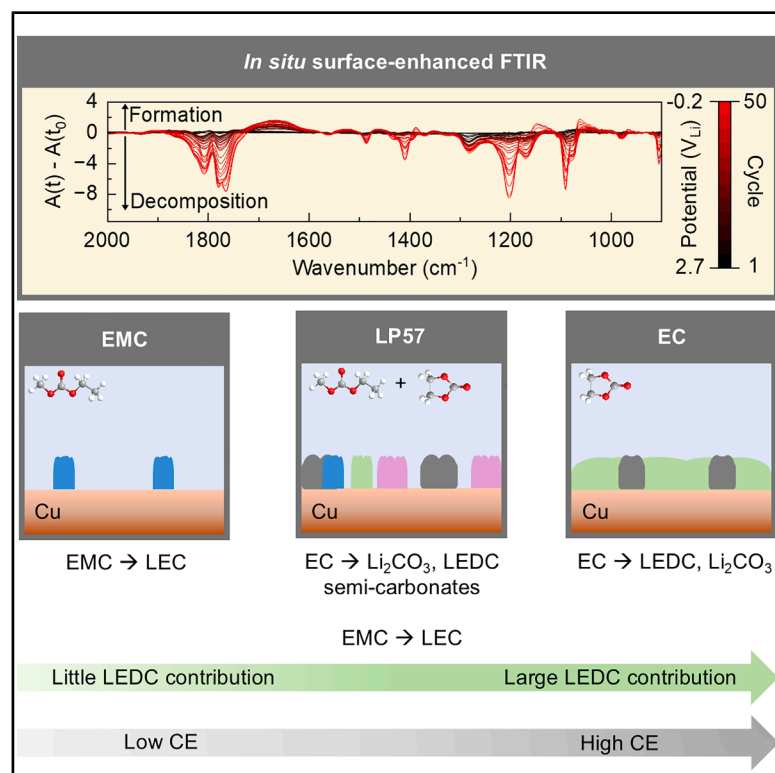


Revealing the lithium solid electrolyte interphase in liquid electrolytes via *in situ* Fourier transform infrared spectroscopy

Graphical abstract



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In brief

The practical use of lithium metal batteries is limited by unstable solid electrolyte interphases (SEIs). Shao-Horn and colleagues have employed *in situ* surface-enhanced FTIR spectroscopy to probe potential- and cycling-dependent electrolyte reduction, demonstrating that a lithium ethylene dicarbonate-based SEI from EC reduction passivates lithium metal surfaces, key to achieving high Coulombic efficiency.

Highlights

- *In situ* surface-enhanced FTIR probes potential- and cycling-dependent SEI
- EC reduces to lithium ethylene dicarbonate starting from pre-plating potentials
- LP57 generates predominantly Li_2CO_3 and semi-carbonates from EC reduction
- EMC reduces into soluble Li alkyl carbonates

Article

Revealing the lithium solid electrolyte interphase in liquid electrolytes via *in situ* Fourier transform infrared spectroscopy

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SUMMARY

Unlocking lithium metal batteries requires a robust solid electrolyte interphase (SEI) capable of sustaining high Coulombic efficiency (CE). Here, we develop *in situ* Fourier transform infrared (FTIR) spectroscopy to directly probe potential- and cycling-dependent formation of an organic SEI in carbonate electrolytes containing ethylene carbonate (EC) and ethyl methyl carbonate (EMC) and systematically correlate interfacial chemistry with CE. In 1.2 M LiPF₆ EC, an organic-dominated SEI comprising lithium ethylene dicarbonate (LEDC) forms starting at pre-plating potentials, yielding the highest CE (~90%). In contrast, 1.0 M LiPF₆ EMC produces primarily soluble lithium ethyl carbonate (LEC) and develops a thick, LiF- and Li₂O-rich, spatially heterogeneous SEI with poor reversibility (<15% CE). LP57 exhibits intermediate behavior, where the emergence of alternative semi-carbonates due to trace water destabilizes the organic SEI. Such observations demonstrate that an inorganic-dominated SEI does not intrinsically ensure high CE and instead high-light organic, LEDC-based interphases as critical to stable cycling.

INTRODUCTION

Li-ion batteries are widely used to electrify consumer vehicles and a broad range of other applications. Carbonate-based liquid electrolytes have been designed to form a stable solid electrolyte interphase (SEI) with carbonaceous anodes, which is electronically insulating and lithium ion conducting in nature.^{1,2} The SEI serves to passivate the electrode by eliminating further consumption of electrolytes during battery operation, critical to realizing high specific energy, high Coulombic efficiency (CE), and long cycle life in Li-ion batteries.^{3–6} Replacing graphite (372 mAh/g) with alternative anode materials has been researched intensively to increase the specific energy of Li batteries. Specifically, using a Li metal anode with a theoretical specific capacity of 3,860 mAh/g^{7,8} can potentially double the gravimetric energy density of current Li-ion batteries,^{4,9} providing the boosted en-

ergy needed for heavy-duty vehicles and electrification of aviation and reducing the cost for widespread electrification in the power and industrial sectors.^{4,8,9}

Significant advances have been made in developing liquid electrolytes to increase the CE of Li plating/stripping and develop stable Li electrodes over the past five decades.¹⁰ Cyclic carbonate-based electrolytes have moderate efficiency (80%–99%),^{11,12} while electrolytes with fluorinated cyclic carbonates and high salt concentrations can achieve high efficiency (up to 99.6%).¹³ The irreversibility can be attributed to continuous consumption of electrolyte components due to incomplete passivation of the SEI on Li and changes in Li morphologies during cycling (i.e., dendritic or dead Li).^{8,14} Unfortunately, the practical use of Li metal batteries is still limited by the CE of Li plating/stripping in liquid electrolytes.^{15,16} Therefore, it is critical to understand the reactivity between Li and liquid electrolytes and

develop design guidelines for new electrolytes for enhanced efficiency.

A large number of *ex situ* measurements, including X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR) spectroscopy, and X-ray diffraction (XRD), have been reported to probe SEI structures and compositions and understand the processes to generate SEIs. For example, Li_2CO_3 and oligomers (or polymers) in the SEI on Li have been reported in 1.5 M LiClO_4 in propylene carbonate (PC).¹⁷ In addition, seminal FTIR spectroscopy and XPS studies from Aurbach et al.¹⁸ have proposed the formation of lithium alkyl carbonates from solvent reduction as the main SEI components on Li for PC-based electrolytes. Lithium ethylene dicarbonate (LEDC; $\text{CH}_2\text{OCO}_2\text{Li}_2$) has been proposed as the key SEI component from ethylene carbonate (EC) reduction on Li from FTIR spectroscopy¹⁹ and nuclear magnetic resonance (NMR) spectroscopy²⁰ studies of EC-based electrolytes. This hypothesis is supported by FTIR spectra between synthetic LEDC²¹ and those collected from plated Li on Ni (cycled in EC-based electrolytes). On the other hand, Wang et al.²² have subsequently reported that EC reduction forms lithium ethylene monocarbonate (LEMC), as evidenced by synthetic LEDC and LEMC, as well as by chemical analysis of an SEI extracted from graphite in LiPF_6 in EC/dimethyl carbonate (DMC). Moreover, XPS has revealed depth-dependent compositions of inorganic components in SEIs, where the compact layer near the Li surface consists of LiF and Li_2O , while the porous layer above contains organic species.^{23,24} These insights provide details of the SEI mosaic structure on Li, first proposed by Peled et al.,²⁵ which consists of (1) compact layers formed near the Li surface, consisting of inorganic species such as Li_2O , Li_2CO_3 , and LiF , which are thermodynamically stable against Li,^{23,25,26} and (2) layers near the electrolyte that mainly consist of oligomer species (polyolefins) and semi-carbonates resulting from carbonate solvent decomposition.^{25,26} Such inorganic-organic composition structures of SEIs have been further supported by cryo-(scanning) transmission electron microscopy (cryo-(S)TEM) of Li/electrolyte interfaces.^{27,28}

Beyond detection of solid SEI species at the surface, gas products of electrolyte reduction have been studied using techniques such as gas chromatography (GC),^{29–33} differential electrochemical mass spectrometry (DEMS),^{34–36} and on-chip electrochemical mass spectrometry (ECMS).³⁷ For example, Novak et al.^{34,35} have utilized DEMS to detect the evolution of ethylene (C_2H_4) centered at 0.5 V_{Li} in EC-based electrolytes in the first cyclic voltammetry, which diminishes in subsequent cycles. The formation of ethylene has been attributed to EC reducing into LEDC or Li_2CO_3 . In addition, CO_2 is detected subsequently at potentials greater than those of ethylene using DEMS with greater sensitivity from 1.0 M LiPF_6 in EC/DMC on graphite.³⁶ Such results are in agreement with recent work of Strehle et al.,³⁸ who have used online electrochemical mass spectrometry (OEMS) to show the detection of CO_2 , CO, and H_2 as minor gas products in addition to C_2H_4 in 1.0 M LiPF_6 in EC/ethyl methyl carbonate (EMC) (3:7 by volume) (LP57). The formation of CO_2 has been attributed to the hydrolysis between EC and OH^- ions. More recently, Thornton et al.³⁷ have reported that CO mainly comes from EMC reduction (1.0 M LiPF_6 in EMC) us-

ing on-chip ECMS, which continues to form for multiple cycles, unlike C_2H_4 in EC-based electrolytes, indicating more stable SEIs formed by EC reduction.

Recent studies of SEIs have focused heavily on the role of inorganic species on the CE of Li plating and stripping.^{39–41} Of significance, Fang et al.³⁹ have recently used titration GC to show that unreacted metallic Li^0 dominates the capacity loss found for liquid electrolytes with low CE, while the formation of the SEI is responsible for the capacity loss associated with liquid electrolytes with high CE. A number of studies have proposed that increasing LiF in the SEI is correlated with increasing CE.^{13,42,43} On the other hand, Hobold et al.⁴⁰ have expanded the previously mentioned titration method to quantify both organic and inorganic SEI components, where they have shown increasing Li_2O concentration improves CE. More recently, Steinberg et al.⁴¹ have pivoted away from Li_2O and instead show that creating more Li_2CO_3 , by exposing Li to CO_2 , can increase the CE of Li plating and stripping and minimize inactive Li^0 buildup. Unfortunately, the titration method⁴⁴ cannot distinguish between lithium carbonate and semi-carbonates, in addition to lacking visibility to alkoxides and oligo/polymeric species. Although these *ex situ* studies have clarified inorganic SEI formation on Li and its correlation with CE, organic species from electrolyte reduction remain poorly understood due to their relative fragility and susceptibility to damage from *ex situ* techniques during sample preparation or acquisition.^{1,20,45} Therefore, *in situ* surface-sensitive techniques are needed to understand organic SEI formation during Li plating and stripping.

Dynamic processes of SEI formation and evolution during the operation of Li metal batteries have been studied by *in situ* spectroscopic techniques, including attenuated total reflection FTIR (ATR-FTIR) spectroscopy and depth-sensitive, plasmon-enhanced Raman spectroscopy (DS-PERS),⁴⁶ which combines surface-enhanced and shell-isolated nanoparticle-enhanced Raman spectroscopy. Among those techniques, infrared (IR)-based techniques are among the most accessible for probing the organic components of the SEI. Goren et al.⁴⁷ have used *in situ* FTIR spectroscopy to report the formation of lithium alkyl carbonate (ROCO_2Li) based on the primary peak feature of $1,680\text{ cm}^{-1}$ and the formation of Li_2CO_3 based on the peak appearance at $1,500\text{ cm}^{-1}$, attributable to PC reduction at $-0.2\text{ V}_{\text{Li}}$ in 0.5 M LiClO_4 in PC. Moreover, the formation of LEDC has been observed for lithiated Au⁴⁸ and lithiated Si⁴⁹ in 1.0 LiPF_6 in EC/diethyl carbonate (DEC) (1:2 by volume), where major peaks at $1,663/1,664$ and $1,318/1,310\text{ cm}^{-1}$ begin appearing at 0.6 V_{Li} and 5 mV_{Li} , respectively, attributable to EC reduction. More recently, Leau et al.⁵⁰ have developed an operando IR fiber-optic evanescent wave spectroscopy method to study SEIs on Cu and other intercalation and alloying negative electrode materials. This work shows comparable growth of semi-carbonates ($1,640\text{ cm}^{-1}$) and Li_2CO_3 ($1,525\text{ cm}^{-1}$) in the SEI from a commercial EC-based electrolyte (1.0 M LiPF_6 in EC/DMC (1:1 by volume); LP30) during voltage cycling, where the lower voltage limit is reduced stepwise from open-circuit voltage (OCV; $\sim 3\text{ V}_{\text{Li}}$) to 0 V_{Li} in five voltage steps. In contrast, the growth of semi-carbonates and Li_2CO_3 ($1,525\text{ cm}^{-1}$) in the SEI in 1.0 LiPF_6 DMC was more gradual during the galvanostatic intermittent titration technique (GITT) protocol and less pronounced than

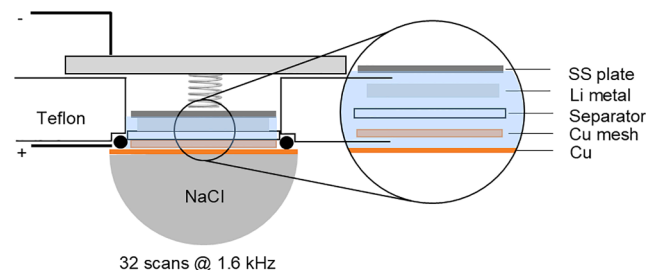
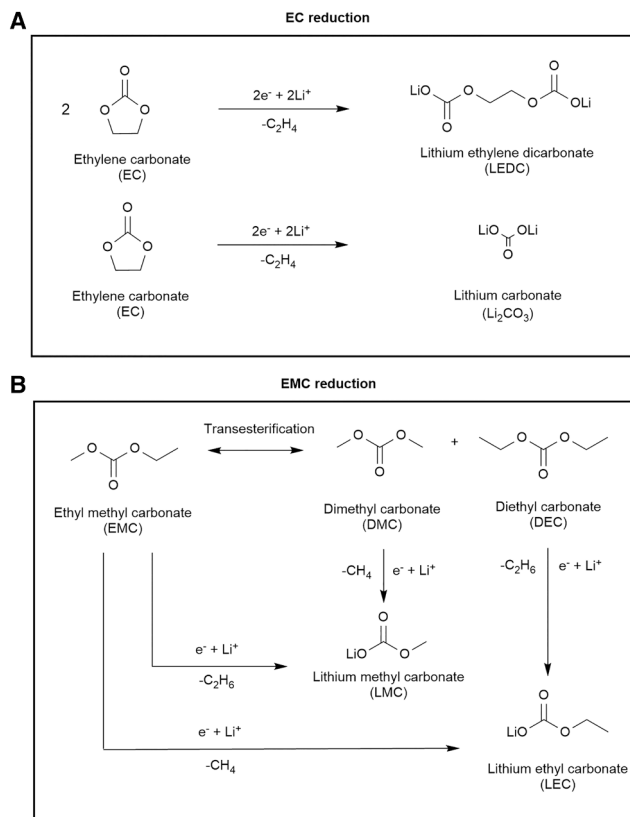


Figure 1. *In situ* FTIR spectroscopy electrochemical cell using a NaCl prism

25 nm Cu was sputtered on top of the NaCl prism to serve as the current collector for the working electrode, and Cu mesh (100 × 100 mesh size, 0.006" opening, open area 30%, 0.0045" wire diameter from McMaster-Carr) was added to the sputtered Cu. Li metal (MTI Corp.) was used as the counter electrode, and 150 μ L of each electrolyte was selected for each measurement. *In situ* FTIR spectroscopy cell assembly and measurement were done inside a glovebox, where the cell was electrically connected to a BioLogic potentiostat outside the glovebox via extension cables and a multi-channel feedthrough (Figure S1).

that noted for LP30, indicating less SEI buildup.⁵⁰ As electrolyte reduction species can be voltage (e.g., Li_2CO_3 can be converted to Li_2O and Li_2C_2 at negative electrode potentials⁴¹), time (cycling), and electrolyte dependent, further *in situ* and operando studies of dynamic changes in SEIs as a function of potential and cycling after Li plating are needed to provide comprehensive information on the formation mechanism of SEI components from electrolyte reduction in realistic Li metal battery operating conditions.

Here, we investigate the growth of SEI on Cu as a function of potential before and after Li plating and as a function of cycling, with the focus on probing the organic SEI species using *in situ* FTIR spectroscopy. An *in situ* FTIR spectroscopy setup (Figure 1) is developed to characterize the operando reduction of liquid electrolytes into organic SEIs on Cu as a function of potential during linear sweep voltammetry (LSV) and galvanostatic cycling. This setup is adapted from that used to reveal potential-dependent oxidative dehydrogenation of carbonate solvents on positive electrode materials reported by Zhang et al.⁵¹ FTIR spectra are collected as a function of potential and cycling in electrolytes including 1.2 M LiPF_6 in EC; 1.0 M LiPF_6 in EMC, DEC, and DMC; and LP57, where the onset potential and growth of SEI species are determined from changes in the differential peak intensities. *In situ* FTIR spectroscopy data are combined with gaseous data obtained from GC coupled with barrier ionization discharge detection and thermal conductivity detection (GC-BID/TCD)²⁹ and ECMS after primary and secondary SEI accumulations to verify organic SEI decomposition pathways. We further incorporate solid-state NMR (SSNMR) and depth-dependent XPS to elucidate the identity, spatial distribution, and relative concentrations of inorganic SEI species. The extent of anion decomposition is further supported by *in situ* liquid NMR measurements focusing on soluble anion-derived species. To connect SEI composition back to Li metal reversibility, scanning electron microscopy (SEM) images reveal the differences in Li deposition morphology as the EC solvent fraction is increased. Collectively, these techniques provide comprehensive informa-



Scheme 1. Reaction pathways for EC reducing into LEDC and Li_2CO_3 and EMC reducing into LMC and LEC based on previous reports

(A) 2 EC molecules can reduce into LEDC and release C_2H_4 gas as a by-product. 1 EC molecule can also be reduced into Li_2CO_3 , producing the same C_2H_4 gas as a byproduct.^{22,26,52,53}

(B) EMC can be directly reduced into LMC and LEC while producing C_2H_6 and CH_4 , respectively. EMC may also undergo transesterification into DMC⁵⁶ and DEC. DMC can then be reduced into LMC, producing CH_4 gas. DEC can similarly be reduced into LEC and produce C_2H_6 .

tion on dynamic changes of SEIs in carbonate electrolytes and elucidate the role of organic SEIs in governing CE.

RESULTS

Electrolyte-dependent gas evolution from SEI formation on Li

We used recently reported techniques²⁹ involving GC-BID/TCD to quantify gas evolution in the formation of SEIs on Li, from which insights into different reduction mechanisms of EC and EMC were obtained. Analyses of gases detected by Li reacting with 1.2 M LiPF_6 in EC revealed that C_2H_4 was the major gas product (81% by volume), as shown in Figure S2A. The formation of C_2H_4 supports EC reduction to form LEDC ($2\text{EC} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{LEDC} + \text{C}_2\text{H}_4$) and Li_2CO_3 ($\text{EC} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4$) in the SEI,^{22,26,52,53} as shown in Scheme 1A. In addition, minor gas products were detected including CO (13%), C_2H_6 (2.4%), and CH_4 (3%), suggesting the formation of Li-coordinated ethylene glycol^{53,54} (LiEG) ($\text{EC} + \text{Li}^+ + \text{e}^- \rightarrow \text{LiEG} + \text{CO}$)

shown in Figure S3 (reaction 2) and lithium ethylene monocarbonate (LEMC) ($2\text{EC} + \text{Li}^+ + \text{H}^+ + 2\text{e}^- \rightarrow \text{CH}_4 + \text{CO} + \text{LEMC}$), as proposed by Hobold et al.³². The dominance of C_2H_4 upon EC reduction by Li can be attributed to more favorable bond cleavage to yield C radicals rather than O radicals.⁵⁵

Analyses of gases detected by Li reacting with 1.2 M LiPF_6 in EMC showed that CH_4 was the majority product (88.5%), with C_2H_4 , C_2H_6 , C_3H_8 , and H_2 as minor gas products (Figure S2B). The formation of CH_4 supports the reduction of EMC to form lithium ethyl carbonate (LEC) (Scheme 1B; Figure S3, reaction 3), while the formation of C_2H_6 is associated with EMC reduction to form lithium methyl carbonate (LMC) (Scheme 1B; Figure S3, reaction 4). The favored generation of CH_4 and LEC over that of C_2H_6 and LMC can be explained by the inductive effect of the ethyl group of LEC, which is greater in comparison to the methyl group of LMC. The minute C_3H_8 detected can come from the termination reaction between the radical products (Figure S3, reactions 3 and 4). Scheme 1B shows the proposed transesterification mechanism of EMC to DMC⁵⁶ and DEC, which can also lead to the formation of LMC and LEC, respectively. Lastly, our measurements using GC-TCD did not detect CO_2 during Li reacting with 1.2 M LiPF_6 in EC or EMC.

Analyses of gases detected from Li reacting with LP57 showed that C_2H_4 was the majority product (65.3%), with CH_4 , CO , C_2H_6 , and H_2 as minor gas products (Figure S2D). The gas products can be attributed individually to each solvent. Ethylene gas formation can be attributed to EC reduction into LEDC or Li_2CO_3 , as stated previously, while CO can be attributed to the reduction of EC into EG. CH_4 and C_2H_6 can come from the reduction of EMC into LEC and LMC, respectively. Such results are in reasonable agreement with the work of Strehle et al.,³⁸ who used OEMS to show the detection of C_2H_4 as the major product, as well as CO_2 , CO , and H_2 as minor products, in LP57. These results indicate that EC reduction dominates in the mixed solvent case.

