

1 Experimental

1.1 Preparation

1.1.1 Preparation of the NCM electrode

LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM, 0.75 g), acetylene black (0.1 g), polyvinylidene fluoride (PVDF, 0.1 g), lithium trifluoromethane sulfonimide (LiTFSI, 0.05 g), and N-methyl pyrrolidone (NMP, 2 mL) were coated onto a single-sided aluminum foil with a thickness of 20 μm after stirring at 25 °C for 24 h. The electrode pieces were vacuum-dried at 65 °C for 24 h and then cut into NCM electrode pieces with a diameter of 12 mm. The active NCM material loading in the electrode was 1.0 mg cm⁻².

1.1.2 Preparation of electrolyte

Polyethylene oxide (PEO, 1 g), LiTFSI (0.33 g), ethylene carbonate (EC, 0.1 g), TPPi (0 or 0.05 g), and acetonitrile (15 mL) were stirred at 25 °C for 24 h to form the SPE solution. In a glove box filled with argon, the SPE solution was added dropwise to the polytetrafluoroethylene mold. The solution was first placed at 25 °C for 24 h and then vacuum dried at 65 °C for 48 h. TPPi-free polymer electrolyte (SPE) and TPPi-containing polymer electrolyte (T-SPE) were prepared. The diameter, thickness and mass of the SPE and T-SPE slices was 20 mm, ~0.1 mm and 0.3 g, respectively.

1.1.3 Preparation of electrolyte/electrode composite

The SPE and T-SPE solutions (1.0 mL) were added dropwise to the surface of the prepared NCM electrode in a glove box, which was first placed at 25 °C for 24 h and then vacuum dried at 65 °C for 48 h. The NCM electrodes prepared with electrolyte supports were named SPE/NCM and T-SPE/NCM, respectively.

1.1.4 Assembly of the batteries

The SPE/NCM and T-SPE/NCM were assembled with lithium foil (diameter of 15 mm, thickness of 0.5 mm) in a glove box filled with argon to form 2025 button batteries, which were named Li|SPE|NCM and Li|T-SPE|NCM batteries, respectively.

Stainless steel (SS) foil (diameter of 12 mm, thickness of 0.5 mm), lithium foil (diameter of 15 mm, thickness of 0.5 mm), and SPE and T-SPE were assembled into 2025 button batteries in a glove box, which were named Li|SPE|Li, Li|T-SPE|Li, SS|SPE|SS, SS|T-SPE|SS, Li|SPE|SS, and Li|T-SPE|SS batteries, respectively.

1.2 Electrochemical measurements

All batteries were allowed to stand at 45 °C for 12 h and then subjected to electrochemical tests. All electrochemical tests in this study were carried out at a temperature of 45 °C.

1.2.1 Electrochemical impedance spectroscopy (EIS)

The EIS tests were performed for Li|SPE|NCM and Li|T-SPE|NCM batteries with NCM as the working electrode by using a Biologic VMP-3 electrochemical workstation. The amplitude was 5 mV, and the frequency range was 10⁵–10⁻² Hz. Before the test, the battery was charged to 4.2 V with a current of 0.1 mA cm⁻².

The EIS tests were performed for Li|SPE|Li, Li|T-SPE|Li, SS|SPE|SS, SS|T-SPE|SS batteries by using a Biologic VMP-3 electrochemical workstation. The amplitude was 5 mV, and the frequency range was 10^5 – 10^{-2} Hz.

1.2.2 Constant current discharge/charge

Constant current discharge/charge tests were performed for Li|SPE|NCM and Li|T-SPE|NCM batteries by using an Arbin BT2000 battery cycler at current densities of 0.1, 0.2, 0.3, 0.4, and 0.5 mA cm⁻² over a voltage range of 3.0–4.2 V. The capacity densities were calculated by using the NCM mass.

1.2.3 Cyclic voltammetry (CV)

The CV tests were performed for Li|SPE|SS and Li|T-SPE|SS batteries with SS as the working electrode by using a Biologic VMP-3 electrochemical workstation. The potential was scanned at a rate of 0.05 mV s⁻¹ from the open-circuit voltage to 5.0 V. The CV tests were performed for Li|SPE|NCM and Li|T-SPE|NCM batteries with NCM as the working electrode by using a Biologic VMP-3 electrochemical workstation. The potential range was 3.0–4.2 V.

