# Supporting information for

# Entropy-driving multi-anionic electrolyte towards Li-ion batteries with high voltage stability and superior temperature adaptability

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#### **Experimental Sections**

#### **Materials** preparation

The LiNi<sub>0.52</sub>Co<sub>0.2</sub>Mn<sub>0.28</sub>O<sub>2</sub> (NCM523) material is purchased from Shanghai Shanshan Tech Co., Ltd, China. The graphite (EP5-H) material is purchased from Shanghai Shanshan Tech Co., Ltd, China. The raw material for configuring the electrolyte and contrastive electrolytes are purchased from Suzhou Duo Duo Chemical Tech Co., Ltd, China.

#### **Preparation of electrolyte**

HE-DIG electrolyte is composed of 0.15 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), 0.15 M lithium bis(fluorosulfon)imide (LiFSI), 0.15 M lithium nitrate (LiNO<sub>3</sub>), 0.15 M lithium difluoro(oxalato)borate (LiDFOB) in Diglyme (DIG). 0.6 M DIG electrolyte is composed of 0.6 M LiTFSI in DIG. Two of the electrolytes are prepared in glove box. The synthesis protocol initiates with volumetric anchoring of the solvent phase, followed by stoichiometric calculation of lithium salt mass based on predetermined molar concentration. Precise gravimetric dosing of the target lithium salt is subsequently executed, followed by agitation on a magnetic stirrer until achieving transparency, ensuring homogeneous ion distribution through controlled dissolution kinetics.

#### Preparation of carbonate precursor

 $Mn_{0.75}Ni_{0.25}CO_3$  carbonate precursor is prepared by the coprecipitation method.  $Na_2CO_3$  and 0.1 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O are used as the precipitant and complexing agent of the reaction. 600 mL 2 mol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> solution is slowly dropped into a tank reactor together with 500 mL 2 mol L<sup>-1</sup> NiSO<sub>4</sub>·6H<sub>2</sub>O and MnSO<sub>4</sub>·H<sub>2</sub>O solution in a molar ratio of 1: 3. The reaction temperature is continuously kept at 55°C and the pH at 7.5. After 12 h of sedimentation, the obtained product is

washed with deionized water thoroughly and dries at 120°C for 24 h to prepare  $Mn_{0.75}Ni_{0.25}CO_3$  precursor.

#### **Preparation of LNMO**

 $Li_2CO_3$  and the prepared precursor above are mixed according to a molar ratio of Li: M  $(Mn_{0.75}Ni_{0.25}) = 1.2$ : 0.8. After evenly grinding, the mixture is calcined at 500°C for 5 h, then calcined at 850°C for 12h to obtain LNMO ( $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ ).

#### Preparation of the 12 Ah pouch cell

When preparing NCM523 cathodes, the NCM523 sample, conductive acetylene black (Super P, SP), and polyvinylidene fluoride (PVDF) are dispersed in the proper amount of N-methylpyrrolidone (NMP), and the mass ratio of m(NMC523):m(PVDF):m(SP) is about 94:1.5:4.5. Then the obtained slurry is pasted on Al foils with a single-side coating surface density of 8 mg cm<sup>-2</sup>. After drying at 95°C and rolling with the compaction density of 3.2 g cm<sup>-3</sup>, the NCM523 cathode is prepared (156 mm×69 mm). The whole process controls the ambient dew point below –35°C.

When preparing the graphite anode, the graphite sample, conductive acetylene black (Super P, SP), carboxylic styrene butadiene latex (SBR), and sodium carboxymethylcellulose (CMC) are dispersed in the proper amount of deionized water, and the mass ratio of m(graphite): m(SBR): m(CMC): m(SP) is about 92:4:1.5:2.5. Then the obtained slurry is pasted on Cu foils with a single-side coating surface density of 5.5 mg cm<sup>-2</sup>. After drying at 95°C and rolling with the compaction density of 1.2 g cm<sup>-3</sup>, the graphite anode is prepared (156 mm×71 mm). The whole process controls the ambient dew point below  $-30^{\circ}$ C.

The NCM523 cathode, the graphite anode, and the separator are stacked into a pouch cell in the form of laminated sheets with about 36 g electrolyte. The 10 µm thick ceramic diaphragm (battery

grade) is chosen as a separator. The capacity of the prepared pouch cell is 12 Ah with a size of 172 mm×74 mm×8 mm. The theoretical energy density is about 200 Wh kg<sup>-1</sup>.

