

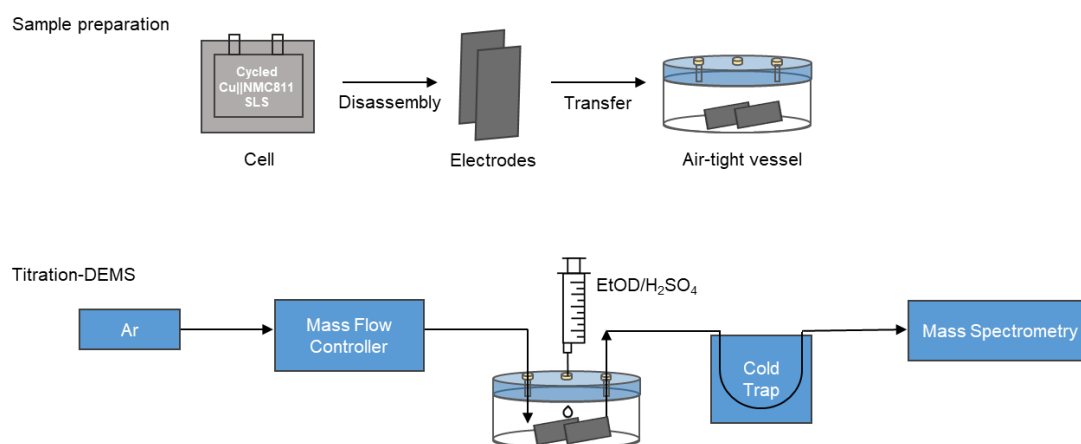
Application-driven design of non-aqueous electrolyte solutions through quantification of interfacial reactions in lithium metal batteries

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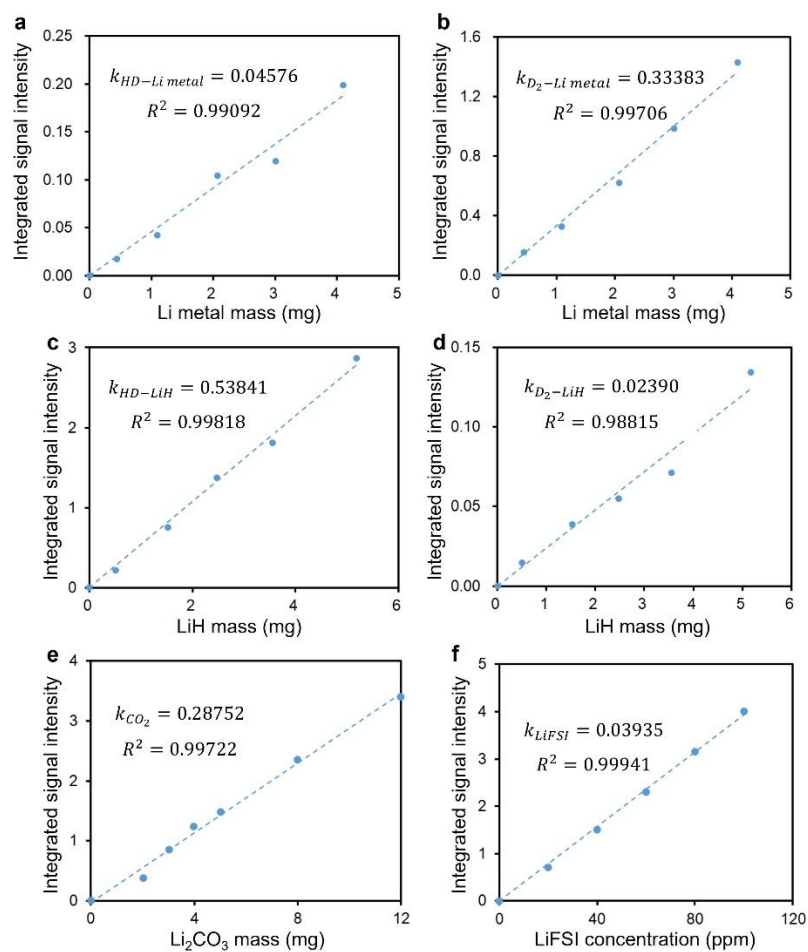
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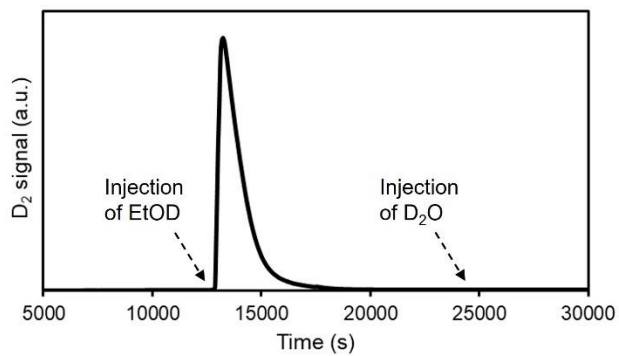
Supplementary Figures 1-34



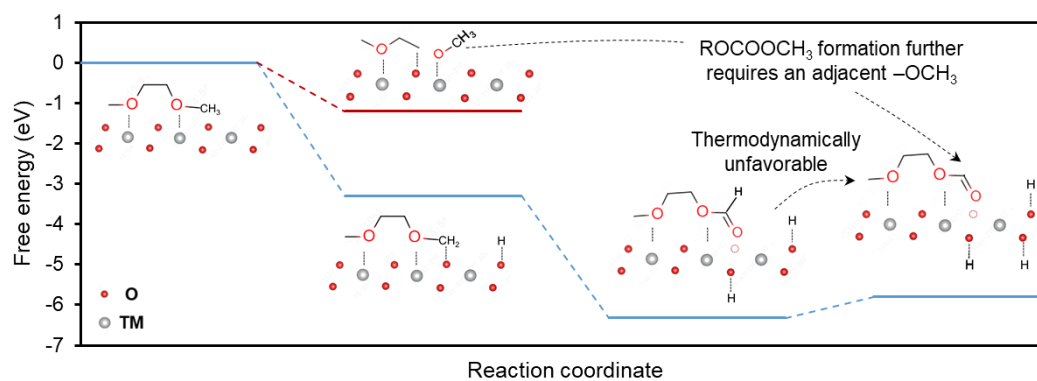
Supplementary Fig. 1 | Schematic diagram of the titration experiment design to carry out the DEMS measurements under argon atmosphere.



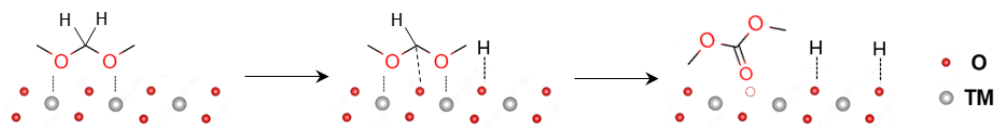
Supplementary Fig. 2 | Calibration curves for T-DEMS and E-G&IC. **a, b**, Linear regression for the peak area of HD (hydrogen deuteride: the diatomic molecule composed of one hydrogen atom and one deuterium atom) (**a**) and D₂ (deuterium gas) (**b**) versus Li metal mass in DEMS results. **c, d**, Linear regression for the peak area of HD (**c**) and D₂ (**d**) versus LiH mass in DEMS results. **e**, Linear regression for the peak area of CO₂ versus Li₂CO₃ mass in DEMS results. **f**, Linear regression for the peak area of the FSI⁻ anion versus LiFSI concentration in IC results.



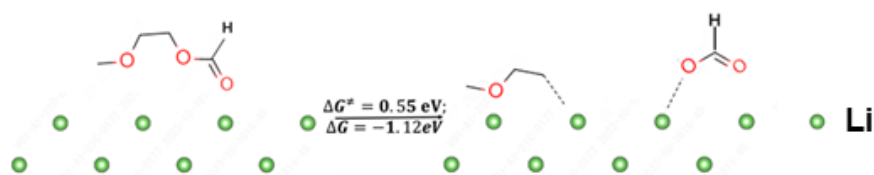
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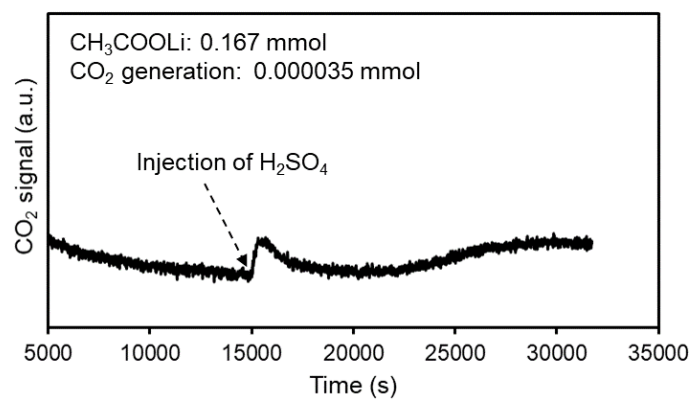
Supplementary Fig. 4 | Simulated pathway of DME oxidation to form ROCOOCH₃. In this figure, TM is the abbreviation for “transition metal”.



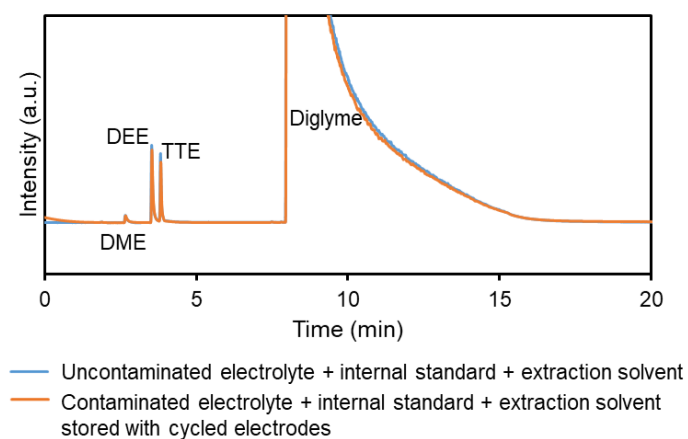
Supplementary Fig. 5 | Theoretical pathway of dimethoxymethane (DMM) oxidation to form $\text{CH}_3\text{OCOOCH}_3$. In this figure, TM is the abbreviation for “transition metal”.



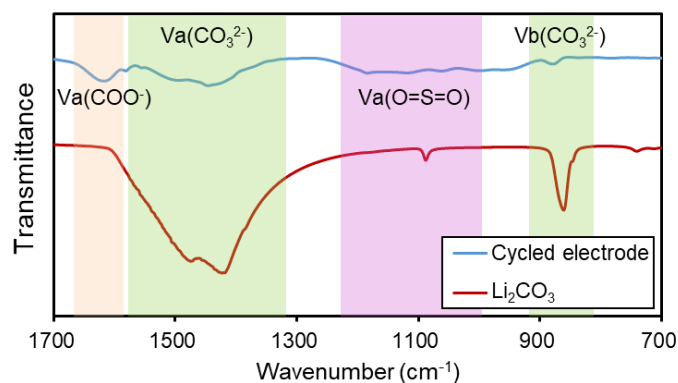
Supplementary Fig. 6 | Simulated thermodynamic and kinetic results for the cross-talk of formate to the Li metal negative electrode to form RCOOLi. Green spheres are Li metal atoms.



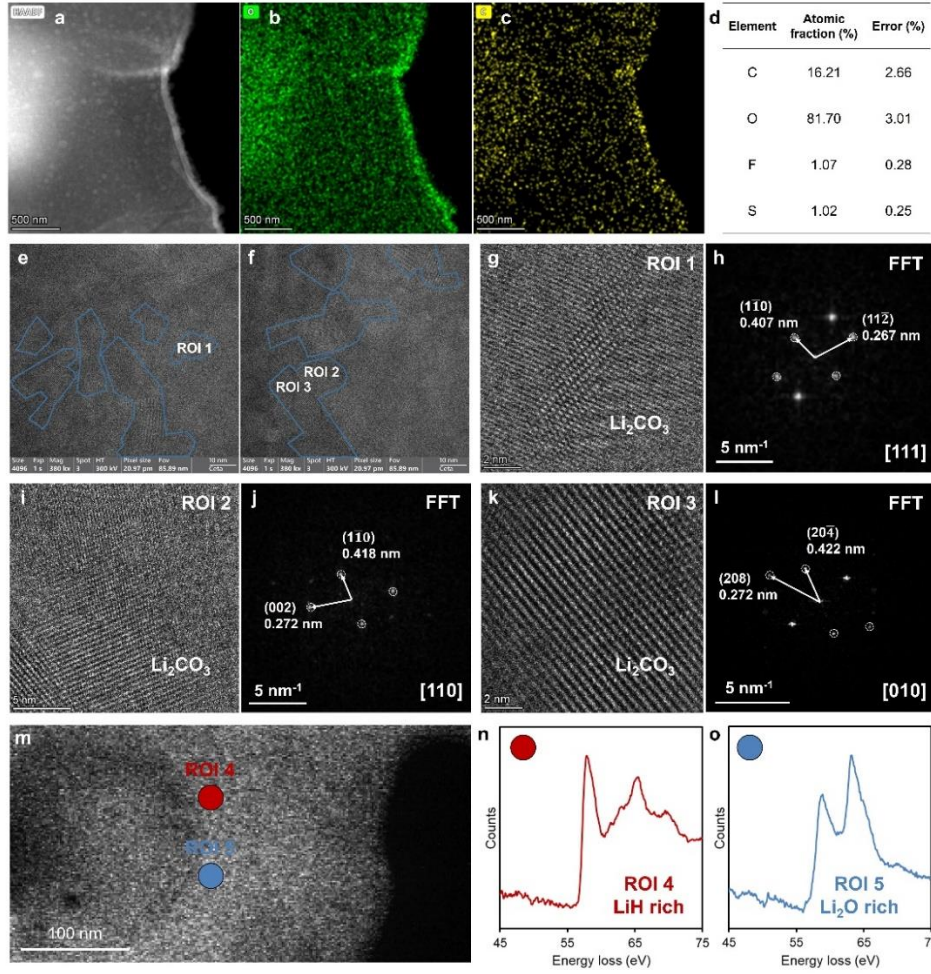
Supplementary Fig. 7 | CO₂ evolution during the titration of CH₃COOLi with H₂SO₄. The detailed discussion can be seen in Supplementary Note 2.



