Supplementary Information

Negative-to-positive electrode soluble species crossover induced accelerated interphasial degradation in lithium-ion batteries

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Experimental Section

Evaluation of coin cells

Graphite and SiO electrodes were fabricated with an active material-to-binder weight ratio of 8:2 (graphite (BTR) or SiO) and polyvinylidene fluoride (PVDF, Kureha KF-1100). The mixed powder was suspended in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich), and the resulting slurry was coated onto Cu foil with a density of 1.5 mg cm^{-2}. The coated electrode was dried at 80 ℃ under vacuum overnight. A 2032-type coin cell was fabricated by stacking Li metal (Honjo metal, 200 μm)/polyethylene (Toray)/negative electrode (SiO or graphite) and 1 *M* $LiPF_6$ in an EC/EMC (3:7=*v*:*v*, Soulbrain) electrolyte, which was injected. The cell was charged using a 0.1 *C* constant current–constant voltage (CC-CV) protocol with a cutoff voltage of 1.0 mV.

The positive electrode was composed of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811, BTR), Super P as a conductive agent, and PVDF (KF-1100, Kureha) as a binder in a weight ratio of 96:2:2. It was dispersed in NMP (Sigma-Aldrich). The resulting slurry was casted onto Al foil with an active-material loading of 8 mg cm^{-2}. The coated electrodes were pre-dried at 80 °C for 3 h and then vacuum-dried at 120 °C for 12 h. The coin cell was fabricated by stacking a Li metal/polyethylene (PE) separator/positive electrode. The electrolyte that had been stored with a negative electrode (SiO or graphite) was injected into the coin cell. Formation cycling of the Li/NCM cell was performed at 0.1 *C* in the CC-CV mode with a cutoff current of 0.05 *C* during charging, followed by CC discharge at 0.1 *C* for three cycles. After the formation cycles, cycling was conducted with 0.5 *C* CC-CV (0.05 *C* cut-off) charging and 0.5 *C* discharging for 200 cycles to evaluate the electrochemical performance.

The accumulated irreversible capacity was calculated as the sum of the irreversible capacity up to the 50th cycle of the Li/NCM half-cell. The irreversible capacity (Q_{irrev}) was defined as follows:

$$Q_{\text{irrev, n}} = Q_{\text{charge, n+1}} - Q_{\text{discharge, n}}$$

NMR analysis after electrolyte storage

After charging the Li/SiO and Li/graphite coin cells, the cells were dismantled in a dry room, and the negative electrodes were immersed in fresh 1.0 *M* $LiPF_6$ in EC/EMC (3:7=*v*/*v*, Donghwa) electrolyte of 6 ml at 60 °C for 7 d. After electrolyte storage tests, NMR analysis (Bruker Ascend 400, USA) was performed using DMSO solvent with the stored electrolyte with constant volume

Electrochemical characterization of coin cells

Electrochemical impedance spectroscopy (EIS) experiments were conducted using NCM/NCM symmetric cells. The cells were reassembled with NCM electrodes from stored SiO/NCM and graphite/NCM pouch cell and 1.0 *M* $LiPF_6$ in an EC/EMC (3:7=*v*:*v*, Soulbrain) electrolyte was injected into the cell. The pouch cells were dismantled in the fully discharged state. The EIS measurements were conducted by applying 5.0-mV voltage perturbation in the frequency range of 10.0 mHz to 3.0 MHz.

The cycling performance of reassembled Li/NCM coin cells was performed. The cells were reassembled with fresh Li metal and NCM electrode from stored SiO/NCM and graphite/NCM pouch cell using 1.0 *M* $LiPF_6$ in an EC/EMC (3:7=*v*/*v*, Soulbrain) electrolyte. The formation process was conducted via 0.1 *C* CC-CV charging (0.05 *C* cutoff) and 0.1 *C* CC discharging. Subsequent cycle performance was conducted with 0.5 *C* CC-CV (0.05 *C* cutoff) Charging and

0.5 *C* CC discharging

Linear sweep voltammetry was conducted using Li/Al coin cells. The cells were fabricated by stacking Li metal/PE separator/Al foil and injecting it into the stored electrolyte. The scan rate was 0.5 mV s^{-1}, and the voltage ranged from the open-circuit voltage to 6.0 V.

