

# Ultra-Low Concentration Gel Polymer Electrolytes Realize Stable and Low-Temperature Lithium–Organic Batteries

Mengjie Li<sup>a,b</sup>, Hang Liu<sup>a</sup>, Hai Su<sup>a</sup>, Zehui Fan<sup>a</sup>, Yuansheng Liu<sup>a</sup>, Jixing Yang<sup>a\*</sup>, Wei Zhu<sup>a</sup>, Qinghao Chen<sup>a</sup> and Yunhua Xu<sup>a\*</sup>

<sup>a</sup>School of Materials Science and Engineering, and Key Laboratory of Advanced Ceramics and Machining Technology (Ministry of Education), Tianjin University, Tianjin 300072, China.

<sup>b</sup>Institute of Technology for Carbon Neutrality, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China.

## Experiment Section

**Materials:** Battery-grade lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), 1,3-dioxolane (DOL) and dimethoxyethane (DME) were purchased from Suzhou DuoDuo Chemical Technology Co., Ltd. LiFePO<sub>4</sub> (LFP) power, Li foils and PP separator were provided by Guangdong Canrd New Energy Technology Co., Ltd. Nafion D520 solution (5 wt% in a mixture of lower aliphatic alcohols and water) was obtained from Dupont Co. Commercial Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (LTO) electrodes were purchased from Shenzhen Kejing Star Technology Co.,.

**Electrodes/Electrolytes Preparation and Cell Assembly:** The synthesis of the 1,3,5-tri(9,10-anthraquinonyl)benzene (TAQB) electrode material and the preparation of the gel polymer electrolyte initiated by Nafion could refer to our previous work.<sup>[1]</sup> Key experimental parameters are summarized as follows: Nafion D520 solution was coated on a PP separator and dried sequentially at room temperature for 1 h and at 60 °C for 6 h, followed by vacuum drying at 60 °C for 24 h. The resulting Nafion-coated separator, with a coating thickness of approximately 3 μm, was then used to initiate the *in situ* gelation of a DOL-based electrolyte (LiTFSI in DOL-DME) and the gelation process was conducted for 16 h. TAQB and LFP electrodes were prepared by mixing TAQB (or LFP), graphene, and polyvinylidene fluoride (PVDF) at a weight ratio of 6:3:1 in N-methyl-pyrrolidone (NMP) to form a uniform slurry. Then, the slurry was smeared on a carbon-coated aluminum foil and the NMP was evaporated at 60 °C for 6 h followed by vacuum drying at 80 °C for 24 h. The mass

1 loading of TAQB (or LFP) is about 0.8~1.2 mg cm<sup>-2</sup>. For TAQB electrodes with high mass  
 2 loading, polytetrafluoroethylene (PTFE) is used as the binder and steel mesh is used as the  
 3 current collector, corresponding to an active material loading of about 8 mg cm<sup>-2</sup>. CR2032-type  
 4 coin cells were assembled in an Ar-filled glove box using Li foil as the anode, LiTFSI in  
 5 DOL/DME (1/1, in volume) with different salt concentrations as the electrolyte, and Nafion-  
 6 coated PP as the separator.

7 **Material Characterizations:** The morphology of the cycled electrodes and separators was  
 8 observed by SEM (S-4800, Hitachi). The surface composition of the cycled Li anode was  
 9 analyzed by X-ray photoelectron spectroscopy (XPS) (ESCALAB 250, Thermo-VG) system.  
 10 <sup>1</sup>H NMR spectra (AVANCE III 400 MHz, Bruker) was used to verify the polymerization of  
 11 DOL with CDCl<sub>3</sub> as the deuterated solvent. Gel permeation chromatography (GPC) (PL-  
 12 GPC50) was conducted to demonstrate the number-average molecular weight (Mn) of the  
 13 synthesized Poly-DOL (PDOL).

14 **Electrochemical Measurements:** Cyclic voltammetry (CV), electrochemical impedance  
 15 spectroscopy (EIS) and the Li-ion transference number ( $t_{Li^+}$ ) tests were performed on Solartron  
 16 Analytical 1470 (AMETEK, USA). The CV curves were scanned at different scan rates with the  
 17 voltage window of 1.5 to 3.0 V for TAQB and 2.7 to 4.0 V for LFP, respectively. For EIS test, the  
 18 frequency range was from 1×10<sup>6</sup> to 0.1 Hz with the voltage amplitude of 5 mV. The ionic  
 19 conductivity of the electrolyte was obtained in symmetrical stainless steel (SS) electrodes by the  
 20 following equation:

$$21 \quad \sigma = \frac{L}{R_b \times S} \quad (1)$$

22 where L and S are corresponding to the thickness and contact area of the separator, R is the bulk  
 23 resistance of the SS-SS cells.

24 The  $t_{Li^+}$  of the electrolyte was evaluated by the steady-state current method using symmetric Li-Li  
 25 cells, which was calculated using the following equation:

$$26 \quad t_{Li^+} = \frac{I^s(\Delta V - I^0 R^0)}{I^0(\Delta V - I^s R^s)} \quad (2)$$

1 where  $\Delta V$  is the applied polarization voltage (10 mV),  $I^0$  and  $I^s$  are the initial and stable currents  
 2 during polarization process, while  $R^0$  and  $R^s$  are the charge-transfer resistances of Li-Li cells before  
 3 and after the polarization respectively.

4 The Li-ion diffusion coefficient ( $D_{Li^+}$ ) is calculated by CV and galvanostatic intermittent titration  
 5 technique (GITT) measurements respectively. From the Randles-Sevcik equation, the  $D_{Li^+}$  could be  
 6 calculated according to the CV curve of electrode material at different scanning rates:

$$7 \quad I_p = 2.69 \times 10^5 n^{1.5} A D_{Li^+}^{0.5} C_{Li} v^{0.5} \quad (3)$$

8 where  $I_p$  is the peak current in the CV curves,  $n$  is the electron transference number,  $A$  is the surface  
 9 area of the electrode,  $D_{Li^+}$  is the diffusion coefficient of Li ions,  $C_{Li}$  is the  $Li^+$  concentration in the  
 10 electrode material and  $v$  is the scan rate.

11 For the GITT measurements, the cells were charged or discharged at a current pulse of 0.1 C for 30  
 12 min, followed by open circuit relaxation for 4 h. The procedure was continued until the voltage of  
 13 the cells reached a preset value. The Li-ion diffusion coefficient ( $D_{Li^+}$ ) according to GITT was  
 14 calculated based on the following equation:

$$15 \quad D_{Li^+} = \frac{4}{\pi \tau} \left( \frac{m_b V_m}{M_B S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (4)$$

16 where  $\tau$  is the constant current pulse time;  $m_b$ ,  $V_m$ ,  $M_B$ , and  $S$  are the mass loading of the active  
 17 material, molar volume, molecular weight, and the area of the electrode-electrolyte interface,  
 18 respectively;  $\Delta E_s$  is the voltage difference between the steady state and the initial state of every step;  
 19 and  $\Delta E_t$  is the change of total voltage during a pulse step excluding the IR drop.

20 The experimental determination of the desolvation energy was achieved by EIS measurements of  
 21 symmetrical Li cells at various temperatures based on the following equation:

$$22 \quad \frac{1}{R_{desolvation}} = A \exp\left(-\frac{E_{desolvation}}{RT}\right) \quad (5)$$

23 where  $R_{desolvation}$  is the charge transfer resistance of symmetrical Li cells;  $E_{desolvation}$  is the activation  
 24 energy of desolvation;  $A$ ,  $R$  and  $T$  are the pre-exponential constant, standard gas constant and the  
 25 absolute temperature, respectively.

26 The rate capability and cycling performance of all batteries were performed on a Neware battery  
 27 testing system (CT-4008T).

1

2 **Theoretical Simulations and Analysis:** All the all-atom molecular dynamics (MD) simulations  
 3 were based on a general AMBER force field<sup>[2]</sup> with the RESP charges<sup>[3]</sup> and were carried out using  
 4 the Gromacs-2022 software package.<sup>[4]</sup> The simulation systems were composed of 962 DME, 286  
 5 DOL, 112 PDOL long chain (the number of repeating unit of -C-C-O-C-O- is 10) and a certain  
 6 amount of Li<sup>+</sup> and TFSI<sup>-</sup> to reach LiTFSI concentrations of 0.1 M and 1.0 M. For the 0.1 and 1.0 M  
 7 GPEs, simulations were conducted with 20 and 200 LiTFSI molecules, respectively. The system is  
 8 a relaxed liquid configuration at 223.15 K and 298.15 K. The total run time was 20 ns NPT for the  
 9 equilibrium MD simulation. We used the relaxed system as a starting configuration. As it is prior to  
 10 system relaxation MD, energy minimization was carried out with a composite protocol of steepest  
 11 descent using termination gradients of 500 kJ mol<sup>-1</sup> nm<sup>-1</sup>. The Nose'-Hoover thermostat<sup>[5]</sup> was used  
 12 to maintain the equilibrium temperature at 223.15 K and 298.15 K and periodic boundary conditions  
 13 were imposed on all three dimensions. The Particle Mesh-Ewald method<sup>[6,7]</sup> was used to compute  
 14 long-range electrostatics within a relative tolerance of  $1 \times 10^{-6}$ . A cut-off distance of 1nm was  
 15 applied to real-space Ewald interactions. The same value was used for van der Waals interactions.  
 16 The LINCS algorithm<sup>[8]</sup> was applied to constrain bond lengths of hydrogen atoms. A leap-frog  
 17 algorithm<sup>[9]</sup> was used with a time step of 2 fs.

18 The solvation states of Li<sup>+</sup> in GPEs was obtained by analyzing the trajectory of MD  
 19 simulations. The de-solvation free energy of each solvation structure is obtained by quantum  
 20 chemistry calculation, which was performed using Gaussian 16 software package. Geometry  
 21 optimizations and energy calculations were performed using B3LYP-D3 functional and TZVP basis  
 22 set, and vibration analysis is carried out to ensure the local minimum value is reached and to obtain  
 23 the thermal correction to Gibbs free energy.

