# **Supporting Information**

# Moderate Li<sup>+</sup>-Solvent Binding for Gel Polymer Electrolytes with Stable Cycling toward Lithium Metal Batteries

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#### 1. Experimental methods

#### 1.1 Materials

Ethylene carbonate (EC), ethyl methyl carbonate (EMC), fluoroethylene carbonate (FEC), methyl 2,2,2-trifluoroethyl carbonate (FEMC), difluoroethylene carbonate(DFEC), Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from DoDochem. poly(ethylene glycol diacrylate) (PEGDA) and azobisisobutyronitrile (AIBN) were purchased from Rhawn. LiFePO4 (LFP) was provided by Wuhan Zhongke Institute of Advanced Technology. LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811) was purchased from Guangdong Canrd New Energy Technology Co.,Ltd. All materials were all used as received. Polypropylene separator (PP) was purchased from Guangdong Canrd New Energy Technology Co.,Ltd.

#### **1.2 Preparation of GPE**

FEC and FEMC were mixed at a volume ratio of 1:1, and 1M LiTFSI was added for full dissolution. 8 wt% of PEGDA and 0.3 wt% of AIBN were dissolved in the mixture of EFC, FEMC and LiTFSI, and mixed thoroughly to obtain the precursor solution. The precursor solution was injected into the separator, and the battery was assembled and sealed. The precursor solution was heated at 60 °C for 12 hours to form the MB-GPE. Similarly, the solvents for HB-GPE were EC and EMC, and for LB-GPE were DFEC and FEMC. 1 M LiTFSI dissolved in 1:1 volume ratio of EC and EMC as commercial liquid electrolyte (LE).

#### **1.3 Material characterization**

FTIR spectra were analyzed using Nexus FTIR spectrometer. Raman spectra were obtained using LabRAM Odyssey (excitation wavelength of 532 nm). X-Ray diffraction (XRD, Bruker, D8 ADVANCE, Cu Ka radiation) was taken to determine the crystallization degree of the GPEs (scan rate =  $10^{\circ}$ /min, Angle range of  $10^{\circ}$  to  $80^{\circ}$ ). Raman spectrometer. The electrolyte and electrode surfaces and cross sections were morphologically analyzed using a scanning electron microscope (JSM-7500F). A differential scanning calorimeter (DSC, TAQ2000) was used to investigate the glass transition temperature (Tg) of the GPEs at a heating rate of  $10^{\circ}$ /min. The changes in SEI composition formed on the lithium metal anode after 20 cycles of the cell were investigated by X-ray photoelectron spectroscopy (Thermo ESCALAB 250Xi) and time-of-flight secondary ion mass spectrometer (IONTOF TOF SIMS 5). A pulsed ion beam of Bi<sup>3+</sup> (20 ns) at 30 keV in high-current mode was used for in-depth analysis, and the samples were sputtered with a Cs<sup>+</sup> (negative) ion beam at 500 eV over an area

of 200  $\mu$ m × 200  $\mu$ m. Typical area of analysis was 50  $\mu$ m × 50  $\mu$ m. the Young's modulus of the gel electrolyte was characterized using an atomic force microscope (Dimension Edge). The average molecular weight of the gel electrolytes was analyzed using gel permeation chromatography (PL-GPC220). The wettability of the electrolytes was tested using a contact angle meter (dataphysics OCA20). The electrodes were obtained after cycling by disassembling the cell and then washed three times with the appropriate solvents to remove the residual electrolyte, which was tested after drying under vacuum.

#### **1.4 Electrode preparation**

NCM811 and LFP cathodes were prepared using a slurry casting technique. Active material, Super P carbon and poly(vinylidene fluoride) (PVDF) were dissolved in N-methyl-2-pyrrolidone with a weight ratio of 8:1:1 to make a slurry and then coated onto a current collector of aluminium foil. The cathodes were dried in a vacuum oven at 110 °C for 12 h. The active loading density of the LFP cathode and NCM811 cathode were 2.5 mg cm<sup>-2</sup>. High-loading NCM811 (9.2 mg cm<sup>-2</sup>) cathodes were purchased from Guangdong Canrd New Energy Technology Co., Ltd. Ultra-thin Li foil (50  $\mu$ m) was purchased from China Energy Lithium Co., Ltd.. LIR2032 type coin cell or pouch cell were tested by LAND measurement system and Neware measurement system with a voltage range of 2.5 - 4 V (LFP) or 3 - 4.3 V (NCM811) at room temperature. The Li||LiFePO4 cells were activated through two cycles at 0.1 C (1 C = 200 mAh g<sup>-1</sup>).

