Supporting Information for:

Enhanced Interfacial Stability of Si Anodes for Li-Ion Batteries via Surface SiO_2 Coating

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This document contains three sections, each of which starts on a new page:

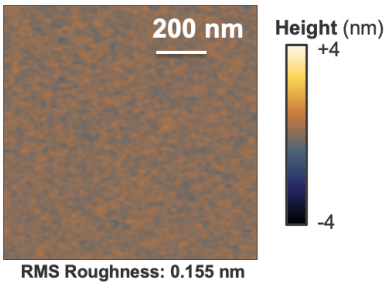
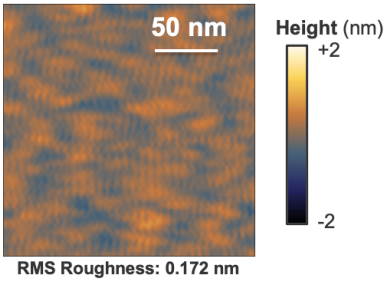
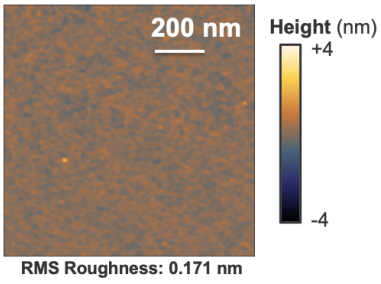
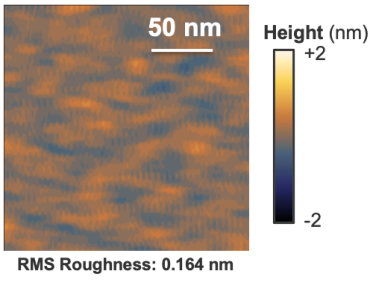
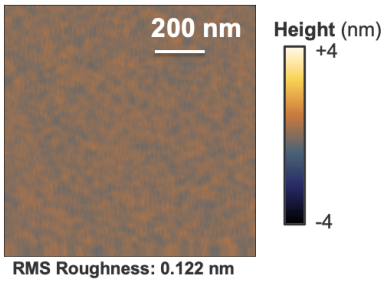
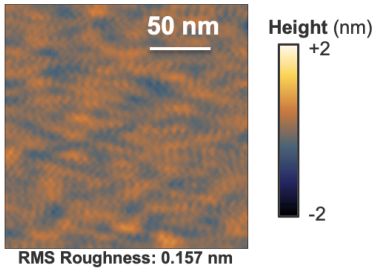
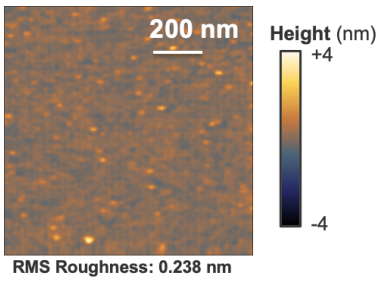
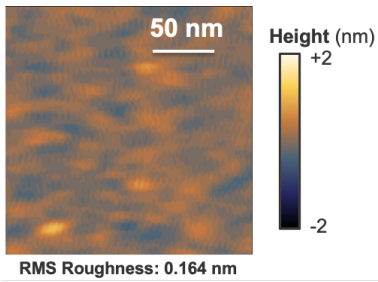
1. Atomic Force Microscopy of pristine oxidized and etched surfaces
2. Full Galvanostatic Cycling and dQ/dV data.
3. Full XPS fitting results, including quantitative analysis.

A list of references is included at the end of the document.

