Supplementary Information (SI) for ChemComm.

Supplementary Information

Regulating Cathode Electrical Double Layer via Electrolyte Engineering for Stable Cycling of NCM811 Cathode at 4.8 V

Experimental Section

Materials preparation

All chemicals are of analytical grade and are used directly without any purification. The following reagents were purchased from Suzhou Dodochem Technology Co., Ltd.: $LiPF_6$ (99.9%), LiBOB (99.8%), EC (99.95%), DEC (99.99%), TEP (99.8%), PFPN (99.5%); 1 in N-methyl-2-pyrrolidone (NMP, 99.9%) was purchased from Sinopharm Chemical Reagent Co., Ltd.; poly(vinylidene difluoride) (PVDF) and acetylene black were purchased from Zhengzhou Jinghong Renewal Energy Technology Co., Ltd.; NCM811 powders and Lithium foil were purchased from Zhejiang Hitrans Lithium Battery Technology Co., Ltd.; CR2025 coin case was purchased from Shanxi Source of Power Battery Materials Co., Ltd.; Aluminum current collector was purchased from Guangzhou Nano New Material Technology Co., Ltd.; Polypropylene separator was purchased from Fujitsu Limited.

Preparation of electrolyte and coin assembly

All operations are carried out under an Ar-filled glove box with an index of O_2 / H_2O < 1 ppm. (1) PED: 1.0 M $LiPF_6$ salt was dissolved in blended ethylene carbonate (EC) and diethyl carbonate (DEC) solvents with a volume ratio of 3: 7, and stir until transparent to obtain PED electrolyte. (2) BPN: LiBOB salt was dissolved in blended triethyl phosphate (TEP) and ethoxy pentafluorocyclotriphosphazene (PFPN) in a molar ratio of 1:4:6, and stir until transparent to obtain BPN electrolyte. The NCM811 electrode was obtained by coating the slurry of NCM811 powders, acetylene black and poly(vinylidene difluoride) with a weight ratio of 8: 1: 1 in N-methyl-2-pyrrolidone solvent onto an aluminum current collector. Dry the slurry for 6 h at 80 °C and punch into disks with diameter of 12 mm. The average mass loading of NCM811 is 4~5 mg. CR2025 coin cells with different electrolytes were encapsulated according to the according to the sequence of cathode, separator, and Lithium foil anode in a glove box for further testing.

Materials characterization

The synthesized material was characterized using Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50), in situ attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR, Nicolet iS50), X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi), scanning electron microscopy (SEM, JEOL 7100F).

The in situ ATR-FTIR measurements were performed using a Nicolet iS50 spectrometer equipped with a diamond ATR crystal and an MCT/A detector. The key experimental parameters included 80 scans for both sample and background, a resolution of 4 cm^{-1}, a spectral range of 400–4000 cm^{-1}. The electrode was prepared by coating NCM811 cathode material on both sides of the current collector and pressing it against the diamond ATR crystal with a minimal amount of electrolyte.

XPS normalization was performed by calculating the atomic percentage of each element from the XPS survey spectra, with the sum of all detected elements normalized to 100%.

Electrochemical characterization

The charge and discharge tests were operated by using LAND system. The Li||NCM811 cell was charged and discharged (1) at 0.1C (1 C = 200 mA h g^{-1}) between 2.50V- 4.40 V in the first three cycles and 0.5C after the third cycle between 2.50 V-4.40 V for 100 cycles; (2) at 0.1C between 2.50V- 4.60 V in the first three cycles and 0.5C after the third cycle between 2.50 V- 4.40 V for 100 cycles; (3) at 0.1C between 2.50V- 4.80 V in the first three cycles and 0.5C after the third cycle between 2.50 V-4.40 V for 100 cycles; (4) at 0.1C between 2.50V- 4.80 V in the first three cycles and 0.5C after the third cycle between 2.50 V- 4.80 V in the next 200 cycles to assess electrochemical performance.

