Supporting Information for

Enhanced Cycling Stability of Ni-Rich Li-Metal Cells Enabled by Dual Vinylene Carbonate and Tris(trimethylsilyl) Borate Electrolyte Additives

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Experimental details

Electrode preparation: The electrode formulation comprises 90 wt.% active material, 5 wt.% acetylene black, and 5 wt.% PVDF (MSE Supplies LLC). NMP serves as the solvent for the PVDF binder. The dissolution of the binder in the solvent is achieved using a SpeedMixer (FlackTek, DAC 330-100 SE) operating at a rotation speed of 2000 rpm for 8 minutes. Active material and acetylene black are meticulously ground in an agate mortar for 20 minutes to ensure thorough mixing. Subsequently, the mixed powder is added to the PVDF solution and subjected to mixing in the SpeedMixer at 2000 rpm for 20 minutes. The resulting slurry is then coated onto aluminum foil and dried at 60°C for 0.5 hours, followed by further drying in a 110 °C vacuum oven overnight. The mass loading is about 4–5 mg/cm^2. The dried cathode is punched into discs with a diameter of 12 mm. SC-NMC811||Li batteries were prepared in an argon-filled glovebox (Vigor) using

CR2032 coin cell components, with lithium chips with a diameter of 15 mm as the anode and glass fiber separators (Whatman GF/D).

Cell testing: The nominal specific capacity of SC-NMC and PC-NMC was set to 200 mAh/g in all electrochemical measurements. Long cycling tests were performed at room temperature on the CT3002 LAND Batteries Tester. All NMC||Li batteries were rested on the LAND tester for 10 hours after assembly to ensure the electrolyte thoroughly infiltrated the electrode. It was then subjected to two cycles of C/3 ratio cycling at 3–4.5 V for activation, followed by cycling at different rates (C/3, 1C, 2C, and 5C) under the same cutoff voltage.

Symmetric cells: Li||Li symmetric cells were also prepared in an argon-filled glovebox (Vigor) using CR2032 coin cell components, with lithium chips (15 mm diameter) as the anode. Li||Li symmetric cells were cycled at the current density of 1 mA/cm^2 and the specific 1 mAh/cm2 capacity. SC-NMC||Li half-cells were prepared and subsequently charged to 4.5 V with a current of 0.1C. The charge was held at 4.5 V for 2 hours. Disassembled charged half-cells and washed the SC-NMC electrodes twice using DMC (dimethyl carbonate). Subsequently, one charged SC-NMC electrode and one pristine SC-NMC electrode are integrated into a single coin cell setup, positioning the charged electrode as the negative electrode and the pristine electrode as the positive electrode. To offset the decreased thickness caused by the lack of lithium anodes, install an extra spacer measuring 0.5mm. Symmetric cells were cycled between -1 V to 1 V at 1C after two cycles of activation at C/3. The SC-NMC||Li half-cell separators were designed with a PP separator layer on the SC-NMC cathode side and a Glass fiber separator layer on the lithium metal side to prevent adhesion between the Glass fiber separator and NMC electrode. One layer of Glass fiber separator was used for the symmetric cell.

X-ray Photoelectron Spectroscopy (XPS): The Kratos Axis Supra XPS (X-ray Photoelectron Spectroscopy) system equipped with Al kα X-ray source was used to probe the interphase composition of SC-NMC cathodes after cycles between 3.0–4.5 V at a rate of 2C. The disassembly of SC-NMC||Li half-cells with four distinct electrolytes with and without additives was performed using a long-nose plier and a diagonal plier in an argon-filled glovebox. After briefly cleaning the electrolyte residual using dimethyl carbonate solvent, the cycled SC-NMC cathodes were recovered and taped onto the sample holder for XPS. The XPS sample holder was sealed in an aluminum laminated film bag in the Ar-filled glove box. The bag was promptly transported to the

XPS room, and the sample was loaded into the XPS vacuum chamber immediately after opening the bag to minimize air exposure. C1s, F1s, O1s, Si1s, P1s, Li1s, B1s, and Si1s spectra were conducted to determine the composition of CEI and SEI.

