

Supplementary Information

Trimethylsilyl azide (C₃H₉N₃Si): A highly efficient additive for tailoring the fluoroethylene carbonate (FEC) based electrolyte in Li-metal batteries

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Experimental Section

Preparation of electrolytes. Lithium hexafluorophosphate (LiPF_6 , Sigma–Aldrich) was used without any pretreatment. Ethyl methyl carbonate (EMC, TCI), fluoroethylene carbonate (FEC, TCI), and trimethylsilyl azide (TSA, Sigma–Aldrich) were purified by molecular sieves until the final water content was <10 ppm, as determined using Mettler–Toledo Karl–Fischer titration without exposure to air. The baseline electrolyte was prepared by dissolving 1 M LiPF_6 in a solution of EMC:FEC = 3:1 (v/v) (EF-31). TSA-added electrolytes were prepared via the addition of different amounts of TSA to baseline electrolyte.

Synthesis of FCG73 cathode. Spherical full-concentration gradient (FCG) $[\text{Ni}_{0.75}\text{Co}_{0.10}\text{Mn}_{0.15}](\text{OH})_2$ precursors were synthesized via the coprecipitation method.^{S1} To obtain Al 2 mol%-doped FCG $\text{Li}[\text{Ni}_{0.75}\text{Co}_{0.10}\text{Mn}_{0.15}\text{O}_2]$ cathode, the obtained FCG $[\text{Ni}_{0.75}\text{Co}_{0.10}\text{Mn}_{0.15}](\text{OH})_2$ precursor was mixed with $\text{LiOH}\cdot\text{H}_2\text{O}$ and $\text{Al}(\text{OH})_3\cdot 3\text{H}_2\text{O}$ (molar ratio of $\text{Li}:(\text{Ni} + \text{Co} + \text{Mn}):\text{Al} = 1.01:0.98:0.02$), followed by calcination at 790°C for 10 h in flowing O_2 . The chemical composition of the prepared $\text{Li}[\text{Ni}_{0.73}\text{Co}_{0.10}\text{Mn}_{0.15}\text{Al}_{0.02}]\text{O}_2$ (FCG73) powders was determined by ICP (OPIMA 8300, Perkin Elmer).

Material characterization. The morphologies of the Li deposited on Cu foil in the Li/Cu cells were observed using scanning electron microscopy (SEM; FEI Nova NanoSEM 450). Because Cu foil was used as the substrate for Li deposition, it was possible to strip the deposited Li completely from the substrate, whereupon we observed a thin film attached to the surface of the Cu foil. This layer was the SEI and was analyzed using X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The chemical compositions of the SEI layer formed on the Li metal were analyzed using XPS (K-Alpha+). The C1s peak (284.8 eV) was utilized as a reference to calibrate the other binding-energy values. To analyze the element distribution in the SEI layer, TEM was performed. The Li metals were washed with EMC to remove the Li residues and then dried under vacuum before the characterizations. To avoid side reactions and the contamination of the electrode by O_2 and moisture, the samples were transported from the glovebox to the SEM and XPS instruments in a hermetically sealed container filled with Ar gas.

