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Supporting Information for

Unraveling the temperature-responsive solvation structure and interfacial chemistry

for graphite anodes

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Experimental section

Electrode preparation

A slurry consisting 94 wt% graphite (Gr, Shanshan Tech Co., Ltd., China) powder, 1 wt% Super-P, and 5 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrolidone (NMP) solvents was coated on Cu foil current collector, followed by being dried at 80 °C in a vacuum oven overnight. Then Gr electrodes were punched into round disks (12 mm in diameter) with an average mass loading of 1~2 mg cm⁻².

Electrolyte preparation

Battery-grade lithium bis(fluorosulfonyl)imide (LiFSI, 99.9%) and fluoroethylene carbonate (FEC, 99.9%) were purchased from DodoChem Co., Ltd. (China), while ethyl difluoroacetate (EDFA, 97%) was provided by Aladdin. Prior to the preparation of electrolytes, pure solvents were dried by 4 Å zeolites for several days. For EDFA-FEC electrolyte, 1871 mg LiFSI was dissolved in 10 mL EDFA/FEC mixtures (9/1 by volume). All preparations were carried out in an argon (Ar)-filled glovebox, where the contents of H₂O and O₂ are less than 0.1 ppm.

Electrochemical measurements

Each CR-2016 type coin cell was fabricated in the Ar-filled glovebox. The Gr||Li coin cells were fabricated by Li metal, Celgard separator, and Gr electrode with 80 μ L electrolyte. Galvanostatic discharge/charge measurements for coin cells were conducted on Landt 2001 A testers and Neware battery test system (CT-4008T-5V10mA-164, Shenzhen, China). Electrochemical impedance spectroscopy (EIS) measurements were carried out on IviumStat electrochemical workstation with an AC amplitude of 10 mV over the frequency range of 100 kHz to 0.1 Hz. For Gr electrodes, the galvanostatic discharge/charge measurements were performed within the potential range of 0~1.5 V (vs. Li⁺/Li) and 1 C corresponds to 372 mAh g⁻¹. The Gr||Li coin cells were first cycled at 0.1 C for 10 cycles at different temperatures (-20, 25, 45 °C) to form solid electrolyte interphase (SEI) films on Gr electrodes with EDFA-FEC electrolyte. Then the Gr||Li cells were used to test the rate capabilities, cycling performance, and low-temperature performance. The low-temperature charge performance of Gr||Li cells with SEI formation at different temperatures was tested after discharging at corresponding SEI formation temperatures. Moreover, the Gr||Li coin cells were harvested after the SEI formation for 10 cycles to fabricate the symmetric Gr||Gr cells for impedance tests under different temperatures. For the electrochemical performance at different temperatures, the cells were placed in a constant temperature and humidity chamber, keeping at least 1.5 h at each temperature before electrochemical measurements.

Materials characterizations

⁷Li- and ¹⁷O-nuclear magnetic resonance (NMR) spectra of EDFA-FEC electrolytes were performed on 500 MHz Bruker NMR spectrometer (Switzerland) under different temperatures. For ⁷Li-NMR, the LiCl/D₂O electrolyte was used as internal standard in a coaxial NMR tube at 25 °C, and acetone-d6 was utilized as locking field substances in a coaxial NMR tube at temperatures other than 25 °C due to the freezing of D₂O in the test temperature lower than 0 °C. Raman spectroscopy analyses were carried out on XploRA Raman microscope (HORIBA Jobin Yvon, France) with 532 nm laser under different temperatures. Fourier transform infrared (FTIR) spectra were conducted on Thermo Fisher Nicolet 6700 spectrometer. Transmission electron microscope (TEM) analysis was carried out on Tecnai G2 F20 S-Twin (America) with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed to explore the composition of SEI on Gr anodes using a Thermo Scientific K-Alpha spectrometer with a monochromatic Al Kα radiation, accompanied with depth profiling which was carried out by Ar⁺ sputtering for 0, 50, 100, 200 s. Time of flight secondary ion mass spectrometry (ToF-SIMS, IONTOF, German) was employed to investigate the chemistry and structure of SEI on Gr anodes. A 30 keV Bi₃++ ion beam was used as the primary beam to detect the samples and a 2 keV Cs⁺ ion

beam was performed for the sputtering of the cycled Gr electrodes with a sputtered area ($300 \ \mu m \times 300 \ \mu m$). All the samples were washed with dimethyl carbonate (DMC) to remove residual electrolytes in an Ar-filled glove box.