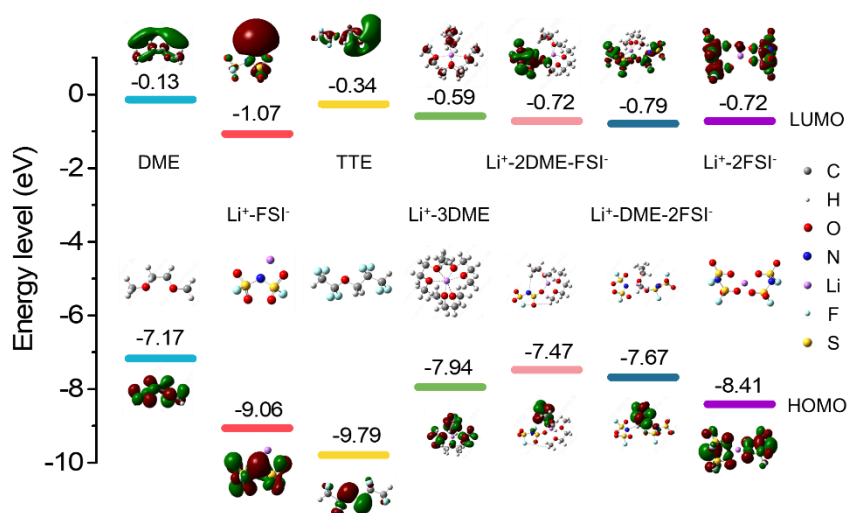
Supplementary Fig. 8 | GC result comparison between an uncontaminated electrolyte and a contaminated electrolyte sampled after being stored with cycled Li metal and NMC811 electrodes for 7 days at 25 °C. During the storage process, the electrolyte and electrodes are sealed in an aluminum-laminated-film pouch. The detailed discussion can be seen in Supplementary Note 3.



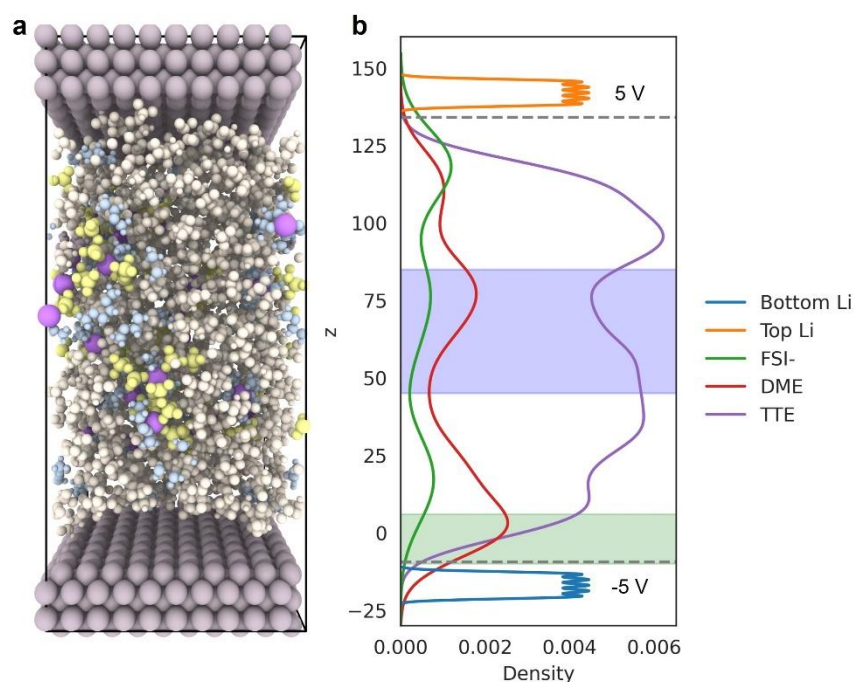
Supplementary Fig. 9 | *Ex situ* FT-IR measurement and analysis of a cycled Cu electrode. A Li₂CO₃ standard sample shows two major peaks at 1490 and 1450 cm⁻¹ (antisymmetric stretching, Va) and a minor peak at 858 cm⁻¹ (bending, Vb), in agreement with previous literature reports¹. The peaks of the Li₂CO₃ standard allow identification of Li₂CO₃ in the rSEI of the cycled negative electrode sample from Cu||NMC811 cell with LiFSI-1.2DME-3TTE electrolyte. The characteristic peaks of COO⁻ and O=S=O species can be observed. The signal of O=S=O originates from LiFSI decomposition intermediates (Fig. 3b), and the signal of COO⁻ likely originates from the cross-talk between the negative electrode and the formate species generated through DME oxidation (Fig. 3d).



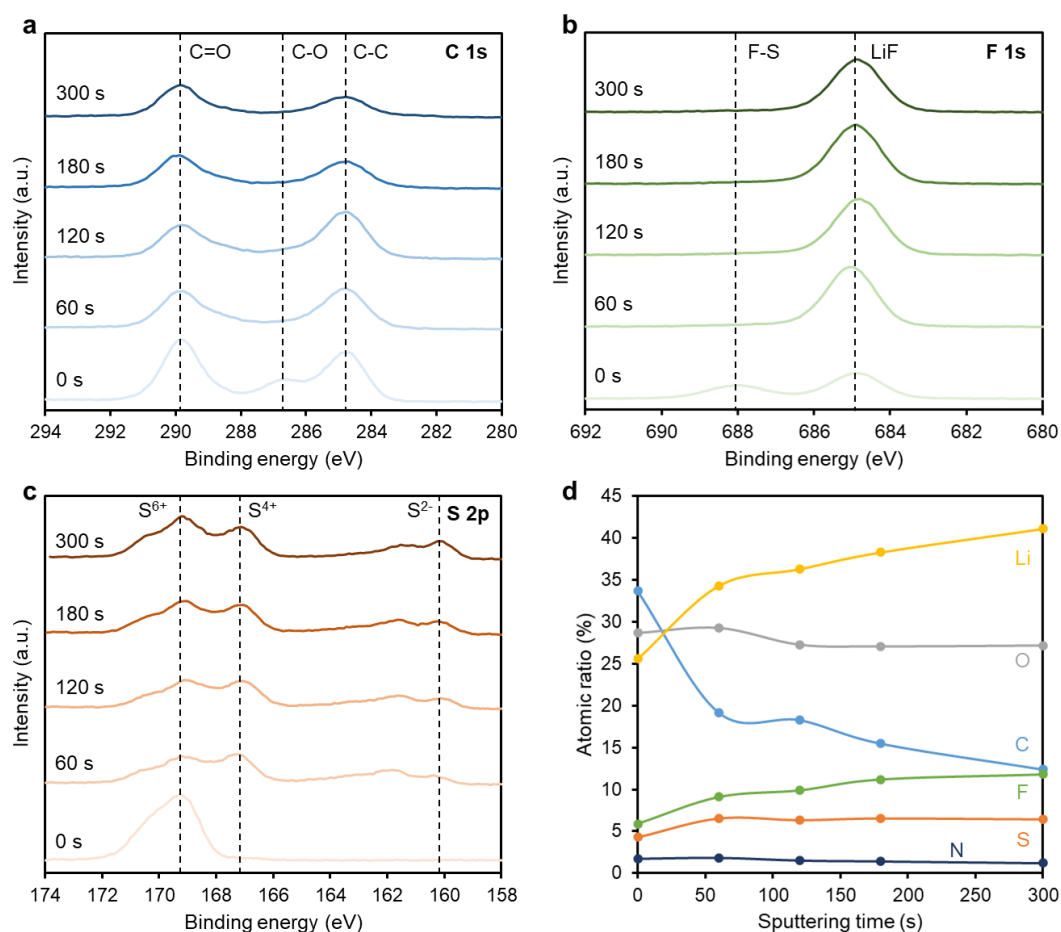
Supplementary Fig. 10 | *Ex situ* cryogenic TEM, STEM, EDS and EELS measurements and analyses of an rSEI. **a, b, c, d,** Cryo-STEM and EDS measurements of an rSEI sample from the Cu TEM grid which was mounted on the Cu electrode of a Cu||NMC811 pouch cell. The sample is mainly composed of carbon and oxygen-based compounds with some fluorine and sulfur-based species. **e, f,** Cryo-TEM images of the rSEI sample in (a). Regions with crystallinity are circled by blue lines. Among them, three regions of interests (ROIs) are further analyzed. **g, h, i, j, k, l,** Enlarged TEM images and corresponding FFT results of the ROIs in (e) and (f). The crystalline structures in ROI 1-3 all correspond to that of Li_2CO_3 ². This result further confirms the presence of Li_2CO_3 in the rSEIs. **m, n, o,** Cryo-STEM image (m) and corresponding EELS Li K-edge fine structures of ROI 4 (n) and ROI 5 (o). Li K-edge fine structure of ROI 4 resembles that of LiH ³. Li K-edge fine structure of ROI 5 resembles that of Li_2O ³. This result confirms the presence of LiH and Li_2O in the rSEIs.



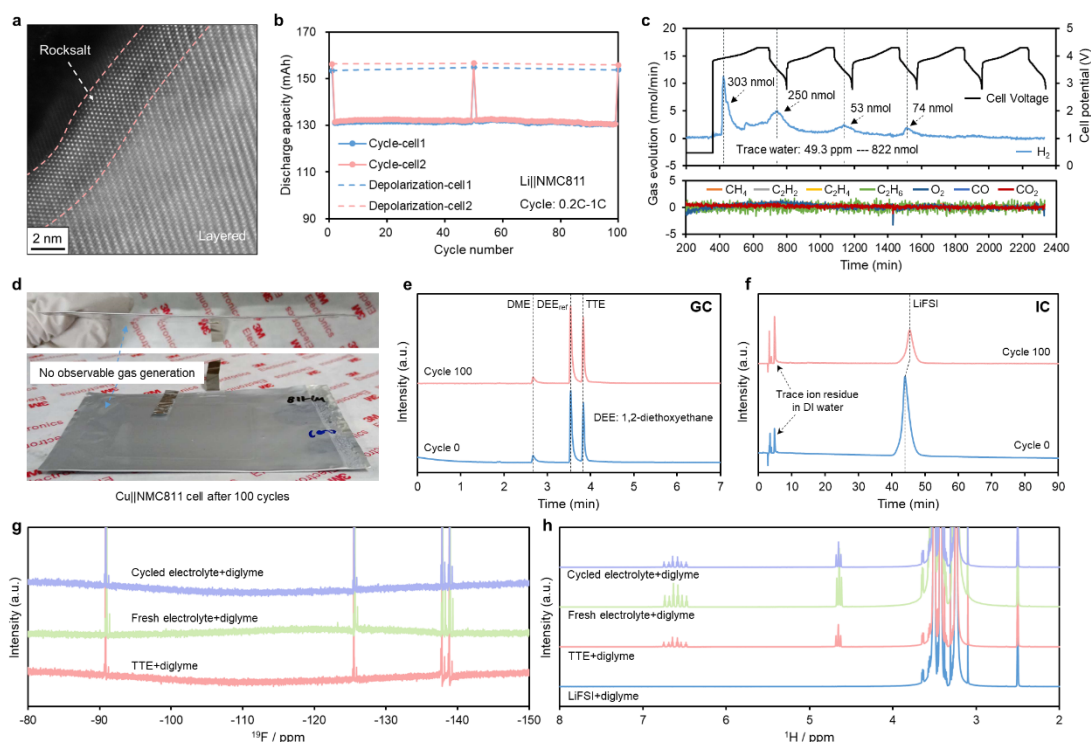
Supplementary Fig. 11 | Simulated HOMO and LUMO of DME, TTE and various solvation structures of a Li⁺ ion. TTE shows a lower LUMO than DME, so it is more prone to reduction. However, when DME is coordinated with a Li⁺ ion, its LUMO decreases to below that of TTE. This is likely the reason that DME decomposes while TTE remains stable in the LHCE since TTE barely coordinates with the Li⁺ ion⁴. When both DME and FSI⁻ anions coordinate with a Li⁺ ion, the LUMO further decreases. The LUMOs of such solvation structures mainly rely on the FSI⁻ anion. Therefore, FSI⁻ anion decomposes much more significantly than DME.



Supplementary Fig. 12 | Molecular dynamics simulation of electrolyte component distributions in the bulk and at interfaces under an applied electric field. In the case of $\{-5\text{ V}, 5\text{ V}\}$ potential range, in order to shield the negatively/positively charged bottom/top electrodes, positively charged $\text{Li}_n\text{DME}_{2n}\text{FSI}_m$ ($m \ll n$) clusters and negatively charged $\text{Li}_n\text{DME}_{2n}\text{FSI}_m$ ($m \gg n$) clusters gather near the electrodes respectively. As a result, electrolyte compositions differ significantly between the bulk (blue region) and the electrode interface (green region), as indicated in Supplementary Table 2. In specific, TTE abundance at the negatively charged bottom electrode interface is significantly lower than that in the bulk. This is possibly an additional cause for its stability during cycling. Meanwhile, since FSI anions are highly coordinated with Li cations in this LHCE formulation, independent diffusion of uncoordinated Li cations towards the negatively charged electrode surface is unlikely. As a result, FSI can be found at non-negligible amounts (making up 8.7 % of the electrolyte, see Table 1) at the negatively charged electrode interface, leading to its reduction during cycling (Fig. 2e).

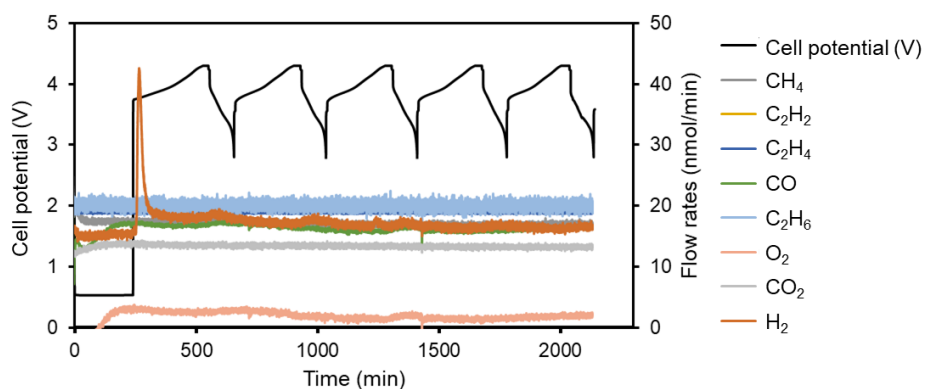


Supplementary Fig. 13 | XPS depth profile of a freshly deposited Li metal negative electrode. a, b, c, C 1s (a), F 1s (b), and S 2p (c) XPS depth profiles showing the energy distributions at different depths (depth increases with sputtering time). d, Changes in the elemental composition with sputtering time. The detailed discussion can be seen in Supplementary Note 4.

