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Operando Ellipsometric Monitoring of Solid Electrolyte Interphase Evolution on Copper: Effects of Electrolyte Chemistry on Interphase Growth Kinetics

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ABSTRACT

The formation and properties of the solid electrolyte interphase (SEI) are considered crucial for cell performance, particularly for negative electrode chemistries that undergo considerable volume and morphological changes during cell operation, such as lithium metal. In this work, the interphase formation kinetics and thickness evolution of the SEI on Cu are monitored via *operando* ellipsometry and correlated with key electrolyte-dependent electrochemical and interphase properties of related lithium metal-based cells. The quantification of SEI growth under potentiodynamic control revealed that the localized high-concentration electrolyte (LHCE) promotes rapid SEI formation at the FSI[−] reduction potential (1.5 V vs. LiLi⁺), followed by a subsequent decrease in growth rate as the Li redox potential is approached. In contrast, the conventional organic carbonate-based electrolyte (CCE) leads to continuously accelerated SEI growth during the cathodic potential sweeps, accompanied by roughly a sixfold higher electrical charge and a thicker interphase of 75 vs. 31 nm with the LHCE. *Ex situ* synchrotron infrared nano spectroscopy (SINS) confirmed a more homogeneous, less rough SEI formation with the LHCE, which, in combination with the identified fast formation kinetics and effectively protective FSI[−]-derived interphase, promotes efficient electrodeposition/-dissolution of Li with a compact morphology.

1 | Introduction

For decades, lithium metal batteries (LMBs) have been heralded as a next-generation energy storage technology by leveraging lithium's exceptional physical properties, particularly its high specific capacity and low standard reduction potential [1, 2]. However, the practical implementation of this cell chemistry has been hindered by challenges with the lithium electrode's stability and structural integrity during repeated charge/discharge [3, 4]. The solid electrolyte interphase (SEI), the protective layer at the Li metal | electrolyte interface, plays a pivotal role in determining major critical performance-determining parameters of the LMB, including active material degradation, electrode's

morphology and Coulombic efficiency (CE) [2, 5–9]. Poor protection of lithium metal leads to continuous side reactions with the liquid electrolyte and inhomogeneous lithium whisker growth, ultimately causing early cell failure [2, 10]. Thus, understanding and controlling the formation and evolution of the SEI is paramount for enabling safe and long-term operating LMBs. As its composition and structure are intimately correlated to the (electro-)chemical behavior of the liquid electrolyte, the right selection of electrolyte components and the design of the Li solvation shell are essential to optimize the protective properties of the SEI [1, 11, 12]. Traditional organic carbonate-based formulations, often used in today's lithium-ion batteries, tend to form

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ineffective, mostly organic SEIs with lithium metal, making those electrolyte formulations unfavorable for LMBs [4, 10, 13, 14]. As a consequence, several new electrolyte classes have been explored in recent years, engineering their properties to enable an effective SEI formation [1, 9, 11, 15–20]. Localized high-concentration electrolytes (LHCE) have recently emerged as a promising concept for stabilizing the Li metal | electrolyte interface. By combining the beneficial solvation structure of high-concentration electrolytes (HCEs) with low viscosity, LHCEs promote a dense lithium morphology and form an inorganic, anion-derived SEI, thereby minimizing electrolyte decomposition during cell operation [15, 16].

The brittle and chemically unstable nature of the few-nanometer-thick interphase layer, however, makes its analysis, especially in an application-oriented environment, challenging. Consequently, key aspects of this pivotal cell component remain unresolved [5]. *Operando* ellipsometry, a powerful, nondestructive technique rarely used in battery research, combines several benefits, making it an attractive tool for analyzing the SEI [21–25]. Here, changes in the polarization state of polarized light upon reflection at an interface are quantified by the amplitude ratio (ψ) and phase difference (Δ) [26]. Using an appropriate model, these physical parameters can be correlated with the optical properties and the thickness of the formed interphases (Figure 1). The technique's high sensitivity to nanoscale films and fast measurement speed enable precise, real-time monitoring of SEI growth under operating conditions [25].

In this study, we quantify how the electrolyte chemistry governs the formation kinetics, interfacial structure, and thickness evolution of the SEI via a custom *operando* ellipsometry setup operated under potentiodynamic conditions. Two representative well-investigated electrolytes were evaluated: an LHCE with high Li metal compatibility and a conventional organic carbonate-based electrolyte (CCE) with limited electrode protective abilities. The SEI growth modes with these two electrolyte chemistries are further correlated with electrochemical features and linked to the performance of related lithium metal-based cells. Complementary *ex situ* synchrotron infrared nanospectroscopy (SINS) and scanning electron microscopy (SEM) analysis allow corroborating the obtained *operando* results and enable correlation with additional interphase properties, in particular, its lateral homogeneity and morphology of underlying Li deposits.

