

Supporting Information

Simultaneous modulation of cathode/anode and electrolyte interfaces via a nitrile additive for high-energy-density lithium-metal batteries

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Experimental

4.1 Materials

The pristine electrolyte was 1 mol L⁻¹ lithium hexafluorophosphate (LiPF₆) dissolved in a 1:1:1 volume ratio of ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (EC/DMC/EMC), obtained from DoDoChem Co., Ltd. Then, succinonitrile (SN) additive was dissolved in the original electrolyte at ratios of 0.5 wt%, 1.0 wt%, and 1.5 wt%, among which the succinonitrile (SN) was purchased from Tokyo Chemical Industry Co., Ltd. The original electrolyte is also referred to as the blank electrolyte or LE electrolyte. The electrolytes containing 0.5 wt%, 1.0 wt%, and 1.5 wt% SN were named as 0.5 wt%-SN, 1.0 wt%-SN, and 1.5 wt%-SN.

4.2 Fabrication of electrodes

Cathode material was NCM811, obtained from Trony Materials Inc and anode material was composed of lithium metal with a diameter of 12 mm, purchased from Neware Technology Co., Ltd. NCM811 powder, acetylene black, and polyvinylidene fluoride (PVDF) were mixed in a ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP) to prepare the NCM811 cathode. Subsequently, the mixture was coated onto aluminum foil and dried at 60 °C in an oven for at least 12 hours. The prepared cathode was cut into discs with a diameter of 11 mm for assembly into CR 2032-type cells within an argon-filled glovebox. The separator utilized was a microporous polypropylene/polyethylene/polypropylene film (Celgard 2325).

4.3 Electrochemical measurements

The cyclic performance and rate capability of Li|NCM811 batteries were evaluated under the conditions of constant temperature at 25 °C and voltage ranging from 2.5 to 4.3 V (1 C=180 mA h g⁻¹) using the LAND electrochemical testing system. Additionally, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted on an electrochemical workstation (CHI660E, China). The CV was performed within a voltage range of 2.5 to 4.5 V at scan rates of 0.1, 0.3, 0.5, 0.7, and 1 mV s⁻¹, while the frequency range for EIS was set from 100 kHz to 10 mHz. The ion conductivity was measured with an Li⁺ blocking symmetric cell based on an EIS analysis at a frequency range from 10⁻² to 10⁶ Hz and an applied amplitude of 10 mV. The impedance was measured on 25°C. The ionic conductivity (σ) was determined according to following equation

$$\sigma = L/RA \quad (1)$$

where L is the pellet thickness, R is the resistance, and A is the area in contact with the electrodes.¹

4.4 Physical characterization

Contact Angle was measured by SZ-CAMC32 (China). Viscosity was measured by Brookfield DV3 (USA). NMR spectra of ¹H, ³¹P, and ¹⁹F nuclei were collected on the Germany Bruker Avance III HD 500MHz spectrometer for electrolytes. Raman spectroscopy was performed on electrolytes by the Japanese Horiba LabRAM HR Evolution model. The morphology and microstructure of electrode surfaces after cycling were studied using Field Emission Scanning Electron Microscopy (SEM, S8230, HITACHI, Japan). The NCM811 cathode was tested by Transmission Electron Microscopy (TEM, FEI Talos F200x, USA). X-ray diffraction (XRD) characterization of cycled electrodes was performed using SmartLab SE, RIGAKU, Japan equipped with Cu K- α radiation,

with a scanning speed of 5° min^{-1} . The chemical composition of cycled electrodes was analyzed using X-ray Photoelectron Spectroscopy (XPS, PHI Quantera II SXM, ULVAC-PHI, Japan). Depth profiling by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was conducted on the PHI nano TOF II (ULVAC-PHI, Inc. Japan). A specialized transfer vessel was employed during sample transfer to facilitate direct transfer from the glove box to the TOF-SIMS vacuum chamber, thus preventing exposure to ambient air. Detection of samples utilized a Bi_3^{++} primary beam at 30 kV, while sputter etching was carried out employing an Ar^+ beam at 3 kV and 100 nA to achieve the desired depth profile. The analysis area measured $100 \times 100 \mu\text{m}^2$, with the sputtering area spanning $400 \times 400 \mu\text{m}^2$.

References

1 K. Oh, J. Kim, S. Kim, D. Oh, S. Han, K. Jung, Z. Wang, L. Shi, Y. Su, T. Yim, S. Yuan and S. Lee, *Advanced Energy Materials*, 2021, **11**, 2101813.

