Mechanism Panel Abstract & Speaker Biography

Multidimensional *Operando* Analysis of Lithium Sulfur Cells with X-ray Radiography

Sebastian Risse[1], Charl J. Jafta[1], Yan Yang[1], Nikolay Kardjilov[2], André Hilger[2], Anika Juhl[3], Simone Mascotto[3], Michael Fröba[3], Ingo Manke[2], Matthias Ballauff[1]

[1] Institute of Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin (HZB), Hahn-Meitner-Platz 1, 14109 Berlin, Germany
[2] Institute of Applied Materials, Helmholtz-Zentrum Berlin (HZB), Hahn-Meitner-Platz 1, 14109 Berlin, Germany
[3] Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King Platz 6, 20146 Hamburg, Germany

INTRODUCTION

Lithium sulfur (Li/S) batteries have a fivefold higher theoretical gravimetric energy density (2680 Wh/kg_{sulfur}) than state-of-the-art lithium ion batteries. [1]–[3] In addition, the abundant raw materials qualify this electrochemical storage system as one of the most promising candidates for the post-lithium-ion-era. However, the strong fading of electrochemical storage capacity with increasing cycle number is still a major obstacle to a broad technical use despite decades of research.[4] The main problems are at hand: During discharge sulfur is converted into Li_2S with a concomitant large volume change of up to 80% that may lead to damage of the cathode structure. Sulfur and Li_2S which are precipitated and dissolved during the operation of the battery are non-conductors and their morphology and crystalline structure will be of central importance for the functioning of the system. In addition to this, the soluble intermediate polysulfides Li_2Sx (x = 3-8) may lead to parasitic side reactions and thereby attack the anode of the system. Clearly, the large number of complicated electrochemical processes occurring on both electrodes at the same time renders the analysis of the Li/S system a difficult task.[5]

Very recently, tremendous progress has been made with the advent of *operando*-techniques that allow to follow electrochemical processes while charging or discharging the Li/S-cell.[6], [7] However, a central problem that could not be resolved so far by these studies is the morphological changes brought about by the deposition and the dissolution of the sulfur particles during cycling of the cell. Here we present the first *operando* study of Li/S cells using X-ray radiography that was partly published elsewhere.[8]

METHODOLOGY

The Li/S cell consists of a carbon cathode which is penetrated by the X-rays (Figure 1). The anode is a lithium foil in which a circular window is cut for the incoming X-rays. The cell can be run much in the way of a standard coin cell and allows us to investigate the voltage as a function of the current. Hence, the impedance can be measured while operating the cell. Moreover, relaxation processes can be measured in different frequency windows. These parameters can be correlated with the morphological changes of the cathodes as visualized by X-ray radiography and the voltage-time curve.

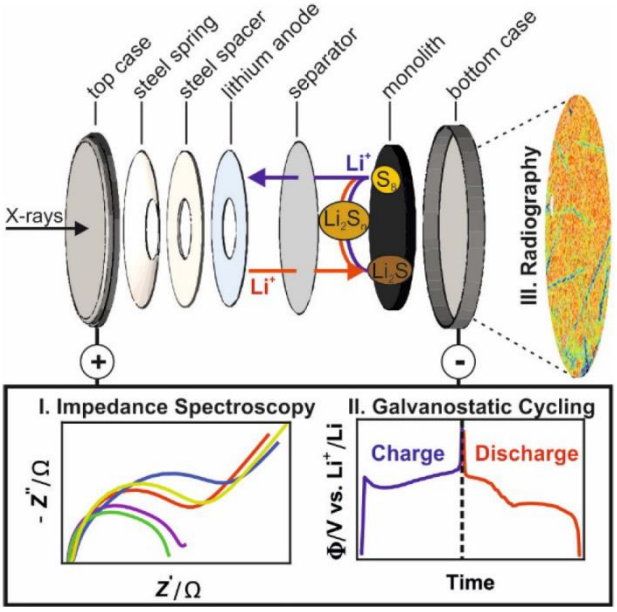

Figure 1: Schematic setup of the *operando* cell that combines *operando* X-ray radiography with impedance spectroscopy and time dependent voltage measurement.

We use two different materials for the cathode, a commercial available activated carbon fiber (ACN) and a synthesised carbon monolith. All experiments start with a partially charged cell (Li_2S_8) containing neither solid sulfur nor solid Li_2S. Hence, the consequences of the generation of solid material upon charging or discharging of the cell, respectively, can be visualized by the radiography experiment. Simultaneous measurement of impedance spectroscopy gives information about relaxation processes related to the deposition and dissolution processes of solid materials.