Evaluation of laminated pouch cells

The positive electrode was prepared using $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811, BTR), Super P, and PVDF (KF-1100, Kureha) in a weight ratio of 95:2.5:2.5. The mixture was dispersed in NMP (Sigma-Aldrich) and casted on 15-μm Al foil. The electrode was pre-dried at 80 °C for 3 h and then dried at 120 °C under vacuum overnight. After vacuum-drying, the electrodes were calendered to an electrode density of 3.2 mg cm^{-3}.

The SiO negative electrode consisted of SiO, flake graphite (SFG6, TIMCAL), poly(acrylic acid) (PAA, Sigma-Aldrich, Mw = 250,000), and poly(vinyl alcohol) (PVA, Sigma-Aldrich, Mw = 19,000–23,000) in a 9:1 ratio, with weight ratios of 70:20:10. The mixture was dispersed in DI water, and the resulting slurry was cast onto a 20-μm Cu foil, resulting in an areal capacity of 3.4 mA h cm^{-2}. The electrode was pre-dried for 3 h and dried at 80 °C under vacuum for 12 h. After vacuum drying, the electrode was dried at 150 °C for 1 h in a vacuum oven to crosslink the PVA and PAA binders.

The graphite negative electrode was composed of graphite (BTR), Super P, styrene–butadiene rubber (SBR, Sigma-Aldrich), and carboxymethyl cellulose (CMC, Sigma-Aldrich) (SBR:CMC = 1:1) in a weight ratio of 90:5:5. The water-based slurry was coated onto the Cu foil, resulting in an areal capacity of 3.57 mA h cm^{-2}, and pre-dried for 3 h. Subsequently, the

electrodes were dried at 80 °C under vacuum for 12 h. The SiO and graphite negative electrodes were calcined to achieve an electrode density of 1.3 mg cm^{-3}.

The pouch cell was assembled by stacking the positive electrode, the polyethylene separator, and the negative electrode. The negative-to-positive capacity (NP) ratio was maintained at 1.08 for the graphite/NCM full cell and at 1.04 for the SiO/NCM full cell. These cells were fabricated with an areal capacity of 3.3 mA h cm^{-2} for the positive electrode. The 1.0 *M* $LiPF_6$ in EC/EMC (3:7=*v*:*v*, Soulbrain) or 0.3 wt% VEC (Chunbo) + 1.0 M $LiPF_6$ in EC/EMC (3:7= *v*:*v*) electrolyte was injected into the pouch cell, followed by aging for 24 h at room temperature to allow the electrolyte to soak into the electrode and separator.

The pouch cell was formed at 0.1 *C* in the voltage range of 2.5–4.2 V, using a CC-CV protocol. After the formation cycle, the cells were subjected to 0.33 *C* CC-CV charge (0.05 *C* cutoff) and 0.33 *C* discharge for three cycles, and then fully charged (SOC 100%), followed by storage of the pouch cell at 60 °C for one week. Subsequently, 0.33 *C* CC-CV charge (0.05 *C* cutoff) and 0.33 *C* discharge cycles were conducted at 25 °C to evaluate the failure of the pouch cell. This process was repeated for 16 weeks with the cells stored at SOC 100%.

ex-situ spectroscopic and morphological analysis of coin and pouch cells

XPS (Thermo Fisher) and SEM (JEOL) were performed to investigate the surface composition and morphological changes in the electrodes. These analyses were applied to (i) the fully charged negative electrode, (ii) electrode stored in electrolyte for 7 d, (iii) Li/NCM coin cells after 200 cycles, and (iv) pouch cells after storage at 60 °C. The electrodes were disassembled in a dry room and dried under vacuum for 12 h after rinsing with EMC. Cross-sectional polishing of the electrodes was performed under cryogenic conditions using an Ar-ion beam

before SEM analysis to observe the cross sections of the electrodes. The electrodes of the Li/NCM half-cells and pouch cells were disassembled in the fully discharged state (state of charge, SOC 0%).

Calculation details

The Li-ion binding energy and adsorption energy were calculated using ORCA software version 4.2.1, through geometry optimization employing the B3LYP functional and the triple-zeta valence polarization basis set.