To verify that the gas byproducts from Li-mediated reduction of electrolyte are comparable to electrochemically generated gas products, we conducted ECMS³⁷ with 1.2 M LiPF_6 EC and LP57, using a polished Cu disk as the working electrode and LFP strips as the counter electrode (Figure S4). We avoided testing 1.0 M LiPF_6 EMC due to solvent volatility, making it unsuitable for our ECMS instrument. The electrolytes were linearly swept from OCV ($\sim 2.7\text{ V}_{\text{Li}}$) down to $-0.5\text{ V}_{\text{Li}}$ and held at that potential for 30 min. Mass-to-charge ratios of 2 (assigned to H_2); 12, 15, and 16 (assigned to CH_4 and its fragments); 27 and 28 (assigned to C_2H_4 and its fragment); and finally 44 (assigned to C_3H_8) were tracked during electrochemistry.

ECMS results for 1.2 M LiPF_6 in EC (Figure S5) showed the formation of H_2 (as measured by $m/z = 2$) and C_2H_4 (as measured by $m/z = 27$) at 1.3 V_{Li} , which is near water reduction into H_2 and OH^- at $\sim 1.5\text{ V}_{\text{Li}}$. Hydroxide ions have been shown to ring open EC to form lithium alkyl carbonates or lithium carbonate.⁵⁷ A second H_2 peak at 0.4 V_{Li} , combined with a small C_2H_3^+ peak at around the same potential, is indicative of EC decomposition, whose reduction potential was found to be centered at 0.5 V_{Li} . At 0 V_{Li} , C^+ ($m/z = 12$), CH_3^+ ($m/z = 15$), C_2H_3^+ ($m/z = 27$), H_2 ($m/z = 2$), and C_3H_8 ($m/z = 44$) mass signals increase due to the Li-induced chemical reduction of solvent into CH_4 , C_2H_4 , and C_3H_8 . The

observation of C_3H_8 at mass 44, combined with the lack of signal at masses 16 and 28, suggests that C_3H_8 may be the recombined ECMS artifact of CH_4 and C_2H_4 . Periodic fluctuations for masses 15 and 27 in Figures S5D and S5F may be due to the physiochemical property of the electrolyte. Gas analysis with LP57 (Figure S7) shows similar behavior of H_2 evolution at 1.3 V_{Li} , but C_2H_4 , as measured by $m/z = 27$ (Figure S7F) and $m/z = 28$ (Figure S7G), is only observed at $\leq 0\text{ V}_{\text{Li}}$. The lack of an ethylene signal at pre-plating potentials in LP57 suggests the reduction of EC into species other than Li_2CO_3 and LEDC. These alternative species will be discussed later by leveraging *in situ* FTIR spectroscopy. At potentials $\leq 0\text{ V}_{\text{Li}}$, CH_4 (Figures S7C–S7E), C_3H_8 (Figure S7B), and H_2 (Figure S7A) are also formed as a result of Li-induced solvent reduction. Unlike EC, both ethylene and methane are also observed at $m/z = 28$ and $m/z = 16$, respectively, and the C_3H_8 signal at $m/z = 44$ is negligible. This could be because the C_2H_4 signal in LP57 is much weaker, suggesting less C_2H_4 evolution. ECMS results for both EC and LP57 agree with reports by Thornton et al.,³⁷ who have shown H_2 , CO , and C_2H_4 evolution during cyclic voltammetry of a Li||graphite cell with 1.0 M LiPF_6 in EMC and 1.0 M LiPF_6 in EC/EMC (3:7 by volume). Therefore, ECMS results highlight that the identity of gaseous byproducts from secondary SEI formation (defined as an electrochemical SEI) is different than gases produced during primary SEI formation (defined as a chemical SEI).

In summary, gas reaction products from reacting EC- and EMC-based electrolytes with LiPF_6 with Li suggest the formation of LEDC, Li_2CO_3 , and LEC as SEI components, which will be further examined by *in situ* FTIR spectroscopy, NMR, and XPS experiments to probe the formation of the SEI as a function of potential in the following sections.

***In situ* FTIR spectroscopy of 1.2 M LiPF_6 in EC: Potential- and cycling-dependent measurements**

Potential-dependent *in situ* FTIR spectroscopy measurements of a Li||Cu cell in 1.2 M LiPF_6 in EC revealed that LEDC grew gradually with decreasing potential from 1.5 V_{Li} , which was accompanied by consumption of EC, and increased sharply upon Li plating below 0 V_{Li} (Figure 2). Beyond LEDC, Li_2CO_3 was present as a minor species and increased more gradually with decreasing potential than LEDC, with no sharp growth upon Li plating. *In situ* FTIR spectra were collected from Cu as a function of potential (Figure S9), which were found to be similar to those of the bulk electrolyte collected by ATR (Figure S16A). Differential spectra subtracted from those obtained at OCV (2.7 V_{Li}) were used to reveal changes associated with electrolyte consumption and the generation of new species as a function of potential (Figure 2A). *In situ* differential FTIR spectra remained largely unchanged up to 1.5 V_{Li} , indicating no significant electrolyte consumption. A number of new peaks centered at $1,670$ and $1,130\text{ cm}^{-1}$ appeared and grew with further potential reduction, which was accompanied by EC consumption as indicated by the reduction of its peak intensities (e.g., $\text{C}=\text{O}$ in free EC molecules at $1,800\text{ cm}^{-1}$ and Li^+ -coordinated EC at $1,770\text{ cm}^{-1}$ in Figure 2A). PF_6^- anions were consumed as indicated by the growth of a negative peak corresponding to a P–F stretching around 850 cm^{-1} in the differential spectra (Figure 2A), which was accompanied by a sharp reduction with Li plating

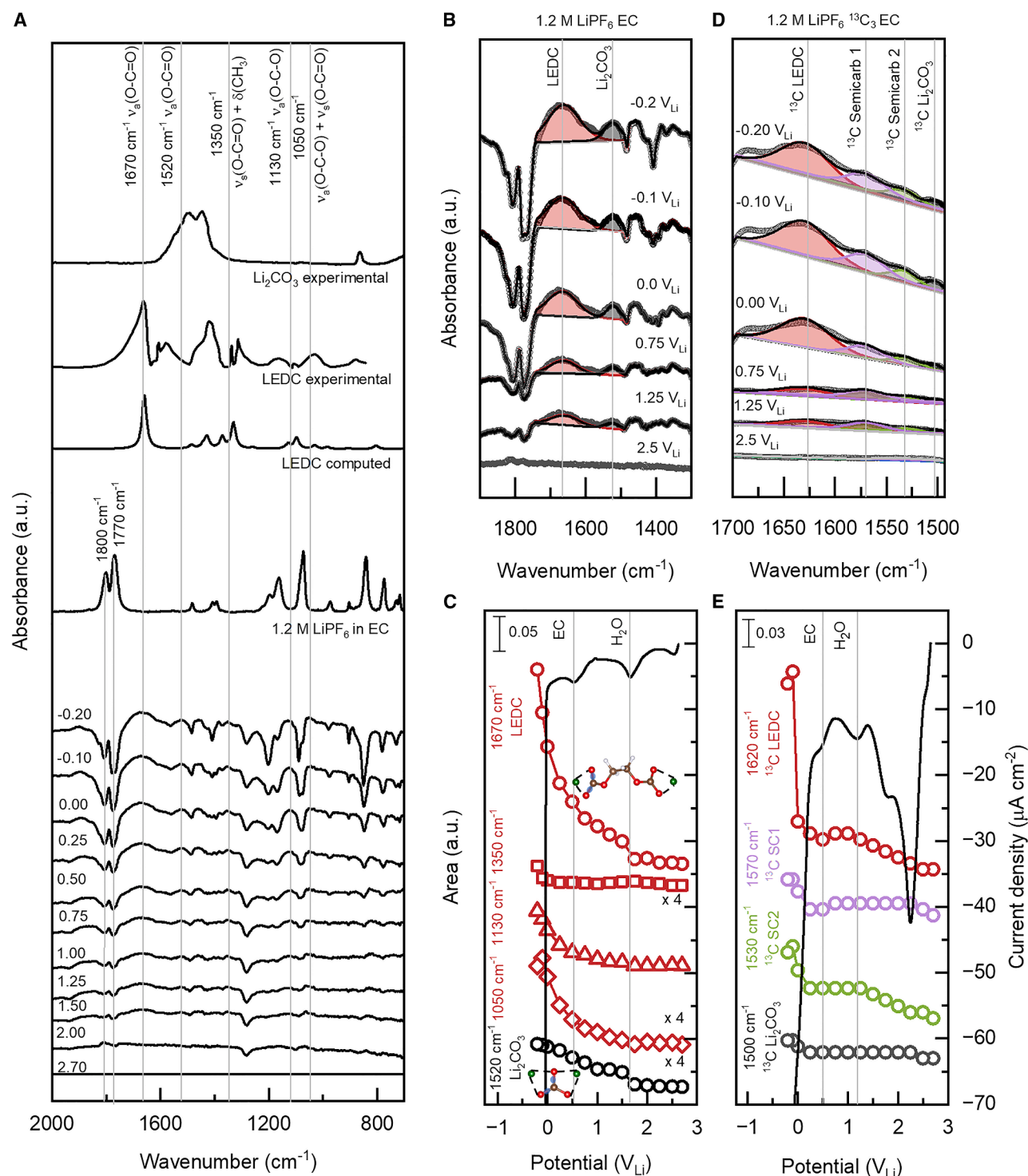


Figure 2. *In situ* FTIR spectra as a function of potential for 1.2 M LiPF₆ in EC and ¹³C₃ EC

(A) Potential-dependent differential spectra with respect to OCV (~ 2.7 V_{Li}) for 1.2 M LiPF₆ in EC from OCV to -0.20 V_{Li}. The *in situ* FTIR spectroscopy cell was linearly swept from OCV (~ 2.7 V_{Li}) down to -0.5 V_{Li} at a scan rate of 0.1 mV/s. As-collected spectra can be found in Figure S9B, and full potential range differential spectra can be found in Figure S9C. The bulk electrolyte on top was collected in ATR mode with a Ge crystal at an incidence angle of 50° . Computed (more details in Figure S10) and synthetic LEDC⁵⁸ and Li₂CO₃ from NIST are included for comparison.

(B) Deconvolution of peak between $1,700$ and $1,450$ cm^{-1} with 1.2 M LiPF₆ EC into LEDC at $1,670$ cm^{-1} (red) and Li₂CO₃ at $1,520$ cm^{-1} (black). Details can be found in Figure S11. A linear background was used, and Gaussian (30%)-Lorentzian (70%) peaks were fit with peak position and FWHM fixed across different potentials.

(legend continued on next page)

below 0 V_{Li} , attributable to reduction of PF_6^- anions ($PF_6^- + 3Li^+ + 2e^- \rightarrow 3LiF + PF_3$).²⁶ These potential-dependent FTIR spectroscopy measurements were reproduced (Figure S17), showing good qualitative agreement and reproducibility.

The pronounced growth of a broad feature centered at $1,670\text{ cm}^{-1}$ (with intensities spanning from $1,700$ to $1,560\text{ cm}^{-1}$) and moderate growth of a peak at $1,130\text{ cm}^{-1}$, especially at potentials below 0 V_{Li} , can be attributed largely to LEDC, corresponding to CO_2 asymmetric stretching^{4–7} and O–C–O asymmetric stretching,⁵⁹ respectively. This assignment is supported by the simulated FTIR spectrum of LEDC (Figure S18), which show two of the strongest peaks associated with asymmetric stretching of O–C=O ($\sim 1,650\text{ cm}^{-1}$) and O–C–O asymmetric stretching ($\sim 1,120\text{ cm}^{-1}$). The calculated result is in agreement with the work from molecular orbital calculations by Zhuang et al.²¹ for O–C=O asymmetric stretching ($1,650\text{ cm}^{-1}$) and O–C–O asymmetric stretching ($1,150\text{ cm}^{-1}$). Small discrepancies between calculated and collected spectra may be due to solvation environment effects. Further support came from ATR spectra of reference LEDC^{21,58,60} (with strong absorbance peaks around $1,660$, $1,310$, and $1,100\text{ cm}^{-1}$ in Figure S19A). In contrast to the work of Wang et al.,²² who report LEMC, we propose the formation of LEDC as the dominant reduction product from EC, as the characteristic peak of LEMC around $3,000\text{ cm}^{-1}$ was not observed (Figure S20). The formation of LEDC can be attributed to EC reduction to generate LEDC and C_2H_4 , as discussed previously.⁵²

Beyond LEDC, a small amount of Li_2CO_3 was detected at $1,520\text{ cm}^{-1}$ (Figure 2C) and grew with decreasing potential. This assignment is supported by the transmission FTIR spectrum of Li_2CO_3 from National Institute of Standards and Technology (NIST) ($1,500$ and 900 cm^{-1} in Figure S18) and density functional theory (DFT) calculations of OCOO asymmetric stretching ($\sim 1,500\text{ cm}^{-1}$ in Figure S18). The formation of Li_2CO_3 can result from EC reduction ($EC + 2Li^+ + 2e^- \rightarrow C_2H_4 + Li_2CO_3$),^{20,61–63} further reduction of LEDC ($LEDC + 2e^- + 2Li^+ \rightarrow 2Li_2CO_3$),⁶⁴ and/or thermal decomposition to Li_2CO_3 , as proposed previously.^{58,65} The reduction of EC in 1.2 M LiPF₆ EC to form LEDC and Li_2CO_3 found in this study is in good agreement with the findings on Au in 1.3 M LiClO₄ in EC from *ex situ* FTIR spectroscopy and XPS measurements (after exposure from 2.0 to 1.0 V_{Li}) by Martins et al.⁶⁶ While LEDC and Li_2CO_3 were found to grow as a function of potential, the presence of other species such as semi-carbonates cannot be excluded completely from differential spectra due to similar peak positions.⁵⁸

Differential FTIR spectroscopy absorbance of different modes associated with LEDC ($\sim 1,670$ and $\sim 1,130\text{ cm}^{-1}$) and Li_2CO_3 ($\sim 1,520\text{ cm}^{-1}$) was plotted as a function of potential in Figure 2C. Beyond these two peaks, minute growth in $1,350$ and $1,050\text{ cm}^{-1}$ was noted. Peak positions were identified by the x intercepts from the first derivative of the differential spectrum (Figure S12), while the lower and upper bounds for the integration of the area were identified via the x intercepts from the second derivative of the differential spectrum (Figure S13). A representative spectrum at -0.2 V_{Li} was chosen to determine the integration bounds, and then the same bounds were applied to all potentials (Figure S21). These intensity changes were overlaid with the reduction current of cathodic LSV in Figure 2C, revealing three reduction processes: around 1.7 V_{Li} , explained by water reduction coupled with EC hydrolysis; 0.5 V_{Li} , attributed to electrochemical reduction of EC to LEDC; and below 0.0 V_{Li} , assigned to the chemical reduction of EC by Li. The small peak centered at $\sim 2.5\text{ V}_{Li}$ is attributed to the reduction of CuO to Cu, which is supported by *in situ* Raman studies.⁶⁷ The reduction peak centered at 1.7 V_{Li} is attributed to water reduction ($H_2O + e^- \rightarrow 1/2H_2 + OH^-$),³⁵ where EC and OH^- can react to form LEMC as reported previously^{64,68} ($EC + Li^+ + OH^- \rightarrow LEMC$). It should be noted, however, that the presence of water in the electrolyte is minute, as the water content measured is less than 30 ppm (Table S3), and no significant intensities were found for the O–H stretching vibration centered at $3,600\text{ cm}^{-1}$ in the as-collected and differential FTIR spectra (Figure S20). LEMC can further react with CO_2 and Li^+ with electron availability to form LEDC.⁶⁸ Therefore, the gradual intensity increase of $\sim 1,670\text{ cm}^{-1}$ starting from 1.8 V_{Li} (Figure 2C) can be attributed to the hydrolysis of EC to form LEMC/LEDC. The reduction peak centered at 0.5 V_{Li} is attributed to the electrochemical reduction of EC to LEDC ($EC + 2Li^+ + 2e^- \rightarrow LEDC + C_2H_4$), which was associated with noticeable growth at $1,670\text{ cm}^{-1}$ (Figure 2C) and moderate growth at $1,130$ and $1,050\text{ cm}^{-1}$.⁵² Previous reports by Deng et al.⁶⁹ calculated a reduction potential of solvated EC molecules between 0.41 and 0.48 V_{Li} . The observed potential-dependent growth of LEDC from EC reduction is in agreement with that from the 1D kinetic Monte Carlo simulation from Persson et al.,⁶⁴ where LEDC increases and becomes the dominant species for SEI interfacing the electrolyte below 0.4 V_{Li} . The large current at potentials below 0 V_{Li} was associated with Li plating and sharp growth at $1,670\text{ cm}^{-1}$, which can be attributed to the chemical reduction of EC to LEDC. The process was not captured by the computational study by Spotte-Smith et al., as

(C) Areas of LEDC peaks at $1,670\text{ cm}^{-1}$ (red circle), $1,350\text{ cm}^{-1}$ (red square) with intensities scaled $4\times$, $1,130\text{ cm}^{-1}$ (red triangle), and $1,050\text{ cm}^{-1}$ (red diamond) with intensities scaled $4\times$ and of Li_2CO_3 at $1,520\text{ cm}^{-1}$ (black) with intensities scaled $4\times$, as a function of potential, overlaid with electrochemical data from LSV. Details for peak area calculation can be found in Figures S11–S13 and Table S1. LSV shows three reduction peaks: CuO to Cu reduction at $>2.0\text{ V}_{Li}$, water reduction centered at $\sim 1.7\text{ V}_{Li}$, and EC reduction centered at $\sim 0.5\text{ V}_{Li}$. The total capacity passed from OCV to -0.5 V_{Li} is $\sim 1.8\text{ mAh cm}^{-2}$. Scale bar for y-axis, area in arbitrary units, is defined for reference.

(D) Deconvolution of peak between $1,685$ and $1,495\text{ cm}^{-1}$ with 1.2 M LiPF₆ $^{13}C_3$ EC into ^{13}C LEDC at $1,620\text{ cm}^{-1}$ (red), ^{13}C semi-carbonate 1 at $1,570\text{ cm}^{-1}$ (purple), ^{13}C semi-carbonate 2 at $1,530\text{ cm}^{-1}$ (green), and $^{13}C\text{ }Li_2CO_3$ at $1,500\text{ cm}^{-1}$ (black). Details can be found in Figure S14. A linear background was used, and Gaussian (30%)–Lorentzian (70%) peaks were fit with peak position and FWHM fixed across different potentials. As-collected and differential with respect to OCV *in situ* FTIR spectra are shown in Figure S15.

(E) Areas of ^{13}C LEDC peak at $1,620\text{ cm}^{-1}$ (red), ^{13}C semi-carbonate peaks at $1,570$ and $1,530\text{ cm}^{-1}$ (purple and green), and $^{13}C\text{ }Li_2CO_3$ peak at $1,500\text{ cm}^{-1}$ (black) as a function of potential, overlaid with electrochemical data from LSV. Details for peak area calculation can be found in Table S2. LSV shows three reduction peaks: CuO to Cu reduction at $>2.0\text{ V}_{Li}$, water reduction centered at $\sim 1.3\text{ V}_{Li}$, and EC reduction centered at $\sim 0.5\text{ V}_{Li}$. The total capacity passed from OCV to -0.5 V_{Li} is $\sim 0.3\text{ mAh cm}^{-2}$. Scale bar for y-axis, area in arbitrary units, is defined for reference.

they reported LEDC to plateau as the potential approached 0 V_{Li} .⁶⁴

The same *in situ* FTIR spectroscopy experiment was repeated using an electrolyte with isotope-labeled $^{13}\text{C}_3$ EC (carbon-13 at all three carbon positions) to show that LEDC and Li_2CO_3 were direct reduction products of EC solvent (Figure S15). Figure 2D shows the deconvoluted $^{13}\text{C}=\text{O}$ asymmetric vibrations at $1,620$ and $1,500\text{ cm}^{-1}$, attributable to ^{13}C LEDC and ^{13}C Li_2CO_3 , respectively. Compared with the LEDC and Li_2CO_3 peak positions at $1,670$ and $1,520\text{ cm}^{-1}$ in unlabeled EC, the isotope-labeled products exhibited a $\sim 20\text{--}50\text{ cm}^{-1}$ downshift. This shift is consistent with simple harmonic oscillator modeling of the $\text{C}=\text{O}$ bond, which predicts a $\sim 20\text{--}30\text{ cm}^{-1}$ downshift, as well as prior experimental reports by Schwenke et al.⁷⁰ showing an $\sim 40\text{ cm}^{-1}$ downshift of Li_2CO_3 peaks upon substitution of ^{12}C with ^{13}C . Potential dependent area tracking of ^{13}C LEDC and ^{13}C Li_2CO_3 peaks in Figure 2E showed growth at 0.5 V_{Li} , corresponding to the reduction potential of EC, thus confirming that these species originate from EC reduction. Two additional semi-carbonate peaks at $1,570$ and $1,530\text{ cm}^{-1}$ were also deconvoluted. The isotope-labeled solvent was not dried with molecular sieves due to material limitations, so as a result, it may contain more water compared to the regular EC electrolyte system, which is also suggested by the larger H_2O reduction peak in the LSV of $1.2\text{ M LiPF}_6\text{ }^{13}\text{C}_3\text{ EC}$ (Figure 2E). The appearance of these semi-carbonate species exclusively in the isotope-labeled electrolyte suggests an OH^- -mediated formation pathway, where OH^- is generated as a product of water reduction. Isotope-labeled EC will continue to be used in this paper to pinpoint the origin of decomposition products in mixed solvent systems.

