Supplementary Information

Revealing the dissolution mechanism of organic carbonyl electrodes in lithium-organic batteries

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1. Experimental Section

1.1 Materials

1,2-Dimethoxyethane (C₄H₁₀O₂, DME), 1,2-diethoxyethane (C₆H₁₄O₂, DEE), 1,2dibutoxyethane (C₁₀H₂₂O₂, DBE), diethylene glycol diethyl ether (C₈H₁₈O₃, DEGDEE), diethyl ether (C₄H₁₀O, EE), ethylene carbonate (C₃H₄O₃, EC), lithium bis(trifluoromethanesulfonyl)imide (LiC₂F₆NO₄S₂, LiTFSI), pyrene-4,5,9,10-tetraone (C₁₆H₆O₄, PTO) and lithium nitrate (LiNO₃) were purchased commercially. All solvents were treated to remove any residual water with 4 Å molecular sieves over 48 h in Ar-filled glovebox before using.

1.2 Preparation of electrolytes and electrode

The different concentration electrolytes (0.5, 1.0, 1.5, 2.0, 2.5 mol kg⁻¹) were obtained by mixing LiTFSI and different solvents. In addition, to enhance the stability of lithium metal anode, LiNO₃ (1% *wt*) was added in electrolytes for battery test. The working electrodes were obtained by mixing the active materials (PTO), conductive (Ketjen black), and binder polyvinylidene fluoride (PVDF) in a weight ratio of 50:40:10, using *N*-methyl-1,2-pyrrolidone (NMP) as the dispersing agent. The slurry was then spread on Al foil and fully dried at 80 °C in a vacuum oven. The mass loading of each electrode was about 0.5 mg cm⁻².

1.3 Preparation of PTO solutions and tests of different spectra

The excess PTO was dispersed in electrolytes, stirred for 30 mins and left 24 h to ensure that the PTO was saturated. The supernatant was removed, and the solutions were diluted for ultraviolet and visible (UV–vis) spectroscopy, Fourier transform infrared spectroscopy, Raman spectroscopy and nuclear magnetic resonance measurements. The partially lithiated electrode and fully lithiated electrode were prepared by discharging to the specified voltages (2.4 V and 1.5 V). Then the electrodes were soaked in 1 m LiTFSI/DME electrolyte for 24 h for the test of UV–vis spectroscopy.

1.4 Electrochemical measurements

The CR2032 coin-type cells were assembled in a glovebox filled with Argon gas where O_2 and H_2O concentrations were kept less than 0.1 ppm. The cells used Celgard

2400 membrane as separator and Li metal foils as anodes. The cycling performance was tested between 1.5–3.6 V vs. Li⁺/Li at 1 C (1 C = 409 mA g⁻¹). The linear sweep voltammetry (LSV) tests were based on Li metal anode and stainless steel cathode with specific electrolyte of 0.1 mV s⁻¹ on the CHI760 electrochemical workstation (ChenHua, Shanghai).

1.5 Characterization

All UV–vis spectra of Li–PTO batteries and electrolytes were obtained by UV–vis spectrophotometry (Agilent Technologies, Cary 60). The special cuvette containing electrodes was used for *in situ* tests. The Fourier transform infrared (FTIR) spectroscopy (Bruker Tensor II Sample Compartment RT-DLaTGS) was utilized to determine the solvent-solute interactions. Raman spectroscopy (Thermo-Fisher Scientific DXR), ¹H nuclear magnetic resonance (¹H NMR, Bruker, AVANCE III 400MHz) and ⁷Li nuclear magnetic resonance (⁷Li NMR, Bruker, AVANCE III 400MHz) were used to distinguish the variations of solvation structures before and after dissolving PTO, in which the D₂O (contained LiCl) or dimethyl sulfoxide-d6 was sealed within a capillary tube and inserted into an NMR tube that contains electrolytes. The cycling performance was tested on the NEWARE battery test system (CT-4008Tn-5V10mA-164, Shen-zhen, China) and LAND testing system (LAND2001CT, Wuhan, China) at specific current density.