The adsorption energy E_{ads} was calculated using the following equation:

$$E_{ads} = E_{OPFOR\text{-}X} - E_{OPFOR} - E_X \text{ (X= SiO, C)}$$

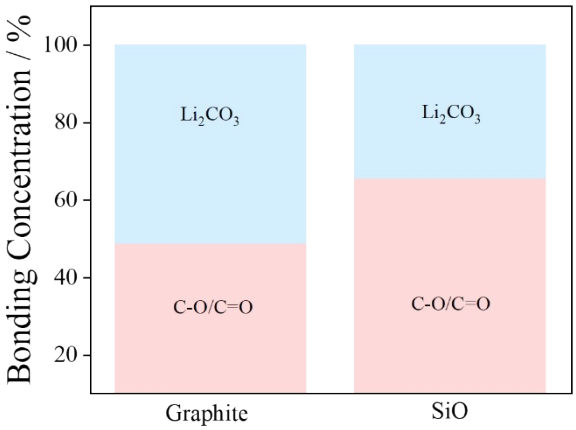

Figure S1. Bonding concentration of graphite and SiO electrode after formation

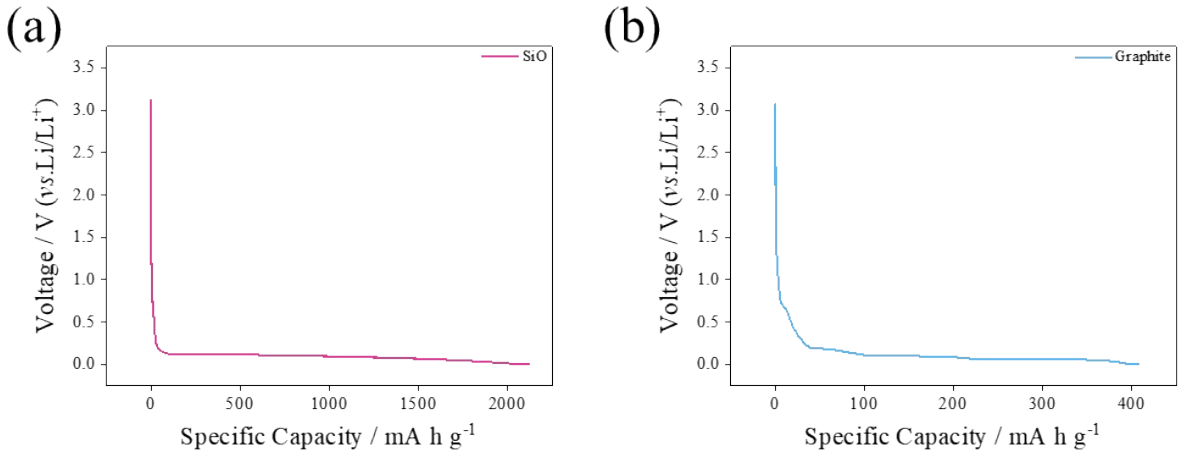

Figure S2. Lithiation voltage profiles of (a) SiO and (b) graphite electrodes