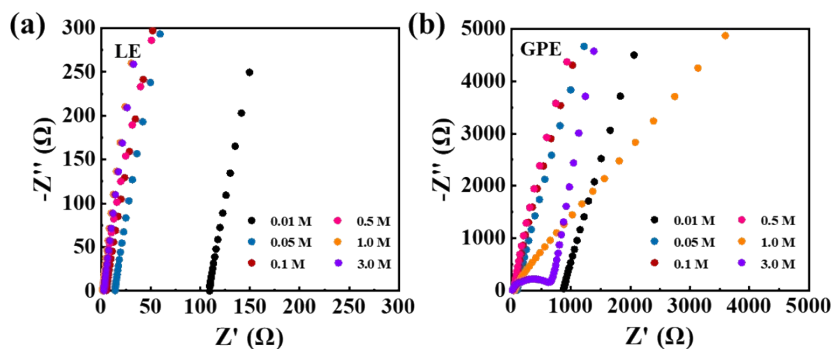
24 The single point energy of the optimized structure was calculated by B2PLYP functional at  
 25 def2-TZVP level of basis set. Assuming the solvation structure of LiA<sub>x</sub>B<sub>y</sub>, where A and B represent  
 26 the solvent molecules around a Li<sup>+</sup>, and x and y represent the number of solvent molecules in each  
 27 solvation structure. The free energy of de-solvation for each solvation structure can be obtained by  
 28 using the following equation:

$$29 \quad \Delta G_{\text{de-solvation}} \left( \text{LiA}_x\text{B}_y \right) = G_{\text{gas}} \left( \text{Li}^+ \right) + xG_{\text{solv}} \left( \text{A} \right) + yG_{\text{solv}} \left( \text{B} \right) - G_{\text{solv}} \left( \text{LiA}_x\text{B}_y \right) \quad (6)$$

1 where  $G_{gas}$  and  $G_{solv}$  represent the Gibbs free energy of gaseous and solvation components,  
2 respectively. For the same structure, the difference between  $G_{solv}$  and  $G_{gas}$  is the free energy of  
3 solvation, which is obtained by deducting the electronic energy calculated using the SMD solvent  
4 model at M052X/6-31G\* level from that calculated without the SMD solvent model.

5       The simulated trajectories in different  $\text{Li}^+$  solvation structures were counted. Using the last 20  
6 ns trajectories, 50 data simulation configurations were taken at equal intervals. The occurrence  
7 frequency of solvation structure was counted according to a radius of 0.3 nm around  $\text{Li}^+$ , and the  
8 de-solvation free energy of each solvation structure was calculated using weighted average method.  
9

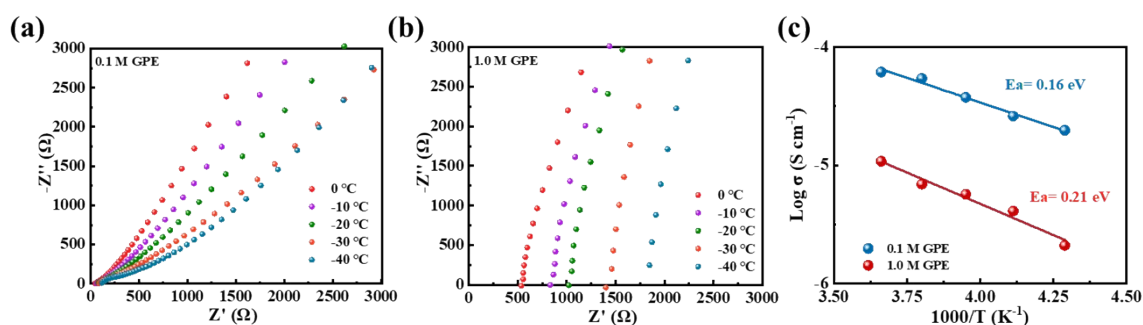
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3 Figure S1. EIS spectra of symmetrical steel cells using (a) LEs and (b) GPEs with different LiTFSI  
4 concentrations from 0.01 to 3.0 M.

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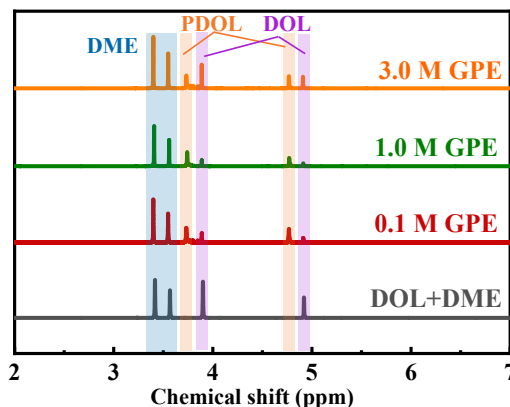


6

7 Figure S2. EIS spectra of symmetrical steel cells using (a) 0.1 and (b) 1.0 M GPEs at different  
8 temperatures. (c) Temperature dependence of the ionic conductivities of 0.1 and 1.0 M GPEs.

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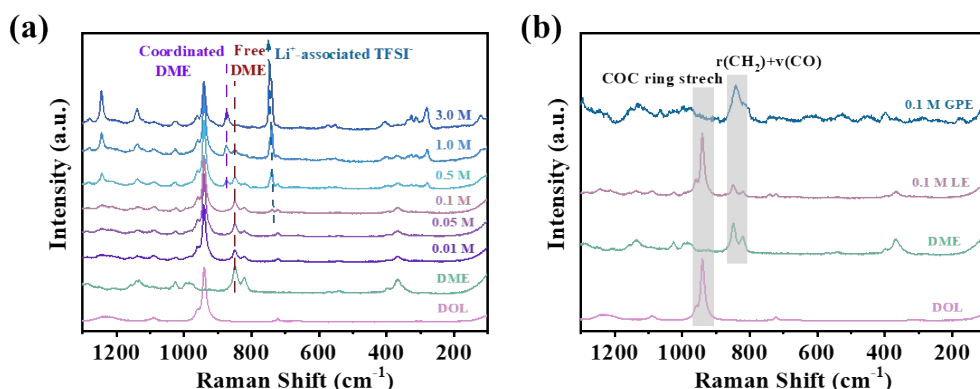
10 As shown in Figure S2, in contrast to the high bulk impedance of the 1.0 M GPE  
11 at low temperatures, the 0.1 M GPE exhibits lower impedance and higher ionic  
12 conductivity over the same temperature range. In addition, the 0.1 M GPE also exhibits  
13 a lower activation energy, indicating a reduced ion transport energy barrier in the  
14 electrolyte.



15

16 Figure S3.  $^1\text{H}$  NMR spectra of GPEs with different LiTFSI concentrations from 0.1 to 3 M and the  
17 corresponding solvent.

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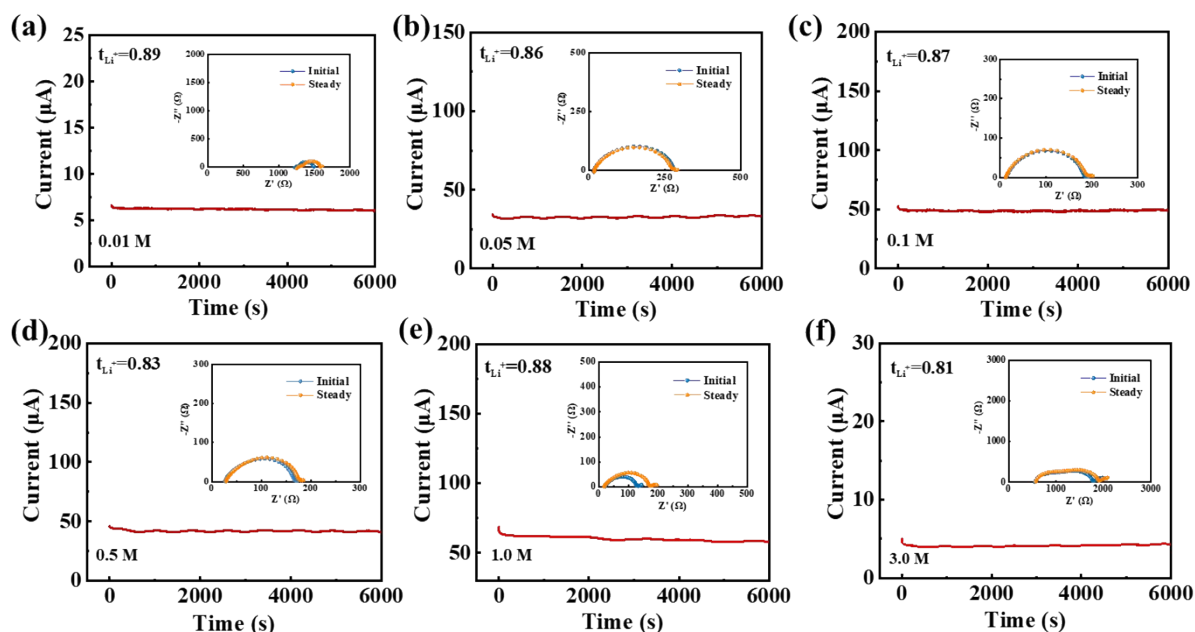


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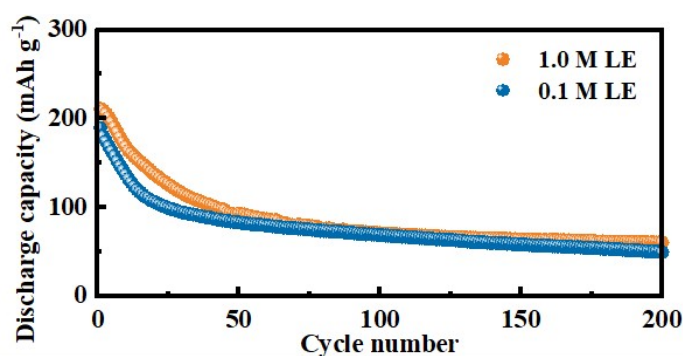
3 Figure S4. (a) Raman spectra of pure solvents and LEs with different salt  
4 concentrations; (b) Raman spectra of pure solvents, 0.1 M LE and 0.1 M GPE.

