

## Regulating Solvation Structure of Acetonitrile-based Electrolyte for Li/NMC811 Battery Cycled at Low Temperature

Lin Liu<sup>a#</sup>, Zulipiya Shadike<sup>a#\*</sup>, Xinyin Cai<sup>a</sup>, Mengwei Hong<sup>a</sup>, Yue Gao<sup>b</sup>, Shuiyun Shen<sup>a</sup>, Junliang Zhang<sup>a\*</sup>

<sup>a</sup>Institute of Fuel Cells, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

<sup>b</sup>State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, Fudan University, Shanghai, China.

# L. Liu and Z. Shadike contribute equally.

\* Correspondence: zshadike@sjtu.edu.cn; junliang.zhang@sjtu.edu.cn

### Experiment

#### Materials

The NMC811 electrode was prepared by mixing  $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$  (NMC811, Canrd), carbon black (Super P Li, TIMCAL), and polyvinylidene fluoride (pvdf, SOLVAY) in N-Methyl-2-pyrrolidone (NMP, anhydrous, Sigma Aldrich) with a mass ratio of 8: 1: 1 together and then coating the formed slurry on the Al foil which was dried at vacuum oven at 80 °C for 12 h. The areal loading of the NMC811 electrode is 3.5 mg cm<sup>-2</sup>. The electrodes were punched into 12mm disks.

The diameter of lithium metal foil (99.9%) was 15.8 mm and the thickness was 450 μm. The separator was purchased from MTI and punched into pieces.

The lithium bis(trifluoromethanesulfonyl)amide (LiFSI), Acetonitrile (AN), 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE), and standard electrolyte containing 1 M lithium hexafluorophosphate ( $\text{LiPF}_6$ ) in Ethylene carbonate (EC) and Ethyl Methyl Carbonate (EMC) mixture (3:7 by volume) were provided by Glat (Shanghai) Information Technology Co., Ltd. and used as received. Electrolytes were prepared in the MIKROUNA glovebox filled with purified Argon (Ar) and H<sub>2</sub>O and O<sub>2</sub> contents were less than 0.01 ppm.

#### Electrochemical Tests

The Li/NMC811 cells were assembled in standard 2032 coin-type cells with 50 μL electrolyte in an Ar-filled glove box. Electrochemical impedance spectroscopy (EIS) measurements and linear sweep voltammetry (LSV) were performed on Gamary Interface 1010E electrochemical workstation. Before EIS measurements, all the cells were activated at 0.1 C for 2 cycles and then charged to 4.4V. Next, EIS measurements were performed in the frequency range from 10<sup>5</sup> to 10<sup>-1</sup> Hz with a voltage amplitude of 10 mV. The electrochemical window of LHCEs was evaluated by LSV at a scanning rate of 10 mV s<sup>-1</sup> at 25 °C. The cells for test were prepared by sandwiching the LHCEs between stainless steel and Li metal in 2032 coin-type cells.

Battery charge/discharge tests were all conducted using NEWARE CT-4008Tn battery test system. The Li/NMC811 cells were cycled between 2.8-4.4 V and 2.8-4.6 V in the galvanostatic mode and allowed to stand for more than 6 hours before being cycled at the corresponding temperature for a full thermal equilibration. All cells were initially activated for three cycles at a rate of 0.1C under the corresponding temperature and voltage conditions before cycling. Li-Cu half cells were prepared by assembling Cu foil (φ 18 mm) as the cathode and Li foils as the anode in CR2032 coin cells. The average coulombic efficiency of Li-Cu cell was measured according to the

second protocol proposed by Zhang et al. <sup>1</sup>. The rate performances of Li/Li symmetric cells were tested at various current densities from 0.5 to 1.5 mA cm<sup>-2</sup> with deposition capacity of 1 mAh cm<sup>-2</sup>.