1.6 Computational Methods

Molecular dynamics (MD) simulations were performed using GROMACS 2023 package.^{1, 2} The electrolyte systems contain 600 molecules of solvents and different quantities of LiTFSI (or LiPF₆) for different concentrations, respectively. The force field parameters for solvents and ions were derived from the general AMBER force field (GAFF),^{3, 4} where all molecular structures were optimized at the level of B3LYP/Def2SVP with Grimme's D3 dispersion correction and the atomic charges were generated from restrained fitting on the electrostatic potential (RESP)^{5, 6} calculated at HF/Def2TZVP, using Gaussian 16.A.03 software.⁷ The atomic charges of ions including Li⁺, TFSI⁻ and PF_6^- were scaled down by a factor of 0.7 to account polarization.⁸ electronic The UV-vis spectra for were computed at

PBEPBE/Def2TZVP using Gaussian 16.A.03 package and the structures were visualized by GaussView 6.0.

In the solvation free energy calculations, the systems consist of 1 PTO (or BQ, AQ and NTCDA) molecule and the electrolyte components corresponding to the different concentration. A total of 26 intermediate states was applied to gradually decouple the electrostatic interaction and van der Waals interactions between cathode and electrolyte. For the decoupling of electrostatic interaction, simulations were performed with the intermediate states at $\lambda = 1.0, 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2$, 0.1, and 0.0. For the decoupling of van der Waals interactions, simulations were performed with the intermediate states at $\lambda = 1.0, 0.95, 0.9, 0.85, 0.8, 0.75, 0.7, 0.65$, 0.6, 0.55, 0.5, 0.4, 0.3, 0.2, 0.1 and 0.0. For each value of λ , a 2 ns NPT (N: number of particles, P: pressure, T: temperature) simulation was performed using the same protocol employed for the simulations of electrolyte systems. This process included the cavitation energy required to create a cavity for PTO by pushing aside solvent molecules. The Bennett's Acceptance Ratio (BAR) method implemented in GROMACS program was used to compute free energy differences for each perturbation.⁹ The calculation of solvation free energy for all cathode in electrolytes has been carried out multiple times, and the average value has been calculated to reduce errors caused by the random distribution of molecules during the calculation process.

In the MD simulations, after being minimized by the steepest-decent algorithm, the systems were further equilibrated in the NPT ensemble using a thermal annealing approach with a total time of 5 ns. The system temperature was initially elevated from 0 K to 400 K in a period of 0.5 ns. After being maintaining at 400 K for 2 ns, the systems were cooled down to 298 K within 0.5 ns and equilibrated at 298 K for an additional 2 ns. Subsequently, a 20 ns NPT simulation was conducted to sample the structures for data analysis. The temperature was controlled by the V-rescale thermostat with a damping time constant of 0.3 ps, while the pressure was maintained at 1 bar using the C-rescale barostat with a time constant of 2 ps. The cutoffs for the short-range electrostatic and van der Waals interactions were set to 1.2 nm. The VMD

software was used to visualize the MD simulation results.¹⁰

The solvation free energy can be decomposed into the proportions of ion-solvation structures and free solvents, which is defined as follows,

$$\Delta G_{\text{free solvents}} = \Delta G_{\text{solvents}} \times x_{\text{free solvents}}$$
$$\Delta G_{\text{ion - solvation structures}} = \Delta G_{\text{total}} - \Delta G_{\text{free solvent}}$$

where $x_{\text{free solvents}}$ represents the percentage of free solvents with respect to the total number of solvents in the simulation box, and $\Delta G_{\text{solvents}}$ is the solvation free energy of PTO in pure solvents. The PTO-electrolyte interaction energy calculations were based on the MD simulations for the systems containing 60 PTO molecules and electrolytes, It contains the interactions of PTO with solvent surrounded Li⁺ (SSL, Li⁺(TFSI⁻)₀), Li⁺-anion single pair (LASP, Li⁺(TFSI⁻)₁) and Li⁺-anion cluster (LAC, Li⁺(TFSI⁻)_{>2}).