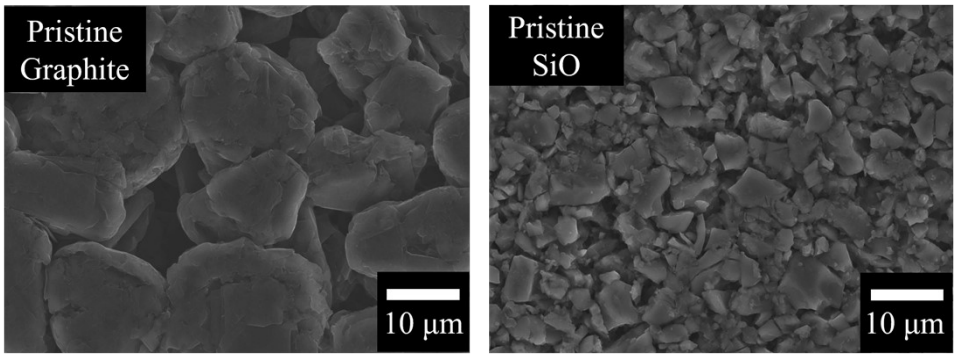

Figure S3. SEM images of pristine graphite and SiO electrodes

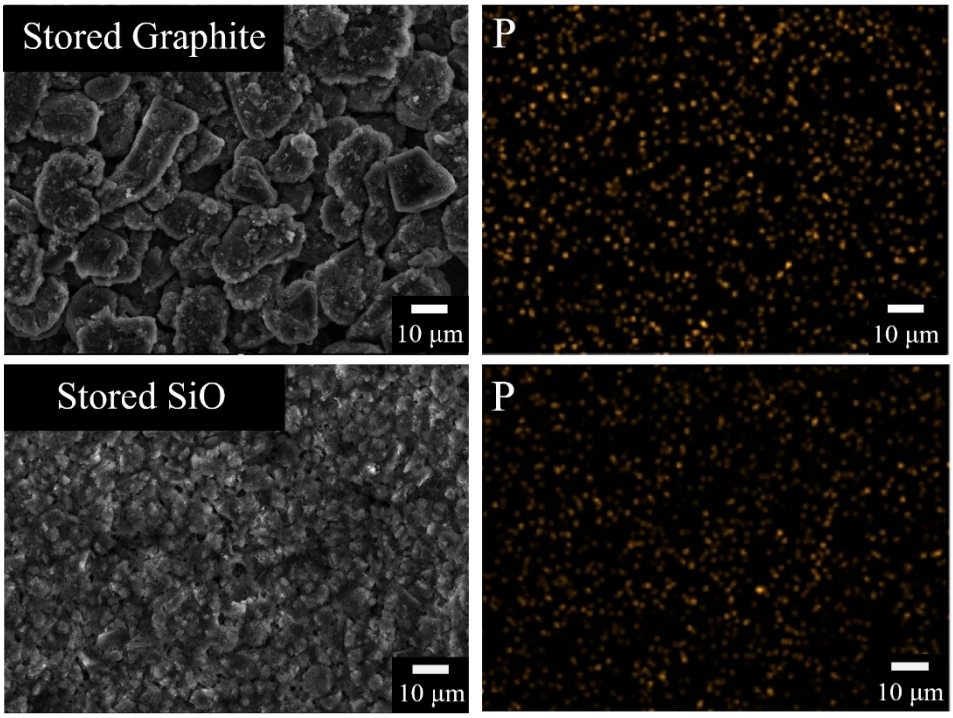

Figure S4. SEM images and corresponding P EDS maps of graphite and SiO electrodes after a week of storage at 60 °C

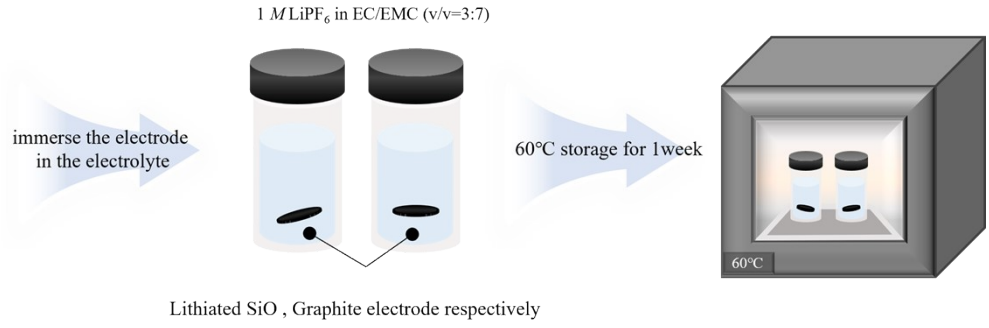

Figure S5. Experimental scheme for electrolyte storage with lithiated negative electrodes

