

## Supporting information

# *In situ* Studies of Solid Electrolyte Interphase (SEI) Formation on Crystalline Carbon Surfaces by Neutron Reflectometry and Atomic Force Microscopy

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Table S1: Fitting results for the X-Ray Reflectometry Measurement (#1, before cycling) in Figure 2 (a).

Component	Thickness / Å	Electron Density / $10^{-6} \text{ Å}^{-2}$	Roughness / Å	$\chi^2$
Carbon 1	119 ± 14	12.99 ± 0.70	59.4 ± 5.7	0.0083
Carbon 2	513 ± 4	14.36 ± 0.19	22.9 ± 5.0	
SiO <sub>2</sub>	30 ± 1	18.9 (fixed)	12.3 ± 0.3	
Silicon	INF	20.10 (fixed)	11.1 ± 0.5	

Table S2: Fitting results for the X-Ray Reflectometry Measurement (#2, before cycling) in Figure 2 (b).

Component	Thickness / Å	Electron Density / $10^{-6} \text{ Å}^{-2}$	Roughness / Å	$\chi^2$
Carbon 1	122 ± 16	11.28 ± 2.98	54.8 ± 10.7	0.0106
Carbon 2	422 ± 10	15.80 ± 0.13	47.5 ± 11.4	
SiO <sub>2</sub>	26 ± 1	18.9 (fixed)	9.7 ± 0.3	
Silicon	INF	20.10 (fixed)	9.8 ± 0.4	

Table S3: Fitting results for the X-Ray Reflectometry Measurement (#1, after cycling) in Figure 2 (c).

Component	Thickness / Å	Electron Density / $10^{-6} \text{ Å}^{-2}$	Roughness / Å	$\chi^2$
SEI 1	74 ± 19	8.30 ± 6.40	57.0 ± 26.8	0.0060
SEI 2	200 ± 48	13.82 ± 2.06	57.7 ± 8.8	
Carbon 1	103 ± 14	10.76 ± 1.32	51.1 ± 14.3	
Carbon 2	451 ± 16	10.20 ± 0.08	46.0 ± 33.5	
SiO <sub>2</sub>	32 ± 8	16.81 ± 0.94	12.3 ± 0.7	
Silicon	INF	20.10 (fixed)	25.3 ± 6.4	

Table S4: Fitting results for the X-Ray Reflectometry Measurement (#2, after cycling) in Figure 2 (d).

Component	Thickness / Å	Electron Density / $10^{-6} \text{ Å}^{-2}$	Roughness / Å	$\chi^2$
SEI 1	80 ± 19	7.92 ± 2.04	49.2 ± 10.4	0.0145
SEI 2	205 ± 48	13.01 ± 1.03	58.0 ± 15.0	
Carbon 1 + 2	545 ± 26	11.37 ± 0.38	48.8 ± 15.3	
SiO <sub>2</sub>	22 ± 1	15.04 ± 0.40	10.5 ± 0.2	
Silicon	INF	20.10 (fixed)	24.7 ± 1.1	

Table S5: Fitting results for the Neutron Reflectometry Measurements obtained during discharging in Figure 3 (a) including thickness (t), scattering length density (SLD) and roughness (R) of the layers.

U	Carbon			SEI			$\chi^2$
	t / Å	SLD / $10^{-6} \text{ Å}^{-6}$	R / Å	t / Å	SLD / $10^{-6} \text{ Å}^{-6}$	R / Å	
OCV	344 ± 1	3.56 ± 0.02	29 ± 1	73 ± 3	0.42 ± 0.03	13 ± 0	0.0036
1,50 V	346 ± 5	3.53 ± 0.06	34 ± 6	48 ± 3	-0.08 ± 0.12	22 ± 1	0.0450
1,25 V	345 ± 4	3.46 ± 0.05	34 ± 5	51 ± 3	-0.10 ± 0.10	34 ± 1	0.0368
1,00 V	345 ± 4	3.45 ± 0.06	31 ± 5	55 ± 3	-0.03 ± 1.10	32 ± 1	0.0448
0,80 V	351 ± 6	3.35 ± 0.07	39 ± 7	55 ± 4	0.01 ± 0.14	27 ± 1	0.0638
0,60 V	350 ± 7	3.12 ± 0.06	35 ± 7	56 ± 5	0.19 ± 0.12	27 ± 1	0.0594
0,50 V	353 ± 11	2.95 ± 0.06	39 ± 8	66 ± 7	0.70 ± 0.08	17 ± 2	0.0353
0,40 V	359 ± 16	2.76 ± 0.06	48 ± 12	81 ± 9	0.54 ± 0.10	28 ± 2	0.0757
0,30 V	371 ± 22	2.69 ± 0.05	74 ± 15	91 ± 13	0.83 ± 0.07	21 ± 2	0.0601
0,20 V	360 ± 32	2.52 ± 0.08	78 ± 22	180 ± 14	0.84 ± 0.10	24 ± 1	0.0572
0,10 V	363 ± 72	2.53 ± 0.24	80 ± 21	184 ± 43	0.80 ± 0.24	15 ± 2	0.0618
0,02 V	375 ± 81	2.53 ± 0.12	96 ± 31	192 ± 28	0.80 ± 0.16	15 ± 2	0.0959