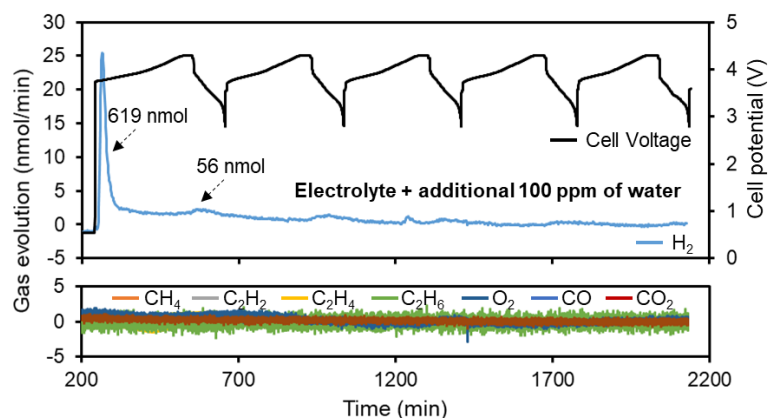


Supplementary Fig. 14 | *Operando* and *ex situ* characterization of Li||NMC811 and Cu||NMC811 cells components. **a**, A HAADF-STEM image of an NMC811 particle surface after 100 cycles. **b**, Cycling of 50 μm Li||NMC811 pouch cells with LiFSI-1.2DME-3TTE electrolyte, including a slow charging/discharging step every 50 cycles to remove the effects of polarization (i.e., “depolarization”). For normal cycling, the cell was cycled under 0.2C-1C. During depolarization, a 50 μm Li||NMC811 cell is charged at 0.05 C (7 mA), and then discharged at 0.05 C to 2.8 V for 10 times with 5 min rest intervals. Since an excess of Li is present at the negative electrode, the capacity obtained during depolarization indicates the total number of active sites of the NMC811-based electrode. The difference between the depolarization capacity (cycling with 0.05C charging and 0.05C discharging rate) and the normal cycle capacity (cycling with 0.2C-1C) indicates the polarization of the cell. **c**, *In situ* DEMS measurements showing the gas generation during the initial five cycles of a Cu||NMC811 pouch cell with LiFSI-1.2DME-3TTE electrolyte cycling under 0.2C-1C at 25 °C. **d**, A digital photo of a Cu||NMC811 cell after 100 cycles. **e**, **f**, **g**, **h**, *Ex situ* GC (**e**), IC (**f**), ^{19}F NMR (**g**) and ^1H NMR (**h**) measurements for various fresh (i.e., uncycled) and cycled electrolytes (after 100 cycles in Cu||NMC811 cell configuration). The “TTE+diglyme”

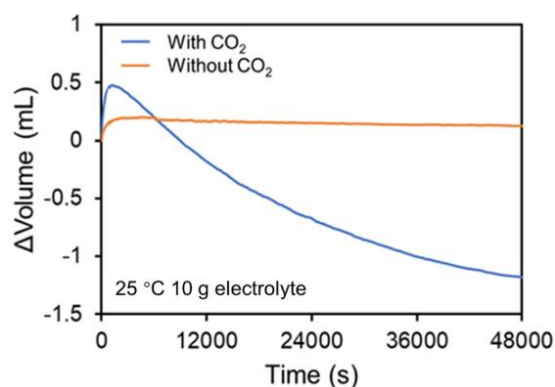
represents a mixture of TTE and diglyme, while the “LiFSI+diglyme” represents a mixture of LiFSI and diglyme.



Supplementary Fig. 15 | Calculated generation rates of different gas species generated in a Li||NMC811 pouch cell with LiFSI-1.2DME-3TTE electrolyte comprising an additional 100 ppm of H₂O at 25 °C in the DEMS experiment. The cell was cycled under 0.2C-1C. The data reported here are the same experimental data reported in Supplementary Fig. 16 but without baseline extraction. The detailed discussion can be seen in Supplementary Note 5.

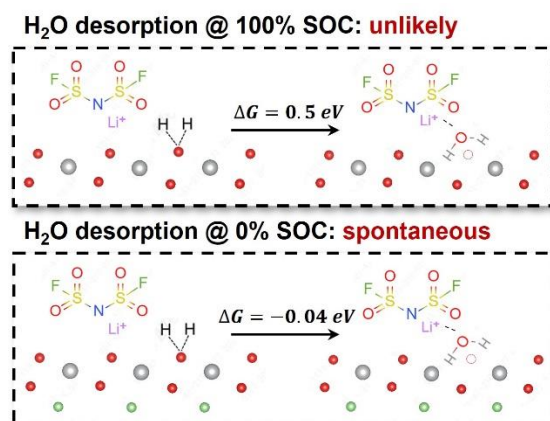


Supplementary Fig. 16 | *In situ* DEMS measurements of a Li||NMC811 pouch cell with LiFSI-1.2DME-3TTE comprising an additional 100 ppm of H₂O at 25 °C under 0.2C-1C. The result shows a further increase in the first peak (619 nmol compared to 303 nmol in Supplementary Fig. 14c). This verifies that this peak is generated due to water decomposition. However, with the additional water, H₂ peaks during subsequent cycling do not increase. This confirms that these H₂ peaks in the later stages are no longer related to the water in the pristine electrolyte.

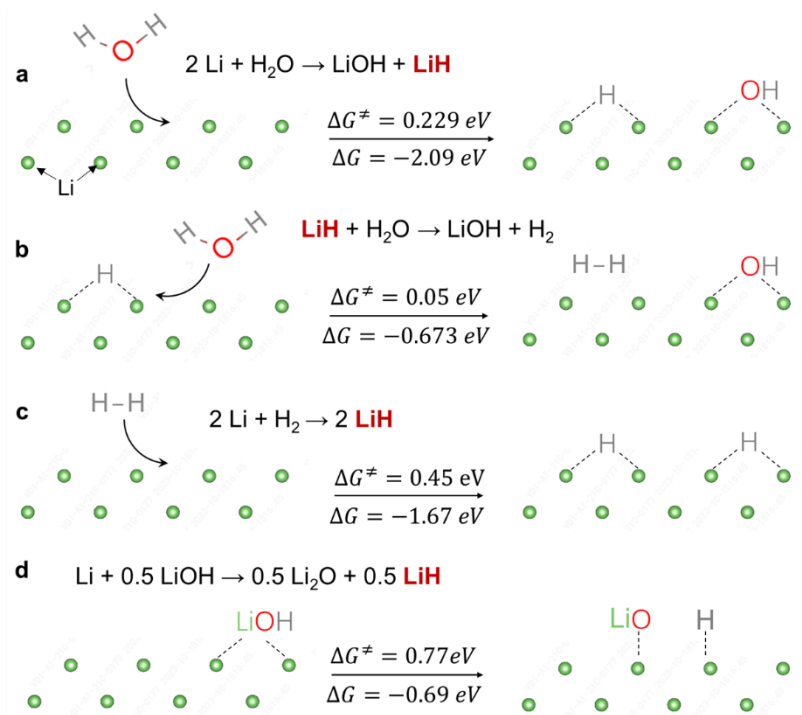


Supplementary Fig. 17 | Measuring the solubility of CO₂ in LiFSI-1.2DME-3TTE.

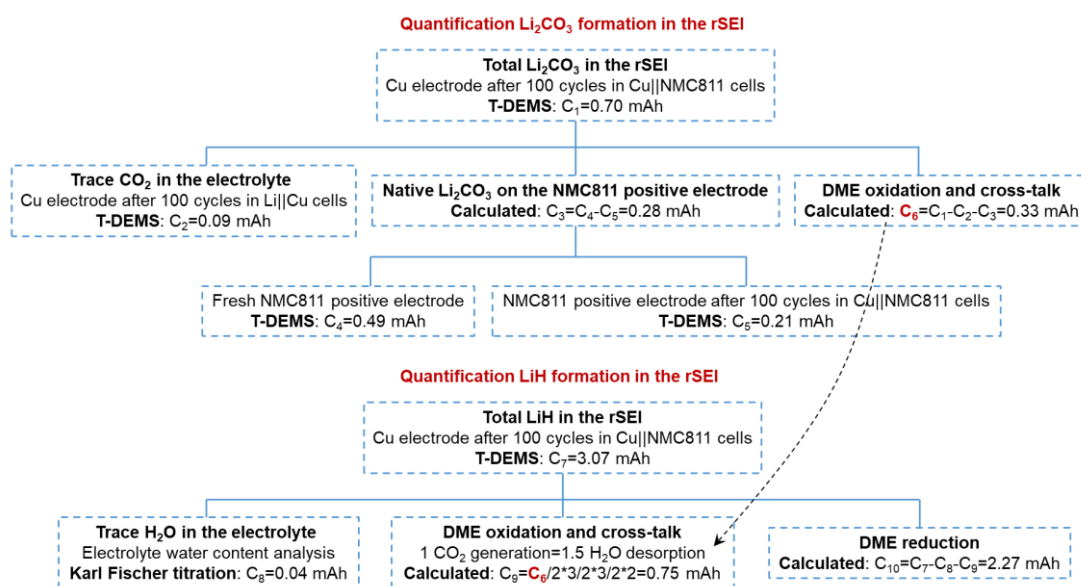
10 g electrolyte was vacuum sealed in an empty pouch. 40 ml of CO₂ gas was injected into the pouch with a syringe, and the pouch was sealed again with duct tape. The shrinkage of the pouch, due to the CO₂ dissolved in the electrolyte solution, was measured with an *in situ* cell volume analyzer. The detailed discussion can be seen in Supplementary Note 6.



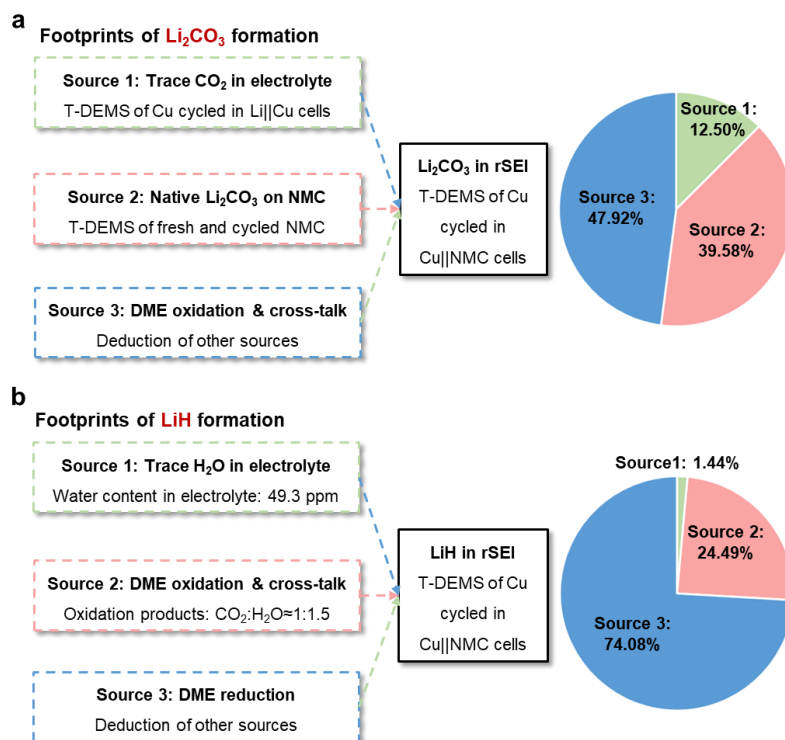
Supplementary Fig. 18 | Free energy simulation results for H₂O desorption on an NMC811 electrode. The positive electrode used for the simulation is NMC811. The Gibbs free energies obtained from *ab initio* simulations confirm that H₂O desorption under a low SOC of 0% SOC (fully discharged) is thermodynamically favorable ($\Delta G < 0$), but not for 100% SOC (fully charged). The detailed discussion can be seen in Supplementary Note 6.



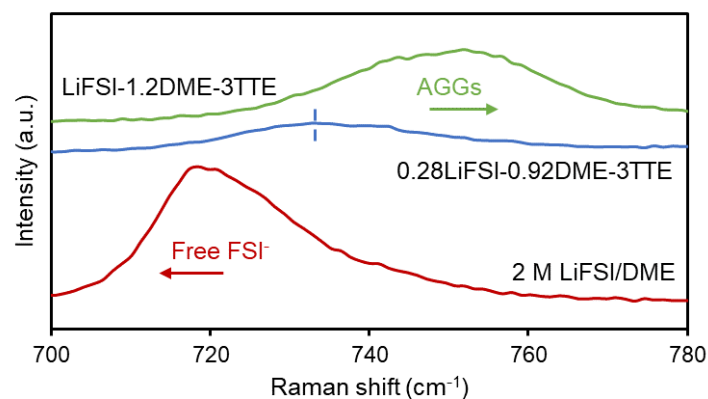
Supplementary Fig. 19 | Simulated reduction pathways of H₂O. a, b, c, d, Activation energy and Gibbs free energy results for the interfacial reactions between Li metal (green spheres) and H₂O (a), LiH and H₂O (b), Li and H₂ (c) and Li and LiOH (d). H₂O, H₂ and LiOH can be reduced by Li metal into LiH. Although LiH can also reduce H₂O into H₂, this pathway likely occurs to a lesser extent, as H₂O (only trace amounts present) is mostly consumed in reaction (a) in producing LiH. When it does, the resulting LiOH and H₂ can react with Li metal to form LiH. Combining (a) for every 1 mol of H₂O, 1 mol of LiOH and 1 mol of LiH are formed and (d) for every 1 mol of LiOH formed, 1 mol of LiH is formed, we make the assumption that the reduction of 1 mol of H₂O ultimately generates 2 mol of LiH.



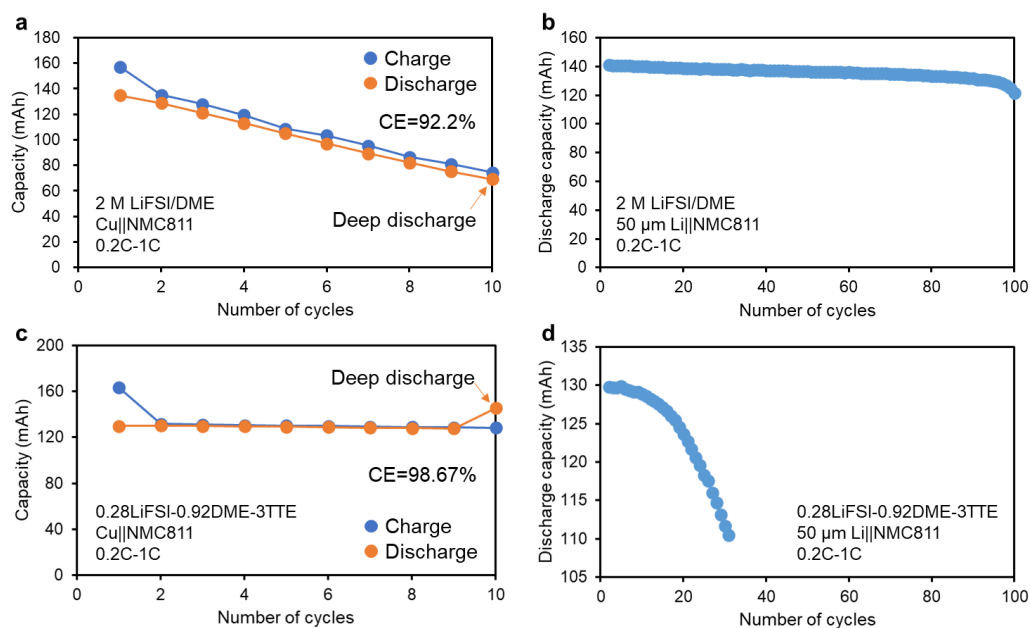
Supplementary Fig. 20 | Schematic diagram for the quantification of Li_2CO_3 and LiH formation in the rSEIs. The capacities of active Li loss caused by forming Li_2CO_3 and LiH are calculated (see Methods). See Supplementary Note 7 for detailed discussion of the calculations.