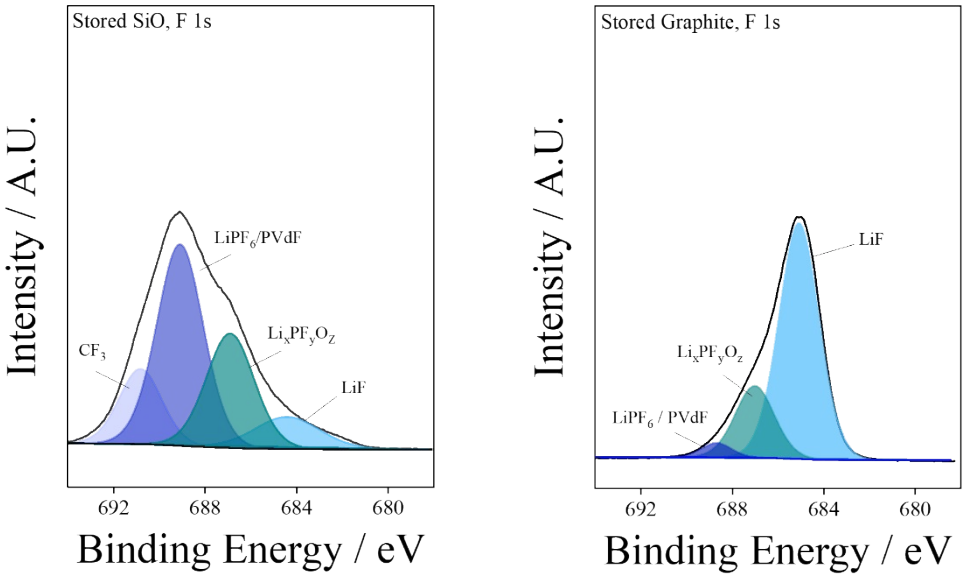

Figure S6. F 1s XPS spectra obtained from stored graphite and SiO electrodes

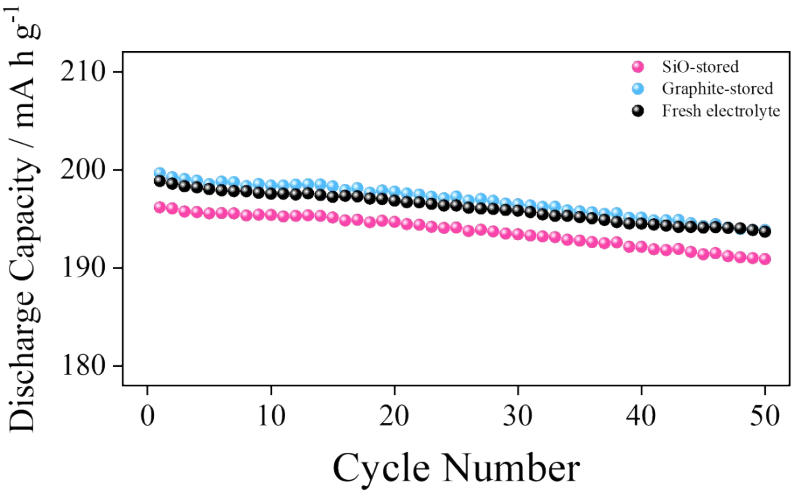

Figure S7. 0.5 *C* Li/NCM811 coin cell cycleability with stored electrolyte and fresh electrolyte

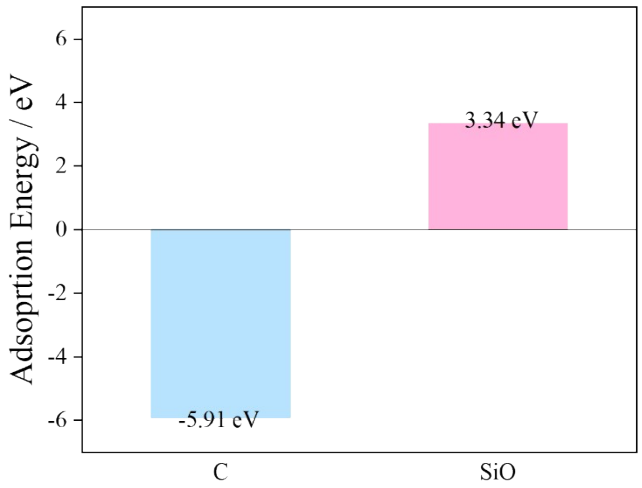

Figure S8. Calculated adsorption energy of degraded product with graphite and SiO electrodes, respectively

