

Effect of cathode on crosstalk in Si-based lithium-ion cells

Minkyu Kim, Zhenzhen Yang*, Seoung-Bum Son, Stephen E. Trask, Andrew Jansen, Ira Bloom*

Chemical Science and Engineering Division, Argonne National Laboratory, 9700 South Cass Avenue, Lemont, IL 60439, USA

* Corresponding author: yangzhzh@anl.gov, ira.bloom@anl.gov

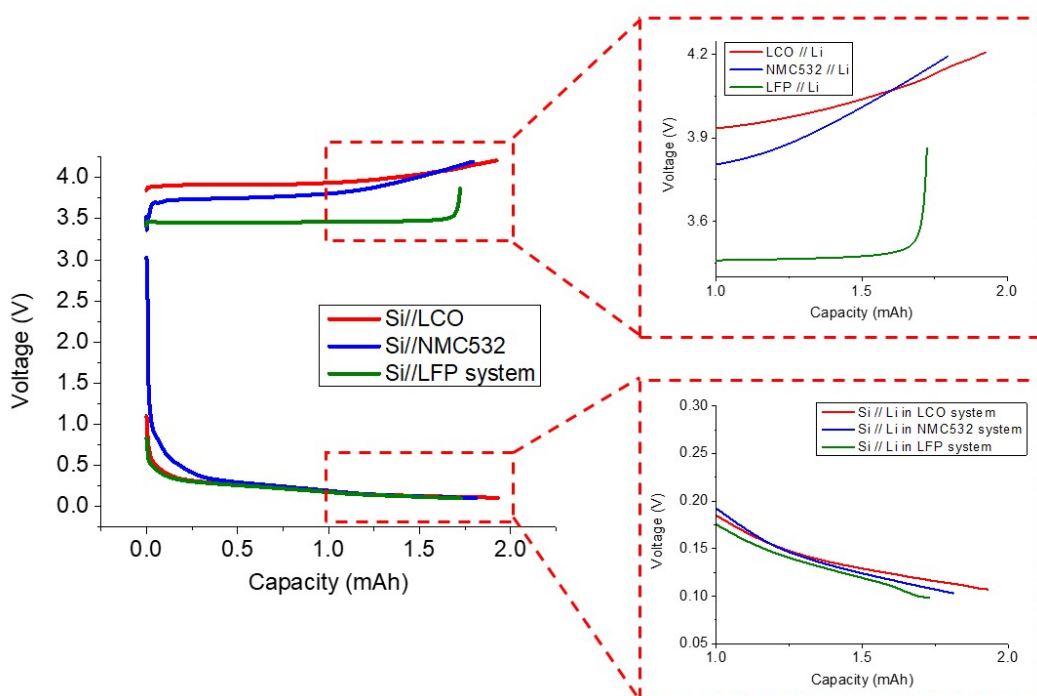


Figure S1. Voltage profiles of the Si electrode or cathode vs. the Li reference electrode from the three systems during the 1st cycle at the formation process.