5 For the Raman shift from 800 to 900  $\text{cm}^{-1}$ , two absorption bands at 820 and 848  
6  $\text{cm}^{-1}$  are attributed to the stretching vibration of  $-\text{CH}_2-\text{O}-\text{CH}_3$  groups in free DME  
7 molecules (Figure S4). In liquid electrolytes, as the LiTFSI concentration increases to  
8 3.0 M, the free DME gradually diminishes, forming  $\text{Li}^+$ -coordinated DME (874  $\text{cm}^{-1}$ ).  
9 Furthermore, with increasing salt concentration, the symmetric C–O–C stretching  
10 vibration peak of DOL at 939  $\text{cm}^{-1}$  remained nearly unchanged, indicating that DOL  
11 molecules preferentially exist as free solvent species rather than coordinating with  $\text{Li}^+$   
12 in the solvation sheath due to the steric hindrance and the low electronegativity of  
13 oxygen atoms. Raman peaks in the range of 730 to 750  $\text{cm}^{-1}$  are assigned to the  
14 formation of  $\text{Li}^+-\text{TFSI}^-$  ion clusters and dissociated ions. As the LiTFSI concentration  
15 increases, the S–N–S vibrational peak of  $\text{TFSI}^-$  shifts to higher wavenumbers,  
16 indicating enhanced formation of  $\text{Li}^+-\text{TFSI}^-$  ion clusters. However, it is challenging to  
17 analyze the solvation structure of GPEs using Raman spectroscopy due to the  
18 overlapping peaks of PDOL and DME in the range of 800–900  $\text{cm}^{-1}$ .

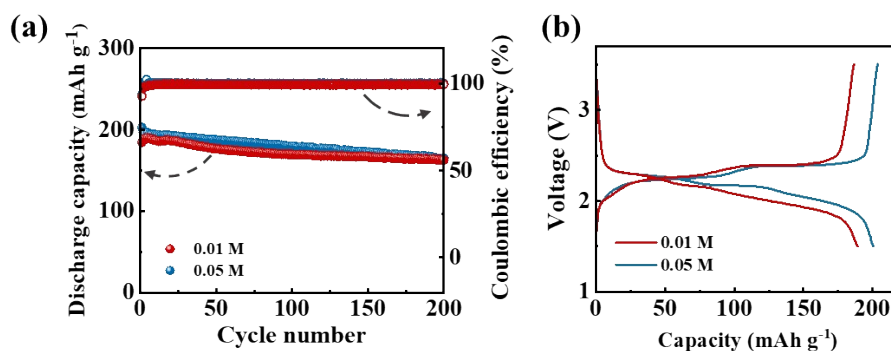
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1  
2 Figure S5. Chronoamperometry profiles of symmetrical Li cells using (a) 0.01, (b) 0.05, (c) 0.1, (d)  
3 0.5, (e) 1.0 and (f) 3.0 M GPEs. Insets: the impedance spectra before and after polarization.  
4

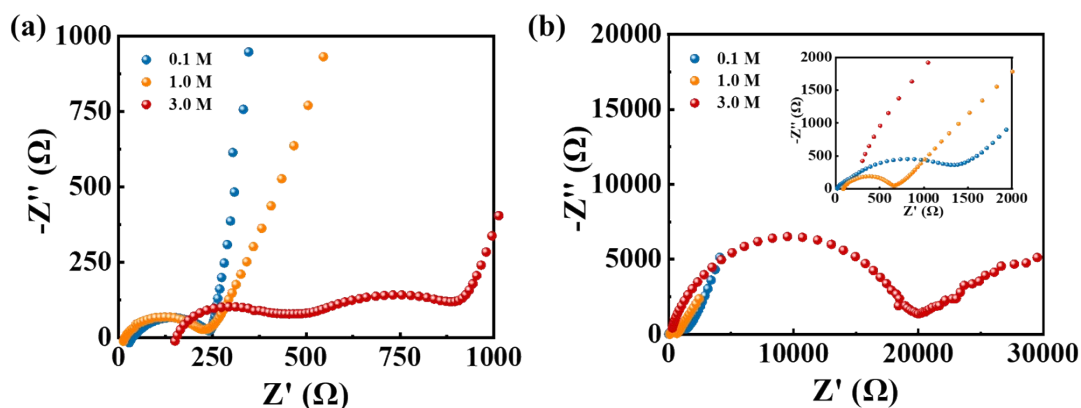


5  
6 Figure S6. Cycling performance of TAQB-Li batteries using LEs with different LiTFSI  
7 concentrations of 0.1 and 1.0 M.  
8

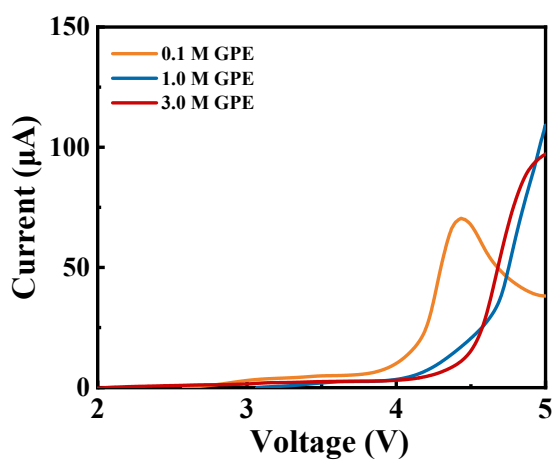


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10 Figure S7. (a) Cycling performance and (b) corresponding charge-discharge curves of TAQB-Li  
11 batteries using GPEs with different LiTFSI concentrations of 0.01 and 0.05 M.  
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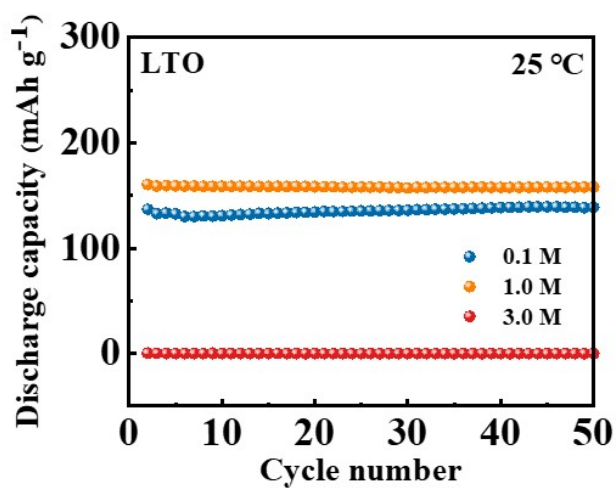