Electrochemical test. Li/Li symmetric-cell tests were conducted using VMP3 Biologic instruments that were set for galvanostatic cycling with a current density of 2.0 mA cm^{-2} . The stripping and plating times were 1 h each. The amount of electrolyte solution used was $100 \text{ }\mu\text{L}$ /symmetric cell. To investigate the kinetic behavior during the Li stripping/plating, the Li/Cu cells were cycled within the voltage range of -0.5 to 1.0 V at a current density of 2.0 mA cm^{-2} . The average Coulombic efficiency was measured using Li/Cu cells. In the Li/Cu cells, the Cu substrate was preconditioned with a single Li deposition/stripping cycle at a capacity of 4 mAh cm^{-2} prior to the deposition of the Li reservoir, and the cutoff voltage was 1.0 V . Then, 4 mAh cm^{-2} Li plating on the Cu substrate was performed, providing the only Li source. Cycling was performed at 0.4 mA cm^{-2} ($Q_C = 0.5 \text{ mAh cm}^{-2}$) for 10 cycles. The final stripping was performed at 0.4 mA cm^{-2} to 1 V . The LMBs were prepared using the FCG73 cathode, an anode made of Li metal foil ($200 \text{ }\mu\text{m}$ thick), a separator (Celgard 2400), and the prepared electrolytes ($75 \text{ }\mu\text{L}$ in each battery). The positive electrodes were prepared by mixing FCG73 as an active material, carbon black (Super P and KS-6), and a polyvinylidene difluoride binder (90:5.5:4.5) on an Al-foil current collector. The active-material loading of the prepared cathodes was ~ 10.0 and $\sim 20.0 \text{ mg cm}^{-2}$. The electrochemical performance was tested between 2.7 and 4.3 V vs. Li/Li^+ at $30 \text{ }^\circ\text{C}$. Prior to long-term cycling, formation cycles at current densities of 0.2 , 0.5 , and 1.0 mA cm^{-2} were conducted. The long-term cycling test was performed at a current density of 2.0 mA cm^{-2} . Electrochemical impedance spectroscopy was performed using a multi-channel potentiostat over the frequency range of 1 MHz to 1 Hz . Electrochemical tests of Li/FCG73 cells were also performed with pouch-type cells ($3 \text{ cm} \times 5 \text{ cm}$).

Table S1. Comparison of the cycling performance of proposed Li/FCG73 battery with previous literatures using FEC containing electrolyte solution.

Cathode	Cathode Loading (mg cm ⁻²)	Voltage Window (V)	Areal capacity (mAh cm ⁻²)	Current density (mA cm ⁻²)	Best Cycling	Ref.
NCM622	~18.3	2.8-4.3	3.3	0.5	90	S2.
NCM333	~13.6	2.7-4.3	2.0	2.0	250	S3.
NCM622	~18.3	2.8-4.3	3.3	2.0	100	S4.
NCM333	~10.0	2.7-4.3	1.5	0.5	250	S5.
NCM523	~12.0	3.0-4.3	1.9	1.8	100	S6.
FCG73	~20.0	2.7-4.3	4.0	2.0	300	This work
	~10.0	2.7-4.3	2.0	2.0	600	

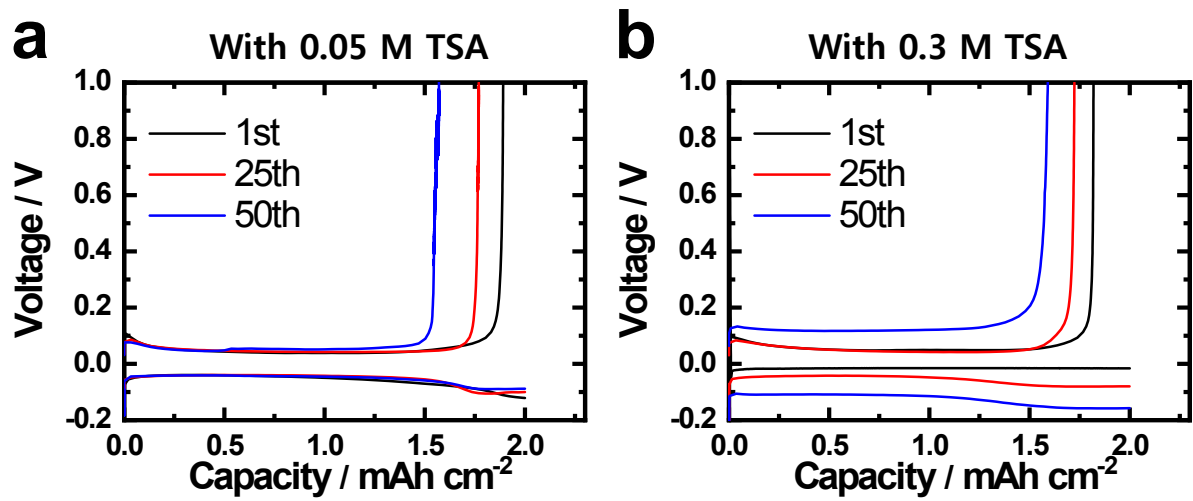


Fig. S1 Voltage profiles of asymmetric Li Cu cells using a different amount of TSA additive at a current density of 2.0 mA cm^{-2} during 50 cycles: (a) with 0.05 M and (b) 0.3 M TSA additive.

