Sulfur speciation for LiS battery materials by Near-Edge X-ray Absorption Fine Structure spectroscopy

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Project: Lithium-Schwefel-Hochenergie Akkumulatoren mit reversiblen Matrix-interkalierten Schwefelkathoden

One way to improve the reversibility and electrochemical use of cathodes is to incorporate electrochemical active sulphur atoms and molecules in the matrix. The sulphur can be either covalently linked or in cavity-like and in sandwich-like structures intercalated so that it cannot be removed or form passive shell around the electrode. Understanding of interaction between the isolated sulphur and carbon matrix is required to obtain fundamental knowledge about function and reliability of LiS batteries. Meanwhile, the distribution of sulphur atoms and their form (clusters films or particles) plays a key role. The process of formation of solvation shell around Li-polyssulphide in the ionic-conductive solvent, transition state to crystallization of sulphide and determination (calculation) of corresponding energy are very important as well.

As a first step the chemical speciation of sulfur by x-ray absorption spectroscopy [1, 2] was chosen. This method requires reference spectra of the sulfur oxidation states. The measurement of such reference spectra is presented here.

Near-Edge X-ray Absorption Fine Structure (NEXAFS)

- $\pi^*$ resonances occur for unsaturated bonds ($=\pi$)
- $\pi^*$ resonances have lower energies and smaller energetic width than the $\sigma^*$ resonances
- resonance energies increase with the bond strength

Experimental set-up

Grazing incidence geometry [3, 4] provides high sensitivity and depth resolution.

High spectral purity => low background in NEXAFS spectra

Calibrated detectors

=> accurate spectral deconvolution

The set-up also allows for reference-free XRF and GI-XRF measurements

Results of the first reference sample set

- significant differences due to the $S$ oxidation state
- up to 9.5 eV shift of $\pi^*$ resonance position
- more than one species visible in the spectra (position of $\pi^*$)

⇒ possible cross contamination during measurements or sample preparation

Results of the second reference sample set

- good agreement with the first sample set
- still more than one species visible in the spectra ⇒ unstable?
- slightly different $\pi^*$ intensity ratios

⇒ sulfur found on the clean substrate without sulfur treatment

Conclusions

The measured NEXAFS spectra are already appropriate as reference spectra for chemical speciation. In addition, literature data is available [1, 2]. The obtained mixing of different oxidation states will reduce the accuracy of quantitative results. Hence we will put further efforts in obtaining better reference samples. Anyway we will start now the investigation of the porous carbon cathode materials.

Perspective

- continuation of the NEXAFS reference measurements
- NEXAFS measurements of sulfur intercalated in porous carbon
- grazing incidence X-ray fluorescence measurements to determine

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References


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