A reversible dendrite-free high-areal-capacity lithium metal electrode

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Reversible dendrite-free low-areal-capacity lithium metal electrodes have recently been revived, because of their pivotal role in developing beyond lithium ion batteries. However, there have been no reports of reversible dendrite-free high-areal-capacity lithium metal electrodes. Here we report on a strategy to realize unprecedented stable cycling of lithium electrodeposition/stripping with a highly desirable areal-capacity (12 mAh cm\(^{-2}\)) and exceptional Coulombic efficiency (>99.98%) at high current densities (>5 mA cm\(^{-2}\)) and ambient temperature using a diluted solvate ionic liquid. The essence of this strategy, that can drastically improve lithium electrodeposition kinetics by cyclic voltammetry premodulation, lies in the tailoring of the top solid-electrolyte interphase layer in a diluted solvate ionic liquid to facilitate a two-dimensional growth mode. We anticipate that this discovery could pave the way for developing reversible dendrite-free metal anodes for sustainable battery chemistries.
Dendritic growth of lithium deposits has plagued the reality of Li-metal-based batteries for approximate four decades, specifically in terms of safety and battery lifetime. The persistent thrust to solve this issue has always been driven by the unprecedented characteristics of lithium electrode, that is, its high theoretical specific capacity of 3,861 mAh g\(^{-1}\) and low electrochemical potential (−3.04 V versus standard hydrogen electrode), for the implementation of high specific energy Li-metal-based batteries. To circumvent the propagation of lithium dendrites, intense studies of metallic lithium electrodes (MLEs) have used strategies for conducting stable lithium electrodeposition such as maintaining a sustained supply of Li\(^{+}\) in the vicinity of MLE surface, the spatial redistribution of Li\(^{+}\) surge along tailored interphase (SEI) films, enhanced Li\(^{+}\) surface diffusivity and the fabrication of Li metal with high surface energy. As a result of these strategies, reversible dendrite-free low-areal-capacity MLEs (0.5–3.0 mAh cm\(^{-2}\)) have been developed. The underlying nature of these advances is closely related to the supply of a locally homogeneous current density or the physical blocking of dendrite growth with less considerations of manipulating lithium electrodeposition kinetics itself.

High areal-capacity and excellent Coulombic efficiency (CE) of MLEs, dependent on the dendrite-free two-dimensional (2D) growth, are highly desirable for the development of high specific energy Li-metal-based batteries. In order for 2D growth mode to prevail, the interlayer transport of deposited lithium adatoms must be fast enough to prevent the onset of nucleation of islands on the yet undeveloped growing islands. Kinetic models and physical arguments indicate that 2D growth should occur when the critical island size (\(I_{\text{crit}}\)) is greater than the separation between 2D nuclei (\(I_{s}\)). To fulfill this condition, enhancing the surface diffusivity of D and nucleation density (decreasing \(I_{s}\)) or reducing the magnitude of the Ehrlich–Schwoebel barrier (\(E_{\text{ess}}\)) by the surfactant (increasing \(I_{\text{crit}}\)) are promising methods, which can be realized by the addition of halogenated salts or enhancing the operating temperature. Yang et al. demonstrated an organic surface modifier to interact with the deposited metal by its functional organic group to yield a 2D growth mode. Based on the well-known mosaic SEI layer model, a possible candidate for a surfactant to decrease \(E_{\text{ess}}\) is oligomer species stemming from the solvent in the battery electrolytes that are spatially inhomogeneously distributed. A unique, promising way of tailoring the top SEI layer, unveiled by Xu et al., is the application of an electrochemically reduced solvation sheath (SS) of Li(solvent)\(^{+}\) under the orientated migration, as long as the reduction potential of the neutral co-solvent falls in a narrow range. Recent advances on reversible Mg electrodeposition obviously manifest the crucial importance of solvent candidate (long-chain ether molecules) that has a high binding energy with Mg\(^{2+}\) to create the robust SS.

