

Electronic Supplementary Information

Table S1. C, O, F and P atomic surface concentrations of the cycled electrodes. *The abnormally high F content at this binding energy (~687 eV) is related to species similar to Li_2SiF_6 . C-O and C-C=O concentrations are for signals at ~286.5 and 289 eV in C1s. O lattice, O=X and O-X concentrations are for signals at ~529.5, 531.5 and 533 eV in O1s. LiF, $\text{Li}_x\text{PO}_y\text{F}_z$, Li_xPF_y concentrations are for signals at ~685, 686.5-687 eV and 688 eV in F1s.

Cycle	C total	C-O	O-C=O	O total	O lattice	O=X-	O-X	F total	LiF	$\text{Li}_x\text{PO}_y\text{F}_z$	Li_xPF_y	P
0	12.8	1.6	1.3	43.1	29.5	13.6						
1	21.6	2.7	1.6	32.0	11.2	17.5	3.3	25.8	17.6	3.4	4.8	2.2
12	16.8	3.0	1.1	40.2	16.8	19.3	4.1	14.7	7.9	2.5	4.3	5.1
35	14.5	2.2	0.3	30.3	6.2	19.9	4.2	27.8	19.5	3.5	3.8	5.8
64	18.5	1.9	0	21.0	1.8	16.4*	2.8	34.3	15.3	10.5*	8.5	5.8
184	17.4	2.4	0	13.0	1.3	9.1*	2.6	48.3	3.5	36.7*	8.1	3.5

Table S2. Metal (Mn, Ni, Co, Si) atomic surface concentrations of the cycled electrodes

Cycle	Mn	Li	Ni	Co	Si
0	11.1	28.2	2.4	2.4	
1	6.9	11.4			
12	7.2	16.0			
35	3.0	18.6			
64	1.1	17.8			1.4
184	1.5	11.0			5.3

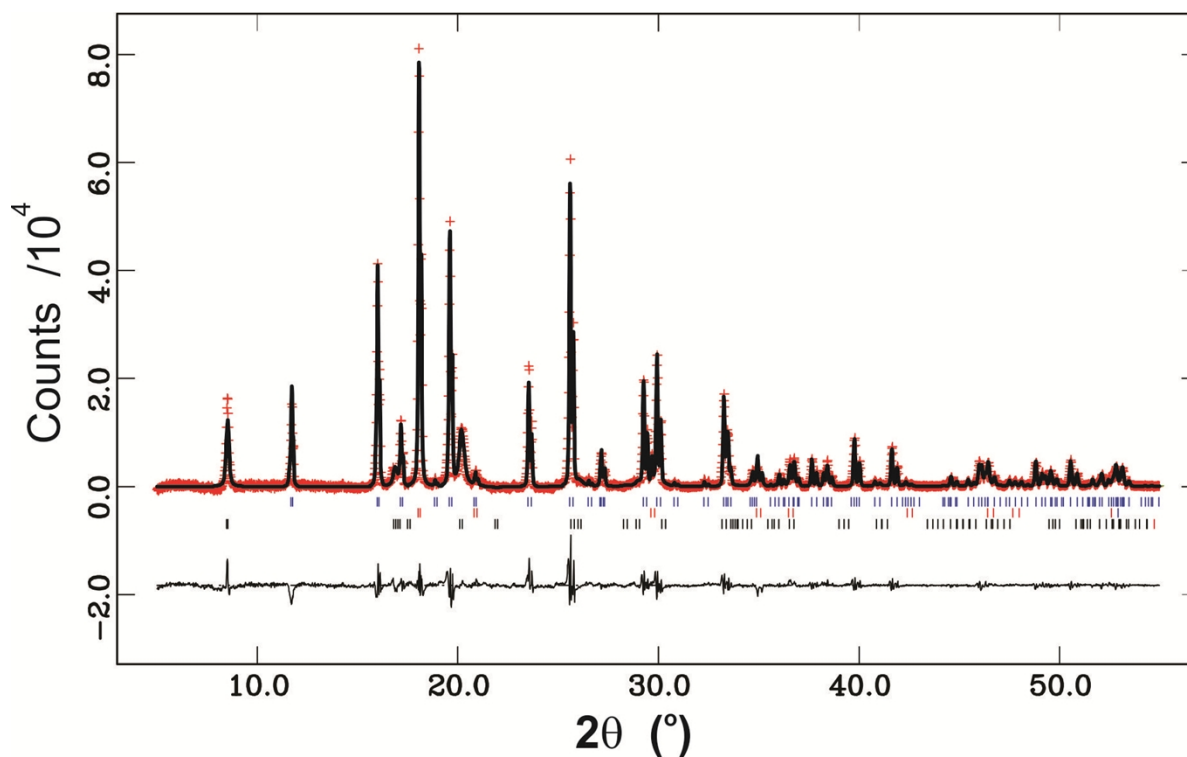


Figure S1. Rietveld refinement of the X-ray diffraction pattern of the pristine thin film deposited at 20 mTorr measured with Mo K_{α} radiation. Blue, red and black vertical bars indicate the reflections of Al_2O_3 substrate, Pt thin film current collector and LNMC thin film. Data were refined with the GSAS/EXPGUI Rietveld refinement package [1-3].