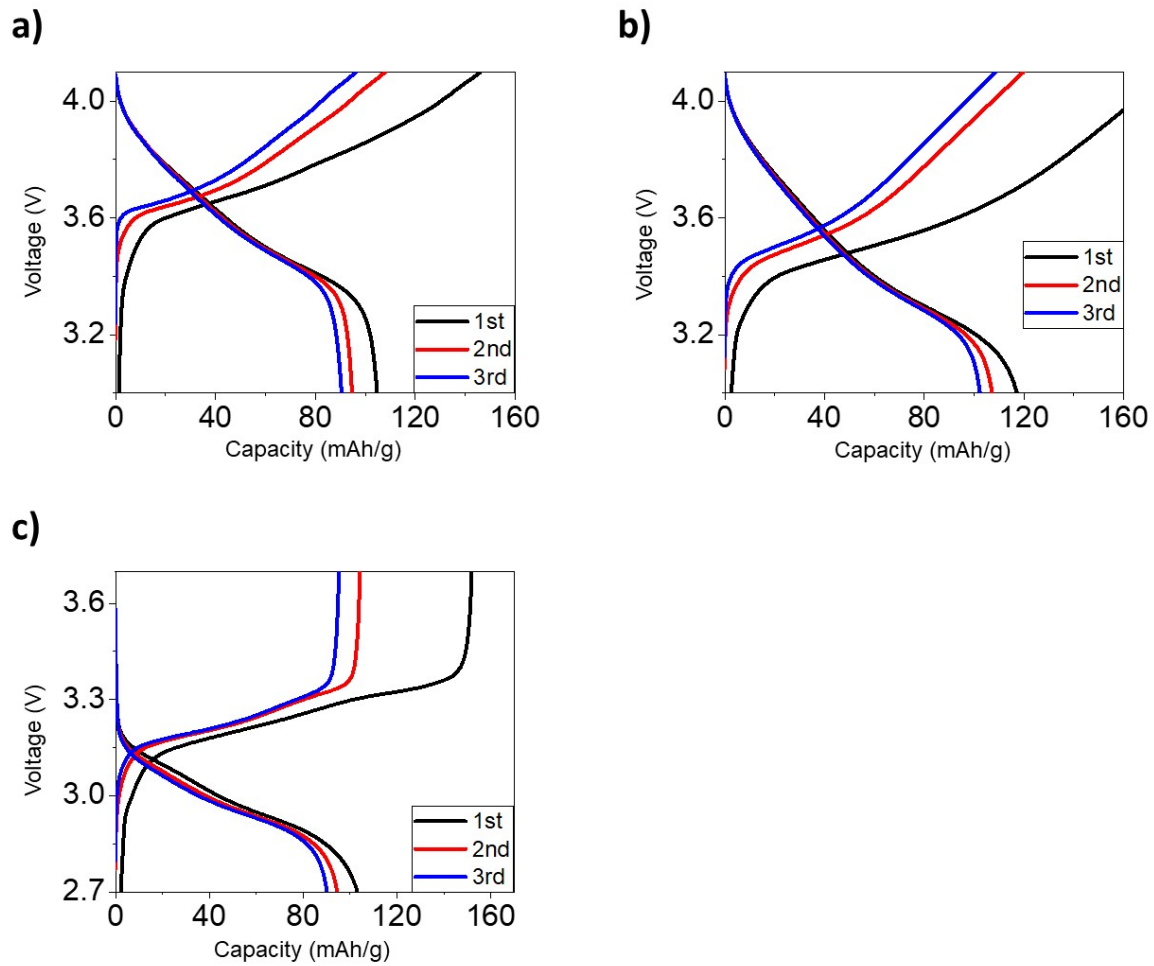


Figure S2. Voltage profiles of a) LCO system, b) NMC532 system, and c) LFP system during the formation process (3 cycles at the C/20 rate).

