## SUPPORTING INFORMATION

# Biomimetic Ant-nest Ionogel Electrolyte Boosts the Performance of Dendrite-free Lithium Batteries

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### **Experimental methods**

Materials. The ionic liquid, N-propyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Py13][TFSI]) from Shanghai Jie Lithium was purchased Cheng company. (LiTFSI,>98%) bis(trifluoromethanesulfonyl)imide was purchased from TCL. 3-Methacryloxypropyltrimethoxysilane was purchased from Guotai-Huarong, China. LiFePO<sub>4</sub> and LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> were purchased from Pulead Technology Industry Company. Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> was obtained from BTR. Formic acid and acetonitrile were purchased from Aldrich. All materials mentioned above are stored in an argon-filled glovebox.

**Ionogel fabrication.** The BAIE electrolytes were prepared by one-step sol-gel method. In a typical experiment, 0.91 g of LiTFSI was first dissolved in Py13 TFSI (4.6 g) and 3-methacryloxypropyltrimethoxysilane (2.8 g) mixture under the magnetic stirring for 3 h, followed by adding 2.5 mL HCOOH. The mole ratio of HCOOH: silane: Py13 TFSI is set as 5.8:1:1. The solution was stirred for 8 min at room temperature, and then transferred into the oven at 70 °C. The

reaction was continued for 48 h, leading to a white colored BAIE. The resulting BAIE was dried in vacuum at 70 °C for 5 days.

**Characterization.** The morphology and Si elemental mapping of the materials were studied using a an FEI Quanta 600 SEM. Energy dispersive spectroscopy (EDS) were examined by the field emission scanning electron microscopy FEI Quanta 600 SEM instrument. TEM and selected area electron diffraction (SAED) were performed with an FEI Tecnai G2 F20 X-TWIN transmission electron microscope. FTIR spectroscopy was conducted using a Nicolet 6700 FTIR spectrometer. Raman spectra were obtained on a Bruker RFS100/S. TGA were carried out with a Netzsch STA 449F3 TGA analyzer. All samples were run in aluminum pans at a heating rate of 10 °C min<sup>-1</sup> from room temperature to 700 °C under an argon flow. The flammability tests of ionogels were performed with an ionogel membrane (the radius is 1.9 cm and the thickness is 0.3 cm) and a flame gun. All the flammability tests were recorded with a digital camera.

**Electrochemical measurements.** The ionic conductivities were measured *via* AC impedance spectroscopy on blocking stainless steel (SS) cells. The structure of the cell is SS/BAIE/SS. The frequency range is 10 mHz-100 kHz with the amplitude voltage of 5 mV. The electrochemical anodic stability of ionogel was analyzed at room temperature using linear sweep voltammetry experiment performed on a Li / BAIE / SS cell at a scan rate of 1.0 mV s<sup>-1</sup>. The electrochemical cathodic stability of ionogel was evaluated by CV experiment at a scan rate of 0.1 mV/s. Symmetric lithium coin cells were assembled and used for interface stability tests and lithium stripping/plating tests. Symmetric lithium coin cells with a Celgard separator were used for ILE as a comparison. The coin cells were assembled by using Li foil as the counter-electrode and SS as the working electrode to study the Coulombic efficiency of Li plating/stripping. In each cycle, a fixed Li areal capacity of 0.3 mAh was deposited onto SS at 0.15 mA cm<sup>-2</sup>, and then stripped by charging to 0.5 V vs Li<sup>+</sup>/Li. The Coulombic efficiency for each cycle was calculated based on the ratio of the capacity of Li stripped to that of Li deposited. A Land battery tester was used for the lithium stripping-plating tests. Lithium metal electrodes were collected after the tests, and further analyzed by SEM.

