Supplemental Information

Solid-State Prealkylation of Electrode Architectures to Tune Solid Electrolyte Interphase Composition

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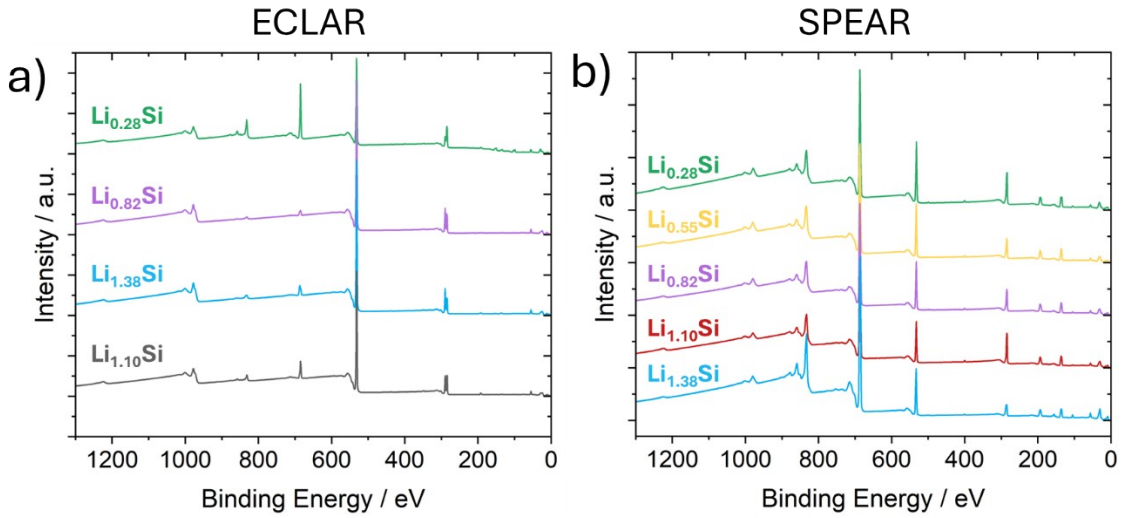

Figure S1. *Wide energy range survey spectra (0–1350 eV) to determine all elements present in the insoluble SEI composition for electrodes prelithiated to varying Li_xSi compositions using* ***a)*** *traditional electrochemical methods versus* ***b)*** *SPEAR after formation. All electrodes were harvested after SEI formation and rinsed in DMC to study the insoluble component of the SEI.*

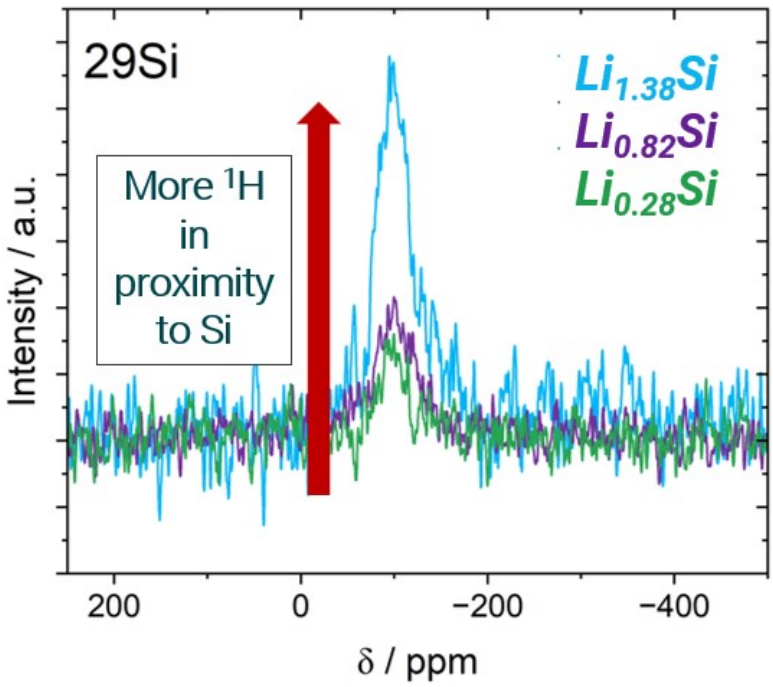

Figure S2. *^{29}Si cross-polarization NMR spectra for Si electrodes prelithiated via SPEAR to $Li_{0.28}Si$, $Li_{0.82}Si$, and $Li_{1.38}Si$ after undergoing 3 C/20 formation cycles in full cell configuration. Note the signal intensity at -98.32 ppm increases as a function of amount prelithiated, suggesting a different SEI with a faster formation process as the prelithiation amount increases. This is consistent with XPS, as surface composition after SEI formation reveals < 1% Si, suggesting a SEI greater than 10 nm in thickness.*