#### **1.5 Electrochemical measurements**

The electrochemical performances of all cells were tested with 2032-type coin cells assembled using Li foil as the anode in an argon-filled glovebox (O<sub>2</sub> and H<sub>2</sub>O <0.1 ppm). Coulombic efficiency (CE) was carried out using Li||Cu cells, which were discharged at a current density of 0.2 mA cm<sup>-2</sup> for 1 h per cycle, and then charged at a current density of 0.2 mA cm<sup>-2</sup> to 1 V. Linear-sweep voltammetry was carried out using Li||stainless steel (SS) asymmetric cells from 2 V to 6 V versus Li/Li<sup>+</sup> at a scan rate of 1 mV s<sup>-1</sup>. Cyclic Voltammetry (CV) was carried out using Li||stainless steel (SS) asymmetric cells from 0 V to 4 V versus Li/Li<sup>+</sup> at a scan rate of 1 mV s<sup>-1</sup>. The EIS of the SS||SS cell and Li||Li cell was carried out from 10<sup>-1</sup> Hz to 10<sup>6</sup> Hz using a 10 mV peak voltage at an open-circuit voltage through an electrochemical workstation (Chi-660e). The ionic conductivity ( $\sigma$ ) was calculated according to the below equation:

#### $\sigma = L / RS$

where R and L refer to the bulk resistance and the thickness of electrolytes, respectively,

and S refers to the contact area of the SS with the solid polymer electrolyte.

The activation energy of Li<sup>+</sup> transport was calculated according to the following equation:

# $\sigma = A \exp(-E_a / RT)$

where A is the pre-exponential factor,  $E_a$  is the activation energy of Li<sup>+</sup> transport, R is the ideal gas constant, and T is the testing absolute temperature.

The Li<sup>+</sup> transference number  $(t_{Li}^+)$  was estimated by the electrochemical polarization method using Li||Li symmetric cell and was calculated by the below equation:

# $t_{Li^+} = I_s(\Delta V - I_0 R_0) / I_0(\Delta V - I_s R_s)$

where  $I_0$  and  $I_s$  are the initial and steady currents during polarization,  $R_0$  and  $R_s$  are the resistance values before and after the polarization, and  $\Delta V$  (10 mV) is the constant applied voltage during polarization. The EIS was tested at the frequency of  $10^{-1}$ - $10^{6}$  Hz with an amplitude of 10 mV at the open-circuit potential.

## 2. Computational methods

The density functional theory calculations of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were performed with the Gaussian 09 and Gauss View 5.0 software package with B3LYP/6-311++G (d, p) basis set level. The electrostatic potential (ESP) calculations were carried out using DMol3 module in Materials Studio software. The geometry optimizations were performed with generalized-gradient approximation (GGA)/BLYP functional and double numerical plus d-functions (DND) basis set. The formula for the binding energy ( $\Delta$ Eb) is as follows:

## $\Delta E_b = E_{total} - \sum E_{frag}$

Where  $E_{total}$  represents the overall electronic energy of the complexes,  $E_{frag}$  denotes the electronic energies of individual fragments.

Molecular dynamic (MD) simulations of three electrolytes are performed using the Forcite module in the Materials Studio software. All the MD simulations employed a condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS III) force field. These models were firstly relaxed by energy minimizing calculations, and then the output models are annealed from 300 to 1000 K for 5 cycles. Further, the electrolytes systems were equilibrated in the isothermal-isobaric ensemble (constant NPT) using the Berendsen barostat with the pressure of 1e<sup>-4</sup> GPa and a constant decay of 0.1 ps for 5 ns. The temperature was set to be 300 K with the Andersen thermostat. The time step is fixed to be 1 fs for the NPT equilibrium. The canonical

ensemble (NVT) at 300 K with total time of 5 ns is further carried out for the production runs and for statistical analysis. Note that long simulation time is necessary for ensuring the equilibrium states of the electrolytes systems.