Table S6: Fitting results for the Neutron Reflectometry Measurements obtained during charging in Figure 3 (b) including thickness (t), scattering length density (SLD) and roughness (R) of the different layers.

U	Carbon			SEI			$\chi^2$
	t / Å	SLD / $10^{-6}\text{\AA}^{-2}$	R / Å	t / Å	SLD / $10^{-6}\text{\AA}^{-2}$	R / Å	
OCV	341 ± 19	2.64 ± 0.03	55 ± 7	124 ± 19	1.15 ± 0.04	11 ± 1	0.0365
1,50 V	349 ± 40	2.63 ± 0.05	60 ± 13	123 ± 13	1.01 ± 0.06	19 ± 2	0.0491
1,00 V	347 ± 58	2.70 ± 0.08	98 ± 21	140 ± 54	0.94 ± 0.10	15 ± 2	0.0711

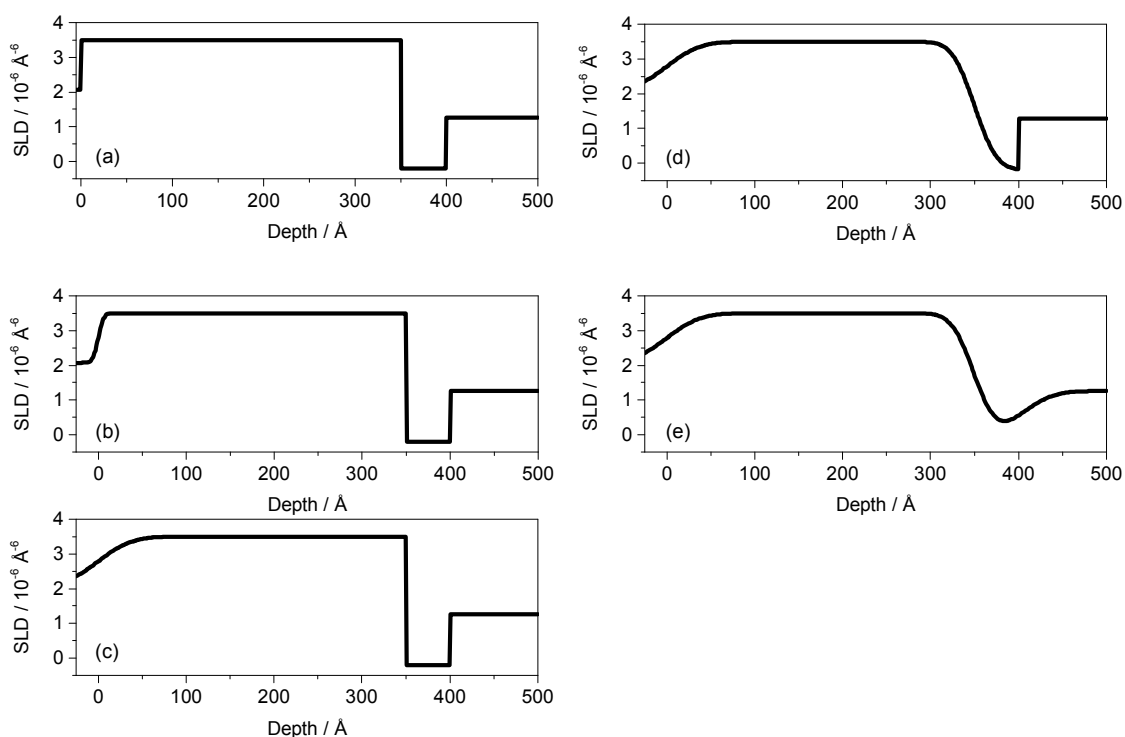


Figure S1. (a) Simulated SLD behavior for three layers (350 Å graphite, 50 Å SEI, electrolyte as fronting) on a silicon backing. The silicon's SLD is  $2.07 \cdot 10^{-6} \text{\AA}^{-2}$ , the graphite's SLD is  $3.5 \cdot 10^{-6} \text{\AA}^{-2}$ , the SEI's SLD is  $-0.2 \cdot 10^{-6} \text{\AA}^{-2}$  and the SLD of the electrolyte is  $1.263 \cdot 10^{-6} \text{\AA}^{-2}$ . The different layers are ideally smooth. (b) Simulated