To validate our manual deconvolution method, two automated FTIR spectroscopy processing techniques were applied. First, we developed an automated peak deconvolution method (see STAR Methods) to reveal the pronounced growth of LEDC in the as-collected FTIR spectra (without differential subtraction), where two unique features at $\sim 1,690$ and $1,640\text{ cm}^{-1}$ (Figure S22) were observed. The automated approach for feature analysis included airPLS⁷¹ baseline subtraction, feature identification, and model construction with minimal user input. The area of the two peaks shown in Figure S22F grew in a similar fashion to the manual deconvolution shown in Figures 2B and 2C. Zhuang et al.²¹ and Xu et al.⁵⁸ observed similar features, which have been attributed to the short and long vibrations of the $\text{O}-\text{C}=\text{O}$ stretch²² of LEDC. In addition, these peaks can be attributed to the formation of lithium alkyl carbonate dimers reported by Matsuta et al.,⁵⁹ domains of LEDC with different solvent molecules of EC, such as LEDC:2DMSO²² or LEMC, which can be formed by hydrolysis of LEDC.²² The physical origin of these two features may also come from FTIR spectroscopy peak degeneracy. The second spectral processing technique we performed was a multivariate curve resolution by alternating least squares (MCR-ALS) algorithm based on Leau et al.'s open source code.⁵⁰ In this algorithm, a matrix D consisting of individual *in situ* spectra is fitted against a matrix composed of pure reference spectra multiplied by a concentration matrix, C , and minimized following an ALS method. Furthermore, goodness of fit is quantified through mean squared error and R-squared

value. The pure reference spectra for bulk electrolyte (LiPF_6 in EC/DMC shown in a color gradient from blue to green) and SEI (Li alkyl carbonates shown in green/DEDOHC shown in dark blue/lithium carbonate shown in turquoise) were collected by Leau et al. and provided in their open source code, which are shown in Figures S23A and S23B. The fitted components and contributions are shown in Figures S23E and S23F. The algorithm identified a negatively increasing contribution for both free and bound EC (Figure S23E) from OCV down to $\sim 0.3\text{ V}_{\text{Li}}$. At this point, the bound EC contribution continued to become more negative, while the free EC contribution appeared to become less negative, suggesting that the free EC is being consumed at a slower rate. As the anode potential becomes more negative, it attracts more Li^+ , and therefore, more bound EC will be available at the interface for reduction compared to free EC. The Li alkyl carbonate contribution from MCR-ALS, shown in Figure S23F, demonstrates a positive value, confirming formation of these species. The Li alkyl carbonate trace increased initially around 2.0 V_{Li} due to OH^- -mediated reduction of EC arising from water reduction ($\text{H}_2\text{O} + \text{e}^- \rightarrow 1/2\text{H}_2 + \text{OH}^-$), consistent with the increase in the LEDC signal at $\sim 1.7\text{ V}_{\text{Li}}$. The Li alkyl carbonate signal from MCR-ALS then increased again at $\sim 0.8\text{ V}_{\text{Li}}$, corresponding to the reduction potential of EC, matching the increase in LEDC starting from 0.5 V_{Li} from the manual deconvolution process. Furthermore, the Li alkyl carbonate trace increased again around 0 V_{Li} at the onset of Li deposition, agreeing well with our manually deconvoluted LEDC increase. Li_2CO_3 contributions from both methods showed similarly weak intensities compared to Li alkyl carbonate/LEDC. While MCR-ALS calculated the contribution as remaining close to 0 throughout, the manual deconvolution method shows weak linear dependence below water reduction potential at $\sim 1.7\text{ V}_{\text{Li}}$. The goodness of fit as measured by the R-squared value was 0.533. Possible areas of error stem from key assumptions built into the MCR-ALS method. First, MCR-ALS assumes a linear mixture model where components combine additively and respond to concentrations independently. Second, it relies heavily on the integrity of input data D and S . As shown in Figure S23C, our as-collected spectra experience significant baseline drift due to changes in potential, detector warming up, or path length changes due to sample thickening. MCR-ALS may interpret these baseline drifts as an additional chemical component. Furthermore, the synthesized and experimentally collected FTIR spectroscopy signal for Li alkyl carbonate and Li_2CO_3 , as seen in Figure S23B, consists of broad, ill-defined features and high levels of noise, thereby lowering the confidence in the input pure spectra, S . Finally, MCR-ALS assumes that spectra of pure components maintain constant peak positions and full width at half-maximum (FWHM) across all potentials. However, the peak positions and shapes of SEI components may change due to changes in the electric field (Stark effect⁷²) or changes in solvation environment.⁷³ Moving forward, only the manual deconvolution method is used due to the similarity in trends obtained from both and the higher adaptability of the manual deconvolution method to different scenarios.

After LSV, the *in situ* FTIR spectroscopy cell was cycled to examine the evolution of LEDC and Li_2CO_3 over 50 cycles

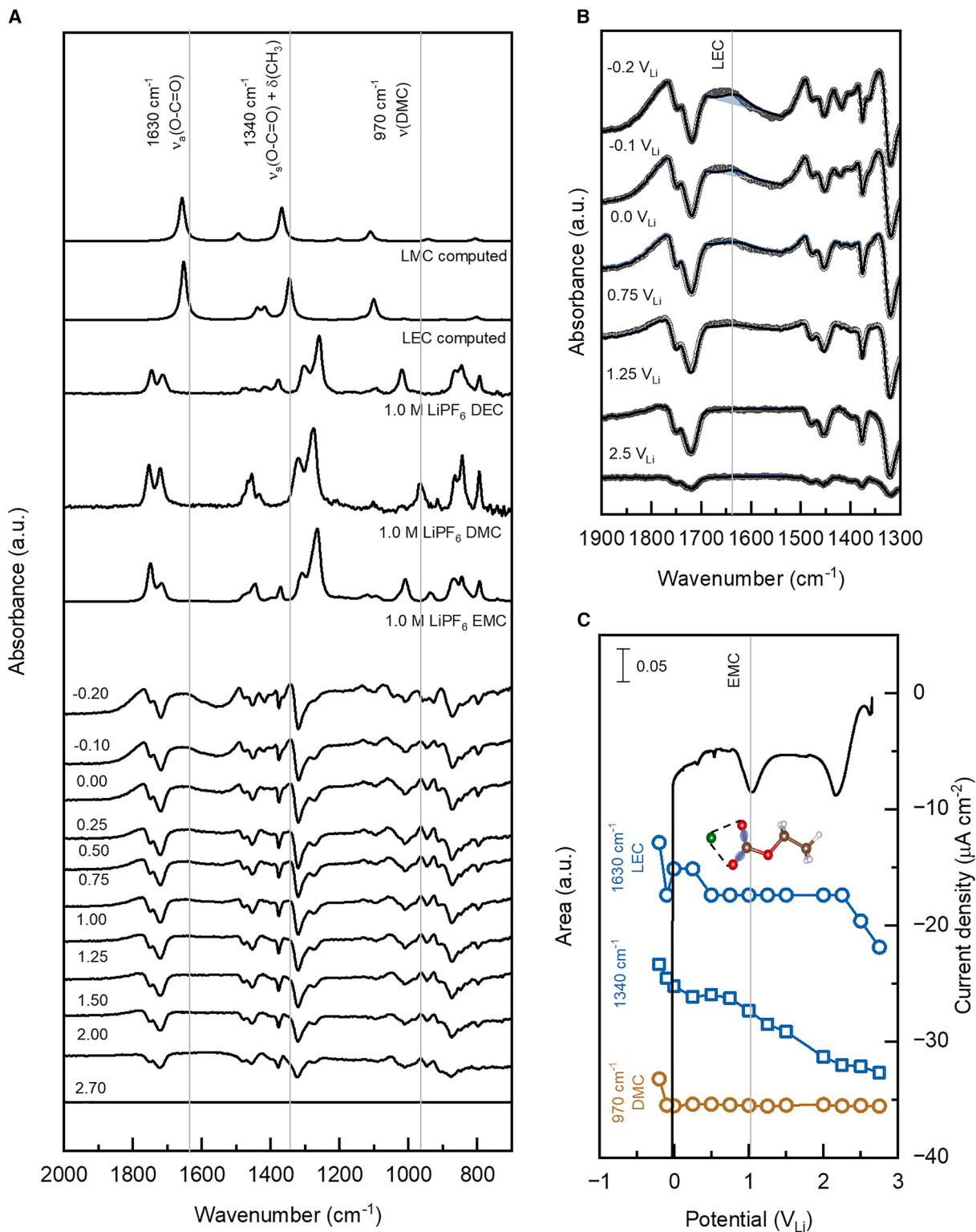


Figure 3. *In situ* FTIR spectra as a function of potential for 1.0 M LiPF_6 in EMC

(A) Potential-dependent differential spectra with respect to OCV ($\sim 2.5 V_{\text{Li}}$) for 1.0 M LiPF_6 in EMC from OCV to $-0.20 V_{\text{Li}}$. The *in situ* FTIR spectroscopy cell was linearly swept from OCV down to $-0.5 V_{\text{Li}}$ at a scan rate of 0.1 mV/s. New peaks corresponding to LEC form at 1,630 and 1,340 cm^{-1} , and DMC at 970 cm^{-1} . The bulk electrolyte on top was collected in ATR mode with a Ge crystal at an incidence angle of 50°. As-collected spectra can be found in Figure S30B, and full potential range differential spectra can be found in Figure S30C. Computational details for LMC and LEC can be found in Figure S10.

(legend continued on next page)

(Figure S24). Galvanostatic cycling of 1.2 M LiPF₆ in EC with the spectroelectrochemical cell shown in Figure S26 averaged around 70% over 50 cycles. A current density of 81.5 $\mu\text{A cm}^{-2}$ was chosen for *in situ* FTIR spectroscopy cycling to ensure that the overpotentials were comparable to those of CR2032 coin cell cycling. The overpotential as measured from Li plating at 0.4 mA cm^{-2} in CR2032 coin cells with 1.2 M LiPF₆ EC after 50 cycles was found to stabilize at ~ 43 mV (Figure S29B). The overpotential for the same electrolyte as measured in the *in situ* FTIR spectroscopy cell at a reduced current density of 81.5 $\mu\text{A cm}^{-2}$ was found to be ~ 25 mV (Figures S24C and S24D), which is comparable to the coin cell measurement. Ensuring that the overpotentials are comparable between coin-cell cycling and *in situ* FTIR spectroscopy cycling is important because larger overpotentials promote the formation of small Li nuclei and contribute to inhomogeneous local current densities for Li plating/stripping.¹⁰ The absorbance peaks of LEDC (1,670 and 1,130 cm^{-1}) were shown to grow gradually upon subsequent cycles of Li stripping and plating (Figures S24A and S24B), indicative of moderate LEDC buildup in the SEI. The peak positions and lower and upper bounds for area integration were determined by the same first- (Figure S27) and second- (Figure S28) derivative methods as those used during LSV. The spectrum of the 50th cycle was used to calculate the peak positions and area integration bounds. Peak assignments are summarized in Table S4 and compared to DFT and literature values. The peaks at $\sim 1,670$ and $\sim 1,130$ cm^{-1} assigned to LEDC grew moderately, more than the peak at $\sim 1,350$ cm^{-1} , while the peak at 1,050 cm^{-1} did not show a measurable change (Figure S24D; Table S5). The growth of the two features of LEDC centered at $\sim 1,670$ cm^{-1} , shown in Figure S24B, remained and grew during cycling. This observation suggests that EC continues to be reduced after the formation of LEDC in the first cycle. The growth of LEDC during cycling in Figure S24D is more moderate than that upon the first Li plating in Figure 2C and is lowered with increasing cycling, indicating gradual passivation of Li with LEDC. This observation is in contrast to the almost complete passivation of graphite in the first cycle,²¹ where limited formation of LEDC is expected beyond the first cycle, as DEMS measurements show that the gas product (ethylene) associated with EC reduction to LEDC rapidly decreases below the noise level after the first cycle for 1.0 M LiPF₆ in EC/DMC.³⁶ Interestingly, no significant increases were found for the peak of Li₂CO₃ (1,520 cm^{-1}) (Figure S24), suggesting no detection of significant conversion from LEDC to Li₂CO₃ from these FTIR spectroscopy measurements. The moderate growth of LEDC and the lack of Li₂CO₃ formation during Li plating and stripping are correlated with reasonably stable overpotentials (Figure S24C) from ~ 15 to ~ 25 mV from the *in situ* FTIR spectroscopy cell and CE close to 90% for 100 cycles from coin cells cycled at 0.4 mA cm^{-2} (Figure S24). This result is in agreement with the hypothesis that LEDC functions as the major

component of the SEI interfacing with the electrolyte, 1.2 M LiPF₆ in EC.

***In situ* FTIR spectroscopy of 1.0 M LiPF₆ in EMC: Potential-dependent measurements**

Potential-dependent *in situ* FTIR spectroscopy measurements for 1.0 M LiPF₆ in EMC in Figure 3 revealed the transesterification of EMC into DMC and DEC (2EMC $\rightarrow$ DMC + DEC) in agreement with previous work,^{38,74} no significant growth of the SEI above 0 V_{Li} , and the formation of some lithium alkyl carbonates in the SEI primarily below 0 V_{Li} .

In situ FTIR spectroscopy measurements for 1.0 M LiPF₆ in EMC were collected as a function of potential from OCV ($\sim 2.7 V_{\text{Li}}$) to $-0.5 V_{\text{Li}}$, where subtle changes were observed in the differential spectra (Figure 3A) and the as-collected spectra shown in Figure S30. Unlike 1.2 M LiPF₆ in EC (Figure 2), no pronounced growth centered at 1,520 cm^{-1} was found for EMC (Figures 3A and 3C), nor significant PF₆[−] consumption as reflected by P–F stretching at 845 cm^{-1} (Figure 3A). A broad feature corresponding to the O–C=O asymmetric stretching with a wavenumber ranging from 1,670 to 1,550 cm^{-1} , centered at $\sim 1,630$ cm^{-1} , was found to grow below 0 V_{Li} , which was accompanied by increased absorbance at $\sim 1,340$ cm^{-1} , attributable to the formation of LEC/LMC based on the IR peak locations and vibrations of reference LEC and LMC shown in Table S7 (e.g., the strong CO₃ asymmetric stretching peak⁵⁸ of LEC at 1,630 cm^{-1}). These assignments are further supported by ATR-FTIR spectra of synthesized LMC and LEC as reported by Xu et al.,⁵⁸ showing strong absorbance in the regions of 1,380–1,300 (LMC/LEC) and 1,150–1,050 (LMC/LEC) cm^{-1} (Figures S19) and in agreement with previous FTIR spectroscopy assignments of lithium alkyl carbonates, including CO stretching and CH₂ deformation^{26,59} at 1,330 and 1,180 cm^{-1} and CH₃ deformation⁵⁹ at 900 cm^{-1} . Moreover, the peak growth at 1,630 cm^{-1} shown in Figure 3A believed to originate from CO₃ asymmetric stretching is small and slightly downshifted compared to the CO₃ from LEDC, a behavior characteristic of LMC/LEC, as supported by the DFT computation in Figure 3A and previous work.⁵⁸ While it is challenging to tell LMC and LEC apart from FTIR spectroscopy alone, GC-BID/TCD data in Figure S2 reveal CH₄ as the major product during reaction with Li. Hence, the formation of LEC is proposed (EMC + e[−] + Li⁺ $\rightarrow$ LEC + CH₄).

The intensity changes of the absorbance at $\sim 1,630$ and $\sim 1,340$ cm^{-1} as a function of potential are shown in Figure 3C, showing the growth of LEC in the SEI below 0 V_{Li} . Peak positions were determined from the x intercept of the first derivative (Figure S32) of a representative potential at $-0.50 V_{\text{Li}}$ (Figure S34), while the lower and upper limits of integration for area were determined by the x intercepts of the second derivative (Figure S33), which are summarized in Table S6. Cathodic

(B) Deconvolution of wide peak between 1,700 and 1,450 cm^{-1} into LEC at 1,630 cm^{-1} (blue). Details can be found in Figure S31. A linear background was used, and Gaussian (30%)-Lorentzian (70%) peaks were fit with position and FWHM constrained between different potentials. Peak positions and lower and upper limits for peak deconvolution are based on the first and second derivatives (Figures S32 and S33).

(C) Areas of LEC peaks at 1,630 cm^{-1} (blue circle) and 1,340 cm^{-1} (blue square), and DMC peak at 970 cm^{-1} (brown circle) with 1.0 M LiPF₆ in EMC as a function of potential. Details can be found in Figures S32 and S33, and Table S6. LSV shows two reduction peaks: CuO to Cu reduction at $>2.0 V_{\text{Li}}$ and EMC reduction centered at 1.1 V_{Li} . The total capacity passed from OCV to $-0.5 V_{\text{Li}}$ is ~ 2.4 mAh cm^{-2} . Scale bar for y-axis, area in arbitrary units, is defined for reference.

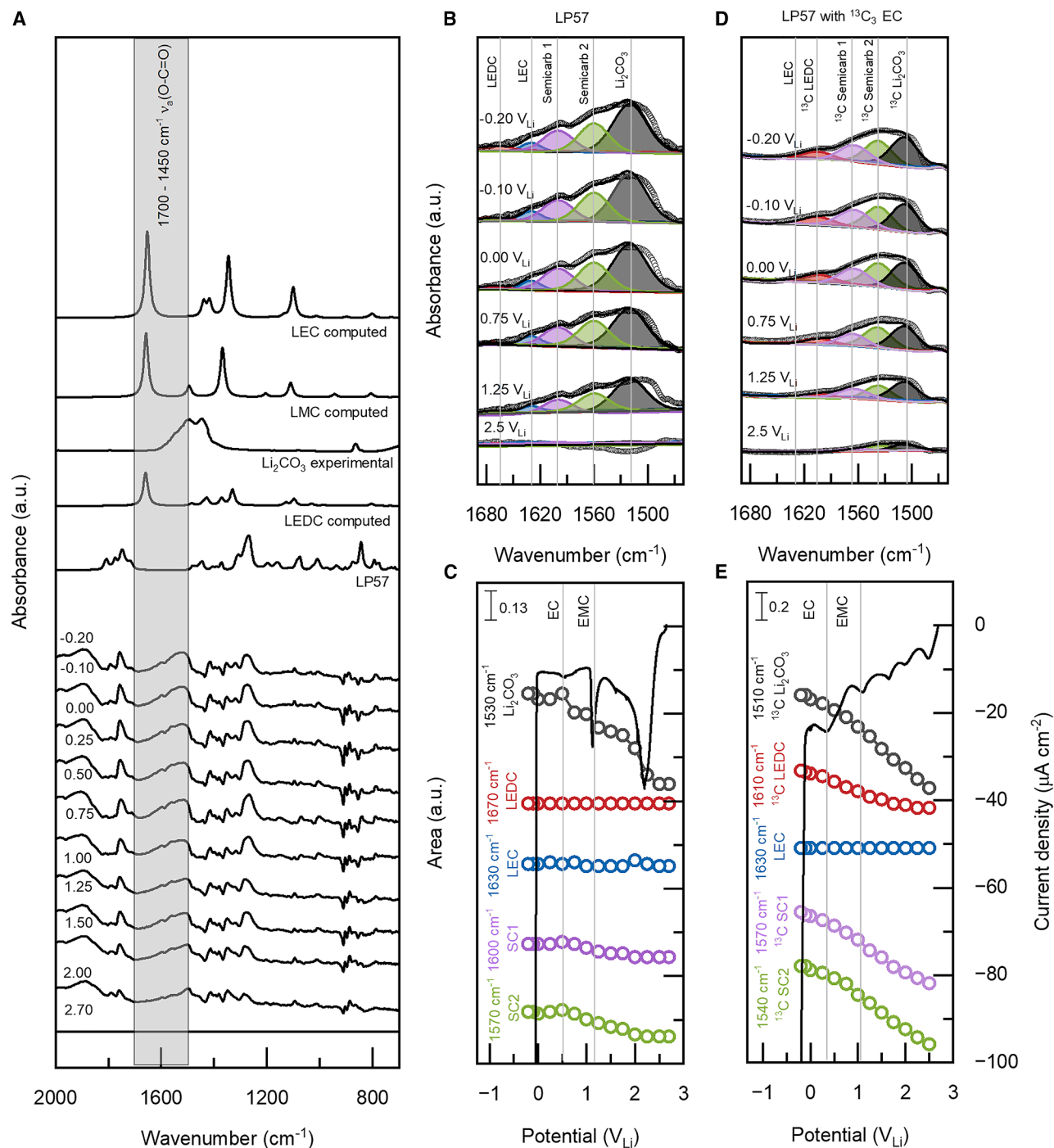


Figure 4. *In situ* FTIR spectra as a function of potential for LP57 and isotope-labeled LP57 with $^{13}\text{C}_3$ EC

(A) Potential-dependent differential spectra with respect to OCV ($\sim 2.7 V_{\text{Li}}$) for LP57 from OCV to $-0.20 V_{\text{Li}}$. The *in situ* FTIR spectroscopy cell was linearly swept from OCV ($\sim 2.7 V_{\text{Li}}$) down to $-0.50 V_{\text{Li}}$ at a scan rate of 0.1 mV/s. Raw spectra can be found in Figure S38B, and full potential range differential spectra can be found in Figure S38C. The bulk electrolyte on top was collected in ATR mode with a Ge crystal at an incidence angle of 50° . Computed (more details in Figure S10) and experimental LEDC⁵⁸ and Li_2CO_3 from NIST are included for comparison.

(B) Deconvolution of large peak between 1,700 and 1,450 cm^{-1} into LEDC at 1,670 cm^{-1} (red), LEC at 1,630 cm^{-1} (blue), Li_2CO_3 at 1,530 cm^{-1} (black), and two additional semi-carbonates at 1,600 and 1,560 cm^{-1} (purple and green). Details can be found in Figure S39. A linear background was used, and Gaussian (30%)-Lorentzian (70%) peaks were fit with position and FWHM constrained between different potentials.

(C) Areas of LEDC (red), LEC (blue), semi-carbonate (purple and green), and Li_2CO_3 (black) peaks as a function of potential. Areas are summarized in Table S8. First and second derivative details can be found in Figures S40 and S41. LSV shows four reduction peaks: CuO to Cu reduction at $>2.0 V_{\text{Li}}$, water reduction

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LSV (Figure 3C) showed one small reduction peak centered at $\sim 2.2 V_{Li}$, attributable to CuO reduction, as mentioned previously,⁶⁷ and another small reduction centered at $\sim 1.0 V_{Li}$, attributable to EMC reduction.⁷⁵ The EMC reduction peak did not produce any visible changes in the FTIR spectra, thus indicating the formation of soluble species. This observation is in agreement with work by Tasaki et al.,⁷⁶ who showed that LMC and LEC are both soluble in DMC. The new peak growth can be assigned to the formation of LEC from EMC reduction by Li, as seen by the peak deconvolution into a single species in Figure 3B. The emergence of LEC below $0 V_{Li}$ can be attributed to the accelerated formation of LEC via the chemical reduction of EMC by the freshly plated Li. The lack of passivation of Li by SEI in the EMC electrolyte is associated with a low CE of $<15\%$ averaged over 100 cycles in coin cells (Figure S29A).

