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Supplementary Information

Ionic protector to proactive mitigate interfacial degradation induced from electrolyte decomposition in lithium-ion batteries

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Experimental Section

Materials Synthesis

The $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ precursor was synthesized via a modified co-precipitation method. Metal sulfates ($NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot H_2O$, 98%, Daejung) were dissolved in deionized water to prepare an aqueous solution with a molar ratio of Ni:Co:Mn = 6:2:2 and a total metal ion concentration of 2.0 *M*. This solution was continuously fed into a reactor (12L capacity) under a controlled N_2 atmosphere. For the co-precipitation process, a 4 mol L^{-1} NaOH solution serving as the precipitating agent and a 10 mol L^{-1} $NH_3 \cdot H_2O$ solution as the chelating agent were introduced simultaneously while maintaining the pH at approximately 11. The reaction was carried out at 50 °C under continuous stirring for 12h to ensure complete precipitation. The resultant precursor was collected and washed multiple times with deionized water at 50 °C until reaching neutral pH, followed by vacuum drying at 120 °C for 12h. The dried precursor was thoroughly mixed with stoichiometric Li_2CO_3 (Li/(Ni+Co+Mn) = 1.08) and subsequently calcined at 920 °C for 12h in air with heating and cooling rates of 5 °C min^{-1} to obtain the single crystal NCM622.

Electrolyte formulation

The background electrolyte consisted of 1.0 *M* $LiPF_6$ dissolved in a mixture of ethylene carbonate and ethyl methyl carbonate (3:7 = *v/v* ratio), containing 2 *wt*.% vinylene carbonate (VC) supplied by EnChem. To prepare the additive-added electrolyte, 0.5 *wt*.% TBNF, supplied by Sigma-Aldrich, was added to the background electrolyte. These electrolytes were used for pouch cell evaluations.

Electrode and cell fabrication

The positive electrode was composed of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NCM), Super P (TIMCAL), and polyvinylidene fluoride (Solef-5130, Solvey) in a 92:4:4 *wt*. ratio. The components were dispersed in *N*-methyl-2-pyrrolidone (Sigma-Aldrich) solvent to form a slurry, which was then coated onto an Al current collector with a mass loading of 14 mg cm^{-2}. The coated electrode was pre-dried at 80 ° C and then vacuum-dried at 120 ° C for 12 h. Electrode calendering was performed to achieve an electrode density of 3.4 g cm^{-3}. The negative electrode was prepared using graphite (BTR), Super P (TIMCAL), styrene-butadiene rubber (SBR, Sigma Aldrich), and carboxymethyl cellulose (CMC, Sigma-Aldrich) (SBR: CMC = 1:1 weight ratio) in a 90:5:5 *wt*.%. The mixture was dispersed in deionized water and cast onto a Cu current collector. The coated electrode was pre-dried at 80 ° C under vacuum for 12 h. A monolayered pouch cell was assembled with the negative electrode, polyethylene separator (PE, Asahi Kasei), and positive electrode. The cell had a negative-to-positive electrode capacity ratio of 1.08. After injecting either the background or TBNF-added electrolyte, the pouch cell was pressed to 1.0 MPa using a jig to evaluate the electrochemical performance.Cell formation was conducted using a constant current (CC)–constant voltage (CV) protocol with a 0.1 *C* CC charge (0.05 *C* cut-off), CV, and 0.1 *C* CC discharge for three cycles at a voltage range of 2.5–4.35 V using a galvanostatic battery cycler (TOYO, Japan). After formation, the cycleability was evaluated at 25 and 45 °C using 1.0 *C* CC–CV charge (0.05 *C* cut-off) and 1.0 *C* CC discharge currents within a voltage range of 2.5–4.35 V. The rate capability of pouch cells was assessed by constant CC-CV charging with 0.5 *C* and 0.05 *C* cut-off current and the discharge currents were varied with 0.1, 0.3, 0.5, and 1.0 *C*-rates at 25 °C.

The identical electrode applied for pouch cell fabrication was comprised to evaluate coin half-cell tests. The 2032 coin cell was fabricated by stacking 200 μm of Li (Honjo metal), PE separator, graphite and positive electrodes, respectively. The 0.1 C CC-CV (0.05 C current cut-off) 1 cycle formation was applied at the voltage range of 5.0 mV to 1.5 V and 2.5 to 4.45 V for graphite and NCM electrodes, respectively. The 25 °C cycle performance was evaluated with 0.5 C at identical voltage swing range applied for formation process.

