Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Material to

Lithium Insertion into Silicon Electrodes Studied by Cyclic Voltammetry and *Operando* Neutron Reflectometry

B. Jerliu[1,*], E. Hüger[1], L. Dörrer[1], B. K. Seidlhofer[2], R. Steitz[2], M. Horisberger[3], H. Schmidt[1,4]

[1]Technische Universität Clausthal, Institut für Metallurgie, AG Mikrokinetik, Robert-Koch-Str. 42, 38678 Clausthal-Zellerfeld, Germany.
[2]Helmholtz-Zentrum Berlin für Materialien und Energie, Soft Matter and Functional Materials, Hahn-Meitner-Platz 1, 14109, Berlin, Germany.
[3]Laboratory for Scientific Developments and Novel Materials, Paul-Scherrer-Institut, 5232 Villigen, Switzerland.
[4]Clausthaler Zentrum für Materialtechnik, Leibnizstraße 9, 38678 Clausthal-Zellerfeld, Germany.

1. Additional Figures

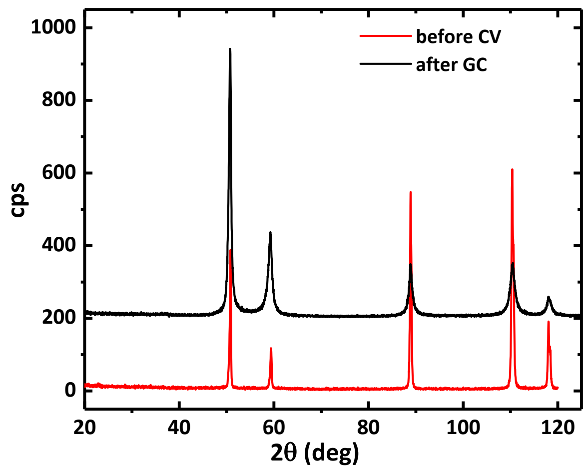

Fig. S1: Grazing incidence X-ray diffraction pattern of the silicon electrode before CV measurements were done (before CV). Only intense sharp Bragg peaks from the copper current collector are visible. Also shown is the pattern of an electrode with a similar silicon thickness of 400 Å after galvanostatic cycling at different charging rates (after GC). No additional peaks are observed. The patterns are shifted for clarity.

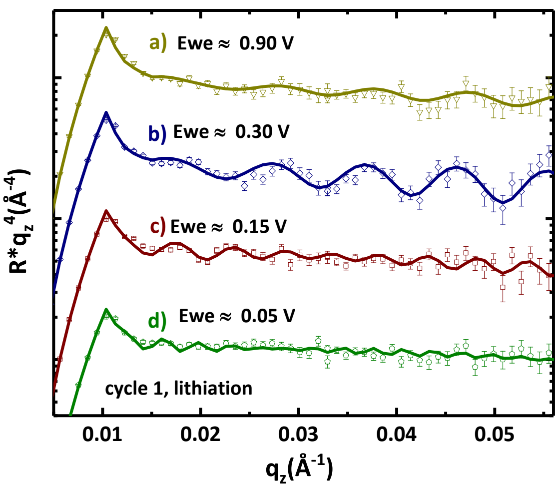

Fig. S2: Neutron reflectivity (R) patterns from Fig. 2(a) of the main manuscript plotted as R q_z^4 vs. q_z.

