In-operando neutron reflectometry studies on lithium insertion into silicon electrodes of Li-ion batteries

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Abstract

Lithium ion incorporation into amorphous silicon electrodes was monitored via in-operando neutron reflectometry in real-time during battery cell operation. Recent results of cyclic voltammetry experiments are presented. These experiments enable us to monitor the enormous volume expansion, the formation and evolution of the SEI (solid electrolyte interphase), the determination of irreversible capacity losses and voltage hysteresis effects during cycling.

1 Introduction

Since Sony has announced the lithium-ion battery in the 1990s, applications based on this energy storage system are rapidly growing and strongly influence our daily life. Due to their high power and energy density together with their long lifespan, lithium-ion batteries are used today in cell phones, laptops, power tools, e-bikes etc. Lithium-ion batteries are expected also to be suitable in the off-grid renewable energy and electrical vehicle sector [1, 2]. This requires the search for new electrode materials for the use in future applications based on lithium-ion battery technology [3].

One of this promising candidates that has been found an enormous attention in the scientific community is amorphous silicon. Amorphous silicon has a high theoretical specific capacity, which is about ten times higher (~ 4200 mAh/g) compared to that of the graphite anode (~ 372 mAh/g), the dominating anode material used in current commercial lithium-ion battery technology [4].

Electrochemical lithiation of amorphous silicon at room temperature occurs via formation of a Li-Si alloy via the following reaction:

$$Si + x\,Li^{+} + x\,e^{-} \rightarrow Li_{x}Si \quad (x \leq 4.2) \tag{1.1}$$

However, bulk amorphous silicon thin film electrode has three major drawbacks which have to be overcome in order to be used in present Li-ion battery applications: (i) The tremendous volume expansion up to 300 % during the lithiation/delithiation process leading to electrode pulverization and loss of contact between the current collector and the electrode material due to mechanical stress (ii) the limited intrinsic conductivity of the semiconductor material and (iii) the continuous re-formation of the SEI during cycling, resulting in electrolyte decomposition, increase of resistance and capacity fading of the battery cell [5, 6].

The aim of this work (originally published in ref. [7] in an extended version) is to investigate the Li-ion incorporation into thin film amorphous silicon via in-operando neutron reflectometry during electrochemical cycling. A better understanding of kinetic processes and interface phenomena at electrode/electrolyte interfaces occurring during electrochemical cycling will lead to an improvement of the battery performance and will help avoiding capacity fading during cycling of the battery cell.

2 Experimental work

The experiments represented in this work were performed on a self -constructed three electrode Li half cell which is sealed against air. This special construction of the electrochemical half cell allow us to carry out in-operando neutron reflectometry experiments in real time under cell operating conditions. An overview, describing the cell configuration is given in *Fig. 1 (a–c)*. More experimental details can be found in our previous published work in ref. [8]. A 10 mm thick SiO_2 substrate was used as a base for the electrode preparation. A 400 nm thick copper layer was deposited on the square shaped SiO_2 substrate (dimensions 50 mm x 50 mm x 10 mm) which serves as a back contact and current collector. The amorphous silicon anode material (thickness ~ 68 nm) was deposited via DC magnetron sputtering on the top of the copper current collector. The electrode material shows a circular design with a diameter of around 40 mm. Both, the reference electrode as well as the counter electrode was made of pure lithium metal foil. We introduce a 20 µm thick microporous polyethylene separator between the working electrode (amorphous silicon anode) and the counter electrode (lithium metal foil) in order to prevent short circuit during electrochemical cycling. As an electrolyte, we used 1 M $LiClO_4$ dissolved in propylene carbonate. The cell was assembled within an argon filled MBraun Glove Box (water and oxygen content < 0.1 ppm). The cell body was made of high density polyethylene material. The electrochemical measurements were done using a computer controlled potentiostate (Gammry, Reference 3000).