Electrochemical Impedance Spectroscopy (EIS): EIS was examined at a discharged state of 3.0 V within a frequency range of 0.01 Hz to 100 kHz on BioLogic SP-300 potentiostat.

Soft X-ray Absorption Spectroscopy (soft XAS): XAS measurements were carried out at the Stanford Synchrotron Radiation Lightsource (SSRL) bending magnet beamline 8–2 at a 55° incidence angle (magic angle) of X-ray incidence. Beamline 8–2 is equipped with multiple spherical gratings as described in Ref [Tirsell NIMA 291 (1990), 511-517].[1] The spectra were recorded using the 1000 lines/mm grating operated with 60x60 um slits for the Ni L-edge data (~0.35 eV resolution). The spot size at the interaction point was around 1 × 1 mm^2 and the total flux was in the order of 10^{10} photons/s for which beam damage was not noticeable even for extended exposure. The data were collected both in the total electron yield (TEY) and total fluorescence yield (TFY) modes using the drain current (amplified by a Keithley picoammeter) for TEY and a Silicon Diode (IRD AXUV-1000) for TFY. The incoming flux was recorded using a nickel grid with an Au sputtered film (i0), collected in TEY, mounted upstream of the end station. Powder or electrode samples were loaded on carbon tape and then stuck to an aluminum sample holder.

Transmission Electron Microscopy: Cryo-TEM experiment was performed on JEOL1400 at the accelerating voltage of 120 kV with a Gatan LN2 transfer specimen holder.

Supporting Figures

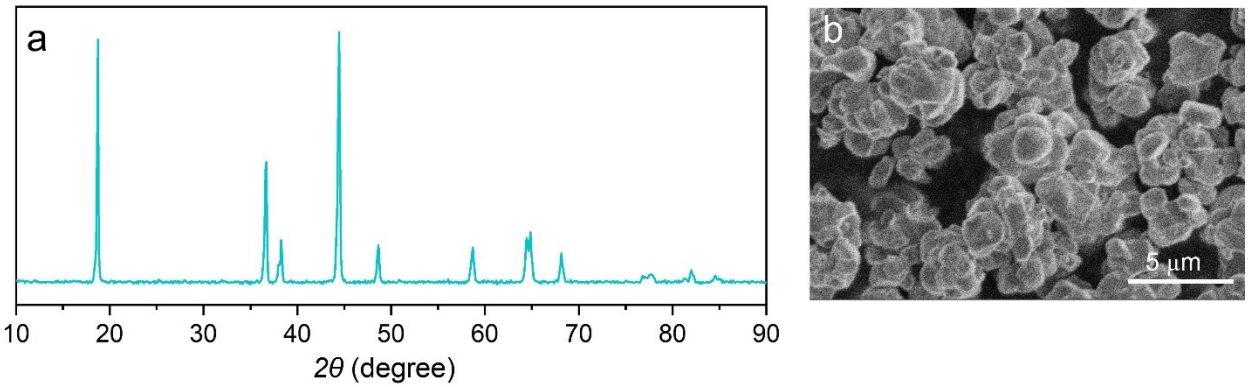

Figure S1 (a) XRD pattern of the single-crystal NMC811 cathode, (b) SEM image of the SC-NMC particles.

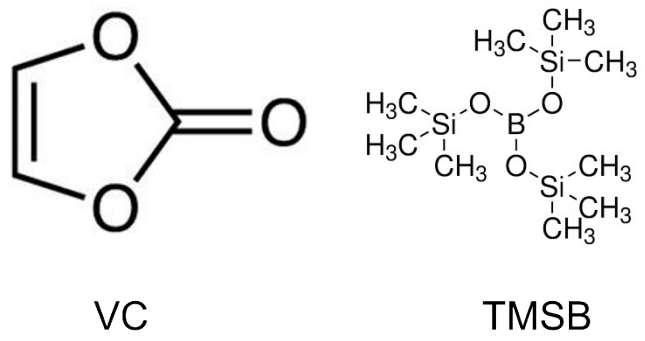

Figure S2 Molecular structure of the two additives used in this work.