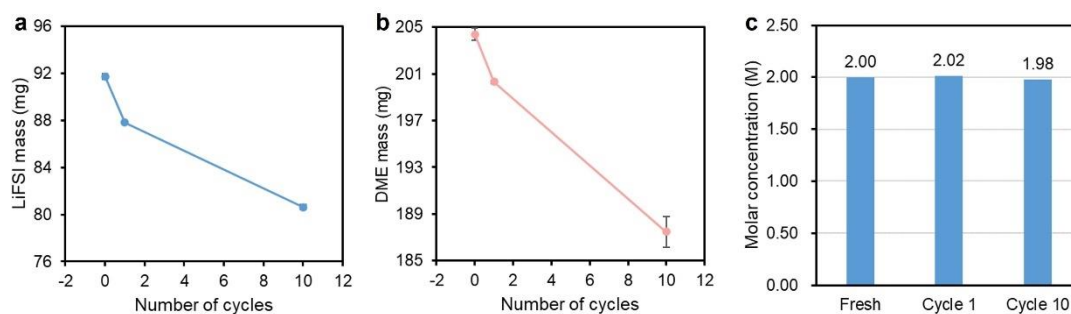
Supplementary Fig. 21 | Distribution of sources contributing to Li_2CO_3 (a) and LiH (b) formation on the negative electrode summarized from Supplementary Fig. 20. DME oxidation and reduction contribute significantly to Li_2CO_3 and LiH accumulation at the negative electrode. The overall formation of Li_2CO_3 and LiH is minimal compared to the formation of LiFSI reduction products.



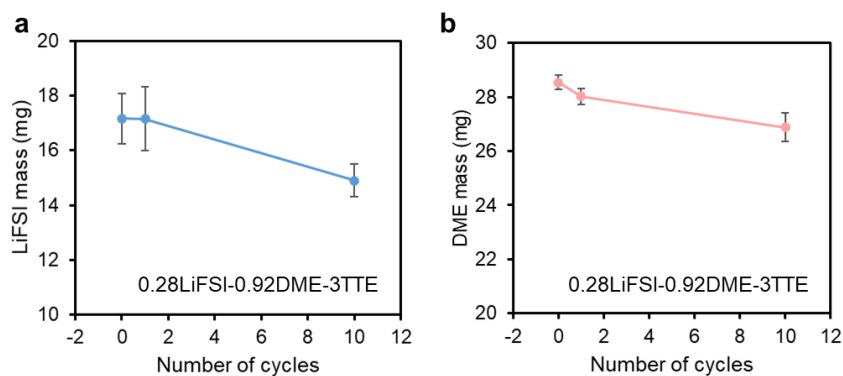
Supplementary Fig. 22 | Raman spectra of LiFSI-1.2DME-3TTE, 0.28LiFSI-0.92DME-3TTE and 2 M LiFSI/DME electrolyte solutions. LiFSI-1.2DME-3TTE is dominated by AGGs (aggregates), while 2 M LiFSI/DME is dominated by SSIPs (solvent-separated ion pairs)⁵. The FSI⁻ peak of 0.28LiFSI-0.92DME-3TTE lies in between those of LiFSI-1.2DME-3TTE and 2 M LiFSI/DME. This proves that 0.28LiFSI-0.92DME-3TTE enables more anion-dominating solvation than 2 M LiFSI/DME and less anion-dominating solvation than LiFSI-1.2DME-3TTE.



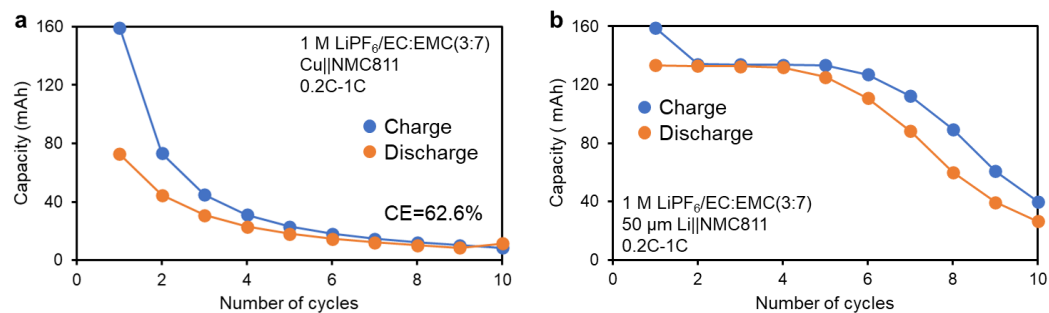
Supplementary Fig. 23 | Cycling performances of Cu||NMC811 and 50 μm Li||NMC811 pouch cells using 2 M LiFSI/DME and 0.28LiFSI-0.92DME-3TTE electrolyte solutions at 25 °C.



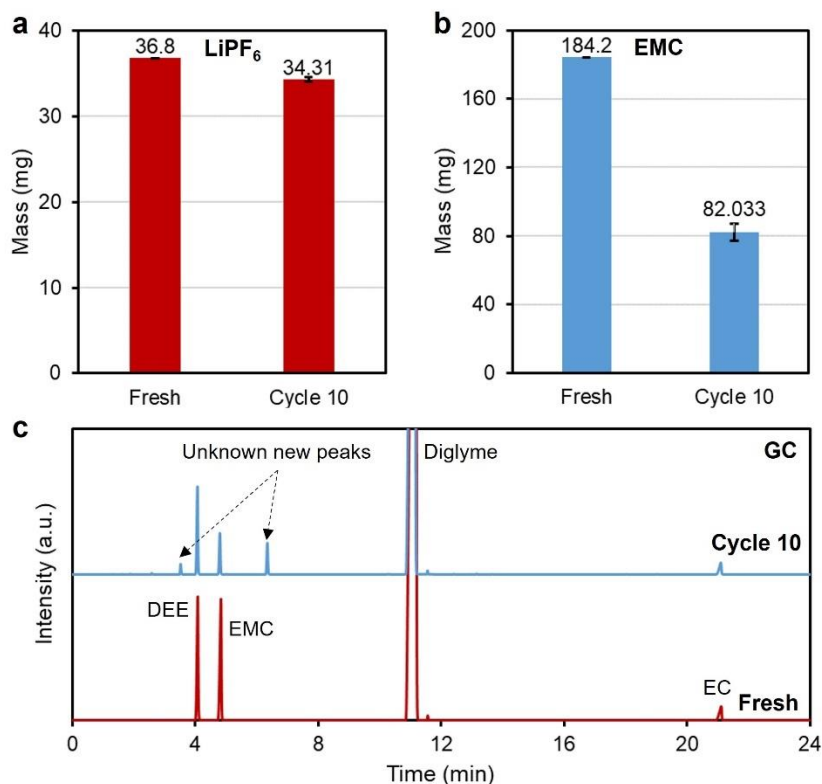
Supplementary Fig. 24 | LiFSI and DME mass variation during the cycling of Cu||NMC811 cells with 2 M LiFSI/DME. a, Evolution of LiFSI mass. **b,** Evolution of DME mass. **c,** Evolution of LiFSI molar concentration in the electrolyte solution. Each data point represents the average of three replicate samples, and the error bars indicate the standard errors. Molar concentrations in (c) were calculated based on the mean values from (a) and (b).



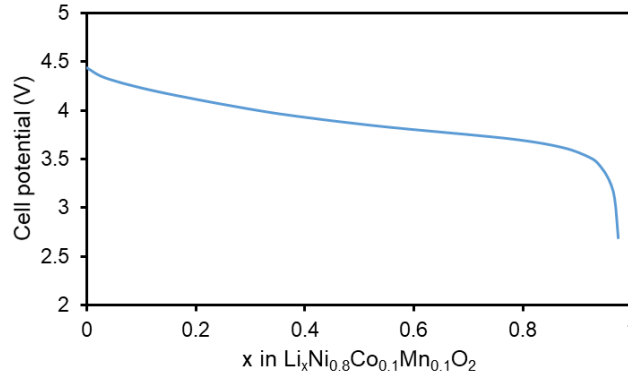
Supplementary Fig. 25 | LiFSI and DME mass variation during the cycling of Cu||NMC811 cells with 0.28LiFSI-0.92DME-3TTE. a, Evolution of LiFSI mass. **b,** Evolution of DME mass. Each data point represents the average of four replicate samples, and the error bars indicate the standard errors.



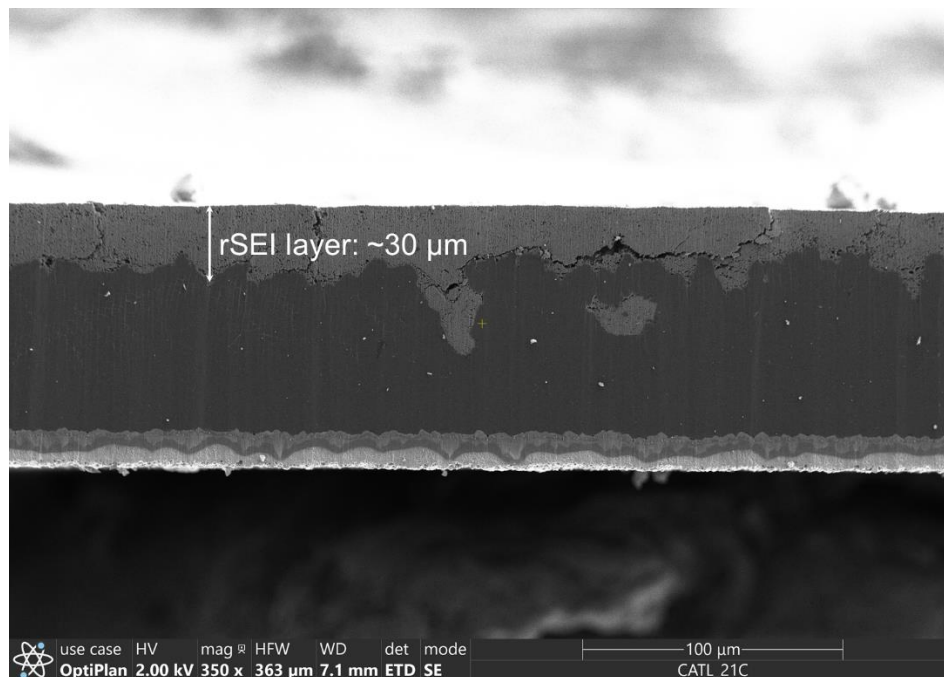
Supplementary Fig. 26 | Cycling performances of Cu||NMC811 (a) and 50 μm Li||NMC811 (b) cells with a 1 M LiPF₆/EC:EMC (3:7, v:v) electrolyte at 25 °C.



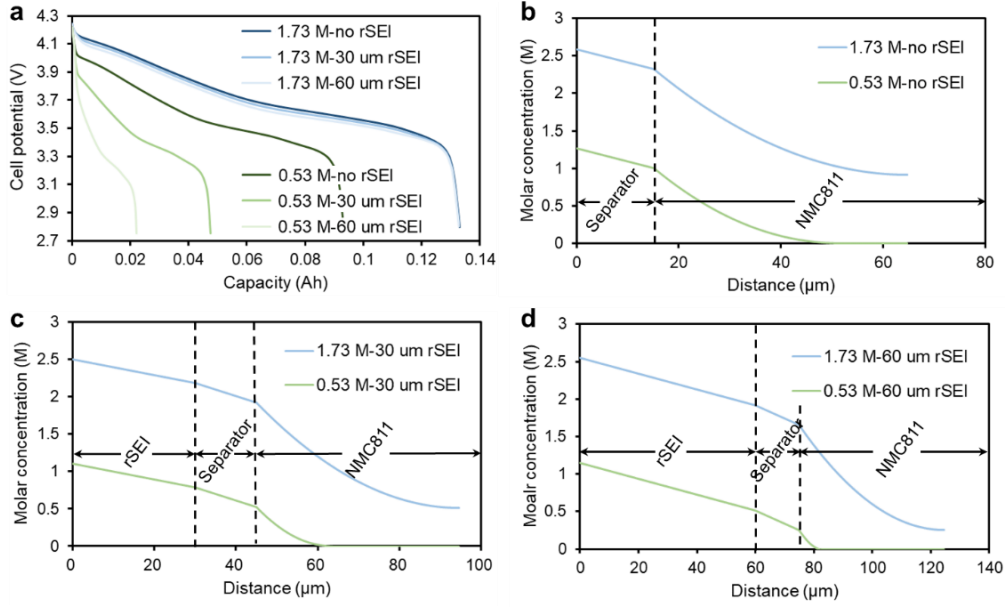
Supplementary Fig. 27 | Evolution of a 1 M $\text{LiPF}_6/\text{EC}:\text{EMC}$ (3:7, v:v) electrolyte during the cycling of 50 μm Li||NMC811 pouch cells. a, Evolution of LiPF_6 mass. **b,** Evolution of EMC mass. Each data point represents the average of three replicate samples, and the error bars indicate the standard errors. **c,** GC results of the extracted electrolyte before and after cycling (the cells were cycled under 0.2C-1C for 10 cycles at 25 $^\circ\text{C}$).



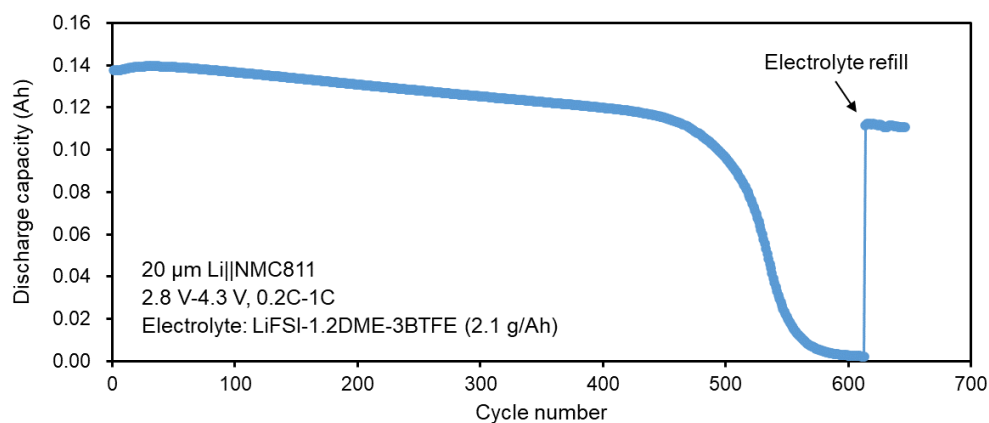
Supplementary Fig. 28 | Open circuit potential profile of a Li||NMC811 cell. Open circuit potential (OCP) values were measured at increments of 2% SOC after allowing the cell to rest for 2 hours at each SOC. A C-rate of 0.33 C was used to tune the SOC values. The cell was first activated by cycling three times between 2.8 and 4.3 V at 0.33 C. The cell was then over-charged to 4.5 V to obtain values for a wider potential range. The resulted OCP data points were connected with smoothing steps to result in this OCP profile.