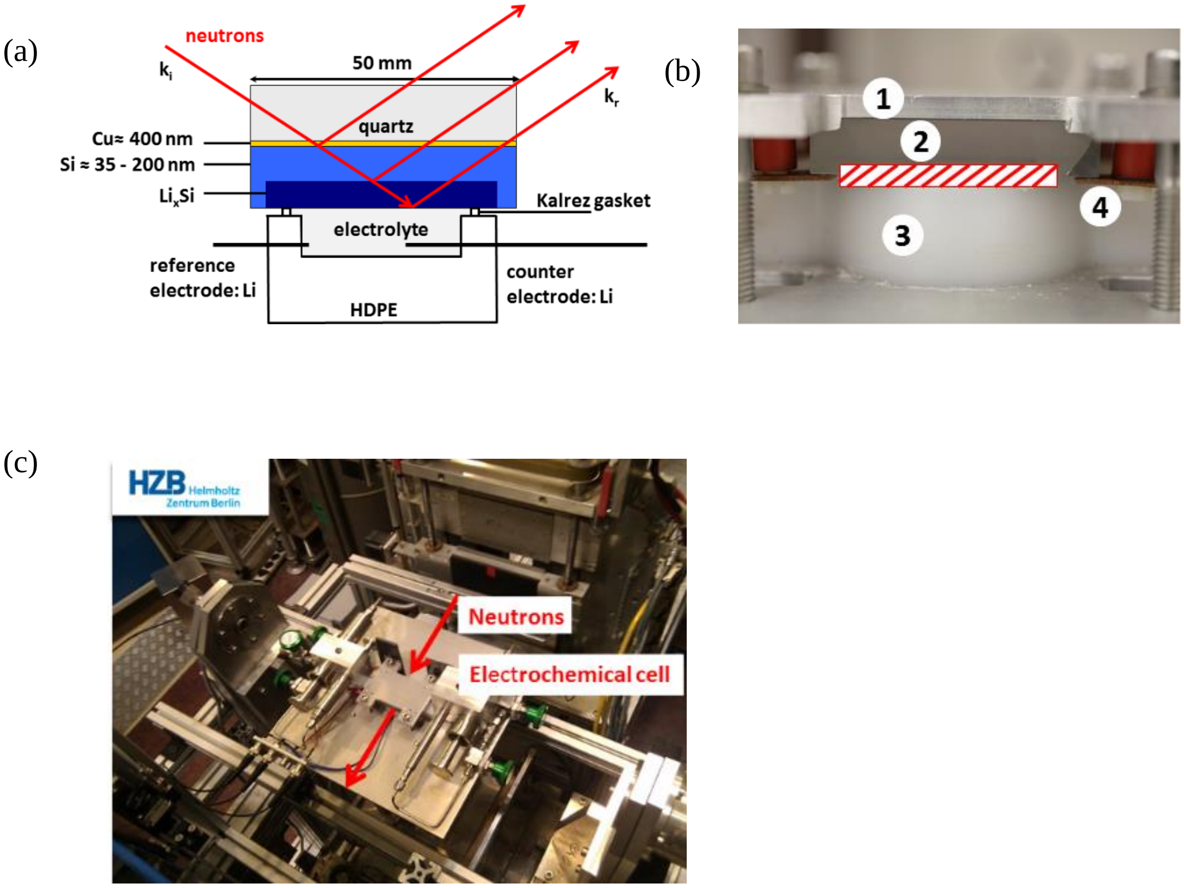

Fig. 1: (a) Schematic sketch of the electrochemical half-cell. (b) Figure of the cell: (1) Aluminium cover platte; (2) SiO_2 Substrate including the electrode material; (3) High Density Polyethylene housing; (4) Electric connections to the Potentiostate. The dashed area represents the incidence area of the neutron beam (not to scale). (c) The mounted electrochemical half-cell at the V6 neutron reflectometer localized at the Helmholz-Zentrum Berlin. After ref. [8].