Herein, we design and demonstrate a diluted solvate liquid (DSIL) composed of the solvent of tetraethylene glycol dimethyl ether (G4 or \(\text{C}_9\text{H}_{18}\text{O}_5\)) and the salt of lithium bis(fluorosulfonyl)imide (LiFSI or Li(N(SO\(_2\)F))\(_2\)) that possesses a robust SS of Li(2G4)\(^{+}\) in the presence of the co-solvent 1,3-dioxolane (DOL or \(\text{C}_3\text{H}_6\text{O}_2\)) to realize high areal-capacity and superior CE of MLEs at ambient temperature. Various in situ or ex situ characterization and simulation tools have been employed to analyse the tailored top SEI layer and observe the growth mode of lithium electrodeposits aiming at correlating our proposed strategy with the 2D growth mode.

**Results**

**Lithium electrodeposition onto Cu.** The co-solvent of DOL (\(E_{\text{h,DOL}} = −1.48\) V versus Li/Li\(^{+}\)) was successfully screened with attempts to decrease the viscosity of LiFSI-2G4 (\(E_{\text{h,G4}} = −1.49\) V versus Li/Li\(^{+}\)) on the premise of the preservation of the solvation manner of Li\(^{+}\) at ambient temperature, as demonstrated by the dominant presence of solvating peak at 870 cm\(^{-1}\) in spite of the added volume of DOL (Supplementary Fig. 1). The composition of LiFSI-2G4-50 vol% DOL was determined by a substantial increase in the ionic conductivity (4.82 \(\times\) 10\(^{-5}\) S cm\(^{-1}\)), double increase in the lithium-ion transference number (0.63), drastic 10-fold decrease in the viscosity (2.98 mPa s), sweeping-dependent electrochemical window (≥5.5 V after five sweeps) and reduced interfacial resistance (57 \(\Omega\) cm\(^2\) after 3 weeks) (Supplementary Figs 2 and 3), as compared with LiFSI-2G4. Cyclic voltammetry (CV) measurements reveal unexpected increases of plating current density (\(I_{p}\)) using the solvate liquid (SIL) of LiFSI-2G4 and the DSIL of LiFSI-2G4-50 vol% DOL in Fig. 1a. After 30 cycles, the onset potential of bulk lithium electrodeposition onto Cu substrate was shifted positively for the SIL and the DSIL; the overpotential for \(I_{p}\) of 5.0 mA cm\(^{-2}\) was −0.16 V for the SIL and −0.07 V for the DSIL as shown in Fig. 1b and Supplementary Fig. 4. Energy dispersive X-ray Cu mapping (purple) of the Cu electrode after CV measurements (premodulation) shows that lithium nuclei were distributed on the Cu surface, some of which are coalesced into a large planar lithium island of 10–30 \(\mu\)m in length with concentrated O elemental mapping in orange (Supplementary Fig. 5). The surface chemistry of MLE after CV premodulation does not initially exhibit the hard-removed inherent contamination from lithium carbides (Li(C\(_x\))) species, however, after 5 min of etching, they instantaneously appear beneath a G4-enriched top-SEI film from the SS of Li(2G4)\(^{+}\) (Supplementary Fig. 6). It is reasonable to assume that a non-thermodynamic-reduced SEI chemistry will take place on the surface of newly formed lithium islands and the uncovered lithium metal substrate, as a result of the preferential reduction of the SS over that of DOL (the decreased decomposition from DOL at the top surface as shown in Fig. 5b).

Morphology evolution of lithium electrodeposits with deposition time was monitored by a home-built visualization Li|Cu cell (see Methods section) as shown in Fig. 1c. Figure 1d and Supplementary Movie 1 show typical images of lithium electrodeposits in a conventional carbonate-based electrolyte at 1.0 mA cm\(^{-2}\) and ambient temperature. In agreement with commonly accepted knowledge, three-dimensional uncontrollable propagation of lithium electrodeposits takes place onto the top of randomly distributed lithium nuclei. However, the distribution of lithium nuclei was uniformized in the case of DSIL as shown in Fig. 1e and lithium electrodeposits with a high spatially homogenization were grown along the spherical Cu surface with time to totally cover Cu surface at 120 min (Supplementary Fig. 7a). After the application of CV premodulation, the distribution of lithium nuclei was even more uniform and a full coverage of Cu was achieved more rapidly. Lithium electrodeposition was observed to grow coaxially and layer by layer as shown in Fig. 1f and Supplementary Movie 2. Even at 5.0 mA cm\(^{-2}\), the same 2D layer-by-layer dendrite-free growth mode was witnessed in Supplementary Fig. 7c and Supplementary Movie 3. However, inhomogeneous and non-coaxial lithium electrodeposition was observed in other electrolytes as shown in Supplementary Fig. 7b–d.

