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Electrode potential influences the reversibility of lithium-metal anodes

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Lithium-metal batteries are a promising technology to address the emerging demand for high-energy-density storage systems. However, their cycling encounters a low Coulombic efficiency (CE) due to the unceasing electrolyte decomposition. Improving the stability of solid electrolyte interphase (SEI) suppresses the decomposition and increases CE. However, SEI morphology and chemistry alone cannot account for CE, and a full explanation is still lacking. Here we report that in diverse electrolytes, the large shift (>0.6 V) in the Li electrode potential and its association with the Li⁺ coordination structure influence the CE. Machine learning regression analysis and vibrational spectroscopy revealed that the formation of ion pairs is essential for upshifting the Li electrode potential, that is, for weakening the reducing ability of Li, which would lead to a high CE with diminished electrolyte decomposition. Various electrolytes with enhanced ion-pairing solution structure are designed to enable a significantly improved CE (>99%).

Lithium metal is an ultimate anode for high-energy-density rechargeable batteries as it presents high theoretical capacity (3,860 mAh g⁻¹) and low electrode potential (-3.04 V versus a standard hydrogen electrode)^{1,2}. However, its low plating/stripping Coulombic efficiency (CE) is the biggest barrier to practical utilization^{3,4}. The low CE is attributed to the thermodynamic instability of a Li/organic electrolyte interface because of the strong reducing ability of Li (refs. ^{3,4}). The electrode potential of Li is located far outside the potential window of an organic electrolyte (Fig. 1a), which induces the reductive decomposition of the electrolyte. In some cases, the reduction products are deposited on the Li surface, serving as a Li⁺-conductive yet electron-insulating layer, referred to as the solid electrolyte interphase (SEI), which may effectively retard further electrolyte decomposition (that is, kinetically extend the potential window)^{5,6}.

SEI is conventionally assumed to be a dominating factor that affects CE. To maximize the effect of SEIs, diverse electrolytes have been designed over the past decades. First, organic carbonates (for example, propylene carbonate (PC) and ethylene carbonate (EC)) were applied as a solvents to form SEI, but the resulting CE (<90%) was far below the requirement (>99.9%) (refs.⁷⁸). Next, ether-based electrolytes (for

example, tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME)) were developed, which exhibited high reduction stabilities, decreasing the gap between their potential window and the Li potential, leading to high CEs^{8,9}. State-of-the-art electrolyte designs focus more on the stability of SEI: for example, concentrated electrolytes, locally concentrated electrolytes with non-polar solvents and weakly solvating electrolytes—which typically employ LiN(SO₂F)₂ (LiFSI)—form LiF-rich inorganic SEIs via preferential reductive decomposition of LiFSI, resulting in high electrochemical/mechanical stabilities and high CEs of \geq 99% (refs. ⁹⁻¹³). However, even in the presence of similar LiF-rich SEIs, there is considerable variation in CEs (90–99%), depending on bulk electrolytes^{9,12-15}. Hence, it is worth exploring a hidden critical factor that could influence CEs.

Here we report the Li electrode potential (E_{Li}) influences the CEs of Li anodes. It is well known that electrode potentials vary significantly depending on the electrolyte^{16,17}. Specifically, E_{Li} is directly linked to the chemical potential of Li⁺ (μ_{Li} ⁺) in the electrolyte, as shown later. Hence, E_{Li} —that reflects the reducing ability of Li—can be controlled via electrolyte design by adjusting μ_{Li} . If E_{Li} is strategically shifted upward (weakening the reducing ability of Li) to decrease the gap from the

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Fig. 1 | **Electrolyte design concept. a**, History of electrolyte concepts for Li-metal batteries. The electrode potential of Li-metal anodes is far from the potential window of non-aqueous electrolytes, leading to a low CE accompanied by severe reductive decomposition of the electrolyte. Here we aim to upshift the electrode potential of Li, thus weakening the reducing ability of Li, to suppress the electrolyte decomposition. Potential is presented with reference to standard hydrogen electrode (SHE). The dashed black lines and red arrow represent the location of $E_{\rm Li}$ and its upward shift, respectively. The oxidation limit of electrolytes (typically over 0 V versus SHE) is not identified after the break-line in the *x* axis, which is not within the scope of this work. **b**, Schematic of an electrochemical cell to measure the electrode potential of Li in various electrolytes with reference to an IUPAC-recommended electrolyte-independent redox species, ferrocene (Fc/Fc⁺) (refs. ^{16,22,23}). The electrode potential of Li was measured as an electromotive force of the cell, which is shown as the red arrow.

potential window, undesirable electrolyte decomposition can be diminished, which would considerably improve the CE of Li anodes (Fig. 1a). This strategy can be validated in analogy with similar cases with higher electrode potential. For example, ultra-high CEs (\geq 99.9%) have been obtained for Na metal anodes with 0.3 V higher electrode potential^{18,19}, and highly reversible Li⁺ intercalation of Li₄Ti₅O₁₂ has been achieved by positioning the electrode potential into the potential window in concentrated aqueous electrolytes^{20,21}. In this study, we demonstrate that the shift of E_{Li} is considerably large (>0.6 V) when Li⁺ is extensively ion paired with counter anions, and higher E_{Li} leads to higher CEs of Li metal anodes. We also identified the spectroscopic features of coordination states that strongly correlate with E_{Li} , which will facilitate the design of high-CE electrolytes for Li-metal anodes. It is important to note here that this work does not disregard the importance of SEI.