1.2.4 Float charge with constant voltage

Before the float charge with a constant voltage test for the Li|SPE|NCM and Li|T-SPE|NCM batteries, the batteries were cycled 3 times at a constant current of 0.1 mA cm⁻² over a voltage range of 3.0–4.2 V. The test batteries were charged to 3.8, 4.0, 4.1, 4.2, 4.3, 4.4, and 4.5 V at 0.1 mA cm⁻² and maintained at each voltage for 10 h, respectively.

2.3 Physical characterization

The Li|SPE|NCM and Li|T-SPE|NCM batteries were cycled 50 times in the voltage range of 3.0–4.2 V at a current of 0.1 mA cm⁻², and then the batteries were charged to 4.2 V. The test batteries in the glove box were disassembled, and the SPE/NCM and T-SPE/NCM electrodes were removed and washed with acetonitrile and 1,2-dimethoxyethane multiple times and then dried at 60 °C for 12 h for subsequent physical characterization.

The Kratos Axis Ultra DLD X-ray photoelectron spectroscopy (XPS) system was used to analyze the original NCM electrode and SPE/NCM and T-SPE/NCM electrodes after 50 cycles. A Hitachi SU8010 scanning electron microscope (SEM) was used to characterize the SEM images of the SPE/NCM and T-SPE/NCM electrodes after 50 cycles. Fourier transform infrared (FTIR) spectroscopy was performed for the original NCM electrode and the SPE/NCM and T-SPE/NCM electrodes after 50 cycles using a Nicolet 6700 infrared spectrometer. The crystal structures of the SPE/NCM and T-SPE/NCM electrodes after 50 cycles were assessed with D8 Focus X-ray diffraction (XRD) using Cu-K α radiation with an incidence angle of 10–80° at a speed of 5° per minute. The chemical composition ration of Li:Ni:Co:Mn for NCM samples were measured by an Agilent 7700 inductively coupled plasma-mass spectrometer (ICP-MS).

2 Density functional theory (DFT) calculation

The geometry optimization and energy calculations for the chosen molecular models were performed in the gas phase using the Gaussian 09 package with the WB97XD functional at the 6-31G(d, p) level of theory.