The molecular structures of EE–PTO, DBE–PTO and DME–PTO were optimized at the level of B3LYP/Def2SVP with Grimme's D3 dispersion correction. The pair interaction energies of PTO and EE (DBE or DME) were computed by the exchanged-scaling second-order symmetry-adapted perturbation theory (sSAPT0)¹¹ with jun-cc-pVDZ basis set, as implemented in PSI4 code.¹²



Fig. S1 (a) Total solvation free energy $|\Delta G|$ and (b) van der Waals component of total solvation free energy $|\Delta G_{vdw}|$ *vs*. electrolyte concentration.



Fig. S2 UV-vis spectra of different electrolytes after dissolving PTO.



Fig. S3 The calculated UV-vis spectra of PTO and PTO-Li⁺. The insides are schematic diagrams of molecular structures.

Compared to the absorption peak of PTO, the absorption peak of PTO–Li⁺ undergoes a significant red shift. After coordinating with Li⁺, the change in carbonyl chemical environment of PTO leads to a shift in the $n\rightarrow\pi^*$ of C=O transition.



Fig. S4 The photographs of different electrolytes and pure solvents after dissolving PTO and let them sit for 24 h.



Fig. S5 The intermolecular interaction energies between PTO and different solvents (EE, DBE and DME).



Fig. S6 Radial distribution function and coordination number of PTO– Li⁺/solvent/TFSI⁻ anion for 1 m DME+PTO (a), 1 m DBE+PTO (b) and 1 m EE+PTO (c).



Fig. S7 Percentage of free solvents vs. electrolyte concentration.

Note that free solvents represent solvents uncoordinated to Li ions. Obviously, the proportion of free solvents in pure solvents is 100%.



Fig. S8 Linear fittings of free solvents contribution in $|\Delta G_{es}|$ for (a) EE, (b) DBE, (c) DME and (d) EC electrolytes.



Fig. S9 The solvent molecule polarity evaluated by dipole moment.



Fig. S10 Dissolution of PTO in EC electrolytes. (a) UV–vis spectra of PTO in different concentrations of EC electrolyte. (b) Variation of absorbance as a function of electrolyte concentration.



Fig. S11 Schematic diagrams of different solvation structures. (a) SSL, (b) LASP and (c) LAC in different electrolytes. The cyan, white, red, blue, orange and pink balls represent C, H, O, N, F and Li, respectively.



Fig. S12 Solvation structures of (a) EE, (b) DBE, (c) DME and (d) EC electrolytes *vs*. electrolyte concentration.



Fig. S13 Raman spectra and corresponding fitting results of 1 m LiTFSI/EE (a), 1 m LiTFSI/DBE (b), 1 m LiTFSI/DME (c) and 1 m LiTFSI/EC (d) electrolytes.

The three parts located at about 740, 745, and 749 cm⁻¹, correspond to free TFSI⁻, CIP, and AGG, respectively.¹³



Fig. S14 Interaction energies between PTO with SSL, LASP, and LAC in (a) EE, (b) DBE, (c) DME and (d) EC electrolytes vs. electrolyte concentration.



Fig. S15 Percentage of free PTO in different electrolytes after dissolving PTO.



Fig. S16 Percentage of free TFSI⁻ in different electrolytes before and after dissolving PTO.

The dissolved PTO enters the solvation structures of the EE, DBE, and DME electrolytes, resulting in the extrusion of TFSI⁻ from the originally solvation structures. Therefore, the amount of uncoordinated TFSI⁻ increases. Conversely, the strong interaction of the PTO with EC leads to the detachment of some EC molecules from the solvation structures resulting in replenishment of TFSI⁻ into the new solvation structures.



Fig. S17 Radial distribution functions and coordination numbers of Li–O of solvent, TFSI⁻ and PTO for different electrolytes before and after dissolving PTO. (a) 1 m EE, (b) 1 m EE+PTO, (c) 1 m DBE, (d) 1 m DBE+PTO, (e) 1 m DME, (f) 1 m DME+PTO, (g) 1 m EC and (h) 1 m EC+PTO are presented, respectively.