Accurate measurement of E_{Li}

We measured E_{11} in 74 different electrolytes (Supplementary Table 1 and Fig. 1). Ferrocene (Fc, at ~1 mM) was introduced into all the electrolytes as an International Union of Pure and Applied Chemistry (IUPAC)-recommended internal standard for electrode potentials^{16,22,23}. Assuming that the electrode potential of Fc/Fc⁺ is constant and independent of the electrolytes^{22,23}, we measured $E_{\rm Li}$ with reference to Fc/ Fc⁺ on a Pt electrode (Fig. 1b). Note that this cell does not contain any liquid junction, thus eliminating the effect of uncertain liquid junction potential¹⁷. Next, we applied the same 74 different electrolytes (without Fc) to Cu|Li cells to test the CEs of Li plating/stripping reactions on Cu (Supplementary Table 1 and Figs. 2 and 3). Liplating was conducted at a constant current density of 0.5 mA cm⁻² for 1 h, followed by Li stripping at the same current density up to a cut-off voltage of 0.5 V. Average CE was calculated from the second to 20th cycles of the three cells for each electrolyte. The first cycle was excluded because it is primarily affected by the SEI formation process. As shown in Supplementary Fig. 4, once the first SEI forms, CEs in the subsequent cycles are distinctly different from the first CE. To compare the data with a standard electrolyte for Li-metal electrodes, E_{1i} (V versus Fc/Fc⁺) was also converted to E_{1i} (V versus Li/Li⁺ in 1 M LiFSI/DME (-3.40 V versus Fc/Fc⁺)).

Correlation of CE and E_{Li}

Figure 2 shows a relationship between E_{Li} and the average CE of Li plating/stripping in 74 different electrolytes. Overall, the average CE increased with increasing E_{Li} , suggesting that the reductive decomposition of electrolytes was suppressed at high E_{Li} (lower reducing ability of Li). On this basis, it is essential to design an electrolyte with $E_{Li} > -3.3$ V versus Fc/Fc⁺, achieving high average CE > 95%. Notably, even at the same E_{Li} , the CEs varied depending on the solvents used; ethers resulted in CEs >90% at -3.3 V versus Fc/Fc⁺, but sulfolane led to low CE of -80%. This was attributed to the difference in the potential windows (that is, the gap between the thermodynamic potential window and E_{Li}) and SEI properties. In the case of ethers, which have wide potential windows in a reductive direction, the E_{Li} of -3.3 V versus Fc/Fc⁺ is sufficiently high to decrease the gap between E_{Li} and the potential windows^{9,12}.

To more clearly demonstrate the effect of E_{1i} on CE, we picked up three ether electrolytes with similar potential windows: 1.5 M LiFSI/ diglyme (G2), 1.5 M LiFSI/DME and 1.5 M LiFSI/dimethoxymethane (DMM). These electrolytes have remarkably varying values of E_{1i} : -3.45 V, -3.38 V and -3.16 V (versus Fc/Fc⁺) and hence, -0.05 V, 0.02 V and 0.24 V (versus Li/Li⁺ in 1 M LiFSI/DME), respectively (Fig. 3b and Supplementary Fig. 5), which are derived from the different solvation energies of Li⁺ (discussed later). The CEs of the Cu|Li cells are shown in Fig. 3c-e. In 1.5 M LiFSI/G2 with the lowest E₁₁ of -3.45 V versus Fc/ Fc⁺ (-0.05 V versus Li/Li⁺ in 1 M LiFSI/DME), significant fluctuations of CEs were observed, suggesting the instability of plated Li with the electrolyte. In 1.5 M LiFSI/DME with slightly higher $E_{\rm Li}$ of -3.38 V versus Fc/Fc⁺ (0.02 V versus Li/Li⁺ in 1 M LiFSI/DME), the fluctuation was still observed, but the CE was slightly improved. In striking contrast, in 1.5 M LiFSI/DMM with the highest E_{Li} of -3.16 V versus Fc/Fc⁺ (0.24 V versus Li/Li⁺ in 1 M LiFSI/DME), highly stable Li plating/stripping was observed, and the CE was remarkably improved up to 99.1% on average over 400 cycles.