The peak growth at 970 cm^{-1} with decreasing potential during *in situ* FTIR spectroscopy measurements of 1.0 M LiPF_6 in EMC (Figure 3A) is indicative of DMC formation as a result of EMC transesterification, where the duration of *in situ* FTIR spectroscopy measurement is similar to that of previous observations.³⁸ Yoshida et al.⁷⁴ first revealed the transesterification of EMC into DMC and DEC through liquid chromatography, which was further studied by Strehle et al.³⁸ The emergence of DMC below $0 V_{Li}$ due to the formation of alkoxide species on freshly plated Li agrees well with Strehle et al.'s observation that the transesterification process of EMC into DMC and DEC is catalyzed by Li alkoxide species. We further examined *in situ* FTIR spectra for 1.0 M LiPF_6 in DMC (Figure S35) and 1.0 M LiPF_6 in DEC (Figure S36) as functions of potential. Differential spectra showed pronounced growth at $1,450$ and $1,340\text{ cm}^{-1}$, while broad features centered at $1,670$ and $1,090\text{ cm}^{-1}$ were observed for 1.0 M LiPF_6 in DMC below $0 V_{Li}$ (Figure S37A), indicative of the formation of LMC ($\text{DMC} + \text{Li}^+ + \text{e}^- \rightarrow \text{LMC} + \text{CH}_4$).^{56,58,77} In contrast, a broad feature at $1,670\text{ cm}^{-1}$ was found to grow sharply below $0 V_{Li}$ for 1.0 M LiPF_6 in DEC (Figure S37B), as well as minute growth at $1,370\text{ cm}^{-1}$, suggesting the presence of LEC ($\text{DEC} + \text{Li}^+ + \text{e}^- \rightarrow \text{LEC} + \text{C}_2\text{H}_6$).^{56,58,77}

In situ FTIR spectroscopy of LP57: Potential-dependent measurements

Potential-dependent *in situ* FTIR spectroscopy measurements for LP57 shown in Figure 4 revealed the formation of Li_2CO_3 , LEDC, LEC, and additional semi-carbonate species when both EC and EMC solvents are present. LSV showed features corresponding to CuO reduction to Cu and water reduction spanning from 2.5 to $1.5 V_{Li}$, as well as EMC reduction at $1.1 V_{Li}$ and EC reduction at $0.5 V_{Li}$, in Figure 4B, in agreement with previous work.³⁴ Differential spectra as a function of potential can be found in Figure 4, and corresponding raw spectra can be found in Figure S38. These

measurements were repeated to show reproducibility (Figure S45). Species and peak assignments compared to literature, DFT, and NIST are shown in Table S10. A broad feature ranging from $1,700$ to $1,450\text{ cm}^{-1}$ grew with decreasing potential from the OCV ($\sim 2.7 V_{Li}$) shown in Figure 4A. We deconvoluted the broad feature into five separate peaks centered at $1,670$ (LEDC), $1,630$ (LEC), $1,600$ (semi-carbonate 1), $1,570$ (semi-carbonate 2), and $1,530$ (Li_2CO_3) cm^{-1} , as shown in Figure 4D. The areas for each species as a function of potential are shown in Figure 4B. While three of the deconvoluted peaks have been previously identified in Figures 2 and 3, two new peaks at $1,600$ and $1,570\text{ cm}^{-1}$ are hypothesized to come from alternative oligomers of semi-carbonate. We further hypothesize that the presence of these oligomers of semi-carbonate is detrimental to cycling efficiency compared to LEDC. To better understand the origin of the semi-carbonate peaks at $1,600$ and $1,570\text{ cm}^{-1}$, LP57 with isotope-labeled $^{13}\text{C}_3$ EC was used to repeat the *in situ* FTIR spectroscopy experiment. If the semi-carbonate species originated from EC, they would experience a $30\text{--}50\text{ cm}^{-1}$ downshift in peak position. The same broad peak from $1,690$ to $1,480\text{ cm}^{-1}$ was observed to grow with isotope-labeled LP57. The broad peak in Figure 4D can be deconvoluted into five peaks: $1,610$ (LEDC), $1,630$ (LEC), $1,570$ (semi-carbonate 1), $1,540$ (semi-carbonate 2), and $1,510$ (Li_2CO_3) cm^{-1} . LEDC and Li_2CO_3 peaks originate from EC, as previously validated in Figure 2D; therefore, a $20\text{--}60\text{ cm}^{-1}$ downshift upon carbon-13 isotope labeling is expected, with the higher-wavenumber LEDC peak experiencing a greater downshift than the Li_2CO_3 peak (Figure S44B). The peak position for LEC, an organic SEI species derived from EMC, stayed relatively constant, with a $<10\text{ cm}^{-1}$ difference, which may be due to experimental error or slight differences in solvation environment. Finally, the two semi-carbonate peaks experienced a $\sim 30\text{ cm}^{-1}$ downshift in peak position, suggesting that they are decomposition products of EC (Figure S44B). The isotope-labeled LP57 *in situ* FTIR spectroscopy experiment was repeated once in Figure S46 to show reproducibility. The decomposition of EC into alternative semi-carbonates is supported by pre-Li-plating ECMS gas profiles in Figure S4, where a lack of C_2H_4 formation above $0 V_{Li}$ points to alternative reduction pathways for EC. The appearance of these semi-carbonate species may be attributed to an elevated water content of $\sim 38\text{ ppm}$ as measured by Karl Fischer (KF) titration, where OH^- from trace water reduction creates alternative reduction pathways for EC into semi-carbonates. Further investigation is necessary to confirm the reaction mechanisms and exact chemical identity of these species.

Following the same method as before for determining the peak position and areas of integration using a representative spectrum at $-0.2 V_{Li}$ (Figure S48), the first- and second-derivative plots are

shoulder peak around $1.7 V_{Li}$, EMC reduction centered at $\sim 1.1 V_{Li}$, and EC reduction centered at $\sim 0.5 V_{Li}$. The total capacity passed from OCV to $-0.5 V_{Li}$ is $\sim 1.8\text{ mAh cm}^{-2}$. Scale bar for y-axis, area in arbitrary units, is defined for reference.

(D) Deconvolution of large peak between $1,690$ and $1,480\text{ cm}^{-1}$ with isotope-labeled LP57 ($^{13}\text{C}_3$ EC) into ^{13}C LEDC at $1,610\text{ cm}^{-1}$ (red), LEC at $1,630\text{ cm}^{-1}$ (blue), ^{13}C Li_2CO_3 at $1,510\text{ cm}^{-1}$ (black), and two ^{13}C semi-carbonate peaks at $1,570$ and $1,540\text{ cm}^{-1}$ (purple and green). Details can be found in Figure S42. A linear background was used, and Gaussian (30%)-Lorentzian (70%) peaks were fit with position constrained between different potentials. Potential-dependent as-collected and differential spectra of the Cu electrode before and after Li plating collected from LP57 with $^{13}\text{C}_3$ EC are shown in Figures S43 and S44.

(E) Areas of ^{13}C LEDC (red), LEC (blue), ^{13}C semi-carbonates (purple and green), and ^{13}C Li_2CO_3 (black) peaks as a function of potential. Areas are summarized in Table S9. LSV shows four reduction peaks: CuO to Cu reduction at $>2.0 V_{Li}$, water reduction shoulder peak around $1.7 V_{Li}$, EMC reduction centered at $\sim 1.1 V_{Li}$, and EC reduction centered at $\sim 0.5 V_{Li}$. The total capacity passed from OCV to $-0.5 V_{Li}$ is $\sim 0.2\text{ mAh cm}^{-2}$. Scale bar for y-axis, area in arbitrary units, is defined for reference.

shown in Figures S40 and S41. Our observations of LEDC and Li_2CO_3 are in agreement with the recent work by Leau et al.⁵⁰ studying the SEI formed on Cu with an EC-based electrolyte LP30, where the growth of semi-carbonate and Li_2CO_3 species centered around 1,640 and 1,525 cm^{-1} , respectively, is observed during GITT cycling down to $\sim 0 V_{\text{Li}}$. The feature at $\sim 1,520 \text{ cm}^{-1}$ began to form around $2.0 V_{\text{Li}}$, coinciding with a large reduction feature spanning from 2.5 to $1.5 V_{\text{Li}}$, which can be attributed to CuO reduction to Cu and water reduction to H_2 and OH^- . Water has been shown to react with EC to form lithium carbonate⁵⁷ ($\text{EC} + \text{OH}^- + \text{Li}^+ \rightarrow \text{Li}_2\text{CO}_3 + \text{HOCH}_2\text{CH}_2\text{OH}$). Starting from $\sim 1.1 V_{\text{Li}}$, a peak at 1,630 cm^{-1} was found to grow, which is assigned to LEC, similar to EMC reduction (Figure 3B). A smaller reduction peak centered at $0.5 V_{\text{Li}}$ was also observed together with an increase in Li_2CO_3 signal, suggesting a 2-electron reduction of EC into Li_2CO_3 ($\text{EC} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{C}_2\text{H}_4 + \text{Li}_2\text{CO}_3$).^{20,61–63} Once again, the peak potential of $\sim 0.5 V_{\text{Li}}$ agrees well with the LSV data from Figure 2B, where EC demonstrated a reduction peak centered around $0.5 V_{\text{Li}}$. At potentials below $0 V_{\text{Li}}$, a third peak at 1,670 cm^{-1} emerges, corresponding to LEDC. By comparing the absolute value of peak areas, we can conclude that Li_2CO_3 is the dominant species, with LEDC and LEC appearing in smaller but similar quantities (Figure 4; peak intensities are shown in Table S8). The prevalence of Li_2CO_3 can be attributed to the electrochemical reduction of EC ($\text{EC} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4$) and the reaction between LEMC and OH^- from water reduction ($\text{LEMC} + \text{Li}^+ + \text{OH}^- \rightarrow \text{HOCH}_2\text{CH}_2\text{OH} + \text{Li}_2\text{CO}_3$).²² This hypothesis is in agreement with gas analysis from reacting Li and LP57 by von Holtum et al.,³⁰ which has revealed the generation of C_2H_4 as the major component (CH_4 as the top minor component, presumably coming from EMC). An explanation for the preferential formation of Li_2CO_3 over LEDC has been previously proposed by Aurbach et al.⁷⁸, who examined the competitive formation of Li_2CO_3 and ROCO_2Li species in EC/DMC mixtures reacted with lithium *tert*-butoxide across varying solvent ratios. Their results showed that Li_2CO_3 dominates at low EC concentrations due to Li^+ outcompeting EC as electrophiles for the carbonate anion, which is initially formed by nucleophilic attack on both carbons of the EC molecule. The water content, as measured by KF titration, was 38 ppm in LP57 compared to 25 and 26 ppm in EC and EMC, respectively (Table S3). Therefore, the possibility that the observed prevalence of Li_2CO_3 originates from elevated water content cannot be excluded.

The average CE over 100 cycles measured in Li||Cu CR2032 half-cells was $\sim 50\%$ (Figure S29), in reasonable agreement with previous work³⁹ and lower than the CE in the 1.2 M LiPF_6 EC electrolyte ($\sim 90\%$). The higher CE associated with LEDC rather than Li_2CO_3 might be attributed to more uniform LEDC coverage on Li compared to that of Li_2CO_3 , which requires further investigation. To better understand how different SEI chemistries in 1.2 M LiPF_6 EC, 1.0 M LiPF_6 EMC, and LP57 influence Li deposition morphology, top-view and cross-sectional SEM images of electrodeposited Li (EDLi) on Cu foil were collected. Samples were prepared by galvanostatically plating Li onto Cu foil at a current density of 0.4 mA cm^{-2} for a total capacity of 2 mAh cm^{-2} , similar to the total charge passed during the LSV portion of the *in situ* FTIR spectroscopy experiments for all three electrolytes (1.8 mAh cm^{-2} for EC, 2.4 mAh cm^{-2} for EMC, and 1.8 mAh cm^{-2} for LP57).

Because Celgard 3501 was used to prepare the samples to ensure smooth removal of the separator from the EDLi on Cu, 1.2 M LiPF_6 in EC encountered a large plating overpotential of $>1.0 V$ (Figure S49A) arising from its viscosity and concentration overpotentials. Along with this large overpotential, Li deposition morphology in the EC electrolyte is dominated by thin needles (Figure S49B), in agreement with accepted Li growth mechanisms where the onset of dendritic growth is proportional to Li diffusivity.⁷⁹ The inflection point in the voltage profile, approximately 30 min into deposition, may correlate with Li^+ depletion at the electrode surface and the onset of dendritic growth. On the other hand, in LP57, larger-diameter whiskers are observed together with larger plates of deposited Li (Figure S49E). The addition of EMC as a diluent serves to decrease viscosity and increase the diffusivity of the LP57 electrolyte,⁸⁰ suppressing dendritic growth and leading to favorable Li deposition morphologies during the initial cycle, irrespective of SEI stability. Furthermore, the plating overpotential in LP57 (Figure S49D) shows an apparent decrease from $\sim 100 \text{ mV}$ at 1 h to $\sim 46 \text{ mV}$ at 5 h, suggesting favorable SEI passivation and improvement of Li plating kinetics. In contrast, the overpotential for 1.0 M LiPF_6 EMC (Figure S49G) shows the opposite trend, increasing from $\sim 230 \text{ mV}$ at 1 h to $\sim 240 \text{ mV}$ at 5 h, which would suggest insufficient passivation and SEI buildup on the electrode surface. SEM images for 1.0 M LiPF_6 EMC show the formation of a thick, porous layer exhibiting significant cracking (Figure S49H). These observations corroborate FTIR spectroscopy findings that the EMC-derived SEI is incapable of passivating the lithium surface from further reactivity. Cross-sectional SEM images (Figures S49C, S49F, and S49I) further revealed a thicker, more porous EDLi layer in EMC compared to LP57. The average thickness across three different sections of the EDLi was ~ 30 and $\sim 14 \mu\text{m}$ for EMC and LP57, respectively. The electrolyte-dependent Li deposition morphology observed here agrees with previous work by Fang et al.,³³ who have used cryo-focused ion beam (cryo-FIB) to observe a thick inactive Li layer in 1.0 M LiPF_6 in EC/EMC and revealed whiskers with lengths up to 80 nm ³¹ embedded in the SEI through cryo-TEM when cycled at a current density of 0.5 mA cm^{-2} . Overall, our results highlight that an increasing EC solvent fraction leads to denser EDLi composed primarily of Li metal deposition aggregates, with the LP57 thickness resembling the $\sim 10 \mu\text{m}$ of ideal 2 mAh cm^{-2} Li deposition, compared to the extremely thick EMC-derived layer, which suggests significant SEI contributions. Increasing the EC solvent fraction has been shown in Figures 2 and 4 to lead to primarily LEDC formation, suggesting the role of LEDC in delivering more uniform and compact Li deposition morphology and thus increasing Li metal reversibility.

NMR to reveal inorganic SEI species

Fluorine and lithium SSNMR were used to chemically resolve the inorganic SEI formed on both Cu and Li in 1.2 M LiPF_6 in EC and 1.0 M LiPF_6 in EMC. Li/Cu samples were extracted from Li||Cu coin cells after LSV from OCV ($\sim 2.70 V_{\text{Li}}$) to 0.1 and $-0.5 V_{\text{Li}}$, followed by a constant voltage hold at the final potential for 1 h. *Ex situ* fluorine SSNMR of Li/Cu electrodes obtained at 0.1 and $-0.5 V_{\text{Li}}$ after cycling in 1.2 M LiPF_6 in EC (Figure 5A) revealed a doublet peak at -74 ppm , corresponding to the PF_6^- that arises from residual salt in the SEI. In addition, we see a peak at -204

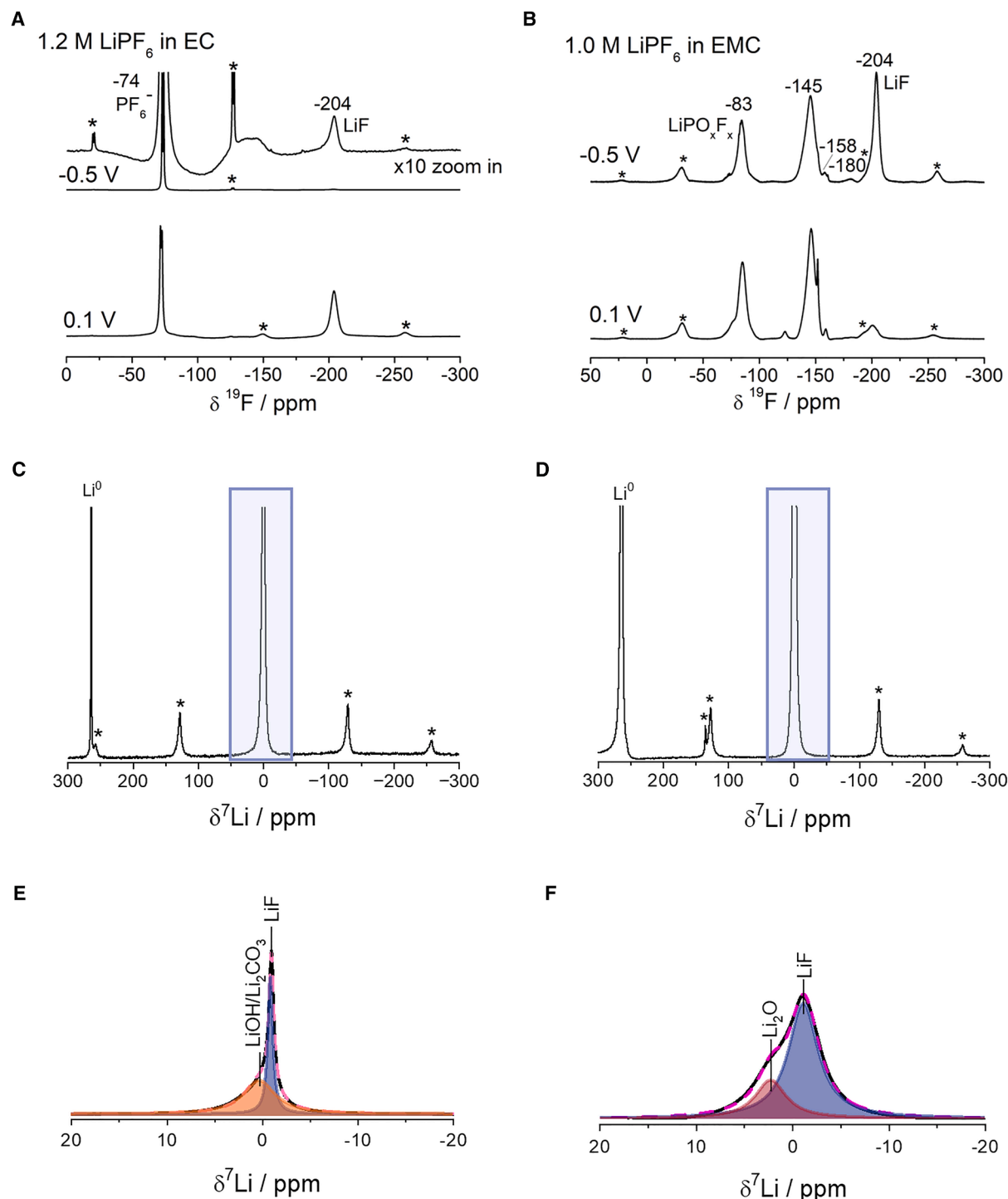


Figure 5. SSNMR measurements of inorganic SEI on SEI formed on Li/Cu electrodes

The SEI was formed in a Li||Cu CR2032 coin cell by linearly sweeping the potential from OCV (~ 2.7 V_L) to the desired potential and holding it for 1 hour. After cycling, the coin cells were disassembled, and solid products from the Cu foil and glass fiber separator were scraped off for analysis. The magic angle spinning (MAS) frequency for all experiments was set to 30 kHz; spinning sidebands are marked with asterisks (*).

(A) ¹⁹F-SSNMR spectra of the SEI formed in the Li||Cu cell using 1.2 M LiPF₆ in EC.

(B) ¹⁹F-SSNMR spectra of the SEI formed in the Li||Cu cell using 1.0 M LiPF₆ in EMC.

(C) ⁷Li-SSNMR spectra for the SEI formed using 1.2 M LiPF₆ in EC. A signal at ~ 246 ppm corresponds to smooth Li metal deposits, while those between 260 and 270 ppm correspond to inhomogeneous Li deposits.⁸⁵

(legend continued on next page)

ppm assigned to LiF, which is higher in intensity at 0.1 V_{Li} than at −0.5 V_{Li}. A detailed analysis of the LiF peak, including longitudinal relaxation measurements (*T*₁), revealed two distinct components. The first component is the low-frequency ¹⁹F-NMR resonance, which is narrower and attributed to crystalline or bulk-like LiF. The second component exhibits a high-frequency ¹⁹F shift that shows a broader line shape, possibly due to structural changes in this fraction of LiF (Figures 5A and S50). Structural changes are supported by ¹⁹F *T*₁ measurements that show that the high-frequency shoulder exhibits faster relaxation compared to bulk LiF, a property that is consistent with differences in local coordination environment, domain size, and/or partial structural modification at the interface. We and others have found a positive correlation between CE and the appearance of this broad, high-frequency shoulder in the ¹⁹F-NMR spectrum of LiF and the associated physical changes.^{81,82} While the signal for LiF at −204 ppm was observed at both potentials, the ¹⁹F-SSNMR peak for the EMC sample is narrower, and the broad shoulder is less pronounced (Figure 5B), consistent with a more ordered structure, which is expected for a lower-CE Li anode. In addition, a number of other F-containing species were observed when the cells were cycled in EMC, including a peak at −83 ppm, ascribed to LiPO_xF_x species such as OPF₂OR or OPF(OR)₂; two single peaks at −158 and −180 ppm, which can be assigned to residual HF; and a peak at −145 ppm, consistent with lithiated fluorides reported previously.^{83,84} ⁷Li-SSNMR experiments performed on these cycled electrodes (Figures 5C–5F) not only confirmed the presence of LiF at −1 ppm but also revealed the presence of LiOH and Li₂CO₃, as indicated by an additional shoulder to the left of the LiF peak for EC (Figure 5E), and the presence of Li₂O, as shown by left peak shoulder (Figure 5F) for EMC. Note that some of the breadth in the ⁷Li-SSNMR spectrum in the EMC sample may also arise from other overlapping compounds identified in ¹⁹F-SSNMR for which the ⁷Li shifts are not known. The multiple F-containing products found for electrodes of EMC also align with *in situ* FTIR spectroscopy data, which show that the EMC electrolyte exhibits greater decomposition of the anion compared to EC (Figure S51).