Spectroscopic and morphological analyses

The crystal structure and phase purity of the samples were investigated using X-ray diffraction (XRD, Rigaku D/Max-2500V) with Cu Kα radiation. The diffraction patterns were collected in the 2θ range of 10-80 degree with a step size of 0.02. Detailed structural analysis was carried out through Rietveld refinement of the XRD patterns using Fullprof.

After cycling, the pouch cells were disassembled in a dry room to reduce the transmutation of cycled electrode morphology and surface at 2.5 V discharge state. The cycled electrodes were washed with dimethyl carbonate (Soulbrain) solvent to remove the residual Li salt and solvent and dried under vacuum for 12 h prior to further analysis. The morphology of cycled electrodes was analyzed using an SEM instrument (JEOL) with a cross-sectional polisher (JEOL). The chemical composition was examined through X-ray photoelectron spectroscopy (XPS, Thermo-Fisher), and ToF-SIMS (ION-ToF). A HR-TEM (ARM-200F, JEOL) analysis was performed to observe the SEI morphology on the graphite surface induced by further electrolytic decomposition. All further analysis was performed in the dry room installed instruments.

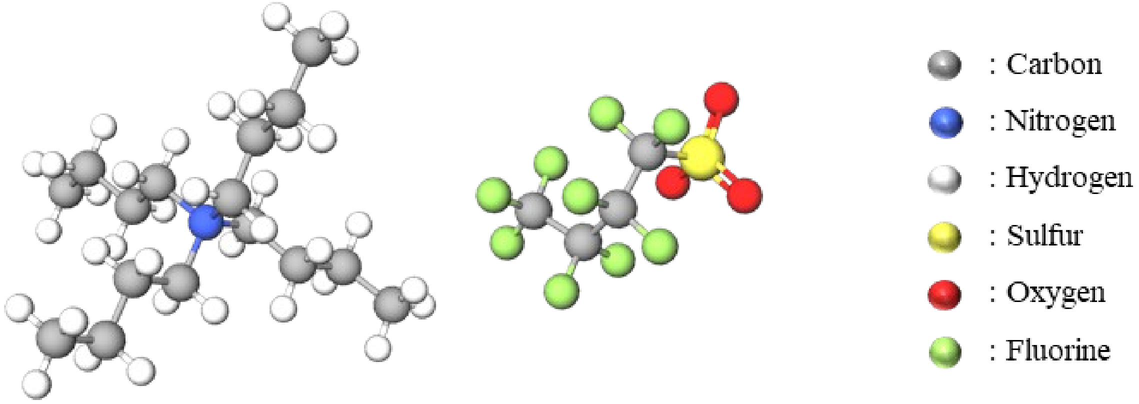

Figure S1. Molecular structure of TBNF additive

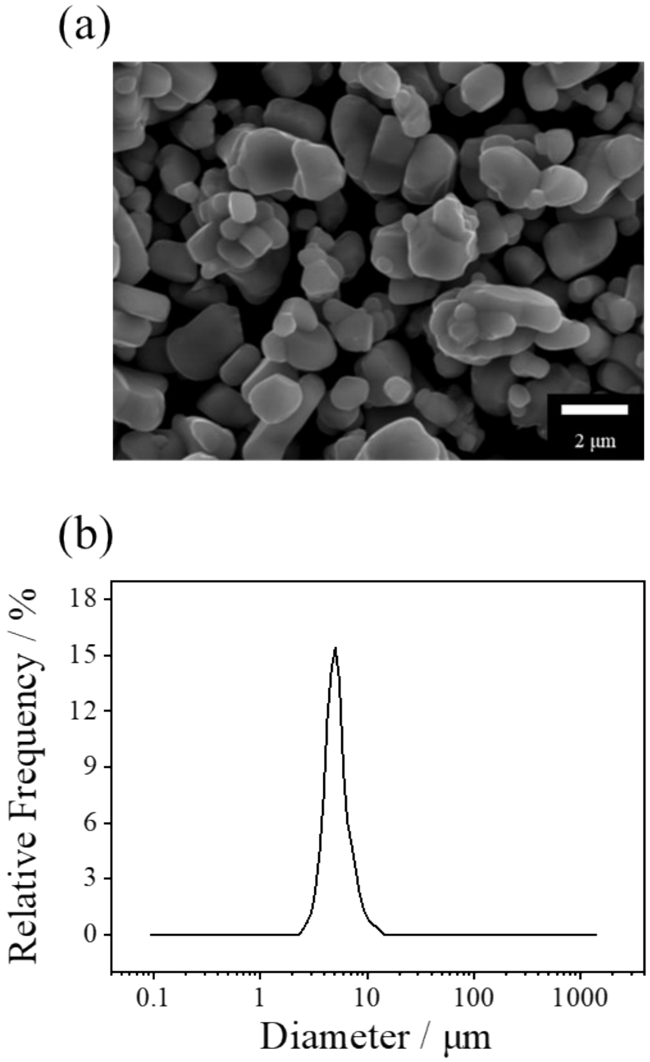

Figure S2. (a) SEM image and (b) particle size distribution profile of synthesized NCM powder

