Experimental report

05/10/2017

Proposal:	**1-04-110**	**Council:**	4/2016
Title:	Operando neutron reflectometry of metallic Lithium layer exposed to polysulfides		
Research area:	Materials		

This proposal is a new proposal

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Local contacts:	Robert CUBITT

Samples: DOL/DME solvent

Instrument	Requested days	Allocated days	From	To
D17	7	7	05/10/2016	12/10/2016

Abstract:

Lithium sulfur (Li/S) cells have a fivefold higher gravimetric energy density than state of the art lithium ion batteries. Furthermore they are environmentally friendly and consist of abundant raw materials. However, the major drawback of this electrochemical system is the pronounced capacity fading with increasing cycle number. A frequently observed degradation process is caused by the "shuttle effect". Soluble polysulfides diffuse to the lithium anode and perform parasitic side reactions which lead to a complex surface chemistry at the anode. We will investigate these degradation processes at the lithium anode with a new operando neutron reflectivity (NR) cell. A lithium layer (50 nm) that is precipitated on a silicon electrode will be exposed to different electrolytes followed by electrochemical cycling. NR is in this respect an especially powerful tool due to its high contrast between the electrode and Li. The NR measurement will be combined with impedance spectroscopy and voltage measurements to get a holistic view of this system. Preliminary results of the lithium precipitation and NR measurements with the operando cell have already proven the feasibility of this

Experimental Report for D17-Experiment 1-04-110

Lithium sulfur (Li/S) cells have a fivefold higher gravimetric energy density than state of the art lithium ion batteries[1]. Furthermore they are environmentally friendly and consist of abundant raw materials. However, the major drawback of this electrochemical system is the pronounced capacity fading with increasing cycle number. A frequently observed degradation process is caused by the "shuttle effect"[2]. Soluble polysulfides diffuse to the lithium anode and perform parasitic side reactions which lead to a complex surface chemistry at the anode[3]. Therefore, it is important to understand the deposition and degradation processes at this electrode. Various investigations were made to analyse the formation of the solid electrolyte interface at the lithium anode[4,5]. As known from Li-ion batteries it is very challenging to resolve the formation of a lithium layer in Li/S cells[6]. The use of neutron reflectometry enables a time-dependent spatial (depth) resolution of these key processes in Li/S cells. Especially the formation of the hardly soluble Li_2S on lithium is of major interest due to its reduction of electrochemically active surface.

Experimment:

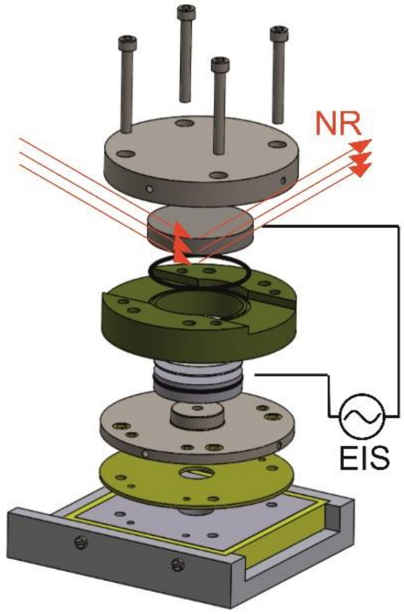

Figure 1: used cell setup

Unfortunately, no glovebox where organic solvents were allowed was available during our experiment at ILL. Therefore we had to change the experiment and investigate only the deposition of lithium on silicon.

The electrochemical cell shown in figure 1 was used. This cell is an improved version of the cell described in the proposal. It consists of a stainless steel stamp which serves as current collector for the counter electrode. On top the counter electrode (in this experiment metallic lithium foil) is deposited. A separator foil (Celgard) is added. The working electrode consists of a silicon wafer (100). Sealings on top and on the bottom ensure an air-tight design of the cell. The cell case itself is made out of PEEK. The space between the 2 electrodes is filled up with an electrolyte which consists of 1M LiPF6 in ethylene carbonate + dimethyl carbonate (1:1 by volume). The contact area of the silicon to the electrolyte is 29.3 cm².

The experiment was carried out by galvanostatic cycling between 0.03 and 3 V. In a first step the current was set to 25 µA. This current was increased to 100 µA because no changes were visible in the cell voltage and also in the reflectometry data. This current was also insufficient so the current was further increased to 250 µA. After each charge and discharge a 3-h- break with open circuit measurement was done to perform long-time reflectometry measurements at two different angles to improve statistics and enlarge the q-range compared to the scans during cycling. Also an impedance spectroscopy was performed in the frequency range of 0.1 Hz to 1 MHz. For improved understanding figure 2 shows a sketch of the different layers.