These improved CEs have thus far been attributed to the enhanced SEI stability. In particular, LiFSI is believed to form stable SEI. In this context, we analysed the surface of cycled Cu using X-ray photoelectron spectroscopy. As shown in Supplementary Fig. 6, LiFSI-derived



Fig. 2 | **CEs of Liplating/stripping depending on** F_{Li} **.** High CEs were, in general, observed in electrolytes with high F_{Li} **.** Li|Cu cells were used for plating/stripping tests under identical conditions. The average CE was calculated from the second to the 20th cycle with three cells. The electrolytes with an identical solvent but different salt concentrations are represented as points with the same colours. Data for each electrolyte are shown in Supplementary Figs. 1–4

and Supplementary Table 1. Inset: cyclic voltammograms of ferrocene in the given electrolytes. We added *x*-axis breaks of 2.4 V to highlight both E_{Li} (0 V) and the redox potentials of ferrocene in the two electrolytes. The shift of E_{Li} (over 0.6 V), which influences the CEs of Li-metal anodes, strongly depends on the electrolytes. HFE, 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether.

components/moieties (LiF, S–N–S, Li–N, S = O and sulfides) were observed for all three ether electrolytes²⁴. Specifically, sulfides, which are reduced forms of LiFSI, were more abundantly observed for 1.5 M LiFSI/G2, which, in turn, showed poor CE²⁴. Hence, SEI chemistries alone cannot account for the varied CEs in the three ether electrolytes. Because SEI can only kinetically suppress the reductive decomposition of the electrolyte, a considerably low E_{Li} (that is, high reducing ability of Li) accelerates the decomposition reaction, leading to a low CE even in the presence of a similar SEI.

Another possible factor that influences CEs is the shape of the deposited Li. Generally, less dendritic deposition decreases the active surface area in contact with the electrolyte, leading to higher CEs. Scanning electron microscopy images show that the morphologies of the deposited Li were similar in the three ether electrolytes (Supplementary Fig. 7). This suggests that the improved CE was not derived from the deposition morphology. On the basis of these observations, we concluded that E_{Li} influences the CE of Li-metal anodes.

With a general theoretical background, we now discuss the dependence of E_{Li} on electrolytes. The E_{Li} was measured as an electromotive force of the cell consisting of six phases (I, II, III, IV, V and VI). T(I)|Pt(II)|Fc, Fc⁺, Li⁺(III)|Li⁺, SEI(IV)|Li(V)|T(VI), where T(I) and T(VI) denote both metal terminals of the cell. On this basis, the E_{Li} is derived as follows:

$$E_{\text{Li}} = \phi^{\text{VI}} - \phi^{\text{I}} = (\phi^{\text{VI}} - \phi^{\text{IV}}) + (\phi^{\text{IV}} - \phi^{\text{III}}) + (\phi^{\text{III}} - \phi^{\text{I}})$$

$$= \frac{\mu_{\text{Li}} + \mu_{e}^{\text{VI}} - \mu_{\text{LI}}^{\text{VI}}}{F} + \frac{\mu_{\text{Li}} + \mu_{e}^{\text{III}} - \mu_{\text{Li}} + \mu_{F}}{F} + \frac{\mu_{Fc} - \mu_{Fc} + \mu_{e}^{\text{III}} - \mu_{e}}{F}$$

$$= \frac{\mu_{\text{Li}} + \mu_{e} + \mu_{e}^{\text{VI}} - \mu_{\text{LI}}^{\text{VI}}}{F} + \frac{\mu_{Fc} - \mu_{Fc} + \mu_{e}^{\text{III}} - \mu_{e}}{F}$$
(1)

where ϕ , μ and F denote the inner potential of each phase (I, II, III, IV, V, VI), the chemical potential of each species in each phase and Faraday constant, respectively. For details on the derivation of the equation, see Supplementary Note 1. According to IUPAC, the redox potential of Fc/Fc⁺, $\phi^{I} - \phi^{III} = -(\mu_{Fc}^{III} - \mu_{Fc}^{+III} - \mu_{e}^{1})/F$, is assumed to be constant

independent of electrolyte compositions. Besides, μ_e^{Vl} and μ_{Li}^{V} are also independent of the electrolyte used. On this basis, the E_{Li} is shown as follows.

$$E_{\rm Li} = \frac{\mu_{\rm Li} + {}^{\rm III}}{F} + {\rm constant}$$
(2)

Notably, E_{Li} is independent of the chemical potential of Li^+ in the SEI (μ_{Li} , P_{Li}). The observed variations in E_{Li} were derived from the different chemical potential of Li^+ in the electrolytes (μ_{Li} , P_{Li}).

Machine learning regression analysis of major descriptor for E_{Li}

By definition, μ_{1i} ^{III} represents the molar Gibbs free energy change when an infinitesimal amount of Li⁺ is added to an electrolyte solution. Because Li⁺ bound to solvent molecule or counter anion, its coordination environment should influence μ_{1i^+} , and hence, E_{Li} . To confirm this, machine learning regression analysis of descriptors was conducted using partial least squares (PLS) regression and a computation-derived descriptor set, such as radial distribution function (RDF), composition, density, dipole moment and highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) values. The inset of Fig. 4a displays diagnostic plots of regression results, showing good agreement between the experimental and PLS-predicted E_{1i} for both validation and test data (root mean squared error, ~0.05 V). Figure 4a presents the normalized prediction function coefficients (relative importance of descriptors) in descending order, indicating that the coordination environment around Li⁺ (especially the coordination to the FSI⁻ anion) is highly relevant for E_{Li} .