Table S1. *Surface Composition % of SEI in electrodes prelithiated using SPEAR method, after sitting in half cells at Voc 100 hours in Gen F3.*

Amount Prelithiated using SPEAR	Li	F	O	C	P	Si	N
$Li_{0.28}Si$	23.3	30.0	17.3	21.0	6.9	0.9	0.6
$Li_{0.55}Si$	26.2	34.9	16.1	14.6	7.1	0.6	0.5
$Li_{0.82}Si$	27.2	33.9	16.0	15.0	6.5	1.0	0.4
$Li_{1.10}Si$	26.9	32.3	13.5	20.3	5.9	0.5	0.6
$Li_{1.38}Si$	35.0	41.2	10.8	7.4	4.2	1.2	0.2

Table S2. *Surface Composition % of SEI in electrodes prelithiated electrochemically, after discharging half cells to targeted Li_xSi amount in Gen F3.*

Amount Prelithiated using ECLAR	Li	F	O	C	P	Si	N
$Li_{0.28}Si$	29.8	15.4	29.0	21.0	1.2	3.3	0.3
$Li_{0.81}Si$	32.0	3.0	42.4	22.1	0.3	0.1	0.1
$Li_{1.38}Si$	31.8	4.3	42.1	21.1	0.5	0.1	0.1
$Li_{2.33}Si$	30.2	6.4	39.8	22.9	0.4	0.2	0.1

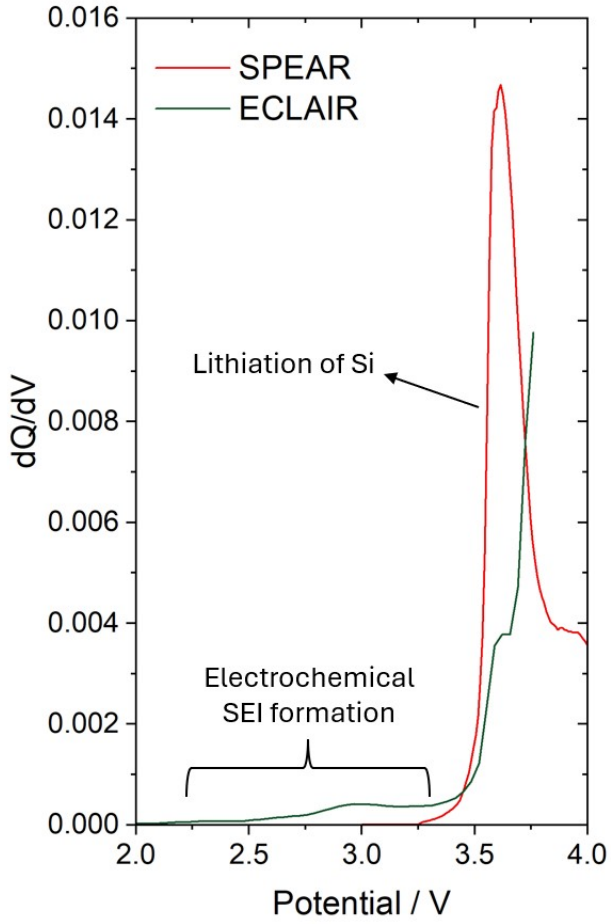

Figure S3. *dQ/dV profiles for the first charge step in ECLAR (**green**) vs. SPEAR (**red**) cells, providing evidence of the different SEI formation mechanisms, where the first charge step for ECLAR was during electrochemical prelithiation, and the first charge step for SPEAR was the first charge after holding at* V_{OC} *to enable stochastic SEI formation.*

