Supplementary Information (SI) for EES Batteries.

Quantifying Silicon Anode Restructuring during Calendar Aging of Lithium-Ion Batteries by Plasma Focused Ion Beam Tomography and Chemical Mapping

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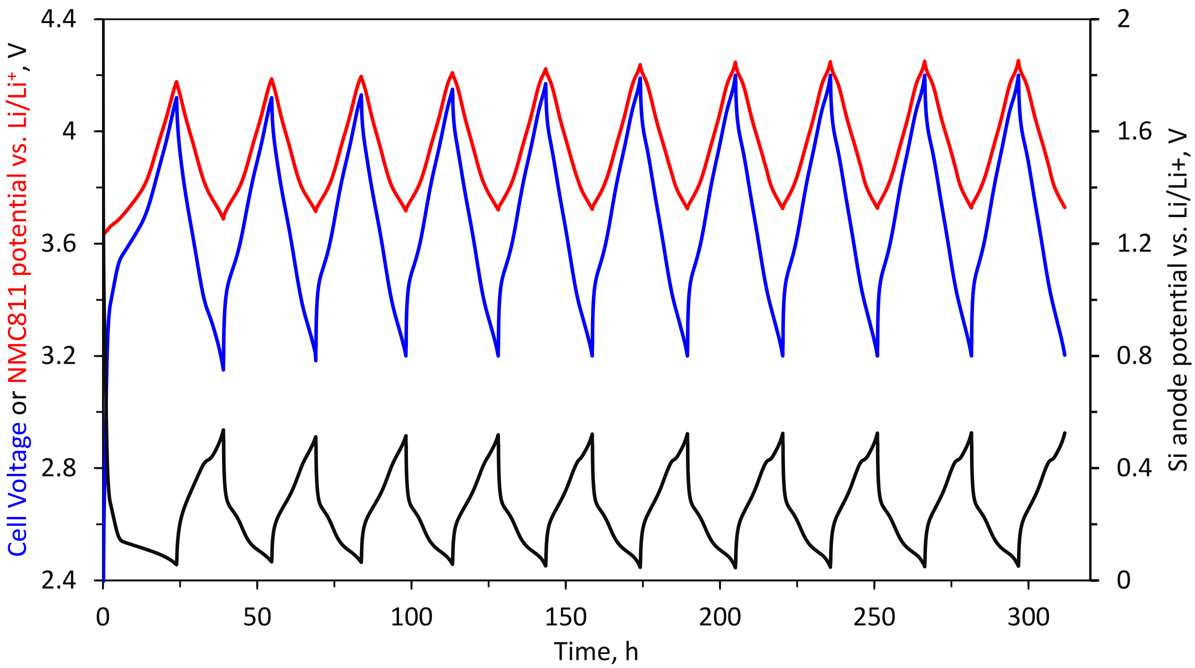

Figure S1 | **Conditioning cycles before aging.** Shown are the Cell voltage (blue), NMC811 electrode (red) and Si electrode (black) potential profiles variation as a function of cycling. See Table S1 for details. The minor plateau around 0.45 V vs. Li/Li^+ seen in the Si electrode delithiation profile is from delithiation of $Li_{15}Si_4$ that is formed during lithiation.

tap charge / rest (wetting) 10x cycles - Full Cell		NMC811 electrode		Silicon electrode		Capacity, mAh/cm2		
#	UCV	LCV	UP	LP	LP	UP	Charge	Discharge	CE, %
1	4.12	3.15	4.18	3.69	0.06	0.54	2.82	1.79	63.30
2	4.12	3.2	4.19	3.71	0.07	0.51	1.84	1.68	91.26
3	4.13	3.2	4.20	3.72	0.06	0.52	1.73	1.70	98.11
4	4.15	3.2	4.21	3.72	0.06	0.52	1.78	1.74	98.12
5	4.17	3.2	4.22	3.72	0.05	0.52	1.81	1.77	98.10
6	4.19	3.2	4.24	3.72	0.05	0.52	1.83	1.80	98.39
7	4.2	3.2	4.25	3.73	0.05	0.52	1.83	1.80	98.68
8	4.2	3.2	4.25	3.73	0.05	0.53	1.81	1.79	98.81
9	4.2	3.2	4.25	3.73	0.05	0.53	1.80	1.78	98.83
10	4.2	3.2	4.25	3.73	0.05	0.52	1.79	1.76	98.06