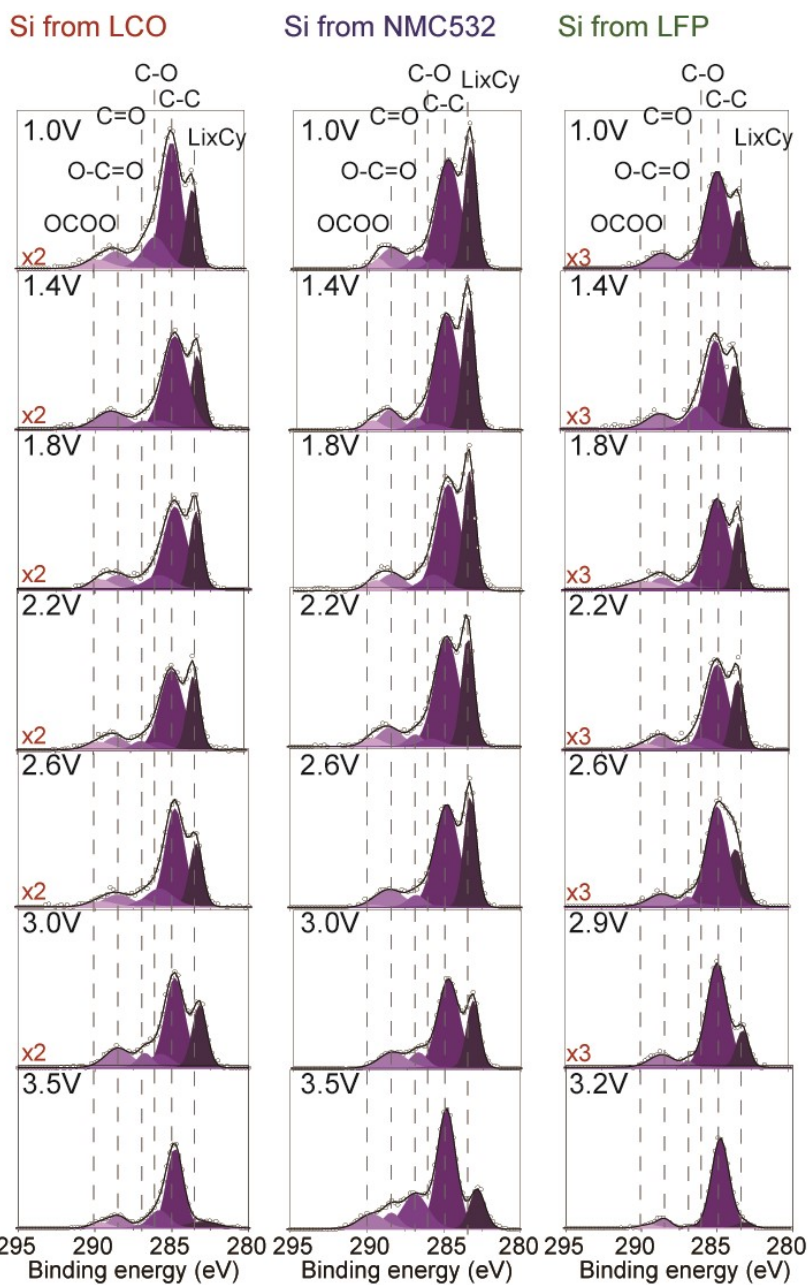


Figure S3. The C 1s XPS spectra of harvested Si extracted from the LCO, NMC532, or LFP system, depending on the pre-set potentials. Black empty circles: measured data. Colored areas: fitted curves of observed components. Black solid lines: envelopes of the fitted curves. “x number” means the intensity multiplied by a factor of *number* to better show the peaks.

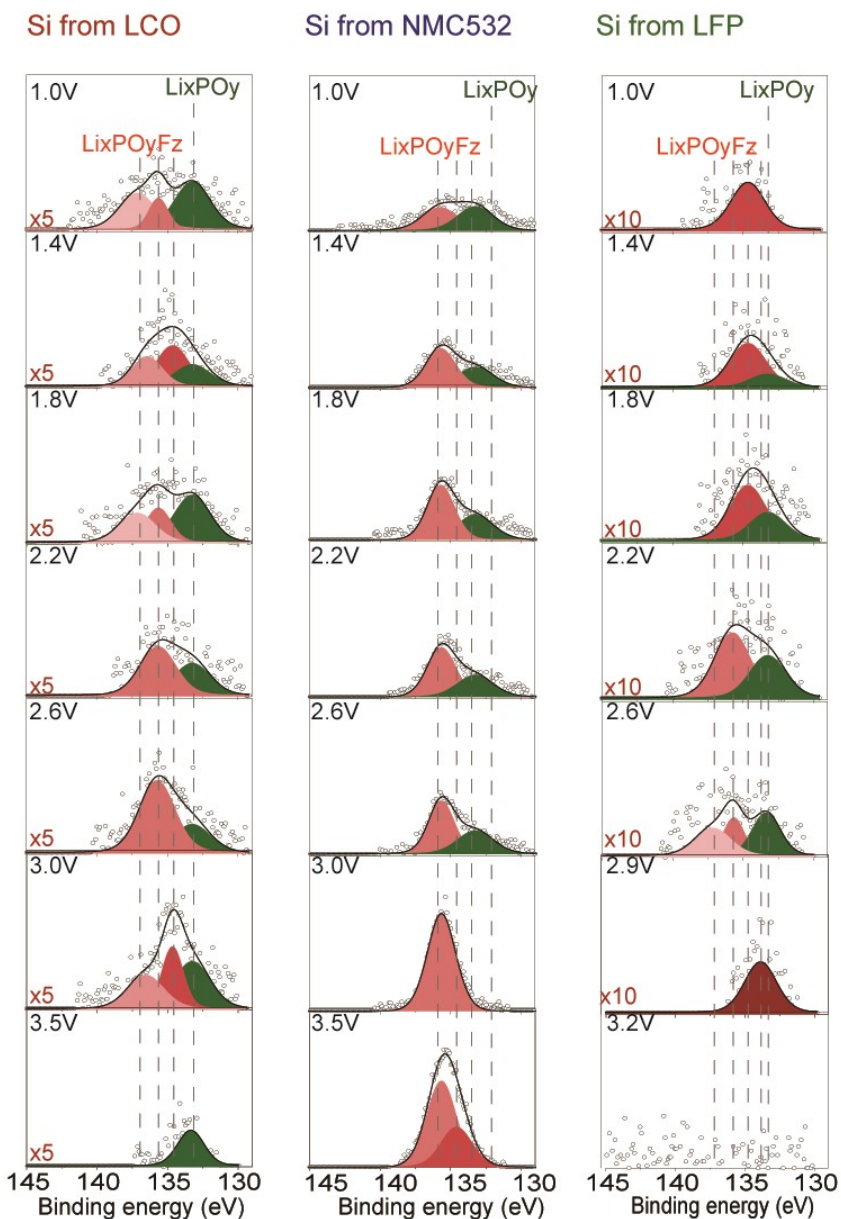


Figure S4. The P2p XPS spectra of harvested Si anodes as a function of charge voltage. Black empty circles: measured data. Colored areas: fitted curves of observed components. Black solid lines: envelopes of the fitted curves. “x number” means the intensity multiplied by a factor of *number* to better show the peaks.