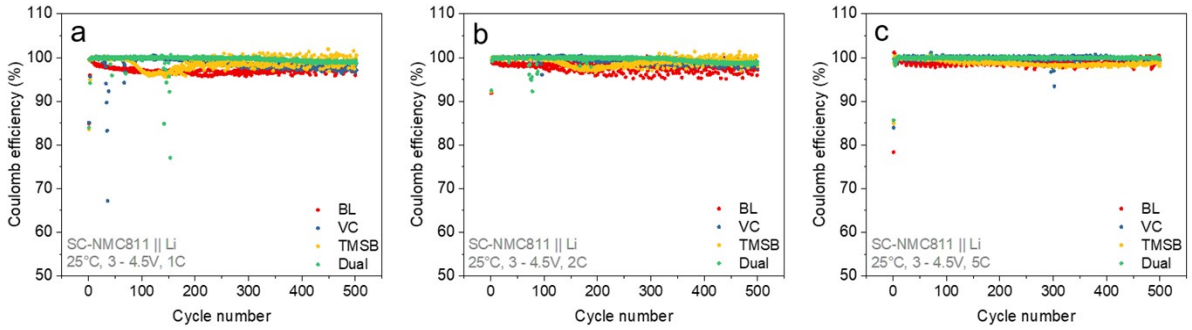

Figure S3 Columbic efficiency of the SC-NMC||Li cells without and with different additives cycled at 1C (a), 2C (b), and 5C (c).

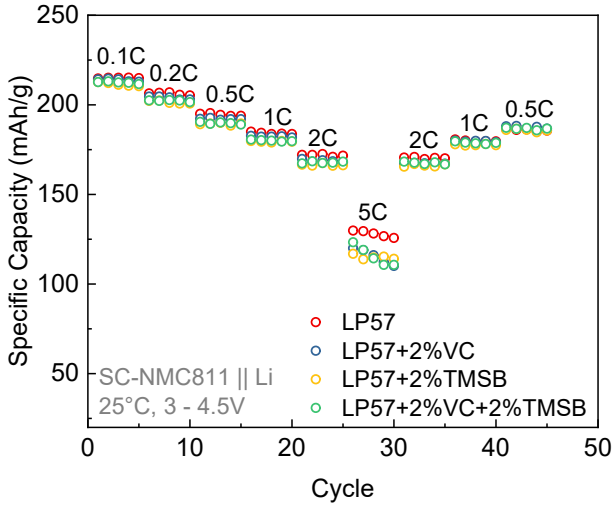

Figure S4 Rate capability of the cells containing SC-NMC cathode, Li metal anode, and electrolyte without or with different additives.