The neutron reflectometry measurements were performed in classical θ/2θ (θ: incidence angle) mode with a monochromatic neutron wavelength of λ ~ 4.6 Å at the V6 Reflectometer at Helmholtz Zentrum Berlin. The neutrons coming from the reactor source are directed through the side of the SiO_2 substrate and are reflected on the SiO_2/Cu/a-Si/electrolyte interfaces. They exit the SiO_2 substrate on the opposite side and are detected by ^{3}He pencil detectors. For further data analysis we used the Motofit simulation software, which is based on the Parratt's recursion algorithm. More detailed information about the experimental setup is given in our previous work [8, 9].

3 Results and discussion

3.1 Neutron reflectometry and electrochemical measurements

The in-operando neutron reflectometry patterns presented in this work were obtained during cyclic voltammetry measurements. Cyclic voltammetry is a widely used electrochemical technique in lithium ion battery research. In general, during the cyclic voltammetry measurement, the potential applied at the working electrode (amorphous silicon anode) is controlled by a reference electrode (lithium metal) and at the same time the resulting current between working and counter electrode is measured. In contrast using a chronopotentiometry (galvanostatic charging) technique, a constant current between the counter and working electrode is applied and the resulting voltage at the working electrode is measured. *Figure 2* show a cyclic voltammetry pattern for an amorphous thin film electrode (thickness 68 nm) recorded at a slow potential sweep rate of 0.01 V s^{-1} for the initial two cycles.

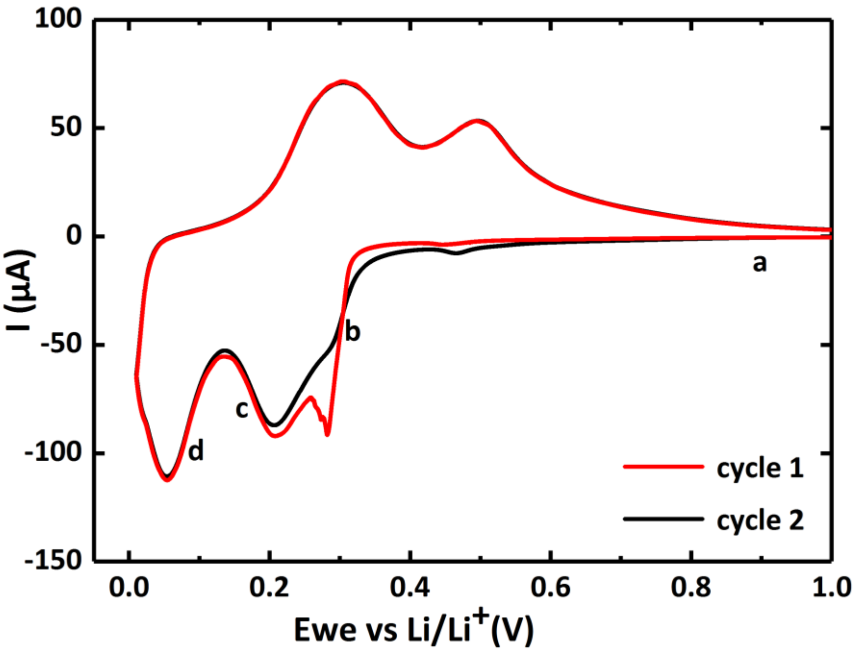

Fig. 2: Cyclic Voltammetry measurement of a 68 nm *thick amorphous silicon electrode at a slow potential scan rate of 0.01 mV s^{-1} in the potential range between 1 V and 0.01 V vs. Li/Li^+ for the initial two cycles. The points a-d refer to Fig. (3). Reproduced from ref. [7] with permission from the PCCP Owner Societies.*

The cyclic voltammetry measurements shown in *Fig. 2* are representative and in good agreement with already published data in literature [10, 11]. We observed four distinct reduction peaks in the cathodic branch and only two in the anodic branch. The two anodic peaks at around 0.3 V and 0.49 V vs. Li/Li^+ stands for Li^+ extraction, whereas the two cathodic peaks at 0.21 V and 0.06 V vs. Li/Li^+ are attributed to Li^+ insertion into amorphous silicon thin film [12 bis 15]. The irreversible capacity loss observed during the first lithiation cycle at 0.28 V is attributed to reduction of native SiO_2 [16].

