

## Sulfur based batteries studied by in-operando S K-edge RIXS and XAS spectroscopy

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Sulfur based batteries are considered as very attractive energy storage devices. Sulfur is one of the most abundant elements in the earth, it is electrochemically active material which can accept up to two electrons per atom. In combination with alkali metals, sulfur forms electrochemical couples with much higher theoretical energy density compared to Li-ion batteries commonly available today. At the moment, the electrochemical couple with Li is most extensively studied. While the main principle of operation is known the relevant operation mechanism(s) is not completely clear. Even more promising is the electrochemical couple with Mg providing almost twofold higher volumetric energy density due to its ability to provide two electrons during oxidation. However, Mg-S batteries are still in the very early stage of research and development and the complex mechanism of sulfur conversion has been less extensively studied.

In order to improve the understanding of sulfur electrochemical conversion and its interactions within electrode, we need to apply new experimental approaches capable to provide precise information about local environment of S in the cathode during battery operation. In our work, resonant inelastic X-ray scattering (RIXS) and XAS measurements at the sulfur K-edge performed in operando mode were used to study the lithium-polysulfide formation during the discharge process. Measurements were performed at ID26 beamline of the ESRF synchrotron using tender X-ray emission spectrometer [1]. Resonant excitation condition enhanced the sensitivity for the lithium-polysulfide detection. On the other hand, the sulfate signal from the electrolyte was heavily suppressed and the self-absorption effects minimized due to fixed excitation energy.

This experimental methodology was used to provide quantitative analysis of sulfur compounds in the cathode of a Li-S battery cell during the discharge process [2]. The high-voltage plateau in the discharge curve was characterized by a rapid conversion of solid sulfur into liquid phase Li polysulfides reaching its maximum at the end of this plateau. At this point the starting point for the precipitation of the Li<sub>2</sub>S from the liquid polysulfide phase was observed. The same approach has been used also for the Mg-S battery revealing similar mechanism as in case of Li-S battery [3]. The electrochemical conversion of sulfur with magnesium proceeds through two well-defined plateaus, which correspond to the equilibrium between sulfur and Mg polysulfides (high-voltage plateau) and polysulfides and MgS (low-voltage plateau).

[1] M. Kavčič et al., *Rev. Sci. Instrum.*, 83, 033113 (2012).

[2] M. Kavčič et al., *J. Phys. Chem. C*, 120, 24568 (2016).

[3] A. Robba et al., *Chemistry of Materials* **29**, 9555-9564 (2017).