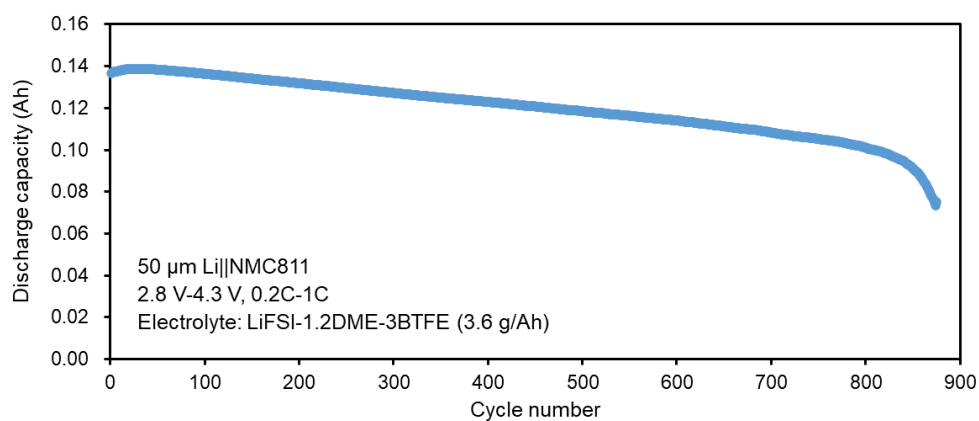
Supplementary Fig. 29 | Cross-section SEM image of a 50 μm Li negative electrode after 250 cycles at 0.2C-1C in a Li||NMC811 cell with LiFSI-1.2DME-3TTE. The cell was adjusted to 50% SOC after 250 cycles at 25 $^{\circ}\text{C}$.



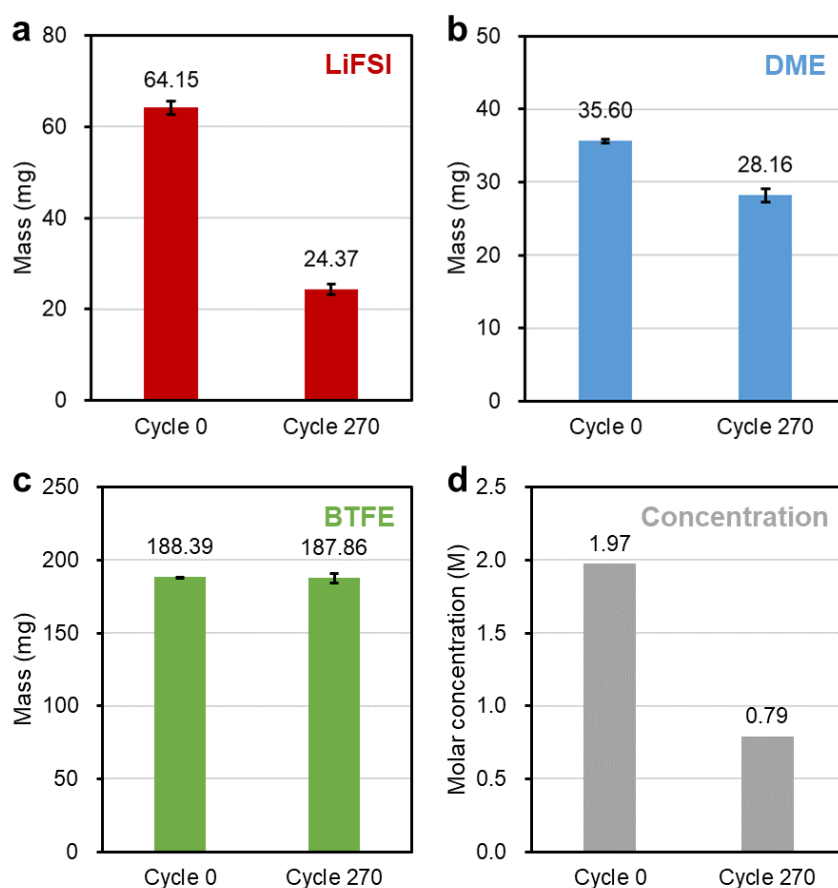
Supplementary Fig. 30 | Electrochemical simulation results under different electrolyte concentrations and different rSEI thicknesses. **a**, Simulated discharge cell potential profiles of Li||NMC811 cells with LiFSI-1.2DME-3TTE (1.73 M) and 0.28LiFSI-0.92DME-3TTE (0.53 M) electrolyte. **b**, **c**, **d**, Simulated concentration distributions of LiFSI-1.2DME-3TTE (1.73 M) and 0.28LiFSI-0.92DME-3TTE (0.53 M) with 0 μm (**b**), 30 μm (**c**) and 60 μm (**d**) accumulated rSEIs at 1000 s into the 1 C (140 mAh) discharge. In this simulation, the rSEI layer was parametrized by its porosity, for which a value of 0.4 was chosen based on its separator-like ionic transport properties (a value of 0.39 was used for the separator in the main text). To simulate transport phenomena in porous media, the classical expression of the effective diffusion coefficient (D_{eff}) is often used: $D_{\text{eff}} = D_0 \cdot \frac{\epsilon}{\tau}$, where D_0 is the intrinsic diffusivity of a material in the absence of structural factors like porosity and tortuosity. Since the empirical measurement of tortuosity is not straightforward, the Bruggeman approximation is often invoked, assuming a power-law relationship between porosity (ϵ) and tortuosity (τ), linked by an empirical parameter known as the Bruggeman parameter (γ): $\tau = \epsilon^{1-\gamma}$. The expression for D_{eff} then becomes: $D_{\text{eff}} = D_0 \cdot \epsilon^\gamma$. We utilized a γ value of 1.5, which is widely adopted as a reasonable approximation for most porous materials⁶.



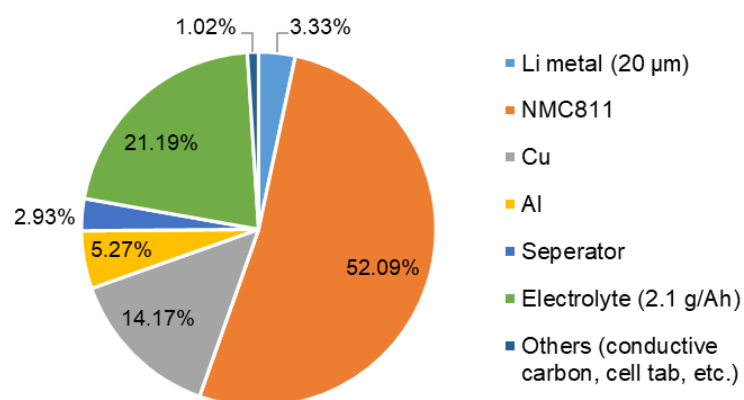
Supplementary Fig. 31 | Prolonged cycling of a 20 μm Li|LiFSI-1.2DME-3BTfE|NMC811 pouch cell (2.1 g/Ah of electrolyte) after end-of-life and electrolyte refill at 25 °C. The initial 485 cycles are the same as reported in Figure 4e in the main text.



Supplementary Fig. 32 | Cycling performance of a 50 μm Li|LiFSI-1.2DME-3BTfE|NMC811 pouch cell (3.6 g/Ah of electrolyte).



Supplementary Fig. 33 | The evolution of electrolyte components and molar concentration of LiFSI-1.2DME-3BTFE at 0 and 270 cycles under 0.2C-1C (25 °C) in 50 μm Li||NMC811 cells. **a, Evolution of LiFSI mass. **b**, Evolution of DME mass. **c**, Evolution of BTFE mass. **d**, Evolution of LiFSI molar concentration in the electrolyte solution. Each data point represents the average of four replicate samples, and the error bars indicate the standard errors. Molar concentrations in (**d**) were calculated based on the mean values from (**a**), (**b**), and (**c**).**



Supplementary Fig. 34 | Calculated percentage of the mass distribution of a LMB applying the pouch cell specifications reported in Supplementary Table 9.

Supplementary Tables 1-10

Supplementary Table 1 | E-G&IC quantification results for the uncontaminated and contaminated electrolyte solutions. The detailed discussion can be seen in Supplementary Note 3.

Component	DME	TTE	LiFSI	Total
Uncontaminated (g)	0.0327	0.2107	0.0566	0.3000
Contaminated (g)	0.0322	0.2105	0.0568	0.2995

Supplementary Table 2 | Solvation environment comparison between the bulk electrolyte and the negatively charged electrode interface for the simulation reported in Supplementary Fig. 12.

	-5 V electrode interface				Bulk electrolyte			
	Li ⁺	FSI ⁻	DME	TTE	Li ⁺	FSI ⁻	DME	TTE
Count	21	11	46	49	29	30	44	174
Ratio	16.6%	8.7%	36.2%	38.6%	10.5%	10.8%	15.9%	62.8%

Supplementary Table 3 | Ion current raw data of the DEMS experiment in Supplementary Fig. 15 at 265 min. The detailed discussion can be seen in Supplementary Note 5.

Gas species	H ₂	CH ₄	C ₂ H ₂	C ₂ H ₄	CO	C ₂ H ₆	O ₂	CO ₂
Ion current ($A \times 10^{13}$)	8.87	3.24	0.34	0.59	30.53	0.55	16.95	1.49

Supplementary Table 4 | Calculated volume fraction of different gas species in the DEMS experiment in Supplementary Fig. 15 at 265 min. The detailed discussion can be seen in Supplementary Note 5.

Gas species	H₂	CH₄	C₂H₂	C₂H₄
Volume fraction	0.00173	0.00069	-0.00117	0.00078
Gas species	CO	C₂H₆	O₂	CO₂
Volume fraction	0.00069	0.00084	0.00012	0.00057

Supplementary Table 5 | Simulated solubilities of gas species in different solvents.

The detailed discussion can be seen in Supplementary Note 6. The solubilities of various gas species in H₂O obtained from both experiment and simulation are presented here. Although discrepancies exist, the trends across gas species are generally similar. Gas solubilities in EC, DMC, EMC, and DME were also simulated. In DME, the solubility of CO₂ is much higher than that of H₂.

	Experimental (g/kg)		Simulated (g/kg)			
	H ₂ O	H ₂ O	Ethylene carbonate (EC)	Dimethyl carbonate (DMC)	Ethyl methyl carbonate (EMC)	DME
NH ₃	529.000	124.547	94.757	83.342	79.426	74.154
CO ₂	1.690	0.060	1.399	3.205	3.622	4.774
C ₂ H ₄	0.149	0.047	1.950	6.188	7.293	7.976
N ₂	0.019	0.020	0.199	0.471	0.502	0.389
CH ₄	0.023	0.004	0.077	0.283	0.363	0.893
CO	0.028	0.003	0.114	0.380	0.474	0.579
O ₂	0.043	0.000	0.017	0.074	0.104	0.165
H ₂	0.002	0.002	0.006	0.012	0.019	0.016

Supplementary Table 6 | Comparing the formulations of 2 M LiFSI/DME with that of the LiFSI-DME-TTE electrolyte after 300 cycles in a Li||NMC811 cell cycled under 0.2C-1C at 25 °C. The detailed discussion can be seen in Supplementary Note 9.

Electrolyte formulation	2 M LiFSI/DME	Cycle 300 formulation (0.28LiFSI-0.92DME-3TTE)
LiFSI : DME (molar ratio)	0.21 : 1	0.31 : 1
LiFSI wt% in the whole electrolyte	30.14 wt%	6.48 wt%
LiFSI molar concentration	2.00	0.53

Supplementary Table 7 | Quantified LiFSI to DME decomposition molar ratio during the first 10 cycles of Cu||NMC811 cells with 2 M LiFSI/DME and 0.28LiFSI-0.92DME-3TTE cycled under 0.2C-1C at 25 °C. The detailed discussion can be seen in Supplementary Note 9.

	LiFSI decomposed		DME decomposed		LiFSI to DME decomposition molar ratio
	(mg)	(mmol)	(mg)	(mmol)	
2 M LiFSI/DME	11	0.059	17	0.188	0.316
0.28LiFSI-0.92DME-3TTE	2	0.012	2	0.018	0.657

Supplementary Table 8 | Single layer stack (SLS) pouch cell configurations. Based on the design of experiment adopted for the cell design and testing reported in this work, the charge/discharge rates and electrolyte injection coefficients are standardized to a cell capacity of 140 mAh. The discussion can be seen in Supplementary Note 12.

Negative electrode current collector (CC)	10 μm Cu foil	
Negative electrode material	0, 5, 10, 15, 20, 50 μm thick Li foil laminated onto the Cu CC (single-sided)	
Separator	12 μm PE + 3 μm coating	
Positive electrode CC	13 μm Al foil	
Positive electrode active material	NMC811 (double-sided)	
Positive electrode active material percentage	96.9%	
Positive electrode material mass loading	17.1 mg/cm^2	
Positive electrode compacted density	3.45 g/cm^3	
Positive electrode area	20.78 cm^2	
Cell discharge capacity	0.2C	147 mAh
	1C	140 mAh
Positive electrode active material theoretical specific capacity	0.2C	206 mAh/g
	1C	196 mAh/g
Positive electrode areal capacity	0.2C	3.53 mAh/ cm^2
	1C	3.36 mAh/ cm^2
Nominal cell potential	0.2C	3.81 V
	1C	3.71 V
Amount of injected electrolyte solution	0.15 g	1.1 g/Ah
	0.2 g	1.4 g/Ah
	0.25 g	1.8 g/Ah
	0.3 g	2.1 g/Ah
	0.5 g	3.6 g/Ah
	0.7 g	5 g/Ah
N/P ratio	Anode-less	0.00
	5 μm Li foil	0.28
	10 μm Li foil	0.57
	15 μm Li foil	0.85
	20 μm Li foil	1.13
	50 μm Li foil	2.83

Supplementary Table 9 | Pouch cell specific energy calculation and projection.

These cell design parameters apply to the cells in Fig. 4e. The cell energy of 0.56 Wh was experimentally measured with the SLS pouch cells. The 50 Ah pouch cell is projected with a higher specific energy than the calculated value based on the electrodes and the electrolyte. This is because the Li metal negative electrodes in a SLS are single-sided, while those in a 50 Ah pouch cell are double-sided.

Cell design parameters	Negative electrode current collectors (CC)	10 μm Cu foil
	Negative electrode material (single-sided)	20 μm Li foil
	Separator	12 μm PE + 3 μm coating
	Positive electrode CC	13 μm Al foil
	Positive electrode active material (double-sided)	NMC811
	Electrolyte injection	2.1 g/Ah
	Cell energy (at 0.2C)	0.56 Wh
Specific Energy	Based on active materials	739 Wh/kg
	Based on electrodes + electrolyte	367 Wh/kg
	Projected for a 50 Ah pouch cell with the same design	389 Wh/kg

Supplementary Table 10 | Specific energy comparison between LMB designs with different Li metal negative electrode thicknesses and electrolyte amounts. The calculated specific energy considers the mass of the whole cell for the 50 Ah pouch cell design. The detailed discussion can be seen in Supplementary Note 12.