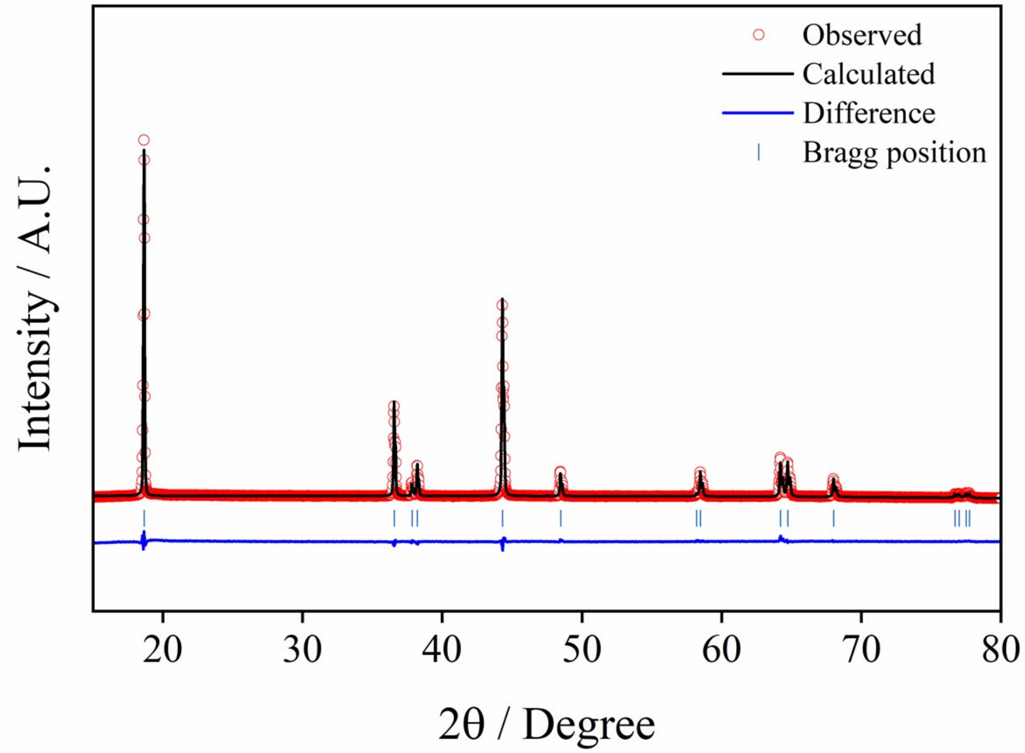

Figure S3. XRD spectra of synthesized NCM powder

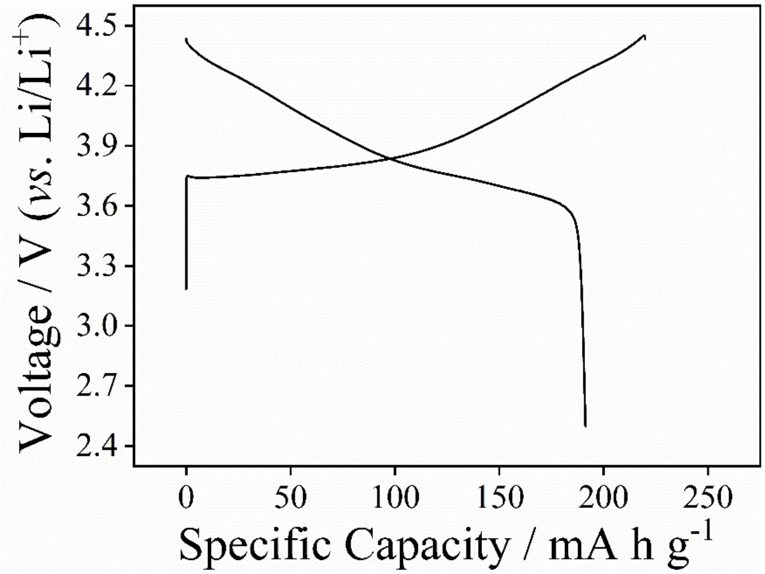

Figure S4. Li half-cell initial voltage profile of synthesized NCM