RESULTS AND DISCUSSION

As shown in Figure 1, the radiography setup allows the monitoring of the cathode of the electrochemical cell under *operando* conditions. The cell was galvanostatically charged and discharged over five cycles with a C-rate of 0.1 C (1h = 168 mAh/g_{sulfur}). Three different X-ray radiography images are shown in Figure 2. They were taken at the end of the first (III) and second (I) charge steps as well as at the end of the second discharge step (II). All X-ray images that were recorded exhibit areas of low transmission that are present from the very first state on. These stains are caused by non-wetted areas of the monolithic carbon cathode. The charged state (Figure 2, III) of the first cycle clearly exhibits macroscopic crystals of sulfur which can be assigned to rhombic α- (Figure 2, α) and monoclinic β-sulfur (Figure 2, β) from their characteristic crystal habit. This finding is in agreement with previous studies using operando X-ray

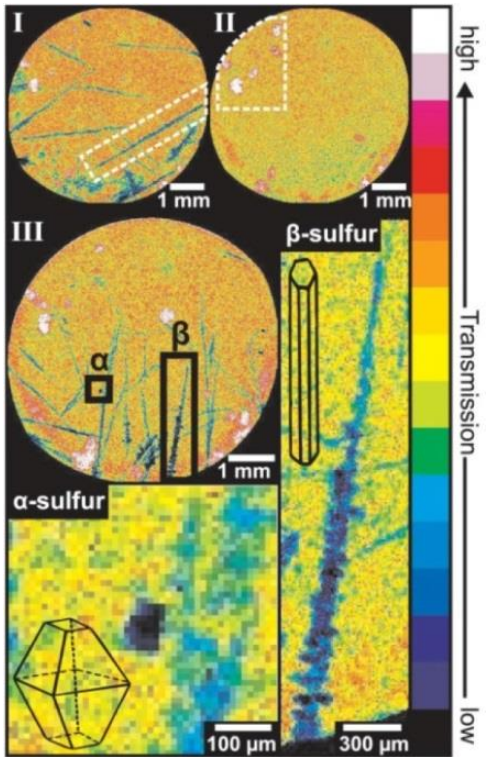

Figure 2: X-ray images: Fully charged (I) and discharged (II) state of the Li/S cell of the 2nd cycle and fully charged state of the 1st cycle (III). Both insets (α, β) magnify the obtained macroscopic sulfur structures. The respective crystal habit of α- and β-sulfur are also inserted into the magnified images (α: rhombic; β: monoclinic).

diffraction (XRD) which also found stable α-sulfur as well the metastable β-sulfur in the charged state of Li/S cells.[9] No macroscopic crystals of Li_2S were monitored in the discharged state. Again this is to be expected since all previous XRD measurements concluded that the Li_2S crystals must be of nanoscopic size.[10], [11]. The time resolved growth of a macroscopic α-sulfur crystal is shown in Figure 3.

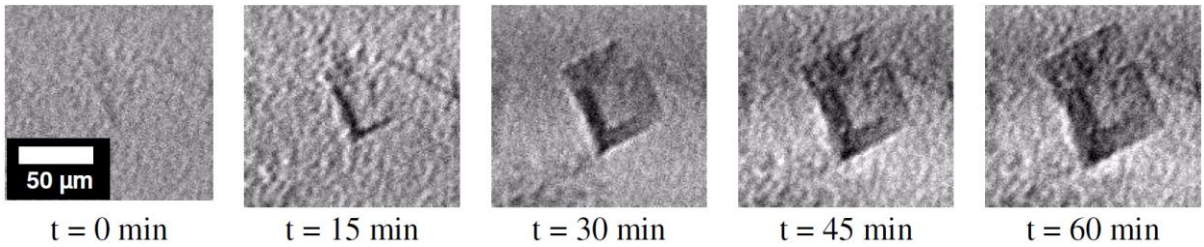

Figure 3: Time resolved growth of a α-sulfur crystal during charge

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Speaker Biography:

Sebastian Risse (*1983) started his physics study at the University of Potsdam (Germany) in 2004 and received his diploma with distinction in 2009. He continued his work in the research field “dielectric elastomer actuators” in the Institute for Applied Physics of Condensed Matter (University of Potsdam) headed by Professor Reimund Gerhard. In 2013 he successfully defended his PhD-thesis entitled “Physical properties of dipole filled silicones for dielectric elastomer actuators”. In the same year he joined the research group of Professor Matthias Ballauff at the Helmholtz-Zentrum in Berlin (Germany) and is at the moment a junior group leader.

The main objective of his research is the investigation of the complex capacity fading processes in lithium/sulfur cells. Therefore he develops novel operando setups that allow the simultaneous performance of several measurement methods. This sophisticated analysis methods yields valuable insights into the operating system. The methods used are small angle neutron scattering, small angle X-ray scattering, X-ray radiography and tomography, energy dispersive X-ray diffraction, electrochemical impedance spectroscopy and cyclic voltammetry.