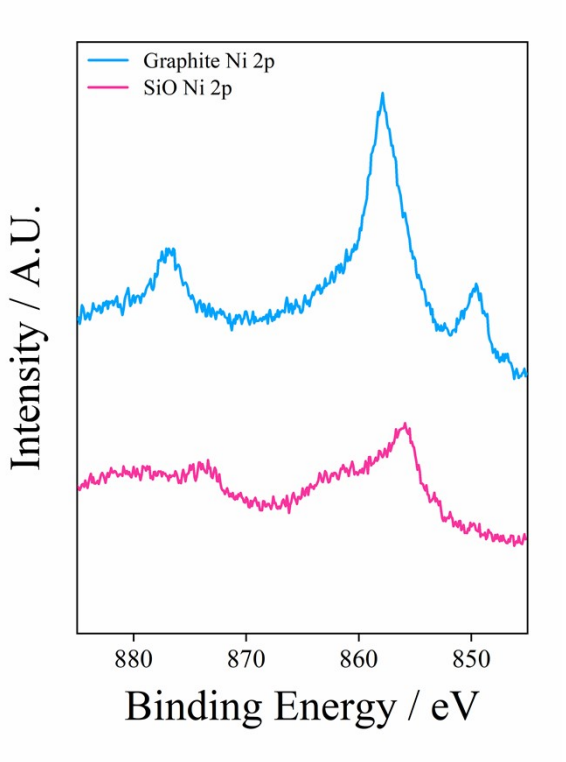

Figure S9. Ni 2p XPS spectra obtained from cycled NCM electrode with SiO and graphite stored electrolytes, respectively

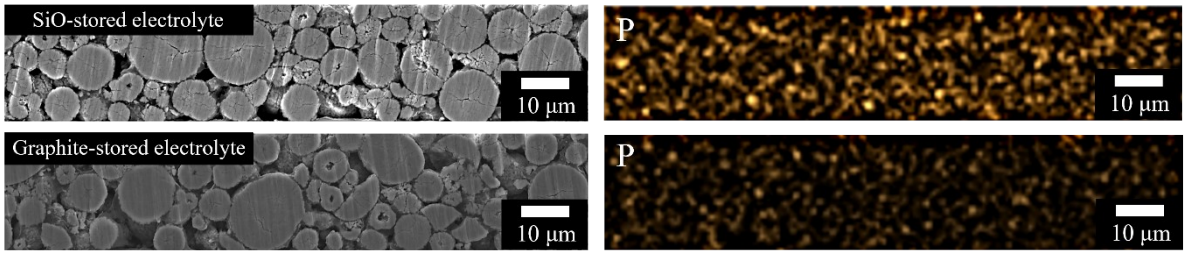

Figure S10. cross-sectional SEM images and corresponding P EDS map of NCM electrodes cycled with SiO-stored and graphite-stored electrolytes, respectively.

Graphite electrode	SiO electrode
	

Figure S11. Optical images of dismantled graphite and SiO electrodes after storage test