Theoretical Calculation

Theoretical calculation was performed using the Material Studio software based on density-functional theory (DFT). Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional of generalized gradient approximation (GGA) was selected to optimize the unit cells on a specific NCM811 crystal surface. The M06-L exchange-correlation functional was used to optimize molecules. The plane-wave energy cutoff was set to be 720 eV and the energy and force convergency threshold were set to 5 ×

10^{-5} eV and 0.1 eV/Å. A vacuum layer with a thickness of 30 Å was introduced along the Z direction to prevent interactions between periodic images. The Gamma-only k-point (1 × 1 × 1) was used to sample the Brillouin zone for all calculations.

The adsorption energy of adsorbates (E_{ads}) on different substrates was calculated by

$$E_{ads} = E_{total} - E_{surface} - E_{molecule}$$

where E_{total}, $E_{surface}$, and $E_{molecule}$ denote the free energy of the adsorbed system, the NCM811 surface, and the molecule, respectively.

The vacuum level was used as the reference standard for the energy levels, set to zero to align the calculated eigenvalues with the absolute energy scale. The highest occupied molecular orbital (HOMO) energy (E_{HOMO}) was taken directly as the negative of the ionization potential (IP) via Koopmans' theorem. All the HOMO calculations were performed using density functional theory (DFT) with the M06-L functional and the DNP4.4 basis set as implemented in Materials Studio. The Kohn–Sham orbital energies were utilized to estimate the frontier molecular orbital energies.

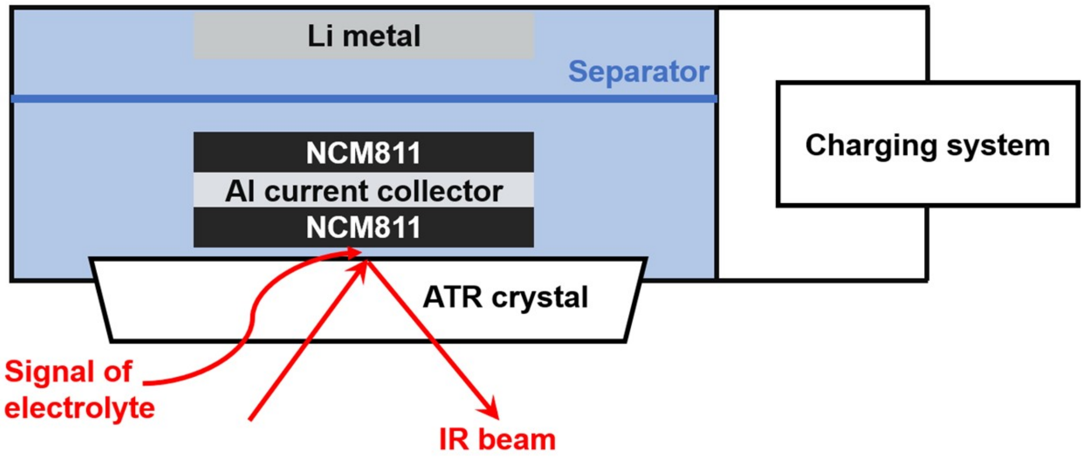

Fig. S1. Schematic diagram of ATR FTIR measuring the electrolyte at the NCM811 surface.

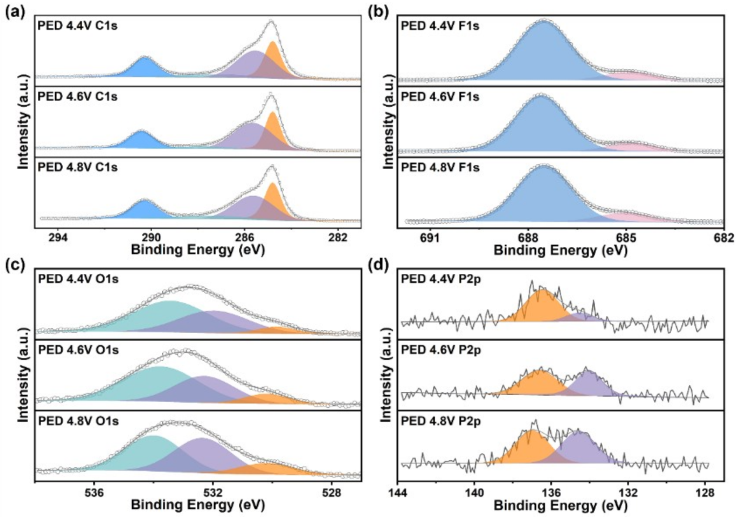

Fig. S2. XPS characterization of CEI on the cathode after 3 cycles in PED electrolytes. (a) C 1s, (b) F 1s, (c) O 1s, (d) P 2p spectra.