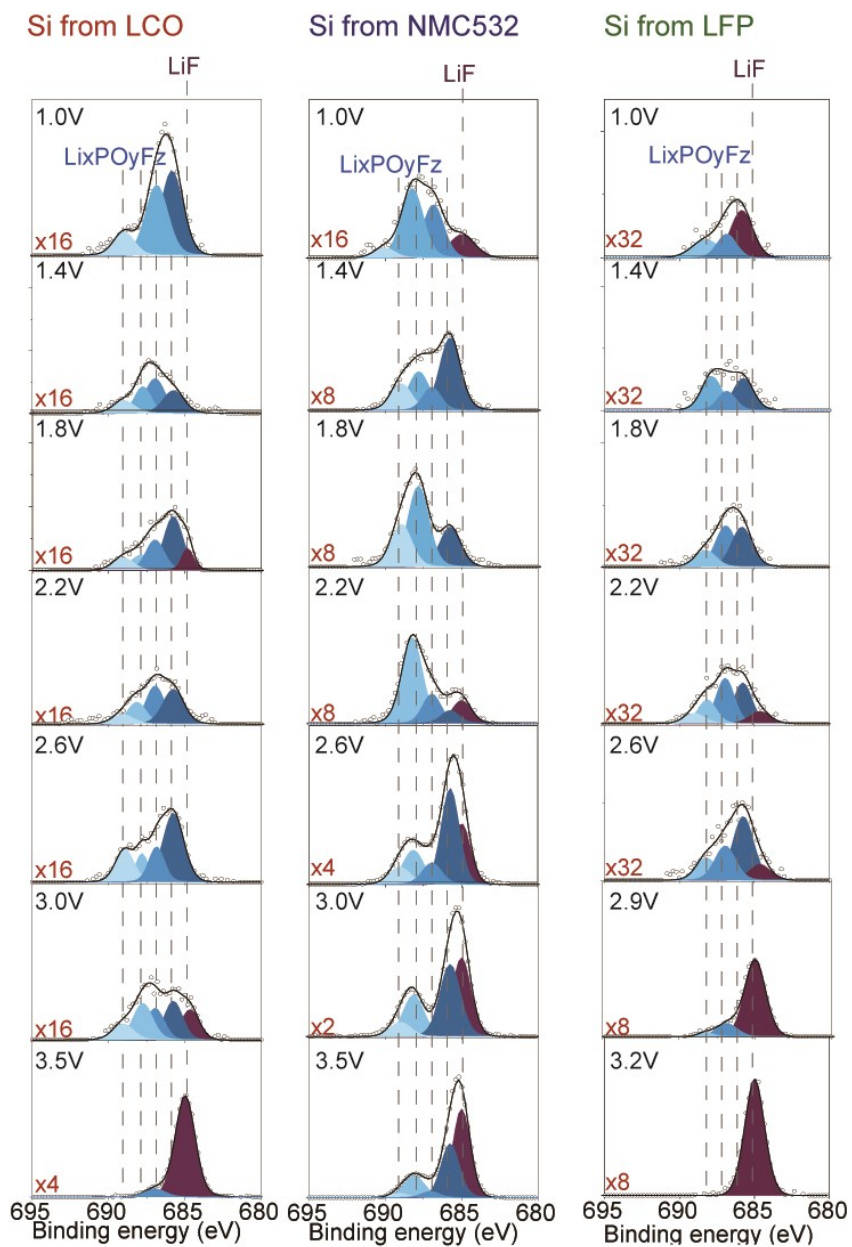


Figure S5. The F1s XPS spectra of harvested Si anodes as a function of charge voltage. Black empty circles: measured data. Colored areas: fitted curves of observed components. Black solid lines: envelopes of the fitted curves. “x number” means the intensity multiplied by a factor of *number* to better show the peaks.