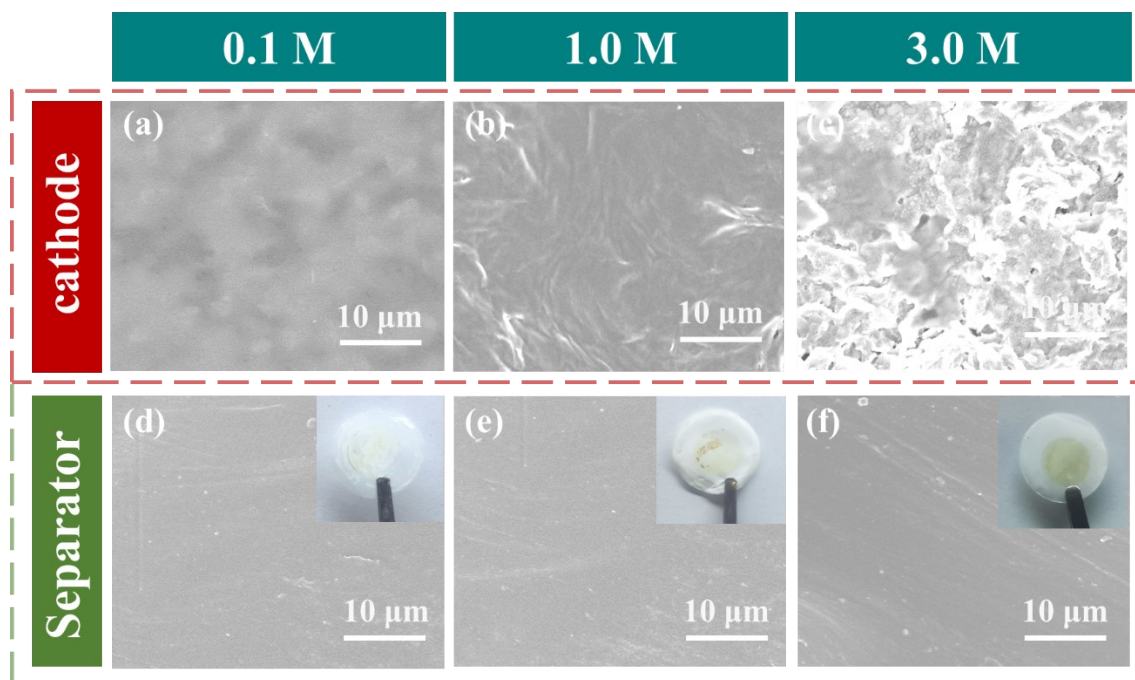
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2 Figure S8. EIS patterns of (a) TAQB-Li and (b) LFP-Li batteries using 0.1, 1.0 and 3.0 M GPEs.  
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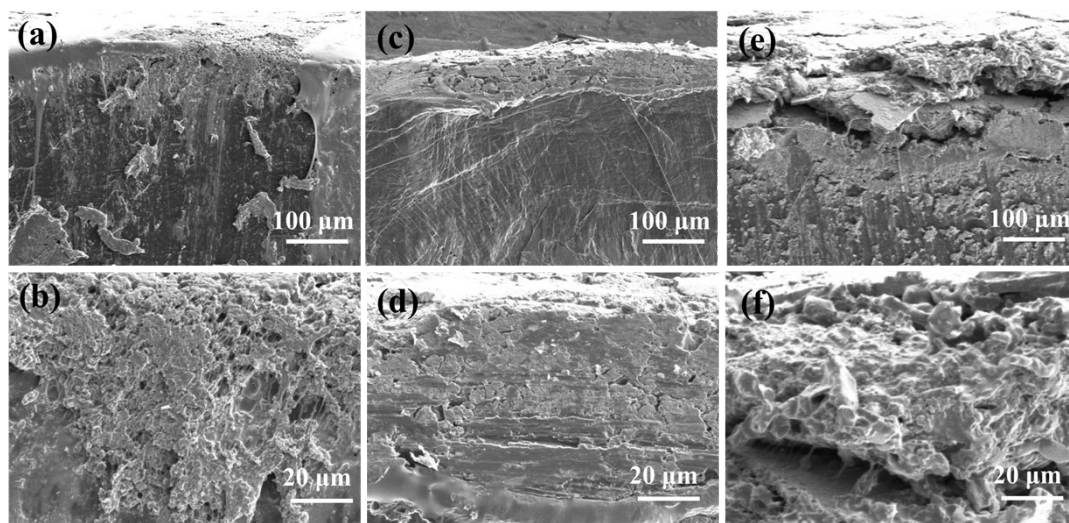
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5 Figure S9. Electrochemical stability windows of GPEs with different salt concentrations.  
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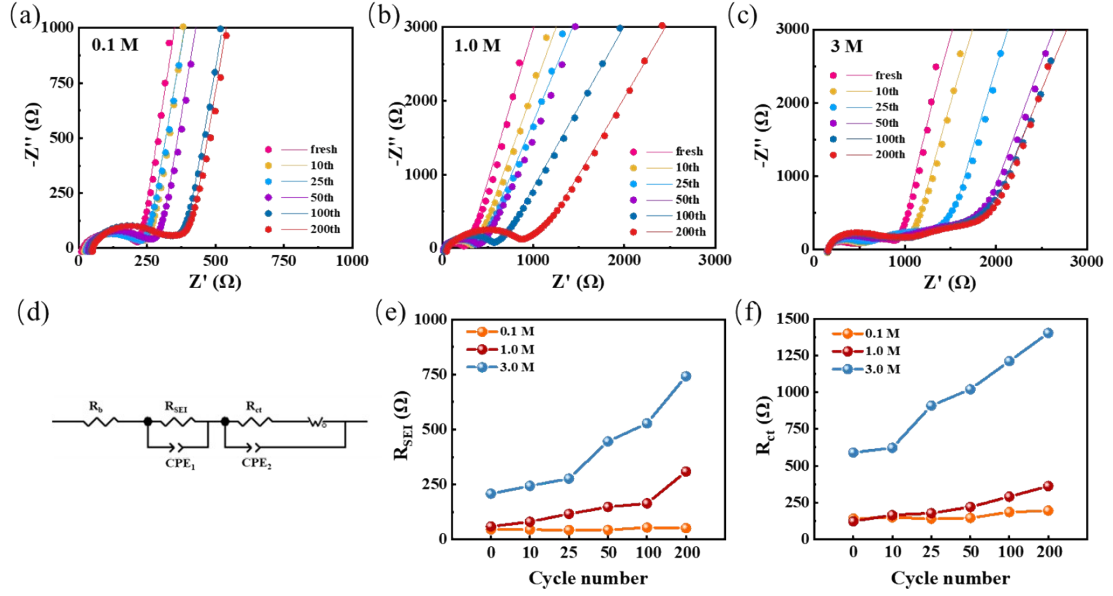
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8 Figure S10. Cycling performance of LTO-Li batteries using GPEs with different salt  
9 concentrations within a voltage window of 1.0–2.5 V.



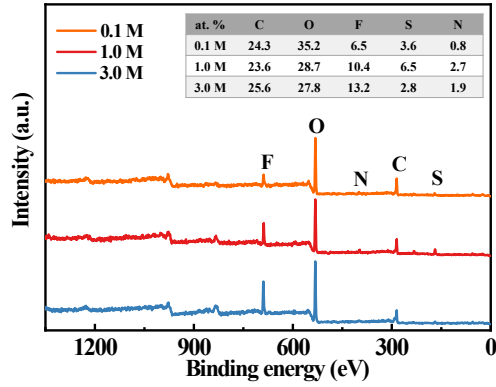
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2 Figure S11. SEM images of (a-c) TAQB cathodes and (d-f) separators using (a,d) 0.1, (b,e) 1.0 and  
3 (c,f) 3.0 M GPEs after 200 cycles. Insets: corresponding photographs of separators.  
4



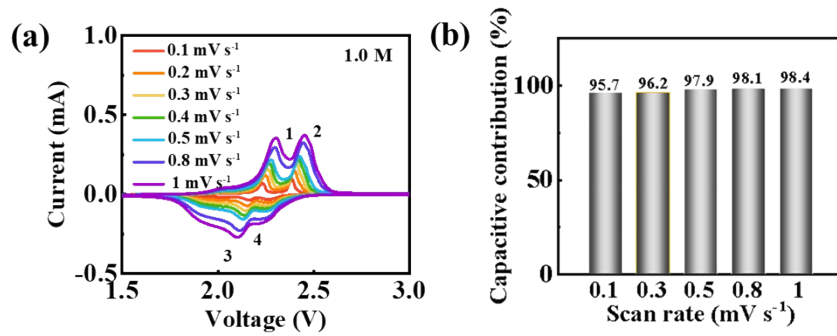
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6 Figure S12. Cross-sectional SEM images of Li anodes cycled in 3.0 M GPEs after (a, b) 50, (c, d)  
7 200 and (e, f) 500 cycles.  
8



1  
2 Figure S13. EIS changes of TAQB-Li cells within 200 cycles using (a) 0.1, (b) 1.0 and (c) 3.0 M  
3 GPEs. (d) The corresponding equivalent circuit for fitting. Changes of (e) the resistance across the  
4 solid electrolyte interphase (SEI) layer ( $R_{SEI}$ ) and (f) charge-transfer resistance ( $R_{ct}$ ) after different  
5 cycles.  
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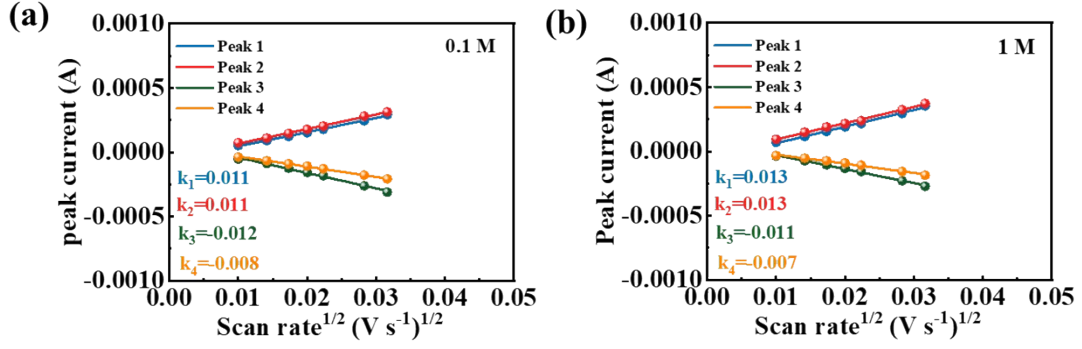


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8 Figure S14. The total XPS spectra from the cycled Li anode with different concentrated GPEs, the  
9 inset table corresponds to atomic ration of elements.  
10



11  
12 Figure S15. (a) CV curves and (b) the capacitive contributions of the TAQB electrode at different  
13 scan rates with 1.0 M GPE.

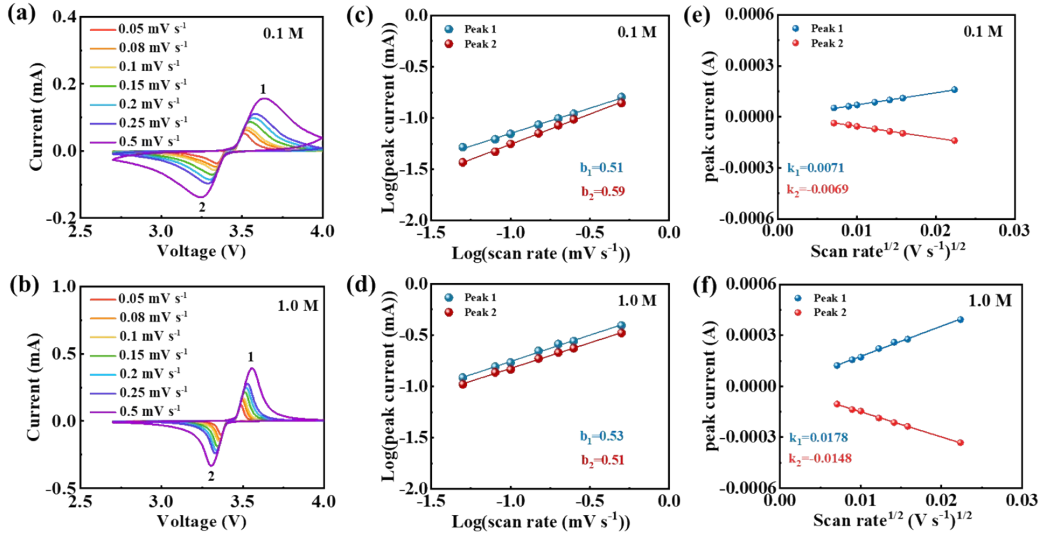
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2

3 Figure S16. The relationships between the peak current and the square root of the scan rate of the  
 4 TAQB-Li cells using (a) 0.1 and (b) 1.0 M GPEs based on CV curves recorded at different scan  
 5 rates.