EIS was employed to determine the ionic conductivity of the electrolyte solution. Symmetric cells were utilized, consisting of a platinum electrode and a graphite electrode symmetrically positioned within the electrolyte. EIS spectra were acquired over a frequency range of 1 Hz to 100 kHz at controlled temperatures using a High and Low Temperature Alternating Humidity and Heat Test Chamber. By analyzing the solution resistance obtained from the EIS spectra at different temperatures, the ionic conductivity was calculated using the equation:

$$\rho = R * l / A$$

Here,  $l$  represents the distance between the electrodes,  $A$  denotes the surface area of the platinum electrode,  $R$  corresponds to the solution resistance, and  $\rho$  represents the resistivity. The reciprocal of the resistivity yields the ionic conductivity. To determine the values of  $l$  and  $A$ , a conductivity calibration solution procured from Guangzhou Zhencui Quality Inspection Technology Co., Ltd. was employed.

### **Spectroscopic Characterization**

**Raman spectra:** Raman spectra were obtained with a Renishaw inVia Qontor Raman spectrometer at an excitation wavelength of 532 nm. To prevent any contamination from air, the solution was put into a glass bottle and tightly sealed in it in an Ar-filled glovebox. The laser was radiated through the glass bottle wall.

After 10 electrochemical cycles, the cells were disassembled and the NMC electrodes were retrieved and rinsed with DMC to remove the residual Li salt on the surface. Then the NMC electrodes were dried at 25 °C under vacuum and used as samples for Transmission Electron Microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) characterization.

**TEM:** The mixture was scraped off from the aluminum foil. Subsequently, the embedded samples were sliced using the Leica EM UC7 ultramicrotome from Leica Microsystems, Germany, and retrieved using a Copper TEM grids (200 mesh). TEM measurements were conducted using a TALOS F200X Transmission Electron Microscope equipped with a Schottky thermal field emission ultra-bright electron gun, operating at 200 kV.

**XPS:** X-ray photoelectron spectroscopy (XPS) measurements were acquired with a K-alpha Thermo system using Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV). The samples were transferred from the argon glove box into the XPS chamber with a vacuum transfer vessel to avoid exposure to air. Sputter depth profiling was carried out using a 2kV Ar<sup>+</sup> ion gun with a raster size of 3 mm. The angle between the surface normal and the ion gun beam was 0°. The binding energy was corrected based on the C 1s spectrum, assigning C-C to 284.8 eV.

**TOF-SIMS:** ToF-SIMS analysis is performed using an ION TOF ToF SIMS 5-100 equipped with a 30 keV Bi-LMIG. For surface analysis, all mass spectra are acquired using the same experimental conditions: the LMIG gun is tuned to deliver Bi<sup>3+</sup> primary ions over a 70 × 70 μm<sup>2</sup> raster size, the mass range is fixed between 0 and 800 u and the number of frames is set to 30 (the primary ion dose was below the static limit 5 × 10<sup>13</sup> ions/cm<sup>2</sup>) for negative polarity. In the depth profiling experiments, each frame spectrum was acquired using the same conditions as for the surface analysis (Bi<sup>3+</sup>, 70 × 70 μm<sup>2</sup> raster size) and a 2 kV Cs sputtering gun was used for etching (with an etching time of 100 μs for each cycle, a sputtered area of 240 × 240 μm<sup>2</sup>, and the Cs current was about 60 nA). Data processing is performed using Surface Lab 7 provided by ION TOF GmbH. All

negative polarity spectra are calibrated using  $C^-$  ( $m/z$  12) and  $O^-$  ( $m/z$  16). Mass resolution ( $C_2H^+$ ,  $m/z$  25) was more than 3437.

Table S1. Electrolyte formula

abbreviation	concentration(mol/L)	molar ratio (LiFSI:AN:TTE)
7M	1	1:2.73:5.66
5.5M	1	1:3.47:5.4
4M	1	1:4.77:4.93

The molar concentration is defined as the molar amount of lithium salt divided by the volume of the “whole solution”. “7M” means the molar amount of lithium salt divided by the volume of AN.