**Cycling stability of MLE.** CE of the Li|Cu cell using the DSIL was found to be strongly dependent on the CV premodulation. In Fig. 2a, the initial CE of the cell was drastically enhanced from 39.0 to 90.5% at 5.0 mA cm\(^{-2}\) and 3.0 mAh cm\(^{-2}\) upon the application of the CV premodulation, where the new calculation...
method (equation 1) takes into account of the $Q_r$—the capacity for residual lithium electrodeposits onto Cu substrate after the CV premodulation. As shown in Supplementary Fig. 8, the $Q_r$ was determined as 0.25 mAh cm$^{-2}$. In Fig. 2a, compared to symmetric lithium plating/stripping in the Li|Cu cell without CV premodulation, distinct difference in the cell overpotential was observed for the Li|Cu cell under the CV premodulation, where the stripping overpotential of 32 mV is much lower than the continuously increasing plating overpotential from 130 to 190 mV, indicating continuous nucleation of lithium electrodeposits on the Cu substrate upon plating and the other side of Li electrode renders lithium electrodeposition in a more facile path. Moreover, the initial CE of the cell surprisingly increases with increasing fixed plating areal capacity in Fig. 2b. The calculated initial CE is 38.4% for 1 mAh cm$^{-2}$, 90.5% for 3 mAh cm$^{-2}$, 95.2% for 5 mAh cm$^{-2}$ and 98.0% for 12 mAh cm$^{-2}$. For long-term cycling tests, the average CE of the cell delivering 3 mAh cm$^{-2}$ is 83.2% for 8 cycles, 99.73% for 500 cycles and 99.86% for 999 cycles in Fig. 2c. From the eighth cycle, the theoretical stripping areal capacity of 3 mAh cm$^{-2}$ can be realized; the average CE of the cell delivering 12 mAh cm$^{-2}$ was calculated to be higher than 99.98% for 450 cycles in Fig. 2d. Two typical plating plateaus were always witnessed in Fig. 2c,d, where the second plateau with higher-plating overpotential regularly follows the first plateau with lower-plating overpotential and the stripping capacity is consistently higher than the plating capacity from the first plateau in each cycle but the overpotential between these two reverse processes is symmetrical. Figure 2e,f show excellent cycling stability of the Li|Li cell delivering the areal capacity of 12 mAh cm$^{-2}$ with the DSIL after CV premodulation at 5.0 mA cm$^{-2}$ and 25°C for 100 cycles (total-charge passed: 8,640 C cm$^{-2}$). No sudden decrease, spikes and erratic fluctuations in the cell potential were observed on cycling. Two distinct plateaus were also observed in the Li|Li cell. Scanning electron microscopy (SEM) top-view and cross-sectional views of lithium electrodes after cycling reveal dendrite-free planar lithium surface with pits and laminated lithium planar films (Supplementary Fig. 9). EDX mapping from the cross-sectional electrodeposited Li presents the concentrated atomic ratio of C and O probably stemming from the SS of Li(2G4)$^+$ (Supplementary Fig. 10$^{27}$). Even at an exceptionally high current density of 10.0 mA cm$^{-2}$, stable cycling was also realized under the same conditions (Supplementary Fig. 11). To the best of our knowledge, this is the first report of a symmetric coin-cell of Li|Li showing superior cycling with a practical high areal-capacity of 12 mAh cm$^{-2}$ at a high current density of 10 mA cm$^{-2}$ and 25°C.