6



7

8 Figure S17 (a, b) CV curves of the LFP electrodes at different scan rates, (c, d) relationships between  
 9 peak current and scan rate and (e, f) relationships between the peak current and the square root of  
 10 the scan rate for the redox peaks using (a-c) 0.1 and (d-f) 1.0 M GPEs of the LFP-Li cells.

11

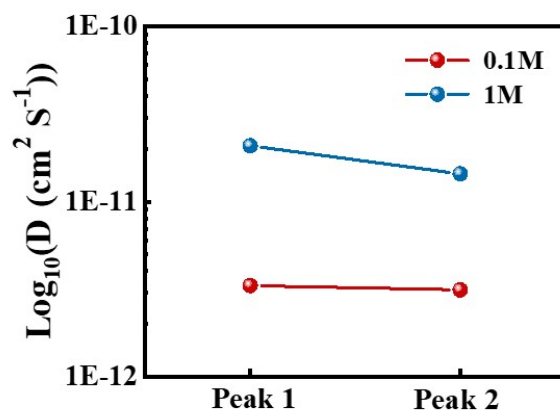
12 The relationship between peak current (i) and the scan rate (v) can be described by Equations  
 13 7 as follows:

$$14 \quad i = av^b \quad (7)$$

15 A b-value approaching 0.5 indicates a diffusion-controlled mechanism, whereas a value near 1  
 16 suggests pseudocapacitive behavior. For LFP electrodes, the corresponding b values are close to 0.5  
 17 in both 0.1 and 1.0 M GPEs, indicating that the Li-storage behavior in LFP is mainly dominated by  
 18 diffusion control, which is completely different from the fast capacitive-dominated Li-storage

1 process observed in TAQB electrodes.<sup>[10]</sup> The apparent chemical diffusion coefficients of Li ions  
 2 ( $D_{Li}^{+}$ ) can be calculated by Randles-Sevcik equation. In contrast to the similar  $D_{Li}^{+}$  values of  
 3 TAQB using 0.1 and 1.0 M GPEs, the  $D_{Li}^{+}$  of the LFP electrode in 0.1 M GPE is nearly an order  
 4 of magnitude lower than that in 1.0 M GPE (Figure S18).

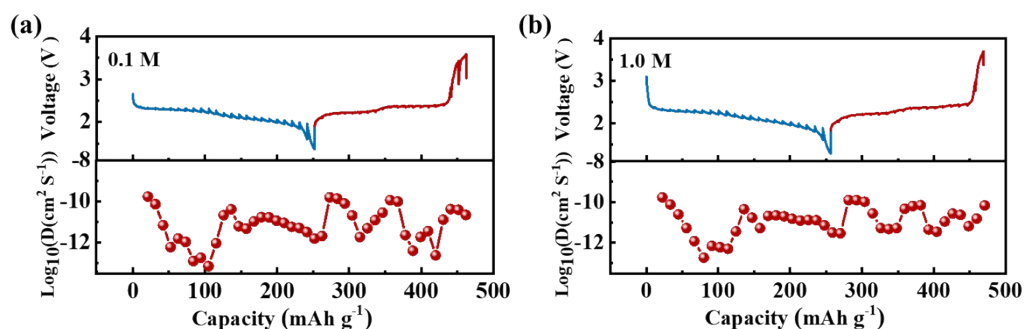
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7 Figure S18. The Li-ion diffusion coefficients of the LFP electrode with 0.1 and 1 M GPEs based  
 8 on Randles-Sevcik equation.

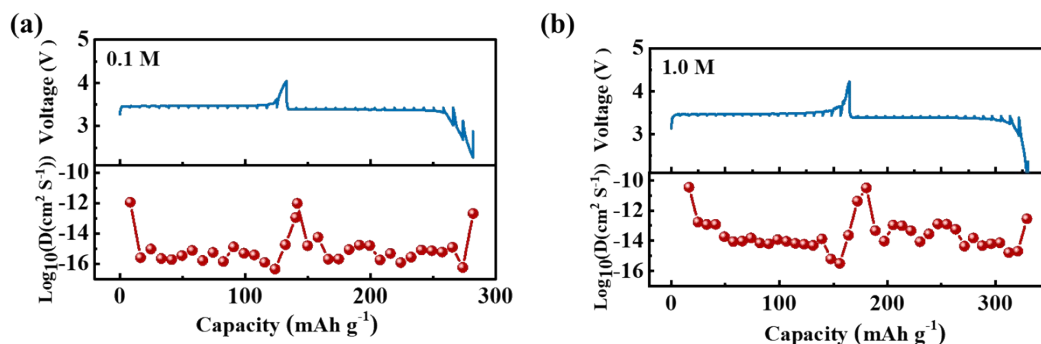
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11 Figure S19 GITT curves of TAQB electrodes and the calculated Li-ion diffusion coefficients tested  
 12 at 25 °C using (a) 0.1 and (b) 1.0 M GPEs.

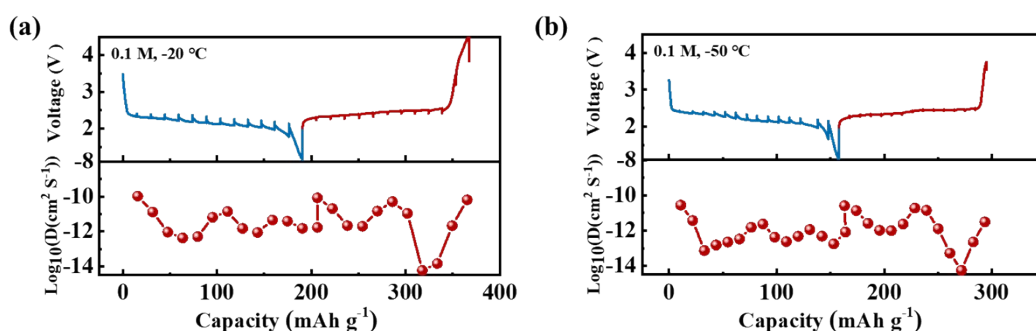
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14

15 Figure S20 GITT curves of LFP electrodes and the calculated Li-ion diffusion coefficients tested at  
 16 25 °C using (a) 0.1 and (b) 1.0 M GPEs.

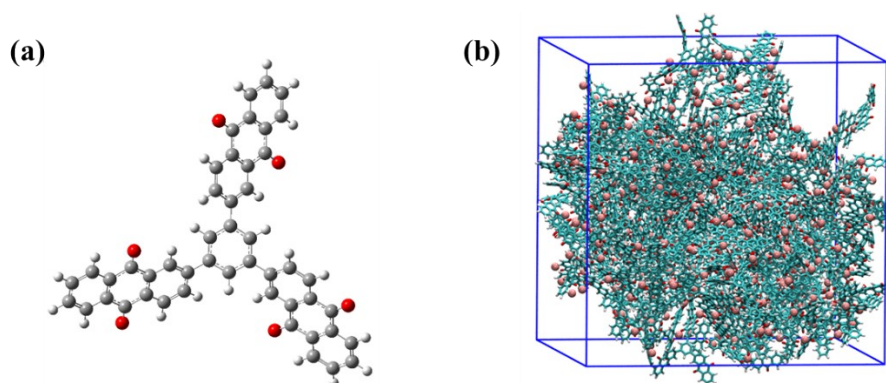
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2

3 Figure S21 GITT curves of TAQB electrodes and the calculated Li-ion diffusion coefficients tested  
 4 at (a) -20 °C and (b) -50 °C using 0.1 M GPE.

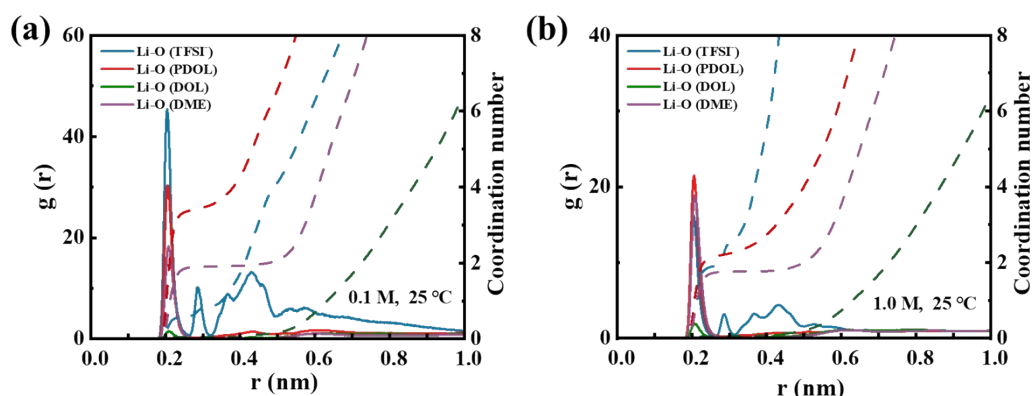
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7 Figure S22 (a) Optimized structure of TAQB by DFT calculation and (b) snapshots obtained from  
 8 MD simulations of the TAQB molecule complexed with two Li<sup>+</sup>.