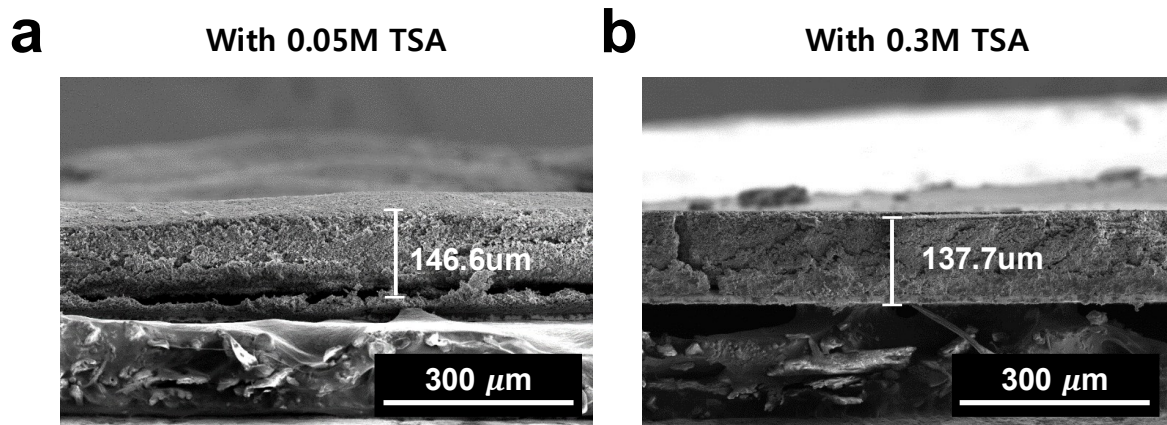


Fig. S2 Cross-section SEM images of accumulated Li layer on Cu foil retrieved from Li/Cu asymmetric after 50 cycles: using (a) 0.05M TSA added electrolyte and (b) with 0.3M TSA added electrolyte.