Table S2. Impedance values of both electrolytes at different temperatures

Electrolyte	T / °C	$R_{SEI}$ / ohm	$R_{CEI}$ / ohm	$R_{ct}$ / ohm
STD	-20	20	1100	799
	25	4.03	8.301	66.36
7M	-20	31.43	70.79	477
	25	12.7	29.44	20.85

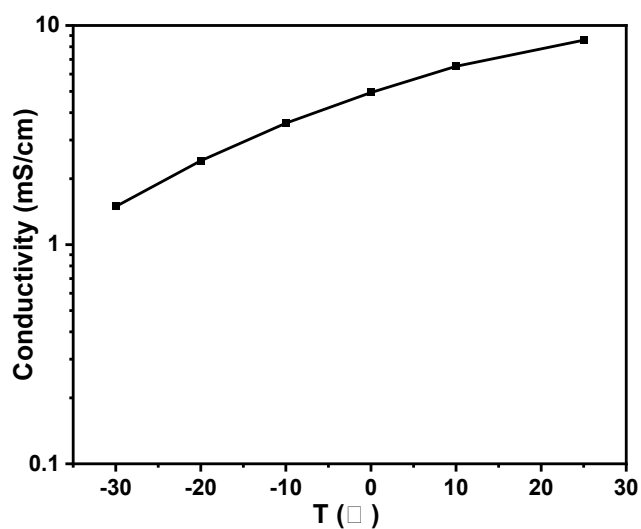


Figure S1. Plots of ionic conductivity–temperature dependence of STD.

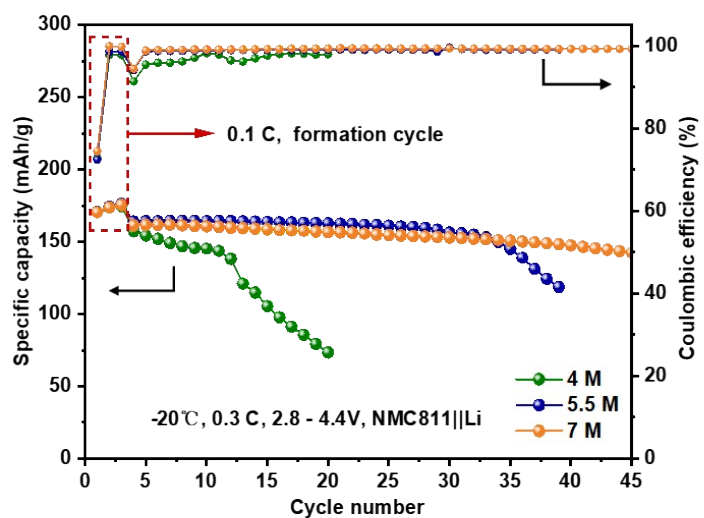


Figure S2. Cycling performances of Li/NMC811 cells in various LHCEs at -20°C.