To verify SSNMR measurements, XPS of the SEI formed on EDLi on Cu foil was performed in two of the three electrolyte systems: 1.0 M LiPF₆ in EMC and LP57. In order to avoid peak convoluting effects from remaining PF₆[−] anions and their potential degradation into LiF and Li_xPO_yF_z species under the x-ray⁸⁶, SEI samples were thoroughly rinsed with solvent prior to XPS measurement. The rinsing solvent was selected to match the electrolyte solvent in which the SEI was formed (i.e., 1.0 M LiPF₆ EMC samples were rinsed with EMC, and LP57 samples were rinsed with EC/EMC [3:7 by volume]) to minimize perturbation of the SEI composition. Due to EC being solid at room temperature, it was not possible to rinse off excess salt from SEI

samples formed in 1.2 M LiPF₆EC. Therefore, we decided to only characterize the SEI formed in 1.0 M LiPF₆ EMC and LP57 electrolytes. In order to distinguish between electrochemically formed SEI (>0 V_{Li}) and chemically formed SEI (<0 V_{Li}), the potential was linearly swept at 1 mV/s down from OCV (~2.7 V_{Li}) to 0.1 or −0.50 V_{Li} and then held at the potential of interest for 3 h to accumulate SEI. High-resolution XPS scans of the 1.0 M LiPF₆ EMC sample at 0.1 V_{Li} in the C1s region (Figure S52A) revealed peaks at 285 eV from C–C/H,⁸⁷ ~286.5 eV from C–O,⁸⁸ and ~289 eV from O–C=O,⁸⁹ which is consistent with the lack of Li₂CO₃ formation observed through *in situ* FTIR spectroscopy (Figure 3C). P2p spectra were assigned as follows: Li_xPO_yF_z (~137 eV) and Li_xPF_y (~135.5 eV), which is consistent with SSNMR observations (Figure 5B). The lack of observation of Li_xPF_y species with SSNMR may be due to the loss of sample during handling. F1s spectra were assigned as follows: LiF (~685 eV),⁹⁰ Li_xPO_yF_z (~687 eV),⁹⁰ and Li_xPF_y (~689 eV).⁹¹ At the negative potential of −0.5 V_{Li}, more reduced moieties of C, P, O, and F were observed in the form of Li₂C₂, Li₃P, Li₂O, and LiF. Depth-dependent XPS measurements for 1.0 M LiPF₆ EMC at 0.1 V_{Li} (Figure S53A) show an organic-rich outer SEI layer (~7 nm), homogenous LiF distribution up to 37 nm, and a Li₂O- and Li_xPF_y-dominant inner SEI from, respectively, 22 and 15 nm of etching onwards. The SEI layer thickness can be approximated by tracking the Li1s signal intensity during etching of the 0.1 V_{Li} sample. In EMC, the SEI is >37 nm thick (Figure S53B), where it is primarily composed of inorganic P, F, and O components (Figure S53A). Upon the addition of EC to 1.0 M LiPF₆ EMC to create the LP57 electrolyte, high-resolution XPS spectra at 0.1 V_{Li} (Figure S52B) showed similar features in the P2p and F1s regions to 1.0 M LiPF₆ EMC. In the C1s spectra, a CO₃ peak at ~290 eV⁹² replaced the carbonyl peak at 289 eV, confirming the presence of Li₂CO₃ SEI species in LP57 observed in Figure 4. In contrast with 1.0 M LiPF₆ EMC, the XPS spectra for LP57 at −0.50 V_{Li} did not show the presence of Li₂O, Li₃P, and Li₂C₂. The lack of a stable SEI in the case of EMC leads to continuous reduction of the electrolyte, whereas LP57 is able to generate a relatively more stable SEI to prevent further reduction of the electrolyte. Depth-dependent XPS spectra in Figure S53D revealed a thinner SEI of approximately 15–22 nm thick, as indicated by the disappearance of the Li1s signal after 22.2 nm of etching. The outer layer of this SEI was dominated by LiF, while the inner layer contained a higher concentration of Li₂O. Organic SEI, as measured by C concentration, showed a relatively stronger presence than P, F, and inorganic O species throughout the entire SEI.

In situ liquid cell NMR was conducted in Li||Li cell/testing configurations (Figure S54) to further probe soluble anion decomposition products. When cycled in 1.2 M LiPF₆ in EC, we observed PO₂F₂[−] at −85.2 ppm (*d*, *J*_{P–F} = 933 Hz) in ¹⁹F-NMR starting at OCV (Figure S55B), which can be attributed to hydrolysis of PF₅

(D) ⁷Li-SSNMR spectra for the SEI formed using 1.0 M LiPF₆ in EMC. A signal at ~246 ppm corresponds to smooth Li metal deposits, while those between 260 and 270 ppm correspond to inhomogeneous Li deposits.⁸⁵

(E) Deconvolution of signals observed around 0 ppm (highlighted with light blue in C), attributed to different SEI phases in 1.2 M LiPF₆ in EC. Fitting details are shown in Figure S50.

(F) Deconvolution of signals observed around 0 ppm (highlighted with light blue in D), attributed to different SEI phases in 1.0 M LiPF₆ in EMC. Fitting details are shown in Figure S50.

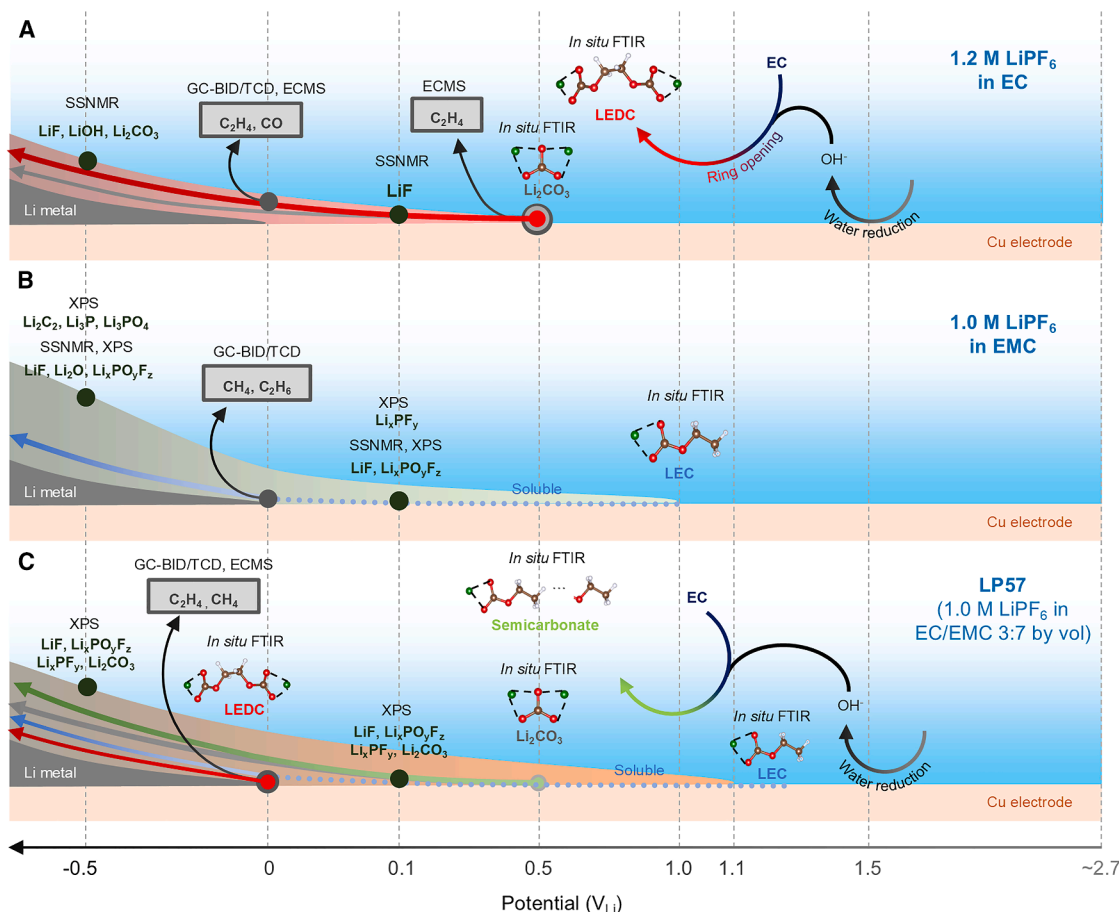


Figure 6. Proposed pathways of potential-dependent carbonate electrolyte reduction onto a Li metal anode

(A) 1.2 M LiPF₆ in EC electrolyte leads to formation of organic LEDC and Li₂CO₃ SEI species as detected by *in situ* FTIR spectroscopy, and inorganic LiF, LiOH, and Li₂CO₃ species as detected by SSNMR. CO and C₂H₄ are the primary gases detected by GC-BID/TCD and ECMS.

(B) 1.0 M LiPF₆ in EMC electrolyte generates soluble organic LEC species that are only observable through *in situ* FTIR spectroscopy at potentials below 0 V_{Li}. Inorganic LiF and Li₂O species are observed through SSNMR, and inorganic Li₂C₂, Li₃P, Li₃PO₄, Li_xPO_yF_z, and Li_xPF_y species are observed through XPS. CH₄ and C₂H₆ are the primary gases observed through GC-BID/TCD.

(C) LP57 electrolyte forms organic LEC, Li₂CO₃, LEDC, and alternative semi-carbonate species as observed by *in situ* FTIR spectroscopy. Inorganic LiF, Li_xPO_yF_z, and Li_xPF_y are observed through XPS. C₂H₄ and CH₄ are the primary gases observed through GC-BID/TCD and ECMS.

(2H₂O + PF₅ → HPO₂F₂ + 3HF)⁹³ or POF₃ (H₂O + POF₃ → HPO₂F₂ + HF).⁹³ Upon LSV to −0.8 V_{Li}, no other peak was observed. On the other hand, ¹⁹F-NMR of *in situ* measurements with 1.0 M LiPF₆ in EMC revealed two doublets at −84.8 (d, J_{P-F} = 929 Hz) and −89.9 (d, J_{P-F} = 1,066 Hz) ppm assigned to PO₂F₂[−] and POF₃ (Figure S55A, right) at OCV, and the POF₃ peak increased with linear voltammetry and reached the maximum at −0.3 V_{Li}, indicating more instability of PF₆[−] in EMC compared to EC. Upon further reduction to −0.5 V_{Li}, the POF₃ signal disappeared, and the PO₂F₂[−] decreased in intensity. At this point, two doublets at −83.9 and −80.8 ppm appeared, with the same J coupling (d, J_{P-F} = 900 Hz), indicating that these new species have a similar coordination environment. Unfortunately, we could not assign the signals at −83.9 (d, J_{P-F} = 900 Hz) and −80.8 (d, J_{P-F} = 900 Hz) ppm, as these particular coupling constants have not been identified in the literature, and the transient nature of these compounds did not allow us

to capture their ³¹P-NMR spectra within the time resolution of the *in situ* experiment (15 min) with sufficient signal-to-noise resolution. The species with the closest J coupling that could arise from the decomposition of LiPF₆ were PO₃F^{2−} (δ_{19F} = −77.0 ppm; d, J_{P-F} = 916 Hz) and PO₂(CH₂CH₃)F[−] (δ_{19F} = −80.7 ppm, d, J_{P-F} = 924 Hz).⁹⁴ These signals were no longer visible after the cell rested for only 10 min, which indicates that these species are metastable, preventing detection with postmortem NMR measurements.

DISCUSSION

In this paper, we have clarified CE trends for 1.0 M LiPF₆ EMC, LP57, and 1.2 M LiPF₆ EC electrolytes by directly connecting cycling performance in coin cells to SEI characterization at the Li metal anode/liquid electrolyte interface (Figure 6). Contrary to conventional wisdom that high CE electrolytes favor an

inorganic SEI, our results show that the best-performing 1.2 M LiPF₆ EC electrolyte with a CE of ~90% produces an SEI dominated by LEDC with a minor contribution from Li₂CO₃, as measured by *in situ* FTIR spectroscopy in Figure 2, whereas the lowest-performing electrolyte 1.0 M LiPF₆ EMC with a CE of <15% exhibits a soluble organic phase (Figure 3) coupled with a thick inorganic SEI (>37 nm) with increasing contributions from LiF and Li₂O based on SSNMR and XPS measurements (Figures 5, S52, and S53). SEM characterization revealed large whisker aggregates and compact Li deposition morphology in EC-derived SEIs, whereas thin whiskers and porous Li deposition morphology were revealed in EMC-derived SEIs. Therefore, inorganic phases do not universally lead to high CE and may in fact be detrimental to CE when present in excess.

The role of organic SEI is further supported by the emergence of distinct semi-carbonate species in the LP57 electrolyte detected by *in situ* FTIR spectroscopy (Figure 4), which we primarily attribute to elevated water content in the electrolyte. Trace water on the order of ~40 ppm may catalyze secondary chemical transformations of LEDC into semi-carbonate species and lithium carbonate. Water-mediated decomposition of the SEI reduces the fraction of mechanically compliant organic SEI components, such as LEDC, and leads to spatial heterogeneity within the SEI. Our preliminary *in situ* FTIR spectroscopy, SSNMR, and XPS findings highlight the sensitivity of organic-rich SEI to electrolyte impurity (e.g., trace water) and further motivate a deeper focus on organic SEIs as a design consideration in the development of high-CE electrolytes.

From a mechanistic point of view, organic SEIs, such as LEDC, provide many beneficial SEI properties compared to their inorganic counterparts. Prior studies have shown that LEDC and similar polymeric carbonate species exhibit elastic moduli on the order of ~1–20 GPa,⁹⁵ substantially lower than those of inorganic SEI components such as LiF and Li₂O (~60–170 GPa),⁹⁵ therefore providing mechanical compliance to accommodate large Li plating/stripping-induced volume changes without fracture. In addition, organic carbonate SEI phases support Li⁺ conductivities in the ~10⁻⁷–10⁻⁹ S cm⁻¹ range,^{96–98} compared to ~10⁻⁹–10⁻¹⁰ S cm⁻¹ for LiF^{99,100} and ~10⁻⁸–10⁻⁹ S cm⁻¹ for Li₂O,¹⁰⁰ reducing interfacial transport limitations during cycling. Finally, numerous studies^{40,101,102} have shown that inorganic SEI phases such as LiF and Li₂O are often spatially heterogeneous and discontinuous, whereas organic SEI components form continuous, conformal interphases. Spatial uniformity leads to homogenous interfacial kinetics and Li⁺ flux across the electrode, thereby promoting smooth, dense Li deposition and suppressing localized current hotspots associated with whisker or dendrite formation.

Taken together, these findings motivate a shift in electrolyte design strategies toward organic-rich SEI under well-controlled drying conditions. Future efforts should prioritize solvents, co-solvents, or additives that form LEDC-like organic interphases, guided by target properties such as elastic modulus, Li⁺ conductivity, and spatial homogeneity.

Limitations of the study

Several methodological and conceptual limitations should be acknowledged when considering the results from this paper. *In*

situ FTIR spectroscopy experiments were performed while plating Li onto roughened electrode surfaces (i.e., Cu mesh), which may influence interfacial reaction pathways and SEI chemistry compared to smoother or more idealized substrates. In addition, the LP57 electrolyte used in this work contained a higher water content (~38 ppm) than typically reported (<20 ppm), which likely contributes to the formation of semi-carbonate species. Future studies that systematically control electrolyte water content are required to isolate intrinsic solvent effects from trace-water-driven reactions. Complementary ECMS measurements similarly may have been susceptible to water contamination during transport from the glovebox to the instrument.

Interpretation of SSNMR data is further constrained by its lack of spatial resolution and by the potential impact of *ex situ* sample preparation and handling on SEI composition. More broadly, direct evidence linking organic SEI chemistry to spatial uniformity and interfacial morphology remains limited in this study. Further spatially resolved techniques—such as atomic force microscopy (AFM) combined with Raman and FTIR spectroscopy or TEM—will be required to survey the distribution of organic SEI phases. Finally, the generalizability of the trends reported here across other solvent and salt chemistries remains uncertain, and observations made under specific current densities, overpotentials, and short experimental timescales may not directly translate to practical battery operation, where extended cycling and aging processes can substantially alter SEI composition and structure.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Yang Shao-Horn (shaohorn@mit.edu).

Materials availability

This study did not generate new unique materials.

Data and code availability

This study did not generate any datasets.

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AUTHOR CONTRIBUTIONS

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DECLARATION OF INTERESTS

The authors declare no competing interests.

DECLARATION OF GENERATIVE AI AND AI-ASSISTED TECHNOLOGIES IN THE WRITING PROCESS

During the preparation of this work, the authors used OpenAI's ChatGPT AI tool to ensure grammatical correctness for the summary and discussion paragraphs. After using this tool/service, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

- KEY RESOURCES TABLE
- METHOD DETAILS
 - Materials and electrolyte preparation
 - ATR and *in situ* FTIR measurements
 - Automated feature identification and analysis
 - CE measurements
 - Quantitative GC-BID/TCD measurements
 - NMR measurements
 - XPS measurements
 - SEM measurements
 - ECMS measurements
 - Ab initio molecular orbital calculations

SUPPLEMENTAL INFORMATION

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REFERENCES

1. Peled, E., and Menkin, S. (2017). Review – SEI: Past, Present and Future. *J. Electrochem. Soc.* 164, A1703–A1719. <https://doi.org/10.1149/2.1441707jes>.
2. Goodenough, J.B., and Kim, Y. (2010). Challenges for Rechargeable Li Batteries. *Chem. Mater.* 22, 587–603. <https://doi.org/10.1021/cm901452z>.
3. Tian, Y., Zeng, G., Rutt, A., Shi, T., Kim, H., Wang, J., Koettgen, J., Sun, Y., Ouyang, B., Chen, T., et al. (2021). Promises and Challenges of Next-Generation “Beyond Li-ion” Batteries for Electric Vehicles and Grid De-carbonization. *Chem. Rev.* 121, 1623–1669. <https://doi.org/10.1021/acs.chemrev.0c00767>.
4. Niu, C., Liu, D., Lochala, J.A., Anderson, C.S., Cao, X., Gross, M.E., Xu, W., Zhang, J.-G., Whittingham, M.S., Xiao, J., and Liu, J. (2021). Balancing interfacial reactions to achieve long cycle life in high-energy lithium metal batteries. *Nat. Energy* 6, 723–732. <https://doi.org/10.1038/s41560-021-00852-3>.
5. He, X., Bresser, D., Passerini, S., Baakes, F., Krewer, U., Lopez, J., Mallia, C.T., Shao-Horn, Y., Cekic-Laskovic, I., Wiemers-Meyer, S., et al. (2021). The passivity of lithium electrodes in liquid electrolytes for secondary batteries. *Nat. Rev. Mater.* 6, 1036–1052. <https://doi.org/10.1038/s41578-021-00345-5>.
6. Winter, M. (2009). The Solid Electrolyte Interphase – The Most Important and the Least Understood Solid Electrolyte in Rechargeable Li Batteries. *Zeitschrift für Physikalische Chemie* 223, 1395–1406. <https://doi.org/10.1524/zpch.2009.6086>.
7. Xu, W., Wang, J., Ding, F., Chen, X., Nasybulin, E., Zhang, Y., and Zhang, J.-G. (2014). Lithium metal anodes for rechargeable batteries. *Energy Environ. Sci.* 7, 513–537. <https://doi.org/10.1039/C3EE40795K>.
8. Cheng, X.-B., Zhang, R., Zhao, C.-Z., and Zhang, Q. (2017). Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* 117, 10403–10473. <https://doi.org/10.1021/acs.chemrev.7b00115>.
9. Xue, W., Huang, M., Li, Y., Zhu, Y.G., Gao, R., Xiao, X., Zhang, W., Li, S., Xu, G., Yu, Y., et al. (2021). Ultra-high-voltage Ni-rich layered cathodes in practical Li metal batteries enabled by a sulfonamide-based electrolyte. *Nat. Energy* 6, 495–505. <https://doi.org/10.1038/s41560-021-00792-y>.
10. Hobold, G.M., Lopez, J., Guo, R., Minafra, N., Banerjee, A., Shirley Meng, Y., Shao-Horn, Y., and Gallant, B.M. (2021). Moving beyond 99.9% Coulombic efficiency for lithium anodes in liquid electrolytes. *Nat. Energy* 6, 951–960. <https://doi.org/10.1038/s41560-021-00910-w>.
11. Ota, H., Shima, K., Ue, M., and Yamaki, J.i. (2004). Effect of vinylene carbonate as additive to electrolyte for lithium metal anode. *Electrochim. Acta* 49, 565–572. <https://doi.org/10.1016/j.electacta.2003.09.010>.
12. Ye, H., Yin, Y.-X., Zhang, S.-F., Shi, Y., Liu, L., Zeng, X.-X., Wen, R., Guo, Y.-G., and Wan, L.-J. (2017). Synergism of Al-containing solid electrolyte interphase layer and Al-based colloidal particles for stable lithium anode. *Nano Energy* 36, 411–417. <https://doi.org/10.1016/j.nanoen.2017.04.056>.
13. Suo, L., Xue, W., Gobet, M., Greenbaum, S.G., Wang, C., Chen, Y., Yang, W., Li, Y., and Li, J. (2018). Fluorine-donating electrolytes enable highly reversible 5-V-class Li metal batteries. *Proc. Natl. Acad. Sci. USA* 115, 1156–1161. <https://doi.org/10.1073/pnas.1712895115>.
14. Horstmann, B., Shi, J., Amine, R., Werres, M., He, X., Jia, H., Hausen, F., Cekic-Laskovic, I., Wiemers-Meyer, S., Lopez, J., et al. (2021). Strategies towards enabling lithium metal in batteries: interphases and electrodes. *Energy Environ. Sci.* 14, 5289–5314. <https://doi.org/10.1039/D1EE00767J>.
15. Zhang, J.-G., Xu, W., Xiao, J., Cao, X., and Liu, J. (2020). Lithium Metal Anodes with Nonaqueous Electrolytes. *Chem. Rev.* 120, 13312–13348. <https://doi.org/10.1021/acs.chemrev.0c00275>.
16. Wang, H., Yu, Z., Kong, X., Kim, S.C., Boyle, D.T., Qin, J., Bao, Z., and Cui, Y. (2022). Liquid electrolyte: The nexus of practical lithium metal batteries. *Joule* 6, 588–616. <https://doi.org/10.1016/j.joule.2021.12.018>.
17. Nazri, G., and Muller, R.H. (1985). Composition of Surface Layers on Li Electrodes in PC, LiClO₄ of Very Low Water Content. *J. Electrochem. Soc.* 132, 2050–2054. <https://doi.org/10.1149/1.2114288>.
18. Aurbach, D., Daroux, M.L., Faguy, P.W., and Yeager, E. (1987). Identification of Surface Films Formed on Lithium in Propylene Carbonate Solutions. *J. Electrochem. Soc.* 134, 1611–1620. <https://doi.org/10.1149/1.2100722>.
19. Aurbach, D., Gofer, Y., Ben-Zion, M., and Aped, P. (1992). The behaviour of lithium electrodes in propylene and ethylene carbonate: The major