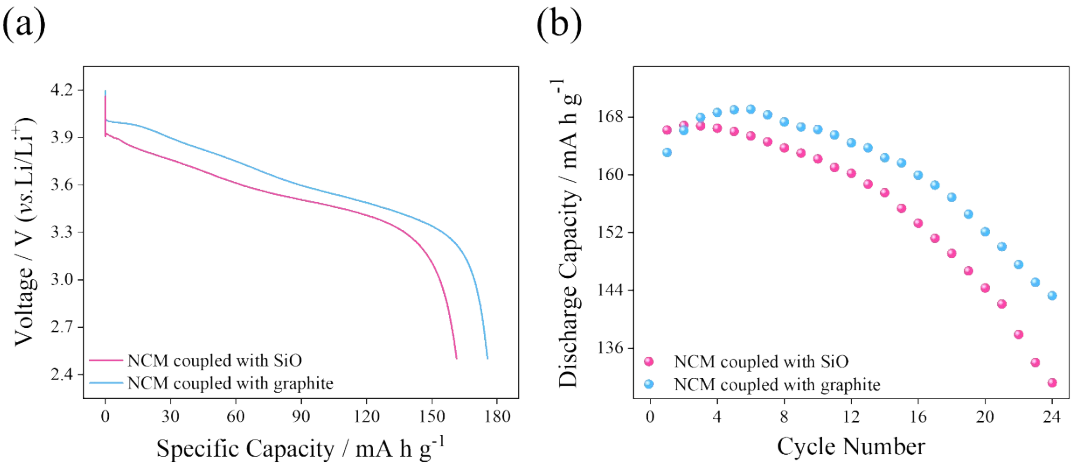

Figure S12. (a) Initial lithiation voltage profiles and (b) 0.5 *C* Cycle performances of Li/NCM811 half-cells obtained from the dismantled NCM electrode at stored SiO/NCM and graphite/NCM pouch cells.

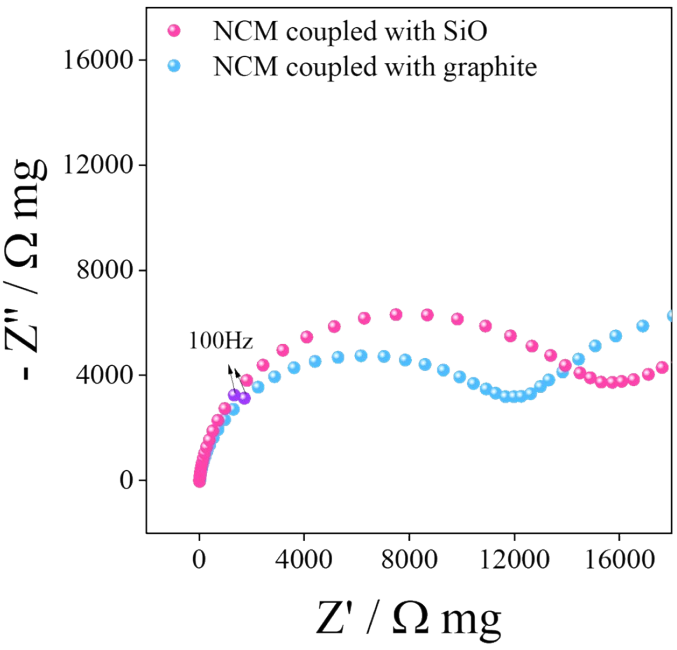

Figure S13. Nyquist plots of NCM/NCM symmetric cells from stored SiO/NCM and graphite/NCM pouch cells.

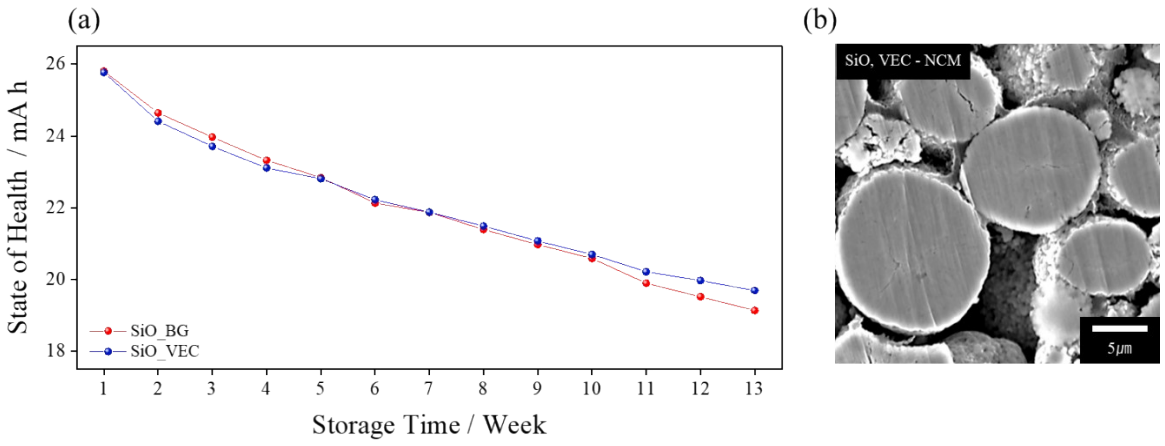

Figure S14. (a) State-of-health of background and VEC-added electrolyte comprised SiO/NCM pouch cells, (b) cross-sectional SEM images of stored NCM electrode with VEC-added electrolyte