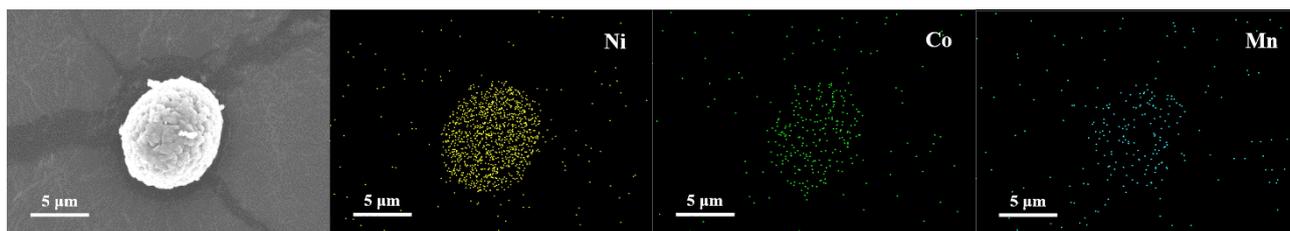


Figure S1 SEM, EDS for original NCM

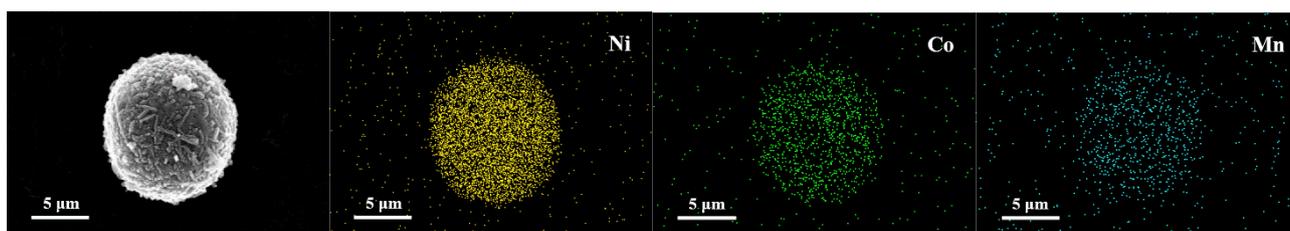


Figure S2 SEM, EDS for SPE/NCM at 4.2 V after 50 cycles

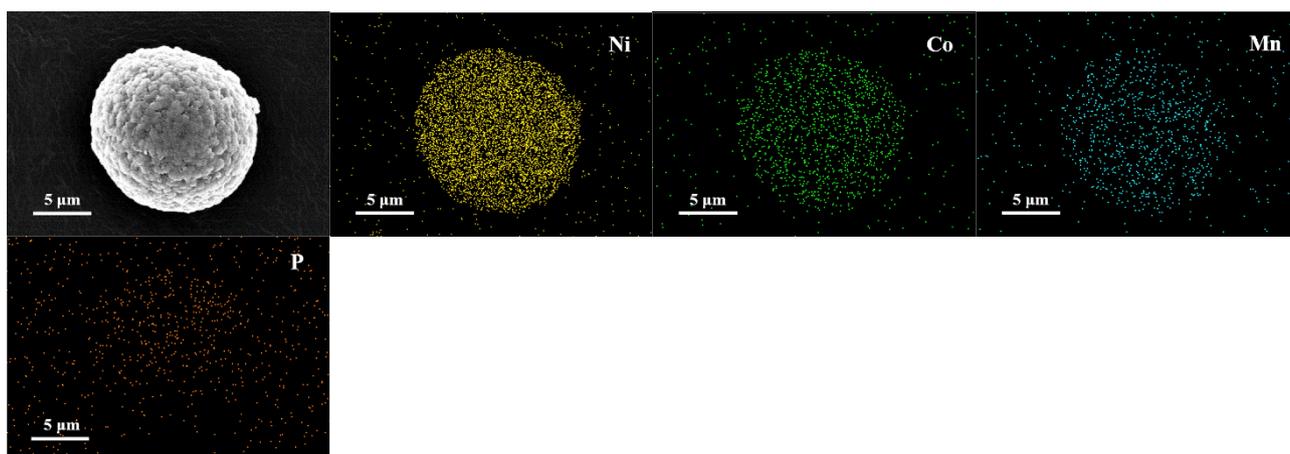


Figure S3 SEM, EDS for T-SPE/NCM at 4.2 V after 50 cycles

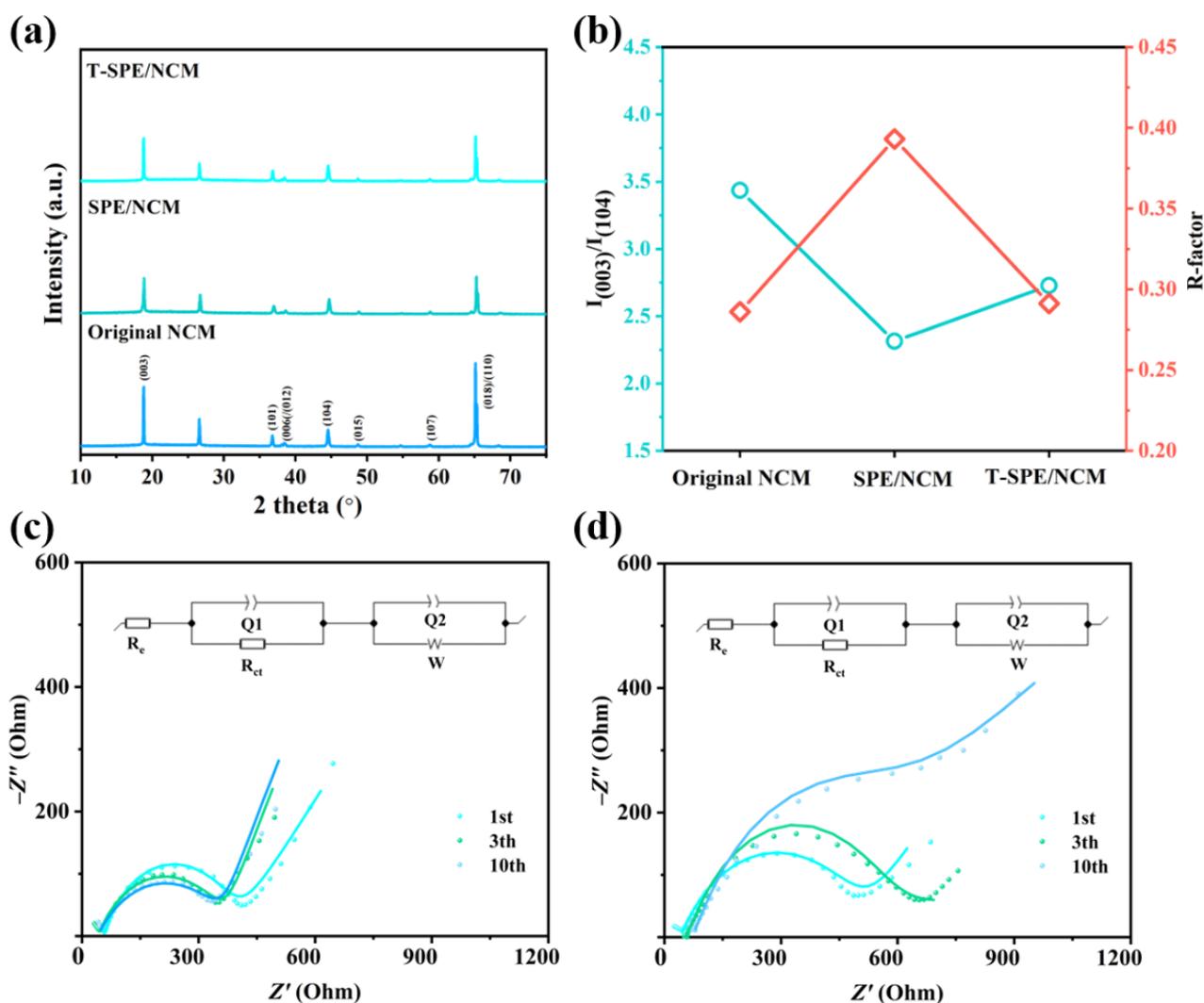


Figure S4 (a) XRD patterns for the original NCM, SPE/NCM and T-SPE/NCM at 4.2 V after 50 cycles. (b) Structural parameters $I_{(003)}/I_{(104)}$ and R-factor calculated from the XRD data. EIS plots and corresponding equivalent circuit for (c) SPE/NCM and (d) T-SPE/NCM at 4.2 V after 1, 3 and 50 cycles. The points show the experimental data, and the lines show the fitting results.

Discussion

The EIS for the test batteries and the corresponding equivalent circuit consist of the solution resistance (R_e), interfacial membrane resistance (R_f), charge transfer resistance (R_{ct}), and the Warburg impedance (Z_w) (Figure S4c,d). The semicircle in the mid-frequency region represents the sum of the impedance (R_{total}) for the charge transfer and interfacial membrane resistance. The R_{total} values for the T-SPE/NCM for the state of full charge at the first, third, and tenth cycles are 456.0, 412.3, and 400.8 Ω , respectively. The decreasing trend for R_{total} indicates that a relatively stable cathode electrolyte interphase (CEI) is formed at the surface of NCM during discharge/charge. TPPi is involved in the formation of CEI. The corresponding R_{total} values for SPE/NCM are 532.4, 605.8, and 1058.4 Ω , respectively, indicating that unfavorable side reactions continue to occur at the NCM surface, and the products of the side reactions

