Experimental report

07/04/2016

Proposal:	**1-04-81**	**Council:**	4/2014
Title:	Lithium Incorporation into SiliconSingle Crystals as a Model System for Anode Materials in Lithium-Ion Batteries		
Research area:	Physics		

This proposal is a new proposal

Main proposer:	**Beatrix-Kamelia SEIDLHOFER**
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Local contacts:	Robert CUBITT

Samples: Si/SiLix/LiClO4/Propylene Carbonate

Instrument	Requested days	Allocated days	From	To
D17	0	5	08/10/2014	13/10/2014
FIGARO User-supplied	4	0		

Abstract:

In the field of automotive transportation lithium-ion batteries with high charge/discharge rates and high power densities are required. These factors are dependent on the diffusion or interface controlled insertion of Li into solid hosts. It is necessary to understand the kinetic processes going on at the electrodes to optimize charging times and to increase the power densities. Within this proposal neutron reflectometry studies on the intercalation of Li into silicon single crystals during galvanostatic charging/discharging at room temperature are planned. We will monitor the formation and movement of the LixSi phase front by the produced changes in reflectivity of the electrode/electrolyte interface. The results will give important information on lithiation mechanism and kinetics, which is the first step in enhancing the properties of Lithium-ion batteries.

Experimental report for D17 Experiment #65032

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08. – 13. October 2014

Scientific background:

Lithium-ion batteries (LIBs) are frequently used as rechargeable power sources for portable devices with further potential for automotive transportation. In the latter case improvements in cycle life, power density, safety and costs of LIBs are required. Here crystalline silicon (c-Si) is a very promising anode material of next generation LIBs due to its high specific capacity of 3579 mAh/g and further advantages like its abundance in the earth crust and well-developed engineering techniques.[1] The current obstacles in utilizing Si anodes are in their slow and in part irreversible charge/discharge processes. During first lithiation an amorphous Li_xSi phase (with x claime ~3.5) develops and migrates into the c-Si anode with a reaction front from of ~1 nm thickness. At full lithiation (full discharge) the a-Li_xSi phase transforms into the crystalline phase c-$Li_{15}Si_4$, which further hinders fast successive charging (delithiation). After the first discharge/charge cycle c-Si is irreversibly turned into a-Si. The amorphization causes a big volume change and deterioration of the anode material.[1] The underlying lithiation kinetics and its pathways are not well explored until now due to the fact that for the latter techniques with a high sensitivity to Li in amorphous phases with a spatial resolution on the nanometer scale and the capability of operando studies are required. The understanding of lithiation kinetics and its pathways -however- is of outmost importance for the understanding of the volume changes, stress evolution, and mechanical failure during the lithiation/delithiation of Si electrodes.

Experiment:

The electrochemical cell was assembled within an argon filled glove box. It is composed of three electrodes, the working electrode which is made of crystalline silicon with (100) orientation and a counter and reference electrode composed of metallic lithium. A circular design with a contact area to the electrolyte of 1288 mm^2 is used. A separator with a thickness of 20 mm is introduced between the two electrodes. As an electrolyte, a 1 M $LiClO_4$ propylene carbonate solution is used.

Electrochemical cycling was carried out using a computer controlled potentiostat. A current of ± 25 μA and ± 100 μA was used for lithiation and delithiation of the crystalline silicon electrode. Figure 1 shows the electrochemical cell mounted at the D17 reflectometer.

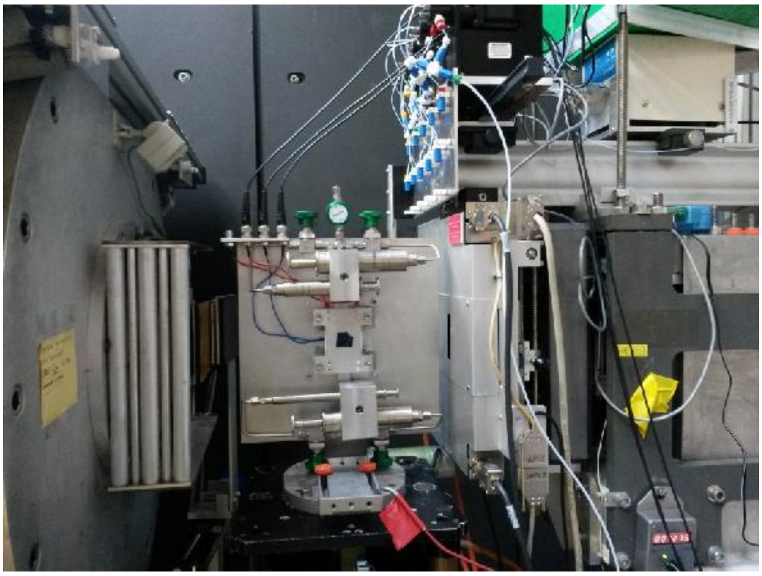

Figure 1: Electrochemical cell at D17

Results:

In Figure 1 the reflectivity curves for the first, second and third lithiation are shown. As the neutron beam impinges the electrode/electrolyte interface from higher to lower SLD, no total external reflection is observed. Bragg analysis of the Kiessig fringes gives the total thickness of the lithiated phase Li_xSi. In dependence of the cycle number, lithiation time and current used, the thickness of Li_xSi increases from 520 Å for the first (-25 µA, 12 hours), to 870 Å for the second (-25 µA, 12 hours) and 2470 Å for the third lithiation (-100 µA, 3 hours). Figure 3 shows the reflectivity curves of the virgin state and after the first, second and third delithiation. The shapes of the neutron reflectivity curves are clearly different form each other.