UCV = Upper cutoff voltage; LCV = Lower cutoff voltage; UP = Upper potential; LP = Lower potential; CE = Coulombic Efficiency

2280 mAh/g-Si

Table S1 | **Details from the conditioning cycles – cell voltages/capacities and electrode potentials.**

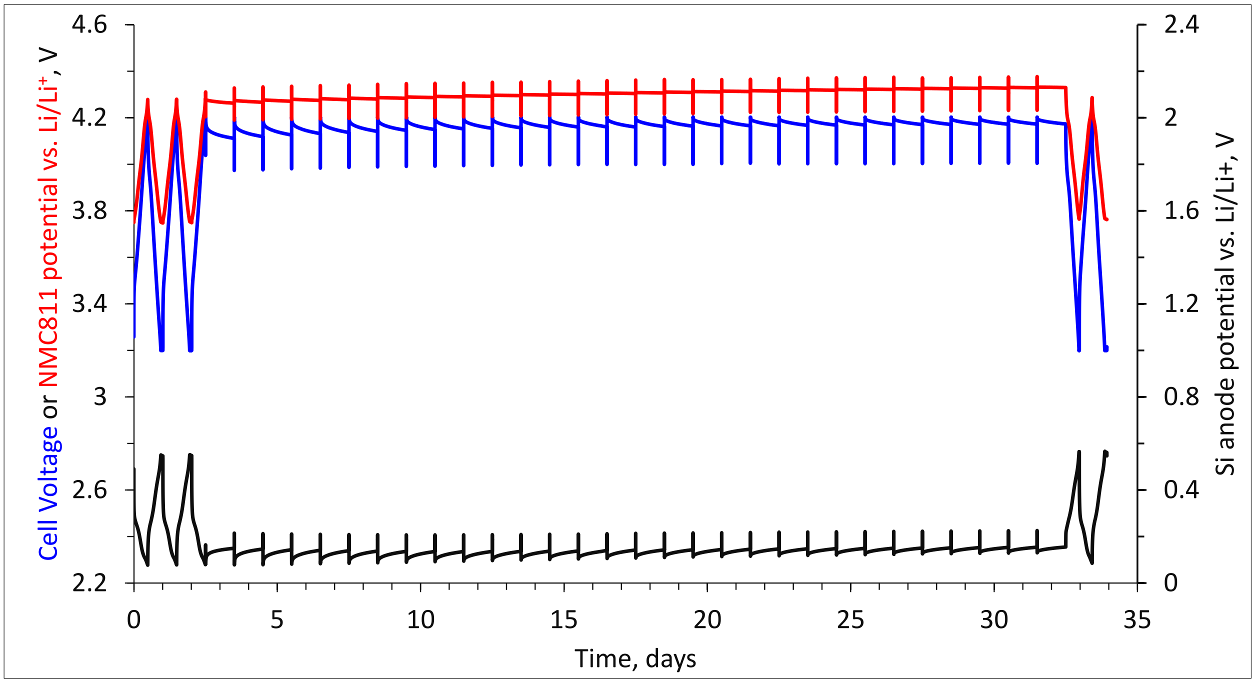

Figure S2 | **OCV-RPT Calendar life aging protocol.** Shown are the Cell voltage (blue), NMC811 electrode (red) and Si electrode (black) potential profiles. The OCV/RPT segment over a 30-day period includes daily current pulses to measure impedance and a daily charge to restore cell voltage to its UCV.