In this context, we analysed the coordination states of Li⁺–FSI⁻ in various electrolytes using Raman spectroscopy. Figure 4b,c show the Raman spectra and their peak positions of the FSI⁻ anion, which represent Li⁺–FSI⁻ ion-pairing states²⁵. Notably, the Raman peak position is strongly correlated with E_{Li} in various electrolytes. E_{Li} increases as FSI⁻ is more extensively ion paired with Li⁺ from solvent-separated ion pairs



Fig. 3 | Reversible Liplating/stripping enabled by electrode potential upshift in a weakly coordinating solvent, DMM. a, Raman spectra of 1.5 M LiFSI/G2, 1.5 M LiFSI/DME and 1.5 M LiFSI/DMM. The peak position between 700 cm⁻¹ and 760 cm⁻¹ represents the coordination condition of Li⁺ and FSI⁻ ion pairs. **b**, E_{Li} with reference to Fc/Fc⁺. **c,d**, Voltage curves of Cu|Li cells with 1.5 M LiFSI/ G2 (blue) and 1.5 M LiFSI/DMM (red) electrolytes. **e**, CE of Li plating/stripping

(SSIPs; solvated Li⁺ without FSI⁻ coordination) to contact ion pairs (CIPs; Li⁺ coordinated with FSI⁻) and aggregates (AGGs; aggregation of ion pairs)²⁵. This correlation agrees well with the machine learning-based prediction that the ion-pairing state of Li⁺ dominates μ_{Li^+} , and thus E_{Li} as well.

Validation and general implications

The relationship between the coordination state, E_{Li} , and CE provides clear insights for developing rational electrolyte design strategies for

reactions measured in Cu|Li cells with the electrolytes. The solid lines represent the smoothed curves obtained with ten-point adjacent averages. Inset: longterm stability of Li plating/stripping with 1.5 M LiFSI/DMM. The upshifted redox potential of Li metal in 1.5 M LiFSI/DMM, which is derived from the anomeric effect of DMM, enables a stable Li plating/stripping reaction with a high CE (-99.1%) over 400 cycles.

Li-metal batteries. As seen in Figs. 2 and 4, the average CEs increased rapidly in the low- E_{Li} range (from -3.5 V to -3.3 V versus Fc/Fc⁺, equivalent to approximately -0.1 V to 0.1 V versus Li/Li⁺ in LiFSI/DME), wherein the coordination state began to be dominated by ion pairs (CIPs). This trend slowed but continued in the high- E_{Li} range (from -3.3 V to -2.9 V versus Fc/Fc⁺, equivalent to 0.1 V to 0.5 V versus Li/Li⁺ in LiFSI/DME), along with the coordination state transition from CIPs to AGGs. This hints that the electrolyte should be designed such that the anion is coordinated to Li⁺ (at least in the state of CIPs) to achieve >95% CE.



Fig. 4 | **Statistical and vibrational correlation between coordination states and** E_{Li} , **a**, Normalized prediction function coefficients (relative importance of descriptors) obtained from machine learning-based PLS regression analysis for E_{Li} . The correlation between the predicted and observed true values of E_{Li} is shown as an inset figure along with the root mean squared error (RMSE). Blue and black circles represent the predicted values based on validation and test data, respectively. The details of the descriptors (d_n) and prediction function coefficients are provided in Methods. The descriptors related to the coordination of FSI⁻ to Li⁺ (red colour) are highly correlated with E_{Li} , **b**, Raman spectra of

position of the FSI⁻ anion in the range of 700–760 cm⁻¹ (S–N–S stretching vibrational mode, v_s (S–N–S)) represents the ion-pairing state of Li⁺–FSI⁻. c, E_{Li} of various electrolytes plotted against the Raman peak positions of the FSI⁻ anion. The Raman spectra of electrolytes composed of sulfolane, EC, PC or FEC, which involve solvent-derived peaks at around 700–760 cm⁻¹, are demonstrated separately in Supplementary Fig. 10. Data for each electrolyte are shown in Supplementary Figs. 1, 9 and 10 and Supplementary Table 1.