Atomic Force Microscopy of pristine oxidized and etched surfaces

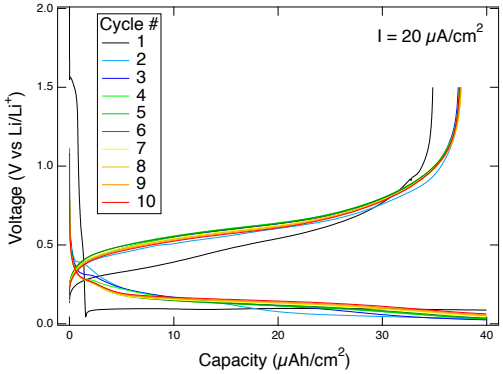
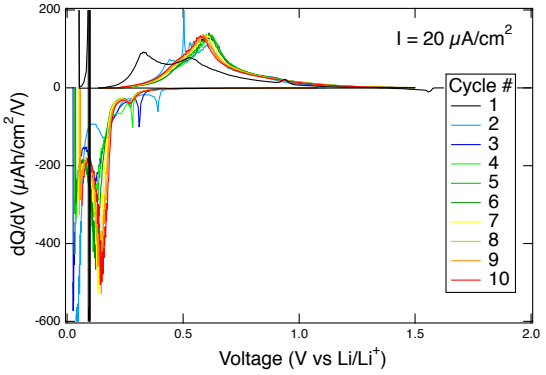
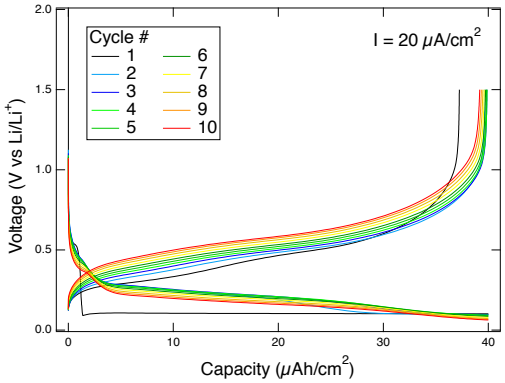
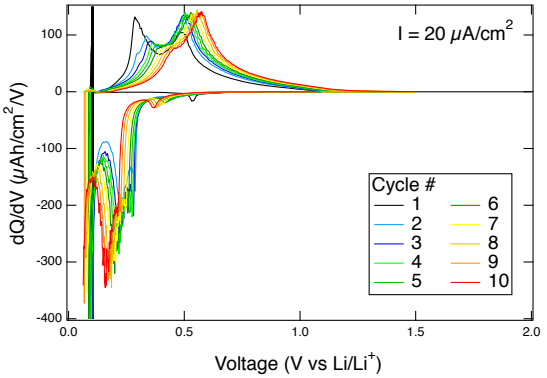
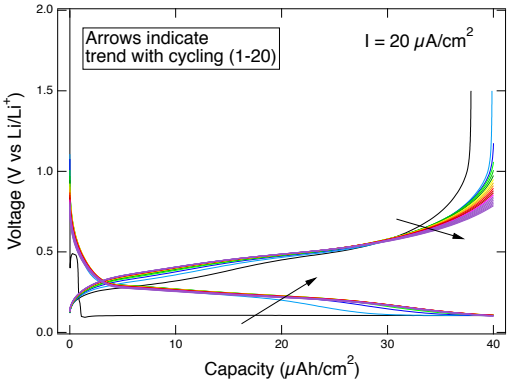
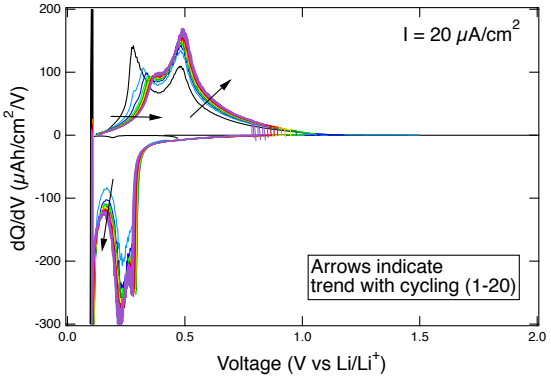
Atomic Force Microscopy (Veeco D5000) was used to image the pristine sample surfaces in tapping mode with Oxford Instruments AC160TS-R3 silicon probes. Thermal and native oxide surfaces were imaged before and after etching in dilute hydrofluoric acid (HF). Etched surfaces correspond to the "No SiO_x" samples described in this manuscript. It can be seen that the impact of HF is minor; root-mean-square surface roughnesses remain below 0.25 nm for all samples.