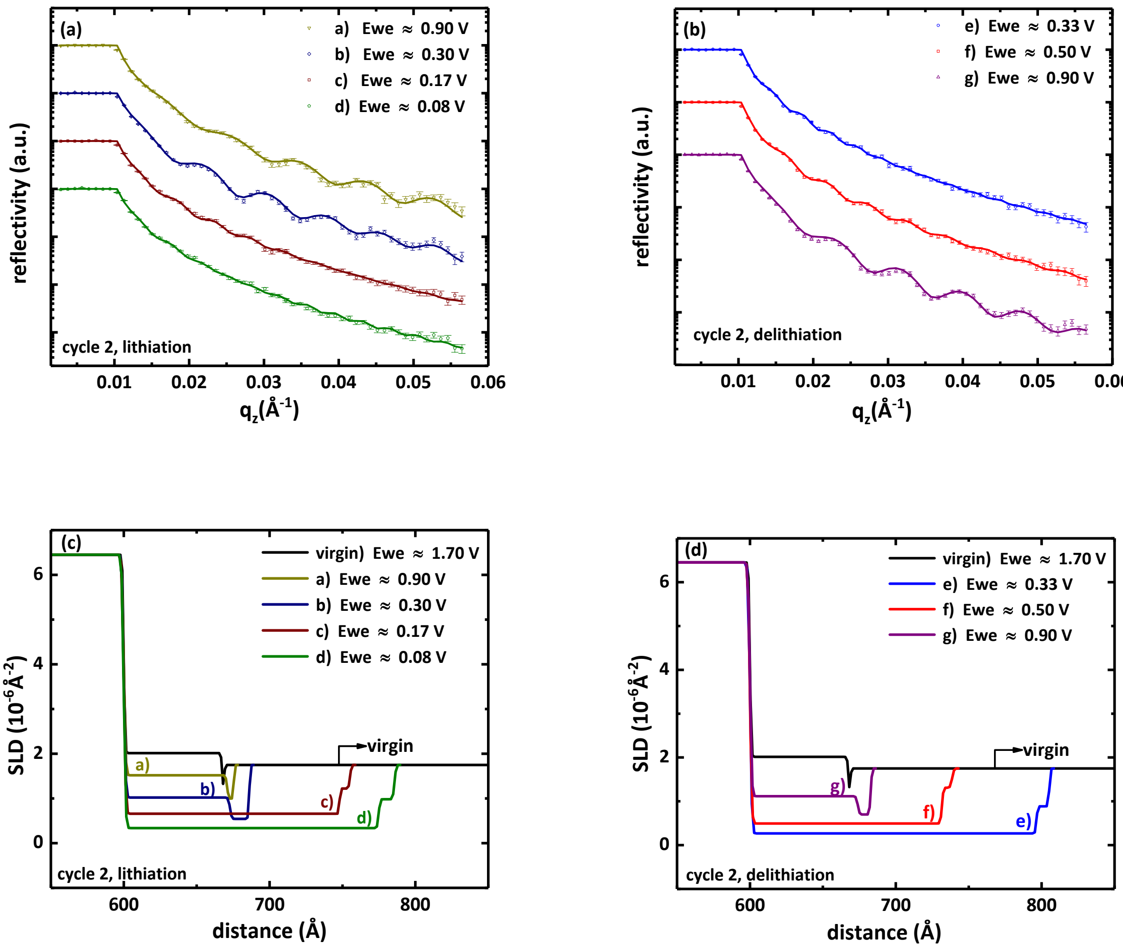

Fig. S3: Neutron reflectometry profiles obtained by operando measurements during the second cycle of the CV measurements at different potentials for (a) lithiation and (b) delithiation. The potentials given correspond to the alphabetic characters of Fig. 1 (main manuscript). Reflectivities are shifted for clarity. Also shown are the fitting results using Motofit (lines). Corresponding SLD profiles to the reflectivity measurements in (a) and (b) for (c) lithiation and (d) delithiation are also given.

2. Electrochemistry

Fig. S4 shows the potential of the working electrode versus relative Li fraction x in a-Li_xSi, which was calculated using the equation

$$x = \frac{I\, t\, M_{Si}}{F\, m_{Si}} \qquad \text{(S1)}$$

where $m_{Si} \approx 1.9 \times 10^{-4}$ g is the actual silicon electrode mass, F = 96487 C/mol is the Faraday constant, and M_{Si} = 28.09 g/mol is the molar mass of silicon. The quantities are calculated for a radius of the circular silicon electrode of 20.25 mm (contact area), a layer thickness of about 680 Å and a mass density of 2.19 g/cm^3. The current I for a given time t is obtained from Fig. 1 of the main manuscript. The curves are similar to galvanostatic lithiation/delithiation curves as found in literature (McDowell et al. 2013) main manuscript and measured in our laboratory on a similar system (see Fig. S5). We get a maximum nominal capacity of about 3700 mAh/g and a Coulombic efficiency of 95.8 % and 98.7 % for the first and second cycle, respectively.

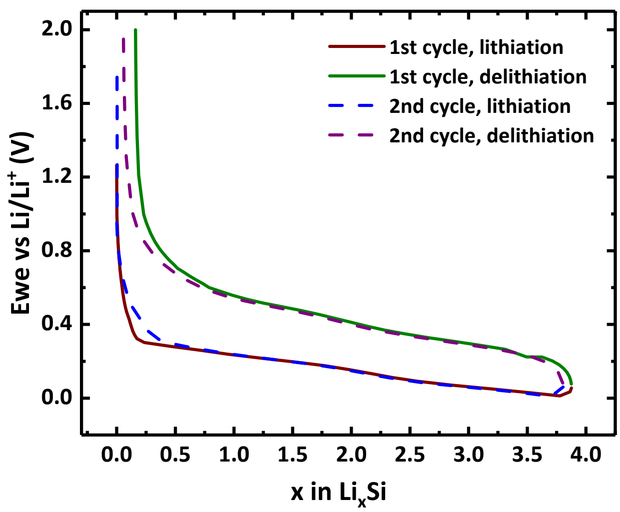

Fig. S4: Electrode potential Ewe as a function of Li fraction x in a-Li_xSi for the two cycles of the CV measurements (x calculated from CV measurements according to eq. (S1)).