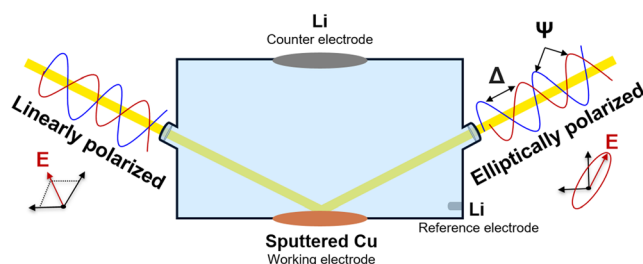


FIGURE 1 | Schematic of the optical cell for the *operando* ellipsometry measurements, exemplifying the measurement principles to monitor the SEI growth during cell operation.

2 | Results

2.1 | Electrochemical Performance

Consistent with prior studies, the selected LHCE (LiFSI in DME/TTE 1:1.2:3 n/n) with lithium bis(fluorosulfonyl)imide (LiFSI), dissolved in dimethoxyethane (DME) and diluted down with 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE), outperforms the CCE (LiPF₆ in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) 3:7 wt%) in LMBs, yielding higher CEs and improved galvanostatic cycling stability [16]. Using a modified Aurbach method [27] (10 mAh instead of 5 mAh reservoir) in CullLi cells, the LHCE reaches a CE of 99.5%, showing a minimal Li loss in each cycle (<0.5%). In contrast, the presence of the organic carbonate-based electrolyte results in poor average CEs of 73.6% under identical conditions, accompanied by a substantial average Li loss (Figure 2a).

This trend is further evident in long-term cycling experiments with CullLi and symmetric LillLi cells, where the CE with the organic carbonate-based electrolyte plummets to 73% after 17 cycles (CullLi) and both CullLi and symmetric LillLi fail after roughly 50 cycles under the stated condition (Figure 2b). In comparison, the LHCE enables a homogeneous Li electrodeposition/dissolution, with an average CE of over 99.4% between the 50th and 200th cycle (in CullLi cells), and sustains a stable operation in LillLi symmetric cells for >600 h (Figure 2c). The cause of cell failure also differs: whereas CCE-based cells experience an exponential increase in overvoltage due to extensive dead Li formation, LHCE-based cells fail due to an internal short circuit, likely caused by dendrite formation. However, the underlying factor is expected to remain the same: the depletion of the liquid electrolyte due to continuous electrolyte consumption. The different failure modes, therefore, likely arise from the electrolyte-specific difference in ion transport kinetics and interphase formation. In organic carbonate-based electrolytes, lithium deposits tend to be nonuniform and whisker-like, leading to the rapid formation of dead Li deposits as electrolyte depletion proceeds and the electroactive electrode area declines [4, 10]. In contrast, the LHCE forms a more protective interphase, promoting denser Li deposition, which limits dead Li accumulation and thereby reduces the exponential rise in interphase resistance toward the cell's end of life [16]. Furthermore, the LHCE's lower ionic conductivity (LHCE, 1.9 mS cm⁻¹ vs. CCE, 7.9 mS cm⁻¹) is expected to increase polarization within the bulk electrolyte. Thus, as the charge carriers are continuously consumed during galvanostatic cycling, Sand's time (i.e., the onset of complete Li⁺ ion depletion at the Li metal | electrolyte interface) shortens, eventually leading to diffusion-limited dendrite growth, which short-circuits the cell.

An in-depth examination of the voltage profiles already provides valuable information about interfacial kinetics, potential mass transport limitations, and morphology at the Li metal | electrolyte interface (Figure 2d). While both liquid electrolyte formulations cause a similar average overvoltage (−0.07 V), the shapes of the overvoltage profiles differ, implying different Li electroplating/dissolution kinetics [28, 29]. In the first cycle, both systems exhibit a large, rapidly decreasing overvoltage, consistent with the breakdown of the native passivation layer (NPL), naturally covering the Li metal surface [30–32]. Already here, the first differences emerge, as the LHCE system exhibits a more pronounced decrease and a lower terminal overvoltage at the end of the first cycle than the organic carbonate-based cell (0.11

