

Supplementary Information

Experimental Section

Preparation of electrolytes

In an Ar-filled glovebox (Mikrouna) with H₂O and O₂ content less than 0.1 ppm, LiTFSI is dissolved into Poly(ethylene glycol) methyl ether acrylate (PEGMEA) and stirred for 30 minutes to forming homogeneous liquid solutions with concentration of 0.35 M, 1 M and 5 M. Poly(ethylene glycol) methyl ether acrylate (PEGMEA) is chosen as the solvent due to the commendable ionic conductivity in both unpolymerized state and polymerized state. LiTFSI is chosen as the lithium salt because of its decent dissociation ability. To prepare solid electrolytes, 0.5 wt% azobisisobutyronitrile (AIBN) was added into the liquid solutions with three kinds of concentration for free radical polymerization. After mixing well, the obtained homogeneous molten precursor was injected into cellulose membrane and heated at 60 °C for 6 hours for the sufficient polymerization. Finally, the solid electrolyte with concentration of 0.35 M, 1 M and 5 M were obtained.

Interfacial characterization

The morphology of Li metal retrieved from Li/Li symmetrical cell was investigated by a field emission scanning electron microscopy (Hitachi S-4800 at 5 kV). Infrared spectra measurements were conducted on a Fourier transform infrared spectrometer (Bruker VERTEX 70). X-ray photoelectron spectroscopy (XPS) was employed to detect the interfacial components on the surface of Li anode and it was performed on a Thermo Scientific ESCA-Lab 250Xi.

In-situ FTIR measurement

In-situ FTIR measurement was carried out on NICOLET 6700. The diamond is transparent to infra-red light and allow the beam to reach the working electrode (Li metal), and the counter electrode (Li metal) positioned aside the composite electrolyte. This configuration ensures good accessibility to the electrode of interest which is

necessary as the infrared beam is incident at an angle to obtain maximum reflection intensity. 50 μm ultrathin Li foils are used in battery assembly for better interfacial observation. The assembly process: First of all, they are stacked in the order of lithium, electrolyte and lithium, and then packaged into the customized electrochemical cell, finally the customized electrochemical cell is sealed by vacuum silicone grease and parafilm.

Deuterium-oxide (D_2O) titration and excess H_3PO_4 (2 M) acid titration:

The *on-line* DEMS system was used to real-time monitor the gas evolution during charge-discharge processes of ECC-DEMSTM Li/Li symmetrical cells. And the *on-line* DEMS system (Hiden Analytical Ltd.) in turn composed of carrier gas cylinder, a mass flow controller (MFC), gas drying bottles, ECC-DEMSTM electrochemical cell (EL-CELL GmbH), self-made cold-trap unit, and mass spectrometer (HPR-20, Hiden Analytical Ltd.). Then, we developed a gas analysis method by replacing the ECC-DEMSTM electrochemical cell of our *on-line* DEMS system with a titration unit. D_2O titration experiments on 50 μm thin lithium metal ($2\text{Li} + 2\text{D}_2\text{O} \rightarrow 2\text{LiOD} + \text{D}_2\uparrow$) is used to estimate the Li and LiH content in cycled Li anode by *on-line* gas analysis MS system. For the identification the moles percentage of LiH and typical SEI components in Li anodes cycled in dilute and concentrated electrolyte respectively, in an Ar-filled glovebox with H_2O and O_2 content less than 0.1 ppm, plated and stripped Li anodes were carefully disassembled from the charged cells, then carefully rinsed with dimethoxyethane (DME, aiming to exclude the effects of lithium salts), dried, weighed and well-sealed in the container of the titration unit. It was noted that, every time, the components of the titration unit were washed with anhydrous alcohol and acetone for several times and dried at 80 $^\circ\text{C}$ for 12 hours under vacuum conditions. After connecting the sample-containing titration unit, the Ar carrier gas was switched to go through the titration unit, then 1 mL D_2O was injected. For quantitative comparison, the intensity signal of D_2 , HD, CO_2 , and CH_3D gas was divided by the intensity of the carrier gas (Ar), the resulting ratio was multiplied by the flow rate (1.5 mL min^{-1}) and