The improved Li plating/stripping CEs obtained with state-of-the-art electrolytes (weakly solvating electrolytes, concentrated electrolytes and locally concentrated electrolytes with non-polar solvents) can be reasonably and consistently explained based on their coordination states and E_{L1} (Figs. 2 and 4). First, weakly solvating electrolytes promote the formation of CIPs and AGGs, thereby upshifting E_{L1} and increasing the CE. This trend is clearly observed in our model electrolytes, namely 1.5 M LiFSI/G2, 1.5 M LiFSI/DME and 1.5 M LiFSI/DMM. The solvation energies were in the following order: G2 > DME > DMM (Supplementary Fig. 8). Notably, G2 is more strongly coordinated to Li⁺ than DME owing to the substantial chelating effect of the three oxygen atoms²⁶. Further, DMM shows the anomeric effect (Supplementary Fig. 8a), which thermodynamically favours a *gauche–gauche* conformation that cannot chelate Li⁺; therefore, DMM is more weakly coordinated to Li⁺ than DME^{27,28}. The Raman peak of FSI⁻ was located at 718 cm⁻¹,

720 cm⁻¹ and 740 cm⁻¹ for 1.5 M LiFSI/G2, 1.5 M LiFSI/DME and 1.5 M LiFSI/DMM, respectively; moreover, the extent of ion pairing was in the order of G2 < DME < DMM (Fig. 3). Importantly, such ion-pairing states are reflected by $E_{\rm Li}$ and the CE; the AGG-dominated 1.5 M LiFSI/DMM showed a 0.29 V higher $E_{\rm Li}$ (-3.16 V versus Fc/Fc⁺, which is 0.24 V versus Li/Li⁺ in 1 M LiFSI/DME) and higher CE than those of the SSIP-dominated 1.5 M LiFSI/G2 (-3.45 V versus Fc/Fc⁺, which is -0.05 V versus Li/Li⁺ in 1 M LiFSI/DME) (Figs. 2 and 3 and Supplementary Figs. 1–4).

Finally, the concept of electrolyte-driven potential upshift can be extended to concentrated electrolytes and locally concentrated electrolytes with non-polar solvents (for example, highly fluorinated ethers and toluene, which are inert towards Li⁺ solvation), both of which have an effect similar to that of weakly solvating electrolytes. With an increasing salt concentration or upon introducing a non-polar solvent, the Raman peak of FSI⁻ gradually shifted from the lower-wavenumber range (~720 cm⁻¹; SSIPs) to the higher-wavenumber range (>730 cm⁻¹; CIPs and AGGs), which also increased E_{1i} and the CE (Fig. 4b,c and Supplementary Figs. 1–4 and 9–11). For instance, both the concentrated LiFSI/DME (salt-to-solvent molar ratio of 1/1.4, n/n) (Supplementary Figs. 2 and 3) and locally concentrated 1.5 M LiFSI/DME:toluene (solvent-to-solvent molar ratio of 3.5:6.5, n:n) (Supplementary Fig. 11) with the ion-pair-dominated solution structure (Raman peak positions at 743 cm⁻¹ and 732 cm⁻¹, respectively) exhibited an enhanced CE with an upshifted E_{1i} (-3.06 V and -3.18 V versus Fc/Fc⁺, which are 0.34 V and 0.22 V versus Li/Li⁺ in 1 M LiFSI/DME, respectively); specifically, these values were higher than those of 1.5 M LiFSI/DME (1/6.0, n/n) (-3.38 V versus Fc/Fc⁺, which is 0.02 V versus Li/Li⁺ in 1 M LiFSI/DME) with the SSIP-dominated solution structure (Raman peak position at 720 cm⁻¹). Thus far, the high CEs obtained using such state-of-the-art electrolytes have been discussed solely based on SEI chemistry; by contrast, the present work proposes the significant variations in E_{1i} (by over 0.6 V) as another contributing factor to the CEs.

Conclusions

We show that the CE of Liplating/stripping is largely influenced by the thermodynamic electrode potential of Li metal (E_{1i}) . An electrolyte with a high E_{Li} , thus weakening the reducing ability of Li metal, can minimize the reductive decomposition of the electrolyte, leading to a high CE. Our machine learning-based regression analysis reveals that E_{11} is substantially affected by Li⁺-FSI⁻ interactions. Correspondingly, E_{1i} is strongly correlated with the Raman shift of FSI, which shows the extent of Li⁺-FSI⁻ ion pairing. On the basis of these insights, highly reversible Liplating/stripping (>99%) was achieved with strongly ion-paired LiFSI/ DMM and LiFSI/DME:toluene electrolytes owing to the anomeric effect and salt concentration-localizing effect by non-polar solvent, respectively. Moreover, this E_{11} -based rationale for better CE is consistent with the high CEs reported for other state-of-the-art electrolytes for Li-metal batteries (for example, weakly solvating electrolytes, concentrated electrolytes and locally concentrated electrolytes). This work does not refute the contribution of the SEI, which kinetically suppresses electrolyte decomposition. There is a possibility that the formation of ion pairs might increase the concentration of the FSI⁻ anion at the negatively charged anode surface, thus promoting the formation of FSI⁻-derived SEI and suppressing the swelling of SEI²⁹. However, we found a case in which CE was remarkably improved with increasing $E_{\rm Li}$, even in the presence of similar FSI⁻-derived SEIs. We believe that the thermodynamic metrics discovered here will provide new opportunities to design next-generation electrolytes for Li-metal batteries.