Over 200 single in-operando neutron reflectometry patterns were continuously measured during the two cyclic voltammetry cycles. An extended neutron reflectivity scan up to q_z = 0.076 Å^{-1} was carried out before the cyclic voltammetry measurement was performed (virgin state). *Figure 3 (a)* shows selected neutron reflectometry patterns observed during the 1st cycle. A single neutron pattern measurement took about ~ 32 minutes. The resulting voltage span during a single NR pattern was around ~ 0.02

V. The observed NR patterns belong to the points a-d in the cathodic branch. The corresponding scattering length density profiles are shown in *Fig. 3 (b).*

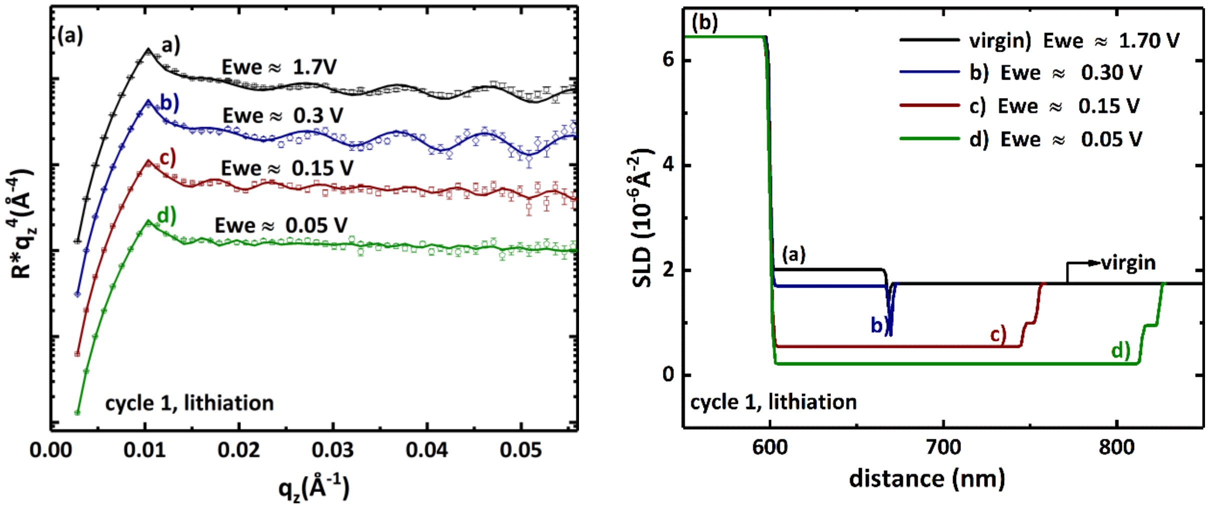

Fig. 3: (a) Neutron reflectometry pattern recorded during the first cycle at different cathodic potentials, together with the fitting results (solid lines) using Motofit. (b) The corresponding SLD profiles of the NR pattern observed in (a). Reproduced from ref. [7] with permission from the PCCP Owner Societies.

In Fig. 3 (a) (a-d) we can observe a change of the NR patterns as a function of the applied electrode potential, resulting from the lithium incorporation into the amorphous silicon electrode. Due to the negative scattering length of lithium a decrease of overall SLD for the a-Li$_x$Si is observed, see *Fig. 3 (b) (a-d). Figure 3 (b) (a-d)* also shows a change of the initial thickness (volume) of the electrode material, due to the Li incorporation. The NR pattern were fitted with the Motofit software using a box-layer model [8].

3.2 Volume and SLD changes of the silicon electrode

For the cyclic voltammetry measurements a 68 nm thick amorphous silicon film was deposited on a 400 nm thick copper current collector. Due to the substrate fixing of the electrode material, we assume a perpendicular expansion of the anode material during lithiation and neglected the expansion in parallel direction completely. So the observed changes in intial thickness L/L$_0$ are correlated to the volume changes V/V$_0$ of the electrode material during the lithiation\delithiation process.