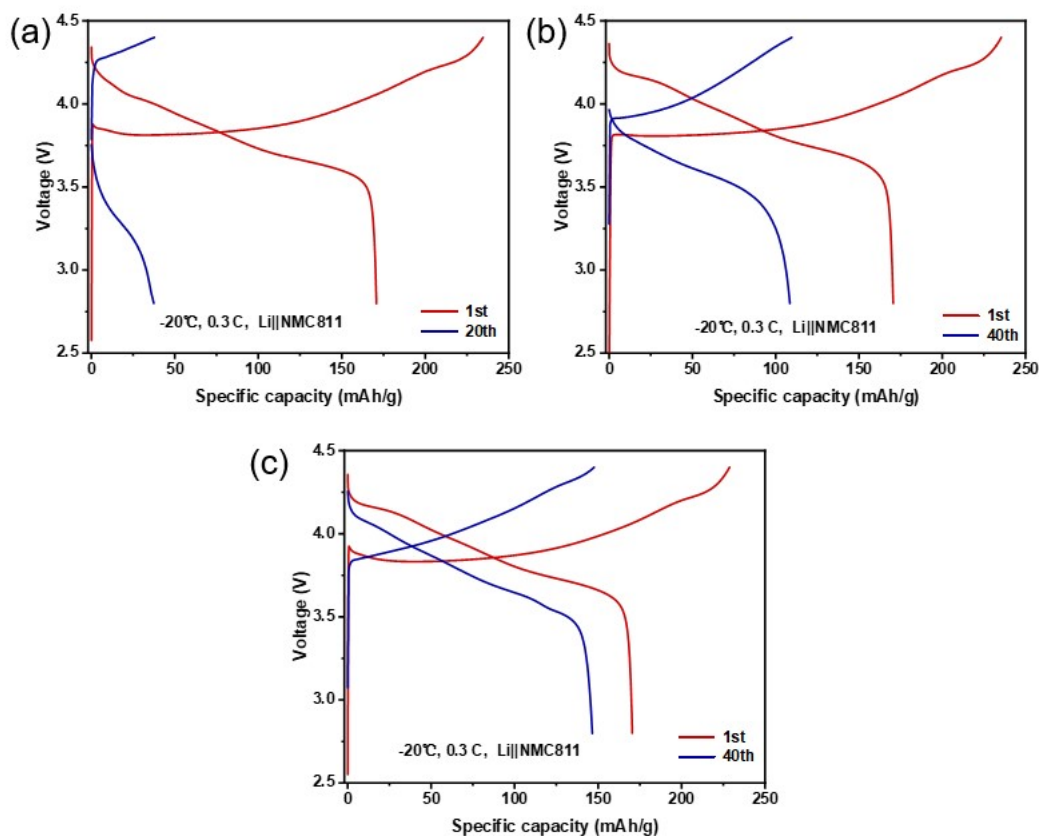


Figure S3. Charge and discharge curves of Li/NMC811 cells in (a) the 4M (b) the 5.5M and (c) the 7M-LHCEs at -20 °C.

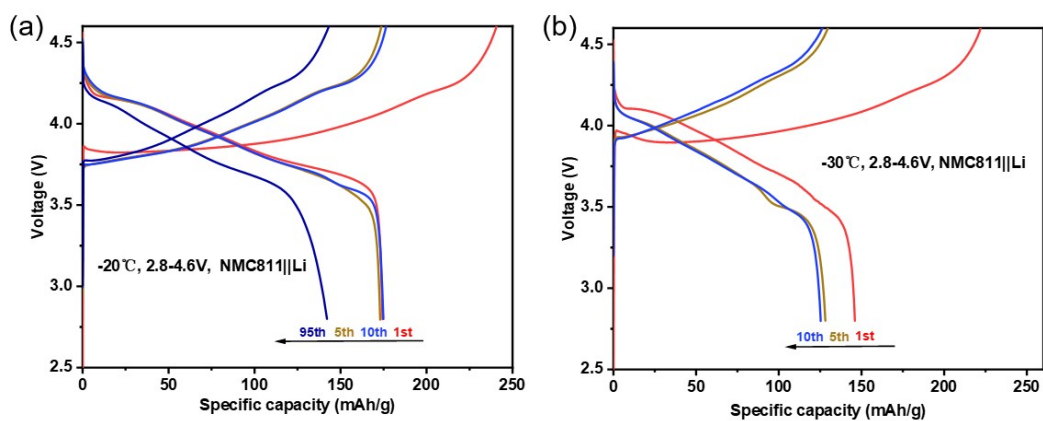


Figure S4 Charge/discharge curves of Li/NMC811 cells at (a)  $-20^{\circ}\text{C}$  and (b)  $-30^{\circ}\text{C}$  within the voltage range of 2.8-4.6V.

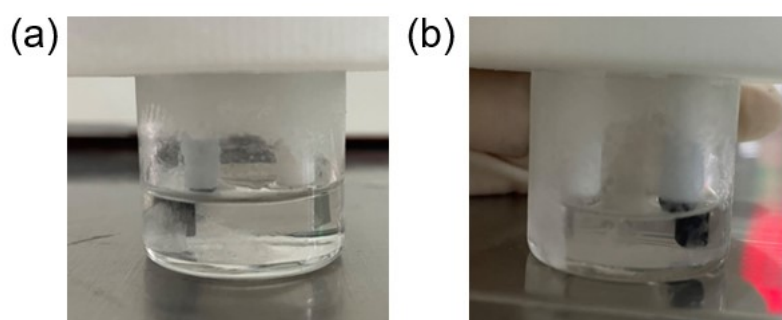


Figure S5. Images of (a) the STD electrolyte at  $-30^{\circ}\text{C}$  and (b) the 7M electrolyte at  $-50^{\circ}\text{C}$ . After the electrolytic cell containing the selected electrolyte is kept at the corresponding temperature for more than ten hours, take it out and take a photo quickly.