Li thickness (μm)	Electrolyte amount (g/Ah)	Specific energy (Wh/kg)
20	2.1	389
0 (anode-less)	2.1	402
20	1.1	434

Supplementary Notes 1-12

Supplementary Note 1: Reliability of CD₃CD₂OD as the titrant for Li and LiH quantification

Deuterated water (D₂O) is routinely used as the titrant for the quantification of Li metal and LiH^{7,8} via *ex situ* titration mass spectrometry measurements of electrodes collected from cycled coin cells. However, as we carry out battery testing in a pouch cell format, a larger amount of Li metal and LiH need to be titrated. As D₂O is highly reactive towards Li metal, when using it to titrate our sample with a significant amount of “dead” Li and LiH, we observed an extremely violent reaction between D₂O and the Li metal in the air-tight titration vessel (Supplementary Fig. 1). Performing such an experiment repeatedly is not safe. Furthermore, an excessive amount of gas was generated at the beginning of titration. This could interrupt the steady flow of the Ar carrier gas, leading to inaccurate results. Therefore, we decided not to use D₂O as the titrant.

Instead, we use ethanol-d₆ (CD₃CD₂OD) as the titrant. CD₃CD₂OD reacts more mildly towards “dead” Li and LiH. To verify that CD₃CD₂OD is a good titrant, we carefully carried out titration-differential electrochemical mass spectrometry (T-DEMS) measurements to confirm that the samples under investigation are completely reacted. After the injection of CD₃CD₂OD into a negative electrode sample (collected after cycling in a pouch cell), a clear deuterium (D₂) signal is detected (Supplementary Fig. 3). After the disappearance of the D₂ signal, D₂O is injected. It can be observed that no further signal appeared. This analytical test verifies the reliability of CD₃CD₂OD as the titrant for the T-DEMS measurements.

Supplementary Note 2: Reliability of H₂SO₄ as the titrant for Li₂CO₃ quantification

Besides Li₂CO₃, other species like ROCOOLi and RCOOLi⁹ could react with H₂SO₄ to generate CO₂. However, these two Li-containing chemical species do not interfere with the quantification of Li₂CO₃ for the reasons discussed below.

1) ROCOOLi is unlikely to form in the LiFSI-1.2DME-3TTE electrolyte

The formation of ROCOOLi from an ether solvent is inherently an oxidation process. Thus, the direct reduction of DME to ROCOOLi on the negative electrode is not possible. Theoretically, ROCOOLi can be formed through DME oxidation at the positive electrode to ROCOOR and subsequent cross-talk with the negative electrode. Such a process would require the carbonyl C in the formate molecule (Supplementary Fig. 4) to lose an additional H atom. This process is thermodynamically unfavorable, according to our simulation. However, even if this happens, it will require the presence of an adjacent -OCH₃ fragment for the generation of ROCOOCH₃ (Supplementary Fig. 4), to initiate the cross-talk with the negative electrode to form ROCOOLi. In contrast, the breakage of a C-O bond could occur in the formate molecule (Fig. 3d), leading to the generation of CO₂. Considering these two pathways, it is unlikely that DME oxidation and cross-talk would lead to the formation of species like ROCOOLi.

The formation of ROCOOLi is highly dependent on the structure of the ether solvent. For example, dimethoxymethane (DMM) is an ether solvent that could undergo oxidation to form CH₃OCOOCH₃. This is because the middle C atom is connected to two O atoms. By losing one H atom during the initial step of the oxidation, this C atom bonds to a lattice O (Supplementary Fig. 5). The loss of an additional H directly lead to the formation of CH₃OCOOCH₃, which could cross-talk to the negative electrode to form CH₃OCOOLi. Therefore, it is essential to highlight that interfacial reaction pathways must be carefully considered case by case.

2) RCOOLi leads to negligible CO₂ generation during T-DEMS

Formate molecules could be produced (Fig. 3d) during DME oxidation. This molecule can activate the cross-talk process with the negative electrode to form species

like RCOOLi (Supplementary Fig. 6). Therefore, we carried out T-DEMS measurements using H_2SO_4 as titrant and CH_3COOLi as the analytical sample to confirm the impact of the latter on CO_2 generation. In the experiment, 0.167 mmol of CH_3COOLi are used for the titration, and only 0.000035 mmol of CO_2 are generated (Supplementary Fig. 7). With this result, it is reasonable to rule out RCOOLi as a CO_2 source and attribute CO_2 generation during H_2SO_4 titration solely to Li_2CO_3 in the sample.

Supplementary Note 3: Selection of the extraction solvent and internal standard for E-G&IC and extraction efficiency

The internal standard (in our case, diethoxyethane, DEE) and extraction solvent (in our case, diglyme) must be highly miscible with the electrolyte components, and the GC peaks must be clearly resolved at different times. Like DME, DEE and diglyme are ethers and exhibit high solubility towards the LiFSI salt. From the GC measurement of an uncontaminated electrolyte (i.e., not in contact with the cell electrodes), it is observed that the DEE and diglyme peaks can be fully resolved from the electrolyte solvents (Supplementary Fig. 8).

Another concern regards the stability of the internal standard and extraction solvent towards the electrodes and rSEIs. We also verified this through a practical experiment. Specifically, a cycled Li metal electrode and a cycled NMC811 electrode were rinsed with DME, dried and paired to assemble a new pouch cell. The electrolyte was first injected to wet the cell for 6 hours, then the internal standard and the extraction solvent were injected for extraction. The cell was vacuum sealed (-90 kPa) in a dry room (relative humidity <1 %) and allowed to rest for 7 days at 25 °C. Afterwards, the extracted electrolyte (labelled as contaminated electrolyte) was measured by GC and IC. The GC results for this “contaminated” electrolyte align with those for the uncontaminated electrolyte sample (Supplementary Fig. 8). A quantitative analysis of IC measurements was also performed to compare the electrolyte formulations. Masses of components in the contaminated electrolyte stored with cycled electrodes showed negligible deviation from the values obtained for the uncontaminated electrolyte (Supplementary Table 1). These results validate the stability of DEE and diglyme towards Li metal, NMC811 and rSEIs and the complete miscibility with the electrolyte solution during the extraction process for an accurate sampling.

Supplementary Note 4: Additional analysis on the chemical composition and distribution of cSEIs

To obtain cSEI samples to characterize in terms of chemical composition and distribution, a Li||NMC811 pouch cell was fully charged at 0.2C to 4.3V and then followed with a constant current-constant potential (CC-CP) protocol with a cutoff current of 0.1C (14 mA). An XPS depth profile was performed on the resulting negative electrode surface (see Methods for sample preparation and measurement details). Before sputtering, F 1s and S 2p spectra show the presence of F-S bonding and S^{6+} and S^{4+} signals (Supplementary Fig. 13). This indicates that the outer layer of the cSEI contains chemical species which are intermediates of the FSI^- anion reduction. After sputtering, these signals are diminished, while LiF and Li_2S (S^{2-}) signals are dominant. This indicates that the inner layer of the cSEI mostly comprises chemical species derived from complete FSI^- reduction. The depth profile of chemical composition also shows that the outer layer of the cSEI is abundant in organic species with a higher C ratio, while the inner layer is more inorganic with higher F and S presence. These results are in agreement with previous reports⁴.

Supplementary Note 5: Quantification of gas generation through *in situ* DEMS measurements

During the DEMS measurement, only a small fraction of the carrier gas (Ar), together with the generated gas, access the MS. However, since the split ratio is constant, it is possible to construct a calibration curve between the ion current signal intensity and the volume fraction of the target gas. In the case of H₂, Ar-H₂ gas mixtures with different H₂ concentrations are introduced into the MS, and the H₂ ion current signal intensities are recorded. The H₂ ion current signal intensity (I_{H_2}) could then be linearly fit against the volume fraction of H₂ (c_{H_2}) in the gas mixture, resulting in the following calibration equation in, the form of $y = ax + b$:

$$I_{H_2} = 6.452 \times 10^{-10} c_{H_2} - 2.287 \times 10^{-13}$$

The numerical values, from left to right, correspond to the slope (a) and intercept (b) of the linear fit. Calibration equations were similarly constructed for other types of gas generated during the DEMS measurement:

$$I_{CH_4} = 8.547 \times 10^{-10} c_{CH_4} - 2.675 \times 10^{-13}$$

$$I_{C_2H_2} = 1.280 \times 10^{-9} c_{C_2H_2} + 1.536 \times 10^{-12}$$

$$I_{C_2H_4} = 2.331 \times 10^{-9} c_{C_2H_4} - 1.749 \times 10^{-12}$$

$$I_{CO} = 3.077 \times 10^{-9} c_{CO} + 9.151 \times 10^{-13}$$

$$I_{C_2H_6} = 3.205 \times 10^{-10} c_{C_2H_6} - 2.146 \times 10^{-13}$$

$$I_{O_2} = 1.280 \times 10^{-9} c_{O_2} + 1.536 \times 10^{-12}$$

$$I_{CO_2} = 9.174 \times 10^{-10} c_{CO_2} - 3.713 \times 10^{-13}$$

We use these calibration equations to analyze the DEMS measurements of the cycled pouch cells. Considering the experiment in Supplementary Fig. 15 as an example, the

flow rate of Ar carrier gas was fixed at 0.6 ml/min. The Ar carry the generated gas into the MS for the measurement (with the same split ratio) and the ion current signal intensity is measured for each gas species. In Supplementary Table 3, we report the ion current intensity raw data at 265 min of the measurement (peak of H₂ generation). Applying the calibration equations, we calculate the volume fraction for each gas species (see Supplementary Table 4). We also calculate the volume fraction of Ar (c_{Ar}) in the measured gas using the following equation:

$$\begin{aligned} c_{Ar} &= 1 - c_{H_2} - c_{CH_4} - c_{C_2H_2} - c_{C_2H_4} - c_{CO} - c_{C_2H_6} - c_{O_2} - c_{CO_2} \\ &= 1 - 0.00173 - 0.00069 - (-0.00117) - 0.00078 - 0.00069 \\ &\quad - 0.00084 - 0.00012 - 0.00057 = 0.99575 \end{aligned}$$

Since the Ar flow rate (r_{Ar}) is fixed at 0.6 ml/min, we can then calculate the generation rate of H₂ (r_{H_2}) using the ratio of the instantaneous volume fractions of Ar and H₂ gas determined at 265 min of the measurement:

$$\begin{aligned} r_{H_2} &= r_{Ar} \times \frac{c_{H_2}}{c_{Ar}} = 0.6 \text{ ml/min} \times \frac{0.00173}{0.99575} \\ &= 1.04 \times 10^{-3} \text{ ml/min} \end{aligned}$$

This volumetric flow rate can then be converted into a molar flow rate using the ideal gas law ($PV = nRT$) at RTP conditions (see Methods, where pressure is atmospheric pressure and given as 0.1 MPa and the temperature is 25 °C):

$$\begin{aligned} n &= \frac{P}{RT} V \\ n(\text{in nmol}) &= \frac{(101.325 \text{ kPa})}{\left(8.314 \frac{\text{kPa} \cdot \text{L}}{\text{mol} \cdot \text{K}}\right) (298.15 \text{ K})} V(\text{in mL}) \times \frac{1 \text{ L}}{1 \times 10^3 \text{ mL}} \times \frac{1 \times 10^9 \text{ nmol}}{1 \text{ mol}} \\ &= 4.088 \times 10^4 \frac{\text{nmol}}{\text{ml}} \times V(\text{in mL}) \end{aligned}$$

where n is the number of moles, P is the pressure (atmospheric pressure), V is the volume, R is the universal gas constant, and T is the absolute temperature.

Thus,

$$\begin{aligned} r_{H_2}(\text{nmol/min}) &= 4.088 \times 10^4 \frac{\text{nmol}}{\text{ml}} \times r_{H_2}(\text{ml/min}) \\ &= 4.088 \times 10^4 \frac{\text{nmol}}{\text{ml}} \times 1.04 \times 10^{-3} \text{ ml/min} \\ &= 42.5 \text{ nmol/min} \end{aligned}$$

Note, the conversion factor, $4.088 \times 10^4 \text{ nmol/ml}$, is often given in the inverse form in units of L/mol, 24.46 L/mol (i.e., RTP molar volume of an ideal gas, equivalent to $2.446 \times 10^{-5} \text{ ml/nmol}$), which can be divided from the volumetric flow rate (ml/min) to give the same results in nmol/min. The generation rates of other gas species can be calculated in a similar manner; they are mapped out for the whole time range of the measurement in Supplementary Fig. 15.

It can be observed that the baselines of different gas species do not perfectly overlap with zero (Supplementary Fig. 15). This is because, in the DEMS measurement of a pouch cell, the solvents in the electrolyte can partially evaporate and flow into the MS as well. The ionized fragments of these solvents could resemble those of the gas species and result in a baseline deviating from zero. The contribution from solvent evaporation to the resulted signal stays rather stable throughout the measurement. Therefore, the baselines of different gas species were extracted to eliminate the signal contribution from the evaporation of the electrolyte's solvent (see Supplementary Fig. 16). Gas generation could then be quantified via integral calculation of the peak areas.

Supplementary Note 6: Evaluation and analysis of the gas generated during the *in situ* DEMS measurements

The presence of Li_2CO_3 on the negative electrode originated from the cross-talk with CO_2 . However, no signal of CO_2 is detected during the *in situ* DEMS measurement on gas generation (Supplementary Fig. 14c). Through simulation, we found that the solubility of CO_2 in DME should be significantly higher than other gas species (Supplementary Table 5), so all the CO_2 generated during *in situ* DEMS could dissolve into the electrolyte resulting in the absence of its signal. To verify this assumption, we experimentally measured the solubility of CO_2 in LiFSI-1.2DME-3TTE. The results are shown in Supplementary Fig. 17. The volume of the control sample without CO_2 injection was reasonably stable during the 13 h testing period. The volume of the sample with CO_2 injection experienced a minor increase at the beginning of the measurement. This was due to a lower initial sample temperature ($\sim 20^\circ\text{C}$) than the silicone oil temperature (25°C). Since the volume of CO_2 gas is more sensitive to temperature than the electrolyte, this initial volume increase was more significant in the CO_2 -injected sample than in the control sample. After peaking, the volume of the CO_2 -injected sample continuously decreases, indicating the solubilization of CO_2 in the electrolyte. Quantitatively, we calculate that 1.7 ml CO_2 dissolved per 10 g electrolyte within 13 hours. Thus, in a Cu||NMC811 SLS pouch cell, if the CO_2 dissolved in the electrolyte could effectively participate in the cross-talk and be incorporated in the SEI of the negative electrode, additional CO_2 , possibly generated during cycling, could continuously dissolve so that no signal of CO_2 gas can be detected during *in situ* DEMS. Therefore, a maximum Li_2CO_3 accumulation rate from dissolved CO_2 , in the absence of gas phase CO_2 , can be calculated as follows:

$$\begin{aligned}
 R_{\text{Li}_2\text{CO}_3}^{\text{max}} &= \frac{pV_{\text{CO}_2}}{RT} \times \frac{2 \text{ mol Li}_2\text{CO}_3}{3 \text{ mol CO}_2} \times M_{\text{Li}_2\text{CO}_3} / (m_{e1} \times t_1) \\
 &= \frac{1.7 \text{ ml CO}_2 \times 101 \text{ kPa}}{8.314 \frac{\text{L} \times \text{kPa}}{\text{K} \times \text{mol CO}_2} \times 298 \text{ K}} \times \frac{2 \text{ mol Li}_2\text{CO}_3}{3 \text{ mol CO}_2} \times 74 \frac{\text{g Li}_2\text{CO}_3}{\text{mol Li}_2\text{CO}_3} \\
 &\quad \div 10 \text{ g electrolyte} \div 13 \text{ h} = 2.63 \times 10^{-5} \frac{\text{g Li}_2\text{CO}_3}{\text{g electrolyte} \times \text{h}}
 \end{aligned}$$

Where p is standard atmospheric pressure, V_{CO_2} is the volume of CO_2 dissolved in 10 g electrolyte after 13 hours, R is molar gas constant, T is the absolute temperature, a factor of 2/3 representing the stoichiometry that 3 moles of CO_2 are required to form 2 moles of Li_2CO_3 (Eq. 3 in the main text), $M_{Li_2CO_3}$ is molar mass of Li_2CO_3 , m_{e1} is the mass of electrolyte, and t_1 is the total time of the solubility experiment.