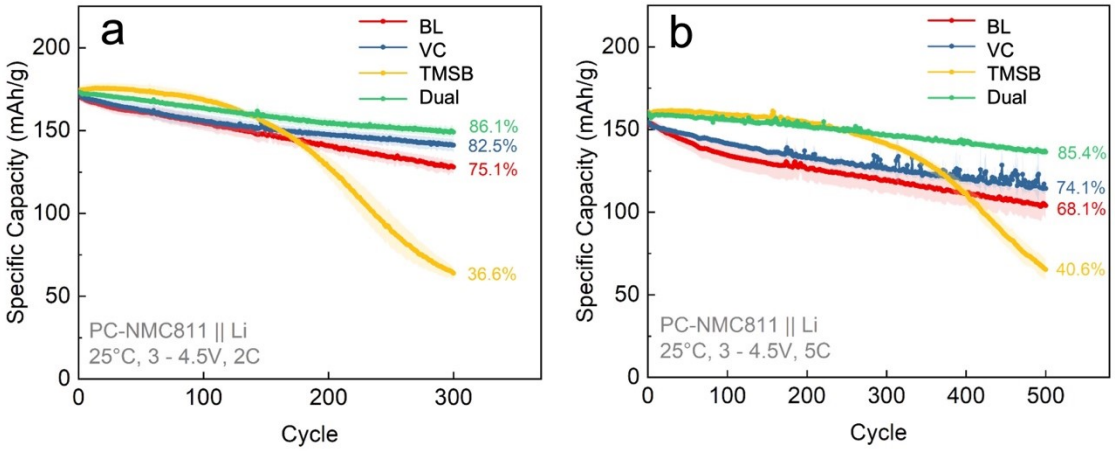

Fig. S5 Long-term cyclability of cells containing PC-NMC as the cathode and Li metal as the anode containing different additives cycled within 3.0–4.5 V vs. Li/Li$^+$. (a) The current rate of 2C and (b) the current rate of 5C.

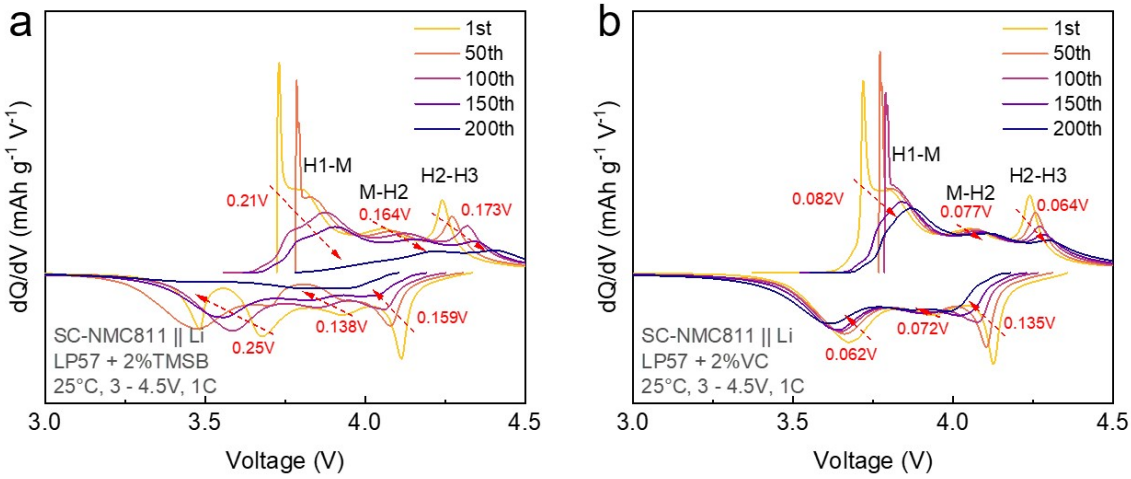

Figure S6 dQ/dV curves of the SC-NMC||Li cells containing (a) TMSB or (b) VC additives cycled at 1C within the voltage range of 3.0–4.5 V vs Li/Li$^+$ at the 1st, 50th, 100th, 150th, and 200th cycles.