[1] H.M. Rietveld, *J. Appl. Cryst.* 2 (1969) 65-71.

[2] A.C. Larson, R.B. Von Dreele, GSAS, General Structure Analysis System; Los Alamos National Laboratory: Los Alamos, NM, 1994.

[3] B.H. Toby, *J. Appl. Cryst.* 34 (2001) 210-213.

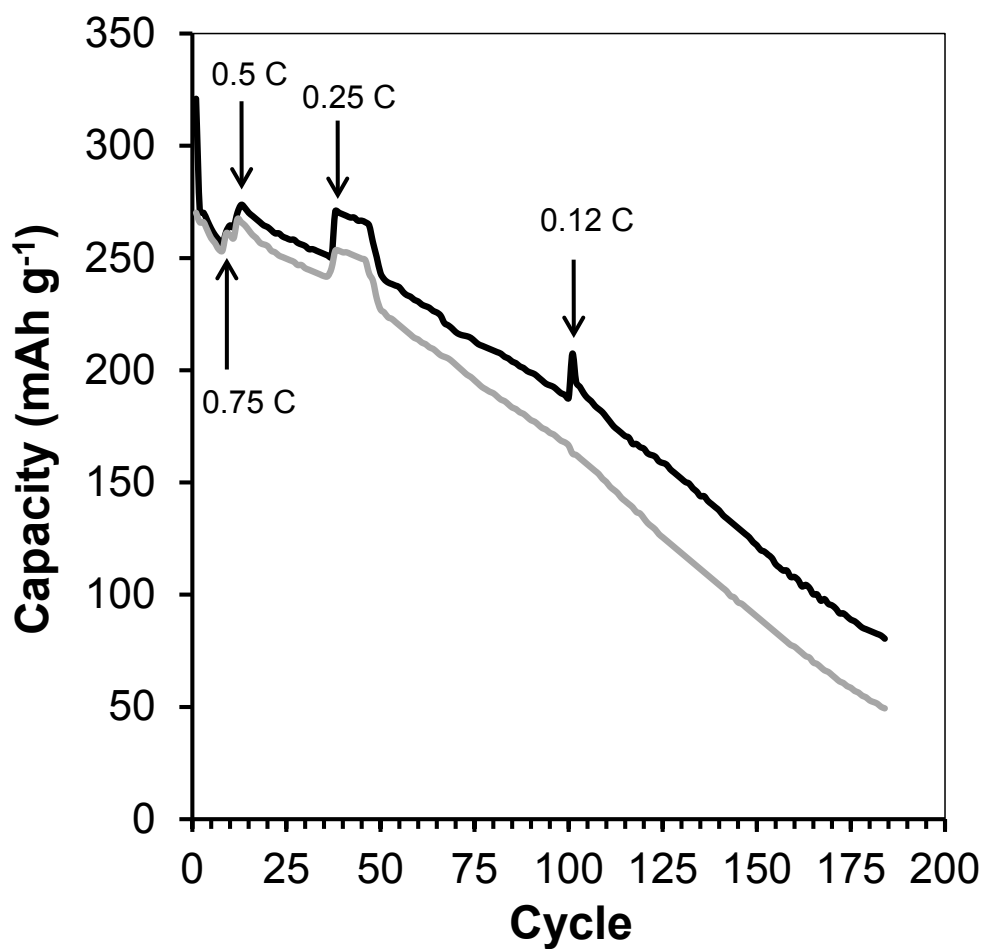


Figure S2. Cycling performance of a thin film electrode grown at 20 mTorr. Gray and black curves are for discharge and charge, respectively. The arrows indicate when the current was decreased during the experiment, from 1 C to 0.75, 0.5, 0.25 and 0.12 C.

