# Tug-of-war Effect Tuned Li Ion Transport Enhances Rate Capability of Lithium Metal Batteries

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#### **Experimental section**

#### Materials

Li foil (China Energy Lithium Co., Ltd.), lithium bis(fluorosulfonyl)imide (LiFSI, 99.5%, Dodo Chem, Suzhou, China), 1,2-dimethoxyethane (DME, 99.5%, Sigma-Aldrich), fluorobenzene (FB, 99%, Aladdin), 1,3,5-Trifluorobenzene (F<sub>3</sub>B, 99%, Aladdin), separator (Celgard 2400), NCM712 power (Ronbay technology Co., Ltd), Commercial NCM712 electrode was supplied by Ronbay technology Co., Ltd. (Ningbo, China), LFP power (Jiangxi Anchi New Energy Technology Co., Ltd.), Commercial LFP electrode was supplied by Jiangxi Anchi New Energy Technology Co., Ltd. (Shangrao, China). Molecular sieves were used to remove the residual water in original solvents.

#### Characterizations

NMR results were carried out with Ascend 600 MHZ (Bruker. Co., Ltd.). A 1 M LiCl in deuterated water was hot sealed in quartz capillary for internal standard. And then, the quartz capillary and electrolyte were put into the NMR tube for test. This method was used to avoid the contact between deuterated water and electrolyte. The ionic conductivities of the electrolytes were recorded by DDS-307A (INESA Scientific Instrument Co. Ltd., Shanghai, China) at selected temperatures.

#### **Electrolyte composition**

For a typical HCE, 1.87 g LiFSI was dissolved into 1.5 ml DME. For the DHCE, 1.87 g LiFSI was dissolved into 1.5 ml DME and 3 ml FB. For the DHCE1, 1.87 g LiFSI was dissolved into 1.5 ml DME, 2.9 ml FB, and 0.1 ml F<sub>3</sub>B. For the DHCE2, 1.87 g LiFSI was dissolved into 1.5 ml DME, 2.8 ml FB, and 0.2 ml F<sub>3</sub>B. For the DHCE5, 1.87 g LiFSI was dissolved into 1.5 ml

DME, 2.5 ml FB, and 0.5 ml F<sub>3</sub>B. The FB-DHCE is LiFSI: DME: FB (1: 1.2: 3 by mol). The FB-F<sub>3</sub>B-DHCE is LiFSI: DME: FB: F<sub>3</sub>B (1: 1.2: 2.8: 0.2 by mol). The preparation and storage of electrolytes are carried out in the glovebox. (H<sub>2</sub>O< 0.1 ppm, O<sub>2</sub>< 0.1 ppm).

#### **Electrochemical measurements**

The electrochemical performance of the coin/pouch cells was conducted on Neware battery test system (CT-4008T-5V10mA-164, Shenzhen, China). Electrochemical impedance spectrometry (EIS) (100 kHz to 0.1 Hz) was conducted using Solartron electrochemical workstation with voltage amplitude of 5 mV, and the EIS plots of cycled Li-NCM 712 cells need to be rested 10 min to obtain a steady voltage before tests. The amount of electrolyte is controlled as 30 µL in coin cell, and 100  $\mu$ L in pouch cell. Li-Cu half cells assembled with Cu foil ( $\phi$  16 mm) as a cathode and Li foils as an anode in CR2032 coin cells. The NCM 712 cathode was made by blending NCM 712 powder, Super P, PVDF with a weight ratio of 8: 1: 1 in NMP solution to form the slurry, and then coated on the Al foil. After drying at 80 °C under vacuum overnight, the obtained electrodes with areal mass loadings controlled to be 4 mg cm<sup>-2</sup>. The Li- NCM 712 cells were galvanostatically cycled between 3 and 4.3 V at 25 °C. The commercial NCM 712 electrode has an areal capacity of 4 mAh cm<sup>-2</sup> and the high-loading Li-NCM 712 cells were galvanostatically cycled between 3 and 4.3 V with long-term cycling and rate tests at 25 °C. For the Li- NCM 712 pouch cell, a 200 and 50 µm Li foil as an anode, and the commercial NCM 712 electrode (3×3 cm) as a cathode, the amount of DHCE2 was controlled at 100  $\mu$ L (3 g Ah<sup>-1</sup>), then, adding separator and packed with an aluminum-plastic film. The pouch cell was galvanostatically cycled between 3 and 4.3 V with a current density of 0.1C at 25 °C. The LFP cathode was made by blending LFP powder, Super P, PVDF with a weight ratio of 8: 1: 1 in NMP solution to form the slurry, and then coated on the Al foil. After drying at 80 °C under vacuum overnight, the obtained electrodes with areal mass loadings controlled to be 1 mg cm<sup>-2</sup>. The Li-LFP cells were galvanostatically cycled between 2.8 and 3.8 V at 25 °C. The commercial LFP electrode has a mass loading of 17.4 mg cm<sup>-2</sup> and the high-loading Li-LFP cells were galvanostatically cycled between 2.8 and 3.8 V with long-term cycling test at 25 °C. For the 6-Ah-grade Li-LFP pouch cell, pouch cells assembly were performed with a semi-automated cell-manufacturing line. Z-folded stacking method was used for winding of the cathode, anode, and separator. Each pouch cell contains 14 layers of double-sided cathodes, as well as 13 double-sided and 2 single-sided anode layers. A 50  $\mu$ m Li foil as an anode, and the commercial LFP electrode (20 mg cm<sup>-2</sup>; 8×8.5 cm) as a cathode, the amount of FB-F<sub>3</sub>B-DHCE was controlled at 3 g Ah<sup>-1</sup>. All the Li metal pouch cells fabrication process including ultrasonic welding, packaging and vacuum sealing with electrolyte injection were assembled in an Ar filled glove box. The pouch cell was galvanostatically cycled between 2.8 and 3.8 V at 0.1C charge and 0.2C discharge at 25 °C.