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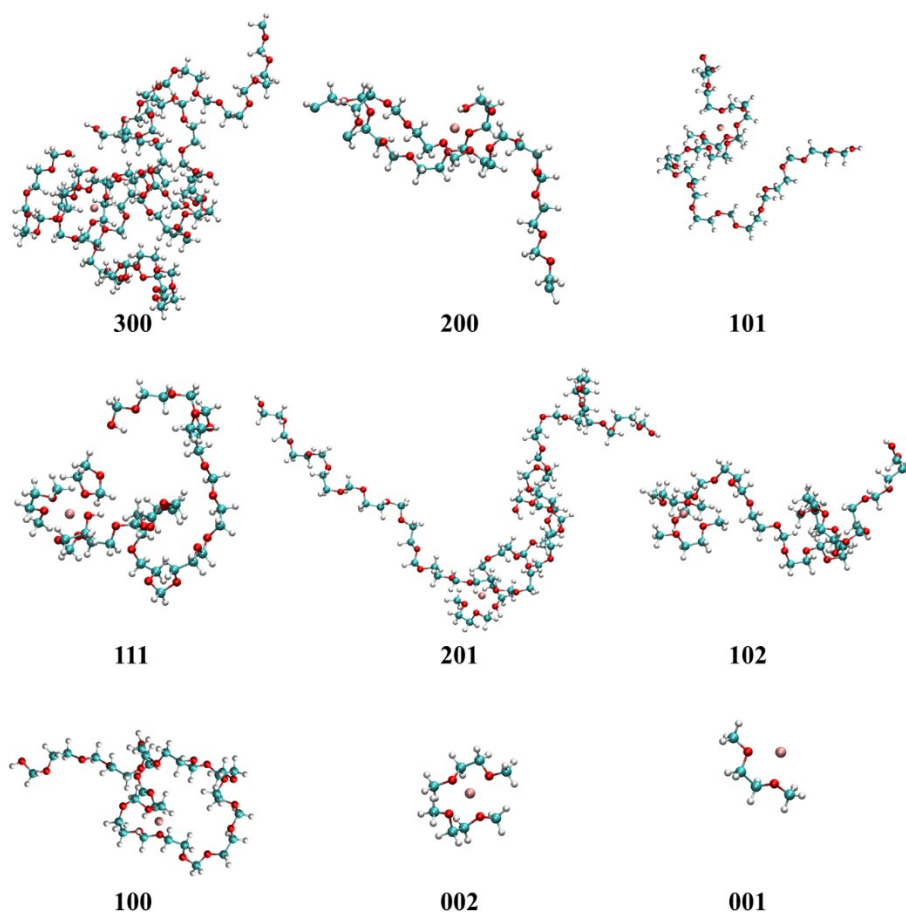
11 Figure S23 Radial distribution functions (RDF) and corresponding coordination numbers of (a) 0.1  
 12 and (b) 1.0 M GPEs at 25 °C.

13

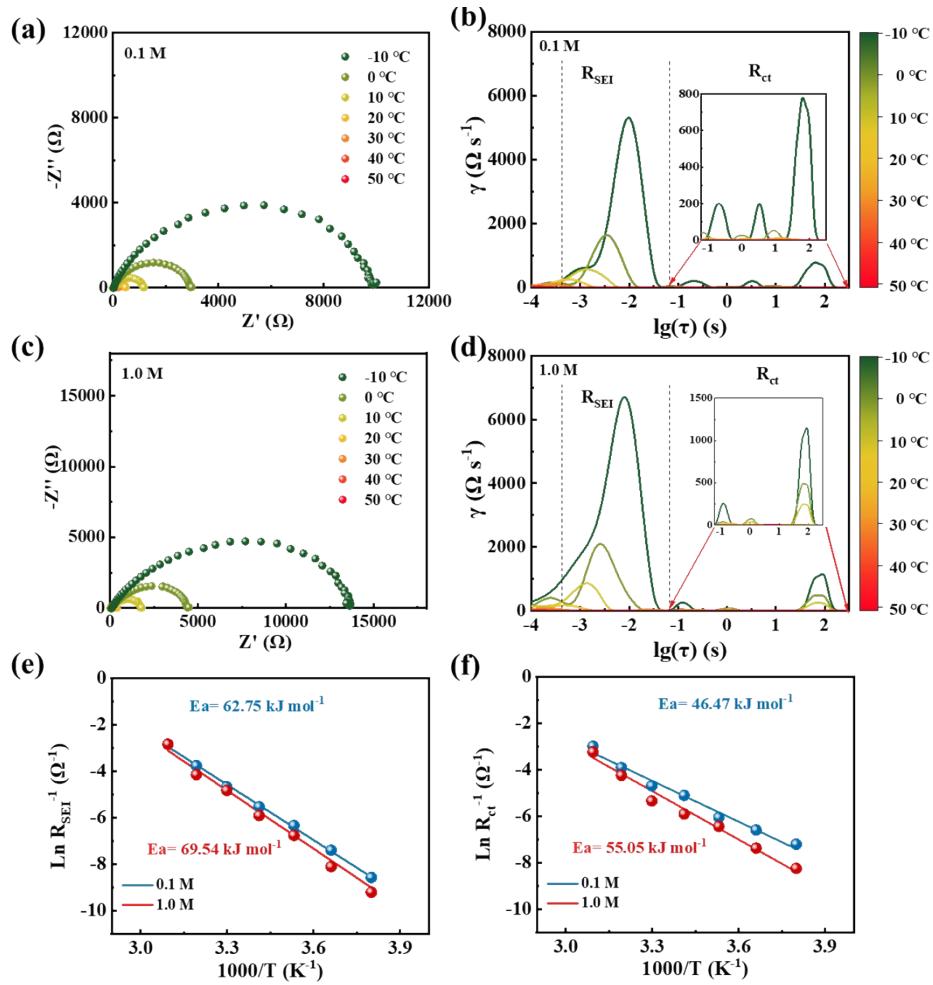
14 As shown in **Figure S23**, within the first solvation shell ( $\leq 3$  Å) of lithium ions,  
 15 DOL molecules contribute minimally to Li<sup>+</sup> coordination, and the Li<sup>+</sup> solvation  
 16 environment is primarily composed of PDOL, TFSI<sup>-</sup>, and DME. Quantitative  
 17 coordination analysis at 25 °C reveals that in 0.1 M GPE, each Li<sup>+</sup> is coordinated by an



1 average of 3.4 PDOL oxygens, 0.7 TFSI<sup>-</sup> oxygens, and 1.9 DME oxygens. Notably,  
 2 increasing the electrolyte concentration to 1.0 M significantly decreased the  
 3 coordination number of PDOL oxygens to 2.2, while that of TFSI<sup>-</sup> increased to 2.0.  
 4

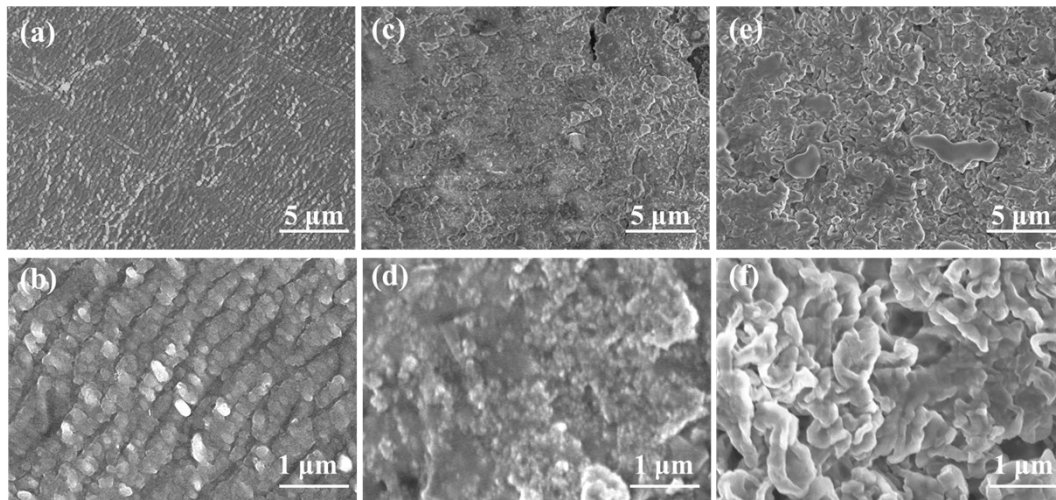


5  
 6 Figure S24 Partial Li<sup>+</sup> solvated structures in GPEs (here xyz represents one Li<sup>+</sup> with x PDOL, y  
 7 DOL, and z DME around 0.3 nm).  
 8  
 9



1  
2 Figure S25. (a-d) EIS spectra and corresponding temperature-dependent DRT distributions of  
3 symmetrical Li cells with (a, b) 0.1 and (c, d) 1.0 M GPEs. The corresponding activation energy of  
4 (e)  $\text{Li}^+$  transport through SEI and (f)  $\text{Li}^+$  de-solvation.

5



6

7 Figure S26. SEM images of the Li metal surface after 50 cycles of Li||Li symmetric cells operated  
8 at  $-50\text{ }^{\circ}\text{C}$  with a current density of  $1\text{ mA cm}^{-2}$  and an areal capacity of  $1\text{ mAh cm}^{-2}$  using (a, b) 0.1,  
9 (c, d) 1.0 and (e, f) 3.0 M GPEs.



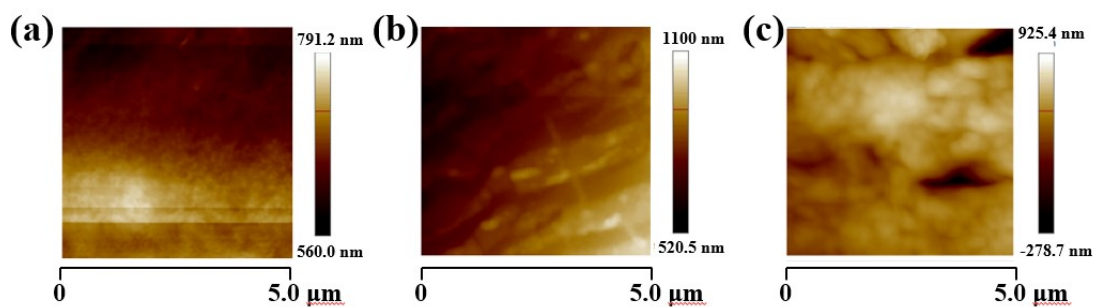


Figure S27. AFM scanning images of the Li metal surface after 50 cycles of Li||Li symmetric cells operated at  $-50^{\circ}\text{C}$  with a current density of  $1\text{ mA cm}^{-2}$  and an areal capacity of  $1\text{ mAh cm}^{-2}$  using (a) 0.1, (b) 1.0 and (c) 3.0 M GPEs.