electrode at areal capacity of 2.5 mA h cm^{-2}

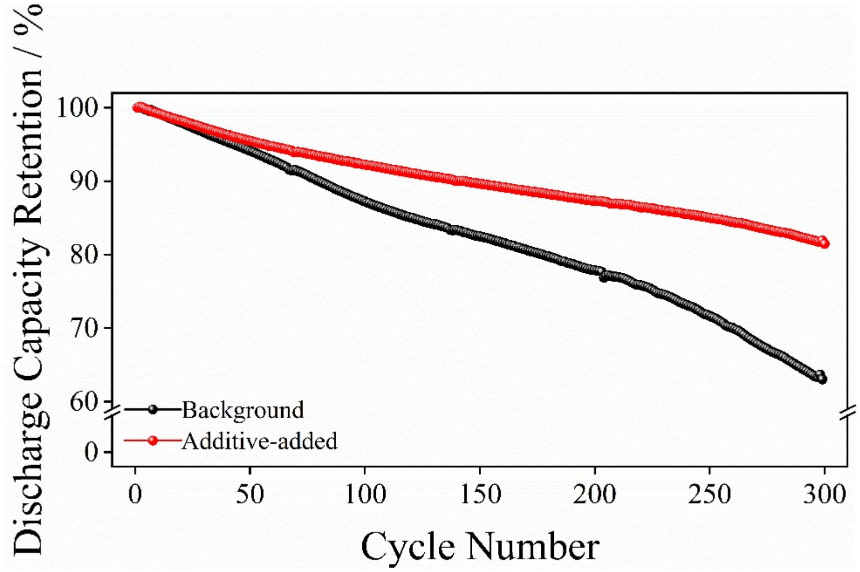

Figure S5. Discharge capacity retention of graphite/NCM pouch cell at 1.0 *C*, 2.5-4.35 V cycling condition