- factors that influence Li cycling efficiency. *J. Electroanal. Chem.* **339**, 451–471. [https://doi.org/10.1016/0022-0728\(92\)80467-I](https://doi.org/10.1016/0022-0728(92)80467-I).
20. Michan, A.L., Leskes, M., and Grey, C.P. (2016). Voltage Dependent Solid Electrolyte Interphase Formation in Silicon Electrodes: Monitoring the Formation of Organic Decomposition Products. *Chem. Mater.* **28**, 385–398. <https://doi.org/10.1021/acs.chemmater.5b04408>.
 21. Zhuang, G.V., Xu, K., Yang, H., Jow, T.R., and Ross, P.N. (2005). Lithium Ethylene Dicarboxylate Identified as the Primary Product of Chemical and Electrochemical Reduction of EC in 1.2 M LiPF₆/EC:EMC Electrolyte. *J. Phys. Chem. B* **109**, 17567–17573. <https://doi.org/10.1021/jp052474w>.
 22. Wang, L., Menakath, A., Han, F., Wang, Y., Zavalij, P.Y., Gaskell, K.J., Borodin, O., Iuga, D., Brown, S.P., Wang, C., et al. (2019). Identifying the components of the solid–electrolyte interphase in Li-ion batteries. *Nat. Chem.* **11**, 789–796. <https://doi.org/10.1038/s41557-019-0304-z>.
 23. Kanamura, K., Tamura, H., and Takehara, Z. (1992). XPS analysis of a lithium surface immersed in propylene carbonate solution containing various salts. *J. Electroanal. Chem.* **333**, 127–142. [https://doi.org/10.1016/0022-0728\(92\)80386-I](https://doi.org/10.1016/0022-0728(92)80386-I).
 24. Kanamura, K., Tamura, H., Shiraishi, S., and Takehara, Z. (1995). XPS Analysis of Lithium Surfaces Following Immersion in Various Solvents Containing LiBF₄. *J. Electrochem. Soc.* **142**, 340–347. <https://doi.org/10.1149/1.2044000>.
 25. Peled, E., Golodnitsky, D., and Ardel, G. (1997). Advanced Model for Solid Electrolyte Interphase Electrodes in Liquid and Polymer Electrolytes. *J. Electrochem. Soc.* **144**, L208–L210. <https://doi.org/10.1149/1.1837858>.
 26. Aurbach, D., Markovsky, B., Shechter, A., Ein-Eli, Y., and Cohen, H. (1996). A Comparative Study of Synthetic Graphite and Li Electrodes in Electrolyte Solutions Based on Ethylene Carbonate-Dimethyl Carbonate Mixtures. *J. Electrochem. Soc.* **143**, 3809–3820. <https://doi.org/10.1149/1.1837300>.
 27. Zachman, M.J., Tu, Z., Choudhury, S., Archer, L.A., and Kourkoutsis, L.F. (2018). Cryo-STEM mapping of solid–liquid interfaces and dendrites in lithium–metal batteries. *Nature* **560**, 345–349. <https://doi.org/10.1038/s41586-018-0397-3>.
 28. Li, Y., Li, Y., Pei, A., Yan, K., Sun, Y., Wu, C.-L., Joubert, L.-M., Chin, R., Koh, A.L., Yu, Y., et al. (2017). Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy. *Science* **358**, 506–510. <https://doi.org/10.1126/science.aam6014>.
 29. Von Holtum, B., Kubot, M., Peschel, C., Rodehorst, U., Winter, M., Nowak, S., and Wiemers-Meyer, S. (2023). Accessing the Primary Solid–Electrolyte Interphase on Lithium Metal: A Method for Low-Concentration Compound Analysis. *ChemSusChem* **16**, e202300451. <https://doi.org/10.1002/cssc.202300451>.
 30. Von Holtum, B., Peschel, C., Rodehorst, U., Wang, D., Shao-horn, Y., Winter, M., Nowak, S., and Wiemers-Meyer, S. (2025). Primary SEI Formation on Lithium Metal – Influence of Film-Forming Additives. *J. Electrochem. Soc.* **172**, 050511. <https://doi.org/10.1149/1945-7111/adce37>.
 31. Ohta, A., Koshina, H., Okuno, H., and Murai, H. (1995). Relationship between carbonaceous materials and electrolyte in secondary lithium-ion batteries. *J. Power Sources* **54**, 6–10. [https://doi.org/10.1016/0378-7753\(94\)02031-W](https://doi.org/10.1016/0378-7753(94)02031-W).
 32. Hobold, G.M., Khurram, A., and Gallant, B.M. (2020). *Operando* Gas Monitoring of Solid Electrolyte Interphase Reactions on Lithium. *Chem. Mater.* **32**, 2341–2352. <https://doi.org/10.1021/acs.chemmater.9b04550>.
 33. Shin, J.-S., Han, C.-H., Jung, U.-H., Lee, S.-I., Kim, H.-J., and Kim, K. (2002). Effect of Li₂CO₃ additive on gas generation in lithium-ion batteries. *J. Power Sources* **109**, 47–52. [https://doi.org/10.1016/S0378-7753\(02\)00039-3](https://doi.org/10.1016/S0378-7753(02)00039-3).
 34. Winter, M., Imhof, R., Joho, F., and Novák, P. (1999). FTIR and DEMS investigations on the electroreduction of chloroethylene carbonate-based electrolyte solutions for lithium-ion cells. *J. Power Sources* **81**, 818–823. [https://doi.org/10.1016/S0378-7753\(99\)00116-0](https://doi.org/10.1016/S0378-7753(99)00116-0).
 35. Imhof, R., and Novák, P. (1998). In Situ Investigation of the Electrochemical Reduction of Carbonate Electrolyte Solutions at Graphite Electrodes. *J. Electrochem. Soc.* **145**, 1081–1087. <https://doi.org/10.1149/1.1838420>.
 36. La Mantia, F., and Novák, P. (2008). Online Detection of Reductive CO[₂] Development at Graphite Electrodes in the 1 M LiPF₆[sub 6], EC:DMC Battery Electrolyte. *Electrochem. Solid State Lett.* **11**, A84. <https://doi.org/10.1149/1.2890756>.
 37. Thornton, D.B., Davies, B.J.V., Scott, S.B., Aguadero, A., Ryan, M.P., and Stephens, I.E.L. (2024). Probing Degradation in Lithium Ion Batteries with On-Chip Electrochemistry Mass Spectrometry. *Angew. Chem.* **63**, e202315357. <https://doi.org/10.1002/ange.202315357>.
 38. Strehle, B., Solchenbach, S., Metzger, M., Schwenke, K.U., and Gas-teiger, H.A. (2017). The Effect of CO₂ on Alkyl Carbonate Trans-Esterification during Formation of Graphite Electrodes in Li-Ion Batteries. *J. Electrochem. Soc.* **164**, A2513–A2526. <https://doi.org/10.1149/2.1001712jes>.
 39. Fang, C., Li, J., Zhang, M., Zhang, Y., Yang, F., Lee, J.Z., Lee, M.-H., Al-varado, J., Schroeder, M.A., Yang, Y., et al. (2019). Quantifying inactive lithium in lithium metal batteries. *Nature* **572**, 511–515. <https://doi.org/10.1038/s41586-019-1481-z>.
 40. Hobold, G.M., Wang, C., Steinberg, K., Li, Y., and Gallant, B.M. (2024). High lithium oxide prevalence in the lithium solid–electrolyte interphase for high Coulombic efficiency. *Nat. Energy* **9**, 580–591. <https://doi.org/10.1038/s41560-024-01494-x>.
 41. Steinberg, K., and Gallant, B.M. (2024). Revealing the Role of Lithium Carbonate at Lithium Metal Anodes Through Study of Gas-Reacted Interphases. *J. Electrochem. Soc.* **171**, 080530. <https://doi.org/10.1149/1945-7111/ad6d92>.
 42. Tan, J., Matz, J., Dong, P., Shen, J., and Ye, M. (2021). A Growing Appreciation for the Role of LiF in the Solid Electrolyte Interphase. *Adv. Energy Mater.* **11**, 2100046. <https://doi.org/10.1002/aenm.202100046>.
 43. Wang, C., Meng, Y.S., and Xu, K. (2019). Perspective—Fluorinating Inter-phases. *J. Electrochem. Soc.* **166**, A5184–A5186. <https://doi.org/10.1149/2.0281903jes>.
 44. Hobold, G.M., and Gallant, B.M. (2022). Quantifying Capacity Loss Mechanisms of Li Metal Anodes beyond Inactive Li⁰. *ACS Energy Lett.* **7**, 3458–3466. <https://doi.org/10.1021/acsenenergylett.2c01845>.
 45. Dedryvère, R., Laruelle, S., Grugeon, S., Gireaud, L., Tarascon, J.-M., and Gonbeau, D. (2005). XPS Identification of the Organic and Inorganic Components of the Electrode/Electrolyte Interface Formed on a Metallic Cathode. *J. Electrochem. Soc.* **152**, A689. <https://doi.org/10.1149/1.1861994>.
 46. Gu, Y., You, E.-M., Lin, J.-D., Wang, J.-H., Luo, S.-H., Zhou, R.-Y., Zhang, C.-J., Yao, J.-L., Li, H.-Y., Li, G., et al. (2023). Resolving nano-structure and chemistry of solid-electrolyte interphase on lithium anodes by depth-sensitive plasmon-enhanced Raman spectroscopy. *Nat. Commun.* **14**, 3536. <https://doi.org/10.1038/s41467-023-39192-z>.
 47. Goren, E., Chusid (Youngman), O., and Aurbach, D. (1991). The Application of In Situ FTIR Spectroscopy to the Study of Surface Films Formed on Lithium and Noble Metals at Low Potentials in Li Battery Electrolytes. *J. Electrochem. Soc.* **138**, L6–L9. <https://doi.org/10.1149/1.2085828>.
 48. Shi, F., Ross, P.N., Zhao, H., Liu, G., Somorjai, G.A., and Komvopoulos, K. (2015). A Catalytic Path for Electrolyte Reduction in Lithium-Ion Cells Revealed by *in Situ* Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy. *J. Am. Chem. Soc.* **137**, 3181–3184. <https://doi.org/10.1021/ja5128456>.
 49. Shi, F., Ross, P.N., Somorjai, G.A., and Komvopoulos, K. (2017). The Chemistry of Electrolyte Reduction on Silicon Electrodes Revealed by

- in situ* ATR-FTIR Spectroscopy. J. Phys. Chem. C 121, 14476–14483. <https://doi.org/10.1021/acs.jpcc.7b04132>.
50. Leau, C., Wang, Y., Gervillé-Mouraviev, C., Boles, S.T., Zhang, X.-H., Coudray, S., Boussard-Plédel, C., and Tarascon, J.-M. (2025). Tracking solid electrolyte interphase dynamics using operando fibre-optic infrared spectroscopy and multivariate curve regression. Nat. Commun. 16, 757. <https://doi.org/10.1038/s41467-024-55339-y>.
 51. Zhang, Y., Katayama, Y., Tatara, R., Giordano, L., Yu, Y., Fraggadakis, D., Sun, J.G., Maglia, F., Jung, R., Bazant, M.Z., and Shao-Horn, Y. (2020). Revealing electrolyte oxidation via carbonate dehydrogenation on Ni-based oxides in Li-ion batteries by *in situ* Fourier transform infrared spectroscopy. Energy Environ. Sci. 13, 183–199. <https://doi.org/10.1039/C9EE02543J>.
 52. Aurbach, D., Ein-Eli, Y., Chusid (Youngman), O., Carmeli, Y., Babai, M., and Yamin, H. (1994). The Correlation Between the Surface Chemistry and the Performance of Li-Carbon Intercalation Anodes for Rechargeable ‘Rocking-Chair’ Type Batteries. J. Electrochem. Soc. 141, 603–611. <https://doi.org/10.1149/1.2054777>.
 53. Mogi, R., Inaba, M., Iriyama, Y., Abe, T., and Ogumi, Z. (2003). Study on the decomposition mechanism of alkyl carbonate on lithium metal by pyrolysis-gas chromatography-mass spectroscopy. J. Power Sources 119, 597–603. [https://doi.org/10.1016/S0378-7753\(03\)00302-1](https://doi.org/10.1016/S0378-7753(03)00302-1).
 54. Shkrob, I.A., Zhu, Y., Marin, T.W., and Abraham, D. (2013). Reduction of Carbonate Electrolytes and the Formation of Solid-Electrolyte Interface (SEI) in Lithium-Ion Batteries. 1. Spectroscopic Observations of Radical Intermediates Generated in One-Electron Reduction of Carbonates. J. Phys. Chem. C 117, 19255–19269. <https://doi.org/10.1021/jp406274e>.
 55. Soto, F.A., Ma, Y., Martínez De La Hoz, J.M., Seminario, J.M., and Balbuena, P.B. (2015). Formation and Growth Mechanisms of Solid-Electrolyte Interphase Layers in Rechargeable Batteries. Chem. Mater. 27, 7990–8000. <https://doi.org/10.1021/acs.chemmater.5b03358>.
 56. Seo, D.M., Chalasani, D., Parimalam, B.S., Kadam, R., Nie, M., and Lucht, B.L. (2014). Reduction Reactions of Carbonate Solvents for Lithium Ion Batteries. ECS Electrochem. Lett. 3, A91–A93. <https://doi.org/10.1149/2.0021409eel>.
 57. Metzger, M., Strehle, B., Solchenbach, S., and Gasteiger, H.A. (2016). Hydrolysis of Ethylene Carbonate with Water and Hydroxide under Battery Operating Conditions. J. Electrochem. Soc. 163, A1219–A1225. <https://doi.org/10.1149/2.0411607jes>.
 58. Xu, K., Zhuang, G.V., Allen, J.L., Lee, U., Zhang, S.S., Ross, P.N., and Jow, T.R. (2006). Syntheses and Characterization of Lithium Alkyl Mono- and Dicarbonates as Components of Surface Films in Li-Ion Batteries. J. Phys. Chem. B 110, 7708–7719. <https://doi.org/10.1021/jp0601522>.
 59. Matsuta, S., Asada, T., and Kitaura, K. (2000). Vibrational Assignments of Lithium Alkyl Carbonate and Lithium Alkoxide in the Infrared Spectra An Ab Initio MO Study. J. Electrochem. Soc. 147, 1695. <https://doi.org/10.1149/1.1393420>.
 60. Gireaud, L., Grugeon, S., Laruelle, S., Pilard, S., and Tarascon, J.-M. (2005). Identification of Li Battery Electrolyte Degradation Products Through Direct Synthesis and Characterization of Alkyl Carbonate Salts. J. Electrochem. Soc. 152, A850. <https://doi.org/10.1149/1.1872673>.
 61. Wang, Y., Nakamura, S., Ue, M., and Balbuena, P.B. (2001). Theoretical Studies To Understand Surface Chemistry on Carbon Anodes for Lithium-Ion Batteries: Reduction Mechanisms of Ethylene Carbonate. J. Am. Chem. Soc. 123, 11708–11718. <https://doi.org/10.1021/ja0164529>.
 62. Naji, A., Ghanbaja, J., Willmann, P., Humbert, B., and Billaud, D. (1996). First characterization of the surface compounds formed during the reduction of a carbonaceous electrode in LiClO₄-ethylene carbonate electrolyte. J. Power Sources 62, 141–143. [https://doi.org/10.1016/S0378-7753\(96\)02401-9](https://doi.org/10.1016/S0378-7753(96)02401-9).
 63. Lundström, R., Gogoi, N., Melin, T., and Berg, E.J. (2024). Unveiling Reaction Pathways of Ethylene Carbonate and Vinylene Carbonate in Li-Ion Batteries. J. Phys. Chem. C 128, 8147–8153. <https://doi.org/10.1021/acs.jpcc.4c00927>.
 64. Spotte-Smith, E.W.C., Kam, R.L., Barter, D., Xie, X., Hou, T., Dwarkath, S., Blau, S.M., and Persson, K.A. (2022). Toward a Mechanistic Model of Solid-Electrolyte Interphase Formation and Evolution in Lithium-Ion Batteries. ACS Energy Lett. 7, 1446–1453. <https://doi.org/10.1021/acsenergylett.2c00517>.
 65. Heiskanen, S.K., Kim, J., and Lucht, B.L. (2019). Generation and Evolution of the Solid Electrolyte Interphase of Lithium-Ion Batteries. Joule 3, 2322–2333. <https://doi.org/10.1016/j.joule.2019.08.018>.
 66. Martins, M., Haering, D., Connell, J.G., Wan, H., Svane, K.L., Genorio, B., Farinazzo Bergamo Dias Martins, P., Lopes, P.P., Gould, B., Maglia, F., et al. (2023). Role of Catalytic Conversions of Ethylene Carbonate, Water, and HF in Forming the Solid-Electrolyte Interphase of Li-Ion Batteries. ACS Catal. 13, 9289–9301. <https://doi.org/10.1021/acscatal.3c01531>.
 67. Herzog, A., Iriawan, H., and Shao-Horn, Y. (2025). Unveiling Solid Electrolyte Interphase Dynamics in Electrochemical Lithium-Mediated Ammonia Synthesis via Operando Raman Spectroscopy. Preprint at ChemRxiv. <https://doi.org/10.26434/chemrxiv-2025-m2jf3>.
 68. Lundström, R., Gogoi, N., Hou, X., and Berg, E.J. (2023). Competing Ethylene Carbonate Reactions on Carbon Electrode in Li-Ion Batteries. J. Electrochem. Soc. 170, 040516. <https://doi.org/10.1149/1945-7111/acceb6>.
 69. Deng, R., Chu, F., Kwofie, F., Guan, Z., Chen, J., and Wu, F. (2022). A Low-Concentration Electrolyte for High-Voltage Lithium-Metal Batteries: Fluorinated Solvation Shell and Low Salt Concentration Effect. Angew. Chem. Int. Ed. 61, e202215866. <https://doi.org/10.1002/anie.202215866>.
 70. Schwenke, K.U., Solchenbach, S., Demeaux, J., Lucht, B.L., and Gasteiger, H.A. (2019). The Impact of CO₂ Evolved from VC and FEC during Formation of Graphite Anodes in Lithium-Ion Batteries. J. Electrochem. Soc. 166, A2035–A2047. <https://doi.org/10.1149/2.0821910jes>.
 71. Zhang, Z.-M., Chen, S., and Liang, Y.-Z. (2010). Baseline correction using adaptive iteratively reweighted penalized least squares. Analyst 135, 1138–1146. <https://doi.org/10.1039/b222045c>.
 72. Sarkar, S., Tseng, C., Maitra, A., Voegtli, M.J., and Dawlaty, J.M. (2021). Advances in Vibrational Stark Shift Spectroscopy for Measuring Interfacial Electric Fields. In ACS Symposium Series, M.R. Berman, L. Young, and H.-L. Dai, eds. (American Chemical Society), pp. 199–224. <https://doi.org/10.1021/bk-2021-1398.ch010>.
 73. Golj, D.R., Dinka, M.O., Sherefedin, U., Belay, A., Gelanu, D., and Megersa, G.D. (2025). Solvent polarity effects on the FTIR spectrum, and thermodynamic and electronic properties of metronidazole and its binding with antibacterial drugs: a DFT and molecular docking study. RSC Adv. 15, 28538–28554. <https://doi.org/10.1039/D5RA02359A>.
 74. Yoshida, H., Fukunaga, T., Hazama, T., Terasaki, M., Mizutani, M., and Yamachi, M. (1997). Degradation mechanism of alkyl carbonate solvents used in lithium-ion cells during initial charging. J. Power Sources 68, 311–315. [https://doi.org/10.1016/S0378-7753\(97\)02635-9](https://doi.org/10.1016/S0378-7753(97)02635-9).
 75. Yi, Z., Zhou, Y., Liu, H., Li, L., Zhao, Y., Li, J., Mao, Y., Su, F., and Chen, C.-M. (2025). Predicting practical reduction potential of electrolyte solvents via computational hydrogen electrode and interpretable machine-learning models. npj Comput. Mater. 11, 135. <https://doi.org/10.1038/s41524-025-01582-w>.
 76. Tasaki, K., Goldberg, A., Lian, J.-J., Walker, M., Timmons, A., and Harris, S.J. (2009). Solubility of Lithium Salts Formed on the Lithium-Ion Battery Negative Electrode Surface in Organic Solvents. J. Electrochem. Soc. 156, A1019. <https://doi.org/10.1149/1.3239850>.
 77. Ein-Eli, Y. (1999). A New Perspective on the Formation and Structure of the Solid Electrolyte Interface at the Graphite Anode of Li-Ion Cells. Electrochem. Solid State Lett. 2, 212. <https://doi.org/10.1149/1.1390787>.
 78. Aurbach, D., Levi, M.D., Levi, E., and Schechter, A. (1997). Failure and Stabilization Mechanisms of Graphite Electrodes. J. Phys. Chem. B 101, 2195–2206. <https://doi.org/10.1021/jp962815t>.