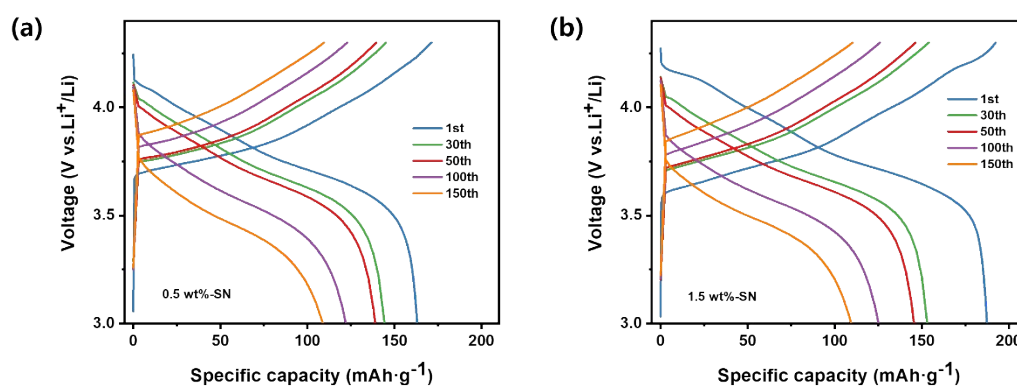


Fig. S1 Voltage profiles of selected cycles for cells (a) with 0.5 wt% SN and (b) with 1.5 wt% SN.

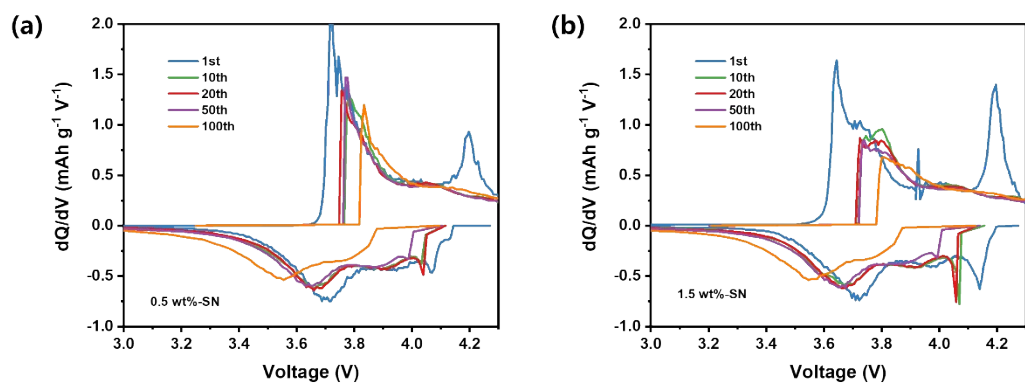


Fig. S2 (dQ/dV) curves of selected cycles for cells (a) with 0.5 wt% SN and (b) with 1.5 wt% SN.

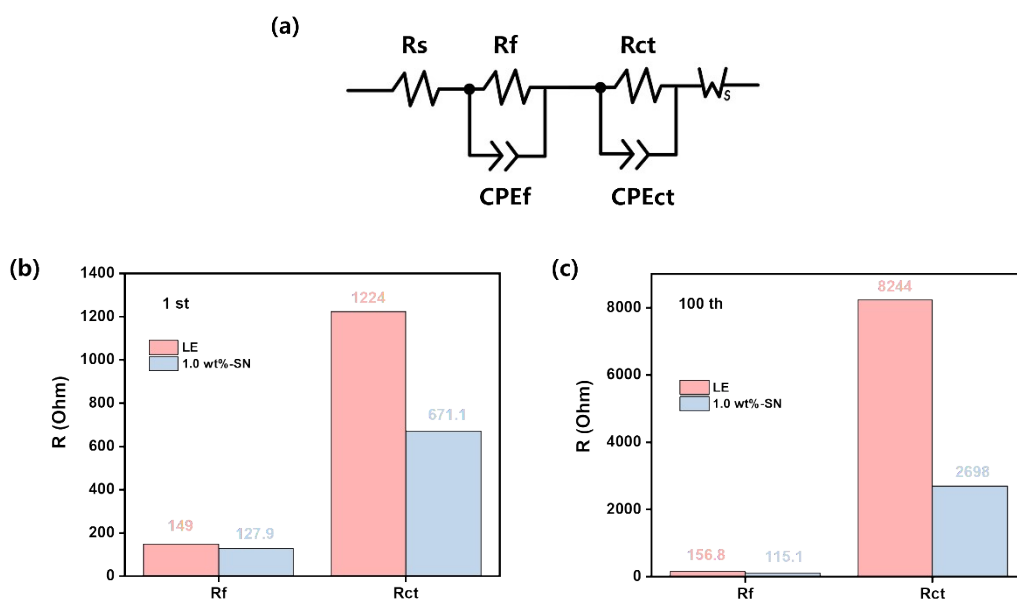


Fig. S3 (a) Representation of the electrochemical impedance via an equivalent circuit. The fitted results of R_f and R_{ct} at (b) 1st cycle and (c) 100th cycle.