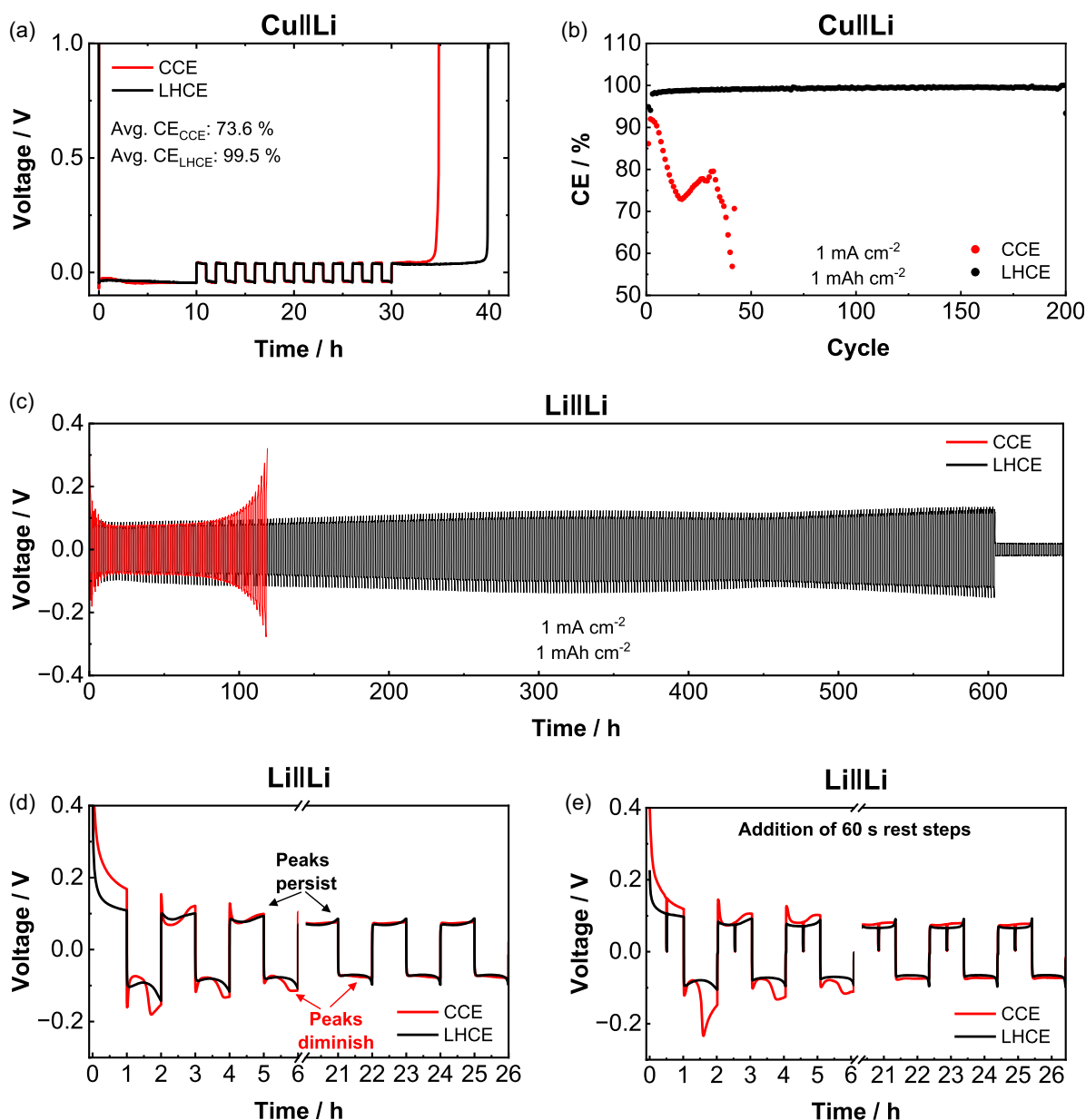


FIGURE 2 | Evaluation of the Li electrodeposition/dissolution efficiency in CuLi cells via (a) a lithium metal reservoir method [27] and (b) long-term galvanostatic cycling. (c) Overvoltage development in symmetric LiLiLi cells and (d) evaluation of the voltage profiles with (e) the inclusion of short rest periods (60 s) before and within every second half-cycle to uncover the origin of the observed voltage peaks.