divided by the weighed sample mass to get the flow rate per unit mass ($\text{umol min}^{-1} \text{mg}^{-1}$, adopting $V_m = 24.5 \text{ L mol}^{-1}$, 25°C , 101 KPa). The amount (umol mg^{-1}) of each gas was determined by plotting the processed data and integrating the peak area exclude the baseline. Then, the mole of D_2 , HD , CO_2 , and CH_3D , and the corresponding mole of Li , LiH , lithium alkylcarbonate (LAC, such as ROCO_2Li and $(\text{CH}_2\text{OCO}_2\text{Li})_2$), and CH_3Li in cycled Li anode were calculated. In subsequent, the total mole amount of Li_2CO_3 is measured by the excess H_3PO_4 (2 M) acid titration on as-obtained D_2O aqueous solution (still conducted in the *on-line* titration MS system).

Molecular dynamics (MD) simulations of the solvation structure:

We performed the MD simulations for electrolyte mixtures (PEGMEA; LiTFSI) to observe the structural changes of the electrolyte mixtures. Firstly, the optimized electrolyte molecules were packed in a periodic box with a 13 \AA linear dimension to construct the bulk systems. The molar ratios used in our simulations was taken from the experimental conditions (6:1, 3:1 and 1: 2 for PEGMEA : LiTFSI). Secondly, MD calculations were performed using the Forcite code with Universal force field. The electrolyte mixtures system was initially relaxed in the NPT (i.e., isothermalisobaric) for 1000 ps to obtain equilibrium. The time step is 1.0 fs. Then, NVT (i.e., isothermal) MD simulations were performed for 1000 ps. Finally, the first-principle calculations of partial density of states were conducted using the plane-wave-based periodic DFT method in CASTEP code. The electron exchange-correlation potential and the core electrons of atoms were treated by the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. The k-points for Brillouin zone were 0.5 \AA^{-1} for bulk calculations and the cutoff energy was set to 400 eV. The convergence tolerance geometry optimization was set to $1.0 \times 10^{-5} \text{ eV atom}^{-1}$ for energy, $3.0 \times 10^{-2} \text{ eV \AA}^{-1}$ for maximum force, $5.0 \times 10^{-2} \text{ GPa}$ for max stress and $1.0 \times 10^{-3} \text{ \AA}$ for maximum displacement, respectively.

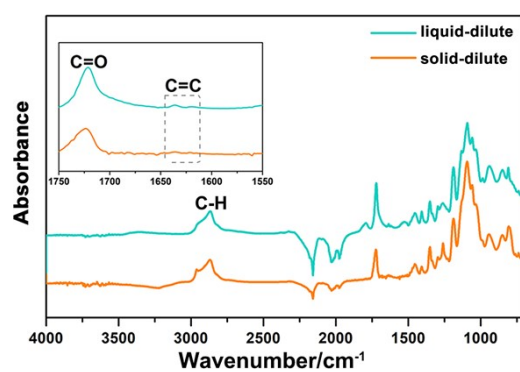


Figure S1. FTIR spectra of liquid dilute electrolyte and corresponding polymerized solid dilute electrolyte.

It can be seen that the peak located at about 1635 cm⁻¹ belonging to the stretching vibration of C=C on PEGMEA disappeared after in-situ polymerization, indicating the completion of aggregation.