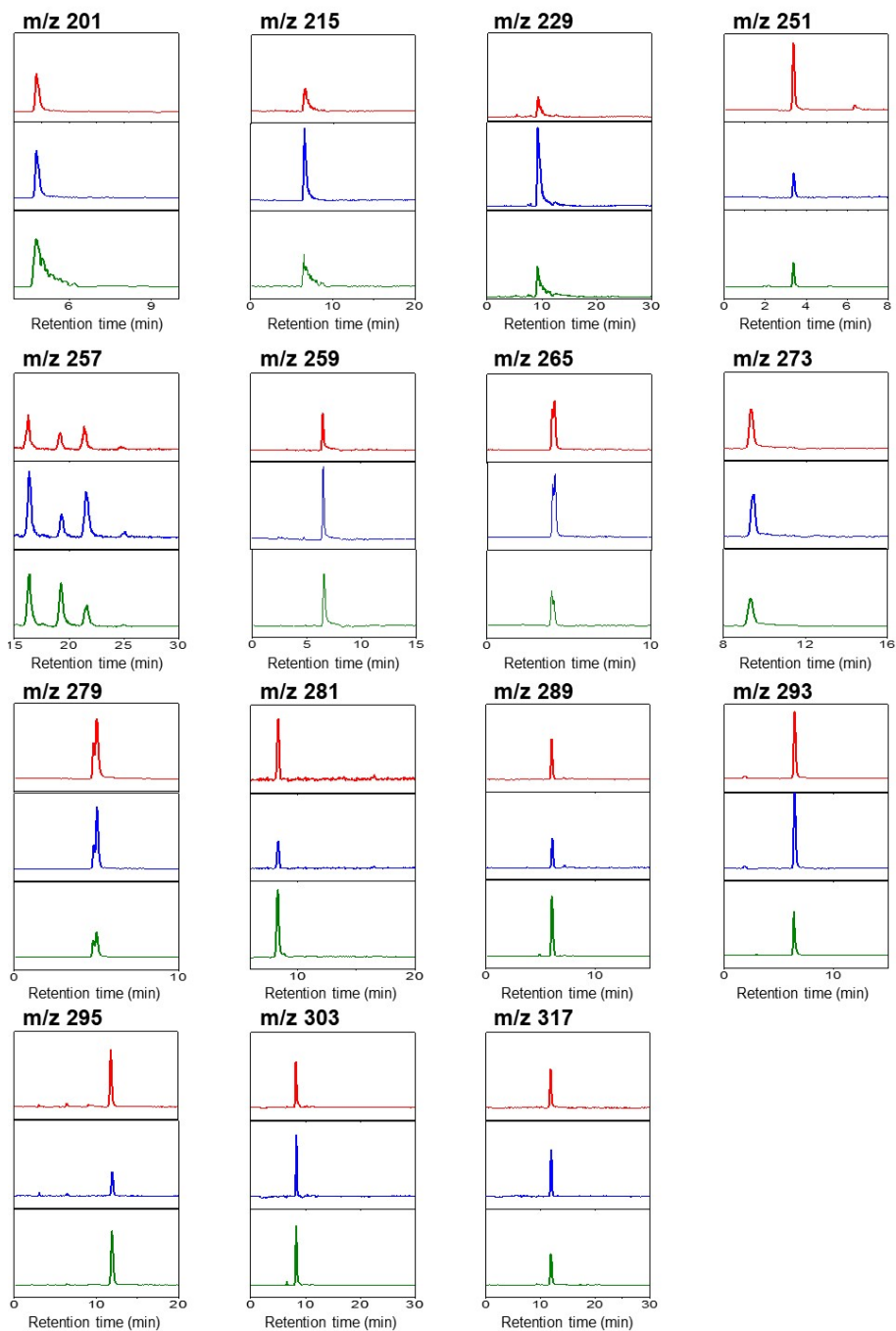


Figure S6. Single-ion chromatograms (SICs) of the aged electrolytes extracted from three systems (Red: LCO, Blue: NMC532, Green: LFP) after 2 cycles at the C/3 rate. Doublets or triplets seen in the SICs of some compounds are probably due to isomers.