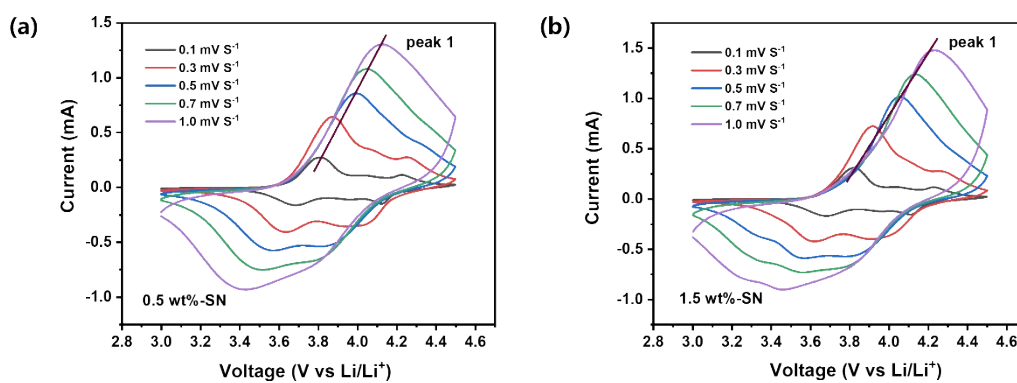


Fig. S4 CV curves recorded at various scan rates (0.1 – 1.0 mV s^{-1}) within a potential window of 3.0 – 4.5 V for (d) 0.5 wt%-SN electrolyte and (e) 1.0 wt%-SN electrolyte.

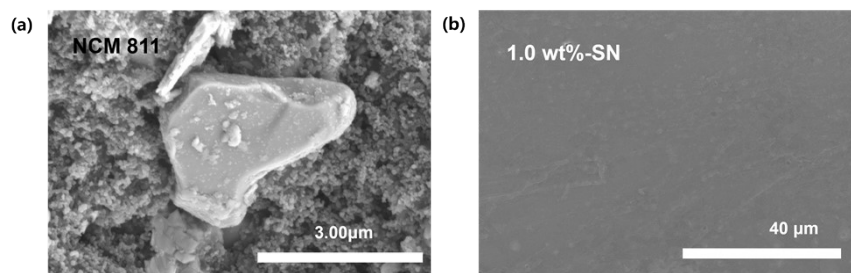


Fig. S5 SEM images of the (a) original NCM811 cathode and (b) lithium metal anode.

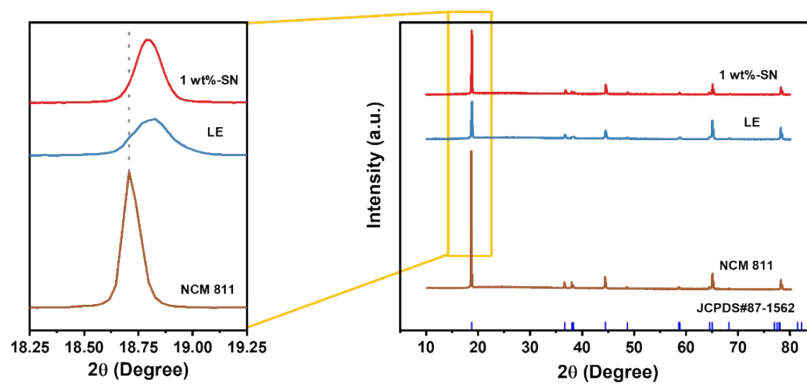


Fig. S6 The XRD test of the NCM811 cathodes after 15 cycles.

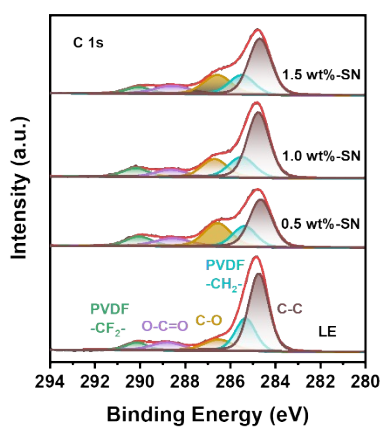


Fig. S7 XPS spectra of C 1s of lithium metal anodes after 100 cycles without SN (LE) and with SN.