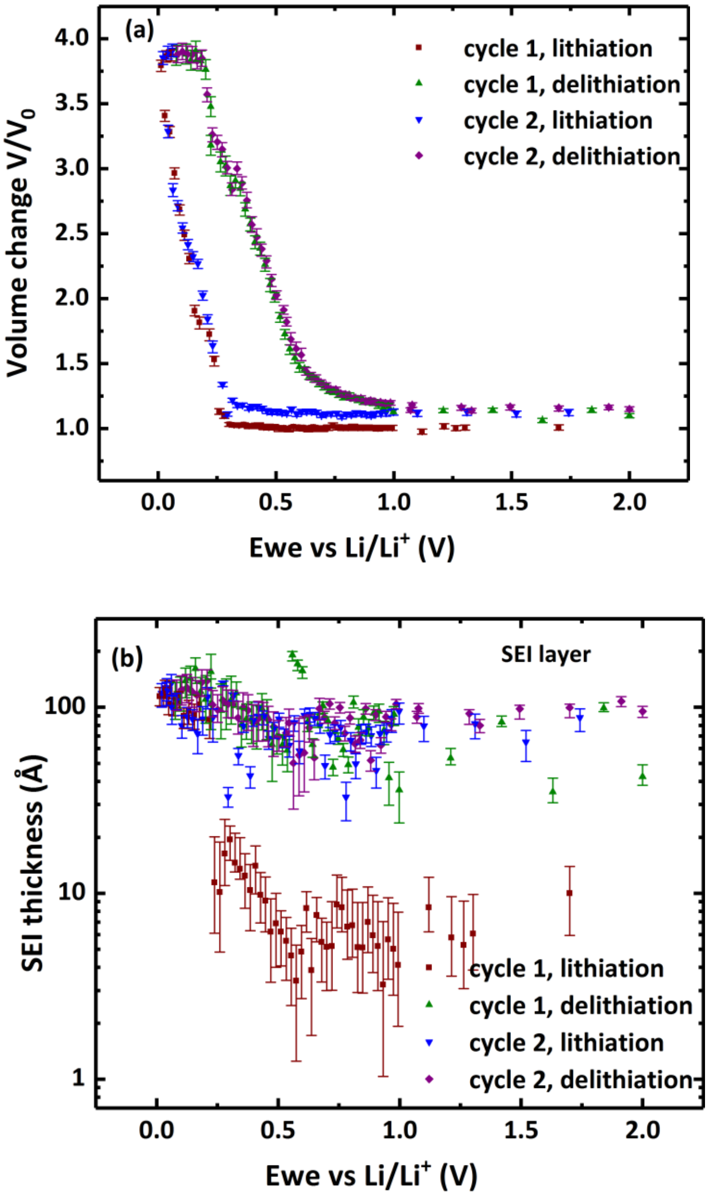

Fig. 4: (a) The relative volume change of the whole electrode material and (b) of the SEI layer thickness as function of the applied voltage on the working electrode. Reproduced from ref. [7] with permission from the PCCP Owner Societies.

Figure 4 (a) and *(b)* represents the relative volume changes of the amorphous silicon film and SEI layer thickness, measured during cyclic voltammetry. A volume expansion of the electrode material up to 390 % is observed. A hysteresis behavior of the of volume changes versus the applied potential is observed and attributed to result from the mechanic stress occurring during lithiation/delithiation process as suggested in the literature [7, 17 bis 19]. The SEI layer (*Fig. 4 (b)*) is formed during the first cyclic voltammetry cycle and grows up to 120 Å for potentials below 0.5 V vs. Li/Li$^+$ and a decrease in thickness down to 70 Å is observed during delithiation. The thickness of the SEI layer varies between 120 Å and 70 Å during cycling.