Conclusions:

The thickness of the lithiated phase increases with each cycle while the total amount of applied current remains the same (300 µA·h). In literature it is noted that c-Si is transformed into a-Si after the first delithiation.[1] We suppose that the first lithiation is inhibited by the virgin, crystalline structure of silicon. The second and third cycle occur faster and easier due to the pre-lithiated respectively amorphous silicon.[2] From Figure 3 it is clearly visible that the Si-electrode in its delithiated state does not return to its initial (virgin) state before lithiation, therefore the electrode reaction is not reversible.

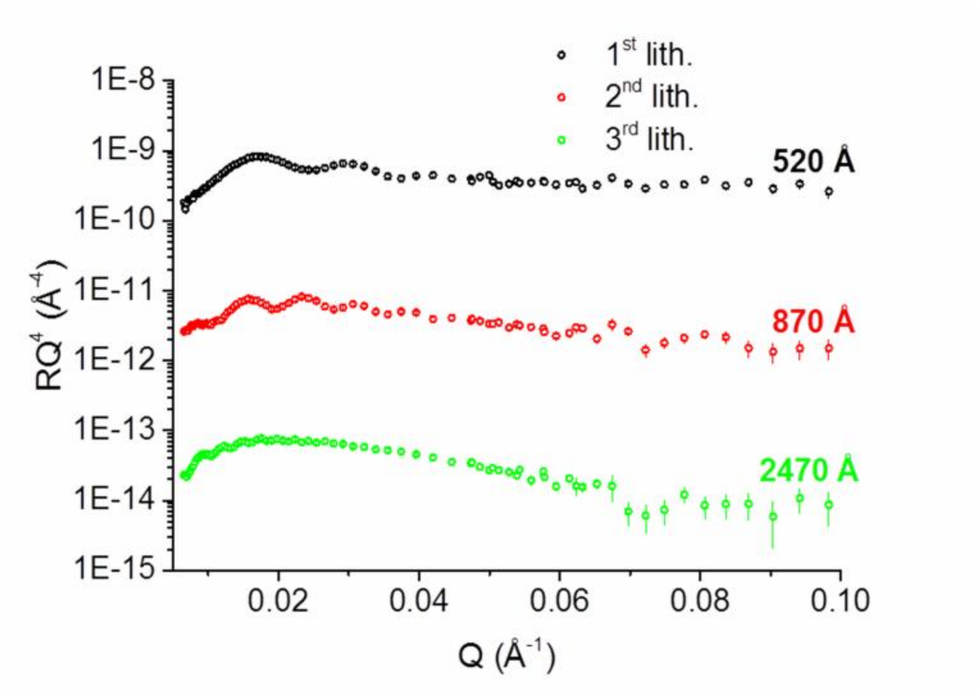

Figure 2: Neutron reflectivity measurements after the 1st, 2nd and 3rd lithiation. The curves are shifted for a better view.

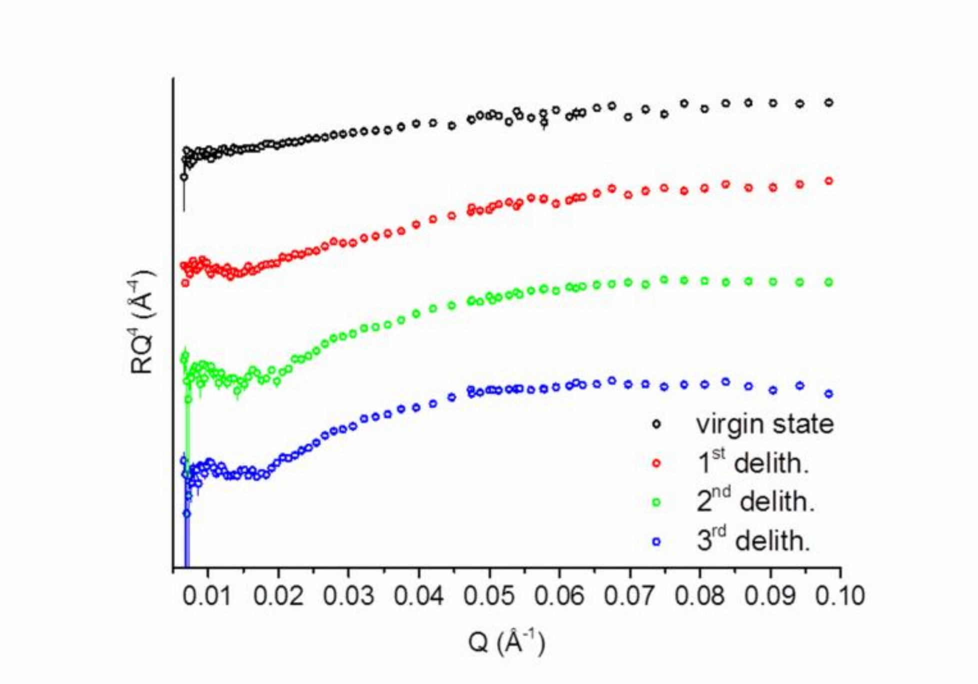

Figure 3: Neutron reflectivity measurements after the 1st, 2nd and 3rd delithiation. The curves are shifted for a better view.

1. M. T. McDowell, S. W. Lee, W. D. Nix, Y. Cui, *Adv. Mater.* 25 (2013) 4966-4985.
2. B.-K. Seidlhofer, B. Jerliu, M. Trapp, E. Hüger, S. Risse, R. Cubitt, H. Schmidt, R. Steitz, M. Baulauff, *submitted to ACS Nano*.