vs. 0.17 V). In subsequent half-cycles, the voltage profiles of the LHCE-based cell exhibit flat plateaus with small, consistent peaks at the beginning and end of the cycle, which persist largely unchanged until cell failure. In contrast, the organic carbonate-based cells display more prominent voltage peaks that decrease in intensity in subsequent cycles before eventually diminishing. The differences in the shapes of the overvoltage profiles already provide valuable insights into the film-forming abilities and nucleation behaviors of the respective electrolyte formulations. The large spikes at the beginning of the first cycles in the organic carbonate-containing cells indicate a high nucleation barrier due to an ineffective SEI formation, whereas the second voltage peaks could be attributed to the complete dissolution of the plated high-surface area Li (HSAL) deposits and the transition to kinetically more hindered stripping of the bulk Li. The subsequent

diminishing of the peaks and evolution toward a flat voltage plateau could reflect an increased uniformity and overall higher effectiveness of the formed SEI; however, the growth of the mossy-like Li deposits and the drastically inflated effective anode area, typical with additive-free organic carbonate electrolytes, is the more likely cause of the lower nucleation barriers [14, 29]. The reduced start and end voltage peaks with the LHCE indicate a much lower nucleation barrier, due to a more effective anion-derived inorganic SEI. The persistence of these small peaks can be attributed to either compact Li deposition, resulting in a modest, consistent nucleation overpotential, or to double-layer effects and Li concentration polarizations in the liquid electrolyte formulation. To distinguish between mass transport limitations and nucleation contributions, short rest steps (60 s) were included between and within every second half-cycle. The persistence of the voltage peaks with both electrolyte formulations

rules out double-layer effects and mass transport limitations as dominant contributors [28], pointing to consistent nucleation-induced overvoltage contributions (Figure 2e).

2.2 | Optical Modeling of Relevant Cell Materials

Prior to investigating the evolution of SEI thickness on Cu electrode, the optical parameters of the various components must be determined to build a suitable model based on the Cauchy transmission equation:

$$n(\lambda) = A + \frac{B}{\lambda^2}$$

This equation describes how the refractive index (n) of a transparent material ($k \approx 0$) depends on the wavelength (λ), with A and B being the coefficients to be determined by fitting the equation at known wavelengths. As negligible light absorption by the forming SEIs is expected, the Cauchy model provides a consistent and straightforward framework for extracting the interphase thickness by correlating changes in the phase shift and amplitude ratio with changes in SEI thickness. In particular, the optical properties of the electrode (here: sputtered Cu), the liquid electrolyte formulations, and the SEI itself need to be determined. First, the optical properties of the Cu electrode in argon were determined (Figure S1a), the modified optical cell filled with the respective electrolyte, and the refractive indices of the solutions determined by fitting the ellipsometric

parameters (Figure 3a). For Cu, the dataset provided by Palik was used, and the parameters were fitted with the Drude–Lorentz model rather than the Cauchy model, due to the significant extinction coefficient ($k > 0$) and the metal's nontransparency.

In contrast, the determination of the SEI's optical parameter is not that straightforward due to the structural and compositional complexity of the interphase layer. Nonetheless, previous studies on this matter [22, 24, 25] and the known compositional information of the SEI with organic carbonate-based electrolytes [33] and LHCEs [16] provide rough estimates of the SEI's refractive index. Accordingly, the SEI's optical parameters used for the Cauchy models were estimated as A 1.45 and B 0.01 and refined by fitting the ellipsometry data after a potential hold at 0.05 V (Figure 3b). The optical constants were determined as A 1.472 and B 0.00937 with a mean square error (MSE) of 18.8 for the organic carbonate-based system (Figure S1b) and 15.0 for the LHCE-based system (Figure 3b), which lie within the ranges reported in similar investigations [25]. To ensure comparability, the determined SEI coefficients were held constant across both cell chemistries and throughout the experiments. However, as SEI composition and nanostructure are expected to differ between two electrolyte chemistries, fixing the refractive indices can bias the absolute thickness obtained from the experiments. Nonetheless, the relative thickness changes with time and potential should remain internally consistent and physically meaningful. Based on the determined optical constants, a stack model was built, including the Cu substrate, the