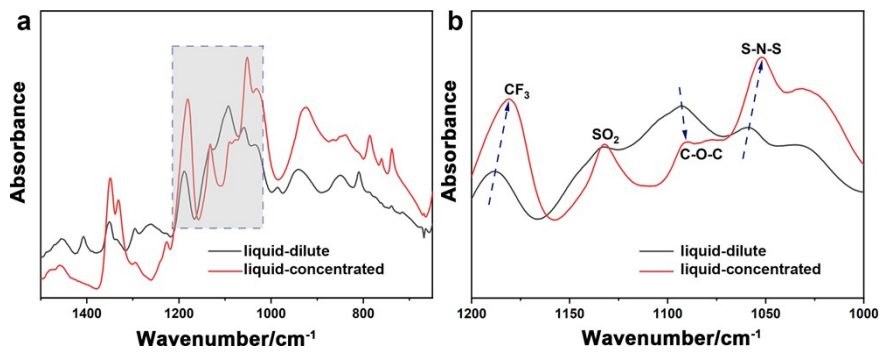


Figure S2. (a) FTIR spectra of liquid dilute electrolyte and liquid concentrated electrolyte and (b) the magnification between 1200 cm^{-1} and 1000 cm^{-1}

Compared to liquid dilute electrolyte, the peaks of CF_3 , SO_2 and S-N-S in concentrated electrolyte all enhanced and exhibited an obvious red shift due to the increase of lithium salt concentration. In the meantime, C-O-C exhibited a red shift due to the interaction with Li^+ .

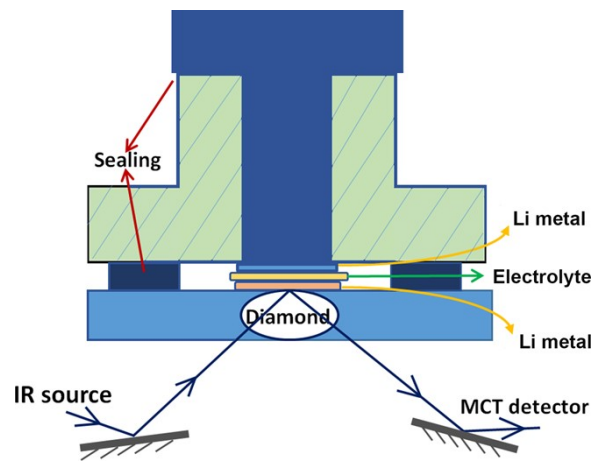


Figure S3. The schematic diagram of the in-situ FTIR measurement.

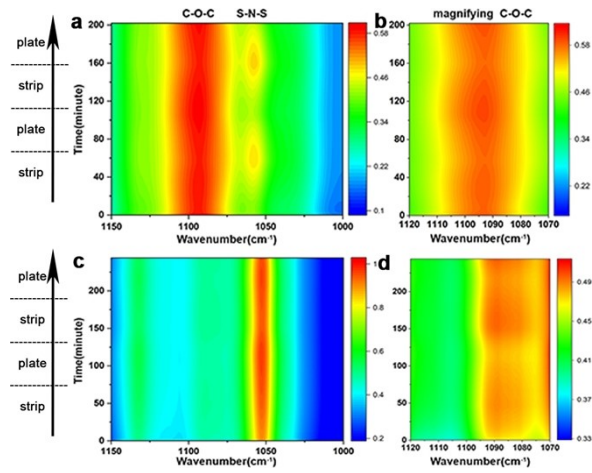


Figure S4. Time-resolved stacked FTIR plots of C–O–C, S–N–S peaks at the interface with electrolytes of (a-b) solid dilute electrolyte and (c-d) solid concentrated electrolyte at the first two lithium stripping and plating cycles.