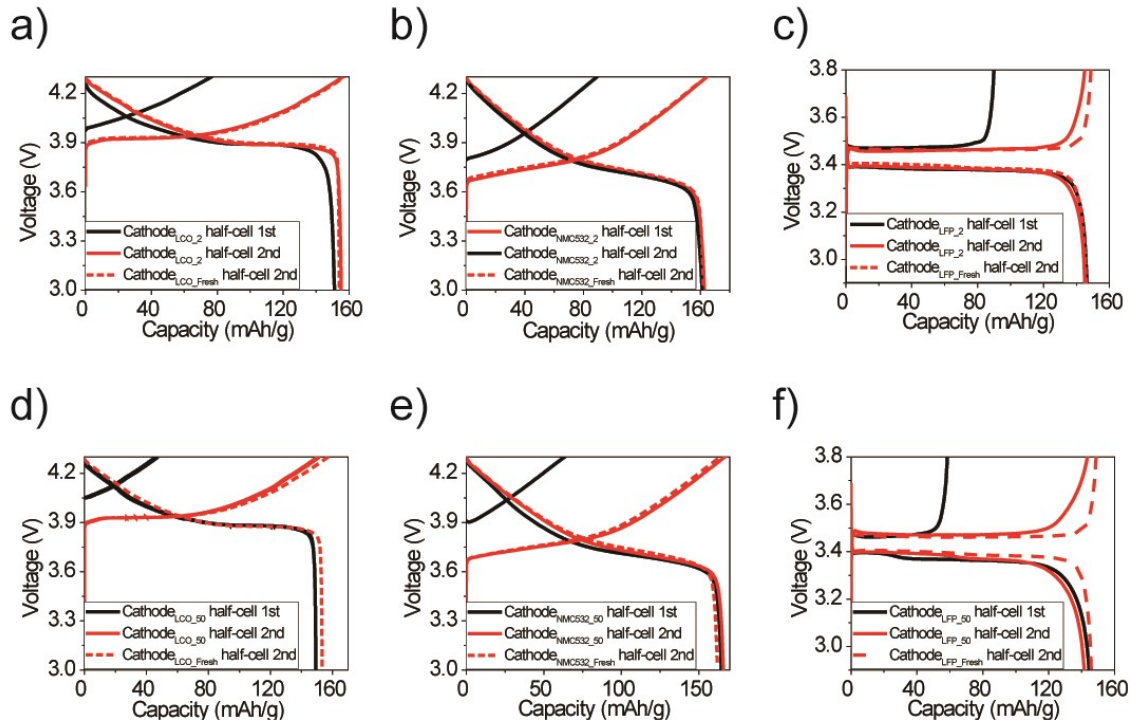


Figure S7. The voltage profiles of harvested- and fresh-cathode/Li half-cells at the C/20 rate. Harvested cathodes come from each full cell system, a-c) after 2 cycles of cycle life test, d-f) after 50 cycles of cycle life test. a) harvested/fresh LCO half-cell, b) harvested/fresh NMC532 half-cell, c) harvested/fresh LFP half-cell. d) harvested/fresh LCO half-cell, e) harvested/fresh NMC532 half-cell, f) harvested/fresh LFP half-cell. Color code for figures: black lines represent the first cycle of the harvested-anode half-cells, and red lines represent the second cycle of the harvested-cathode half-cells. The second cycle of fresh-cathode half-cells (red, dashed lines) is included for reference.