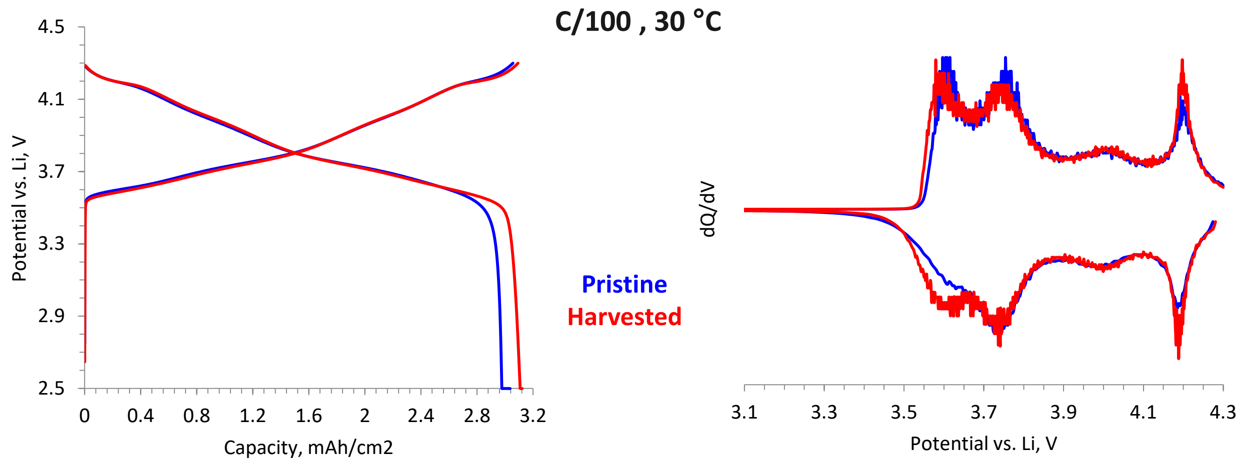

Figure S3 | **Data from pristine and harvested NMC811 electrodes.** (a) Potential profiles of an as-prepared electrode (blue) and an electrode harvested from a cell after 8-months of calendar-aging (red), cycled in cells with a Li-metal counter electrode. (b) Differential capacity vs. NMC811 electrode potential plots derived from the data in (a).