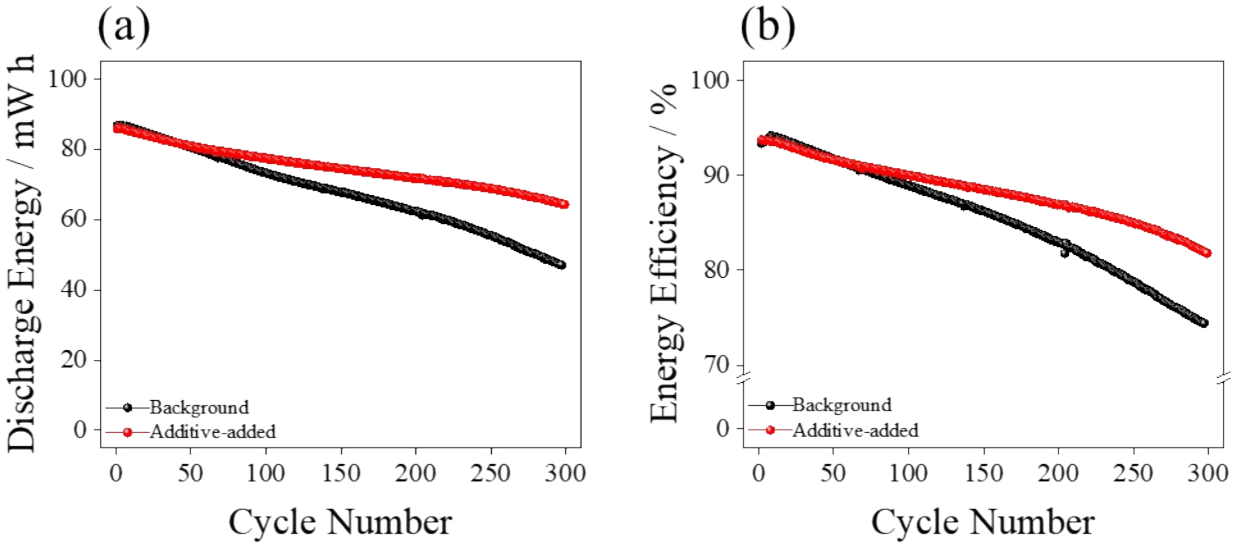

Figure S6. (a) Discharge energy and (b) energy efficiency of graphite/NCM cells with background and additive-added electrolytes, respectively

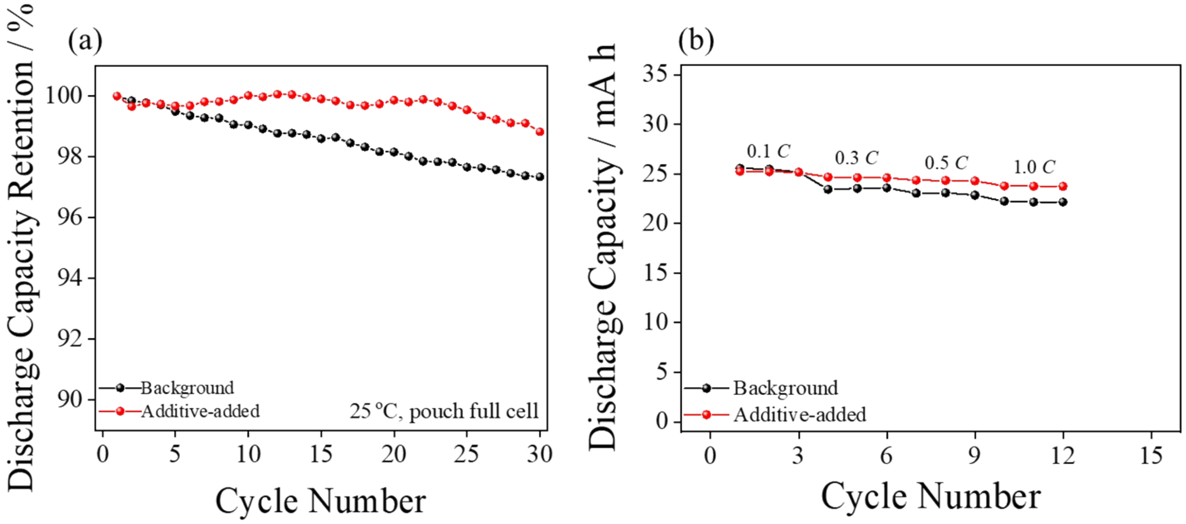

Figure S7. (a) cycle and (b) rate performances obtained from graphite/NCM pouch cell with background and additive-added electrolytes at 25 °C