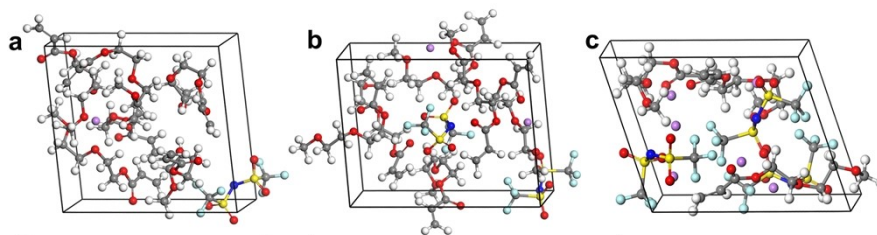


Figure S5. DFT-MD simulations of coordination situation in electrolytes with different PEGMEA units to LiTFSI molar ratios: (a) 6:1, (b) 3:1 and (c) 1:2. The hydrogen, lithium, carbon, nitrogen, oxygen, fluorine, phosphorus, and sulfur atoms are represented by white, purple, grey, blue, red, green, orange, and yellow, respectively.

Coordination behavior between solvent and lithium salt with different concentration is indicated by MD simulations for the understanding of local interactions and speciation. The 6:1 system has an absolutely solvent dominated structure with a small fraction of the lithium salt distributed in solvent. In the high salt concentration system of 1:2, the salt-rich domains are particularly prominent. A significant increase in the number of Li^+ ions coordinating to PEGMEA is demonstrated.

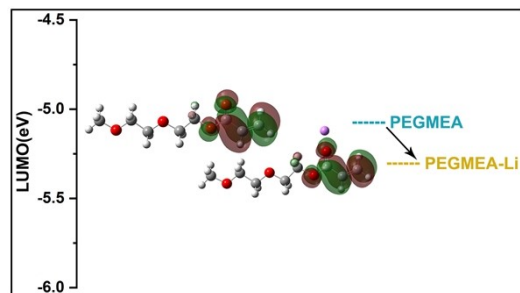


Figure S6. Comparisons among the LUMO levels of pure solvent [PEGMEA] and ion-solvent complexes [Li⁺-ion-PEGMEA].

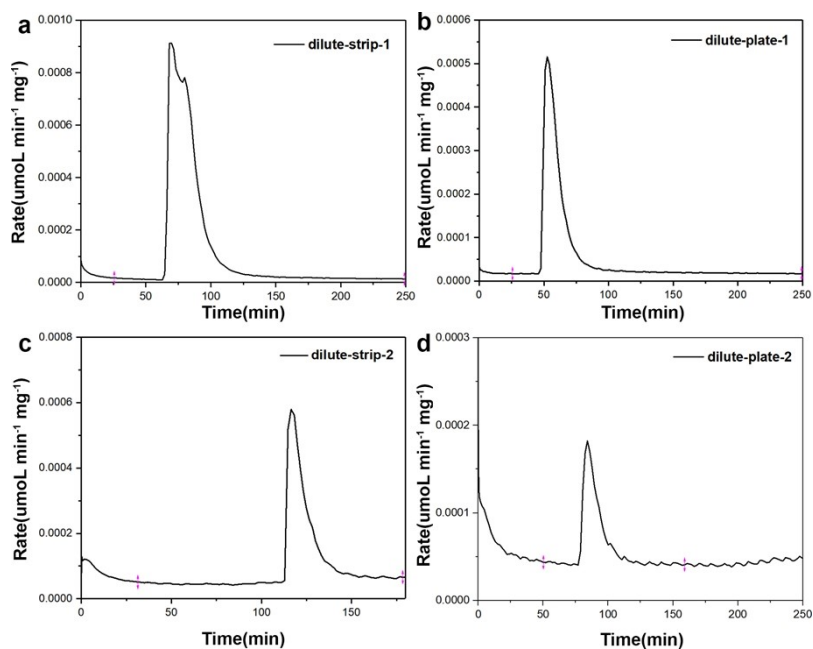


Figure S7. The CO_2 gas evolution rate curve after H_3PO_4 titration on the as-obtained D_2O aqueous solution (after D_2O titration on lithium metal cycled in dilute electrolyte): (a) Li metal after stripping process in the first cell; (b) Li metal after plating process in the first cell; (c) Li metal after stripping process in the second cell; (d) Li metal after plating process in the second cell (mg^{-1} , divided by the sample mass for D_2O titration)