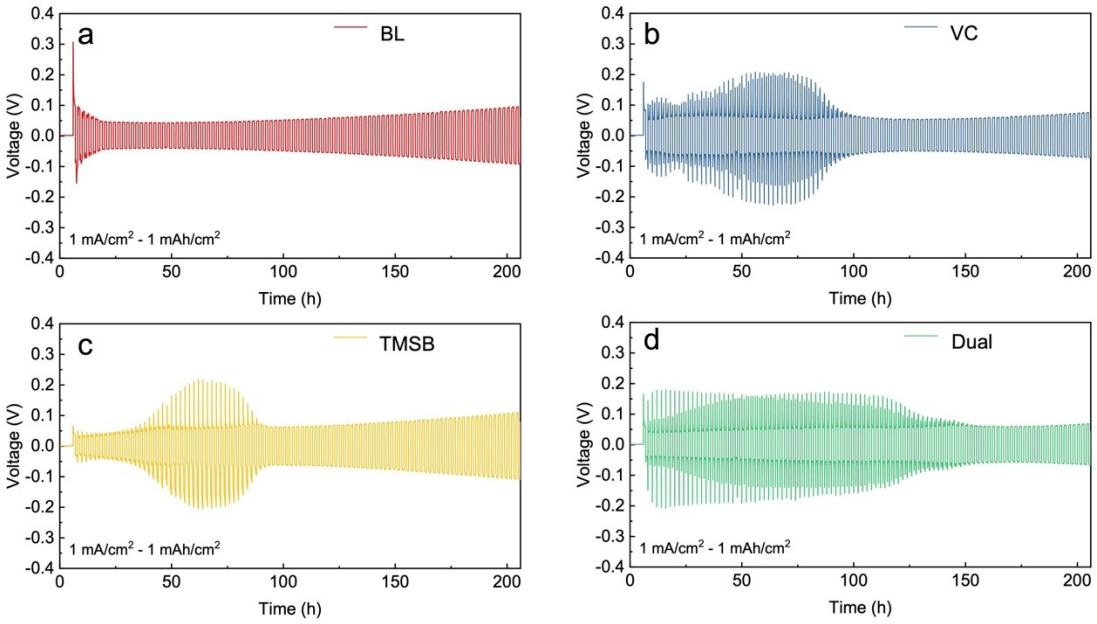

Figure S7 Cycle stability of Li||Li symmetric cells with (a) BL, (b) VC additive, (c) TMSB additive, and (d) dual additives at the current rate of 1 mA/cm^2.

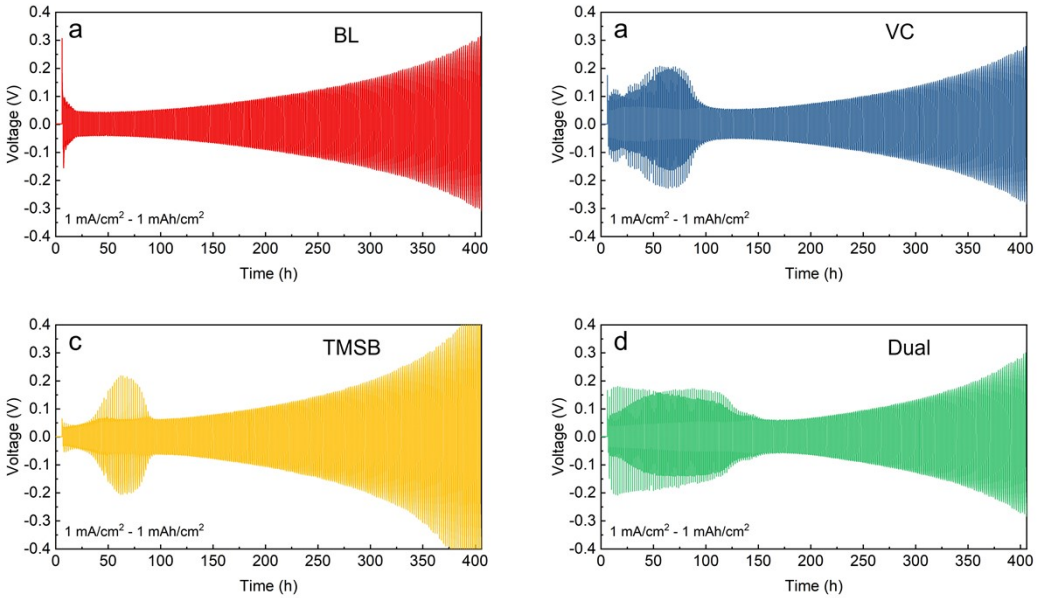

Figure S8 Cycle stability of Li||Li symmetric cells with (a) BL, (b) VC additive, (c) TMSB additive, and (d) dual additives at the current rate of 1 mA/cm^2 for 400 h.