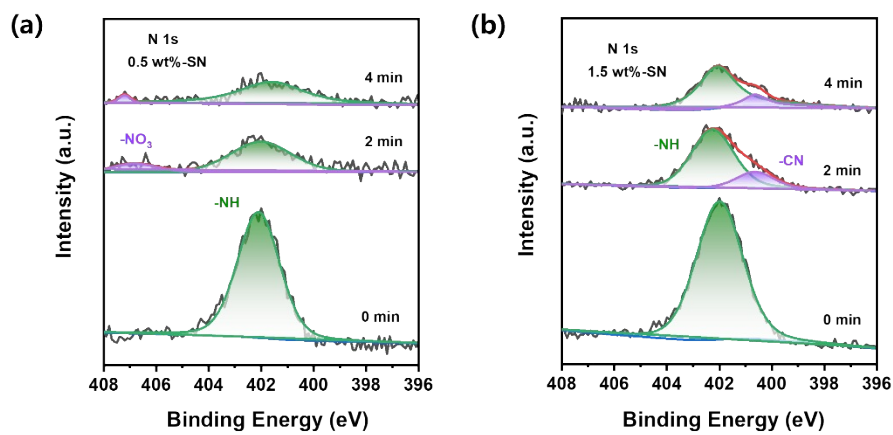


Fig. S8 XPS spectra of N 1s of lithium metal anodes after 100 cycles without SN (LE) and with SN.

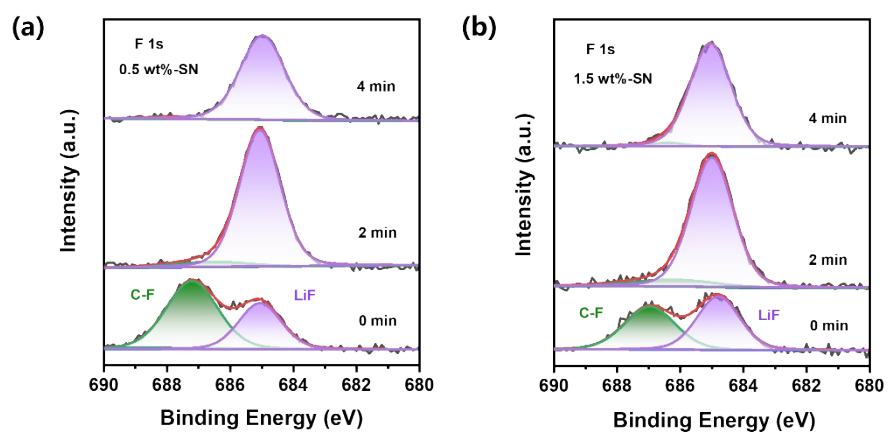


Fig. S9 XPS spectra of F 1s of lithium metal anodes after 100 cycles without SN (LE) and with SN.

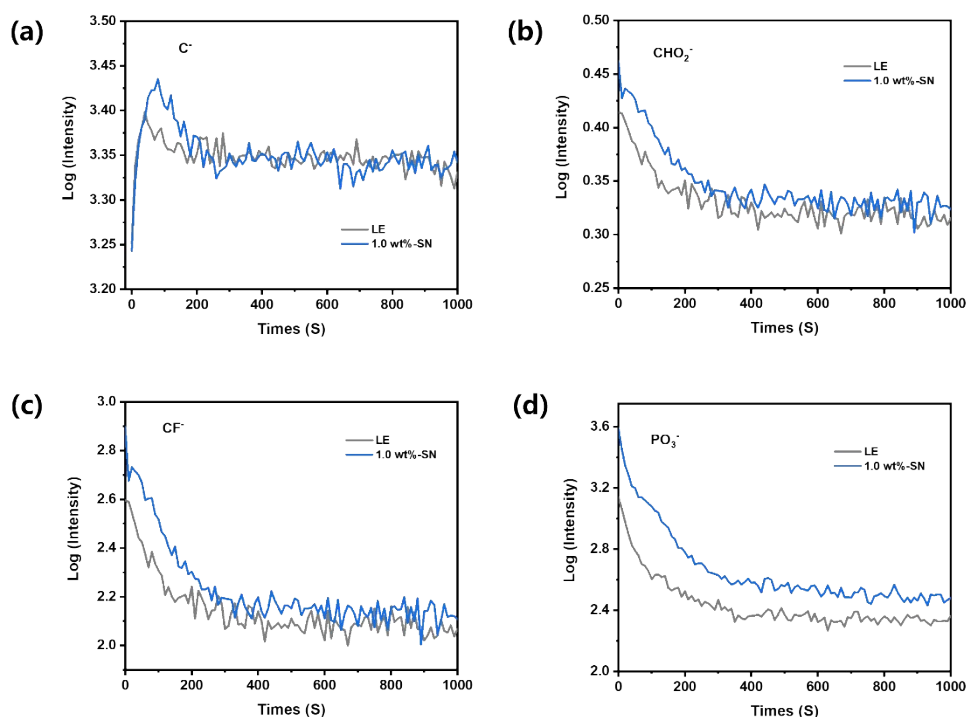


Fig. S10 (a-d) TOF-SIMS depth profiles of interested species.