Experimental report

13/02/2019

Proposal:	**1-04-138**	**Council:**	4/2018

Title: Operando neutron reflectometry of lithiated silicon protected by an artificial SEI

Research area: Materials

This proposal is a new proposal

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Samples: LiPF6 in C3H4O3 + C3H6O3

Instrument	Requested days	Allocated days	From	To
FIGARO	4	0		
D17	4	4	08/10/2018	15/10/2018
SUPERADAM	4	0		

Abstract:

Silicon electrodes for Li-batteries have a ten times higher gravimetric energy density than current graphite electrodes. They consist of nonhazardous, abundant raw materials, which are widely used in industry. This electrode has also possible applications in future battery systems, for example Lithium-Sulfur batteries. The major drawback of this electrode system is the strong capacity. The silicon electrode is lithiated and serves as a lithium reservoir. It was shown that Aluminum oxide is a stable artificial SEI, which hinders electrolyte decomposition. To further improve the performance of silicon electrodes the formation and stability of the SEI-layer on the silicon anode and the migration of lithium in and out of the anode needs to be investigated. This knowledge helps to improve the long-term performance of this electrode system. Neutron Reflectometry (NR) is an excellent tool for these investigations.We want to investigate the (de-)lithiation of a crystalline silicon electrode coated with 5nm of AlOx with operando NR and impedance spectroscopy over several (e.g. 10) cycles. This work is the last part of the PhD-thesis of Arne Ronneburg.

Experimental Report: 1-04-138, D17, 8.10.-15.10.2018

Abstract

Silicon electrodes have an eleven times higher gravimetric energy density than state of the art anodes for Lithium ion batteries. They are based on the reaction of silicon and metallic lithium which form an alloy instead of an intercalation mechanism. . The major drawback of this battery system is the strong capacity fading with increasing cycle number. This is caused by the volume expansion up to 310% during lithiation causing mechanical fracture of the silicon and exposes new electrode surface to the electrolyte generating a constant growth of the solid-electrolyte-interphase layer (SEI)1. Also it was shown that aluminum oxide is a stable artificial SEI which hinders electrolyte decomposition. To further push the commercialization of this system also the long term behavior needs to be investigated. Neutron Reflectometry (NR) is an excellent tool for these investigations due to the good scattering length density (SLD) contrast of lithium and silicon.

Experiment

Unfortunately, the experiment completely failed. In total, 5 cells were build, but none of them worked, even though they were tested excessively in the lab before. Back home we did further experiments and data analysis to understand the reason for this failure. Also the cell was slightly modified to increase the pressure at the lithium electrode and therefore enhance electrical conductivity. (Figure 1) The overall Resistance of the electrolyte, the electrodes and contacts dropped by a factor of 2.

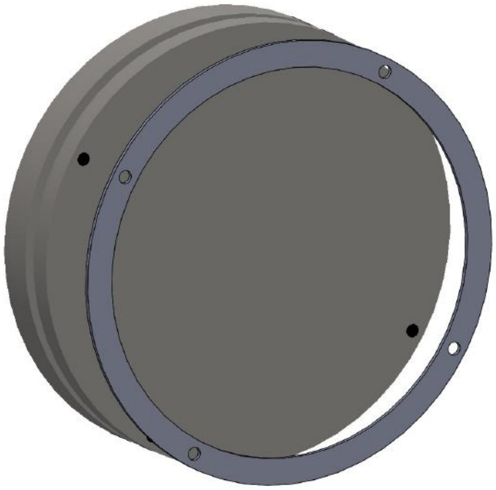

Figure 1: modified current collector for lithium electrode.

Figure 2 shows a series of reflectivity measurements (virgin state and during "lithiation") done at one of these cells and the corresponding voltage- and current-plot. Clearly differences in reflectivity can be found before (VS_initial) and after (VS_end) wetting of the cell. Slight changes can also be found at initial and final state of the galvanostatic lithiation. These changes do not correspond to lithium insertion since (A) the voltage is too high (approx. 1V) and (B) higher changes were expected. Afterwards the voltage was ramped down followed by an potentiostatic step at 10 mV which is below the lithiation potential (approx. 70 mV for the final crystalline phase). Here also no changes can be found, so lithiation does not took place.