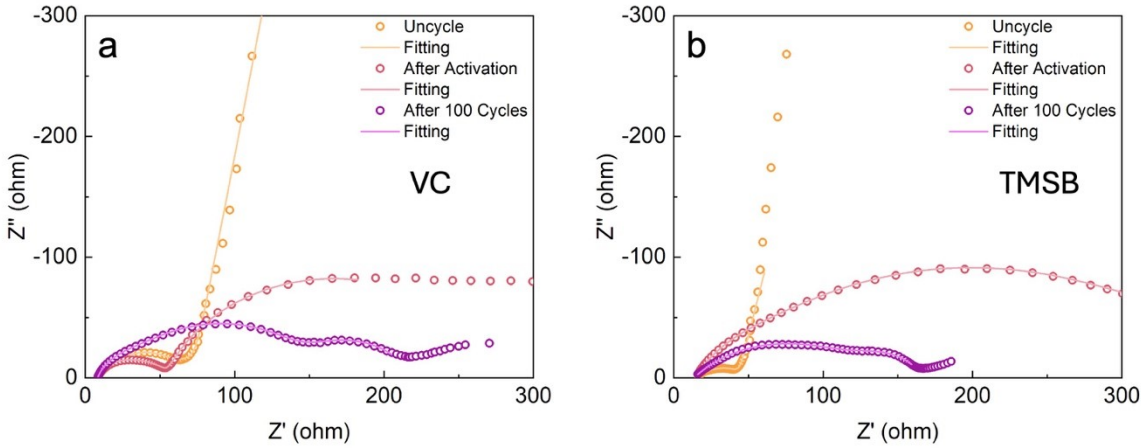

Figure S9 Nyquist plot of the SC-NMC||Li cells before cycling, in the discharge of 3.0 V after two activated cycles at C/3, and after 100 cycles at 2C containing different electrolyte additives (a) VC and (b) TMSB additives.

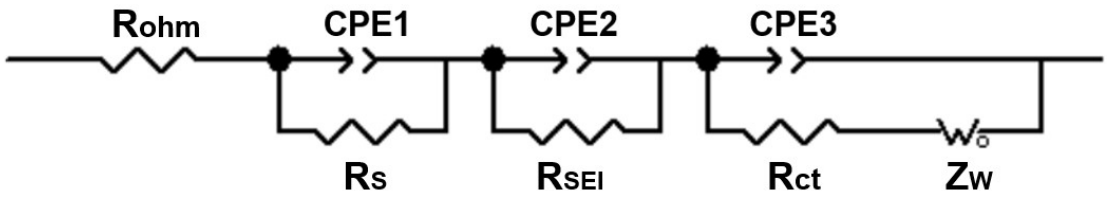

Figure S10 Equivalent circuit model of the cells containing SC-NMC811 cathode and Li metal anode.