Methods

Electrochemical study

The electrolytes were prepared by dissolving lithium bis(fluorosulfonyl) imide (LiFSI, LiN(SO₂F)₂, Nippon Shokubai) into the given solvents in an Ar-filled glove box. All the electrochemical tests were performed at room temperature. Cyclic voltammetry was conducted using a VMP3 potentiostat (BioLogic) to evaluate E_{11} in a three-electrode cell consisting of a Pt working electrode and Li-metal counter and reference electrodes with various electrolytes containing 1 mmol l⁻¹ ferrocene (Fc, Sigma Aldrich). The redox potential of Fc/Fc⁺ was measured with reference to Li/Li⁺, and E_{Li} of various electrolytes was quantified assuming that the potential of Fc/Fc⁺ is constant according to IUPAC recommendations^{16,22,23}. Electrochemical Liplating/stripping tests were performed using half cells (Cu|Li) with various electrolytes without Fc. The coin-cell parts (stainless-steel positive and negative cases, springs, spacers and polypropylene O-rings) were purchased from Hoshen. A glass fibre separator (GC50, Adventec) with a large pore size was selected to immerse electrolytes (Fig. 2). In some experiments, a polypropylene (PP, Cellgard) membrane was used as an optimized separator to obtain long-term cycling data (Fig. 3). Note that the trend of the CE based on the redox potential of Li in the various electrolytes did not change with

different types of separators. Cu foil (Fuchikawa Rare Metal) and Li foil (Honjo Metal) were used without further treatment. The Li plating/stripping tests were conducted with a charge–discharge unit (TOSCAT-3100, Toyo System) at a constant current density of 0.5 mA cm⁻² for 1 h during Li plating on Cu and up to a cut-off voltage of 0.5 V during Li stripping. The area of Li deposited on the Cu foil was 1.13 cm² (diameter = 1.2 cm). The average CE was calculated from the second to the 20th cycle using three cells. The CE in the first cycle (SEI formation process) was excluded because we focused on the CE after SEI formation.

Materials characterization

The liquid structure of the electrolytes was studied using Raman spectroscopy (NRS-5100 spectrometer, JASCO) with a laser excitation wavelength of 532 nm. The resolution of the Raman spectrometer was 0.8 cm^{-1} . To avoid air contamination, the electrolytes were sealed in quartz cells in an Ar-filled glove box, and the laser was irradiated through a quartz window. All the Raman peaks of the electrolytes were calibrated with a standard Si peak (520.7 cm⁻¹).

The surface morphology and chemical composition were evaluated using scanning electron microscopy (Hitachi S4800) and X-ray photoelectron spectroscopy (PHI5000 VersaProbe II, ULVAC-PHI) with a monochromatised Al K α X-ray source. The cycled Cu electrodes in the given electrolytes were rinsed with DME several times in an Ar-filled glove box and transferred into the chambers without exposure to air by using a transfer vessel.

Computational study

Molecular dynamics (MD) simulations were performed to determine the geometrical properties of 74 different electrolytes. The atomic charges of all molecules and ions were obtained using gas-phase density functional theory (DFT) calculations with the B3LYP exchange functional and cc-pvdz basis set, and the general AMBER force field³⁰ was employed as the Lennard-Jones parameter. The time step was set to 1 fs using the SHAKE method, which constrains the bond distances between hydrogen atoms and heavy atoms. The sizes of the simulation cells were adjusted by MD simulations in isobaric-isothermal (NPT) ensemble at 1 bar and 298 K. Then, using MD simulations in canonical (NVT) ensemble at 298 K, the systems were equilibrated for 1 ns, followed by 1 ns production runs. The quantum chemical properties of ten different solvent molecules (EC, PC, fluorinated ethylene carbonate (FEC), fluorinated ethyl methyl carbonate (FEMC), G2, DME, DMM, THF. 1,4-dioxane and sulfolane) were evaluated using gas-phase DFT calculations at the B3LYP/cc-pvdz level. The Amber16 and Gaussian16 packages were used for MD simulations and DFT calculations, respectively.

In the solvation energy calculations (Supplementary Fig. 8), the structures of G2, DME and DMM were optimized by using the three-dimensional reference interaction site model (3D-RISM) theory³¹. To remove the excess charge in the system, the effective screening medium and reference interaction site model (ESM-RISM) theory was used to calculate the solvation-free energies of Li⁺ in the 1.5 M LiFSI/G2, 1.5 M LiFSI/DME and 1.5 M LiFSI/DMM electrolytes. The modified quantum ESPRESSO code³² was used to perform 3D-RISM and ESM-RISM calculations using $40 \times 40 \times 40 \text{ Å}^3$ and $20 \times 20 \times 63.5 \text{ Å}^3$ unit cells, respectively; here, only the target molecule/ion was treated quantum mechanically using DFT, whereas the other molecules/ions were treated based on the implicit solvent model using the RISM method. The exchange correlation energies were calculated using the Perdew-Burke-Ernzerhof generalized gradient approximation with the plane-wave basis set and ultrasoft pseudopotential scheme. The cut-off energies were set to 40 Ry and 320 Ry for the wave functions and augmented charge, respectively. The Brillouin zone was sampled using only the Γ point (1 × 1 × 1k-point mesh). The molar ratio of molecules/ ions in RISM was determined based on the experimental results for each electrolyte. For the RISM calculations, the same atomic charge and force field were used as in the MD simulations.

