery. First we have recorded a full K-L RIXS maps on a set of chemically prepared  $\text{Li}_2\text{S}_x$  sample standards characterized by different Li:S stoichiometric ratios ( $0 < x < 2$ ). A significant improvement in resolution was achieved using RIXS spectroscopy compared to standard S K-edge XAS spectra.

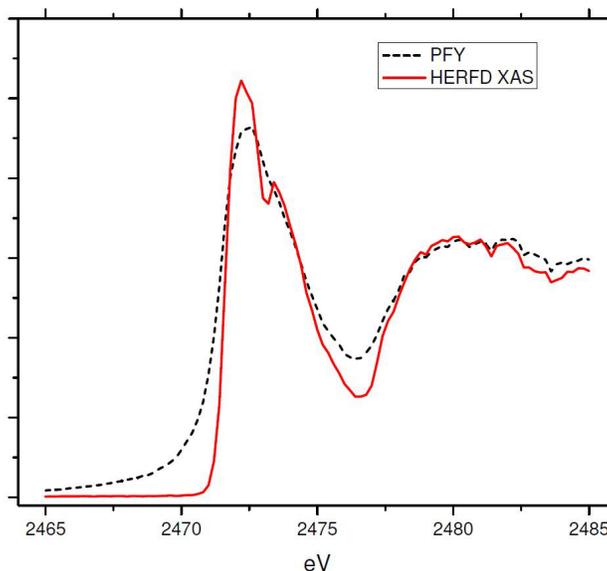


Figure 1: The S K-edge partial fluorescence yield (PFY) spectrum and high energy resolution fluorescence detected (HERFD-XAS) recorded on the  $\text{S}_8$  standard sample using the emission spectrometer.

After measuring the standard samples we have successfully performed also in operando measurements of the (Li-S) battery during one full discharge cycle (C20). Based on the HERFD spectra recorded on  $\text{Li}_2\text{S}_x$  standards two excitation energies were chosen and RXES spectra were acquired during the discharge process. Within this process the reduction of S to  $\text{Li}_2\text{S}$  proceeds through a complicated equilibrium mixture of compounds that are typically dissolved in the electrolyte in the form of long and short chain polysulfides (PS). As seen from Figure 2, the sensitivity for the detection of polysulfides was drastically enhanced in our experiment due to resonant emission spectroscopy and this enabled us to follow precisely the formation of PS through the process. Since we have used a fixed excitation energy only one minute was needed to record a single spectrum which was important to avoid the radiation damage of the battery.

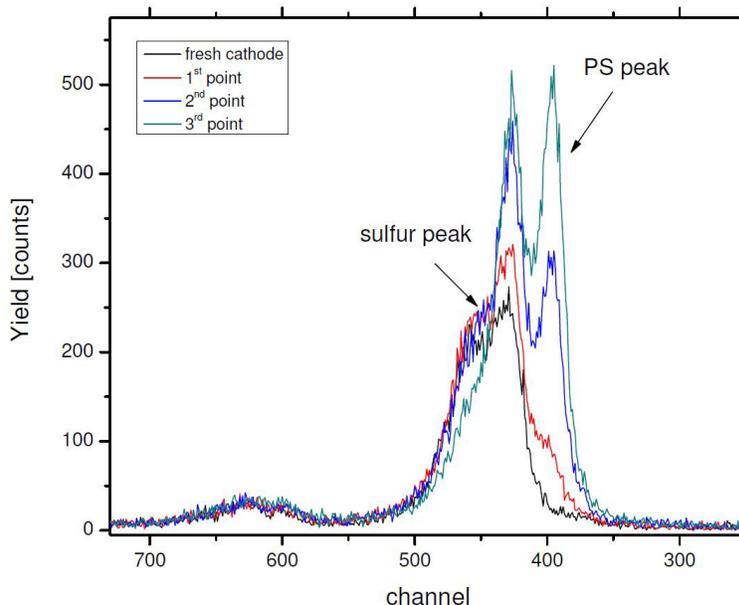


Figure 2: A sequence of first three resonant KL emission spectra of the LiS battery during the discharge process. Fixed excitation energy of 2470.3 eV was used corresponding to the PS peak in the HERFD spectra. Due to very high sensitivity the formation of PS is detected right from the start of the discharge process. The sulfate electrolyte peak is completely suppressed due to resonant excitation.

So far we can conclude that the experiment proved to be successful. As expected the resonant emission approach has turned to be superior over standard XAS spectroscopy. More elaborated treatment of the experimental data is still going on. However, based on first very preliminary treatment of the data recorded we believe that upon further analysis all main goals of this proposal could be achieved.