Quantum chemistry calculations

Density functional theory (DFT) calculations were carried out using Gaussian 16 software package. The molecular geometrical configurations were optimized at the B3LYP/6-311G(d, p) level. Frequency analysis was done at the same time to ensure the obtained optimized stationary point. The binding energy (E_b) between solvent molecules and Li⁺ ions was calculated as following:

$$E_b = E_{total} - E_{Li} + - E_{solvent}$$

where E_{total} stands for the total energy of the complexes of solvent molecules coordinated with Li⁺; E_{Li^+} and E_{solvent} refer to the energy of the individual Li⁺ ion and solvent molecule, respectively.

Molecular dynamics (MD) simulations

Molecular dynamics (MD) simulations were carried out via the Forcite module, with electrolyte molar ratios obtained from the experimental results. Molecular forces were calculated by using the condensed-phase optimized molecular potentials for atomistic simulation studies II (Compass II) force field. Atomic partial charges were computed by the RESP2(0.5) method with the aid of Multiwfn.¹⁻³ Moreover, the Solvation Model Based on Density (SMD) was used at the B3LYP-D3(BJ)/def2-TZVP level. The acetone with a relative permittivity of 20.5 was chosen as the solvent for calculation. Using Amorphous Cell module, the initial structures of the electrolytes were established by randomly placing the Li⁺, FSI⁻ anions, EDFA solvents and FEC additives. The MD simulations were carried out at different temperatures (-20, 25, 45 °C). Using Nosé-Hoover thermostat and a Parrinello-Rahman barostat, the initial configuration was equilibrated for 1 ns in isothermal-isobaric ensemble (NPT) to

maintain at different temperatures and a pressure of 1 bar with timesteps of 0.5 fs. Another 10 ns simulation was then carried out in the canonical ensemble (NVT) under Nosé-Hoover thermostats at different temperatures. The radial distribution functions (RDFs) analysis was generated using the final 8.75 ns. The equilibrium structures of the MD simulations were extracted every 1000 frames for the calculation of the projected density of states (PDOS), which is determined by calculating the single point energy using CP2K/Quickstep software. The Grimme dispersion correction was performed to all atoms in combination with the molecularly optimized double- ζ basis set (DZVP-MOLOPT-SR-GTH) and the Perdew Burke Ernzerhof (PBE) generalized gradient approximation (GGA). The energy cutoff is 400 Ry, and the SCF convergence's target accuracy is 1.0×10^{-6} .

Temperatures(°C)	Coordination numbers		
	O (EDFA)	O (FEC)	O (FSI⁻)
45	2.49	0.63	2.29
25	2.63	0.79	2.09
-20	2.99	1.20	1.58

Table S1 The coordination numbers of the primary solvation sheath of Li^+ (within 3.0 Å) in the EDFA-FEC electrolyte under different temperatures.



Fig. S1 FTIR spectra of different solvents, EDFA+FEC mixed solvents and 1 M LiFSI in EDFA-based electrolytes under room temperatures.



Fig. S2 (a) ¹⁷O-NMR of the EDFA-FEC electrolyte under different temperatures and (b) the corresponding enlarged view of carbonyl O on FEC.



Fig. S3 Raman spectra of different solvents, EDFA+FEC mixed solvents and 1 M LiFSI in EDFA-based electrolytes under room temperatures.



Fig. S4 (a) Raman spectra of the EDFA-FEC electrolyte under different temperatures. The corresponding enlarged part of Raman spectra for (b) S-N-S stretching vibration of FSI⁻ and (c) carbonyl of EDFA solvents.



Fig. S5 Raman spectra of the 1 M LiFSI/EDFA electrolyte under different temperatures (-20, 25 and 45 °C).

The temperature-variable Raman was performed on the 1 M LiFSI/EDFA electrolyte to better confirm the enhanced Li^+ -FSI⁻ interaction at elevated temperatures, which excludes FEC because of its interference peak position at around 731 cm⁻¹ from the Raman spectra (Fig. S3). As shown in Fig. S5, when the temperature increases from -20 °C to 45 °C, the band of S-N-S stretching vibration of FSI⁻ anions exhibits a blueshift, well confirming the enhanced Li^+ -FSI⁻ interaction with elevated temperatures.



Fig. S6 (a) The structures and corresponding binding energies of $Li^+(EDFA)_n$ complexes and $Li^+(FEC)_n$ complexes (n represents the coordination numbers of solvents). (b) The binding energies of the $Li^+(EDFA)_{2.49}$, $Li^+(EDFA)_{2.63}$ and $Li^+(EDFA)_{2.99}$ calculated via linear interpolation. (c) The binding energies of the $Li^+(FEC)_{0.63}$, $Li^+(FEC)_{0.79}$ and $Li^+(FEC)_{1.20}$ complexes calculated via linear interpolation.