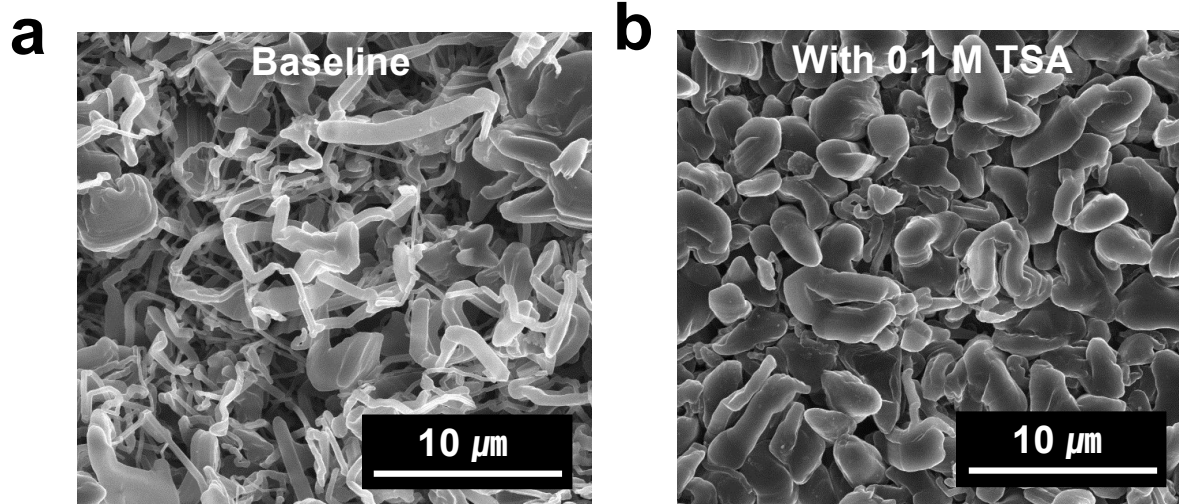


Fig. S3 Comparison of SEM images of deposited Li morphologies from Li/Cu cells using different electrolyte solutions: (a) baseline electrolyte and (b) 0.1M TSA-containing electrolyte.

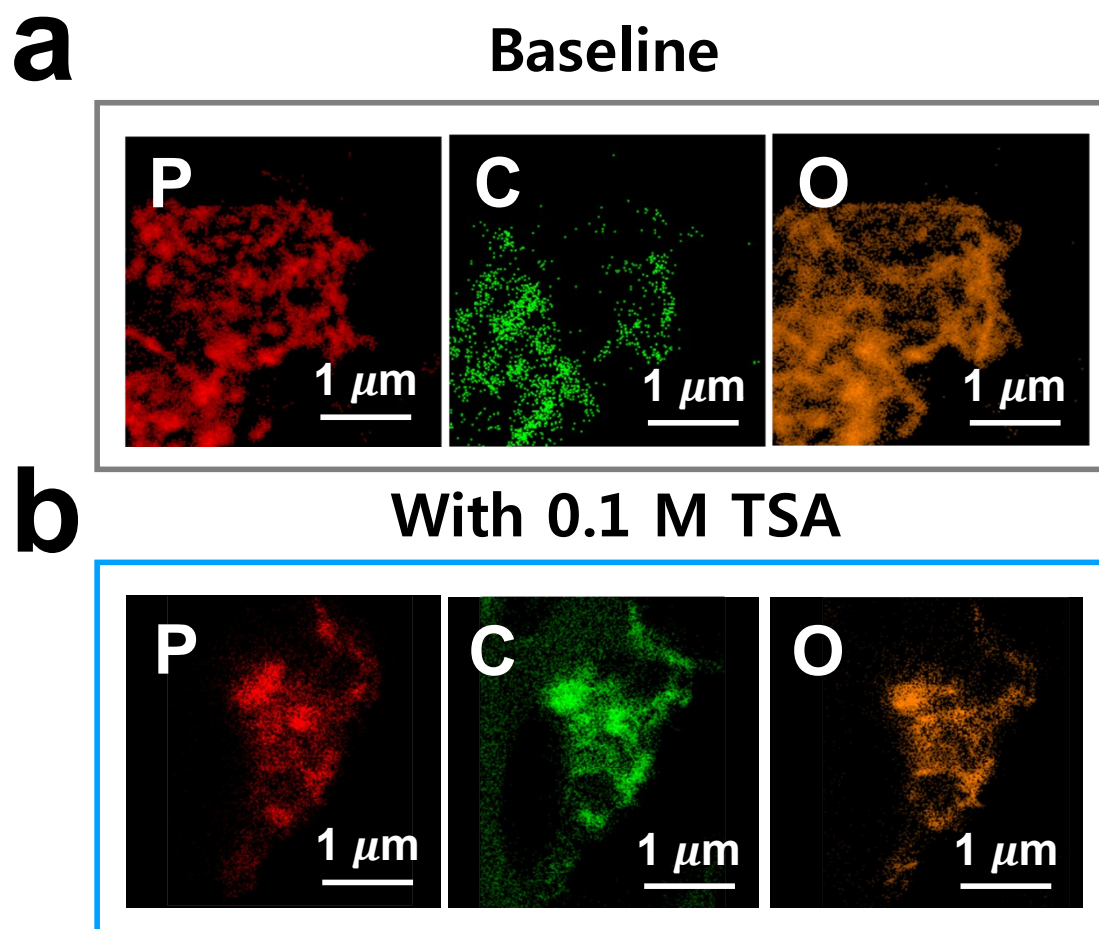


Fig. S4 TEM EDX mapping images of the SEI layer derived from Li/Cu cells using different electrolyte solution: (a) baseline electrolyte and (b) 0.1M TSA-containing electrolyte.