Fabrication and measurement of solid-state lithium-ion batteries. The cathode electrode was composed of 80 wt% active material, 10 wt% PVDF binder and 10 wt% carbon black. The N-methylpyrrolidone (NMP) was used as solvent for homogenizing all components. The LiFePO<sub>4</sub> and

LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> slurries were coated on an aluminum plate, and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> slurry was coated on a copper plate. Two methods were used to assemble the solid-state lithium metal cells. One is the conventional method: stacking the as-prepared ionogel membrane on a cathode, followed by a lithium metal electrode in type 2032 coin cell. Another method is injection printing. The electrode surface was covered with a solvent precursor using a syringe and then transferred to a vacuum oven at 70 °C for 7 days. The thickness of the electrolyte is controlled at about 30  $\mu$ m to ensure that there is sufficient thickness to prevent the battery from shorting. Then, the ionogel-coated cathodes is stacked with a lithium metal to form a solid-state battery. The assembled cells were aged for 7 days at 30 °C before electrochemical testing. The galvanostatic experiment was performed under different charging/discharging rate and different temperature. The Li/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> coin cell collected after the galvanostatic experiment was disassembled in a glovebox. The Lithium metal electrode, ionogel electrolyte and cathode electrode were washed with methyl ethyl carbonate and stored for SEM analysis.

#### Figures



X=organic functional group R=alkyl bridge OR'=alkoxy group

Figure S1 Typical chemical structure of a tri-alkoxy silane coupling agent.



Figure S2 Selected area electron diffraction (SAED) of X-SiO $_2$ 



Figure S3 SEM images of the X-SiO<sub>2</sub> scaffolds. BAIE-0 (a), BAIE-0.4 (b) and BAIE-1.0 (c).



Figure S4 Raman spectra of BAIE-2.0 (closed squares), fitted with F1 and F2 band.



Figure S5 FT-IR spectra of ILE, BAIE-1.0, BAIE-0 and X-SiO<sub>2</sub>.



**Figure S6** TGA profiles of ILE, BAIE-0 and BAIE-1.0 from room temperature up to 700 °C under an argon flow.



Figure S7 Nyquist plots of BAIE-1.0 at different temperature.



**Figure S8** Nyquist plot of the impedance spectra of the symmetrical Li/BAIE-1.0/Li cell before and after 7 cycles at a current density of 0.032 mA cm<sup>-2</sup>.



**Figure S9** Cyclic voltammograms of the  $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}$  cell at 60 °C with a scan rate of 0.1 mV/s using BAIE-1.0 as the electrolyte. *Inset*: partial enlarged view.



**Figure S10** Capacity and Coulombic efficiencies *versus* cycle number for the  $Li/Li_4Ti_5O_{12}$  cells at 30 °C (a) and 60 °C (b).



Figure S11 Voltage profiles of the Li plating/stripping on SS electrode with current densities of 0.15  $MA \text{ cm}^{-2}$  at room temperature.



**Figure S12** SEM images of the lithium metal after 1000 cycles at  $Li/Li_4Ti_5O_{12}$  cell with BAIE-1.0 electrolyte. Surface images of lithium metal before a) and after b) removal of the ionic liquid. c) EDS of the lithium metal.

Table S1 Chemical structure, functionality and abbreviation of the possible silane coupling agent for

## immobilizing ionic liquid. R'=methyl or ethyl.

Structure	Functionality
OR' OR' OR' OR'	Methacryl
OR' OR'-Si OR'	Glycidoxy
OR' OR'—Si— OR'	Vinyl
OR' OR'—Si OR' NH <sub>2</sub>	Amino
OR' SH OR' SH	Mercapto
OR'	Alkyl
$\begin{array}{c c} & OR' & O\\ & OR' & & \\ OR' & & \\ & OR' & & \\ & OR' & & \\ \end{array} \\ \end{array} \\ \begin{array}{c} OR \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	Azide

Table S2 Summary of the compositions of BAIE samples used in this study.