#### Characterization

Time of flight secondary ion mass spectrometry (TOF-SIMS, *PHI nanoTOF* II) is used to determine the species of atomic units near the surface (about 40 nm depth; sputtering time is ~3nm/min SiO<sub>2</sub> depth) of the NCM523 cathode and then forms 3D-mapping images. The ionic conductivity of the electrolytes is measured by *DDSJ-319L* (INESA SCIENTIFIC INSTRUMENT CO., LTD, Shanghai) ionic conductivity meter. Raman spectra of the electrolyte and its components were collected to analyze the solvation complexes (RENISHAW, wavelength of excitation laser: 532.8 nm).

#### **Electrochemical Measurement**

Galvanostatic charge/discharge (GCD) tests are conducted on half-cells and 12Ah-pouch cells controlled by the NEWWARE battery testing system. Before testing, the batteries are kept quiet at the same temperature for 2 hours. To evaluate the Li<sup>+</sup> storage performance of the graphite anode, coin-type (CR2025) half-cells were fabricated by coupling NCM523-based electrodes with metal lithium. The NCM523-based electrodes were prepared by mixing active materials, super P and polyvinylidene fluoride solution (NMP as a solvent, mass percentage of 6.5%) with a mass ratio of 8:1:1. The slurry was coated on aluminum foils and dried at 120°C for 12h. The electrode was punched into circle with diameters of 12 mm, in which the average mass loading of cathodes were 2-4 mg cm<sup>-2</sup>. The assembling process of half-cells were carried in a glovebox filled with pure Ar. The Whatman glass fiber (GF/D) was selected as the separator. 0.15 M LiTFSI, 0.15 M LiFSI, 0.15 M LiDFOB in Diglyme (DIG), 0.6 M LiTFSI in DIG and 15%LiPF<sub>6</sub>, 11%EC, 25%DMC, 5%PC, 35%EMC, 6%FEC, 3%PS (Ester) were used as electrolyte.

Tafel polarization curve tests are conducted on CR2025-type coin batteries recorded on an electrochemical workstation (CHI660E). Before testing, the batteries are kept quiet at the same temperature for 2 h. Electrochemical impedance spectroscopy (EIS) is recorded on an electrochemical workstation (CHI660E) in the frequency range of 0.01~100000 Hz. Cyclic voltammetry (CV) was measured by the electrochemical workstation (CHI660E, Chenhua, Shanghai).

#### Simulation details and methods

Quantum chemistry calculations were first performed to optimize molecular geometry of DGM (diglyme) molecule, DFOB, FSI, NO<sub>3</sub>, and NTF<sub>2</sub> anions using the Gaussian 16 package [1] at B3LYP/6-311+G(d,p) level of theory. The atomic partial charges on these molecules and ions were calculated using the ChelpG method at the same level of theory (the B3LYP hybrid functional and the 6-311+G(d,p) basis set). The atomistic force field parameters for all ions and solvent molecules are described in the AMBER format and are taken from a previous work [2]. The cross-interaction parameters between different atom types are obtained from the Lorentz-Berthelot combination rule.

A modeling system was constructed and the detailed system composition is listed in Table 1. All atomistic simulations were performed using GROMACS package with cubic periodic boundary conditions [3]. The equations for the motion of all atoms were integrated using a classic Verlet leapfrog integration algorithm with a time step of 1.0 fs. A cutoff radius of 1.65 nm was set for short-range van der Waals interactions and real-space electrostatic interactions. The particle-mesh Ewald (PME) summation method with an interpolation order of 5 and a Fourier grid spacing of 0.15 nm was employed to handle long-range electrostatic interactions in reciprocal space. All simulation systems were first energetically minimized using a steepest descent algorithm, and

thereafter annealed gradually from 700 K to room temperatures (300 K) within 10 ns. All annealed simulation systems were equilibrated in an isothermal-isobaric (NPT) ensemble for 20 ns of physical time maintained using a Nosé-Hoover thermostat and a Parrinello-Rahman barostat with time coupling constants of 0.4 and 0.4 ps, respectively, to control the temperature at 300 K and the pressure at 1 atm. Atomistic simulations were further performed in a canonical ensemble (NVT) for 40 ns, and simulation trajectories were recorded at an interval of 100 fs for further structural and dynamical analysis.

Representative ion structures were extracted from extensive atomistic simulations, and these solvation structures were adopted as starting configurations for additional DFT calculations. DFT calculations were performed using the Gaussian 16 software [1] at the same level of theory (B3LYP/6-311+G(d,p)) and with Grimme's-D3 (gd3bj) dispersion correction to obtain the corresponding optimized coordination structures and thereafter binding energies.