A Li/SPE/Li cell was tested by AC impedance and DC polarization to calculate transference number  $t_{Li}^{+}$  from Bruce-Vincent-Evans equation:

$$t_{Li^+} = \frac{I_{ss} \left( \Delta V - I_0 R_0 \right)}{I_0 \left( \Delta V - I_{ss} R_{ss} \right)}$$

The applied polarization voltage is 10 mV ( $\Delta$ V).  $I_0$  and  $I_{ss}$  are read from time-dependence current curve, and  $R_0$  and  $R_{ss}$  represent the initial resistance and the steady-state resistance of the passivating layer on the lithium electrode, respectively.

#### Pulsed-Field Gradient Nuclear Magnetic Resonance (PFG-NMR) Measurements

Diffusion coefficients of Li<sup>+</sup>, and FSI<sup>-</sup> were measured using <sup>7</sup>Li, and <sup>19</sup>F PFG NMR,

respectively, using a vendor-supplied stimulated echo sequence (Dbppste, VNMRJ) on a 600-MHz NMR spectrometer (Agilent) equipped with a 5-mm z-gradient probe with a maximum gradient strength of ~31 T m<sup>-1</sup>. The echo heights were recorded as a function of gradient strength and fitted with the Stejskal–Tanner equation50,  $S(g) = S(0) \exp[-D_i(\gamma_i \delta g)^2(\Delta - \delta/3)]$ , where S(g) and S(0) are the echo heights at gradient strengths of g and 0, respectively.  $D_i$  is the diffusion coefficient and  $\gamma_i$  is the gyromagnetic ratio, where i is <sup>7</sup>Li, <sup>19</sup>F,  $\delta$  is the length of the gradient pulse, and  $\Delta$  is the duration between the encoding and decoding gradient pulses. The values of  $\delta$  and  $\Delta$  were fixed at 2 and 80 ms for <sup>7</sup>Li; 1 and 10 ms for <sup>19</sup>F, respectively. The gradient strength was varied in 16 equal steps with an appropriate maximum gradient strength to achieve a full decay of the echo profiles.

#### **Computational Details**

Ab inito molecular dynamics (AIMD) simulations were performed on the electrolytes using in the canonical (NVT) ensemble at 300K. In addition, the constant temperature of the AIMD simulation systems was controlled using the Nosé thermostat method with a Nosé-mass parameter of 0.1. Our structure is simulated by 17.5 Å×17.5 Å×17.5 Å cell. These initial structures were firstly relaxed using a cell made classical molecular dynamics simulation method with the force field. A time step of 1 fs was used in all AIMD simulations. A Monkhorst-Pack k-point mesh grid scheme (1× 1 × 1) was used Upon quasi-equilibration of the system, a total of 15 ps AIMD simulations were carried out for each mixture system. The AIMD trajectory of the final 5 ps was used to obtain radial distribution functions of Li-O<sub>DME</sub>, Li-O<sub>FSI</sub> and  $F_{(FB/F3B)}$ -H<sub>DME</sub> pairs.

#### **Supplementary Figures**



**Figure S1.** Chronocurrent curves of the Li symmetric cells with different electrolytes, (a) HCE, (b) DHCE, (c) DHCE1, (d) DHCE2, (e) DHCE5 (Insert: the EIS spectra before and after DC polarization).



**Figure S2.** The <sup>19</sup>F NMR spectra of FB, F<sub>3</sub>B and different electrolytes



**Figure S3.** The <sup>1</sup>H NMR spectra of FB without Li salt (a) and with Li salt (d); DME without Li salt (b) and with Li salt (e); 3FB without Li salt (c) and with Li salt (f).



**Figure S4.** (a-b) LSV plot of different electrolytes. (Scan rate:  $1 \text{ mV s}^{-1}$ ). (c) Frontier molecular orbital energies of the LiFSI, DME, FB and F<sub>3</sub>B molecules. Fermi level of the Li metal anode and high-voltage cathode.