Figure S1 Electrostatic potential(ESP) analysis of different solvents.



Figure S2 Calculation of binding energy between Li<sup>+</sup> and different solvents.



Figure S3 Snapshots views of the simulated coordination structures of (a) HB-GPE (b)

MB-GPE (c) LB-GPE obtained by MD simulation.



Figure S4 Pictures of the state of MB-GPE before and after thermal polymerization.



Figure S5 The contact angle test on the precursor solutions of HB-GPE, MB-GPE and LB-GPE.



Figure S6 Cross-section and surface morphology of MB-GPE impregnated the separator.



Figure S7 EDS analysis of MB-GPE impregnated the separator.

The surface and cross-sectional morphology of MB-GPE was analyzed using SEM, revealing a uniform and dense coverage on the separator surface. X-ray energy dispersive spectroscopy (EDS) confirmed the uniform distribution of carbon and fluorine elements, indicating that MB-GPE effectively penetrated the separator voids.



Figure S8 Gel permeation chromatography Analysis of LB-GPE and MB-GPE.



Figure S9 Raman spectra of EC and FEC.

The peak at 715 cm<sup>-1</sup> in HB-GPE belongs to the characteristic peak of EC, while the peak at 730 cm<sup>-1</sup> in MB-GPE is assigned to the characteristic peak of FEC.



Figure S10 Dissolution states of precursor solutions of HB-GPE, MB-GPE and LB-GPE at different lithium salt concentrations

We further supplemented the dissolution experiments with different concentrations of lithium salts. When the concentration of lithium salts increases to 4 mol/L, the LB-GPE precursor solution is difficult to fully dissolve the lithium salt, and the solution is turbid. While HB-GPE and MB-GPE precursor solutions are still able to fully dissolve and the solution is clarified.



Figure S11 Electrochemical float test for (a) HB-GPE and (b) LB-GPE



Figure S12 Chronoamperometry profile collected from (a) symmetric Li|HB-GPE|Li cell and (b) symmetric Li|LB-GPE|Li cell at 25 °C. Insets show the EIS plots of Li||Li cell before and after chronoamperometry.



Figure S13 Young's modulus mapping of the bare PP separator.



Figure S14 Flammability test of the LB-GPE



Figure S15 (a) XRD patterns of HB-GPE, LB-GPE and MB-GPE. (b) DSC curves of HB-GPE, LB-GPE and MB-GPE.

As illustrated in Fig. S15a, all GPEs show a broad diffraction peak between  $15^{\circ}$  and  $25^{\circ}$  in XRD patterns, indicating the formation of amorphous phases. The diffraction peak of LB-GPE is sharper than that of HB-GPE and MB-GPE. The amorphous region provides additional transport channels for lithium-ion migration in addition to that provided by the solvent. We further performed DSC analyses of GPEs with different Li<sup>+</sup>-solvent binding, and MB-GPE had the lowest T<sub>g</sub> (-2.34 °C). In contrast, HB-GPE only shows a melting heat absorption peak during the warming process, and no significant glass transition temperature can be observed. Additionally, a clear exothermic peak of crystallization occurs in LB-GPE and no glass transition temperature can be found (Fig. S15b). Undoubtedly, the moderate Li<sup>+</sup>-solvent binding design can improve the thermal stability of MB-GPE with no significant heat absorption or exothermic peaks.



Figure S16 Physicochemical properties of MB-GPE, FEC-GPE and FEMC-GPE. (a) Ionic conductivities of MB-GPE, FEC-GPE and FEMC-GPE. (b) LSV curves of MB-GPE, FEC-GPE and FEMC-GPE. (c) Critical current density test of the symmetric Li| FEC-GPE |Li cell. (d) Critical current density test of the symmetric Li| FEMC-GPE |Li cell. (e) The chronoamperometry profile of Li symmetric cells with FEC-GPE. The inset shows the Nyquist plots before and after polarization. (f) The chronoamperometry profile of Li symmetric cells with FEMC-GPE.