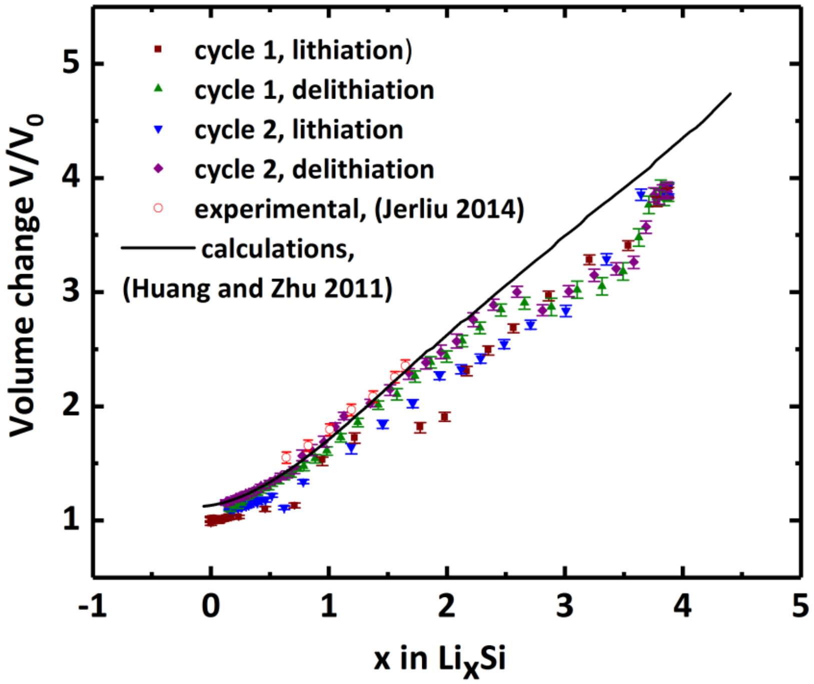

Fig. 5: (a) *Relative Volume changes (V/V$_0$) of the a-Li$_x$Si versus Li fraction x. The black solid line shows atomistic calculations, as given in ref. [20]. Literature data of relative volume changes of amorphous silicon during galvanostatic lithiation experiments are also shown in ref. [9]. Reproduced from ref. [7] with permission from the PCCP Owner Societies.*

Figure. 5 show the theoretical calculated volume expansion data (black solid line) of amorphous silicon film, based on atomistic calculations reported in ref. [20] together with experimental data measured during galvanostatic cycling done by our group ref. [9]. The slope calculated from the volume composition curve for the represented galvanostatic and cyclovoltametric mesurements in *Fig. 5* is in agreement with atomistic calculations reported in ref. [20]. Further detail on the cyclic voltammetry experiment and analysis can be found in ref. [7].