**Figure S5.** (a-b) Li-Cu tests toward different electrolytes. Voltage response of Li-Cu cells in c) DHCE, d) DHCE2. (0.5 mA cm<sup>-2</sup>, 0.5 mAh cm<sup>-2</sup>), e) DHCE, f) DHCE2. (3 mA cm<sup>-2</sup>, 1 mAh cm<sup>-2</sup>)



**Figure S6.** Voltage profiles of the Li-NCM712 batteries in different electrolytes. (a) DHCE. (b) DHCE2. (Cathode loading: 4 mg cm<sup>-2</sup>, 3-4.3 V, 1 C)



**Figure S7.** Voltage profiles of the Li-NCM712 batteries in different electrolytes. (a) DHCE. (b) DHCE2. (Areal capacity: 2 mAh cm<sup>-2</sup>, 3-4.3 V)



**Figure S8.** Voltage profiles of the Li-NCM712 batteries cycled with different current density in selected electrolytes. (Areal capacity: 2 mAh cm<sup>-2</sup>, 3-4.3 V)



**Figure S9.** (a) Nyquist plots of the Li/Li symmetric cells with different electrolytes at temperatures ranging from -10 to 20 °C. (b) Comparison of the activation energies (E<sub>a</sub>) values for desolvation in the corresponding electrolyte.



**Figure S10.**Rate performance of Li–NCM712 batteries toward different electrolytes (NCM712 areal capacity: 4 mAh cm<sup>-2</sup>).



**Figure S11.** The charge-discharge curves of Li–NCM712 batteries at different rate using (a) DHCE and (b) DHCE2 (NCM712 areal capacity:  $4 \text{ mAh cm}^{-2}$ ).



**Figure S12.** Voltage profiles of the Li-NCM712 batteries in different electrolytes. (a) DHCE. (b) DHCE2. (Areal capacity: 4 mAh cm<sup>-2</sup>, Li: 50  $\mu$ m, 3-4.3 V)



**Figure S13.** Cycling peformance of Li-NCM712 coin cell under practical condition. (Areal capacity: 4 mAh cm<sup>-2</sup>, Li: 50  $\mu$ m, electrolytes: 3 g Ah<sup>-1</sup>, 3-4.3 V)



**Figure S14.** Voltage profiles of Li-NCM712 coin cell under practical condition. (Areal capacity: 4 mAh cm<sup>-2</sup>, Li: 50  $\mu$ m, N/P: 2.3, E/C: 3 g Ah<sup>-1</sup>, 3-4.3 V)



**Figure S15.** Voltage profiles of Li-NCM712 pouch cell under challenging condition. (Areal capacity: 4 mAh cm<sup>-2</sup>, E/C: 3 g Ah<sup>-1</sup>, 3-4.3 V)



**Figure S16.** Rate performance of Li–LFP batteries toward different electrolytes (loading: 17.4 mg cm<sup>-2</sup>).

![](_page_12_Figure_4.jpeg)

**Figure S17.** The charge-discharge curves of Li–LFP batteries at different rate using (a) FB-DCHE and (b) FB-F<sub>3</sub>B-DHCE (loading: 17.4 mg cm<sup>-2</sup>).

![](_page_13_Figure_0.jpeg)

**Figure S18.** Voltage profiles of Li-LFP coin cell under practical condition. (loading: 17.4 mg cm<sup>-2</sup>, Li: 50  $\mu$ m , E/C: 3 g Ah<sup>-1</sup>, 2.8-3.8 V)

![](_page_13_Figure_2.jpeg)

**Figure S19.** Voltage profiles of Li-LFP pouch cell under practical condition. (loading: 20 mg cm<sup>-2</sup>, Li: 50 μm, N/P: 2.9, E/C: 3 g Ah<sup>-1</sup>, 2.8-3.8 V)

## Supplementary Tables

Electrolytes	Ionic conductivity	$T_{Li}^+$	Li <sup>+</sup> conductivity	FSI <sup>−</sup>
	(mS cm-1)		(mS cm <sup>-1</sup> )	conductivity
				(mS cm <sup>-1</sup> )
HCE	3.51	0.3	1.053	2.457
DHCE	6.12	0.45	2.754	3.366
DHCE1	6.03	0.55	3.3165	2.7135
DHCE2	5.95	0.65	3.8675	2.0825
DHCE5	5.86	0.52	3.0472	2.8128

**Table S1.** Detail the ionic conductivity of different electrolytes at 30 °C.

**Table S2.** The mass of each part of the Li-NCM712 pouch cell.

Electrolyte type	DHCE2	
NCM 712 areal capacity	22 mg/cm <sup>2</sup>	
Active materials content	97 %	
Areal capacity	4 mAh/cm <sup>2</sup>	
Average Voltage	3.7 V	
Li foil (50µm)	23.4 mg	
Al foil (8µm)	18.9 mg	
Separator (20µm)	8.1 mg	
Electrolyte	130 mg	
Dimension	3*3 cm	
Gravimetric energy density	≥330 Wh/kg	

### Note: The calculation of gravimetric energy density.

The calculation of gravimetric energy density is based on the following equation:

$$E_{g} = \frac{VC}{\sum m_{i}}$$
(1)

In this equation, V is the average working voltage of Li-MNC712 pouch cell (3.7 V), C is the actual capacity of each cycle,  $m_i$  is the all mass of each part including cathode, anode, electrolyte, separator, and current collector shown in **Table S2**.