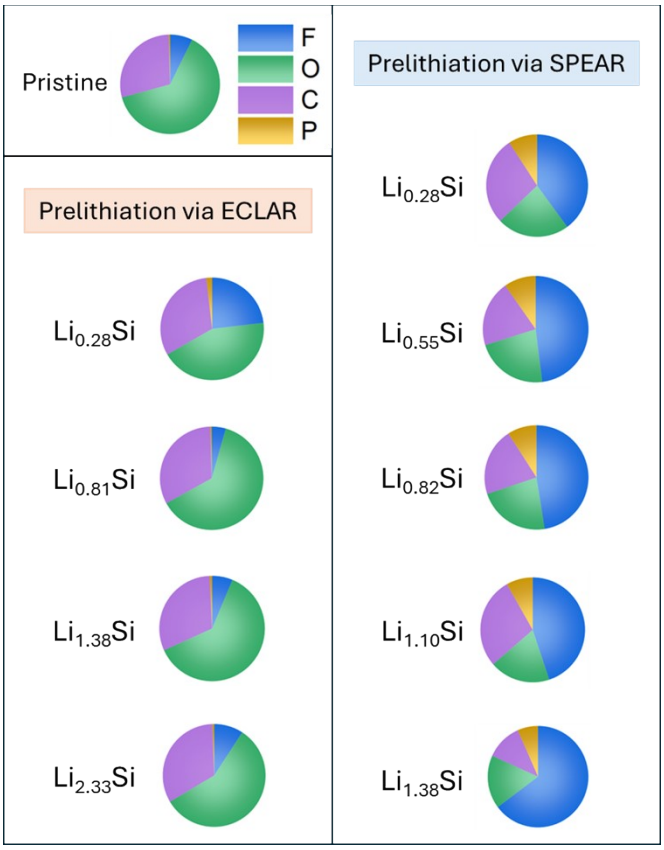

Figure S4. *Elemental P, F, C, and O % SEI composition for electrodes prelithiated to Li_xSi via traditional electrochemical methods (**left**) versus SPEAR (**right**). Note these are compositions of the insoluble SEI component, as all electrodes were harvested from the cells before rinsing in DMC prior to XPS analysis.*

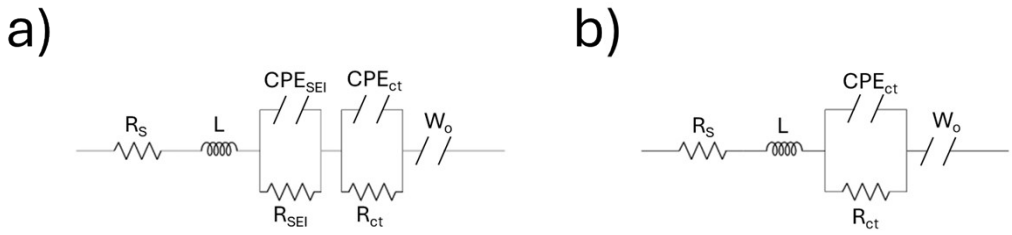

Figure S5. *Equivalent circuit models (with elements labeled) used to fit the Nyquist plots for cells prelithiated using* ***a)*** *ECLAR to $Li_{0.28}Si$, $Li_{0.81}Si$, and $Li_{1.38}Si$ and SPEAR to$Li_{1.38}Si$, and* ***b)*** *SPEAR to $Li_{0.28}Si$ and $Li_{0.82}Si$.*

Table S3. *Fit values for each equivalent circuit component for Nyquist plots taken of ECLAR vs. SPEAR prelithiated cells prior to electrochemical cycling. ECLAR and SPEAR cells were prelithiated to the specified, targeted Li_xSi stoichiometries.*

	ECLAR			**SPEAR**		
	$Li_{0.28}Si$	**$Li_{0.81}Si$**	**$Li_{1.38}Si$**	**$Li_{0.28}Si$**	**$Li_{0.82}Si$**	**$Li_{1.38}Si$**
R_S	12.1	14.7	16.3	6.1	13.4	7.1
L	5.23E-7	9.18E-7	1.02E-6	3.97E-7	1.23E-6	5.28E-7
CPE_{SEI} - T	1.41E-5	2.32E-6	1.65E-6	7.24E-4	1.21E-4	1.59E-4
CPE_{SEI} - P	0.95	0.95	0.95	0.53	0.55	0.85
R_{SEI}	53.6	2.4	4.4	3.2	14.7	51.1
CPE_{ct} - T	2.28E-5	3.10E-5	3.53E-5	-	-	5.64E-4
CPE_{ct} - P	0.70	0.73	0.77	-	-	0.45
R_{ct}	147.5	4.3	1.1	-	-	9.5
W_o - T	4.97E-4	2.04E-3	9.08E-3	1.41E-4	1.76E-4	2.67E-4
W_o - P	0.60	0.47	0.48	0.22	0.70	0.79