 Table 1. The modeling system and detailed system composition of HE-DIG.

	system		
Li-DFOB	15		
Li-FSI	15		
Li-NTF2	15		
Li-NO3	15		
DGM	725		
Nr. of atoms	17290		
System size	$(5.6538 \text{ nm})^3$		

Electrolyte	Initial specific capacity (mAh g <sup>-1</sup> )	Rate (C)	Temperature rate (°C)
HE-DIG (this work)	139.8	0.5	25
HE-DIG (this work)	76.2	0.5	-20
1.2 M LiPF <sub>6</sub> in EC: EMC: MP (20: 60: 20 vol%) <sup>4</sup>	~135	0.5	25
1.0 M LiPF <sub>6</sub> in EC: DMC (3: 7 vol%), 0.5 wt% TMEB <sup>5</sup>	~140	0.5	25
1 M LiFSI in 2-Me DOL <sup>6</sup>	~125	0.5	25
1.0 M LiPF6 in EC: DMC (3: 7 vol%) <sup>7</sup>	~70	0.5	-20
1.2 M LiPF <sub>6</sub> in EC: EMC: MP (20: 60: 20 vol%) <sup>4</sup>	~60	0.5	-20
1.2 M LiPF <sub>6</sub> in EC: EMC (3:7 vol%) <sup>4</sup>	~50	0.5	-20
1.0 M LiPF <sub>6</sub> EC: EMC (7.5: 4.8 molar ratio) <sup>8</sup>	~60	0.1	-30

**Table 2.** The comparison table for the performance of NCM523 relative to other electrolytes.



## Figure S1.

The charge/discharge curves of the NCM523 half-cells based on 0.6 M DIG and HE-DIG electrolytes at 1 C at 25°C.



**Figure S2.** The snapshot acquired through MD simulations of Ester (a) and 0.6 M DIG (b).



**Figure S3.** The coordination number N(r) and RDF g(r) of Li-O (solvent) of Ester.



**Figure S4.** The RDF g(r) and coordination number N(r) of Li-O(anions) of HE-DIG.



# Figure S5.

The LSV curves of the Li||Spacer batteries based on 0.6 M DIG and HE-DIG at 25°C and -20°C.



## Figure S6.

The Raman curves and the fitting results of HE-DIG, 0.6 M DIG electrolytes and DIG solvent.



## Figure S7.

The ionic conductivity of the three electrolytes (HE-DIG, 0.6 M DIG and Ester) at 25°C and -20°C.



## Figure S8.

The discharge-dependent *in-situ* EIS and fitted curves of the Li||Li batteries based on HE-DIG (a) and Ester (b) at 25°C.



#### Figure S9.

The variation of the fitted impendence variations of solution resistance ( $R_s$ ) and charge transfer resistance ( $R_{ct}$ ) based on HE-DIG (a, c) and Ester (b, d) at 25°C and -20°C.



## Figure S10.

The DRT curves of discharge of Li||Li batteries based on HE-DIG (a) and Ester (c). The related homologous 2D intensity color maps of HE-DIG (b) and Ester (d) at  $-20^{\circ}$ C.



#### Figure S11.

The discharge-dependent *in-situ* EIS curves and DRT curves of graphite||Li batteries based on 0.6 M DIG (a, b), Ester (c, d) and HE-DIG (e, f). The variation of the fitted impendence variations of  $R_s$  and  $R_{ct}$  based on 0.6 M DIG (g), Ester (h) and HE-DIG (i) at 25°C.



**Figure S12.** The cycle performance of NCM523 half-cells based on HE-DIG and Ester at 0.5 C at 25°C.



## Figure S13.

The cycle performance of NCM523 half-cells based on HE-DIG and Ester at 1 C and at -20°C based on constant-voltage charge and galvanostatic discharge.



**Figure S14.** The cycle performance of NCM523 half-cells based on 0.6 M DIG at 0.5 C, at 25°C and –20°C.



### Figure S15.

The electrochemical rate capability of NCM523 half-cells based on HE-DIG and Ester at 25°C (a) and -20°C (b).



## Figure S16.

The charge/discharge curves of NCM523 half-cells based on HE-DIG (a) and Ester (b) at 1 C at  $25^{\circ}$ C.



## Figure S17.

The cycle performance of HE-DIG and Ester based on LNMO half-cells at 0.5 C at 25°C.



**Figure S18.** The multiple rates of HE-DIG and Ester based on LNMO half-cells at 0.5 C at 25°C.



## Figure S19.

The XRD patterns of the NCM523 pristine and the cycled NCM523 cathodes after 100 cycles at 0.5 C based on HE-DIG and Ester at  $25^{\circ}$ C and  $-20^{\circ}$ C



## Figure S20.

The SEM of the NCM523 pristine and the cycled NCM523 after 100 cycles at 0.5 C based on HE-DIG and Ester at  $-20^{\circ}$ C

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