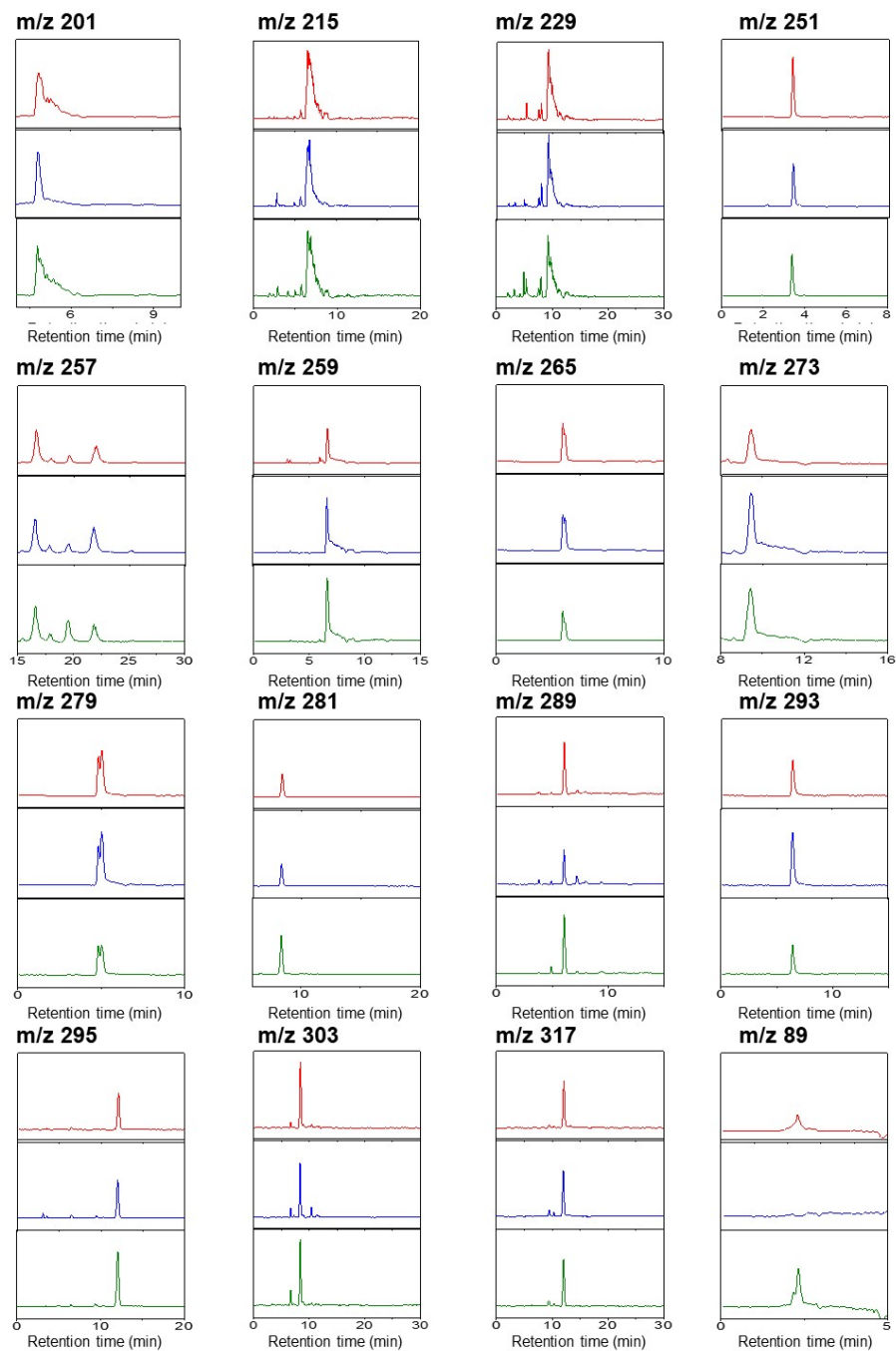


Figure S8. Single-ion chromatograms of the aged electrolytes extracted from the three cell systems (Red: LCO, Blue: NMC532, Green: LFP) after 50 cycles at the C/3 rate.

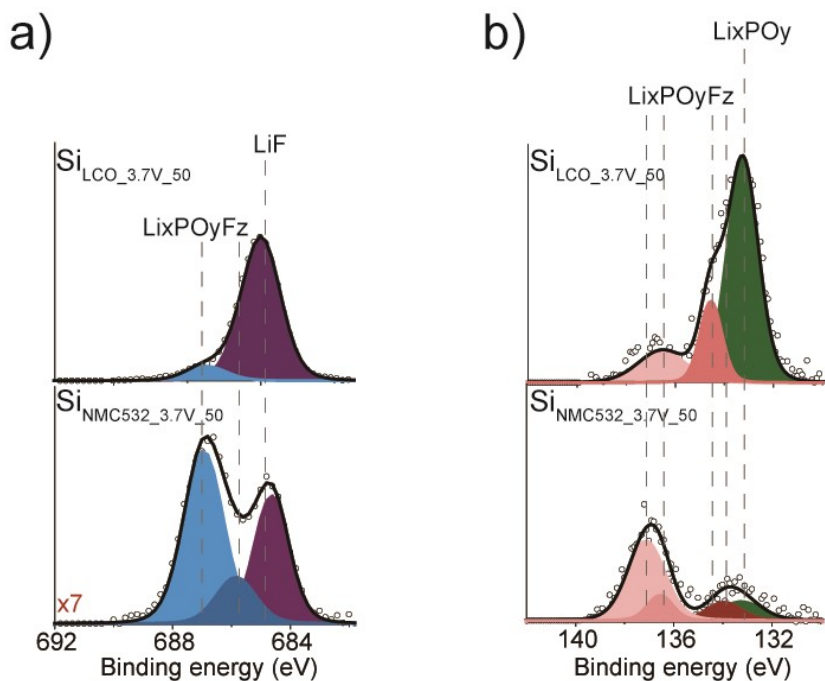


Figure S9. XPS analysis of the harvested Si extracted from LCO and NMC532 systems after 50 cycles at the C/3 rate cycled between the voltage limits of 2.7 V and 3.7 V. a) F 1s spectra; b) P 2p spectra. Black empty circles: measured data. Colored areas: fitted curves of observed components. Black solid lines: envelopes of the fitted curves. “x number” means the intensity multiplied by a factor of *number* to better show the peaks.