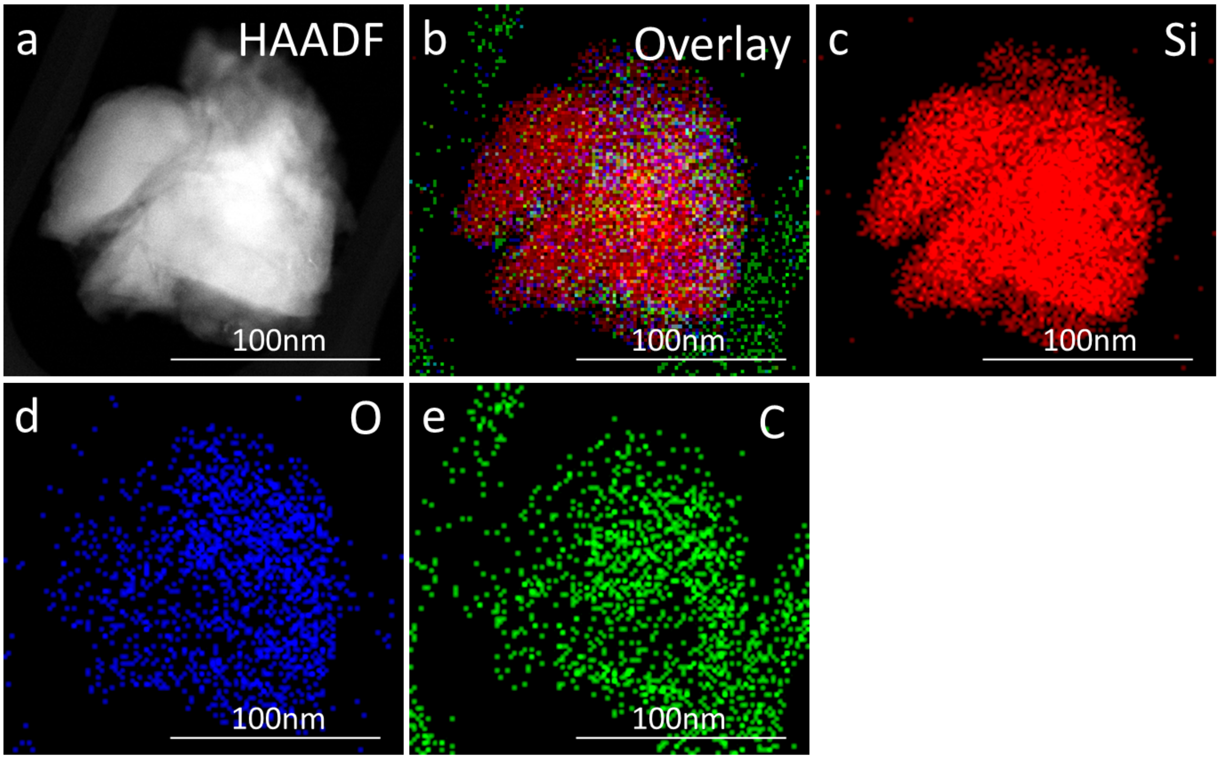

Figure S4 | **HAADF image and EDS Maps of a Si nanoparticle from a pristine electrode.**

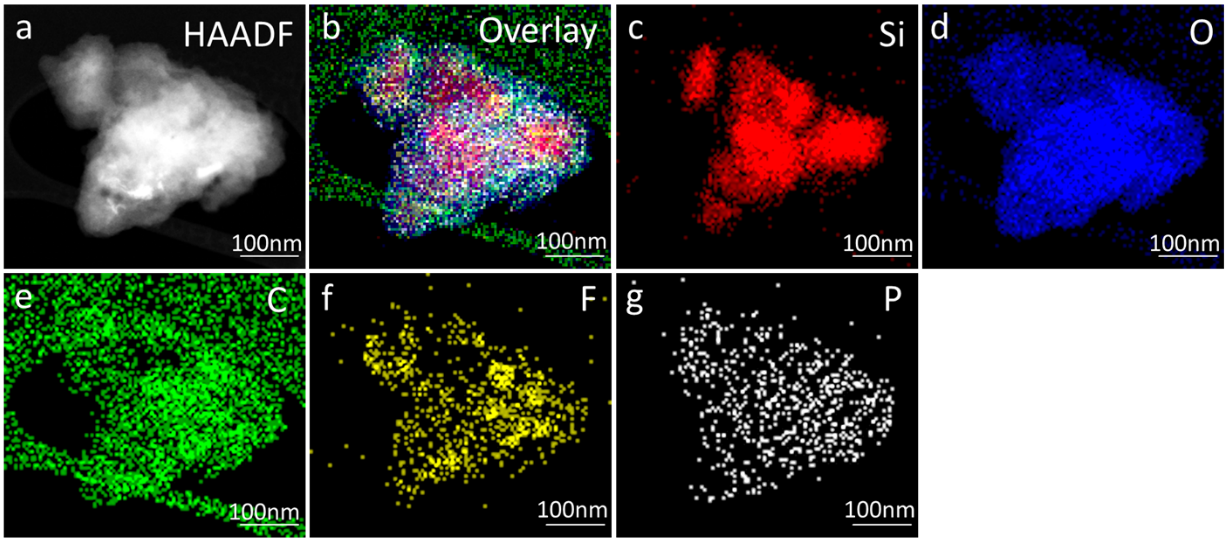

Figure S5 | **HAADF image and EDS Maps of a Si nanoparticle from an electrode after conditioning cycles.** Portions of the holey-carbon grid (used for mounting of TEM samples) are seen in the C-map.