From the Li_2CO_3 quantification result (0.38 mAh after 40 cycles, Fig. 2d), we can also calculate the experimental Li_2CO_3 accumulation rate:

$$\begin{aligned}
 R_{Li_2CO_3}^{exp} &= \frac{C_{Li_2CO_3}}{C_{lithium} \times M_{Li} \times n_{Li}} \times M_{Li_2CO_3} / (m_{e2} \times n \times t_2) \\
 &= \frac{0.38 \text{ mAh}}{3860 \frac{\text{mAh}}{\text{g}} \times 7 \frac{\text{g}}{\text{mol}} \times 2} \times 74 \frac{\text{g } Li_2CO_3}{\text{mol}} \div 0.3 \text{ g electrolyte} \\
 &\div (40 \times 6 \text{ h}) = 7.23 \times 10^{-6} \frac{\text{g } Li_2CO_3}{\text{g electrolyte} \times \text{h}}
 \end{aligned}$$

Where $C_{Li_2CO_3}$ is the total equivalent lithium capacity for Li_2CO_3 , $C_{lithium}$ is the theoretical specific capacity of lithium metal, M_{Li} is the molar mass of lithium, n_{Li} is the number of moles of Li in a mole of Li_2CO_3 , $M_{Li_2CO_3}$ is the molar mass of Li_2CO_3 , m_{e2} is the mass of electrolyte injected in the cell, n is the cycle number, and t_2 is the total time per cycle.

Since $R_{Li_2CO_3}^{exp} \ll R_{Li_2CO_3}^{max}$, it is reasonable to assume that only a small amount of CO_2 is generated during cycling. This small amount of CO_2 can then be dissolved in the electrolyte and subsequently cross-talk and react with the Li negative electrode to form a small amount of Li_2CO_3 . For this reason, no signal of CO_2 gas was observed during *in situ* DEMS measurement.

Another interesting phenomenon is that several additional peaks of H_2 were observed at the end of the cell discharge (Supplementary Fig. 14c). When 100 ppm of H_2O are added to the electrolyte solution used for the cycling of the Li||NMC811 pouch cell, the H_2 signals did not increase (Supplementary Fig. 16). This feature indicates that

the formation of H_2 is not directly associated with the initial water contents in the electrolyte solution. If we look at the DME oxidation pathway (Fig. 3d), we observe that the molecule could lead to the increasing density of surface-bonded hydrogen. When two hydrogen atoms bond to one oxygen atom, *ab initio* simulation results confirm the likelihood of H_2O desorption (Supplementary Fig. 18) under a low SOC of 0%SOC rather than 100%SOC. Based on this analysis, we assume that the cross-talk of the desorbed H_2O is the origin of the H_2 signals at the end of discharges. The H_2 signal became not detectable after several cycles, possibly due to either the formation of the rock-salt phase that passivates the NMC811 particles' surface (Supplementary Fig. 14a) or the change in the morphology of the electrodeposited Li metal at the negative electrode (which favours an increase of the surface area) so that H_2O is promptly reduced to LiH.

Supplementary Note 7: Quantification of Li_2CO_3 and LiH

For the quantification of Li_2CO_3 and LiH formed in the rSEI (schematically shown in Supplementary Fig. 20), we assume that all the CO_2 generated on the NMC811-based positive electrode undergo cross-talk and reacts with Li metal at the negative electrode. We also assume that all the hydrogen atoms absorbed on the NMC811 electrode surface, due to DME oxidation, are released in the form of H_2O , and all the H_2O in the electrolyte fully reacts with Li metal.

1. Li_2CO_3

The total active Li loss to form Li_2CO_3 in the rSEI on the Cu electrodes of Cu||NMC811 cell after 100 cycles was $C_1=0.70$ mAh, which was quantified by T-DEMS (Fig. 2d). There are three sources of Li_2CO_3 : 1) trace CO_2 dissolved in the electrolyte, 2) native Li_2CO_3 on the NMC811 positive electrode, and 3) DME oxidation and cross-talk.

- 1) To quantify the Li_2CO_3 that originated from trace CO_2 dissolved in the electrolyte, we performed T-DEMS on a Cu electrode cycled 100 times in a Li||Cu half-cell under the same areal capacity as the NMC811 positive electrode. At this stage all the CO_2 dissolved in the electrolyte likely converted into Li_2CO_3 on the Cu electrode. Through this approach, active Li loss through reduction of CO_2 dissolved in the electrolyte to form Li_2CO_3 was measured to be $C_2=0.09$ mAh.
- 2) Native Li_2CO_3 on the NMC positive electrode could decompose into CO_2 during charging, which then cross-talks to form Li_2CO_3 on the negative electrode. To calculate this quantity, the quantity of Li_2CO_3 on NMC811 positive electrodes before and after 100 cycles were measured using T-DEMS. These quantities were translated into Li capacity through Eq. 12 in the main text. From this analysis, the active Li loss through the decomposition and cross-talk of the native Li_2CO_3 on the NMC811 positive electrode was determined to be $C_3=0.28$ mAh.
- 3) To determine the amount of Li_2CO_3 derived from DME oxidation and the cross-talk of the resulting CO_2 , the active Li loss from the previous two origins were deducted from the total Li loss to form Li_2CO_3 in the rSEI, which resulted in $C_6=0.33$ mAh.

2. LiH

The total active Li loss to form LiH in the rSEI on the Cu electrodes of Cu||NMC811 cell after 100 cycles was $C_7=3.07$ mAh, which was quantified by T-DEMS (Fig. 2d). The origins of LiH on the negative electrode are: 1) trace H_2O in the electrolyte, 2) DME oxidation and cross-talk, and 3) DME reduction.

- 1) To determine the amount of LiH originating from trace H_2O , H_2O content in the electrolyte was first measured by Karl Fisher titration (822 nmol H_2O , Supplementary Fig. 14c). Under the assumption that the reduction of 1 mol of H_2O results in 2 mol of LiH (detailed in Supplementary Fig. 19), 1644 nmol of LiH are generated. Using the molar mass and specific capacity of Li (values shown in Eq. 11 of the main text), the active Li loss due to the trace H_2O in the electrolyte can be calculated to be $C_8=0.04$ mAh.
- 2) The amount of LiH resulting from DME oxidation and cross-talk is calculated in the following manner. We start with the value C_6 , which is the amount of Li_2CO_3 obtained via DME oxidation and cross-talk, given in equivalent capacity of Li. Since there are 2 mol of Li for every mole of Li_2CO_3 , C_6 should be divided by a factor of 2 to obtain the number of moles of Li_2CO_3 . According to the stoichiometry for the cross-talk reaction, shown in Eq. 3 in the main text, 3 mol of CO_2 generate 2 mol of Li_2CO_3 . Thus, the equivalent amount of CO_2 involved in producing Li_2CO_3 is obtained by multiplying by a factor of 3/2. As seen in the DME oxidation pathway in Fig. 3d, the oxidation of 1 molecule of DME to form a molecule of CO_2 is accompanied by the breaking of three C-H bonds (the bonding of three H radicals to the lattice O corresponds to the generation of 1.5 H_2O molecules). Thus, a second factor of 3/2 should be considered going from the amount of CO_2 to H_2O . As discussed above, each mole of H_2O results in 2 mol of LiH, hence a factor of 2. Through these relations, active Li loss due to DME oxidation and cross-talk to form LiH can be calculated as $C_9=0.75$ mAh.
- 3) The amount of LiH resulting from DME reduction is calculated by deducting the active Li loss from the previous two origins from the total Li loss involved in

forming LiH in the rSEI, which resulted in $C_{10}=2.27$ mAh.

We can also try to relate LiH formation to DME reduction with the quantification results on the electrolyte decomposition through E-G&IC. $C_{10}=2.27$ mAh of active Li was lost through DME reduction into LiH, corresponding to 0.08 mmol of LiH (using conversion factors from Eq. 11 in the main text) after 100 cycles. From the DME reduction pathway demonstrated in Fig. 3c, it would require at least 0.08 mol of DME to result in 0.08 mol of LiH. From the electrolyte quantification results (Fig. 2e), 0.06 mmol of DME decomposed after 100 cycles. These independent analysis results are roughly aligned, giving results on the same order of magnitude. Slight discrepancies are reasonable given experimental errors of the many techniques employed.

Supplementary Note 8: Calculation of LiFSI molar concentration in electrolytes.

The Cu||NMC811 or Li||NMC811 SLS pouch cells with 2.1 g/Ah electrolyte (LiFSI-1.2DME-3TTE) contain the same mass of Li salt (56.6 mg), DME (32.7 mg) and TTE (210.7 mg). The density of DME is 0.868 g/cm³, and the density of TTE is 1.533 g/cm³. And the molar mass of LiFSI is 187 g/mol.

For the fresh electrolyte, the molar amount of Li salt can be calculated as:

$$N_{fresh\ EL}^{LiFSI} = 56.6\text{mg} \div \frac{187\text{g}}{\text{mol}} = 0.3027\text{ mmol}$$

The volume of electrolyte can be calculated as:

$$V_{fresh\ EL} = \frac{32.7\text{mg}}{0.868\text{g/cm}^3} + \frac{210.7\text{mg}}{1.533\text{g/cm}^3} = 0.1751\text{ ml}$$

Thus, the Li salt molar concentration can be calculated as:

$$C_{fresh\ EL}^{LiFSI} = 0.303\text{ mmol} \div 0.175\text{ ml} = 1.7287 \frac{\text{mmol}}{\text{ml}} = 1.7287 \frac{\text{mol}}{\text{L}} \approx 1.73 \frac{\text{mol}}{\text{L}}$$

As for the electrolyte after 300 cycles in Li||NMC811 cells, the mass of Li salt, DME and TTE are 16.3 mg, 25.4 mg and 209.5 mg, respectively. Hence, the Li salt molar concentration can be calculated as follow:

$$\begin{aligned} N_{300cycle\ EL}^{LiFSI} &= 16.3\text{ mg} \div \frac{187\text{g}}{\text{mol}} = 0.0872\text{ mmol} \\ V_{300cycle\ EL} &= \frac{25.4\text{ mg}}{0.868\text{g/cm}^3} + \frac{209.5\text{ mg}}{1.533\text{g/cm}^3} = 0.1659\text{ ml} \\ C_{300cycle\ EL}^{LiFSI} &= 0.0872\text{ mmol} \div 0.1659\text{ ml} = 0.5256 \frac{\text{mmol}}{\text{ml}} \approx 0.53\text{ mol/L} \end{aligned}$$

Supplementary Note 9: Failure mechanisms of LMBs with different non-aqueous electrolyte solution systems

A broadly adopted understanding in battery research attributes cell capacity decay to non-ideal solvation structures¹⁰. However, additional factors need to be considered. Non-ideal solvation structures¹¹ lead to low cell's CE and fast Li inventory loss, but they do not always lead to immediate cell failure. To demonstrate this, we tested a 2 M LiFSI/DME electrolyte solution in a Li metal cell configuration. The original LiFSI-1.2DME-3TTE formulation changed to 0.28LiFSI-0.92DME-3TTE after 300 cycles in a 50 μm Li||NMC811 SLS pouch cell (Fig. 3h), and this final composition has a higher LiFSI to DME molar ratio (0.31:1) than 2 M LiFSI/DME (0.21:1) (Supplementary Table 6). This means that 0.28LiFSI-0.92DME-3TTE has higher salt-derived anion participation in the solvation environment, which is verified through Raman measurements (Supplementary Fig. 22). These two electrolyte formulations were then used to cycle Cu||NMC811 cells. Using 2 M LiFSI/DME, the cell capacity continuously decays, demonstrating a lifetime CE of 92.2% (Supplementary Fig. 23a). In contrast, 0.28LiFSI-0.92DME-3TTE enables stable cell cycling, with a lifetime CE of 98.7% (Supplementary Fig. 23c). Analysis of the electrolyte decomposition during cell cycling shows that the decomposition of the LiFSI-derived species and DME solvent is hindered in 0.28LiFSI-0.92DME-3TTE (Supplementary Figs. 24 and 25). As the decomposition of LiFSI and DME in 2 M LiFSI/DME and 0.28LiFSI-0.92DME-3TTE electrolytes can be quantified (mass loss over 10 cycles from Supplementary Figs. 24 and 25 tabulated in Supplementary Table 7), the corresponding consumption of LiFSI and DME in moles can be calculated (Supplementary Table 7). The mole ratio of LiFSI decomposed to DME decomposed (i.e., LiFSI to DME decomposition molar ratio) increased from 0.316 in 2 M LiFSI/DME to 0.657 in 0.28LiFSI-0.92DME-3TTE.

These results suggest that while the 0.28LiFSI-0.92DME-3TTE formulation has a Li-ion solvation shell with more FSI⁻ species, producing an improved and more stable SEI and thus resulting in a higher lifetime CE, it fails more rapidly (Fig. 3i, Supplementary Fig. 23d, <40 cycles) in a 50 μm Li||NMC811 SLS pouch cell. The cell

with 2 M LiFSI/DME could sustain stable cycling for more than twice as long (Supplementary Fig. 23b, ~100 cycles). Therefore, we can assume that the change in the Li-ion solvation environment in the LiFSI-DME-TTE electrolyte due to FSI decomposition is not the direct cause of cell failure.

Another possible failure mechanism is the degradation of the Li metal negative electrode. After 300 cycles, the electrolyte composition changes because of its components' degradation. The negative electrode also degrades, leading to impedance growth¹². Therefore, we used 0.28LiFSI-0.92DME-3TTE to assemble and test an uncycled 50 μ m Li||NMC811 cell. This cell failed rapidly as well (Fig. 3i, <40 cycles). This result supports the claim that negative electrode degradation is not the main cause of cell failure. Nevertheless, negative electrode degradation did contribute to capacity decay to a certain extent, and this will be discussed below.

We finally consider the LiFSI concentration in the electrolyte. LiFSI has a molar concentration of 0.53 M and weight percentage of 6.48 wt.% in 0.28LiFSI-0.92DME-3TTE, in contrast to the 2 M and 30.14 wt.% in 2 M LiFSI/DME. These data suggest that the 50 μ m Li||NMC811 cell failure is associated with ion depletion during discharging caused by inadequate Li-ion concentration in the electrolyte. This is also discussed via electrochemical simulations in the main text (Figs. 3j and 3k).