Owing to the electrostatic repulsion of the negative polarization of the anodes, the Li⁺-anion binding is usually neglected in the Li⁺ desolvation energy calculations.^{4, 5} Therefore, the interaction between different amounts of solvents (EDFA and FEC) and Li⁺ has been investigated by DFT calculations. The binding energy shows an increasing tendency as more EDFA solvents coordinate with Li⁺, so do FEC solvents (Fig. S6a). This means that the desolvation process would become more difficult. According to the coordination number in the first solvation sheath of Li⁺ obtained from the MD simulations (Fig. 1d-f), the coordination numbers of EDFA solvents at 45, 25 and -20 °C are 2.49, 2.63 and 2.99, respectively. The desolvation energy of Li⁺(EDFA)_n complexes can be evaluated via linear interpolation (n represents the coordination numbers of EDFA solvents at different temperatures), which yields -105.7, -108.9 and -117.1 kcal mol⁻¹ for the Li⁺(EDFA)_{2.49}, Li⁺(EDFA)_{2.63} and Li⁺(EDFA)_{2.99} complexes (Fig. S6b), respectively. In addition, according to the MD simulations, the coordination numbers of FEC solvents at 45, 25 and -20 °C are 0.63, 0.79 and 1.20, respectively. The desolvation energy of Li⁺(FEC)_n complexes can also be evaluated via the same method ((Fig. S6c), which shows that the Li⁺ desolvation energy is -31.8, -39.9 and -58.4 kcal mol⁻¹ for the Li⁺(FEC)_{0.63}, Li⁺(FEC)_{0.79} and Li⁺(FEC)_{1.20}, respectively. Therefore, the weakened Li⁺-solvent interaction with elevated temperatures would help lower the Li⁺ desolvation energy and facilitate the desolvation process at the electrolyte/electrode interface.



Fig. S7 The S2p spectra of the inner SEI films with different Ar^+ sputter durations for Gr anodes with SEI formation at (a) 45, (b) 25 and (c) -20 °C.

The SEI formed at 45 °C exhibits the highest content of anion-derived S-contained products in the inner layer of SEI. Moreover, the SEI formed at 25 °C shows slightly higher content of anion-derived S-contained products than that formed at -20 °C. The increased content of anion decomposition products with temperatures corresponds to the solvation structure with more anion participation at higher temperature.



Fig. S8 The O1s spectra of the Gr anodes with SEI formation at different temperatures of (a) 45, (b) 25 and (c) -20 °C.



Fig. S9 The C1s spectra of the SEI film surface formed at different temperatures for Gr anodes.

The lowest content of C-O and C-C/C-H species can be observed from the SEI formed at 25 °C, indicating the generation of SEI film with low organic content at 25 °C. Moreover, the SEI formed at -20 °C exhibits the highest content of C-C/C-H species, suggesting the formation of organic-rich SEI on Gr anodes. This corresponds to more solvents participating in the solvation sheath of Li⁺ at low temperature. However, the SEI formed at 45 °C shows slightly higher C-C/C-H species than that formed at 25 °C.



Fig. S10 The O1s spectra of (a) the pristine Gr electrode and (b) the Gr electrode resting in the EDFA-FEC electrolyte at 45 °C for 5 days.

In the O1s spectra, the intensity of C-O peak of the Gr electrode resting in the EDFA-FEC electrolyte at 45 °C is obviously stronger than that of the pristine Gr electrode, indicating the increase of organic components at the surface of Gr electrode. This can be ascribed to the slight thermal reduction of solvents at the higher temperature of 45 °C, which can explain the higher content of organic components in the SEI formed at 45 °C.



Fig. S11 (a) The C1s spectra of Gr anodes after discharging to 0 V (Li^+/Li) at 25 °C. (b) The C1s spectra of Gr anodes resting in the electrolyte at 45 °C for 3 days after discharging to 0 V (Li^+/Li) at 25 °C.

According to the C1s spectra, the Gr anodes in lithiation stage exhibit the distinctly higher content of C-F, CO_3^{2-} and C-O species after resting in the electrolyte at 45 °C, indicating the reduction decomposition of fluorinated solvents during the rest of the battery. Combined with the O1s spectra of pristine Gr anodes resting in the electrolyte at 45 °C (Fig. S10), it is jointly confirmed that the content of organic components in the SEI formed at 45 °C is higher than that formed at 25 °C.



Fig. S12 Contour plots of the F1s spectra of the Gr anodes with SEI formation at different temperatures of (a) 45, (b) 25 and (c) -20 °C. The fitted F1s spectra of the inner SEI films with different Ar⁺ sputter durations (50 s and 100 s) for Gr anodes with SEI formation at (d) 45, (e) 25 and (f) -20 °C. It should be noted that LiF species are derived from the joint reduction decomposition of the fluorinated solvents (including EDFA and FEC solvents) and FSI⁻ anions.