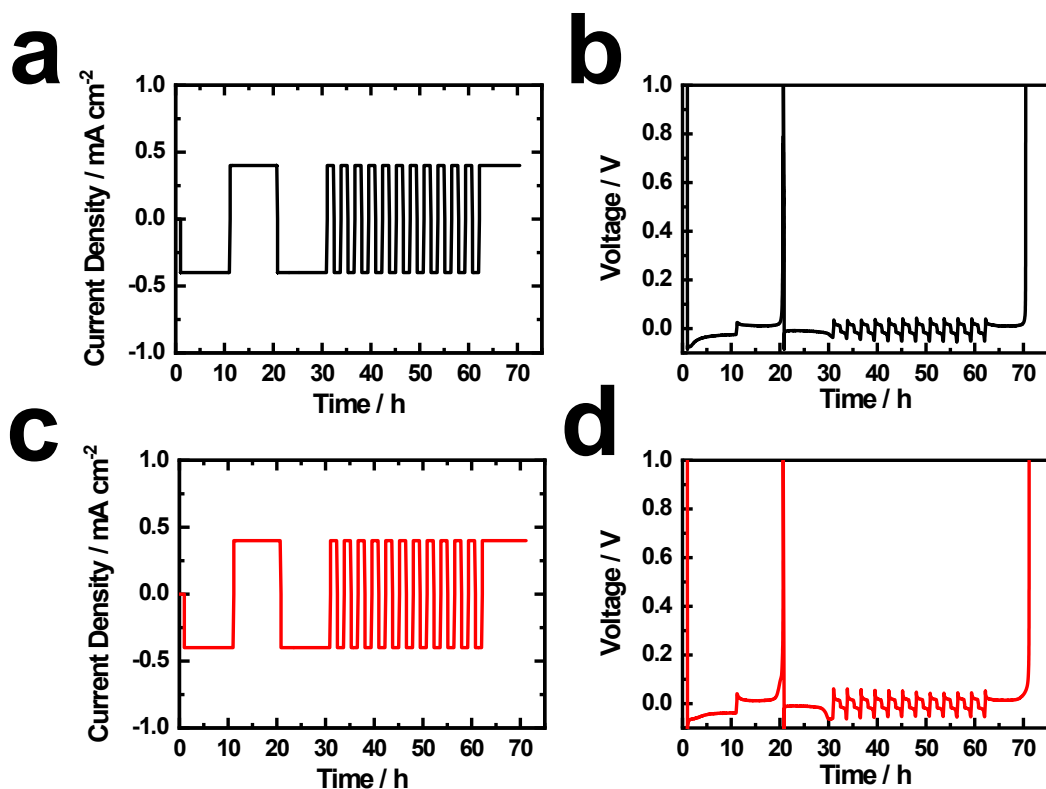


Fig. S5 (a and c) The constant current protocol and (b and d) the measured voltage versus time plot for the Li/Cu cells. (a, b) baseline electrolyte and (c, d) 0.1M TSA-containing electrolyte.

From the Li/Cu cells in Fig. S5, we could calculate the average coulombic efficiency of the electrolyte following two equations.

$$1. \quad CE_{avg} = \frac{nQ_C + Q_S}{nQ_C + Q_T}$$

In this method, a given amount of charge (Q) is used to deposit Li onto the Cu substrate first as a Li reservoir, then a smaller portion of this charge (Q_c) is used to cycle Li between working and counter electrodes for n cycles. After n cycles (where, the number of cycles n is 10), a final exhaustive strip of the remaining Li reservoir is

performed to the cut-off voltage. The final stripping charge (Q_s), corresponding to the quantity of Li remaining after cycling, is measured.