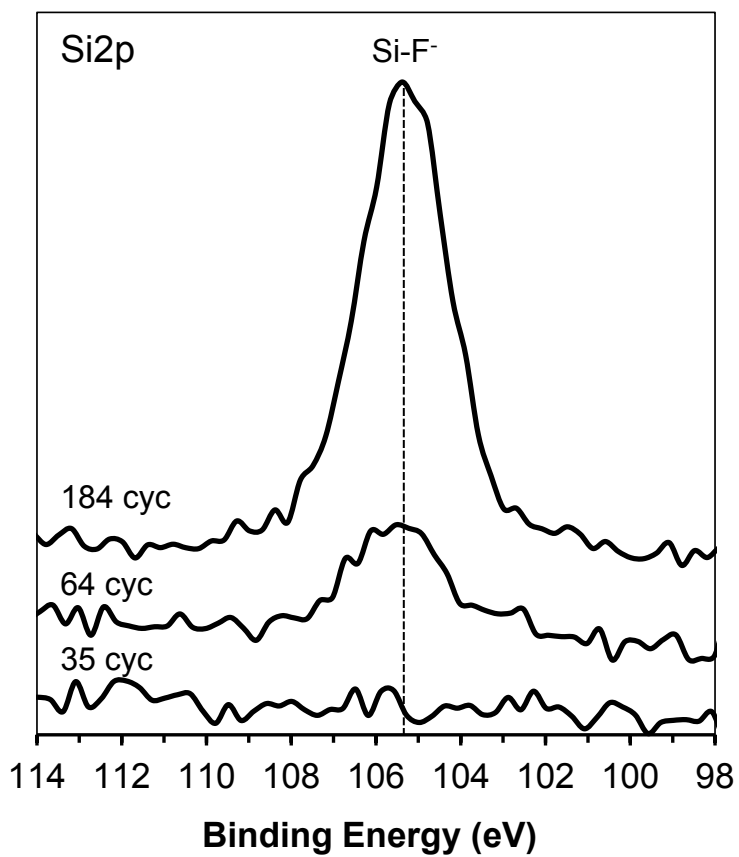


Figure S3. Si2p XPS spectra of electrodes cycled 35, 65 and 184 times. The data is from the survey scans.