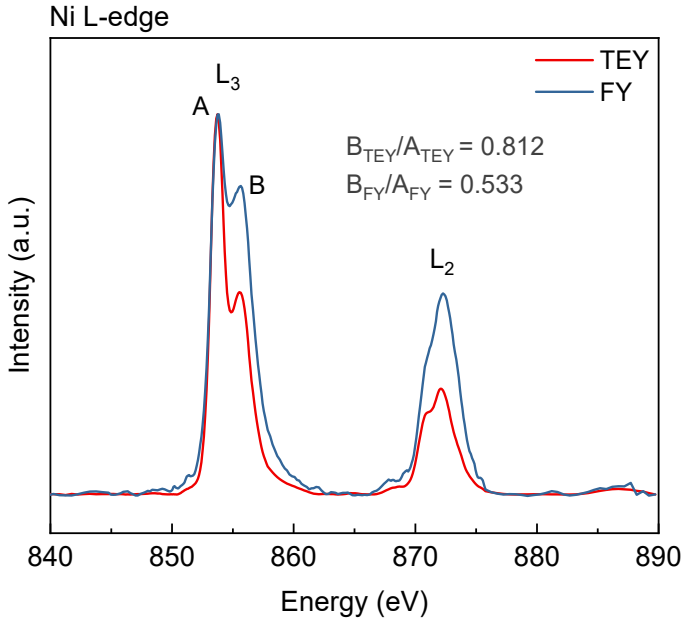

Figure S11 Soft XAS of Ni *L*-edge of the pristine SC-NMC811 cathode.

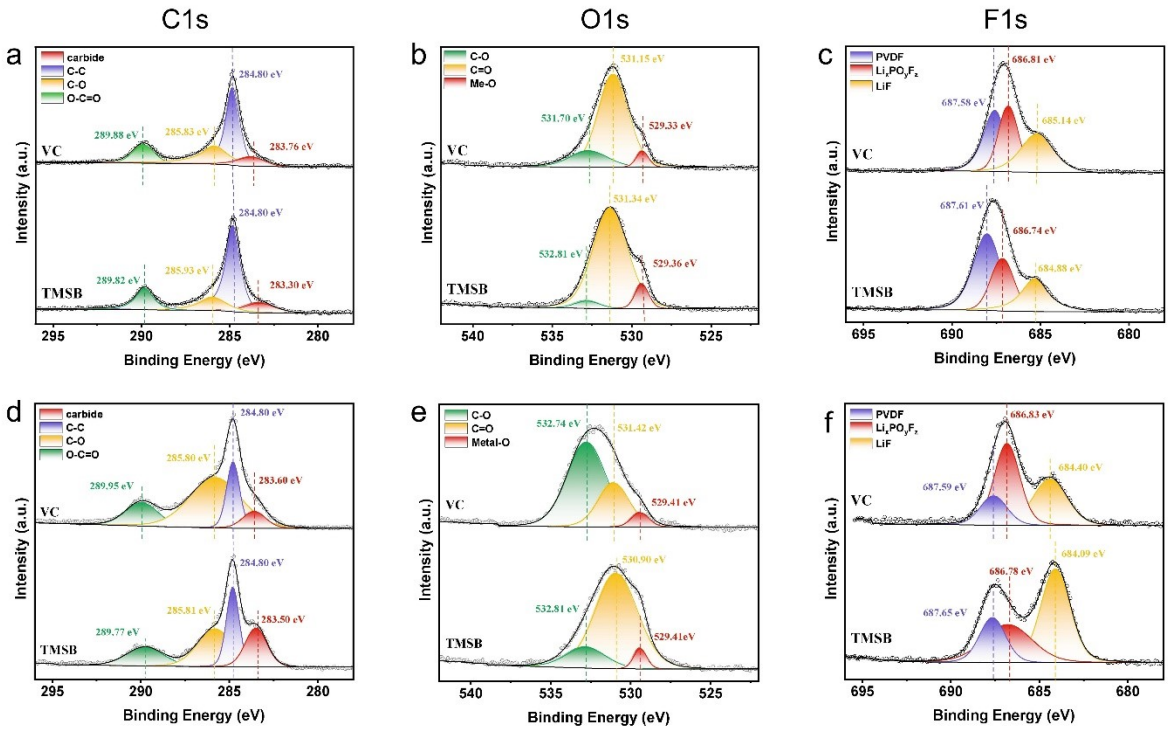

Figure S12 XPS analysis of the cycled SC-NMC cathodes of (a) C1s (b) O1s (c) F1s after the activation cycles and (d) C1s (e) O1s (f) F1s after 100 cycles with VC and TMSB additives.