FEMC has the lowest binding energy (-1.66 eV) with Li<sup>+</sup> in the designed solvent system (FEC: -2.0 eV). Gel electrolytes with both high and low Li<sup>+</sup>-solvent binding have certain advantages in electrochemical performance, and the homogeneous optimization of all performance can be achieved by combinatorial design of electrolytes with ultimate moderate Li<sup>+</sup>-solvent binding (MB-GPE).



Figure S17 Critical current density test of the symmetric Li||Li symmetrical cell with HB-GPE and LB-GPE.



Figure S18 Impedance evolution of the Li||Li symmetrical cells with HB-GPE, MB-GPE and LB-GPE during different storage times.



Figure S19 Rate capability of Li|GPE|Li cells with HB-GPE, MB-GPE and LB-GPE



Figure S20 CV testing of HB-GPE, MB-GPE and LB-GPE.



Figure S21 EIS analysis of Li|GPE|Li symmetric batteries before and after cycling



Figure S22 Surface morphology of lithium foil after cycling of Li $\|$ Li symmetric cells with HB-GPE, MB-GPE and LB-GPE



Figure S23 Capacity-voltage curves of Li||Cu cells with (a, b) HB-GPE and (c, d) LB-GPE GPE

The Li||Cu cells with MB-GPE show polarization voltages of 82, 40 and 46mV at cycle 1, 50 and 150, respectively. The smaller polarization voltages indicate excellent stability for MB-GPE in the lithium deposition-stripping process, whereas the polarization voltages of the cells using HB-GPE are 108 and 99mV at cycle 1 and 50, respectively. The polarization voltages of the cells with LB-GPE are 134, 97, and 161 mV at cycle 1, 50, and 150, respectively, and the larger polarization voltages correspond to the poorer lithium deposition morphology.



Figure S24 Galvanostatic discharge/charge voltage profiles of Li||LFP cells using HB-GPE and LB-GPE at 0.5 C at charge cut-off voltage of 4.0 V.



Figure S25 Galvanostatic discharge/charge voltage profiles of Li $\|$ LFP cells using HB-GPE and LB-GPE at 1 C at charge cut-off voltage of 4.0 V.



Figure S26 Galvanostatic discharge/charge voltage profiles of Li||NCM811 cells with HB-GPE and LB-GPE at 0.5 C at charge cut-off voltage of 4.3 V.



Figure S27 XPS spectra of (a) C 1s, (b) F 1s, and (c) O 1s in LFP cathode with HB-GPE after 20 cycles. XPS spectra of (d) C 1s, (e) F 1s, and (f) O 1s in LFP cathode with MB-GPE after 20 cycles. XPS spectra of (g) C 1s, (h) F 1s, and (i) O 1s in LFP cathode with LB-GPE after 20 cycles.



Figure S28 ToF-SIMS depth profiles of the HB-GPE and MB-GPE derived SEIs after 20 cycles

The lithium metal surface after cycling with HB-GPE contains a large amount of organic component ( $C_2HO$ ), which is always more than that of the LiF inorganic component with increasing etching depth. Therefore, the poor interfacial formation

Table S1 The calculated coordination numbers of the $Li^+/X$ pairs(=O)								
	EC(=O)	EMC(=O)	FEMC(=O)	FEC(=O)	DFEC(=O)	TFSI <sup>-</sup> (=O)	PEGDA (-O/=O)	
HB- GPE	0.4	0.29				0.48	0.48/0.05	
MB- GPE			0.06	0.19		0.61	0.48/0.07	
LB- GPE			0.1		0.08	0.8	0.42/0.07	

ability of HB-GPE is not conducive to the long-term stable cycling of lithium metal batteries.

Table S2. HOMO/LUMO energies of molecules.						
Molecules	LUMO(eV)	HOMO(eV)	HOMO-LUMO gap			
EC	0.61	-8.20	8.81			
EMC	0.95	-7.93	8.88			
FEMC	0.41	-8.50	8.91			
FEC	0.25	-8.65	8.9			
DFEC	-0.26	-9.12	8.86			
LiTFSI	-1.43	-9.77	8.34			