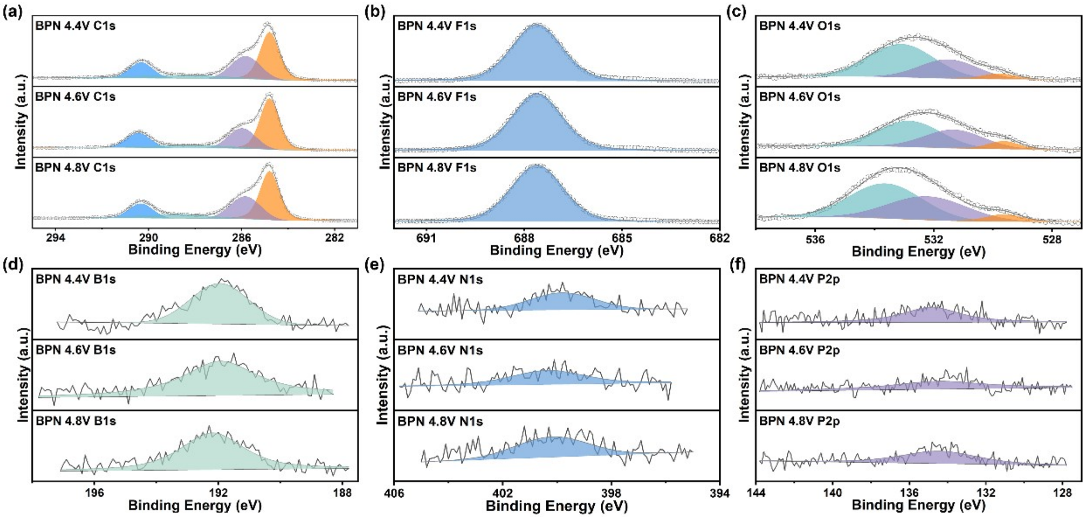

Fig. S3. XPS characterization of CEI on the cathode after 3 cycles in BPN electrolytes. (a) C 1s, (b) F 1s, (c) O 1s, (d) B 1s, (e) N 1s, (f) P 2p spectra.

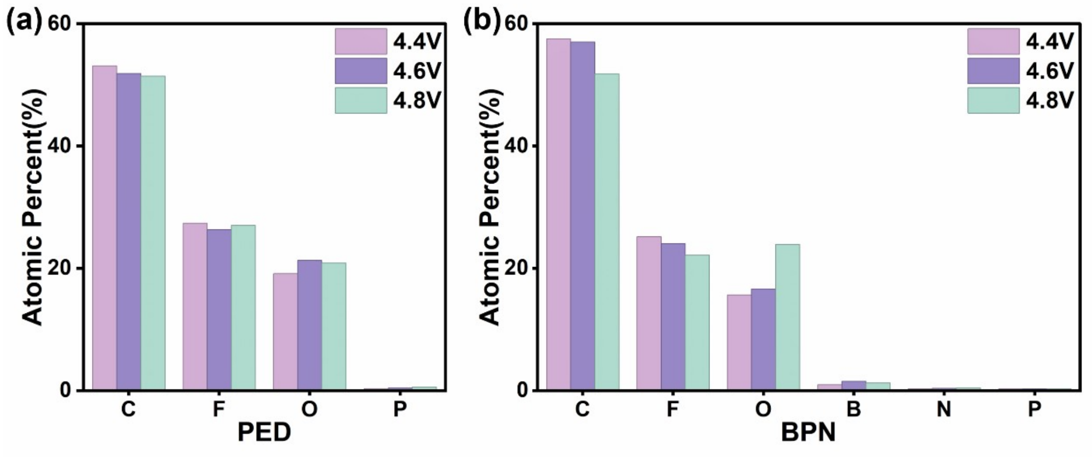

Fig. S4. Relative content of all the elements of CEI on NCM811 in PED (a) and BPN (b) after 3 formation cycles under different cutoff voltages.