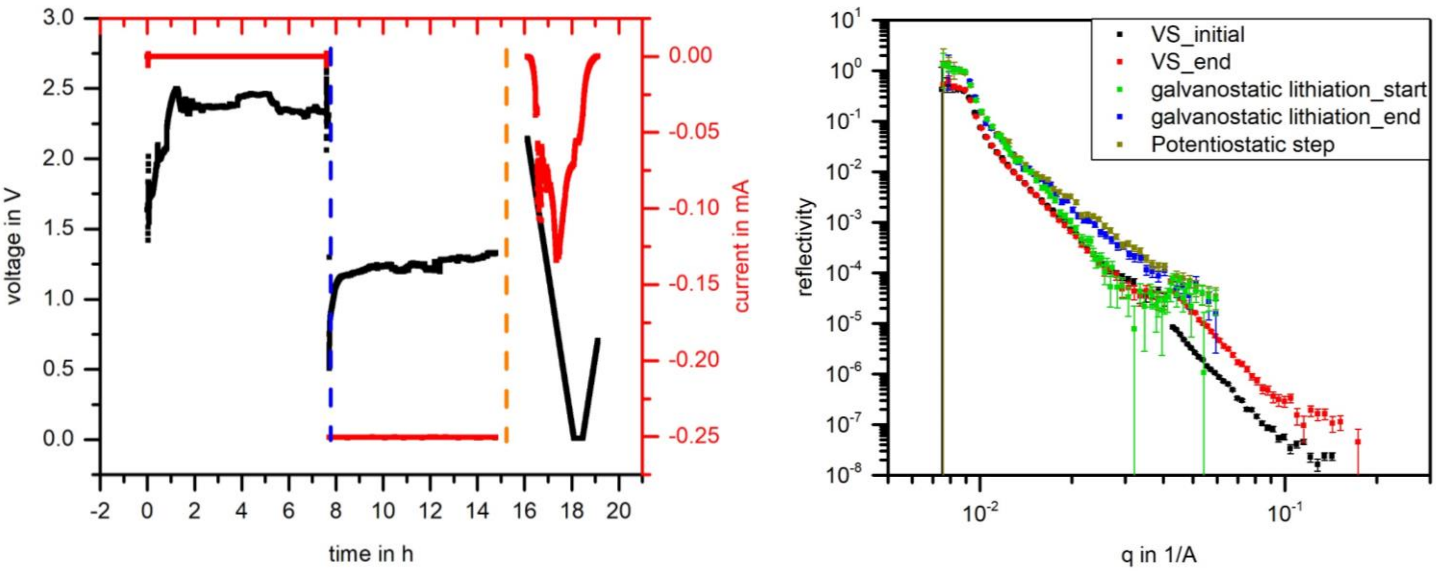

Figure 2 Results obtained during experiment 1-04-138 at D17. On the left: Voltage (black) and current (red) as function of time. The blue dashed line shows the end of the wetting process (Virgin state- VS). The orange dashed line shows the end of the galvanostatic lithiation. On the right: Reflectivity curves.

Measurements with the improved cell are shown in figure 4. The difference in reflectivity (V6 instrument@BERII, Berlin) in the final states can be found easily corresponding to the increased contrast caused by the insertion of lithium. Also the electrochemical response corresponds to the expectations. During OCP-periods (current equal to zero) impedance spectroscopies were done. This causes virtual fluctuations on the voltage which does not affect the overall cell state. The performance over several cycles was also tested in our lab (figure 3). Here the reversibility can be seen over 5 cycles. The plateau around 1V corresponds to side reactions. The aim of this experiment was to investigate the origin and influence of these side reactions on the solid-electrolyte-interface layer as well as the lithium profile in the silicon.