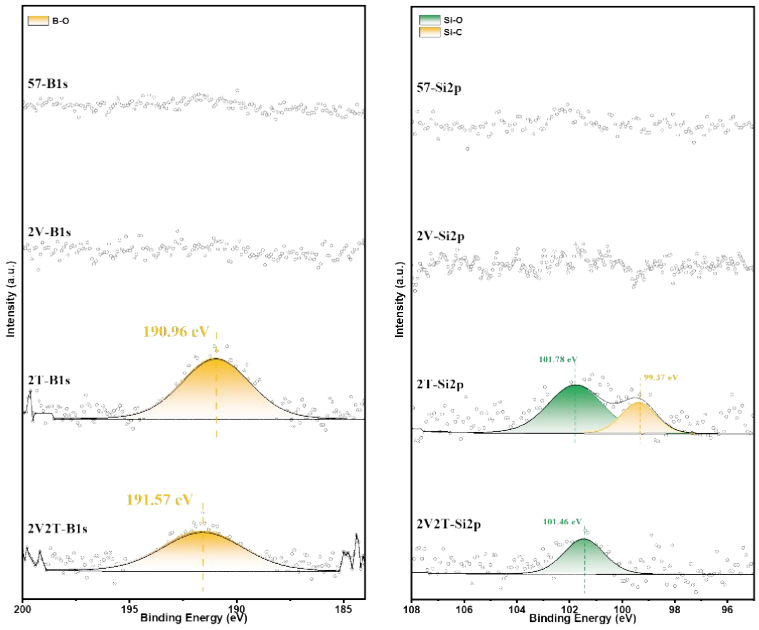

Figure S13 XPS analysis of the cycled SC-NMC cathodes of (a) B1s, and (b) Si2p after the activation cycles and (d) C1s (e) O1s (f) F1s after 100 cycles at 1C between 3.0–4.5 V vs. Li/Li^+.

Supporting Table 1: The EIS fitting data of the SC-NMC||Li cells.

	R_{SEI} (Ω) Uncycled	Rct (Ω) Uncycled	R_{SEI} (Ω) After activations	Rct (Ω) After activations	R_{SEI} (Ω) After 100 cycles	Rct (Ω) After 100 cycles
LP57	73.3	/	137.63	189	49.4	115.6
VC	44.5	/	45.76	225.6	138.7	70.5
TMSB	30.3	/	353.44	400.1	116.8	36.7
Dual	14.9	/	46.61	172.7	91.1	43.2

Supporting Table 2: XPS surface composition and fitting of C1s, O1s, F1s peaks.

		BL (%)		VC (%)		TMSB (%)		Dual (%)	
		activation	100 cycles	activation	100 cycles	activation	100 cycles	activation	100 cycles
C1s	Carbide	27.4	7.4	10.6	8.8	11.5	21.8	14.5	0
	C-C	27.4	31.3	47.2	18.7	58	26.1	52.2	25
	C-O	33.3	38.9	26.7	55.8	15	34.1	19.3	52.8
	CO_3	11.8	22.4	15.5	16.6	15.6	18	14	22.2
O1s	C-O	42.5	14.7	17	57.4	4.6	16.5	12.6	54.5
	C=O	52.5	82.1	77.6	39.5	86.9	78.4	71.6	31.9
	M-O	5	3.2	5.4	3	8.5	5.1	15.9	13.6
F1s	PVDF	14	31.2	32.4	17.4	48.9	19.7	44.1	39.3
	$Li_xPO_yF_z$	16.7	21.2	32.6	47.5	27.5	32.1	35.4	44
	LiF	69.3	47.6	35	35.1	23.6	48.2	20.5	16.7

1. Tirsell, K. G.; Karpenko, V. P., A general purpose sub-keV X-ray facility at the Stanford Synchrotron Radiation Laboratory. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment* **1990,** *291* (1), 511-517.