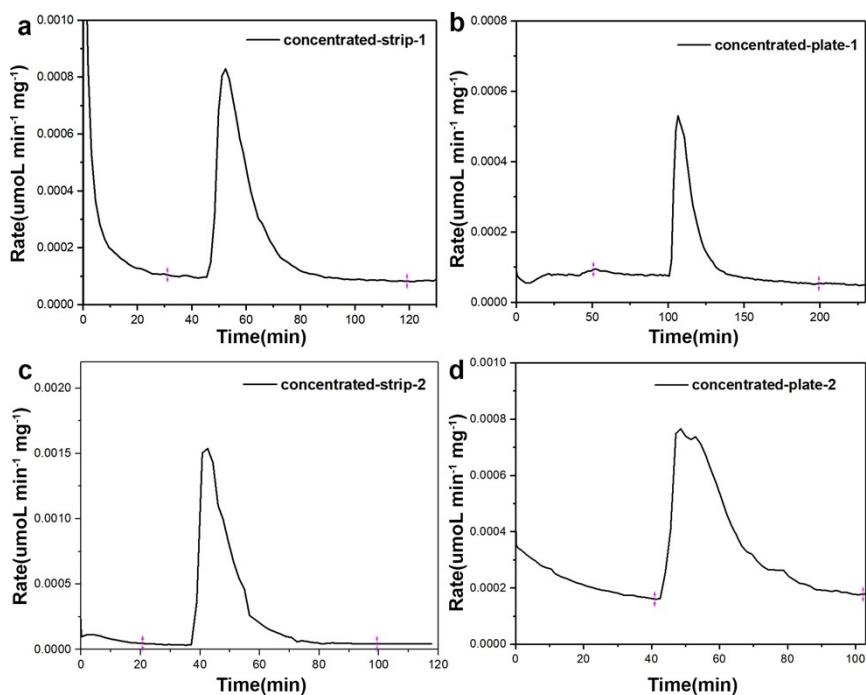


Figure S8. The CO₂ gas evolution rate curve after H₃PO₄ titration on the as-obtained D₂O aqueous solution (after D₂O titration on lithium metal cycled in concentrated electrolyte): (a) Li metal after stripping process in the first cell; (b) Li metal after plating process in the first cell; (c) Li metal after stripping process in the second cell; (d) Li metal after plating process in the second cell (mg⁻¹, divided by the sample mass for D₂O titration)

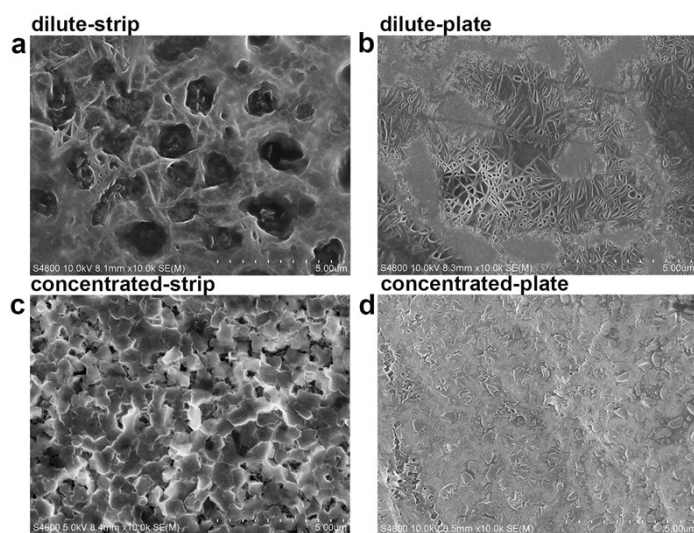


Figure S9. Typical SEM images of the morphologies of Li metal after stripping process and plating process in (a, b) dilute electrolyte and (c, d) concentrated electrolyte.