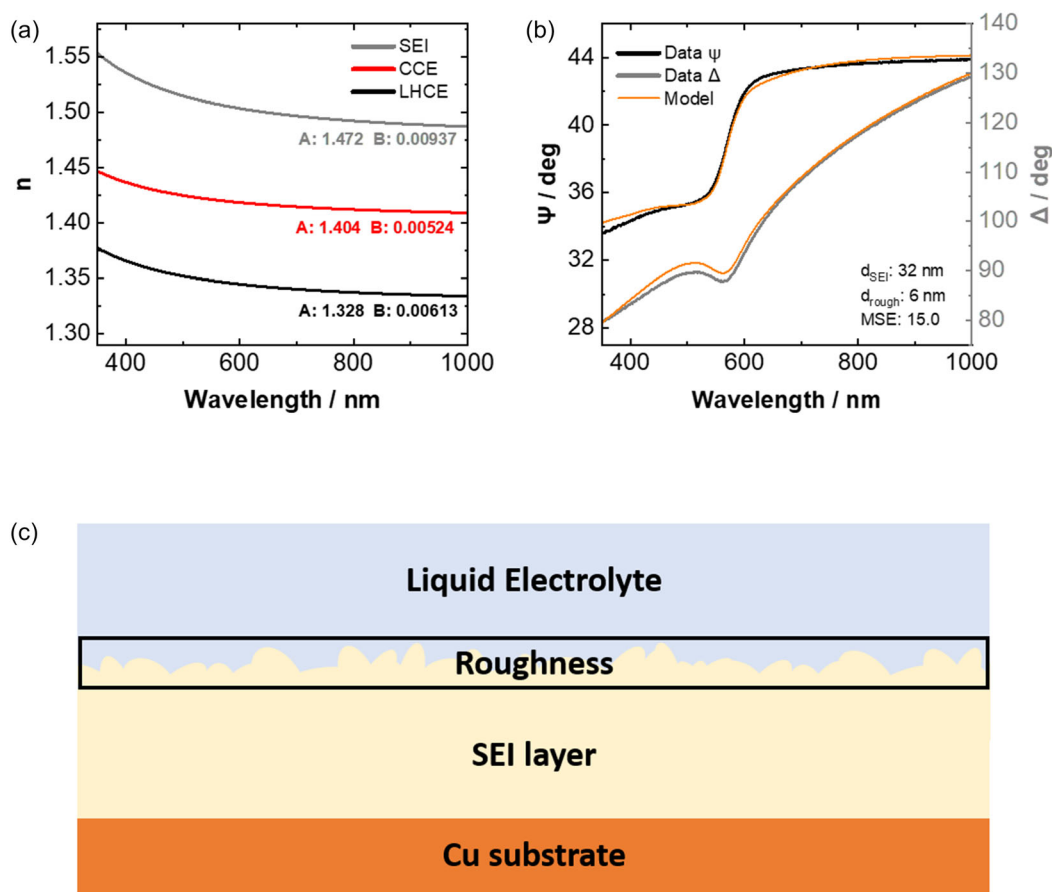


FIGURE 3 | (a) The determined optical constants of the considered electrolyte formulations and the SEI by fitting the data with a Cauchy model in the operando ellipsometry setup. (b) Fitting of the optical data after a 12 h potential hold at 0.05 V vs. LiLi^+ to determine the optical constants of the SEI with the LHCE. (c) Schematic of the modeled layer stack.

forming SEI layer with its surface roughness, and the liquid electrolyte (Figure 3c). With this, the thickness of the SEI and roughness layers were modeled throughout the experiment, while the optical parameters were held constant. The roughness was modeled as an additional theoretical layer via an effective medium approximation (EMA) with a 50% filling fraction [34, 35].

2.3 | Operando Observation of the SEI Thickness Evolution

To investigate the growth and dissolution of the SEI in the presence of the investigated electrolyte solutions at different operating

potentials, a protocol involving potential sweeps (1 mV s^{-1}) and potential holds (2 h each) was employed, and the changes in ψ and Δ were continuously recorded (Figures S3, S4).

Under open circuit conditions and during the initial potential hold at 2 V (vs. LiLi^+ for all given potentials), both electrolytes cause slow interphase layer growth, reaching approximately 2 nm in thickness (Figure 4). As potential decreases, the growth behaviors begin to diverge. With the CCE, the SEI grows continuously as the operating potential decreases, with accelerated growth near the Li plating potential (0.05 V vs. LiLi^+). The SEI thickness peaks during the reverse scan at 26 nm before contracting to 9 nm after returning to 1 and 2 V. In contrast, the SEI