SLD behavior with a roughness of 5 Å at the silicon surface. (c) Simulated SLD behavior with a roughness of 30 Å at the silicon surface. (d) Simulated SLD behavior with a roughness of 30 Å at the silicon surface and a roughness of 20 Å at the carbon surface. (e) Simulated SLD behavior with a roughness of 30 Å at the silicon surface, 20 Å at the carbon surface and 30 Å at the SEI surface. Even though the SEI roughness remains unchanged, the overlapping SLDs of the electrolyte and the SEI lead to an averaged SLD in the diagram.

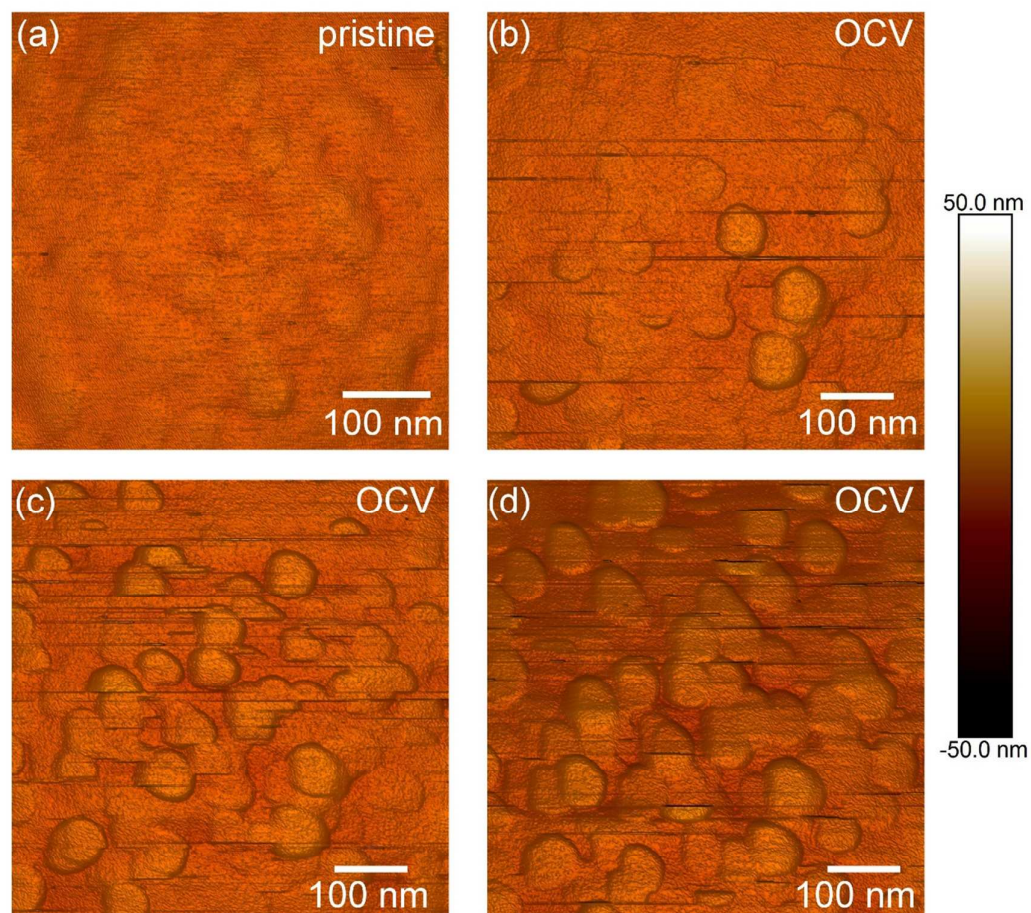


Figure S2. AFM images of (a) the pristine model electrode surface, (b) the model electrode at OCV after 24 min in contact with the electrolyte, (c) the model electrode at OCV after 28 min in contact with the electrolyte, (d) the model electrode at OCV after 33 min in contact with the electrolyte. Images (b)-(d) were taken at the same surface spot of the model electrode, while (a) was taken at a different surface spot.