79. Bai, P., Li, J., Brushett, F.R., and Bazant, M.Z. (2016). Transition of lithium growth mechanisms in liquid electrolytes. *Energy Environ. Sci.* **9**, 3221–3229. <https://doi.org/10.1039/C6EE01674J>.
80. Xu, K. (2004). Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **104**, 4303–4417. <https://doi.org/10.1021/cr030203g>.
81. Svirinovsky-Arbeli, A., Juelsholt, M., May, R., Kwon, Y., and Marbella, L.E. (2024). Using NMR spectroscopy to link structure to function at the Li solid electrolyte interphase. *Joule* **8**, 1919–1935. <https://doi.org/10.1016/j.joule.2024.04.016>.
82. Liu, X., Li, S., Yuan, C., Zheng, B., Cheng, G., Chen, Y., Lu, X., Gu, D., Lv, B., Li, H., et al. (2025). Probing the heterogeneous nature of LiF in solid-electrolyte interphases. *Nature* **646**, 102–107. <https://doi.org/10.1038/s41586-025-09498-7>.
83. Lebens-Higgins, Z.W., Halat, D.M., Faenza, N.V., Wahila, M.J., Mascheck, M., Wiell, T., Eriksson, S.K., Palmgren, P., Rodriguez, J., Badway, F., et al. (2019). Surface Chemistry Dependence on Aluminum Doping in Ni-rich LiNi_{0.8}Co_{0.2}-yAl₂O₃ Cathodes. *Sci. Rep.* **9**, 17720. <https://doi.org/10.1038/s41598-019-53932-6>.
84. Clément, R.J., Kitchaev, D., Lee, J., and Ceder, G. (2018). Short-Range Order and Unusual Modes of Nickel Redox in a Fluorine-Substituted Disordered Rocksalt Oxide Lithium-Ion Cathode. *Chem. Mater.* **30**, 6945–6956. <https://doi.org/10.1021/acs.chemmater.8b03794>.
85. Chang, H.J., Trease, N.M., Iltott, A.J., Zeng, D., Du, L.-S., Jerschow, A., and Grey, C.P. (2015). Investigating Li Microstructure Formation on Li Anodes for Lithium Batteries by *in Situ* ⁶Li/⁷Li NMR and SEM. *J. Phys. Chem. C* **119**, 16443–16451. <https://doi.org/10.1021/acs.jpcc.5b03396>.
86. Oyakhire, S.T., Gong, H., Cui, Y., Bao, Z., and Bent, S.F. (2022). An X-ray Photoelectron Spectroscopy Primer for Solid Electrolyte Interphase Characterization in Lithium Metal Anodes. *ACS Energy Lett.* **7**, 2540–2546. <https://doi.org/10.1021/acsenenergylett.2c01227>.
87. Matthew, J. (2004). Surface analysis by Auger and x-ray photoelectron spectroscopy. *Surf. Interface Anal.* **36**, 1647. <https://doi.org/10.1002/sia.2005>.
88. Ago, H., Kugler, T., Cacialli, F., Salaneck, W.R., Shaffer, M.S.P., Windle, A.H., and Friend, R.H. (1999). Work Functions and Surface Functional Groups of Multiwall Carbon Nanotubes. *J. Phys. Chem. B* **103**, 8116–8121. <https://doi.org/10.1021/jp991659y>.
89. Kozłowski, C., and Sherwood, P.M.A. (1985). X-ray photoelectron-spectroscopic studies of carbon-fibre surfaces. Part 5.—The effect of pH on surface oxidation. *J. Chem. Soc., Faraday Trans. 1* **81**, 2745. <https://doi.org/10.1039/f19858102745>.
90. Verdier, S., El Ouatani, L., Dedryvère, R., Bonhomme, F., Biensan, P., and Gonbeau, D. (2007). XPS Study on Al[sub 2]O[sub 3]- and AlPO[sub 4]-Coated LiCoO[sub 2] Cathode Material for High-Capacity Li Ion Batteries. *J. Electrochem. Soc.* **154**, A1088. <https://doi.org/10.1149/1.2789299>.
91. Lu, Y.-C., Mansour, A.N., Yabuuchi, N., and Shao-Horn, Y. (2009). Probing the Origin of Enhanced Stability of “AlPO₄” Nanoparticle Coated LiCoO₂ during Cycling to High Voltages: Combined XRD and XPS Studies. *Chem. Mater.* **21**, 4408–4424. <https://doi.org/10.1021/cm900862v>.
92. Appapillai, A.T., Mansour, A.N., Cho, J., and Shao-Horn, Y. (2007). Microstructure of LiCoO₂ with and without “AlPO₄” Nanoparticle Coating: Combined STEM and XPS Studies. *Chem. Mater.* **19**, 5748–5757. <https://doi.org/10.1021/cm0715390>.
93. Hestenes, J.C., Sadowski, J.T., May, R., and Marbella, L.E. (2023). Transition Metal Dissolution Mechanisms and Impacts on Electronic Conductivity in Composite LiNi_{0.5}Mn_{1.5}O₄ Cathode Films. *ACS Mater. Au* **3**, 88–101. <https://doi.org/10.1021/acsmaterialsau.2c00060>.
94. Guillot, S.L., Peña-Hueso, A., Usrey, M.L., and Hamers, R.J. (2017). Thermal and Hydrolytic Decomposition Mechanisms of Organosilicon Electrolytes with Enhanced Thermal Stability for Lithium-Ion Batteries. *J. Electrochem. Soc.* **164**, A1907–A1917. <https://doi.org/10.1149/2.0671709jes>.
95. Park, S., Kim, S., Lee, J.-A., Ue, M., and Choi, N.-S. (2023). Liquid electrolyte chemistries for solid electrolyte interphase construction on silicon and lithium-metal anodes. *Chem. Sci.* **14**, 9996–10024. <https://doi.org/10.1039/D3SC03514J>.
96. Li, Z., Chen, Y., Yun, X., Gao, P., Zheng, C., and Xiao, P. (2023). Critical Review of Fluorinated Electrolytes for High-Performance Lithium Metal Batteries. *Adv. Funct. Mater.* **33**, 2300502. <https://doi.org/10.1002/adfm.202300502>.
97. Wang, Y., and Hao, F. (2022). Interactions Between Solid Electrolyte Interphase and Lithium Dendrite. *J. Electrochem. Energy Convers. Storage* **19**, 040801. <https://doi.org/10.1115/1.4054339>.
98. Schafzahl, L., Ehmann, H., Kriechbaum, M., Sattelkow, J., Ganner, T., Plank, H., Wilkening, M., and Freunberger, S.A. (2018). Long-Chain Li and Na Alkyl Carbonates as Solid Electrolyte Interphase Components: Structure, Ion Transport, and Mechanical Properties. *Chem. Mater.* **30**, 3338–3345. <https://doi.org/10.1021/acs.chemmater.8b00750>.
99. He, M., Guo, R., Hobold, G.M., Gao, H., and Gallant, B.M. (2020). The intrinsic behavior of lithium fluoride in solid electrolyte interphases on lithium. *Proc. Natl. Acad. Sci. USA* **117**, 73–79. <https://doi.org/10.1073/pnas.1911017116>.
100. Guo, R., and Gallant, B.M. (2020). Li₂O Solid Electrolyte Interphase: Probing Transport Properties at the Chemical Potential of Lithium. *Chem. Mater.* **32**, 5525–5533. <https://doi.org/10.1021/acs.chemmater.0c00333>.
101. Han, B., Zou, Y., Xu, G., Hu, S., Kang, Y., Qian, Y., Wu, J., Ma, X., Yao, J., Li, T., et al. (2021). Additive stabilization of SEI on graphite observed using cryo-electron microscopy. *Energy Environ. Sci.* **14**, 4882–4889. <https://doi.org/10.1039/D1EE01678D>.
102. Chen, Z., Wang, B., Li, Y., Bai, F., Zhou, Y., Li, C., and Li, T. (2022). Stable Solvent-Derived Inorganic-Rich Solid Electrolyte Interphase (SEI) for High-Voltage Lithium-Metal Batteries. *ACS Appl. Mater. Interfaces* **14**, 28014–28020. <https://doi.org/10.1021/acsami.2c06934>.
103. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H., et al (2016). Gaussian 16, Revision C.01.
104. Fairley, N., Fernandez, V., Richard-Plouet, M., Guillot-Deudon, C., Walton, J., Smith, E., Flahaut, D., Greiner, M., Biesinger, M., Tougaard, S., et al. (2021). Systematic and collaborative approach to problem solving using X-ray photoelectron spectroscopy. *Appl. Surf. Sci. Adv.* **5**, 100112. <https://doi.org/10.1016/j.apsadv.2021.100112>.
105. Massiot, D., Fayon, F., Capron, M., King, I., Le Calvé, S., Alonso, B., Durand, J., Bujoli, B., Gan, Z., and Hoatson, G. (2002). Modelling one- and two-dimensional solid-state NMR spectra. *Magn. Reson. Chem.* **40**, 70–76. <https://doi.org/10.1002/mrc.984>.
106. Trimarco, D.B., Scott, S.B., Thilsted, A.H., Pan, J.Y., Pedersen, T., Hansen, O., Chorkendorff, I., and Vesborg, P.C.K. (2018). Enabling real-time detection of electrochemical desorption phenomena with sub-monolayer sensitivity. *Electrochim. Acta* **268**, 520–530. <https://doi.org/10.1016/j.electacta.2018.02.060>.
107. Osawa, M. (1997). Dynamic Processes in Electrochemical Reactions Studied by Surface-Enhanced Infrared Absorption Spectroscopy (SEIRAS). *Bull. Chem. Soc. Jpn.* **70**, 2861–2880. <https://doi.org/10.1246/bcsj.70.2861>.
108. Lieber, C.A., and Mahadevan-Jansen, A. (2003). Automated Method for Subtraction of Fluorescence from Biological Raman Spectra. *Appl. Spectrosc.* **57**, 1363–1367. <https://doi.org/10.1366/00037020322554518>.
109. Zhao, J., Lui, H., McLean, D.I., and Zeng, H. (2007). Automated Autofluorescence Background Subtraction Algorithm for Biomedical Raman Spectroscopy. *Appl. Spectrosc.* **61**, 1225–1232. <https://doi.org/10.1366/000370207782597003>.

110. Adams, B.D., Zheng, J., Ren, X., Xu, W., and Zhang, J. (2018). Accurate Determination of Coulombic Efficiency for Lithium Metal Anodes and Lithium Metal Batteries. *Adv. Energy Mater.* 8, 1702097. <https://doi.org/10.1002/aenm.201702097>.
111. Leißing, M., Winter, M., Wiemers-Meyer, S., and Nowak, S. (2020). A method for quantitative analysis of gases evolving during formation applied on LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ || natural graphite lithium ion battery cells using gas chromatography - barrier discharge ionization detector. *J. Chromatogr. A* 1622, 461122. <https://doi.org/10.1016/j.chroma.2020.461122>.
112. Hestenes, J.C., May, R., Sadowski, J.T., Munich, N., and Marbella, L.E. (2022). Resolving Chemical and Spatial Heterogeneities at Complex Electrochemical Interfaces in Li-Ion Batteries. *Chem. Mater.* 34, 232–243. <https://doi.org/10.1021/acs.chemmater.1c03185>.
113. Cossi, M., Rega, N., Scalmani, G., and Barone, V. (2003). Energies, structures, and electronic properties of molecules in solution with the C-PCM solvation model. *J. Comput. Chem.* 24, 669–681. <https://doi.org/10.1002/jcc.10189>.
114. Tomasi, J., Mennucci, B., and Cammi, R. (2005). Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* 105, 2999–3093. <https://doi.org/10.1021/cr9904009>.
115. Schaftenaar, G., and Noordik, J.H. (2000). Molden: a pre- and post-processing program for molecular and electronic structures. *J. Comput. Aided Mol. Des.* 14, 123–134. <https://doi.org/10.1023/A:1008193805436>.

STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Lithium hexafluorophosphate (LiPF ₆), battery grade, ≥99.99% trace metals basis	Sigma-Aldrich	CAS#21324-40-3
Ethylene carbonate (EC), battery grade, ≥99%, acid <10 ppm, H ₂ O < 10 ppm	Sigma-Aldrich	CAS#96-49-1
Ethylene carbonate- ¹³ C ₃ , 99 atom % ¹³ C, 97% CP	Sigma-Aldrich	CAS#1173023-62-5
Ethyl methyl carbonate (EMC)	Gotion	Lot#4017-87
LP57	Gotion	Lot#SSDE-MIT-72
Dimethyl carbonate, battery grade, ≥99.9%, acid <10 ppm, H ₂ O < 10 ppm	Sigma-Aldrich	CAS# 616-38-6
Diethyl carbonate, battery grade, ≥99%, acid <10 ppm, H ₂ O < 10 ppm	Sigma-Aldrich	CAS#105-58-8
Lithium Foil (0.75 mm thick x 19mm W x 3000 mm L) for Li-ion Battery R&D, 22g/bag -MF-Li25	MTI Corporation	SKU: MF-Li25
Whatman® circles, borosilicate glass grade GF/F filter discs 0.7 μm pore size	Sigma-Aldrich	UNSPSC Code: 40161507
Composite Copper Foil (Cu/PET/Cu) as Battery Current Collector (180/280mm W x 6.5 μm T x 50m L) - CuPET-65u	MTI Corporation	SKU: CuPET-65u180
Celgard® 3501 25μm Monolayer Microporous Membrane (PP) Surfactant Coated	Celgard	https://celgard.shop/products/celgard%C2%AE-3501
Molecular sieves, 3 Å	Sigma-Aldrich	CAS#308080-99-1
Lithium iron phosphate (LFP) electrode sheets	NEI Corporation	Lot#S19-494935
Deposited data		
Automated peak identification and analysis	This paper	https://github.com/milesmsmith/AutoMatIR
Software and algorithms		
Gaussian16	Frish et al. ¹⁰³	https://gaussian.com
Python version 3.9	Python Software Foundation	https://www.python.org
ChemDraw Professional 22.2.0	PerkinElmer	https://www.perkinelmer.com/category/chemdraw
CasaXPS Version 2.3.24PR1.0	Fairley et al. ¹⁰⁴	http://www.casaxps.com/berlin/index.htm
MultiPak	ULVAC-PHI, Inc.	https://www.phl.com/surface-analysis-equipment/system-software/multipak-data-reduction-software.html
Origin 2024	OriginLab Corporation	https://www.originlab.com/
Spectragryph, optical spectroscopy software	Friedrich Menges	https://www.effemm2.de/spectragryph/about.html
MCR-ALS decomposition of the paper “Tracking solid electrolyte interphase dynamics using operando fibre-optic infrared spectroscopy and multivariate curve regression”	Leau et al. ⁵⁰	https://zenodo.org/records/11122131
DMFit software	Massiot et al. ¹⁰⁵	https://nmr.cemhti.cnrs-orleans.fr/dmfit/

(Continued on next page)

Continued

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Other		
Bruker Tensor II	Bruker	https://www.bruker.com/en/products-and-solutions/infrared-and-raman/ft-ir-routine-spectrometer.html
Pike Vee-Max II attenuated total reflection accessory	Pike Technologies	https://www.piketech.com/wp-content/uploads/2019/12/350-001300-03-VeeMAX-II.pdf
Sputter-AJA-ChamberLoad	AJA International	https://www.ajaint.com/system-multitchamber
Cu mesh (100 × 100 mesh size, 0.006" opening, open area 30%, 0.0045" wire diameter)	McMaster-Carr	9224T87
Bruker Avance NEO 600 MHz spectrometer equipped with a 1.9 mm HXY MAS Bruker NMR probe	Bruker	https://www.bruker.com/en/products-and-solutions/mr/nmr/avance-nmr-spectrometer.html
Bruker Avance III 400 spectrometer equipped with a triple resonance broadband observe (TBO) probe head	Bruker	https://www.bruker.com/en/products-and-solutions/mr/nmr/avance-nmr-spectrometer.html
PHI Versaprobe II XPS	ULVAC-PHI, Inc.	https://www.phi.com/index.html
Zeiss Merlin high resolution microscope	Zeiss	https://www.zeiss.com/microscopy/us/products/sem-fib-sem/sem.html
Electrochemistry mass spectrometry	SpectroInlets ¹⁰⁶	https://spectroinlets.com/ec-ms-premium/
GC-2010 Plus	Shimadzu	https://www.ssi.shimadzu.com/products/gas-chromatography/index.html#top
BID-2010 Plus	Shimadzu	https://www.shimadzu.com.ua/chromatographic-equipment/tracera-gc-2010plus-bid?lang=en
TCD-2010 Plus	Shimadzu	N/A
SP-300	Biologic	https://www.biologic.net/products/sp-300/
SP-150	Biologic	https://www.biologic.net/products/sp-150e-potentiostat/
VMP3	Biologic	https://www.biologic.net/products/vmp-3e-potentiostat/
CR2032 Coin Cell Cases (20mm D x 3.2 mm T) with SS304 & SS316 Option - 100 pcs/pack - CR2032CASE	MTI Corporation	SKU: CR2032CASE316
Stainless Steel Spacer for CR20XX Cell (15.8 mm Dia. x 1.0 mm) - 100 pcs/pck-CR20SPA10	MTI Corporation	SKU: CR20SPA10
Stainless Steel Spring (Belleville Washers) for CR2032 Cases - 100 pcs/pck-CR20Be-Spring	MTI Corporation	SKU: CR20SPR
FEP (fluorinated ethylene polypropylene copolymer) NMR tube	Wilmad LabGlass	SKU: family-3628-18294

METHOD DETAILS

Materials and electrolyte preparation

Cu mesh was rinsed with isopropanol (IPA) and then dried in an oven at 60°C overnight before bringing it into MBraun glovebox (<0.5 ppm H₂O and <0.5 ppm O₂). 9.5 mm diameter Cu mesh was punched for the spectroelectrochemical cell. Li foil was brushed with a vegetable brush to remove native passivation film before being punched for cell assembly.

Electrolytes include 1.0 M LiPF₆ in ethylene carbonate (EC)/ ethyl methyl carbonate (EMC) (3:7 by volume) (LP57, battery-grade, Gotion), 1.2 M LiPF₆ (>99.99% battery-grade, Aldrich) in EC (battery-grade, Aldrich) and ¹³C₃ EC (99% purity, Aldrich), 1.0 M LiPF₆ (>99.99% battery-grade, Aldrich) in EMC (battery-grade, Gotion). Isotope labeled ¹³C₃ EC (99 atom %, 97% CP) was obtained from

Sigma Aldrich. The electrolytes (except for LP57) were prepared by mixing LiPF_6 in EC/ $^{13}\text{C}_3$ EC or EMC in the glove box (<1.0 ppm O_2 and <1.0 ppm H_2O). All solvents except for EC and $^{13}\text{C}_3$ EC were dried using activated 3 Å molecular sieves for at least 24 h. LiPF_6 salt was dried in a Buchi at 60°C and under vacuum for at least 12 h. EC was heated above its melting point of 40°C before mixing with the salt to produce a liquid electrolyte of 1.2 M LiPF_6 in EC.

ATR and *in situ* FTIR measurements

FTIR spectra of bulk electrolytes containing EC or EMC and 20–25 μL sample of the electrolyte solution was dropped onto a germanium (Ge) crystal for ATR measurements inside a glovebox. The measurements were taken at an incidence angle of 50° and consist of 32 scans. Attenuated total reflection (ATR) spectrum of bulk 1.2 M LiPF_6 in EC was shown for comparison in Figure 2A, which included three different regions, including EC (1801 cm^{-1} , 1482 cm^{-1} , 1408 cm^{-1} , 1163 cm^{-1} , 973 cm^{-1} , 773 cm^{-1} , and 718 cm^{-1}), Li^+ -coordinated EC (1768 cm^{-1} , 1195 cm^{-1}) and PF_6^- anion ($\sim 841\text{ cm}^{-1}$) (more details in Figure S16A). In addition, ATR spectrum of bulk 1.0 M LiPF_6 in EMC was shown for comparison in Figure 3A, which revealed features coming from EMC (1751 cm^{-1} , 1447 cm^{-1} , 1390 cm^{-1} , 1270 cm^{-1} , 1010 cm^{-1} , 937 cm^{-1} , 875 cm^{-1} , and 794 cm^{-1}), Li^+ -coordinated with EMC (1717 cm^{-1} and 1309 cm^{-1}), and finally PF_6^- anion (844 cm^{-1}) (more details in Figure S16B). Moreover, ATR-FTIR spectroscopy measurements for LP57 was shown in Figure 4A, which revealed peaks at 1808, 1774, 1406, 1372, 1197, 1163, 1075, 777 cm^{-1} coming from EC, and 1748, 1717, 1447, 1390, 1309, 1270, 1010, 937, 875, and 794 cm^{-1} originating from EMC (Figure S16C).

An *in situ* FTIR spectro-electrochemical cell was developed by leveraging recent work by Zhang et al.,⁵¹ as shown in Figure 1. A sodium chloride (NaCl) hemisphere (diameter 20 mm, Pier optics) was used as the optical prism, with Cu as the current collector (sputtered in Sputter-AJA-ChamberLoad system at $\sim 0.5\text{ Å s}^{-1}$ for 25 nm, as measured by an electrochemical quartz crystal microbalance), and the prism was pressed against a Teflon cell. The nano-structured Cu layer serves to enable surface-enhanced infrared absorption spectroscopy (SEIRAS),¹⁰⁷ enabling molecular vibrations within only a few nanometers of the interface to be selectively probed. The cell was assembled in an argon-filled glovebox ($[\text{H}_2\text{O}]$ and $[\text{O}_2] < 0.5$ ppm, MBraun). Sputtered Cu was used as the working electrode, and a lithium metal foil (MTI Corp.) was employed as the counter electrode, separated by two pieces of Whatman GF/F separator, with 150 μL of electrolyte. Cu mesh from McMaster Carr was added to improve surface enhancement and increase surface area for SEI formation. A stainless-steel plate was used as a spacer on top of the Li foil, and a spring was compressed by a cap on top.