Figure S1. Atomic Force Microscopy images (left: 1 × 1 µm, right: 0.2 × 0.2 µm) and associated root-mean-square surface roughness values for thermal and native oxide surfaces before and after HF etching.

	1 × 1 µm	**0.2 × 0.2 µm**
Thermal SiO_2		
Thermal SiO_2, etched (No SiO_x)		
Native SiO_x		
Native SiO_x, etched (No SiO_x)		

Full Cycling and dQ/dV Data

Figure S2. All galvanostatic cycles, and dQ/dV plots derived from them, corresponding to Figures 1 and 4 of the main manuscript. Discontinuities have been removed from the dQ/dV plots. Ten cycles are shown for "No SiO_x" and native SiO_x, and 20 cycles for thermal SiO_2.

	Cycling Data	**dQ/dV Data**
No SiO_x		
Native SiO_x		
Thermal SiO_2		

Full XPS Fitting Results

During XPS measurement Si 2p, C 1s, O 1s, Li 1s, F 1s, and P 2p core levels were acquired and fitted. All peaks were fitted together to ensure that the peaks for a given bond are consistent across both core levels. Bonds are identified based on a characteristic binding energy difference between the associated core levels[1]. Si 2p, F 1s and P 2p levels were provided in Figures 2 and 3 of the main manuscript. This section shows all fitted C 1s, O 1s, and Li 1s core levels, in Figures S3-S5. The pristine levels are omitted for Li 1s because those samples had negligible Li. Across all figures, the same component is shaded with the same color, e.g. LiF is turquoise in both F 1s and Li 1s.

Furthermore, the quantitative fit results are tabulated in Tables S1-S3. For each phase present in each core level, the peak position in eV and atomic % is tabulated. The atomic % refers to the analysis volume (~4-6 nm deep), which differs in its sensitivity to lower layers depending on the thickness of upper layers.

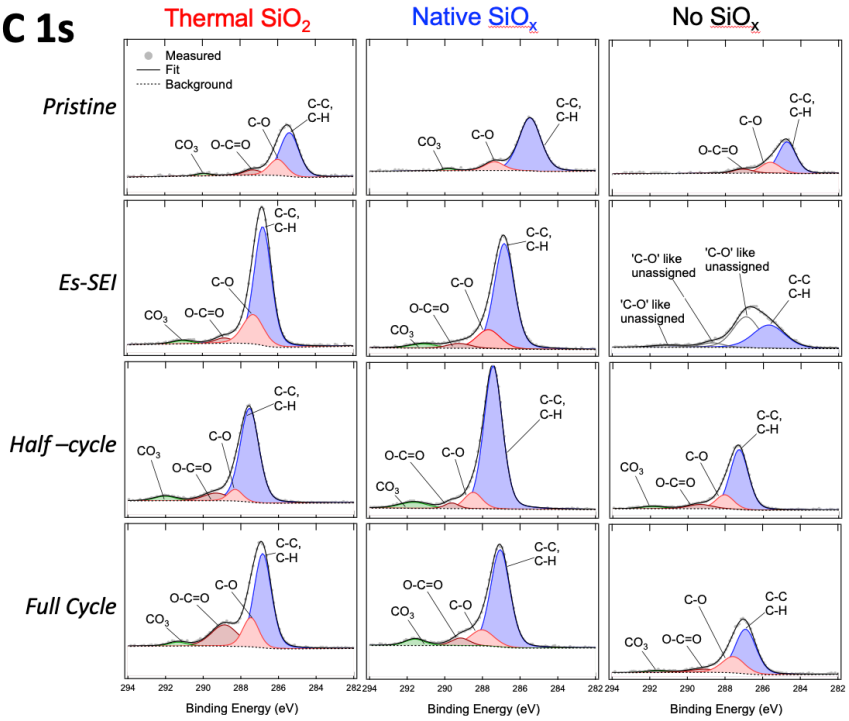


Figure S3. Fitted C 1s core level XPS data for the three Si surfaces investigated. For each surface, spectra acquired on pristine samples, at 115 mV (early stage SEI, es-SEI), after half a cycle (lithiated) and after a full cycle (delithiated) are shown from top to bottom. All panels use the same scale on both axes and all panels share the legend of the top-left panel. The following bonds are shaded: C-C/C-H (blue), C-O (light red), O-C=O (dark red), CO_3 (green).