reduce the ion transport capacity of the interface. The stable interfacial film formed by TPPi during the NCM discharge/charge process can effectively inhibit the oxidation of the electrolyte, reduce the consumption of NCM and electrolyte, and improve the cycle life for the test batteries.

According to the EIS data of SS|SPE|SS, SS|T-SPE|SS symmetrical batteries, the ionic conductivities of SPE, T-SPE were calculated with Equation S1.

$$\sigma = L/(R_b \cdot A) \quad (S1)$$

σ is the ionic conductivity of SPE, L is the thickness, A is the area, and R_b is the resistance of the test battery.

Table S1 Ionic conductivities of SPE, T-SPE at various temperatures.

	Ionic conductivity (S cm ⁻¹)		
	25 °C	45 °C	60 °C
SPE	9.84×10 ⁻⁷	8.29×10 ⁻⁵	2.33×10 ⁻⁴
T-SPE	4.65×10 ⁻⁷	2.49×10 ⁻⁴	6.79×10 ⁻³

Table S2 Atomic ratios of Li:Ni:Co:Mn for the NCM samples.

	Atomic ratios of Li:Ni:Co:Mn
Original NCM electrode	1.009:0.792:0.112:0.100
SPE/NCM electrode after 50 cycles	0.941:0.745:0.107:0.100
T-SPE/NCM electrode after 50 cycles	0.981:0.778:0.117:0.100

Discussion

Compared with the content of Li and Ni, the absolute content of Mn remains nearly unchanged during charge/discharge, so the atomic ratio of Mn is reasonably fix to 0.1 as a reference value. As shown in Table S2, the atomic ratio of Co is almost unchanged while the content of Li and Ni are both decreased after 50 cycles. As a result of the Ni/Li disordering, the Ni ion at the Li layer would migrate from bulk to surface via the empty channel and it thus led to loss of Ni. It can be observed that T-SPE coating effectively suppressed the undesired Ni/Li disordering and therefore stabilized the structure upon cycling. Moreover, T-SPE coating could also reduce the consumption of active Li⁺ caused by side reaction in batteries.