For electrolyte systems that demonstrate preferential decomposition among their components, attention must be devoted to analyzing the measurements associated with the cell failure. When the Li salt-derived components decompose much faster than solvent molecules (like in LHCEs), there is a risk of ion depletion after long-term cycling. However, when the main solvent decomposes much faster than the salt-derived components, there is a risk of dynamic viscosity increase or even formation of a precipitate. These are the additional factors that could lead to cell failure besides solvation environment, Li inventory loss, or electrode degradation.

To provide a more holistic picture, we further analyze the failure of 50 μ m Li||NMC811 cells using 2 M LiFSI/DME and a conventional carbonate-based 1 M LiPF₆/EC:EMC (3:7, v:v) electrolyte solution.

In 2 M LiFSI/DME, both the solvent DME and the salt-derived components decompose rapidly, but the LiFSI molar concentration remains stable during short cycling (Supplementary Fig. 24). This indicates that, in the short term, major Li-ion depletion or salt precipitation is unlikely. Cell failure could either be caused by insufficient electrolyte amount to wet the porous structures of the electrodes, or the depletion of Li inventory. The dominant factor relies on the balance between the amount of the electrolyte and the thickness of the Li metal negative electrode.

When using 1 M LiPF₆/EC:EMC (3:7, v:v) as the electrolyte, both Cu||NMC811 and Li||NMC811 cells failed before the 10th cycle. Through a lifetime CE calculation (see Methods), Cu||NMC811 cells exhibited a CE of 62.6% (Supplementary Fig. 26). This is expected for a Li cell operating with a carbonated-based electrolyte solution. Through GC and IC measurements and analyses, it can be observed that the LiPF₆ salt mass loss is minor (Supplementary Fig. 27a), whereas the EMC solvent mass loss is major (Supplementary Fig. 27b). The results of EC are not shown due to its high boiling point (243 °C), which could lead to inaccurate GC results (the GC gasification temperature is 250 °C). Since solvent decomposition is the predominant effect for the cell with the 1 M LiPF₆/EC:EMC electrolyte, it is expected that the electrolyte dynamic viscosity would increase during cycling, thus leading to possible salt precipitation. Meanwhile, through the GC results, we observed the generation of unidentified signals (Supplementary Fig. 27c) in the cycled electrolyte, possibly attributed to soluble species generated through EMC reduction. These features suggest that the electrolyte decomposition detrimentally affects the cell's CE. Therefore, we speculate that the Li inventory will be depleted of Li ions before LiPF₆ precipitation happens. This could be the possible main factor for the failure of the 50 μm Li|1 M LiPF₆/EC:EMC|NMC811 cells.

To summarize, the failure mechanisms of LMBs are strongly correlated to electrolyte decomposition and need to be studied case by case. This is because electrolyte decomposition pathways are highly dependent on different salts, solvents and their formulations. E-G&IC or other analytical methods for electrolyte

quantification¹⁰ should be adopted as baseline characterization approaches for application-driven design of non-aqueous electrolyte solutions.

Supplementary Note 10: Impact of rSEI accumulation on cell's discharge capacity decay

Within the first 10 cycles, for a 50 μm Li|0.28LiFSI-0.92DME-3TTE|NMC811 cell, the delivered discharge capacity values are in line with the expected values (Fig. 3i), considering the theoretical capacity of the electrodes' active materials and the cell design. However, this is not the case for the 50 μm Li|LiFSI-1.2DME-3TTE|NMC811 cells after 300 cycles (Fig. 3e). This difference could be associated with the accumulation of rSEI on the Li negative electrode. In this supplementary note, we provide a detailed discussion of this phenomenon.

Supplementary Fig. 29 shows the *ex situ* SEM image of the cross-section of a Li metal negative electrode of Li||NMC811 SLS cell after 250 cycles at 50% SOC. A porous layer with a thickness of ~ 30 μm can be observed on the surface of the Li metal electrode. We identify this porous layer as the accumulated rSEI. The rSEI morphology resembles the schematic on the right part of Fig. 1b. Such a porous rSEI layer behaves like a separator, being electrochemically inactive as the SEI components are generally electronically insulating and possess negligible ionic conductivities. When the liquid electrolyte solution wets the porous rSEI framework, Li ions are given access to the underlying negative electrode and can be electrodeposited as Li metal. Thus, while the rSEI layer still allows for ion transport, its accumulation makes the Li-ion transport pathway more tortuous, but how this impacts the cell's discharge capacity is dependent on the salt concentration in the electrolyte. To further analyze this aspect, we carried out electrochemical simulations.

Based on the electrochemical simulation reported in the main text (Fig. 3k), we added another layer of porous rSEI, which was treated as an additional porous separator. We compared the Li||NMC811 cell discharge potential profiles and concentration distributions under three different rSEI thicknesses (0 μm , 30 μm , 60 μm) and two electrolyte formulations: LiFSI-1.2DME-3TTE (1.73 M LiFSI in DME/TTE) and 0.28LiFSI-0.92DME-3TTE (0.53 M). Supplementary Fig. 30a shows the simulated cell discharge potential profiles. For LiFSI-1.2DME-3TTE (1.73 M, blue curves), the

increase in the rSEI thickness only mildly decreases the discharge potential plateau but does not diminish the total cell discharge capacity. In contrast, in the cell with the 0.28LiFSI-0.92DME-3TTE (0.53 M, green curves) electrolyte, the increase in rSEI thicknesses leads to a discharge capacity loss. Supplementary Figs. 30b-d show the concentration distribution under different conditions. It can be observed that a decrease in the discharge capacity is associated with Li-ion depletion in the electrolyte. For LiFSI-1.2DME-3TTE (1.73 M), although a thicker rSEI aggravates the concentration gradient in the NMC811-based positive electrode, the Li-ion depletion effect is minor, thus not strongly affecting the cell's discharge capacity. In summary, the rSEI cause only a minor increase of the ohmic polarization (potential drop due to resistance in the system) and concentration polarization (potential drop arising from the formation of concentration gradients at the Li metal electrode interface or in the porous NMC811 electrode), while the cell's discharge capacity is detrimentally affected by Li-ion depletion in the electrolyte.

When the 0.28LiFSI-0.92DME-3TTE (0.53 M) electrolyte is used, the discharge capacity in a cycled cell (30 μm rSEI) is lower than that in a freshly assembled and uncycled cell (no rSEI) because the farther and more tortuous ion transport results in greater Li-ion depletion (Supplementary Figs. 30a-c). It should be noticed that the simulated cell discharge capacity in a freshly assembled and uncycled cell is lower than the actual experimental initial discharge capacity reported in Fig. 3i. The difference between the simulation and experimental results lay in the use of commonly used parameters (diffusion coefficient, porosity, tortuosity, etc. for typical porous systems) in the electrochemical simulation which may not exactly represent our specific cell system. Nevertheless, the simulation outcomes support the following claims:

1. When the Li salt concentration is sufficiently high (i.e., in excess of a specific threshold value that varies with the system and cycle number), the accumulation of rSEI has little effect on the discharge capacity (e.g., for 1.73 M, no rSEI vs. 60 μm rSEI).
2. When the Li salt concentration falls below a certain threshold value, the

concentration of salt-derived Li-ion present in the electrolyte in the positive electrode after loss through the rSEI cannot sustain cell cycling. Since an increase in the rSEI thickness amplifies the depletion of the Li-ion, it detrimentally affects the cell discharge capacity (e.g., for 0.53 M, no rSEI vs. 60 μm rSEI).

In the case of the Li||NMC811 cell failure, the accumulation of rSEI is not the main contributing process. Fig. 4c shows that cycling can be extended if a larger amount of electrolyte is used. Because the SEI formation in cells with the 0.28LiFSI-0.92DME-3TTE electrolyte is mainly salt anion-derived (Supplementary Figs. 22-25, Supplementary Table 7), the accumulated rSEIs should be similar under 2.1 g/Ah and 3.6 g/Ah of electrolyte. The key difference is that overall electrolyte concentration during cycling is better maintained under 3.6 g/Ah as the larger mass of the electrolyte could buffer the salt components' decomposition process in forming the SEI. This analysis supports the assumptions that in Li metal cells containing LHCE solutions i) the rSEI accumulation is not detrimental to cell cycling when the electrolyte concentration is above a certain threshold value, and ii) an inadequate electrolyte concentration is the main cause of the cell failure.

Supplementary Note 11: Characterization of the decomposition products in cycled LiFSI-1.2DME-3BTFE electrolyte solution

Since different diluents possess different physicochemical properties, it is reasonable to think that the LiFSI-1.2DME-3BTFE followed a different interfacial reaction pathway from LiFSI-1.2DME-3TTE, which ultimately results in an extension of the cell cycle life (Fig. 4e). Therefore, we also quantified the LiFSI-1.2DME-3BTFE electrolyte decomposition process. The results are presented in Supplementary Fig. 33.

The quantification verified that the LiFSI-1.2DME-3BTFE followed the same decomposition pathway as LiFSI-1.2DME-3TTE. The salt-derived electrolyte components are those that decompose the most (note the LiFSI mass loss in Supplementary Fig. 33a), while the DME solvent shows a lower mass loss, experiencing less decomposition during cycling (Supplementary Fig. 33b). The BTFE mass is almost unchanged, demonstrating a lack of decomposition during cell cycling (Supplementary Fig. 33c). These results rule out the possibility of BTFE decomposition to facilitate SEI formation. There is still the possibility of BTFE impacting the solvation environment of Li ions to alter the SEI formation, growth and stability. However, this latter aspect should not be the reason for the long cell cycle life since the CE of the Li|LiFSI-1.2DME-3BTFE|NMC811 is lower than that of Li|LiFSI-1.2DME-3TTE|NMC811 (Fig. 4f). This suggests that even if BTFE had impacts on solvation, the SEI ability to support cell cycling is worsened. Concerning the concentration of the electrolytes in 50 μm Li|NMC811 cells, the BTFE-based electrolyte shows a LiFSI molar concentration of 0.79 M after 270 cycles (Supplementary Fig. 33d), in contrast to 0.66 M and 0.53 M of the TTE-based electrolyte after 250 and 300 cycles, respectively (Fig. 3h). Although a higher electrolyte concentration could help prevent Li-ion depletion and promote improved cell performance, as also supported by the electrochemical simulations, the 0.79 M electrolyte concentration does not show a significant improvement in cell cycling performance. However, it should be pointed out that the decomposition of LiFSI showed a gradually decelerating trend during cycling, for example, the mass of LiFSI decomposed between the 250th cycle and 300th cycle is

obviously decreased compared with that between the 1st cycle and 50th cycle (Fig. 3f). This could be attributed to an improved Li deposition morphology with lower surface area, a result of the repeated Li plating/stripping that gradually removes the passivation layer on the Li metal negative electrode and provide more homogeneous nucleation sites. The reduction in exposed Li metal surface area results in fewer reactions with the electrolyte, leading to reduced LiFSI decomposition over time. Furthermore, the BTFE-containing electrolyte solution (Fig. 4e, 4.1 mS/cm) demonstrates a higher bulk ionic conductivity than the TTE-containing electrolyte (Fig. 4e, 2.1 mS/cm). This suggests a possibly higher diffusion coefficient in the BTFE-containing electrolyte, which could help alleviate the concentration gradient and avoid Li-ion starvation.

Supplementary Note 12: Discussions on the importance of cell parameters for practical LMB development

The practical development of LMBs should focus on two key requirements: long cell life and high specific energy. To maximize the first requirement, thick Li metal electrodes and high electrolyte usage can be implemented. However, these two implementations are at the expense of specific energy. In particular, electrolyte plays a more crucial role in adversely impacting the cell specific energy. Based on the cell design reported in Supplementary Table 9, we calculate the mass ratio of various cell components (Supplementary Fig. 34). The Li metal negative electrode only accounts for 3.3% of total BOM (Bill of Materials) weight, whereas the electrolyte solution accounts for 21.2%. Therefore, even by shifting to an “anode-less” cell design (i.e., where after the cell assembly, the active material at the negative electrode is initially absent), the improvement of the specific energy can be calculated as 13 Wh/kg (Supplementary Table 10). In contrast, by halving the electrolyte mass in the cell, a 45 Wh/kg increase in the cell’s specific energy can be calculated (Supplementary Table 10).

Also, considering that currently, 5-20 μm thick Li metal on Cu current collector can be mass produced efficiently and Li_2CO_3 raw material cost is $\sim \$10,000$ per tonne^{13,14}, their impact on the total cost of the LMBs production is minor. Therefore, in improving the specific energy of a cell, the effect of decreasing the Li thickness at the negative electrode is not as high as decreasing the mass of the electrolyte and the current collectors (e.g., via composition change or thickness reduction) as well as using positive electrode active materials with high energy content. The state-of-the-art reports CE of 99.6%-99.9% for $\text{Cu}||\text{NMC811}$ and $\text{Li}||\text{NMC811}$ cells, and long cell’s cycling life (600-800 cycles) for $\text{Li}||\text{NMC811}$ cells using 20 μm Li foils (Fig. 4a), but the cell’s specific energy is highly dependent on the electrolyte quantity used (Fig. 4c). Therefore, urgent research efforts should be focused on extending the electrolyte durability (number of cycles that can be sustained with a certain amount of electrolyte) in prolonged cell cycling.

In this regard, it is crucial to consider if high CE values are associated with prolonged electrolyte durability during the cell's cycling. In current academic research studies, scientists generally associate the interfacial reactions, CE performance, electrolyte durability and cell cycle life with the solvation environment of the Li ions in the bulk electrolyte solution. However, practical LMB advancements cannot be realized without resolving the complex relations between cell design parameters (e.g., electrode porosity) and cycle life¹⁵⁻²². Although a tailored solvation environment could lead to the formation of more effective SEI at the negative electrode and higher cell CEs, it does not guarantee high electrolyte durability. The findings presented in this manuscript show that the CE and electrolyte durability could be deconvoluted. Indeed, different electrolytes could lead to a similar cell's CE while showing varying capabilities to support long-term consumption and cycle life (Figs. 4e and 4f).

Recent research works¹⁵⁻²² proposed tailored electrolyte materials and formulations to advance research towards practical LMB development. Nevertheless, the CE of anode-less LMBs cells or other cells with Li-free working electrodes and Li counter electrodes (e.g., Li||Cu cells) reported has rarely exceeded 99.9%^{23,24}. Compared to the CE value of ~99.85% of Li||NMC811 cells with LiFSI-1.2DME-3TTE (Fig. 4b), first reported in 2019⁴, the advancement is very minor and contribute little to the transition to a high technology readiness level for LMBs¹³. Achieving a CE > 99.99% is the ultimate goal. However, the reaching this goal for LMBs is, from a practical perspective, very unlikely because of the inherent instability associated with SEI evolution during LMB cycling, compared to the SEIs formed in Li-ion batteries (Figs. 1a and 1b). Thus, we suggest that researchers focus more on understanding how to improve electrolyte durability to reach the ultimate goal of developing practical LMBs as commercial products.

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