### Sweeping time-dependent positively charged lithium substrate.

To elaborate the key role of CV premodulation, CV measurements were performed under different conditions in Fig. 3a. CE of lithium electrodeposition was found to strongly rely on the sweep rate and potential range. During the first cathodic sweep at 5.0 mV s$^{-1}$, the lithium stripping rate from the lithium is faster than the lithium electrodeposition rate on the Cu substrate (0 to $-0.3$ V). The lithium plating rate increased in the range of $-0.3$ to $-0.2$ V, possibly due to the change of deposition sites from the Cu–Li interface to Li–Li interface on Cu in Fig. 3c. A substantial amount of lithium stripped from the lithium anode remained in the bulk electrolyte and participated in the reverse step of lithium electrodeposition onto lithium cathode to render...
CE greater than 100% at 5.0 mV s\(^{-1}\). During the first anodic sweep, lithium electrodeposition onto lithium cathodes is observed to be facilitated at low sweep rate (that is, the longer span for creating positively charge lithium anodes to adsorb multidentate solvent of G4 and then facilitate lithium electrodeposition kinetics) in Fig. 3b. At a higher sweep rate of 50 mV s\(^{-1}\), the similar evolution was usually witnessed at the fourth sweep. During the second cathodic sweep at 5.0 mV s\(^{-1}\), the plating current density for lithium electrodeposition onto Cu is comparable to the first stripping current density but twice higher than the first plating current density in Fig. 3c. Lithium electrodeposition takes place onto previous residual lithium electrodeposits in the ensuing cathodic sweeps. As a result, the Li|Cu cells should be regarded as the Li–Li|Cu–Li cells from the electrodeposition takes place onto previous residual lithium.

After CV premodulation, galvanostatic lithium electrodeposition/stripping was performed on Cu substrate for a short period to observe the formation of lithium electrodeposits by SEM as shown in Fig. 3d. Two distinct plateaus were again produced. Large planar patch-like lithium electrodeposits with ca. 30 \(\mu\)m in width were observed to grown onto the smaller lithium particles generated from the CV premodulation and to coalesce with neighbouring analogues.

To further study the impact of CV premodulation ahead of the bulk lithium electrodeposition, in situ CV/quartz crystal microbalance (QCM) measurements were performed using three-electrode cells in the range of 0–3.1 V in different electrolytes. No increase in the peak current was observed in the electrolyte of LiPF\(_6\)-EC-DEC (Supplementary Fig. 13a). The peaks during the cathodic and anodic sweeps are comparable for SIL and DSIL (Supplementary Fig. 13b,c) with an unexpected increase in the current density that are ascribed to underpotential deposition/stripping\(^{35}\). During the second anodic sweep, the continuous increase in the mass of the Ni substrate using DSIL presents solid evidence that G4 is supposed to interact with positively charged lithium deposits derived from the underpotential deposition during the second cathodic sweep at 0.95 V in Fig. 3e. However, the increase in the mass of the Ni substrate during the second anodic sweep for SIL was not observed, which suggests that G4 is not facile to interact with the positively charged lithium deposits in the high viscous SIL. After four sweeps, Ni-coated quartz crystal has been coated by underpotential-deposited lithium. From 3.0 to 1.5 V, the slight decrease in the mass implies de-adsorption of G4 from positively charged lithium on Ni (Supplementary Fig. 13c). The irreversible mass of \(\Delta m_{\text{irr}}\) upon cycling, referring to the accumulation of SEI, was observed to be negligible for the DSIL electrolyte when the cycling number increased to five (Supplementary Fig. 13d), but continuously increased for the SIL and carbonate-based electrolytes. According to the slope of the two curves arising from the potential zone of 1.3 to 0.42 V and 1.3 to 2.65 V\(^{36}\), the molar mass of the species for electrodeposition/stripping was calculated as 6.94 g mol\(^{-1}\) that is close to that of Li (Supplementary

**Figure 2** | **Cycling stability of MLE.** Electrochemical performance of lithium electrodeposition/stripping on Cu or Li electrode in the DSIL of LiFSI-2G4-50 vol% DOL at 5.0 mA cm\(^{-2}\) and 25 °C. (a) Impact of CV premodulation on the first CE. (b) Dependence of the fixed plating capacity of Li|Cu cells on the first CE after CV premodulation; (c,d) voltage versus capacity profile for the Li|Cu cell under CV premodulation with a fixed plating capacity of 3.0 mAh cm\(^{-2}\) (c) and 12 mAh cm\(^{-2}\) (d); voltage versus time (e) and voltage versus capacity (f) profile for Li|Li cells after CV premodulation with an areal capacity of 12 mAh cm\(^{-2}\).
cycles of Li|Cu cell at 5.0 mVs
the CE of lithium electrodeposition during CV measurements of a Li|Cu cell at 25°C. The first anodic sweep at different sweep rates (c) the first two cycles of Li|Cu cell at 5.0 mVs⁻¹ and 25°C in the range of −0.3−3.0 V (d) two plateaus of lithium electrodeposition onto Cu electrode with CV premodulation at 5.0 mA cm⁻², 3.0 C cm⁻² and 25°C along with two typical images of morphology of lithium electrodeposits at different height positions. Scale bar, 20 μm. (e) In situ CV/QCM study on the underpotential Li deposition/stripping in the second cycle using three-electrode cell, where Ni-coated quartz crystal was used as the working electrode and Li as the reference and counter electrode, respectively.