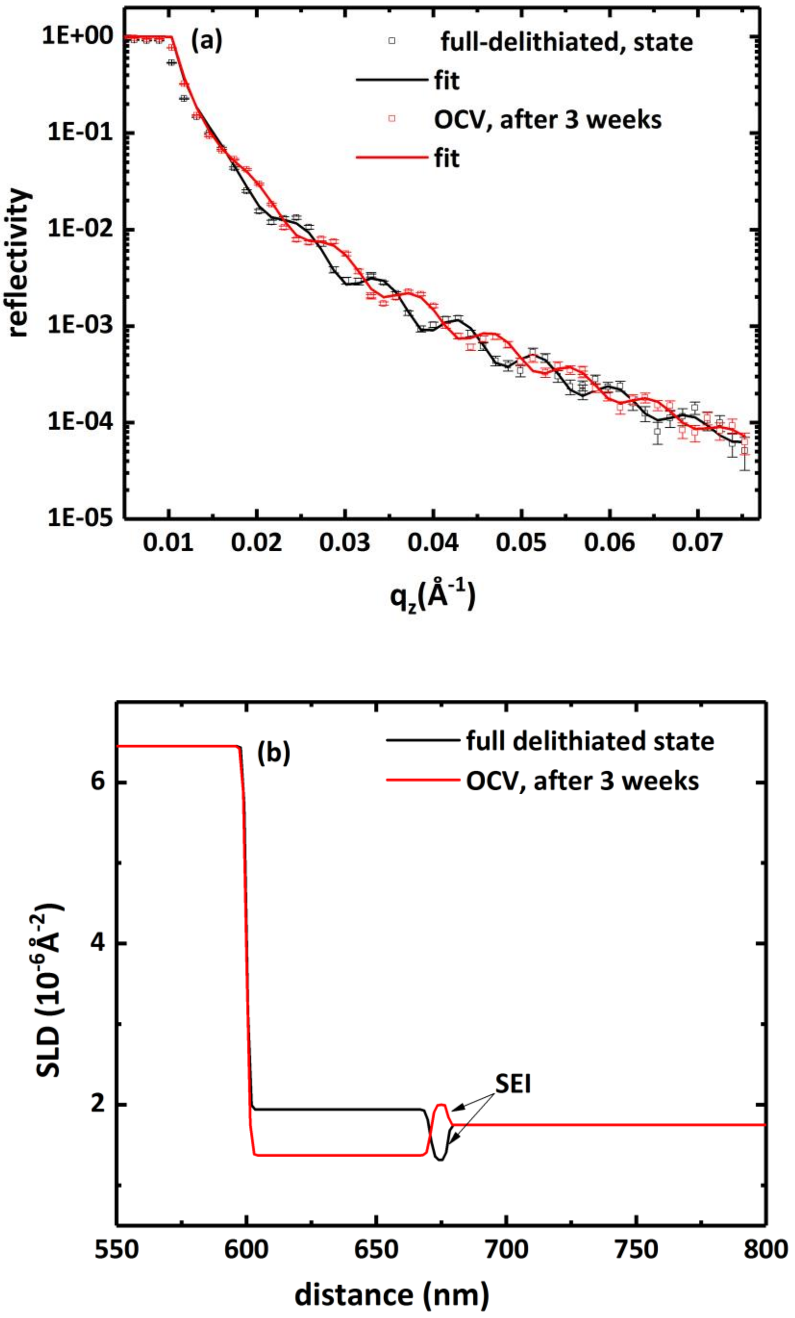

Fig. 6: (a) NR reflectivity patterns of a 68 nm thick amorphous silicon electrode in the full delithiated state (black square) after cycling galvanostatically with a current of 10 µA. Also shown is the same sample measured again after three weeks under open circuit conditions (red squares). The corresponding fits are also shown. (b) The corresponding SLD profiles for the NR measurements in Fig. 6 (a).

In context to battery performance also a possible reaction of the electrode/SEI and the electrolyte without electrochemical driving force is important. *Fig. 6 (a)* shows NR patterns of an amorphous silicon thin film electrode (~ 68 nm thickness) in the delithiated state. In this case electrochemical cycling was done galvanostatially at a low current of only 10 µA. The corresponding SLD is given in *Fig. 6 (b).* The SEI is clearly seen (arrow). In the fully discharged state the SEI is enriched with lithium as indicated by the lower SLD compared to the main a-Li_xSi layer. After three weeks of storing at open circuit conditions the sample was re-measured. We found that the NR pattern is modified. SEI and Li_xSi layer did not change significantly in thickness but the SLD of the SEI is enhanced while that of the Li_xSi layer is decreased. This can qualitatively be explained with the fact that the amount of Li initially stored in the SEI layer is diffused into the a-Li_xSi. In addition, also small amounts of Li from the electrolyte might be introduced additionally into the electrode (not electrochemically driven) in order to fulfil the Li mass balance. The fact that the SLD of the SEI is enhanced (meaning Li depleted) is difficult to understand. A possible explanation might be that the SEI is not depleted in Li (negative scattering length) but enriched with ions from the electrolyte leading to a high SLD like Cl (high positive SLD). Battery performance is strongly affected by the properties of the SEI layer. If the SEI layer is not stable also under open circuit conditions the inherent instability of the system is augmented. Possibly an artificial SEI might be a solution to the problem.

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