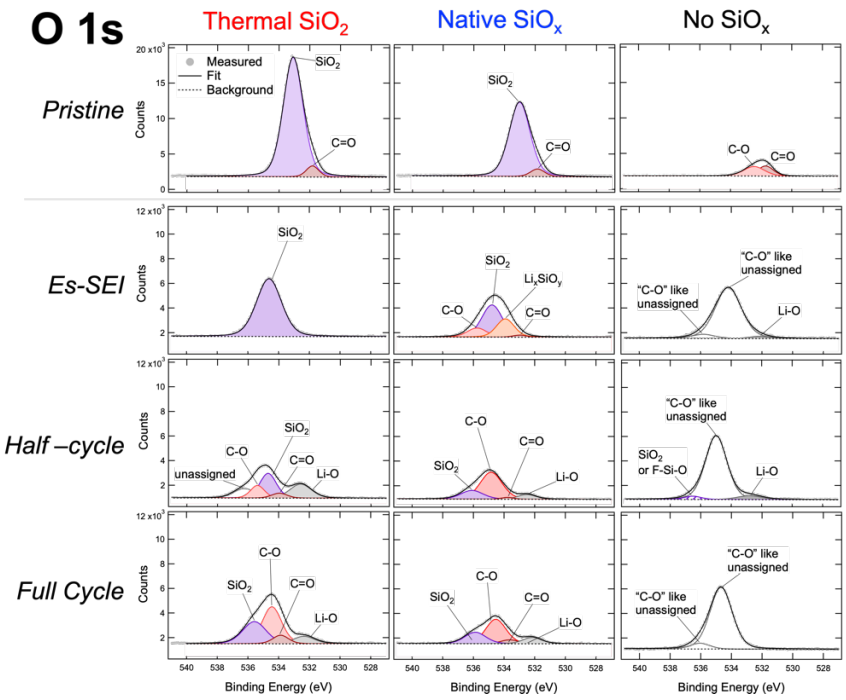


Figure S4. Fitted O 1s core level XPS data for the three Si surfaces investigated. For each surface, spectra acquired on pristine samples, at 115 mV (early stage SEI, es-SEI), after half a cycle (lithiated) and after a full cycle (delithiated) are shown from top to bottom. All panels use the same binding energy scale, and apart from the pristine spectra all panels use the same vertical scale. All panels share the legend of the top-left panel. The following components are shaded: SiO_2 (purple), Li_xSiO_y (orange), C-O (light red), C=O (dark red), Li-O (grey). Li-O is a bond that could originate from Li_xSiO_y, Li_2O, or LiOH. Where peaks could not be unequivocally assigned, they remain unassigned, but this should not be taken as evidence that the phases seen in other panels are absent.