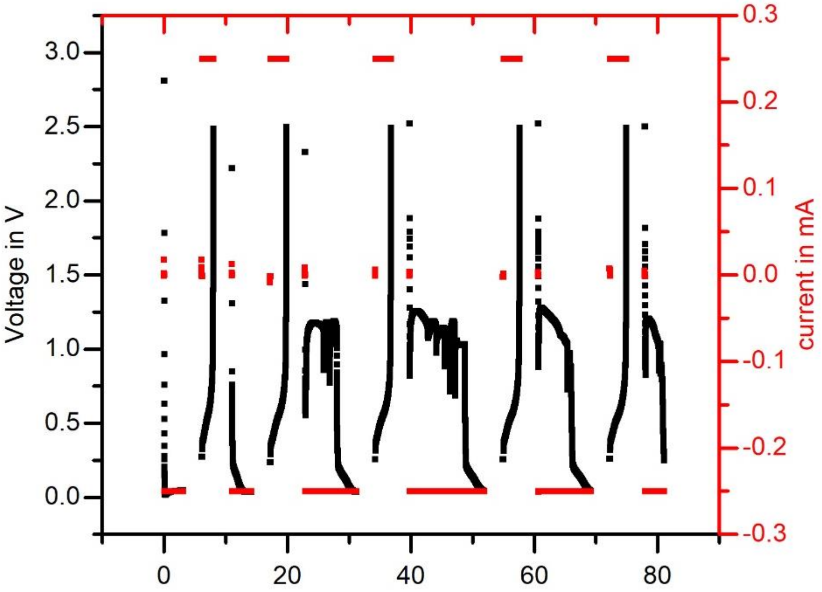

Figure 3: Lithiation/Delithiation behavior of the neutron cell over 5 cylces. The plateau around 1V is associated with side reactions occuring in the SEI.

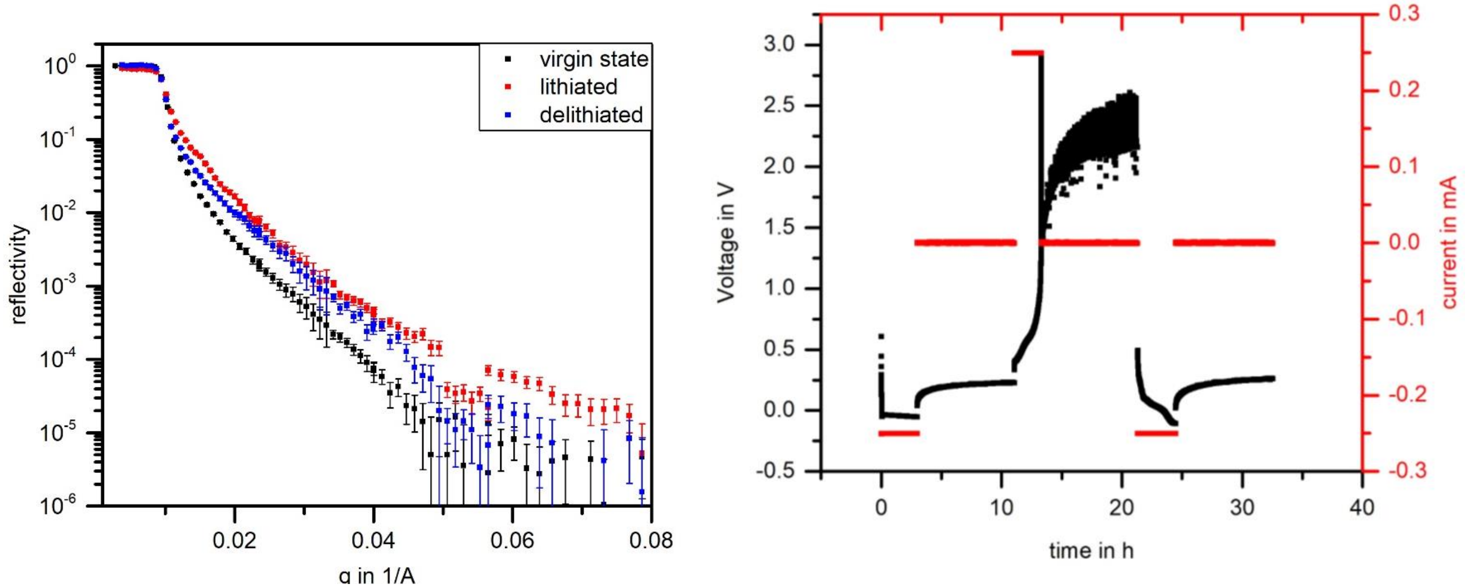

Figure 4: left: in situ NR measurements done at V6/BERII. The difference between the lithiated and delithiated state can be seen easily and corresponds to expectations. Right: corresponding Voltage and current data as function of experimental time. The broad voltage signal around 20h was generated by impedance spectroscopies

Conclusion and summary

The cell used during this experiment showed a bad performance because of missing electrical contact of the lithium. A modification was done improving the overall electrical contact by a factor of two. In situ measurements with the modified cell were done demonstrating the performance of the cell and ongoing side reactions which were the subject of study for the proposed experiment.