After assembly, the cell was first rested for 6 h at OCV at room temperature. Next, linear sweep voltammetry was performed using SP-300 (Biologic). At the same time during linear voltage sweeping, *in situ* FTIR measurements were performed on a Tensor II (Bruker) FTIR equipped with deuterated triglycine sulfate (DTGS) detector inside of an argon-filled glovebox. The FTIR spectra were acquired in the single-reflection mode using an attenuated total reflection (ATR) accessory (Pike Vee-Max II, Pike Technologies) at an incident angle of 65° . The spectral resolution was 4 cm^{-1} and the scan velocity was 1.6 kHz. Each spectrum was measured by superimposing 32 interferograms. All spectra were collected in the form of absorbance according to $\log(I_0/I_1)$, where I_0 and I_1 are the background spectra (blank Cu surface without electrolytes) and *in situ* spectrum of the sample, respectively. Differential spectra were generated by subtracting the OCV spectrum from all subsequent spectra. For *ex situ* measurements on pristine electrolytes, the spectra were acquired in the ATR mode using a Ge prism (Pier optics) at an incident angle of 50° . Spectral settings were the same as *in situ* measurements. While we assign the observed species based on DFT and solution ATR spectra, other species such as semicarbonates cannot be excluded, because there could be other features in the convoluted bands. Although the penetration depth and optical constants are similar among the electrolytes, the enhancement provided by the sputtered nano-structured Cu can vary because it is sensitive to subtle differences in the nanostructure. For this reason, our analysis focuses on differences in SEI composition rather than on quantitative comparisons.

DFT computed reference spectra agreed well with experimentally observed peaks. In 1.2 M LiPF_6 EC, using the C=O asymmetric stretching mode as reference, computed LEDC (1658 cm^{-1}) has less than 4 cm^{-1} discrepancy with literature values (1660 cm^{-1}), where experimentally measured peak position aligns well with both. In the case of EMC, computed LEC has a C=O asymmetric peak at 1650 cm^{-1} , showing a 20 cm^{-1} upshift from our experimentally observed LEC peak around 1630 cm^{-1} . The discrepancies between DFT computed reference spectra and experimentally obtained could be because the DFT calculations were performed assuming an isolated, monomer structure, whereas in real systems lithium alkyl carbonates may exist in more stable forms, such as Li-coordinated LEDC clusters or as dimers.⁵⁹ To compare experimentally observed vibrational positions with DFT calculated ones, a scaling factor needs to be considered.

The FTIR spectra were primarily analyzed manually by examining differential changes between the spectra collected and a defined reference state. During the first plating cycle, the reference sample was defined as the spectrum at the open-circuit potential, while for subsequent cycles, the spectrum collected before cycling was defined as the reference sample. This manual analysis for 1.2 M LiPF_6 EC was complemented and validated with an automated approach for identifying and separating peaks in the original FTIR spectra.

Automated feature identification and analysis

The automated method enabled the connection of features observed in the reference samples to trends in the experimental data and differential spectra. The automated approach for feature analysis included baseline subtraction, feature identification, and model construction with minimal user input. Baseline subtraction was performed using the adaptive iteratively reweighted penalized least squares (airPLS) algorithm developed by Zhang et al.⁷¹ A generic baseline subtraction function was created for the reference

spectrum and subsequently applied to each related spectrum, preserving subtle relative differences in absorbance. Feature identification was carried out by tuning a peak-finding algorithm on the baseline-subtracted spectra and their derivatives, based on the prominence of the peaks. The identified features were then clustered using a density-based clustering algorithm, which grouped features identified within a defined wavenumber range. Parameters such as minimum prominence, the number of features, and the wavenumber range were adjusted for each dataset. The centroid of each feature cluster was used to construct a composite mathematical model consisting of a sequence of Gaussian functions, each centered near the centroid of the feature clusters.

To address the challenge of analyzing large and complex spectrochemical datasets from *in situ* characterization studies, an automated framework for identifying and analyzing features in FTIR spectra was developed. This framework consists of three main steps: (1) baseline subtraction, (2) feature identification, and (3) modeling, enabling the estimation of changes in specific features within complex IR spectra relative to a reference condition.

Baseline subtraction is a crucial preprocessing step for background correction in spectroscopic datasets, allowing for the comparison of feature prominence across datasets using a common reference point. Three algorithms for baseline subtraction were benchmarked to assess their ease of use and effectiveness in enhancing feature prominence while minimizing relative differences between spectra. For example, the prominence of the asymmetric bending of CO₂ in LEDC during the initial plating cycle for 1.2 M LiPF₆ in EC was compared across different baseline correction methods and against uncorrected data.

To preserve subtle relative absorbance differences that might otherwise be diminished or exaggerated by a generic baseline subtraction approach, a single baseline subtraction function was defined for each dataset using the system's reference state (e.g., the open-circuit voltage during the initial plating cycle) and applied uniformly across all spectra in the dataset. This ensured features were aligned closer to the reference point without introducing relative differences between spectra.

The three algorithms used to generate the baseline subtraction functions were: (1) the adaptive iteratively reweighted penalized least squares (airPLS) method by Zhang et al.,⁷¹ (2) a polynomial-based method by Lieber et al.,¹⁰⁸ and (3) a polynomial-based method by Zhao et al.¹⁰⁹ All three methods improved the prominence of the LEDC peak compared to uncorrected spectra, but the airPLS method was preferred because it is fully automated, whereas the polynomial-based approaches required manual tuning of polynomial degrees.

In modeling and analysis, it is essential to identify physically meaningful peaks and remove other artifacts. This was accomplished by identifying features based on their prominence in the IR spectra and their first derivatives. Identified features across related spectra were clustered using the density-based spatial clustering of applications with noise (DBSCAN) algorithm. DBSCAN was particularly useful for this application as it clusters one-dimensional datasets without requiring prior knowledge of the number of clusters. It effectively identified clusters corresponding to physically relevant peaks while ignoring noise artifacts that did not consistently appear throughout the dataset.

A composite Gaussian model was constructed by using the centroids of feature clusters as inputs for a multi-component Gaussian function, enabling detailed analysis of feature behavior. This composite model was demonstrated to fit IR spectra over both large (Figure S22) and small frequency ranges. While modeling over a large frequency range provides a general representation of the spectra with a relatively consistent mathematical model, challenges with model convergence and inconsistencies make it less practical for studying individual features in complex systems. Conversely, focusing on a small frequency range allows for more accurate representation of single features but may lose context provided by neighboring features.

CE measurements

CR2032 coin cell parts were bought from MTI Corp. Coin cell parts were initially sonicated in isopropanol (IPA) or ethanol for 10 min and then dried in an oven at 60°C. Coin cells were assembled with 16 mm diameter Cu as the working electrode, 14 mm diameter Li as the counter electrode, two layers of 19 mm diameter Whatman GF/F separators, and 100 μ L of electrolyte pipetted in four increments of 25 μ L for equal distribution. Assembled CR2032 cells were placed in battery holders (Adam Tech) and then connected to VMP3 potentiostat (Biologic) for cycling. Cell cycling protocol was based on method 1 from Adams et al.¹¹⁰ Method 1 over 100 cycles was chosen to get a better understanding of long-term cycling behavior under the largest Li metal anode volume expansion and contraction conditions. Cells were initially rested for 6 h, followed by a formation step consisting of 0.1 mA cm⁻² plating for a total charge of 0.2 mAh cm⁻² and 0.1 mA cm⁻² stripping for a total charge of 0.3 mAh cm⁻². Finally, cells were cycled at a current density of 0.4 mA cm⁻² for a total charge of 0.4 mAh cm⁻² for each charging (stripping) and discharging (plating) step. CE for each cycle was calculated by dividing the measured stripping charge by the measured plating charge. Average CE was calculated by averaging the CE per cycle over 100 cycles.

Quantitative GC-BID/TCD measurements

Electrolytes were prepared in cyclic olefin polymer (COP) vials in an argon atmosphere glovebox using an AX224 scale by Sartorius (Göttingen, Germany) with weight precision of 1 mg for each compound. The sample preparation was performed according to von Holtum et al.²⁹

Quantitative GC measurements were carried out on a GC-2010 Plus system. For the quantification, a BID-2010 Plus and a TCD-2010 Plus detector were used (all Shimadzu, Kyoto, Japan). Injections were performed manually with a 0.5 mL or a 0.025 mL headspace-syringe. The system is controlled by the LabSolutions software (version 5.90) by Shimadzu (Kyoto, Japan). The resulting chromatograms were evaluated with the Postrun Analysis editor (version 5.90) from Shimadzu (Kyoto, Japan). For

chromatographic separation of the GC-BID measurements a PLOT gas separation column RT-Msieve 5 A (30 m × 0.32 mm × 30 μm) and a packed RT-ShinCarbon ST (80/100, 2.0 m × 0.53 mm for GC-TCD, both by Restek (Bad Homburg, Germany) were utilized. GC parameters and calibration were conducted and adapted according to Leißing et al.,¹¹¹ using a gas mix by Westfalen AG (Münster, Germany) together with a gas mixing device (GMS-2CH by QCAL Messtechnik GMBH, Oberostendorf, Germany).

These absolute volumes were calculated by using the following equation:

$$V_{\text{abs}} = V_{\text{vial}} \cdot \frac{V\% \cdot V_{\text{cal}}}{100 \cdot V_{\text{inj}}}$$

where V_{vial} is the calculated volume of the COP vials, $V\%$ is the determined percentage volume of the respective gas according to the calibration, V_{inj} is the injected volume of the sample, and V_{cal} is the injection volume of the calibration (500 μL).

NMR measurements

Cells were disassembled in an Ar-filled glovebox ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.5$ ppm) to retrieve the Li SEI attached to the glass fiber separator and copper foil in the Li/Cu cells. While no visible SEI layer was present on the copper foil, when the glass fiber separator and the Cu foil were peeled apart, we could see that the SEI was coated on the glass fiber. The SEI-coated glass fiber was dried overnight *in vacuo*, then cut into small pieces inside the glovebox and loaded into a 1.9 mm o.d. ZrO_2 rotor for analysis with SSNMR. All SSNMR experiments were performed on a Bruker Avance NEO 600 MHz spectrometer equipped with a 1.9 mm HXY MAS Bruker NMR probe head performed at room temperature. ^{19}F SSNMR experiments were performed using a single 90° pulse-acquire, with a 90° pulse length of 2.73 μs, a cycle delay of 30 s, and between 256 and 1024 scans. ^{19}F SSNMR spectra were externally referenced to LiF at -204 ppm. ^7Li SSNMR experiments were performed using a single 90° pulse-acquire, with a 90° pulse length of 3.144 μs, a recycle delay of 100 s, and 64 scans. Longitudinal relaxation, T_1 times, were measured using the saturation recovery pulse. Fitting and analysis were performed using Origin software. Spectral fitting and deconvolution were performed using the DMFit software.¹⁰⁵

We collected *in situ* solution NMR measurements using a previously reported *in situ* electrochemical NMR tube cell design^{93,112} where here we make a symmetric cell employing Li metal strips cut from Li metal ribbon as electrodes (Figure S54). We tested the same three electrolytes used in the *in situ* FTIR experiments: 1.0 M LiPF_6 in EMC, 1.2 M LiPF_6 in EC and 1.0 M LiPF_6 in EC/EMC (3:7 by volume) (LP57). For the electrochemical protocol, we used a linear sweep voltammetry (LSV) protocol, where we swept from the starting open circuit voltage (OCV) (near ~ 0 V_{Li} for each symmetric cell) to -0.8 V_{Li} using a sweep rate of 0.1 mV/s, such that the entire *in situ* experiment lasted 2 h 13 min. Accordingly, we plate Li metal on the working electrode and strip from the counter electrode, producing a negative current. Electrolyte decomposition species generated at the working electrode diffuse easily to the measurement area upon which we can detect them with ^{19}F solution NMR. All cells were visually inspected after the experiment to confirm that Li plating occurred on the working electrode, as the Li microstructures were readily visible in this transparent cell design.

The symmetric flood cell (Figure S54) contains the two Li metal electrodes (each having dimensions 1 mm × 1 mm × 20 mm, surface area 0.82 cm²) and the desired electrolyte (350 μL) assembled in a 3.65 mm outer diameter FEP (fluorinated ethylene polypropylene copolymer) NMR tube (Wilmad LabGlass, dried at 60°C overnight prior to use), sealed with epoxy. The tube cell is then submerged into a 5 mm o.d. glass NMR tube containing 0.1 mL DMSO- d_6 (for locking and shimming) and secured in place with Teflon tape, allowing us to collect high resolution ^{19}F NMR during electrochemical cycling. Electrodes were placed into the tube approximately 25 mm from the bottom of the FEP liner, completely submerged in electrolyte. Each Li metal anode was connected via heat-shrink chemically resistant electrical insulation tubing to a 22 cm long pure Cu wire, whereby upon heat-treating the tubing, the shrinkage electrically connects the Li metal anode to the Cu wire within the tubing. The heat-shrink tubing prevented cell shorting along the length of the NMR tube. The counter Li electrode (from which we strip during the electrochemistry step), was wrapped in a single layer of Celgard 2325 separator (dried at 60°C for 24 h prior to use).

Prior to the experiment, the *in situ* cell was connected to double shielded wires which were connected to an electromagnetic shield (NMR Service, GmbH). Once the cell was inserted into the NMR magnet, the shield was placed on top of the upper magnet bore. The double shielded wires extended out from the other side of the shield to connect to a Biologic SP-150 potentiostat for the electrochemical protocol. Solution NMR experiments were performed on a Bruker Avance III 400 spectrometer equipped with a triple resonance broadband observe (TBO) probe head. One-dimensional (1D) ^{19}F (30° single pulse, 3 s recycle delay, 32 scans, internally referenced to PF_6^- electrolyte salt at -74.5 ppm) spectra were recorded at room temperature. Prior to acquisition, the sample was locked to DMSO- d_6 and shimmed, which was key for detecting the dilute species reported in this work. For *in situ* NMR, ^{19}F spectra (128 scans, 30° single pulse, 3 s recycle delay, 32 scans, internally referenced to PF_6^- electrolyte salt at -74.5 ppm) were collected sequentially during the length of the electrochemistry protocol, where each spectral acquisition was 7 min and 2 s long, defining the time resolution of the *in situ* experiment. A single ^{19}F spectrum was acquired before electrochemical protocol began for each cell.

XPS measurements

Li || Cu half cells were built and scanned at 1 mV/s from OCV (~ 2.7 V_{Li}) to either 0.1 V_{Li} or -0.5 V_{Li} , followed by a 3 hour constant voltage hold. Immediately afterward, the batteries were disassembled inside the glovebox and the Cu electrode was extracted. In order to avoid peak convoluting effects from remaining PF_6^- anions and their potential degradation into LiF and $\text{Li}_x\text{PO}_y\text{F}_z$ species under the x-ray⁸⁶, SEI samples were thoroughly rinsed with solvent prior to XPS measurement. The rinsing solvent was selected

to match the electrolyte solvent in which the SEI was formed (i.e., 1.0 M LiPF₆ EMC samples were rinsed with EMC, and LP57 samples were rinsed with EC/EMC (3:7 by volume)) to minimize perturbation of the SEI composition. Due to EC being solid at room temperature, it was not possible to rinse off excess salt from SEI samples formed in 1.2 M LiPF₆EC. Therefore,⁸⁶ we decided to only characterize the SEI formed in 1.0 M LiPF₆ EMC and LP57 electrolytes. 4 × 50 μL increments of EMC were used to rinse the electrode, which was then placed inside the antechamber to dry under vacuum for at least 6 h. After drying, a sample roughly equal to 1/8th of total electrode area was cut off and placed on double-sided insulating tape. Finally, the sample was loaded into an air free XPS transfer vessel to transfer to the XPS instrument.

All XPS data were collected on a PHI VersaProbe 2 XPS with an Al Kα source. All measurements were performed using X-ray settings of 200 μm, 50 W, and 15 kV. Ion and electron neutralization were used for all XPS measurements to avoid charging of the sample. Survey, high resolution, and depth profile scans were collected using pass energies of 187.85 eV, 23.5 eV, and 117.4 eV, respectively. Ar⁺ sputtering settings of 1kV, 0.7 μA, and 2 mm × 2 mm were used. Etch rate was calibrated to a SiO₂ reference and determined to be 3.7 nm/min. Total etch time was 10 min with 2-min intervals and alternating w/Zalar rotation.

Relatively atomic concentrations from survey and depth profile were quantified using MultiPak software after taking into consideration corrected RSF values. High resolution spectra were processed in CasaXPS 2.3.23 software.¹⁰⁴ All spectra were calibrated to C-C/H peak at 248.8 eV. All spectra were smoothed using Savitzky-Golay with a smoothing window of 7. Shirley background was applied and peak shapes were defined using Gaussian-Lorentzian in a 30:70 ratio. FWHM were typically constrained from 1 eV to 2 eV. For P2p spectrum, area of p1/2 was constrained to be half of p3/2, and the two peaks were constrained to a 1.16 eV separation.

SEM measurements

Batteries with 19 mm diameter Cu as working electrode, 15 mm diameter Li as counter electrode, 2 × 19 mm Celgard 3501 separators, and 75 μL of electrolyte were assembled inside a glovebox. The three electrolytes of interest came from the same batch as the one used for FTIR and cell cycling measurements. To achieve early-stage Li deposition morphology, a galvanostatic protocol applied a total capacity of 2 mAh cm⁻² at a current density of 0.4 mA cm⁻². In the case of EC, high viscosity of the electrolyte led to cell polarization and premature termination of the galvanostatic protocol, leading to a plated capacity of ~0.5 mAh cm⁻².

The batteries were disassembled inside the glovebox and the working electrode was extracted. 2 × 100 μL increments of EMC was used to rinse the electrode of any Li salt. Excess solvent was absorbed with a Kimwipe. After drying, Cu foil with electrodeposited Li was cut with scissors and mounted onto an SEM stub. An air-free transfer process to the SEM was used.

High-resolution SEM imaging was performed using a Zeiss Merlin microscope. Top-view images were typically acquired at an acceleration voltage of 5 kV and a probe current of 100 pA. Cross-sectional imaging was obtained by tilting the sample holder by 50°–55°, followed by tilt correction to ensure accurate determination of Li layer thickness.

ECMS measurements

Electrochemistry–mass spectrometry (ECMS) was performed using the Spectrolnlets interface system.¹⁰⁶ A silicon-on-insulator microchip with an internal volume served as a microscopic headspace, equilibrating with the working volume to deliver electrochemical products to the vacuum chamber without differential pumping.¹⁰⁶ The system comprised a Pfeiffer Vacuum QMG electronics unit with a QMA 125 mass analyzer and a Biologic SP-300 potentiostat.

The detachable module was dried in a 60°C oven for over 2 h. Prior to use, the polychlorotrifluoroethylene (PCTFE) electrochemical cell, Cu working electrode (polished with a 1 μm alumina powder to a mirror finish), and syringes were boiled in deionized (DI) water, ultrasonicated in ethanol for 1 h and dried overnight at 60°C. The lithium iron phosphate (LFP) strips (NEI Corporation) were dried in a Buchi oven at >100°C under vacuum for at least 24 h. Before each run, the cell was assembled onto the module (see Figure S4), and evacuated in an antechamber before glovebox transfer for electrolyte injection to minimize air contamination. 1 mL of fresh electrolyte was introduced via a syringe inside the Ar glovebox, and the module was returned to the ECMS instrument. Helium was flowed at 1 mL min⁻¹, with outlet pressure set to 1025–1035 mbar. Openings were sealed with parafilm, punctured with needles to prevent pressure buildup. The system lines were then evacuated to <10⁻³ mbar for interfacing with MS chamber.

During the ECMS run, the mass spectrometry and the corresponding open circuit potential was performed for >0.5 hours to allow the mass signals to equilibrate and to allow a sufficient record of baseline signal evolution for baseline subtraction. A linear sweep voltammetry at 3 mV s⁻¹ was performed to Li plating region, where the inflection point of the current was used to demarcate the Li⁺/Li potential (0 V_{Li⁺/Li}). The LSV was followed by Li-plating at constant current of –120 μA cm⁻²_{geo} for 0.5 hours, followed by a long (>1 hour) open circuit potential.

Baseline subtraction and data processing. Given the decaying baseline in raw mass signals, the spectra were first normalized to the carrier gas signal (He, m/z = 4). Then, the normalized mass signals were corrected using a composite exponential–diffusive background model of the form:

$$y(t) = Ae^{-\frac{t}{\tau}} + \frac{B}{\sqrt{t + t_0}} + C$$

Where A and τ in the first term describe a fast exponential relaxation, B and t_0 account for the slower diffusion-limited tail characteristic of gas transport and detector stabilization, and C represents the steady-state baseline. The parameters were fitted to the regions outside the electrochemical event (excluding masked time intervals defined as the 1.5 hour period since the start of linear sweep), and the fitted background were subtracted from the normalized signal to obtain the background-corrected trace.

Ab initio molecular orbital calculations

The interaction of Li^+ with carbonate molecules (LEDC, LEMC, LEC, LEM and Li_2CO_3) was computed by density functional theory (DFT) with the Gaussian16 suite.¹⁰³ Geometry optimizations were performed at B3LYP/6-31G(d,p) level of theory. To account for solvation effects, we employed a conductor-like polarizable continuum model (CPCM)^{113,114} with a dielectric constant = 46.8. Simulated infrared spectra of the optimized molecular structures of Li^+ complexes in the implicit solvent were obtained from the computed vibrational frequencies using a Lorentzian bandwidth of 10 cm^{-1} with the program Molden.¹¹⁵