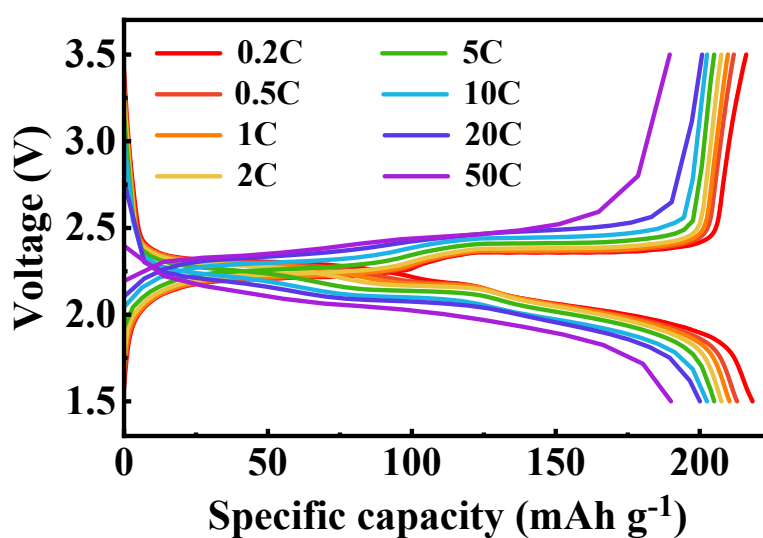


Figure S28. Charge-discharge curves of TAQB-Li battery using 0.1 M GPE with different current densities.

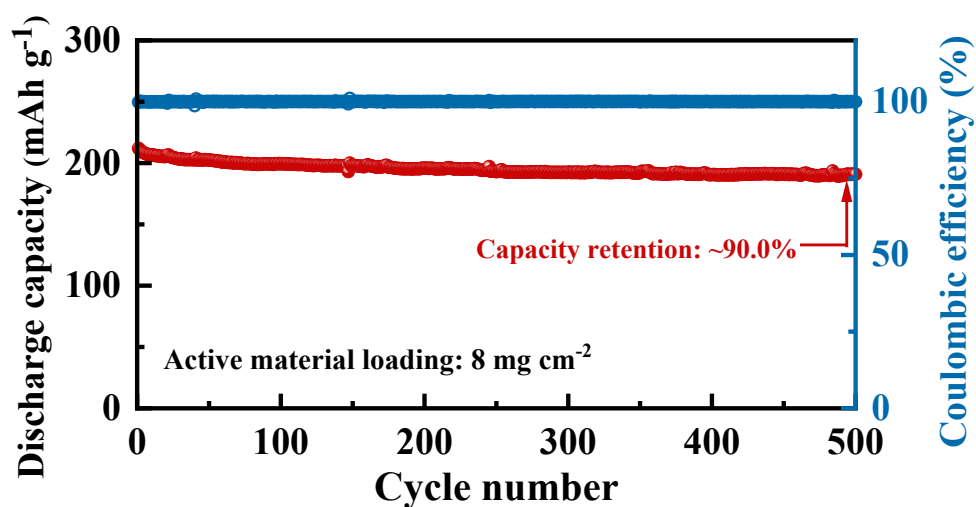
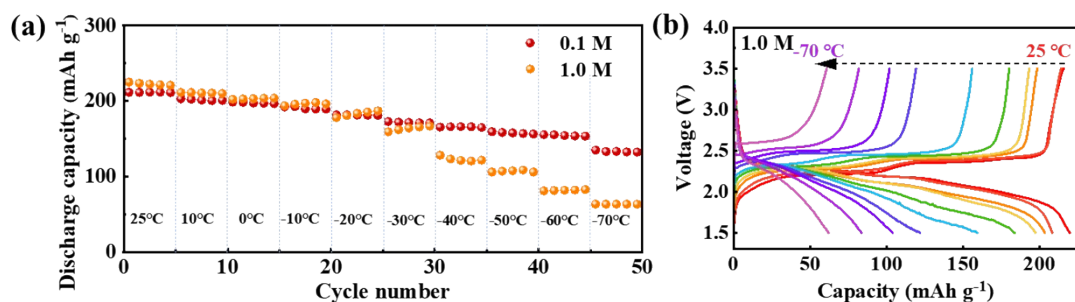


Figure S29. Cycling performance of TAQB-Li cells with a high active material loading of  $8\text{ mg cm}^{-2}$  using 0.1 M GPE at 0.2 C.

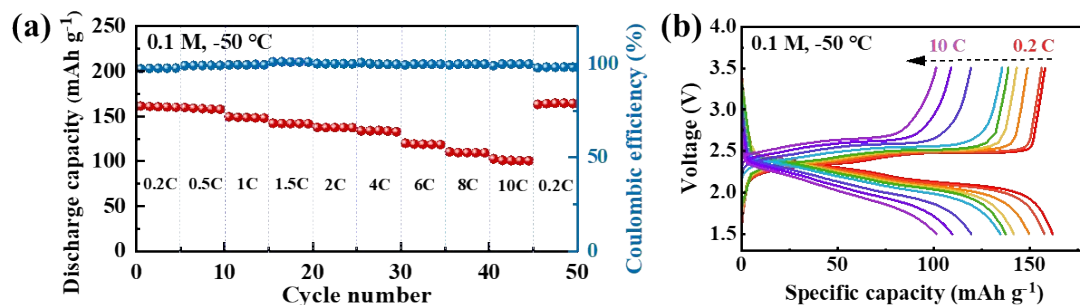
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2

3 Figure S30. (a) Discharge capacity of TAQB-Li cells with 0.1 M and 1.0 M GPEs at different  
 4 temperatures with a current density of 0.2 C and (b) the corresponding charge-discharge curves  
 5 with 1.0 M GPE.

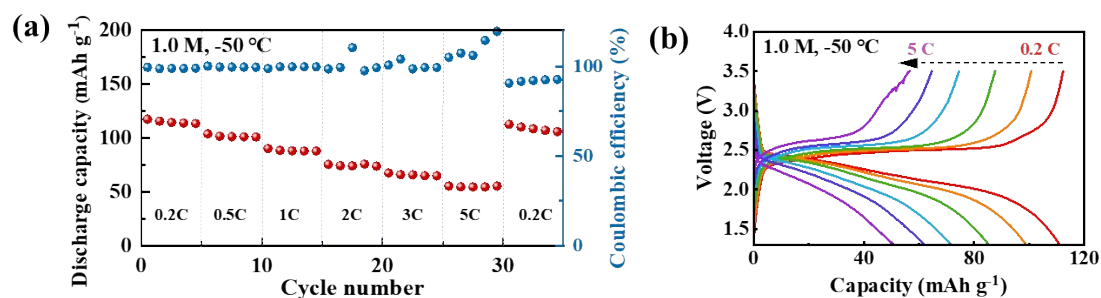
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7

8 Figure S31. (a) Rate performance of TAQB-Li cells with 0.1 M GPE and (b) the corresponding  
 9 charge-discharge curves at -50 °C.

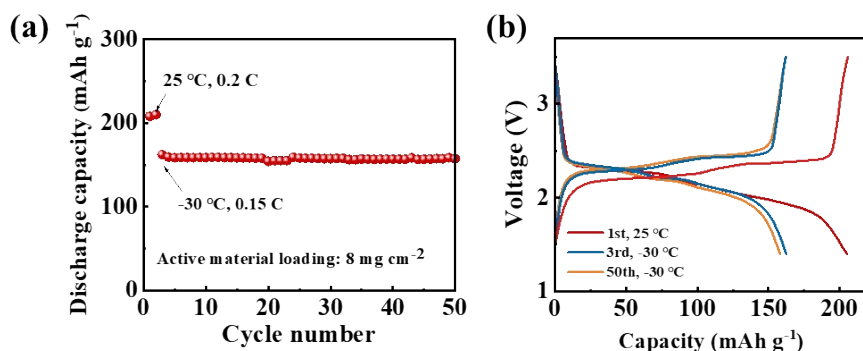
10



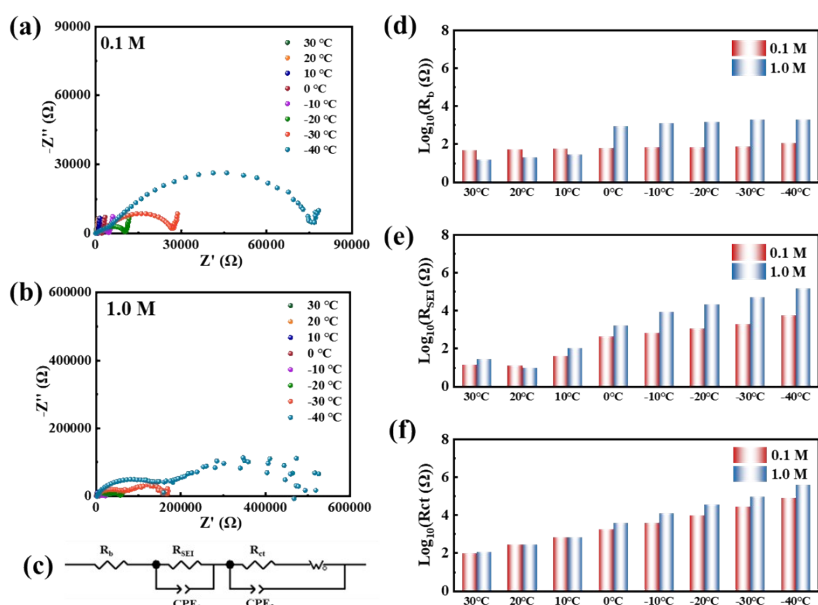
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12 Figure S32. (a) Rate performance of TAQB-Li cells with 1.0 M GPE and (b) the corresponding  
 13 charge-discharge curves at -50 °C.

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1  
2 Figure S33. (a) Cycling performance of TAQB-Li cells with a high active material loading of 8 mg  
3 cm<sup>-2</sup> using 0.1 M GPE at -30 °C and (b) the corresponding charge-discharge curves.