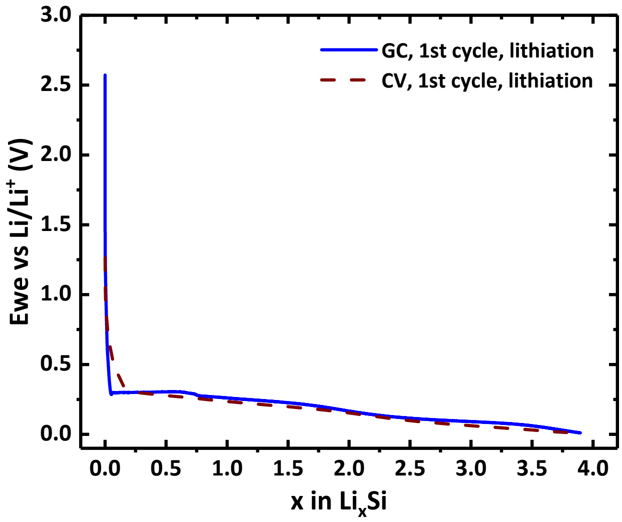

Fig. S5: Electrode potential Ewe as a function of Li fraction x in Li_xSi during lithiation as calculated from electrochemical measurements (first cycle) according to eq. (S1) for the CV measurements shown in S4 and for galvanostatic charging of a different but similar silicon electrode with 40 µA (GC).

3. Additional Tables

Tab. S1: Layer thickness and scattering length density (SLD) of the a-Li_xSi layer and of the SEI as obtained from the fits in Fig. 3(a, b) of the main manuscript for the first cycle at different potentials. Fitting was done between 0.003 and 0.055 Å^{-1} using the Motofit program package and the Generic algorithm. The parameters of the quartz block, of the copper layer and of the electrolyte as given in Tab. 1 of the main manuscript for the virgin state were kept fixed during the fit. Error limits correspond to a 10 % increase of χ^2 of the best fit with respect to the fitted parameter only. For details see manuscript.

CV, cycle 1		Amorphous Li_xSi			SEI
		Thickness (Å)	SLD (x 10^{-6} Å^{-2})	Thickness (Å)	SLD (x 10^{-6} Å^{-2})
	virgin, Ewe ~ 1.70 V	674 ± 7	2.01 ± 0.05	10 ± 4	0.92 ± 0.32
a)	Ewe ~ 0.90 V	681 ± 13	1.75 ± 0.12	5 ± 4	0.50 ± 0.90
b)	Ewe ~ 0.30 V	686 ± 6	1.70 ± 0.22	19 ± 5	0.64 ± 0.28
c)	Ewe ~ 0.16 V	1213 ± 22	0.54 ± 0.14	90 ± 14	0.99 ± 0.26
d)	Ewe ~ 0.05 V	2142 ± 37	0.21 ± 0.11	104 ± 17	0.95 ± 0.23
e)	Ewe ~ 0.33 V	1864 ± 23	0.09 ± 0.13	119 ± 19	0.83 ± 0.28
f)	Ewe ~ 0.50 V	1307 ± 18	0.50 ± 0.11	69 ± 13	0.99 ± 0.26
g)	Ewe ~ 0.90 V	731 ± 5	1.33 ± 0.12	92 ± 7	0.97 ± 0.16

Tab. S2 Layer thickness and scattering length density (SLD) of the a-Li_xSi layer and of the SEI as obtained from the fits in Fig. S3 for the second cycle at different potentials. Fitting was done between 0.003 and 0.055 $Å^{-1}$ using the Motofit program package and the Generic algorithm. The parameters of the quartz block, of the copper layer and of the electrolyte as given in Tab. 1 of the main manuscript for the virgin state were kept fixed during the fit. Error limits correspond to a 10 % increase of χ^2 of the best fit with respect to the fitted parameter only. For details see manuscript.

CV, cycle 2		Amorphous Li_xSi			SEI
		Thickness (Å)	SLD ($x\ 10^{-6}\ Å^{-2}$)	Thickness (Å)	SLD ($x\ 10^{-6}\ Å^{-2}$)
	virgin, Ewe ~ 1. 70 V	67 4± 7	2.01 ± 0.05	10 ± 4	0.92 ± 0.32
a)	Ewe ~ 0.90 V	709 ± 7	1.51 ± 0.14	46 ± 9	0.99 ± 0.16
b)	Ewe ~ 0.30 V	728 ± 5	1.02 ± 0.11	132 ± 5	0.54 ± 0.20
c)	Ewe ~ 0.17 V	1480 ± 20	0.66 ± 0.10	72 ± 13	1.21 ± 0.15
d)	Ewe ~ 0.08 V	1748 ± 26	0.34 ± 0.12	108 ± 20	0.98 ± 0.31
e)	Ewe ~ 0.33 V	1965 ± 19	0.26 ± 0.10	88 ± 13	0.88 ± 0.23
f)	Ewe ~ 0.50 V	1316 ± 12	0.49 ± 0.01	69 ± 15	1.31 ± 0.16
g)	Ewe ~ 0.90 V	741 ± 5	1.23 ± 0.14	90 ± 7	0.75 ± 0.15