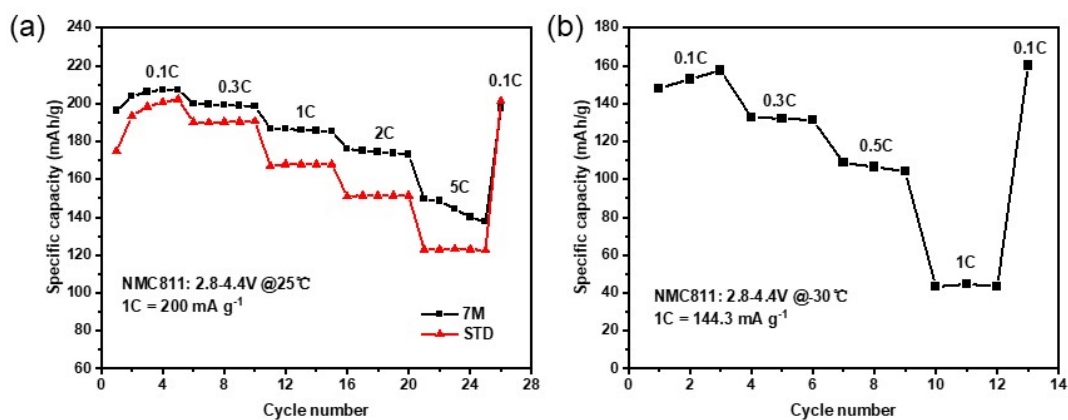


Figure S6 Rate performance of Li||NMC811 cells in (a) 7M-LHCE and STD electrolytes at room temperature, and (b) 7M-LHCE at  $-30^{\circ}\text{C}$ .

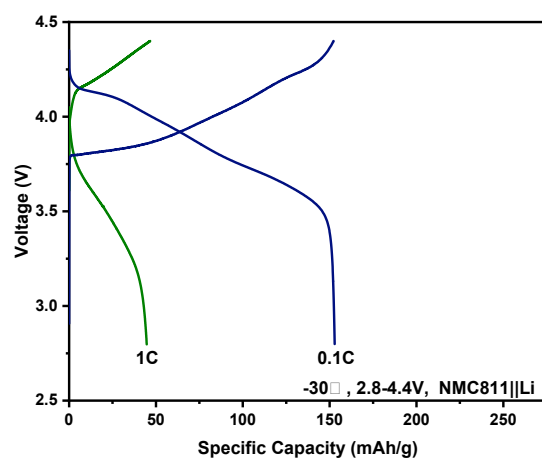


Figure S7 Low temperature charge/discharge curves of Li/NMC811 cells at current rates of 0.1 C and 1C, respectively.

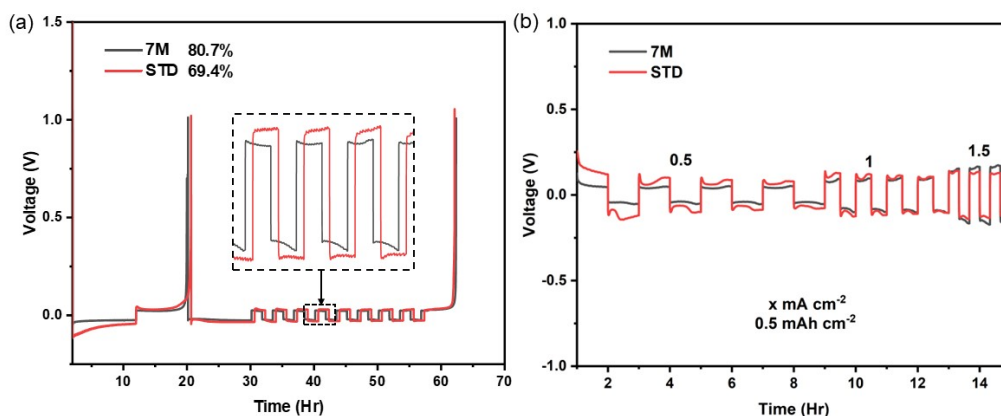


Figure S8 (a) Average coulombic efficiency measurements of Li|Cu cells and (b) rate performance of Li/Li symmetric cells in 7M-LHCEs and STD electrolyte. (The lithium deposition capacity was fixed at 1 mAh cm<sup>-2</sup>).