From equation 1, the average coulombic efficiency of the electrolytes was determined to be 92.2 % for baseline electrolyte and ~ 96 % for modified electrolyte with 0.1 M TSA additive.

$$2. \quad CE_{avg} = \frac{Q_{dissolution}}{Q_{deposition}}$$

In this method, a given amount of Li metal is plated ($Q_{deposition}$) onto the Cu substrate which has no Li in the initial state, followed by stripping Li metal from the Cu substrate to a cut-off voltage. All the removal Li ($Q_{dissolution}$) has been stripped from the surface of the Cu substrate.

From equation (2), the average coulombic efficiency of the electrolytes was determined to be 99.84 % for baseline electrolyte and 99.95 % for modified electrolyte with 0.1 M TSA additive.

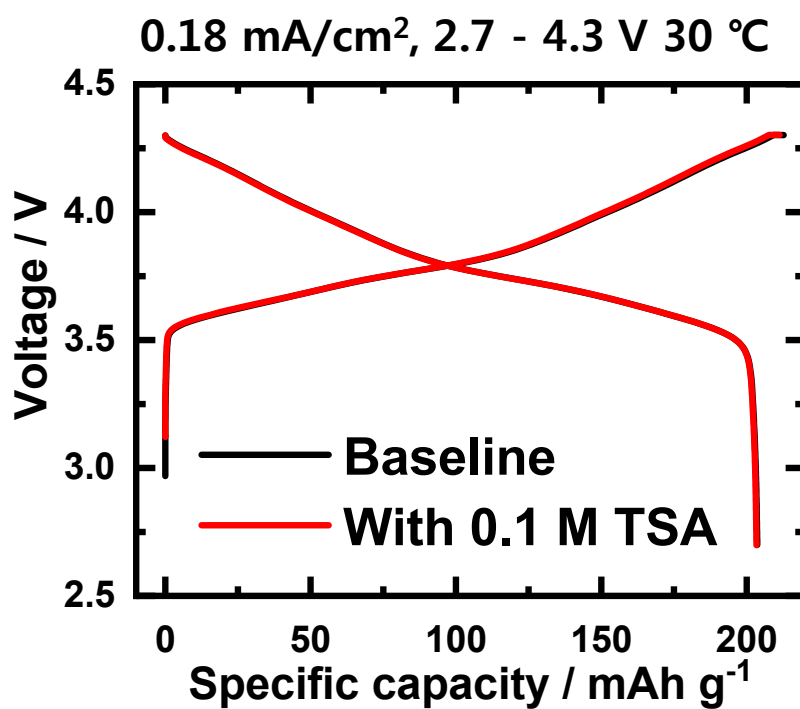


Fig. S6 Initial charge-discharge voltage profiles of Li/FCG73 batteries depending on with / without TSA additive in the electrolyte solution at 0.1 C.