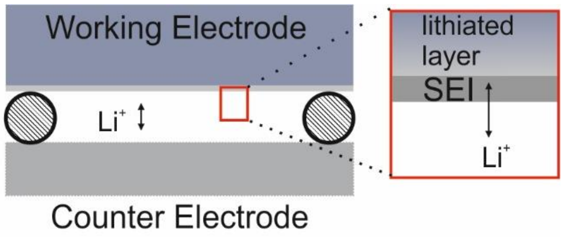

Figure 2: Sketch of the layer plot in the cell

Results

Figure 3 shows the voltage profile of the cell over the whole experiment stacked together with the measured neutron reflectivity. In total four cycles of lithiation and delithiation was investigated using impedance spectroscopy and neutron reflectometry. The reflectometry data of the virgin state as well as of the individual lithiated and delithiated states are shown in figure 4. The solid lines show the best obtained fit results. It can be found that after the voltage dropped the reflectivity increases dramatically, especially in the region of lower values for the scattering vector. This indicates the deposition of lithium. No well-defined fringes can be found indicating rough, not well defined layers.

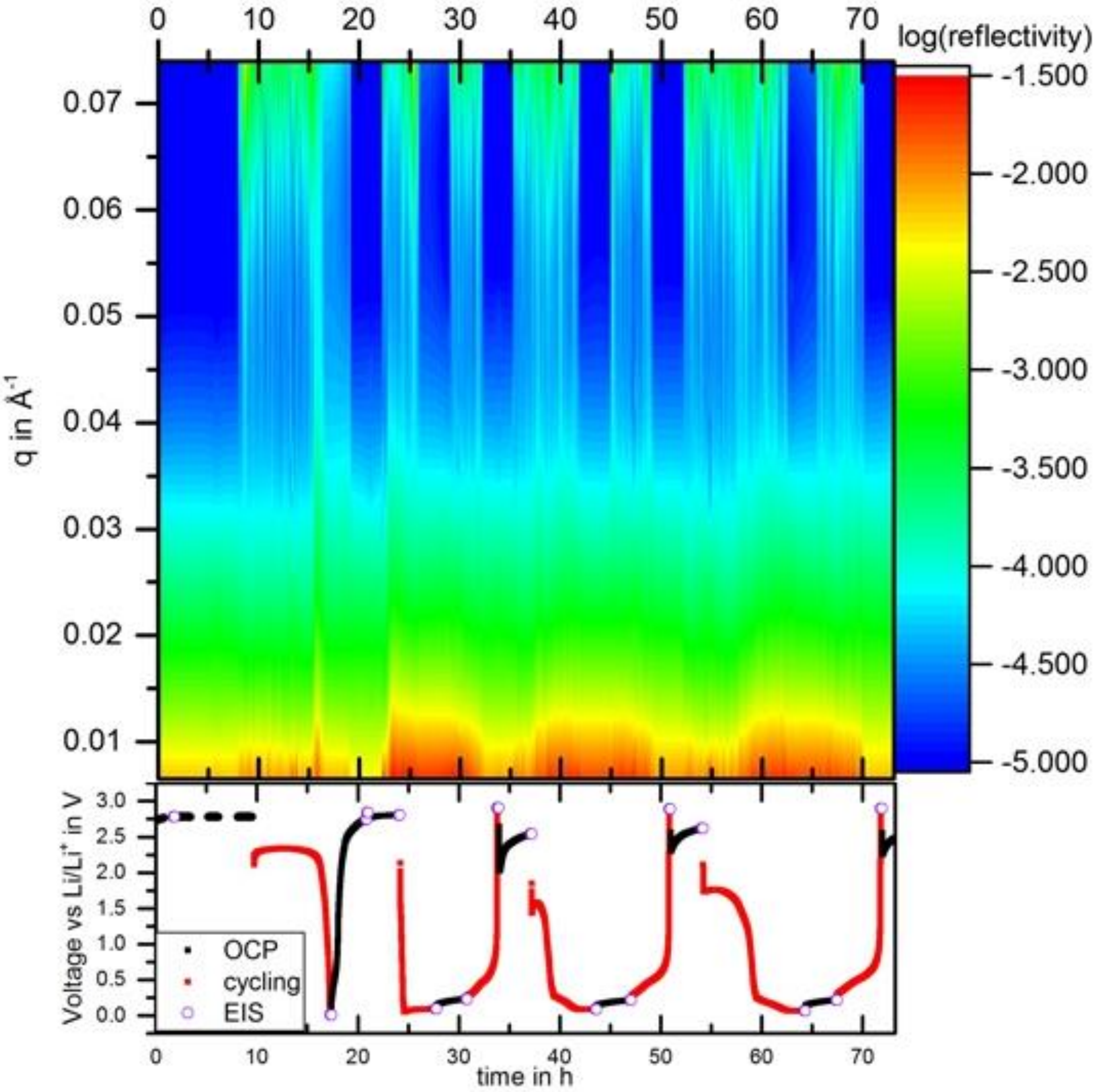

Figure 3: Voltage-time curve over the whole experiment stacked together with the reflectivity-time curve of the whole experiment.