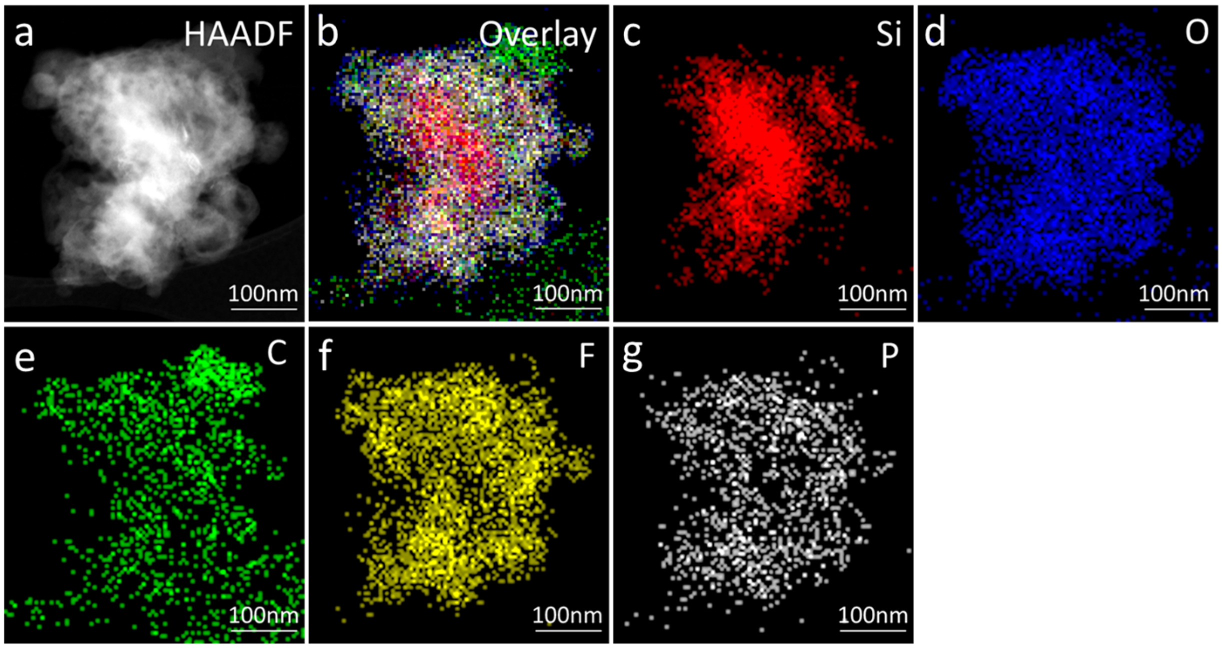

Figure S6 | **HAADF image and EDS Maps of a Si nanoparticle from an electrode after calendar aging.**

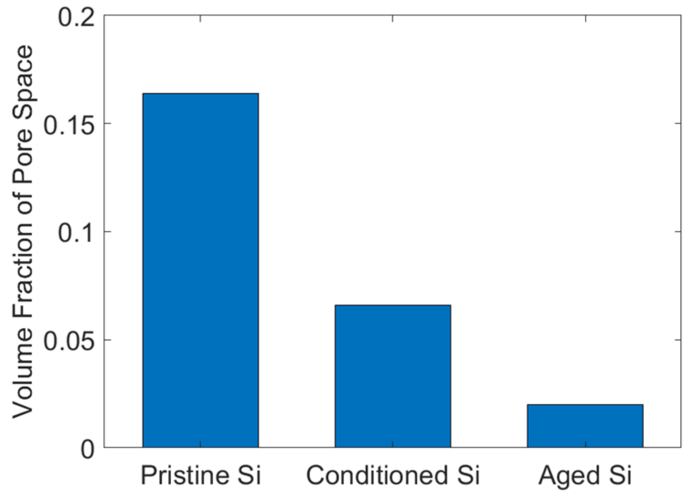

Figure S7 | **Quantification of the volume fraction of pore space for the pristine, conditioned, and aged electrode.** The volume fraction was calculated for the bulk of the electrode material and does not include void space created from surface delamination.

Video S1 | **Cross-sectional frames of the pristine Si sample after the two-step alignment process (“SEMvid_Pristine.avi” attached in supporting files).** Alignment algorithms were developed to minimize frame-by-frame drifting of the electrode cross-section.

Video S2 | **Cross-sectional frames of the pristine Si sample after the two-step alignment process (“SEMvid_Conditioned.avi” attached in supporting files).** Alignment algorithms were developed to minimize frame-by-frame drifting of the electrode cross-section.

Video S3 | **Cross-sectional frames of the Calendar Aged Si sample after the two-step alignment process (“SEMvid_Aged.avi” attached in supporting files).** Alignment algorithms were developed to minimize frame-by-frame drifting of the electrode cross-section.