Impact of CV premodulation. In situ Li|Cu visualization cell using the DSIL was also used to record the morphology evolution in the first two cycles at 5.0 mA cm⁻² and 1.5 mAh cm⁻² and ambient temperature under the CV premodulation as shown in Fig. 4a and Supplementary Movie 4. Upon the second plating, the potential declined slowly to reach the bulk deposition zone (<0 V), indicating underpotential lithium electrodeposition took place in the galvanostatic deposition mode in the presence of positively charged lithium residuals with adsorbed multidentate G4 solvents. Upon the second stripping, the appearance of black SEI layers changed from the previous random way into a mossy-film-growing mode before 0.5 V, which may be associated with ensuing 100% CE in Fig. 2c. A symmetric cell of Li|Li was applied by CV premodulation in the potential range of −0.3−0.3 V and the impedance evolution of the cell was real-time monitored with cycling as shown in Fig. 4b-d. Compared to the cell with LiPF₆-EC-DEC, the cell with the DSIL exhibits drastic increases in the lithium plating and stripping current density in the fourth cycle and large dendrite lithium particles were observed on Cu substrate (Supplementary Fig. 14d,e). After the galvanostatic deposition of lithium at 5.0 mA cm⁻² and 3.0 C cm⁻² with CV premodulation (Fig. 3d), patch-like lithium electrodeposits onto Cu were still present (Supplementary Fig. 14f).

Favourable surface film chemistry. As to the surface chemistry of Li or Cu electrodes, the elemental depth profile of the Cu substrate after CV premodulation was found akin to the top-SEI film of Li metal surface in Fig. 5a. The reduction species of (CH₂,CH₂OH)₂O⁻ and (CH₂,CH₂O–) from reduced DOL, possessing two characteristic peaks at 288.6 eV and 286.2 eV, were found in the outmost SEI layer (0–1 min), respectively, 39,40. For the F 1s spectra, the majority of LiF is detected at the outermost surface (10–20 s), compared to the continuing increase contribution of LiF with depth in the case of LiPF₆-EC-DEC and LiFSI-2G4 (Supplementary Fig. 16). The Li 1s spectra distinctly display that Li₂O is the main constituent of the inner-SEI film...
(20–40 min) with little contribution from Li$_2$S and Li$_2$CO$_3$/LiOH mainly comprises the top-SEI film with small fraction of LiF. O 1s spectra present a clear transition after 5 min etching as well; the main inner contribution of Li$_2$O from the FSI(-F) is further determined. However, negative shifts of O 1s and Li 1s spectra to Li$_2$S and Li$_2$CO$_3$ with little contribution from LiF by the spontaneous dimerization reaction between FSI(-F) and Li$_2$S$_2$. CV premodulation could also impart the complete coverage of MLE regardless of the presence of the contaminant of Li$_x$Cy as illustrated in Fig. 5c. The sweeping rate was 10 mV s$^{-1}$. Impedance evolution of the symmetrical Li|Li cell with cycle number using LiFSI-2G4-50 vol% DOL and (d) LiFSI-2G4-50 vol% DOL. (e) Evolutions of $R_{f,x}$ and $R_{c,x}$ for the symmetrical Li|Li cell using LiFSI-2G4-50 vol% DOL during and after the CV premodulation.