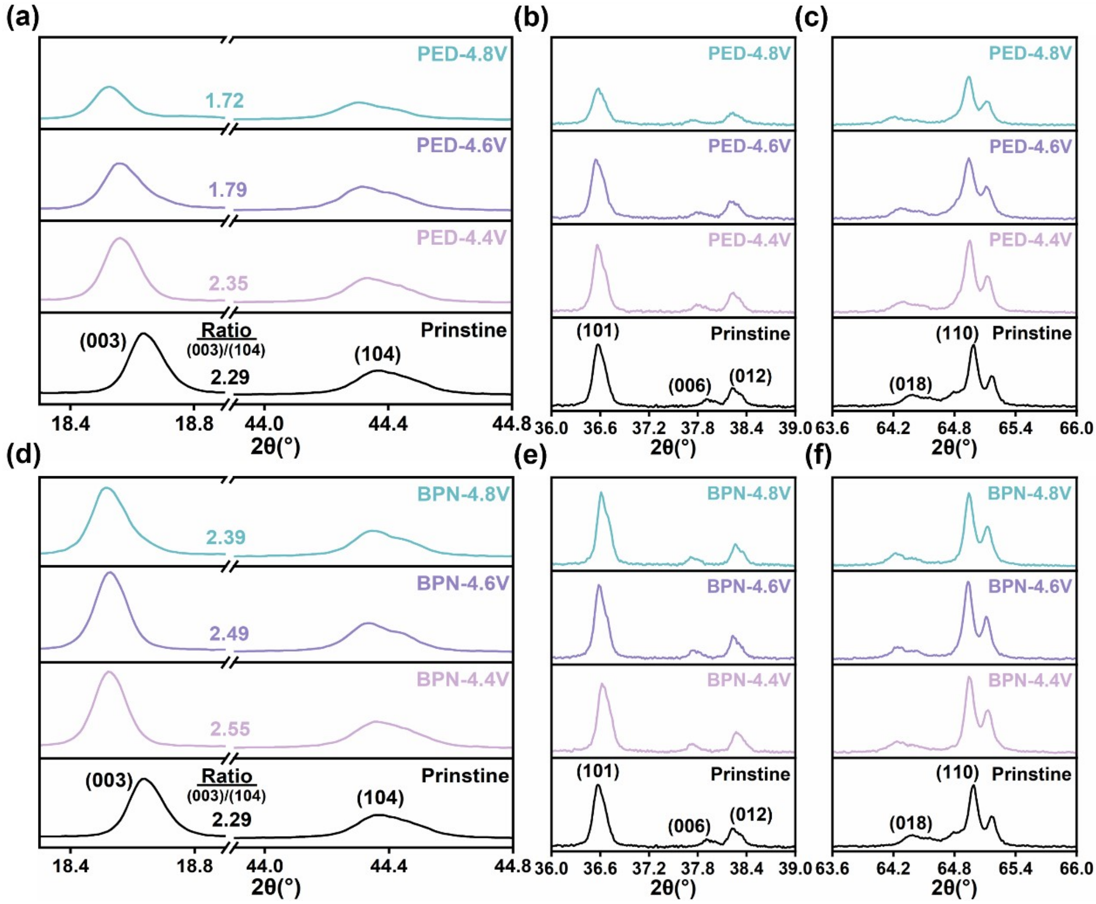

Fig. S5. XRD patterns of NCM811 cathodes after cycling in different electrolytes. PED electrolyte: (a) (003) and (104) peaks; (b) (006) and (012) peaks; (c) (018) and (110) peaks. BPN electrolyte: (d) (003) and (104) peaks; (e) (006) and (012) peaks; (f) (018) and (110) peaks.