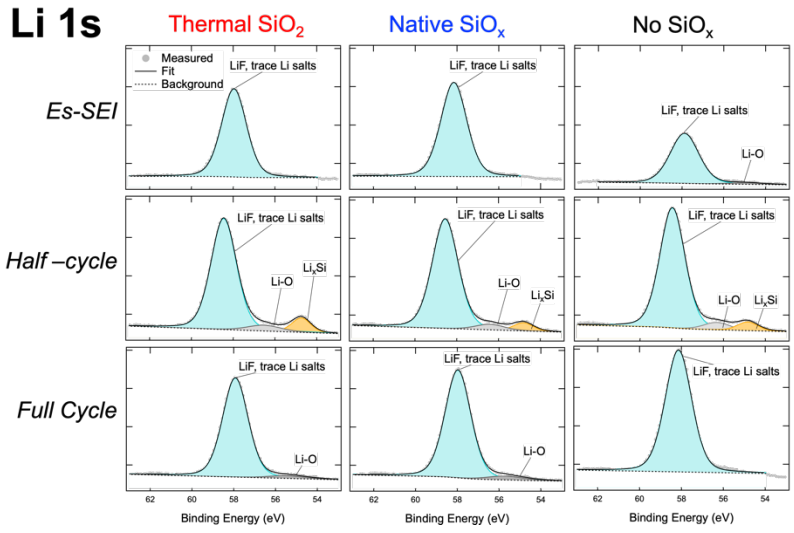


Figure S5. Fitted Li 1s core level XPS data for the three Si surfaces investigated. For each surface, spectra acquired at 115 mV (early stage SEI, es-SEI), after half a cycle (lithiated) and after a full cycle (delithiated) are shown from top to bottom. Spectra on pristine samples showed only trace lithium. All panels use the same scale on both axes, and share the legend of the top left panel. The following phases are shaded: LiF (turquoise), Li-O (grey), and Li_xSi (yellow). Li-O is a bond that could originate from Li_xSiO_y, Li_2O, or LiOH.

Thermal SiO_2, 1.4 nm, compositions

Table S1. Quantitative fitting results to XPS data of thermal SiO_2. For each phase present in each core level, the peak position in eV and atomic % is tabulated. The atomic % refers to the analyzed volume, which differs in its sensitivity to lower layers depending on the thickness of upper layers. "$LiPF_6$ dec. prod." denotes a $LiPF_6$ decomposition product. Li-O denotes a bond that could be present in Li_xSiO_y, Li_2O, or LiOH.

	Pristine		**Early-stage SEI**		**Half-cycle**		**Full cycle**	
	Position	at.%	Position	at.%	Position	at.%	Position	at.%
Fluorine								
LiF			687.08	33.32	687.65	36.62	687.09	32.56
P-F			688.78	4.95	689.19	1.89	688.3	3.93
P-F					690.33	1.41	689.72	3.72
Oxygen								
SiO_2	533.09	30.83	534.63	6.58	534.71	1.64	535.58	2.26
Li-O					532.59	1.21	532.35	0.69
unassigned					536.26	0.80		
C-O					535.4	0.71	534.44	3.11
C=O	531.83	1.84			533.97	0.31	533.87	0.59
Carbon								
C-C, C-H	285.38	5.59	286.8	8.30	287.54	6.33	286.84	6.44
C-O	286	1.86	287.31	2.47	288.3	0.60	287.47	1.82
O-C=O	287.33	0.62	291.08	0.26	289.33	0.66	291.35	2.19
CO_3	289.96	0.22	288.86	0.38	292.03	0.35	288.87	0.28
Silicon								
Si	99.06	45.19	99.49	6.76			99.4	2.64
Li_xSi					97.93	1.22		
SiO_2	103.63	13.59	105.69	3.00	105.14	0.43	106.12	0.42
F-Si-O					107.09	0.18		
Li_xSiO_y					103.34	0.67	104.24	0.56
unassigned							103.1	0.10
Phosphorous								
$LiPF_6$ dec. prod.			137.42	0.45	138	0.51	137.15	1.14
$LiPF_6$ dec. prod.					139.85	0.15	137.99	0.57
Lithium								
Li_xSi					54.75	3.64		
LiF and other salts			57.96	33.53	58.45	38.10	57.93	36.97
Li-O					56.53	2.58	55.47	1.43

Native SiO_x, 1.3nm, compositions

Table S2. Quantitative fitting results to XPS data of native SiO_x. For each phase present in each core level, the peak position in eV and atomic % is tabulated. The atomic % refers to the analysed volume, which differs in its sensitivity to lower layers depending on the thickness of upper layers. "$LiPF_6$ dec. prod." denotes a $LiPF_6$ decomposition product. Li-O denotes a bond that could be present in Li_xSiO_y, Li_2O, or LiOH.