**Discussion**

The strong interaction between G4-derived top-SEI film and the incoming Li cations could retard the surge of lithium ions during the nucleation stage$^{15,42}$ (Supplementary Figs 18 and 19). However, the lower-binding energy from the weak metallic bond of Li–Li or Li–Cu cannot inhibit the occurrence of local lithium surges. Besides, compared to surface diffusion on a terrace, there is a higher activation energy barrier of $E_{a,s}$ for an adatom to move over a descending step$^{19}$. The preferred location of LiF in the top-SEI layer could enhance the surface diffusivity$^{20}$, in turn, the G4-derived top-SEI film, by thermodynamic reduction and preferential electrochemical reduction from the SS, to function as the surfactant to reduce the overpotential plateau could be ascribed to the lithium dendrite formation in the ensuing electrodeposition with a high deposition capacity (Supplementary Figs 5b and 14d).

Two distinct plateaus of Li|Cu cells and Li|Li cells in Fig. 2 indicate the first lower-overpotential plateau should be associated with the lithium electrodeposition onto top of residual lithium electrodeposits in a growing fashion of dendrite-free 2D large planar lithium particles at higher positions (Fig. 3d); the higher overpotential plateau could be ascribed to the lithium electrodeposition onto pristine Cu surface or bottom lithium surface directly at lower positions. One can see the lithium stripping capacity is consistently higher than the lithium plating capacity.

**Figure 4 | Impact of CV premodulation.** (a) In situ morphology evolution and chronopotentiometric curves of Li|Cu cell using the LiFSI-2G4-50 vol% DOL at 5 mA cm$^{-2}$ and ambient temperature under the CV premodulation in the first two cycles, where lithium electrodeposition and stripping time were fixed as 18 min (1.5 mAh cm$^{-2}$). Scale bar, 100 μm. (b) CV of Li electrodeposition/stripping in the symmetrical Li|Li cell for 10 cycles using different electrolytes at 25 °C. The sweeping rate was 10 mV s$^{-1}$. Impedance evolution of the symmetrical Li|Li cell with cycle number using (c) LiPF$_6$-EC-DEC and
Figure 5 | Favourable surface film chemistry of Li in the DSIL with the CV premodulation. (a) Elemental depth profile of surface film chemistry of Li after CV premodulation in the DSIL of LiFSI-2G4-50 vol% DOL. (b) C 1s spectra of Li immersing in different electrolytes without etching. (c) Schemes of the modification of surface film chemistry of Li in the SIL of LiFSI-2G4 after the introduction of DOL and CV premodulation.

originating from the first plateau, indicating that dendrite-free large planar lithium particles are pivotal for complete lithium stripping. Moreover, the higher overpotential plateau regularly follows the lower overpotential plateau, suggesting 2D layer-by-layer growth mode prevails in our experiments evidenced by the continuously increasing plating overpotential and otherwise three-dimensional lithium dendrite growth is expected to occur on the top surface of lithium electrodeposits instantly with a shorter electrodeposition path. The fraction of the second plateau for cells delivering high areal-capacity (> 5 mAh cm⁻²) is so large that the lithium electrodeposition on Cu substrate at lower spots have sufficient time to grow till the coalescence with the top lithium electrodeposition layer within the unidirectional galvano-static plating process. However, in the case of low areal-capacity, the arrival time for the coalescence of these two layers should be substantially delayed (after eight cycles for the cell delivering 3 mAh cm⁻²) to result in the initial fluctuations of CE.

Favourable surface chemistries of Li in contact with DSIL, on the grounds of the outmost layer of oligomers from DOL, the descending top-layer of LiF, Li₂S, and Li₂S, the inner-layer of Li₂O, have been reported to enhance the cycling stability of metallic lithium deposition. The final negligible Δmₜₐᵢ upon cycling indicates a stable SEI film can be generated onto Li metal in contact with DSIL that leads to excellent cycleability of Li|Li cells with steady cell potentials.

In summary, we have reported evidences that CV premodulation is a viable strategy to generate a homogenous top-SEI cloth by preferential electrochemical reduction of the SS to fully cover MLEs with a low Eₓᵢₐ to enhance the 2D growth mode in the presence of sweeping time-dependent positively charged lithium using the novel DSIL. DOL plays an important role in generating preferably localized SEI gradients of MLEs to sustain the excellent cycling performance. Reversible MLEs can then deliver an exceptionally high areal-capacity of 12 mAh cm⁻² at high-current densities and ambient temperature. With the CV premodulation, the couple of Li/DSIL could be an appealing alternative for beyond lithium ion batteries. The proposed strategy could also be imposed to develop other reversible dendrite-free high-areal-capacity metallic anodes (for example, Na, Mg, Zn and Al) for sustainable battery chemistries.