Fig. S18 IR spectra analysis of different samples. (a)-(c) correspond to 0 m and 1 m LiTFSI/EE, LiTFSI/DBE, and LiTFSI/DME electrolytes with dissolved PTO, respectively. (d) corresponds to solid sample of LiTFSI. (e) corresponds to 1 m LiTFSI/EC and 1 m LiTFSI/EC+PTO electrolytes.



Fig. S19 Raman spectra and corresponding fitting results of 1 m LiTFSI/EE (a), 1 m LiTFSI/DBE (b), 1 m LiTFSI/DME (c) and 1 m LiTFSI/EC (d) electrolytes with dissolving PTO.



Fig. S20 (a) Optical photo of the brand new 1 m LiTFSI/DME electrolyte with dissolved PTO. (b) Optical photo of adding Li to the electrolyte with dissolved PTO. (c-d) Optical photo of solution changes at different reaction times between electrolyte with dissolved PTO and Li. (e) Optical photo of Li.

The 1 m LiTFSI/DME electrolyte with dissolved PTO will react with lithium metal. Over time, under the influence of lithium metal, the 1 m LiTFSI/DME electrolyte with dissolved PTO will gradually change from an orange solution to a purple solution.



Fig. S21 UV-vis spectra and corresponding optical photos of PTO at (a) unlithiated (pristine), (b) partially lithiated (discharge 2.4 V) and (c) fully lithiated states (discharge 1.5 V) in 1 m LiTFSI/DME electrolyte.



Fig. S22 LSV curves of 1 m LiTFSI/EE, LiTFSI/DBE, and LiTFSI/DME electrolytes.



Fig. S23 The 2nd normalized voltage-capacity profiles of PTO with 1 m LiTFSI/EE, 1 m LiTFSI/DBE and 1 m LiTFSI/DME electrolytes.



Fig. S24 Coulombic efficiencies during cycles.

Carbonyl cathodes	Electrolytes	Current density	Initial capacity (mAh g ⁻¹)	Capacity retention (Cycle number)	Ref.
2,6-dimethoxy-9,10- anthraquinone	4 M LiTFSI/DOL/DME	0.2 C	200	73% (80)	14
2,5-diamino-1,4- benzoquinone	1 M Litfsi/tegdme/ Dol	0.05 C	~388	~80% (10)	15
9,10-anthraquinone	2 M LiTFSI/DOL/DME /LiNO ₃	0.2 C	205	85% (100)	16
2,2'-bis(3-hydroxy-1,4- naphthoquinone)	2 M LiTFSI/DOL/DME /LiNO3	0.2 C	307	76% (100)	16
4,4'-dimethyl-1,1'- bi(cyclohexa-3,6-diene)- 2,2',5,5'-tetraone	2 M LiTFSI/DOL/DME /LiNO ₃	0.2 C	404	84% (100)	16
5,5'-bibenzofuran- 4,4',7,7'-tetraone	2 M LiTFSI/DOL/DME /LiNO ₃	0.2 C	310	69% (100)	16
2,2'-binaphthyl- 1,1',4,4'-tetraone	2 M LiTFSI/DOL/DME /LiNO ₃	0.2 C	322	78% (100)	16
1,4,5,8- naphthalenetetracarboxylic dianhydride	4 M LiTFSI/DOL/DME	50 mA g^{-1}	173	66% (100)	17
pyrene-4,5,9,10-tetraone	β -Li ₃ PS ₄	1 C	~400	72% (100)	18
pyrene-4,5,9,10-tetraone	LiTFSI/HFE-4/ DEMMEA-TFSI	1 C	~245	78% (1000)	19
pyrene-4,5,9,10-tetraone	1 m LiTFSI DBE/LiNO ₃	1 C	348	76% (300)	This work

Table S1. Comparison of the performance in the present study with other Li–carbonyl batteries.



Fig. S25 Solvation free energies of PTO in LiPF_6 electrolytes vs. electrolyte concentration.



Fig. S26 Solvation free energies of different cathodes. (a) BQ, (b) AQ and (c) NTCDA in LiTFSI electrolytes *vs.* electrolyte concentration. The molecular structure formulas of cathodes are shown inside the plots.

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