

**Experiment title:**

Electrochemical processes within Mg-S batteries studied by operando RIXS and XAS at the sulfur K edge

Experiment number:

CH-5124

Beamline:**Date of experiment:**

from: 16/03/2017

to: 22/03/2017

Date of report:

29/08/2017

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We have successfully performed *in-operando* sulfur K-edge resonant inelastic X-ray scattering (RIXS) and X-ray absorption (XANES) measurements on the magnesium sulfur (Mg-S) battery to study the reduction/oxidation mechanism occurring in the electrochemical cell during the discharge. All measured spectra were collected in fluorescence mode from the back side of the cathode using the high resolution Johansson type x-ray emission spectrometer. The battery was prepared in the in-situ Swagelok cell with a 6 μm mylar foil plated with aluminum (500 \AA) on the side facing the cathode. The cell was mounted in the vacuum chamber of the spectrometer with the front window tilted at 45° relative to the incident beam and discharged to 0.1 V vs Mg/Mg²⁺ using a Bio-Logic SP200 galvanostat/potentiostat at a current density of C/60 (27.9 mA/g). First excitation energy for RIXS measurements was selected at the sulfur pre-edge resonance to enhance sensitivity for the polysulfide detection. The resonantly enhanced polysulfide signal was followed with high sensitivity and accuracy along the discharge process. The measured spectra were successfully described as linear combinations of the polysulfide component and of pure sulfur (Figure 1a). For the detection of MgS slightly higher (about 2 eV) excitation energy was used. While pure sulfur and polysulfides yield the same characteristic line for this particular excitation energy, the MgS doublet is shifted towards lower emission energy by approximately 0.5 eV and this was used to resolve the MgS component and follow its intensity through the discharge (Figure 1b).. Complementary to RIXS also sulfur XANES spectra were recorded with the photodiode installed in the vacuum chamber of the spectrometer. Principle component analysis (PCA), of the whole set of *in operando* spectra showed that a set of four principal components completely describes all XANES spectra: sulfur, sulfate groups in the electrolyte, Mg-polysulfides (MgS_x), and magnesium sulfide (MgS). Using linear combination fits we obtained relative amounts of four sulfur-containing compounds (sulfur, MgS_x, MgS_{electrochem.} and electrolyte) in the cathode during the first discharge.

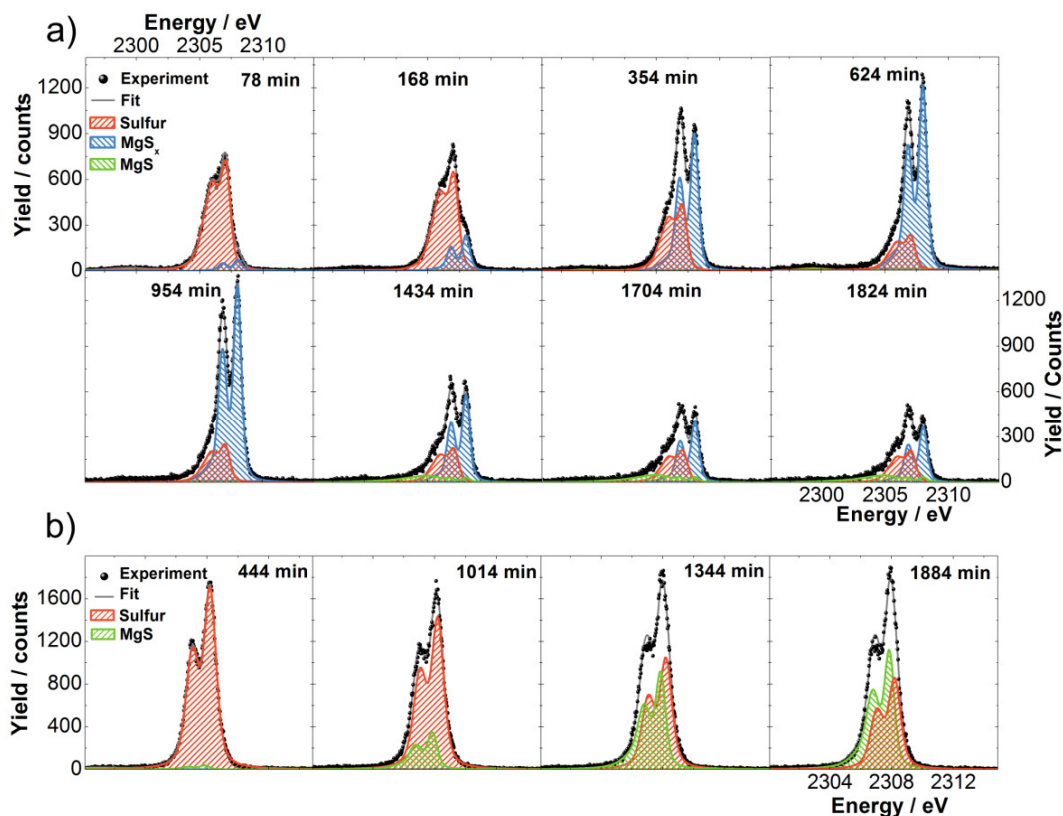


Figure 1: a) A sequence of normalized *in operando* sulfur RIXS spectra at the excitation energy of the polysulfide pre-edge resonance recorded at different times through the discharge. A linear combination fit is used to decompose the measured spectra into MgS_x (blue color) and sulfur (red color) component, which are followed through the discharge. b) A sequence of four *in operando* sulfur RIXS spectra at the second excitation energy recorded at different times towards the end of the discharge. A linear combination fit using reference spectra of sulfur and MgS standards is used to separate the MgS signal (green color) from the rest of the sulfur signal (red color).

The general evolution of separate sulfur components during the discharge determined from both sets of spectra are consistent with each other providing a clean, reliable picture of sulfur electrochemistry within the Mg-S battery. The electrochemical conversion of sulfur with magnesium proceeds through two well-defined plateaus in the voltage diagram. Our experimental results revealed that these correspond to the equilibrium between sulfur and polysulfides (high-voltage plateau) and polysulfides and MgS (low-voltage plateau). We have also observed that the electrochemically precipitated MgS ($MgS_{\text{electrochem}}$) has a different local structure from the synthesized MgS.

Based on these results we can conclude that the experiment was successful and the main goals of the proposal were fully achieved. Our results will contribute substantially towards understanding of reduction/oxidation mechanism occurring in the Mg-S battery, which is one of the most promising electrochemical couples but still in the very early stage of research. The paper with the main results of the experiment is already in preparation and will be submitted soon.