Fig. S13 The normalized depth profiles of the representative fragments of the SEI formed at (a) 45 °C, (b) 25 °C and (c) -20 °C.



Fig. S14 Discharge/charge curves of the Gr anodes with SEI formation at (a) -20 °C, (b) 25 °C and (c) 45 °C under different rates. (d) The corresponding discharge medium voltage of the Gr anodes with SEI formation at different temperatures under different rates.

The Gr anode with SEI formation at 25 °C exhibits the higher discharge medium voltage, indicating the smaller polarization. This corresponds to the higher capacity and better rate capability for the Gr anodes with SEI formation at 25 °C. However, the Gr anode with SEI formation at 45 °C shows the lowest discharge medium voltage, suggesting the largest polarization and poor rate performance.



Fig. S15 (a) The charge curves of Gr||Li half cells with SEI formation at different temperatures (-20, 25 and 45 °C) under -20 °C at 0.1 C after discharging at corresponding SEI formation temperatures and (b) the enlarged plot.



Fig. S16 Discharge/charge curves of the Gr anodes with SEI formation at different temperatures (-20, 25 and 45 °C) under low temperatures at 0.1 C.



Fig. S17 Discharge/charge curves of Gr anodes with SEI formation at different temperatures (-20, 25 and 45 °C) under low temperature of -45 °C at 0.05 C.



Fig. S18 Discharge/charge curves of Gr anodes with SEI formation at different temperatures (-20, 25 and 45 °C) under low temperature of -20 °C.



Fig. S19 The discharge/charge performance of Gr anodes with high mass loading (~10 mg cm⁻²) at 0.1 C under -20 °C.

The Gr anode with SEI formation at 25 °C shows the smallest polarization than that with SEI formation at -20 °C and 45 °C under the temperature of -20 °C. Moreover, it can achieve a reversible capacity of 303 mAh g⁻¹ at 0.1 C, corresponding to a capacity retention of 88.9% compared to that at 25 °C. It should be mentioned that the achieved reversible capacity for the Gr anode formed SEI at 25 °C is slightly lower than the Gr anode with low mass loading (336 mAh g⁻¹) due to the increased ion transport resistance. However, it is still superior to the cells with SEI formation at -20 °C (203 mAh g⁻¹) and 45 °C (256 mAh g⁻¹). The results confirm the superiority of the SEI formed at 25 °C, which is consistent with the Gr anodes with low mass loading.



Fig. S20 The charge capacity retention of Gr||Li half cells with SEI formation at different temperatures (-20, 25 and 45 °C) under low temperatures of (a) -30 and (b) -40 °C at 0.1 C after discharging at corresponding SEI formation temperatures.

It can be detected from Fig. S20a that Gr anodes with SEI formation at 25 °C exhibit a low overpotential of ~0.21 V with high capacity retention of 98.7% at low temperature of -30 °C, which is superior to those with SEI formation at -20 °C and 45 °C. As a sharp comparison, the charging process of the Gr anode formed SEI at 45 °C displays the largest overpotential of ~0.31 V with the lowest capacity retention of 96.1%. When the charging process is performed at the temperature of -40 °C, the Gr anode with SEI formation at 25 °C shows a slight increase of overpotential (~0.31 V) compared to its overpotential at -30 °C and it still exhibits the highest capacity retention (98.5%) compared to those with SEI formation at -20 °C and 45 °C.



Fig. S21 The charge capacity retention of Gr||Li half cells with SEI formation at different temperatures (-20, 25 and 45 °C) under ultra-low temperatures of (a) -50, (b) -60 and (c) -70 °C) at 0.1 C after discharging at corresponding SEI formation temperatures. (d) The charge specific capacity of Gr||Li cells with SEI formation at different temperatures under -70 °C at 0.1 C after discharging at corresponding SEI formation temperatures. (e) The charge polarization voltage (medium voltage) of Gr||Li half cells with SEI formation at different temperatures.



Fig. S22 (a-e) The Nyquist plots obtained from Gr||Gr cells with SEI formation at different temperatures (-20, 25 and 45 °C) under ultra-low temperatures. (f) The fitted resistance values of SEI films formed at different temperatures (-20, 25 and 45 °C).



Fig. S23 The activation energy of the SEIs formed at different temperatures (-20, 25 and 45 °C).



Fig. S24 The cycling performance and corresponding discharge/charge curves of Gr anodes with SEI formation at different temperatures (-20, 25 and 45 °C).

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