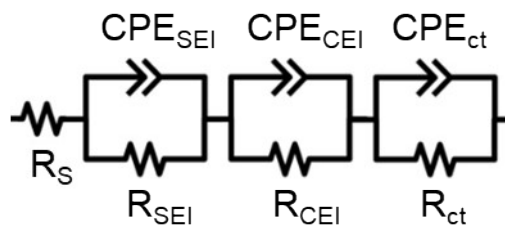


Figure S9. The equivalent circuit designed to analyze the impedance.

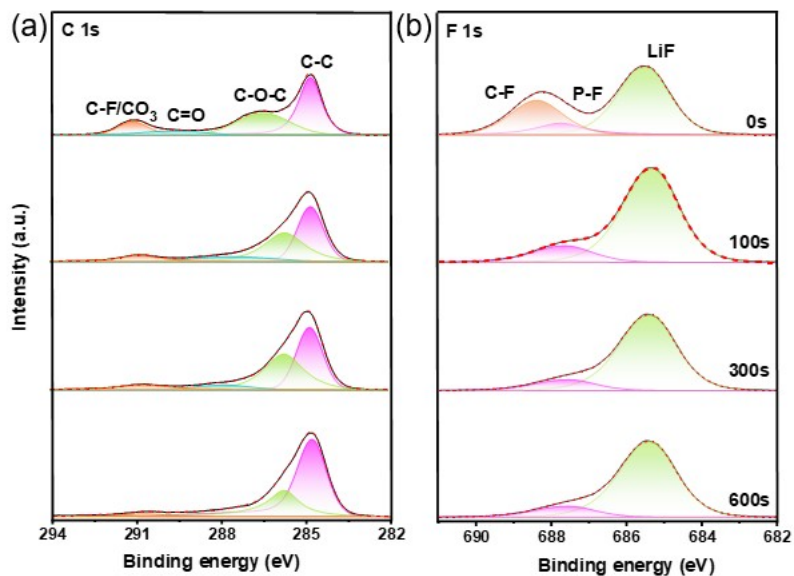


Figure S10. XPS spectra of the NMC811: (a) C 1s and (b) F 1s. The NMC811 cathodes were cycled 10 cycles in the STD electrolyte.

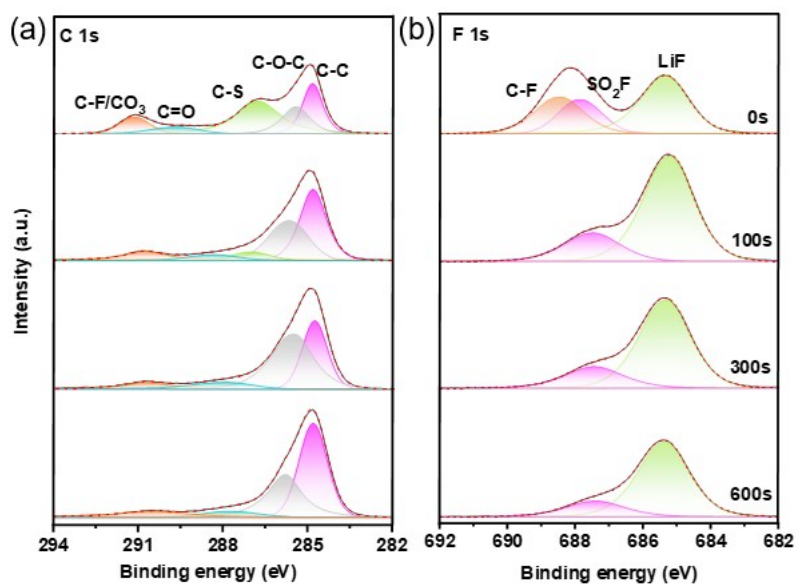


Figure S11. XPS spectra of the NMC811: (a) C 1s and (b) F 1s. The NMC811 cathodes were cycled 10 cycles in the 7M electrolyte.

References:

- [1] B. D. Adams , J. Zheng , X. Ren , W. Xu and J. G. Zhang , *Adv. Energy Mater.*, 2018, **8** , 1702097.