4  
5 Figure S34. EIS changes of TAQB-Li cells under different working temperatures using GPEs with  
6 different LiTFSI concentrations of (a) 0.1 and (b) 1.0 M. (c) The corresponding equivalent circuit  
7 for fitting. Values of (d) the bulk resistance ( $R_b$ ), (e)  $R_{SEI}$  and (f)  $R_{ct}$  under different working  
8 temperatures.

9  
10 Table S1. The cost at different concentration in 1 dm<sup>-3</sup> LiTFSI DOL-DME electrolyte.

| Concentration<br>(mol dm <sup>-3</sup> ) | Weight of salt<br>(g) | Weight of solvent<br>(g) | Cost<br>(CNY) |
|--|-----------------------|--------------------------|---------------|
| 0.01                                     | 2.87                  | 961.42                   | 31.71         |
| 0.05                                     | 14.2                  | 953.21                   | 42.80         |
| 0.1                                      | 28.1                  | 943.14                   | 56.39         |
| 0.5                                      | 129.55                | 869.65                   | 155.64        |
| 1.0                                      | 236.12                | 792.44                   | 259.89        |
| 3.0                                      | 522.75                | 584.80                   | 540.29        |

According to the quotation of the electrolyte company, we calculated the total cost of 1 dm<sup>-3</sup> electrolyte. Wherein, the unit prices of DOL, DME and LiTFSI are 30, 30 and 1000 CNY kg<sup>-1</sup> respectively. Obviously, the cost of low-concentration electrolytes is much lower than the high-concentration electrolytes.

Table S2 The electrochemical performance of TAQB-Li batteries using GPEs with different LiTFSI concentrations

| Salte concentration (M) | Initial specific capacity (mAh g <sup>-1</sup> ) | Capacity retention after 200 cycles |
|-------------------------|--|-------------------------------------|
| 0.01 M                  | 190  | 87%                                 |
| 0.05 M                  | 202.8  | 82%                                 |
| 0.1 M                   | 211.3  | 97%                                 |
| 1.0 M                   | 215  | 95%                                 |
| 3.0 M                   | 205.1  | 80%                                 |

Table S3 The electrochemical performance of LFP-Li batteries using GPEs with different LiTFSI concentrations

| Salte concentration (M) | Initial specific capacity (mAh g <sup>-1</sup> ) | Capacity retention after 200 cycles |
|-------------------------|--|-------------------------------------|
| 0.1 M                   | 147.2  | 77%                                 |
| 1.0 M                   | 155  | 97%                                 |
| 3.0 M                   | 91.8   | Nearly 100%                         |

Table S4. The Li-ion diffusion coefficients of the TAQB electrode with 0.1 and 1.0 M GPEs based on Randles-Sevick equation.

| Electrolyte | Peak 1 (cm <sup>2</sup> s <sup>-1</sup> ) | Peak 2 (cm <sup>2</sup> s <sup>-1</sup> ) | Peak 3 (cm <sup>2</sup> s <sup>-1</sup> ) | Peak 4 (cm <sup>2</sup> s <sup>-1</sup> ) |
|-------------|---|---|---|---|
| 0.1 M       | 1.2×10 <sup>-10</sup>                     | 1.2×10 <sup>-10</sup>                     | 1.4×10 <sup>-10</sup>                     | 6.3×10 <sup>-11</sup>                     |
| 1.0 M       | 1.7×10 <sup>-10</sup>                     | 1.7×10 <sup>-10</sup>                     | 1.2×10 <sup>-10</sup>                     | 4.8×10 <sup>-11</sup>                     |

Table S5. The Li-ion diffusion coefficients of the LFP electrode with 0.1 and 1.0 M GPEs based on Randles-Sevick equation.

| Electrolyte | Peak 1 (cm <sup>2</sup> s <sup>-1</sup> ) | Peak 2 (cm <sup>2</sup> s <sup>-1</sup> ) |
|-------------|---|---|
| 0.1 M       | 3.3×10 <sup>-12</sup>                     | 3.1×10 <sup>-12</sup>                     |
| 1.0 M       | 2.1×10 <sup>-11</sup>                     | 1.5×10 <sup>-11</sup>                     |

1 Table S6 A summary of various solvated structures and the corresponding de-solvation  
2 energies in 0.1 M GPE system

| Solvated<br>structure | 223.15 K          |   | 298.15 K          |   |
|-----------------------|-------------------|---|-------------------|---|
|                       | Frequency<br>(Hz) | De-solvation<br>energy<br>(kJ mol <sup>-1</sup> ) | Frequency<br>(Hz) | De-solvation<br>energy<br>(kJ mol <sup>-1</sup> ) |
| 300                   | 123               | 453.2   | 110               | 445.7   |
| 200                   | 299               | 463.5   | 231               | 458.8   |
| 101                   | 103               | 459.5   | 116               | 451.2   |
| 111                   | 102               | 469.8   | 95                | 461.4   |
| 001                   | 44                | 358.3   | 60                | 350.3   |
| 201                   | 157               | 376.8   | 182               | 371.9   |
| 102                   | 153               | 468.1   | 152               | 454.2   |
| 003                   | 51                | 498.3   | 51                | 490.6   |
| 002                   | 51                | 474.8   | 42                | 463.3   |
| Average               |                   | 448.5   |                   | 436.4   |

3 Note:

4 300 represents one Li ion with three PDOL, zero DOL, and zero DME around 0.3 nm,

5 101 represents one Li ion with one PDOL, zero DOL, and one DME around 0.3 nm,

6 111 represents one Li ion with one PDOL, one DOL, and one DME around 0.3 nm,

7 and so on.

8

9 Table S7 A summary of various solvated structures and the corresponding de-solvation  
10 energies in 1.0 M GPE system

| Solvated<br>structure | 223.15 K          |   | 298.15 K          |   |
|-----------------------|-------------------|---|-------------------|---|
|                       | Frequency<br>(Hz) | De-solvation<br>energy<br>(kJ mol <sup>-1</sup> ) | Frequency<br>(Hz) | De-solvation<br>energy<br>(kJ mol <sup>-1</sup> ) |
| 100                   | 1138              | 529.5   | 1144              | 520.5   |
| 200                   | 951               | 463.5   | 980               | 458.8   |
| 101                   | 2548              | 459.5   | 2506              | 451.2   |
| 002                   | 1202              | 474.8   | 1197              | 463.3   |
| 001                   | 1276              | 358.3   | 1360              | 350.3   |
| 102                   | 692               | 468.1   | 730               | 454.2   |
| 111                   | 55                | 469.8   | 45                | 461.4   |

|         |     |       |     |       |
|---------|-----|-------|-----|-------|
| 110     | 594 | 515.3 | 500 | 510.1 |
| 010     | 68  | 363.3 | 385 | 356.4 |
| 210     | 663 | 479.4 | 544 | 471.5 |
| 301     | 51  | 516.2 | 51  | 511.6 |
| 300     | 8   | 453.2 | 9   | 445.7 |
| 011     | 62  | 367.3 | 50  | 361.4 |
| 120     | 125 | 516.8 | 136 | 510.7 |
| 003     | 203 | 498.3 | 192 | 490.6 |
| Average |     | 462.7 |     | 449.6 |

1

2 Table S8 Electrochemical performance comparison of organic batteries in our work and the  
3 previous reports.

| Electrolyte  | Cathode/anode                                       | Cycling stability at RT (capacity retention@cycle life) | Rate performance at LTs       |                                | Ref.     |
|--|---|---|-------------------------------|--------------------------------|----------|
|  |   |   | Condition (rate, temperature) | LT vs. RT                      |          |
| 0.1M LiTFSI+ PDOL-based GPE  | TAQB/Li   | 74%@2000  | 10C, -50°C                    | 101mAh g <sup>-1</sup><br>50%  | Our work |
| ~1 M LiTFSI/EA in DCM (1/4, v/v)                                   | PI/Li   | 69%@100   | 10C, -70 °C                   | 9 mAh g <sup>-1</sup><br>14%   | [11]     |
| 1.8 M LiTFSI in EA   | PTPAn/PNT CDA                                       | 83%@500   | 5C, -50 °C                    | 45 mAh g <sup>-1</sup><br>52%  | [12]     |
| 1 M LiFSI <sub>0.8</sub> TFSI <sub>0.2</sub> in HME/HEP (1/1, v/v) | PTCDA/Li  | 71%@200   | 0.1C, -40 °C                  | 75 mAh g <sup>-1</sup><br>57%  | [13]     |
| 1 M LiPF <sub>6</sub> in EC/EMC (3/7, v/v)                         | PTO-2TH/Li  | 59%@4000  | 0.5C, 2 °C                    | 141 mAh g <sup>-1</sup><br>49% | [14]     |
| 1 M LiFSI in BTFE/DME (5/1, v/v)                                   | NCM811/Li   | 94%@200   | 0.2C, -40 °C                  | 109 mAh g <sup>-1</sup><br>54% | [15]     |
| 1 M LiPF <sub>6</sub> in MTFP/FEC (9/1, v/v)                       | NCM811/Li   | 80%@250   | 0.1C, -50 °C                  | 149 mAh g <sup>-1</sup><br>79% | [16]     |
| 2.5 M LiFSI in DPE/DIPE(1/1, v/v)                                  | LFP/Li  | 84%@150   | 0.1C, -20 °C                  | 92 mAh g <sup>-1</sup><br>59%  | [17]     |
| 2.1 M LiTFSI in MTBE/THF (3/1, v/v)                                | LFP/Li  | 87%@1400  | 0.2C, -40 °C                  | 106 mAh g <sup>-1</sup><br>69% | [18]     |
| 1.0 M LiDFOB in FEC/DMS/IF (4/7/9, v/v/v)                          | LiCoO <sub>2</sub> /Li                              | 95% @500  | 1/15C, -70 °C                 | 120 mAh g <sup>-1</sup><br>60% | [19]     |
| 1.0 M LiFSI in DMM   | Li <sub>4</sub> Ti <sub>5</sub> O <sub>12</sub> /Li | 77% @200  | 0.1C, -40 °C                  | 100 mAh g <sup>-1</sup><br>60% | [20]     |

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