Methods

Preparation of diluted solvate ionic liquids. G4 (LBG, Kishida Chemical) and LiFSI (LBG, Kishida Chemical) were mixed in different molar ratios in an Ar-filled glove box. The mixtures of LiFSI-xG4 (x: the molar ratio of G4 to LiFSI) were stirred for 24 h at room temperature and the as-prepared homogenous electrolytes were stored and handled in the glove box. Blends of 1,3-dioxolane (DOL, 99%, Sigma-Aldrich) and LiFSI-2G4 were then combined using a pipette (Gilson Inc.) and stirred for an additional 24 h. The final residual moisture in all mixtures was determined to be <20 p.p.m., measured with a Karl Fischer moisture metre (KEM, MKC-510). The 1 M LiPF₆-EC-DEC (Kishida Chemical, 1:1 v/v) electrolyte was used for comparison. The other lithium salt evaluated in this work was lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), LiTFSI (98%) was obtained from Wako Chemicals and dried overnight under vacuum at 150 °C. The washing solvent of 1,2-dimethoxyethane-DME (LBG, Kishida Chemical) and dimethyl carbonate-DMC (anhydrous, >99%, Sigma-Aldrich) was used to remove the residual electrolyte of glyme-lithium salt mixtures and LiPF₆-EC-DEC on Li or Cu electrodes, respectively.

Cell assembly. In situ visualization Li|Cu cell: An extra-thin Cu wire (99.9%, Nilaco Corp.) with a diameter of 100 μm penetrated through a rigid-thick rubber ring, whose inner part (8–12 mm in length; 0.025–0.038 cm² in surface area) was employed as the working electrode for the lithium electrodeposition and outer part was used as the current collector. A disposable needle was then inserted into the rubber ring in the vertical direction, whose inner part was mounted by a Li rod using as the counter electrode and reference electrode and outer part acted by the current collector. The rubber ring was then sandwiched by two glass slides and injected by the electrolytes in the glove box. Electrodeposition of lithium onto Cu wire was carried out at ambient temperature (25 ± 2 °C) by an automatic polarization system (Hokuto Denko, HSV-110) using the current range of 10 μA. In situ observation of evolution of lithium electrodeposits with time was realized by a digital microscope (Keyence VHX-1000).
Sweeping rate of 50 mV s⁻¹ for 5–30 scans using a Solartron 1285 potentiostat; the capacity corresponding to the residual lithium plating capacity, \( Q_{p} \), the fixed plating capacity, and \( Q_{s} \) the capacity corresponding to the residual lithium electrodeposits after the CV premodulation. In situ CV/QCM: The Ni (QA-A9M-Ni) and Cu (QA-A9M-Cu) sputtered quartz crystal electrode was a 9 MHz AT-cut quartz (Seiko EG&G). The Ni (surface area 0.1963 cm²) on the solution side was employed as the working electrode in a three-electrode cell system in connection with QCM (Seiko EG&G: PS-P800), where Li metal was used for the reference and counter electrode. The theoretical mass sensitivity was 9.57 × 10⁻⁴ g Hz⁻¹. CV measurements were performed within a range of 0.0–3.5 V for 1 M LiPF₆-EC-DEC at ambient temperature with a sweeping rate of 10 mV s⁻¹ in the glove box.

The authors declare that the data supporting the findings of this study are available within the article and its Supplementary Information files. All other relevant data supporting the findings of this study are available on request.

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Author contributions
H.W. and N.I. conceived and designed the experiments. H.W. prepared the electrolytes and performed the electrochemical, in situ observation, Raman spectroscopy measurements. H.W. and H.K. conducted XPS measurements. H.W. and H.S. carried out in situ CV/QCM measurements. H.W. and X.S. performed the theoretical computations and simulations. H.W., M.M., Y.M., Y.T., O.Y. and N.I. discussed the results and analysed the data. H.W. and N.I. wrote the manuscript.

Additional information
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