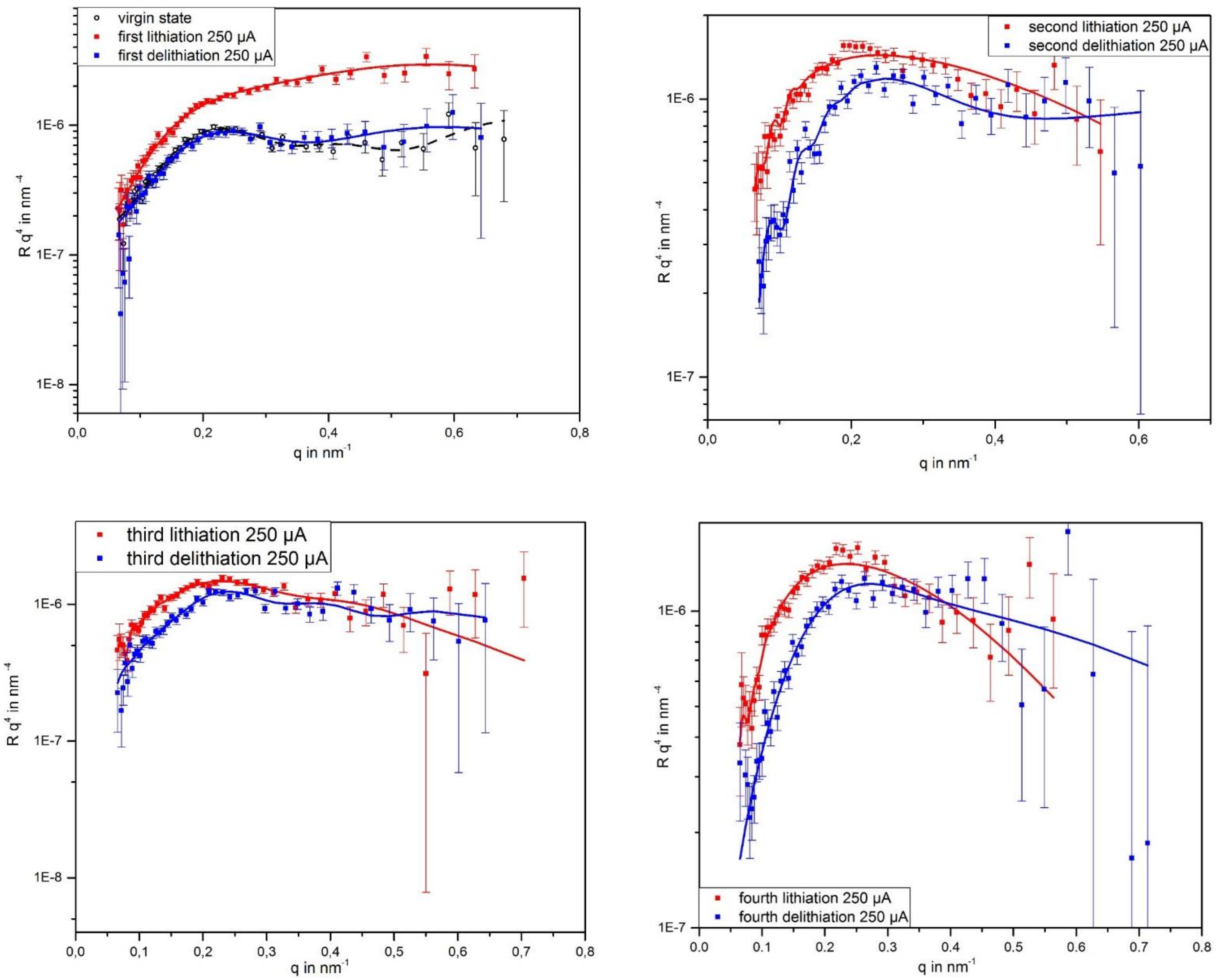

Figure 4: Reflected intensity times scattering vector to the power of 4 vs the scattering vector of the static scans in lithiated and delithiated state

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