Machine learning analysis

A machine learning analysis using the PLS regression method³³⁻³⁵ was conducted to estimate the dominant physical factor affecting the upshift of E₁₁. The following were adopted as the descriptors (explanatory variables): $d_{1,2,3}$ = vectors derived from RDF around Li⁺ (Li⁺-FSI⁻, Li^+ -solvent, Li^+ - Li^+), $d_{4,5,6}$ = vectors derived from the number distribution function (NDF) around Li⁺ obtained by the integral of the RDF $(Li^+ - FSI^-, Li^+ - solvent, Li^+ - Li^+), d_7 = intermolecular interaction energy$ of the electrolyte (per atom), d_8 = mass density of the electrolyte, $d_{9,10,11,12}$ = elemental ratio (O, F, C, H) of the electrolyte, d_{13} = molecular ratio of the solvent to Li salt, d_{14} = dipole moment of the solvent, d_{1516} = energies of the HOMO and LUMO of the solvent, d_{17} = formation energy of the solvent and d_{18} = binding energy of the solvent to Li⁺. The geometrical (d_{1-8}) and quantum chemical properties (d_{14-18}) were obtained by MD simulations and DFT calculations, respectively. Further, 80% of the dataset was randomly selected and used for training/ validation, while test predictions were performed on the remaining 20%. A ten-partition cross-validation method was adopted, and seven latent variables were used in this study. The importance of d_{1-6} was given as the maximum value among those in each bin (0.5 Å interval) of the RDF and number distribution function. By linearly combining these descriptors (d_n) , E_{Li} was fitted as

$$E_{\rm Li} = \sum_{n=1}^{18} \beta_n d_n + \beta_0$$
 (3)

where β_n represents the prediction function coefficients describing the degree of contributions of each descriptor to the value of E_{Li} , and β_0 is the intercept of the function. The normalized values of β_n are shown in Fig. 4a.

Data availability

All the relevant data are included in the paper and its Supplementary Information.

References

- 1. Lin, D., Liu, Y. & Cui, Y. Reviving the lithium metal anode for high-energy batteries. *Nat. Nanotechnol.* **12**, 194–206 (2017).
- Liu, B., Zhang, J.-G. & Xu, W. Advancing lithium metal batteries. Joule 2, 833–845 (2018).
- Zhang, X., Yang, Y. & Zhou, Z. Towards practical lithium-metal anodes. Chem. Soc. Rev. 49, 3040–3071 (2020).
- 4. Zhang, Y. et al. Towards better Li metal anodes: challenges and strategies. *Mater. Today* **33**, 56–74 (2020).
- 5. Cheng, X.-B. et al. A review of solid electrolyte interphases on lithium metal anode. *Adv. Sci.* **3**, 1500213 (2016).
- Tikekar, M. D., Choudhury, S., Tu, Z. & Archer, L. A. Design principles for electrolytes and interfaces for stable lithium-metal batteries. *Nat. Energy* 1, 16114 (2016).
- Aurbach, D., Ein-Ely, Y. & Zaban, A. The surface chemistry of lithium electrodes in alkyl carbonate solutions. J. Electrochem. Soc. 141, L1–L3 (1994).
- 8. Ue, M. & Uosaki, K. Recent progress in liquid electrolytes for lithium metal batteries. *Curr. Opin. Electrochem.* **17**, 106–113 (2019).
- Yu, Z. et al. Molecular design for electrolyte solvents enabling energy-dense and long-cycling lithium metal batteries. *Nat. Energy* 5, 526–533 (2020).
- Suo, L., Hu, Y.-S., Li, H., Armand, M. & Chen, L. A new class of solvent-in-salt electrolyte for high-energy rechargeable metallic lithium batteries. *Nat. Commun.* 4, 1481 (2013).
- Gao, X., Chen, Y., Johnson, L. & Bruce, P. G. Promoting solution phase discharge in Li–O₂ batteries containing weakly solvating electrolyte solutions. *Nat. Mater.* **15**, 882–888 (2016).
- Jiao, S. et al. Stable cycling of high-voltage lithium metal batteries in ether electrolytes. *Nat. Energy* 3, 739–746 (2018).