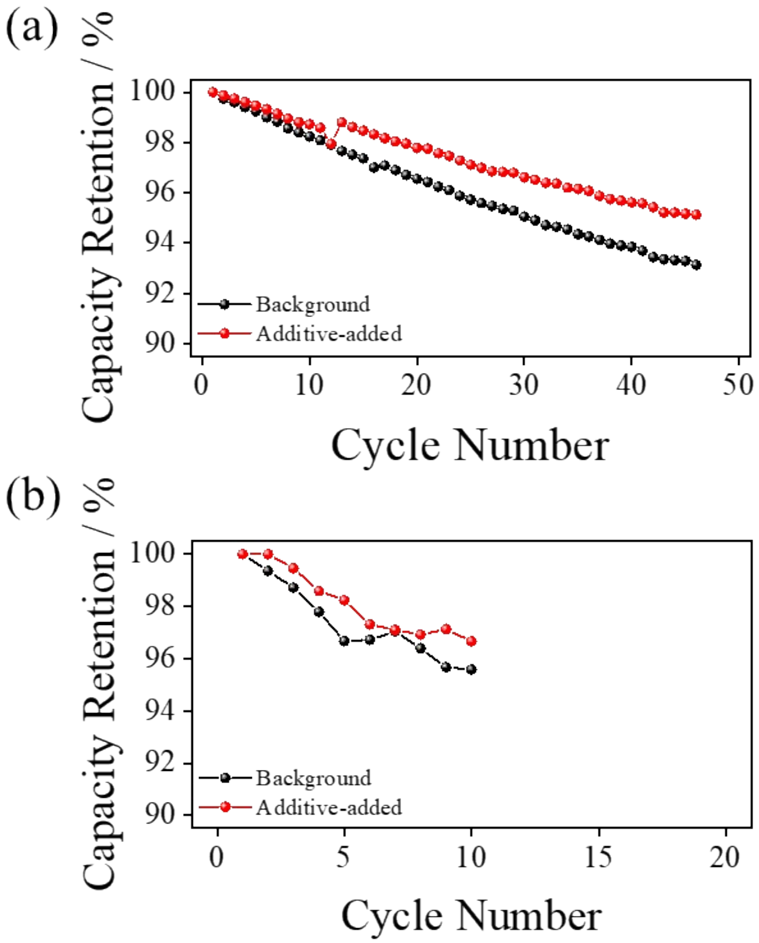

Figure S8. Coin half-cell cycle performances of (a) NCM and (b) graphite electrodes with background and additive-added electrolytes at 25 °C and 0.5 *C*-rate

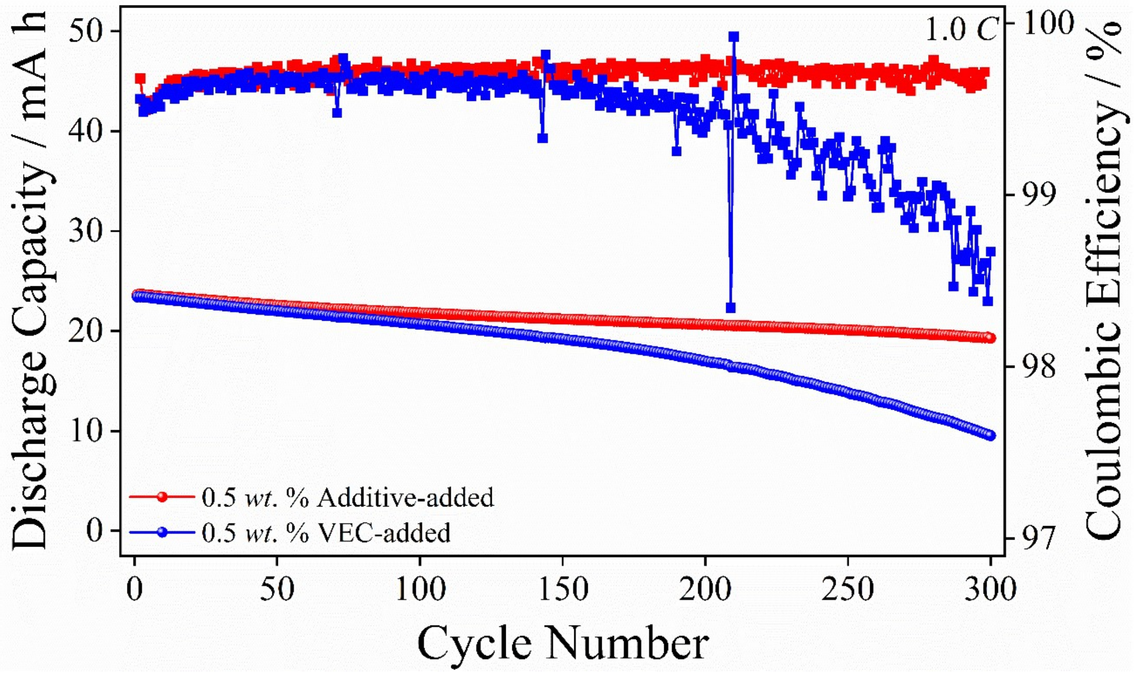

Figure S9. Cycleability obtained from graphite/NCM pouch cell with additive and VEC-added electrolytes

Table S1 Crystallographic parameters obtained from Rietveld refinement on the powder XRD patterns of single crystal NCM622

	a-axis (Å)	*c*-axis (Å)	Volume (Å^3)
NCM622	2.86879	14.25018	101.57