	Pristine		**Early-stage SEI**		**Half-cycle**		**Full cycle**	
	Position	at.%	Position	at.%	Position	at.%	Position	at.%
Fluorine								
LiF			687.3	36.62	687.75	35.68	687.16	36.03
P-F			689.2	3.97	689.75	3.24	689.11	4.66
Oxygen								
SiO_2	533.02	22.28	534.8	0.77	536.1	0.79	535.88	1.02
Li-O			533.9	1.41	532.52	0.35	532.17	0.5
C-O			535.8	2.88	534.85	2.42	534.54	2.09
C=O	531.85	1.56	533	0.12	533.77	0.09	533.63	0.3
Carbon								
C-C, C-H	285.48	8.61	286.85	8.12	287.44	9.72	287.06	7.07
C-O	287.37	1.21	287.69	1.74	288.5	1.06	288.02	1.42
O-C=O			289.25	0.45	289.64	0.28	289.16	0.51
CO_3	289.82	0.19	291.15	0.45	291.68	0.63	291.59	0.47
Silicon								
Si	99.12	55.56	99.44	5.06			99.44	3.15
SiO_2	103.55	8.21	106.05	1.36	107.01	0.43	106.46	0.44
Li_xSi					97.91	0.64		
Li_xSiO_y			104.45	0.23	103.44	0.25	103.75	0.25
Phosphorous								
$LiPF_6$ dec. prod.			136.79	0.67	137.94	0.54	137.41	0.41
$LiPF_6$ dec. prod.			138.75	0.37	139.76	0.23	139.11	0.38
Lithium								
Li_xSi					54.81	2.17		
LiF and other salts			58.16	35.67	58.56	39.27	57.98	39.34
Li-O					56.41	2.18	55.73	1.95

No SiO_x, compositions

Table S3. Quantitative fitting results to XPS data of SiO_x-free Si. For each phase present in each core level, the peak position in eV and atomic % is tabulated. The atomic % refers to the analysed volume, which differs in its sensitivity to lower layers depending on the thickness of upper layers. "$LiPF_6$ dec. prod." denotes a $LiPF_6$ decomposition product. Li-O denotes a bond that could be present in Li_xSiO_y, Li_2O, or LiOH.

	Pristine		**Early-stage SEI**		**Half-cycle**		**Full cycle**	
	Position	at.%	Position	at.%	Position	at.%	Position	at.%
Fluorine								
LiF			687	23.13	687.66	35.64	687.25	30.16
P-F			687.87	3.15	689.34	1.57	687.91	8.2
P-F			689.97	5.48	690.86	3.76	690.46	4.96
Oxygen								
SiO_2/F-Si-O					536.53	0.22		
Li-O			532.14	0.24	532.8	0.37		
C-O	531.71	3.02						
C=O	532.46	3.79						
"C-O" like, unassigned			534.2	7.56	534.99	5.38	534.68	5.44
"C-O" like, unassigned			535.83	0.52			536.06	0.45
Carbon								
C-C, C-H	284.74	5.46	285.69	3.78	287.29	3.84	286.91	3.3
C-O	285.62	2.02			288.06	0.88	287.57	1.3
O-C=O	287.07	0.77			289.35	0.35	289.12	0.32
CO_3					291.89	0.18	291.63	0.14
"C-O" like, unassigned			286.9	4.06				
"C-O" like, unassigned			288.69	0.5				
"C-O" like, unassigned			291.09	0.29				
Silicon								
Si	99	84.06	99.21	19.65			99.57	0.47
SiO_2					107.44	0.07		
Li_xSi					97.95	0.61		
Li_xSiO_y					102.6	0.11		
Phosphorous								
$LiPF_6$ dec. prod.			136.12	0.65	136.05	0.25	135.89	0.14
$LiPF_6$ dec. prod.			137.32	2.49	138.02	2.34	137.71	2.58
Lithium								
Li_xSi					54.84	2.3		
LiF and other salts			57.88	27.5	58.45	39.63	58.15	42.55
Li-O			55.02	0.98	56.33	2.5		

References

1. Wood, K. N.; Teeter, G., XPS on Li-Battery-Related Compounds: Analysis of Inorganic SEI Phases and a Methodology for Charge Correction. *ACS Applied Energy Materials* **2018,** *1* (9), 4493-4504.