- Fan, X. et al. Highly fluorinated interphases enable high-voltage Li-metal batteries. Chem 4, 174–185 (2018).
- 14. Chen, M. et al. Marrying ester group with lithium salt: cellulose-acetate-enabled LiF-enriched interface for stable lithium metal anodes. *Adv. Funct. Mater.* **31**, 2102228 (2021).
- Ko, J. & Yoon, Y. S. Recent progress in LiF materials for safe lithium metal anode of rechargeable batteries: is LiF the key to commercializing Li metal batteries? *Ceram. Int.* 45, 30–49 (2019).
- Mozhzhukhina, N. & Calvo, E. J. Perspective—the correct assessment of standard potentials of reference electrodes in non-aqueous solution. *J. Electrochem. Soc.* 164, A2295–A2297 (2017).
- 17. Kim, S. C. et al. Potentiometric measurement to probe solvation energy and its correlation to lithium battery cyclability. *J. Am. Chem.* Soc. **143**, 10301–10308 (2021).
- Seh, Z. W., Sun, J., Sun, Y. & Cui, Y. A highly reversible room-temperature sodium metal anode. ACS Cent. Sci. 1, 449–455 (2015).
- Doi, K. et al. Reversible sodium metal electrodes: is fluorine an essential interphasial component? *Angew. Chem. Int. Ed.* 58, 8024–8028 (2019).
- 20. Yamada, Y. et al. Hydrate-melt electrolytes for high-energy-density aqueous batteries. *Nat. Energy* **1**, 16129 (2016).
- 21. Ko, S. et al. Lithium-salt monohydrate melt: a stable electrolyte for aqueous lithium-ion batteries. *Electrochem. Commun.* **104**, 106488 (2019).
- 22. Gagne, R. R., Koval, C. A. & Lisensky, G. C. Ferrocene as an internal standard for electrochemical measurements. *Inorg. Chem.* **19**, 2854–2855 (1980).
- Gritzner, G. & Kůta, J. Recommendations on reporting electrode potentials in nonaqueous solvents: IUPC commission on electrochemistry. *Electrochim. Acta* 29, 869–873 (1984).
- 24. Yamada, Y. et al. General observation of lithium intercalation into graphite in ethylene-carbonate-free superconcentrated electrolytes. ACS Appl. Mater. Interfaces **6**, 10892–10899 (2014).
- Han, S.-D., Borodin, O., Seo, D. M., Zhou, Z.-B. & Henderson, W. A. Electrolyte solvation and ionic association. *J. Electrochem. Soc.* 161, A2042–A2053 (2014).
- Zhang, C. et al. Chelate effects in glyme/lithium bis(trifluoromethanesulfonyl)amide solvate ionic liquids. I. Stability of solvate cations and correlation with electrolyte properties. J. Phys. Chem. B 118, 5144–5153 (2014).
- Wiberg, K. B. & Murcko, M. A. Rotational barriers. 4. Dimethoxymethane. The anomeric effect revisited. J. Am. Chem. Soc. 111, 4821–4828 (1989).
- Tvaroška, I. & Bleha, T. Lone pair interactions in dimethoxymethane and anomeric effect. *Can. J. Chem.* 57, 424–435 (1979).
- 29. Zhang, Z. et al. Capturing the swelling of solid–electrolyte interphase in lithium metal batteries. *Science* **375**, 66–70 (2022).
- Wang, J., Wolf, R. M., Caldwell, J. W., Kollman, P. A. & Case, D. A. Development and testing of a general amber force field. J. Comput. Chem. 25, 1157–1174 (2004).
- Nishihara, S. & Otani, M. Hybrid solvation models for bulk, interface, and membrane: reference interaction site methods coupled with density functional theory. *Phys. Rev. B* 96, 2–3 (2017).
- 32. Giannozzi, P. et al. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J. Phys. Condens. Matter* **21**, 395502 (2009).

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- Spiegelman, C. H., Bennett, J. F., Vannucci, M., McShane, M. J. & Coté, G. L. A transparent tool for seemingly difficult calibrations: the parallel calibration method. *Anal. Chem.* 72, 135–140 (2000).
- Marini, F., Roncaglioni, A. & Novič, M. Variable selection and interpretation in structure—affinity correlation modeling of estrogen receptor binders. J. Chem. Inf. Model. 45, 1507–1519 (2005).
- Jalem, R., Aoyama, T., Nakayama, M. & Nogami, M. Multivariate method-assisted ab initio study of olivine-type LiMXO₄ (main group M²⁺-X⁵⁺ and M³⁺-X⁴⁺) compositions as potential solid electrolytes. *Chem. Mater.* 24, 1357–1364 (2012).

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Author contributions

Y.Y. and A.Y. conceived and directed the projects. T.O., S.K. and Y.Y. proposed the concepts of the electrolyte design and electrode potential control. A.Y., N.T. and M.N. proposed the strategy and direction of the machine learning approach. S.K. and T.O. performed the experiments and analysed the data. T.S., N.T. and M.N. performed the computational and machine learning analyses. S.K., N.T., M.N., Y.Y. and A.Y. wrote the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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