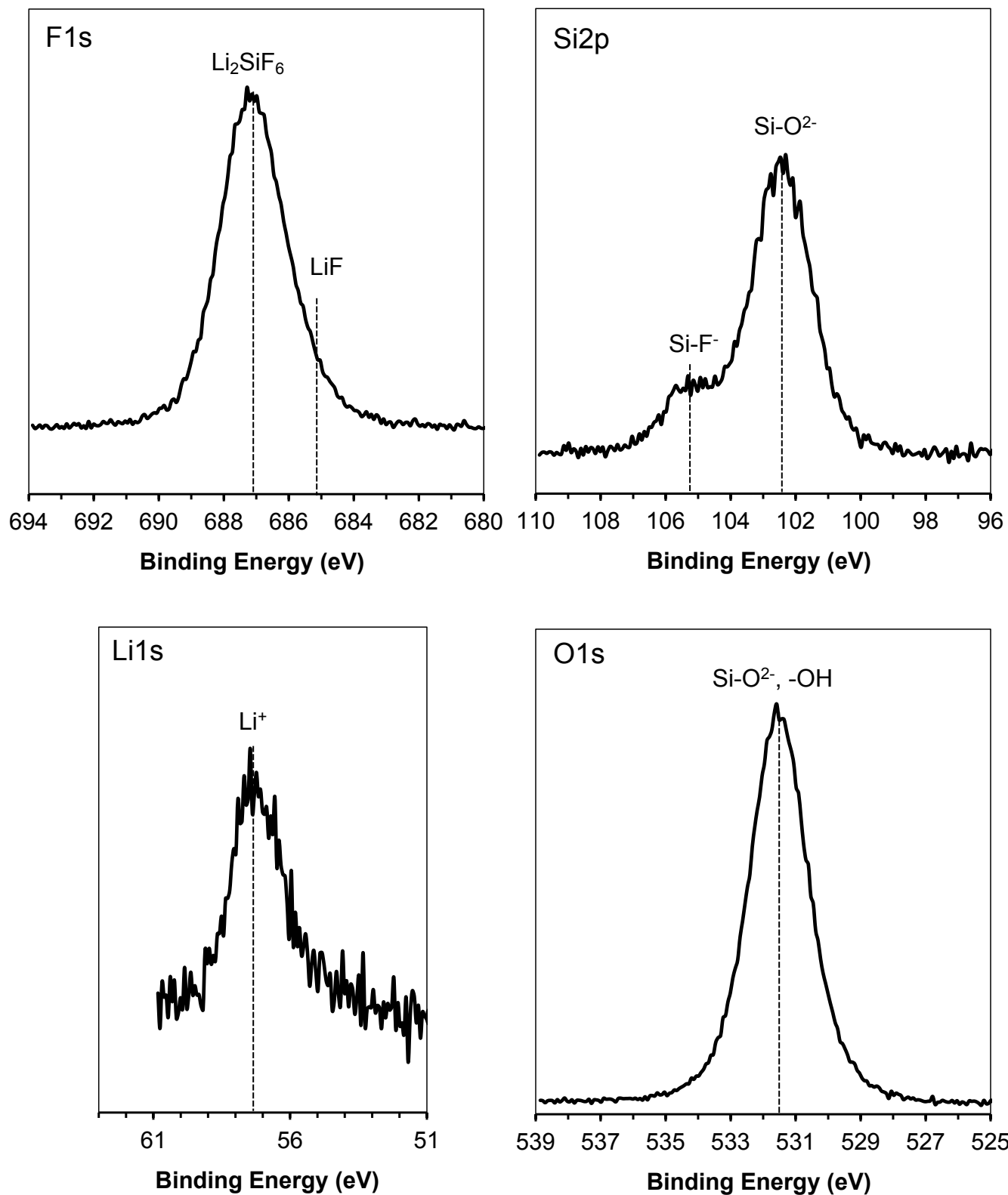


Figure S4. F1s, Si2p, Li1s and O1s high resolution XPS spectra of as-received Alfa Aesar Li_2SiF_6 reference powder.

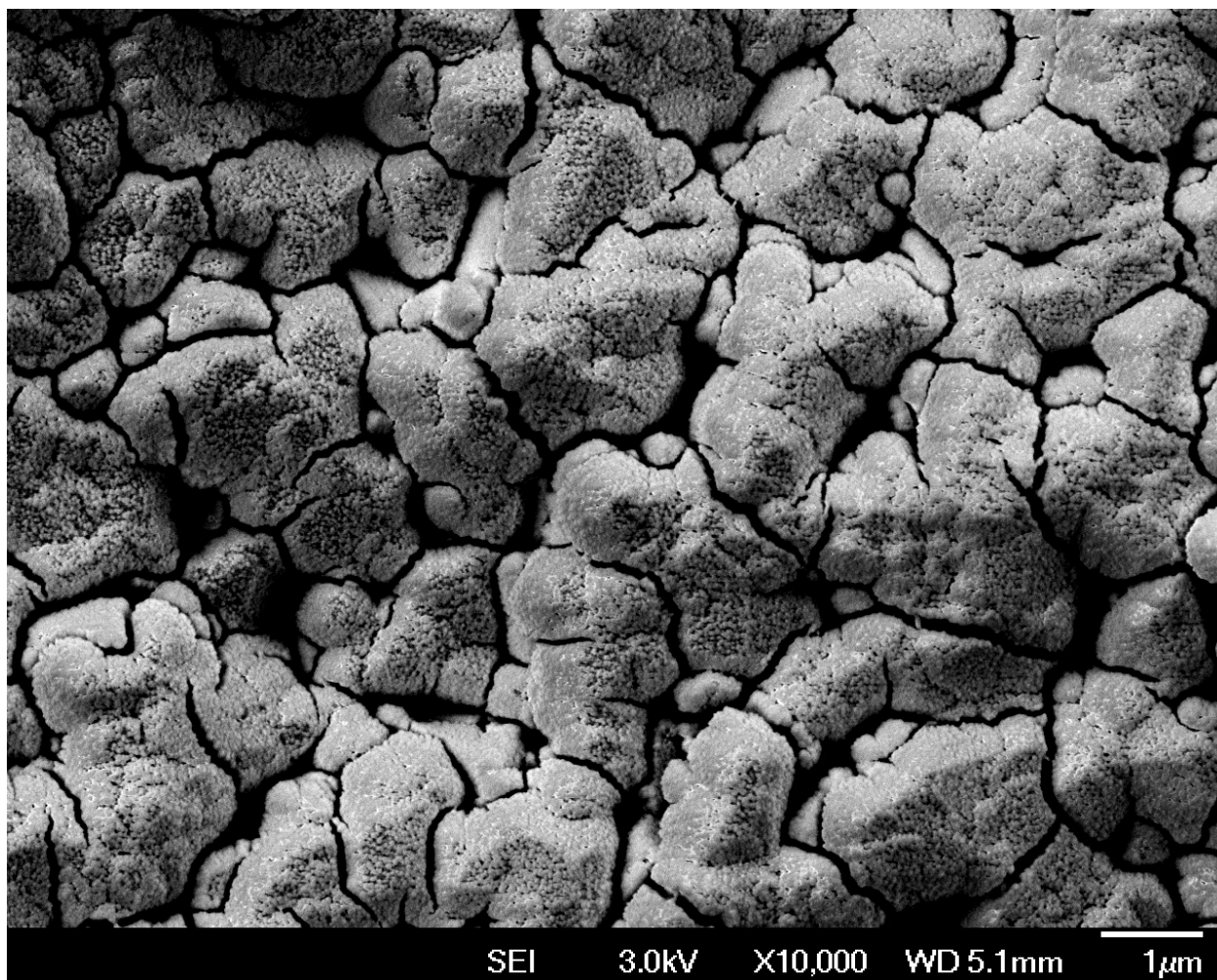


Figure S5. SEM micrograph of a film grown at 20 mTorr and annealed at 700°C in O₂.