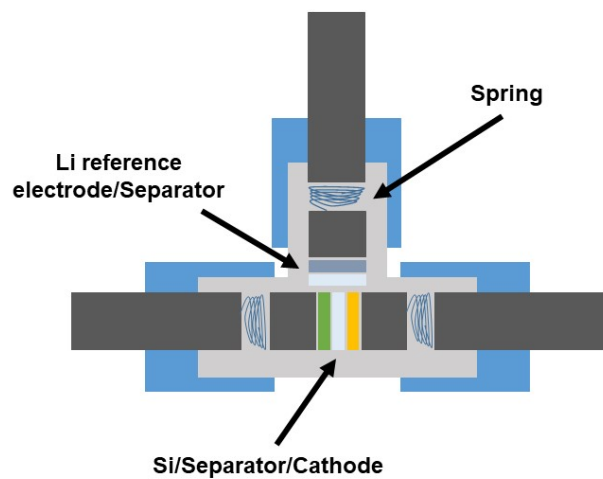


Figure S10. Configuration of the three-electrode “T”-cell used in the experiments. The dark gray rectangles in the schematic represent stainless steel rounds used as the current collectors.

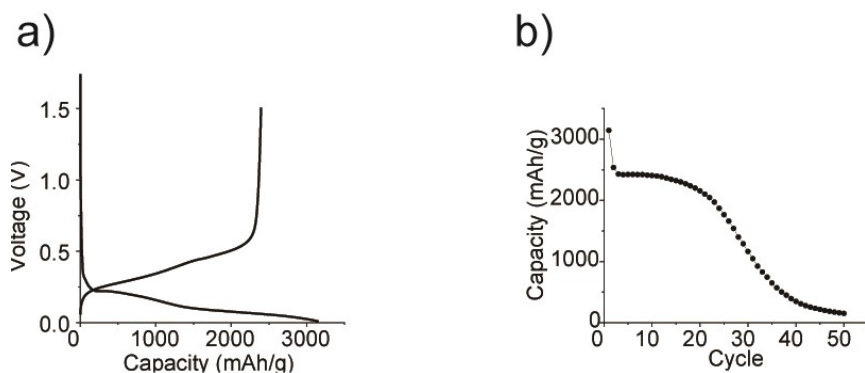


Figure S11. Electrochemical properties of fresh Si//Li half-cell. a) Capacity vs. Voltage curves of 1st cycle. Initial coulombic efficiency is ~76%. b) Cycle number vs. capacity curves during 50 cycles. C-rate was C/20, and potential window was between 0.01-1.5V.

Table S1. The 1st lithiation capacity and coulombic efficiency of three half-cells with harvested Si from each system after 2 cycles at the C/3 rate

After 2 cycles at the C/3 rate	Si _{LCO_2} half-cell	Si _{NMC532_2} half-cell	Si _{LFP_2} half-cell
The 1 st Lithiation capacity (mAh/g _{Si})	2316	2646	2687
Coulombic efficiency (%)	67.1	88.7	93.1
The 2 nd Lithiation capacity (mAh/g _{Si})	1359	2345	2569
Coulombic efficiency (%)	82.4	89.1	96.6

Table S2. The amount of Li loss in each system, after 2 cycles at the C/3 rate. Capacity loss is defined as the difference in the 2nd charge capacity between fresh and harvested cathode half-cells in Fig. 6c–e.

After 2 cycles at the C/3 rate	LCO	NMC532	LFP
Absolute Li loss capacity (mAh)	1.695	1.215	1.025
Li loss amount relative to the 2 nd charge capacity of fresh cathode/Li half cell (%)	51.5	45.7	38.1

Table S3. The 1st lithiation capacity and coulombic efficiency of three half-cells with harvested Si from each system after 50 cycles at the C/3 rate

After 50 cycles at the C/3 rate	Si _{LCO_50} half-cell	Si _{NMC532_50} half-cell	Si _{LFP_50} half-cell
The 1 st Lithiation capacity (mAh/g _{Si})	1316	1554	2420
Coulombic efficiency (%)	24.3	38.5	74.8

Table S4. The amount of Li loss in each system, after 50 cycles at the C/3 rate. Capacity loss is defined as the difference in the 2nd charge capacity between fresh and harvested cathode half-cells in Fig. 7c–e.

After 50 cycles at the C/3 rate	LCO	NMC532	LFP
Absolute Li loss capacity (mAh)	2.209	1.673	1.579
Li loss amount relative to the 2 nd charge capacity of fresh cathode/Li half cell (%)	69	61.9	59.3