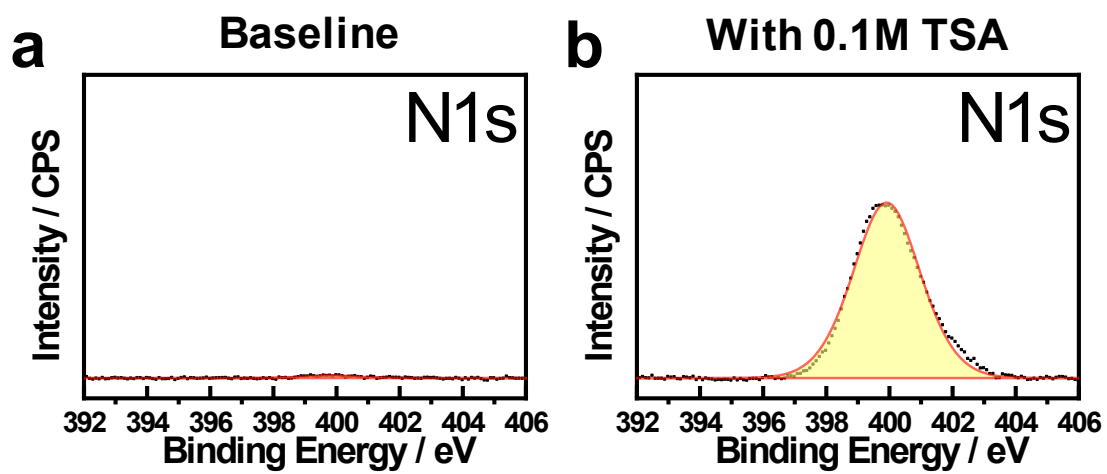


Fig. S7 XPS spectra of N 1s of the cycled Li metal recovered from Li/FCG73 batteries using different electrolyte solution: (a) baseline electrolyte and (b) 0.1M TSA-containing electrolyte.

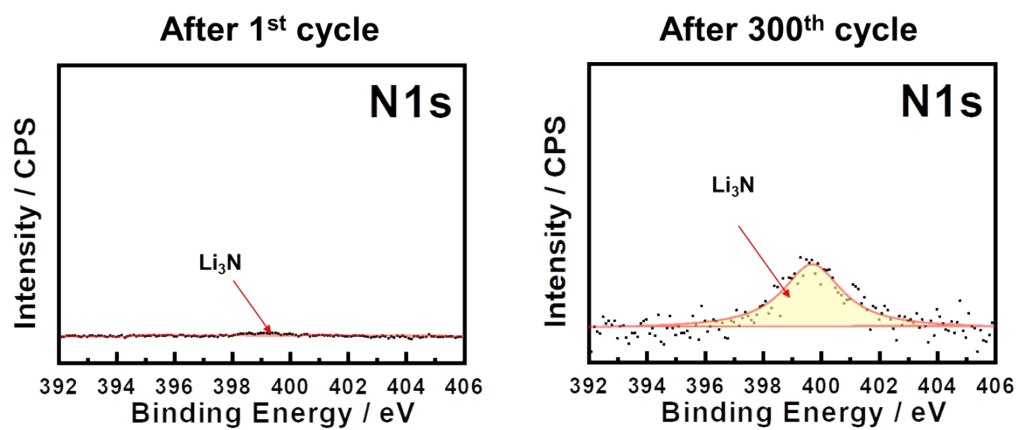


Fig. S8 XPS spectra of N 1s for FCG73 cathode after (a) 1st cycle and (b) 300th cycle cycled in Li/FCG73 battery using 0.1 M TSA-containing electrolyte.

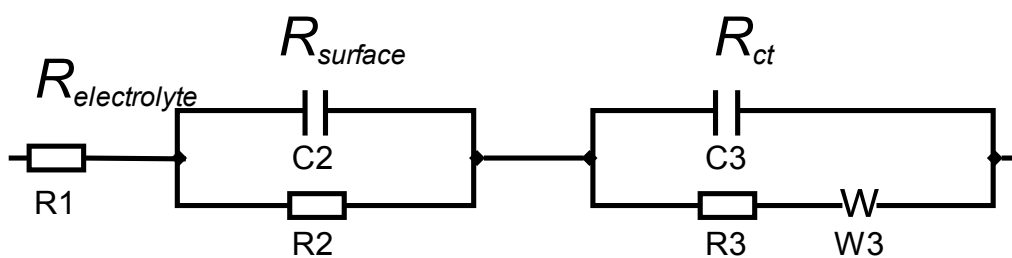


Fig. S9 Equivalent circuit model for EIS analysis.

Table S2. $R_{\text{electrolyte}}$, R_{suf} and R_{ct} of Li/FCG73 batteries using different electrolytes.

	$R_{\text{electrolyte}}$	R_{suf}	R_{ct}
Baseline	54.8 Ω	194.8 Ω	596.4 Ω
With 0.1 M TSA	14.2 Ω	29.5 Ω	136.3 Ω

References in supplementary information

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