Samula	Sample compositions					
Sample	LiTFSI /g	3-Methacryloxypropyltrimethoxysilane/g	Py13 TFSI/g			
BAIE-0	0	2.8	4.6			
BAIE-0.4	0.364	2.8	4.6			
BAIE-1.0	0.910	2.8	4.6			
BAIE-1.5	1.365	2.8	4.6			
BAIE-2.0	1.820	2.8	4.6			

Table S3 Ionic conductivity ( $\sigma$ ), activation energy ( $E_a$ ) and coefficient of determination ( $R^2$ ) of

electroly	ytes.
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Samplas	Ionic	Conductivit	$E_{\rm a}[{\rm eV}]$	<b>D</b> 2		
Samples	0°C	30°C	60°C	80°C	(10-80°C)	К
ILE	0.12	1.28	4.60	8.26	0.34	0.998
BAIE-0.4	0.65	2.10	4.75	6.41	0.22	0.999
BAIE-1.0	0.33	1.37	3.60	5.54	0.26	0.998
BAIE-1.5	0.10	0.63	1.98	3.15	0.31	0.996
BAIE-2.0	0.04	0.36	1.24	2.00	0.34	0.995

**Table S4** The parameters for calculating the specific energy of the  $Li/LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$  cell with BAIE-1.0 electrolyte.

	Design parameters	Weight of Materials / mg	Weight percentage / %
A	node current collector	none	0
Lithium electrode		1.5	7.0
Electrolyte (20 µm thick)		2.0	9.3
Cathada	Active material	15.0	69.8
Catnode	Binder and additives	1.6	7.4
Cathode current collector (Al Foil, 5 μm thick) <sup>1</sup>		1.4	6.5
	Total weight	21.5	100

The energy density (*E*) were calculated according to the following equations:  $E=Q \cdot V_{avg}/\Sigma M_i$ , Where *Q* is the capacity,  $V_{avg}$  is the average voltage of Li/LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> cell, and  $\Sigma M_i$  is the total weight of electrode component except cell-housing.

Table S5 The	performance of	different	solid-state	Li/Li <sub>4</sub> Ti <sub>5</sub>	$_{5}O_{12}$	lithium	metal	batteries.
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Electrolyte	Date	Ionic conductivity	Cycles	Dis.	CE.	Ref.

		/ S cm <sup>-1</sup>		Capa.		
Biomimetic Ant-nest Ionogel Electrolyte	2017	1.37×10⁻³ (30 °C)	3000	5C 110	99.8%	Our wor k
Gel polymer electrolyte						
Poly(aryleneether)basedpolymer(LiPHFE) / EC-MC	2017	0.41×10⁻³ (25 °C)	800	1C ~90	-	2
PMMA-IL / LiTFSI- PC	2016	3.13×10⁻³ (25 °C)	500 10	1C 126 5C ~100	99%	3
PEO-SiO <sub>2</sub> / LiTFSI- PC	2015	5×10 <sup>-3</sup> (ambient temperature)	150	1C 138	Over 90%	4
PVDF-HFP/LiTFSI- LiF-PC	2014	1.3×10 <sup>-3</sup>	300	1C ~150	-	5
PVDF-HFP /Al <sub>2</sub> O <sub>3</sub> / LiTFSI-PC	2014	1×10 <sup>-3</sup> (25 °C)	1000	5C ~130	close to 100%	6
Polyimide / LiPF <sub>6</sub> - EC-EMC-DMC	2014	2×10 <sup>-3</sup> (25 °C)	200	5C ~146.8	99.3%	7
PVDF / LiTFSI-IL- VC	2014	4.4×10⁻³ (25 °C)	200	0.5C 133	99%	8
Polymer / LiTFSI-IL	2014	0.64×10⁻³ (25 °C)	100	1C ~64	98%	9
Quasi-solid electrolyte						
LiTFSI-clay / IL	2015	3.35×10⁻³ (120 °C)	150	1C ~50	-	10
SiO <sub>2</sub> -IL-TFSI / PC	2014	1×10 <sup>-3</sup> (25 °C)	500	1C 128	>95%	11
SiO <sub>2</sub> -IL / PC	2014	6×10 <sup>-4</sup> to 5×10 <sup>-3</sup> (25 °C)	2000	3C ~118	90%	12

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