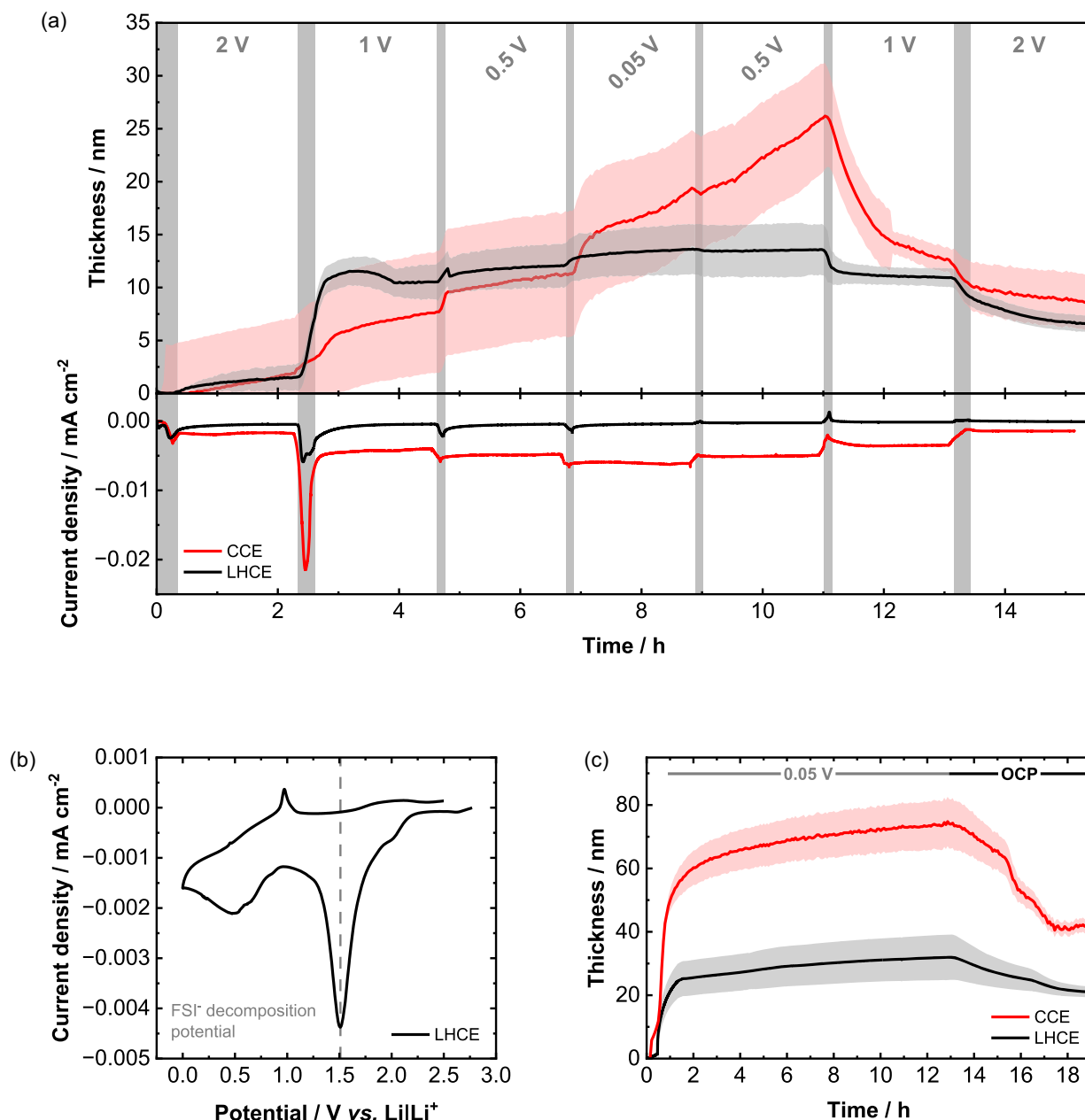


FIGURE 4 | (a) SEI thickness evolution during the potential hold protocol (top) and the corresponding current densities during the cathodic sweep (bottom). The vertical gray bars represent the voltage sweeps (1 mV s^{-1}) between the potential holds (vs. LiLi^+). (b) Cyclic voltammogram (reductive) of the cell containing the investigated LHCE formulation, showcasing the distinct reductive current peak at 1.5 V vs. LiLi^+ . (c) Evolution of the SEI thickness during the 12-h potential hold at 0.05 V vs. LiLi^+ and the following 6-h rest step (open circuit potential (OCP) conditions). The shaded areas above and below the graphs depict the determined roughness of the SEI layers throughout the experiments.

derived from the LHCE exhibits rapid SEI growth from 2 to 1 V, reaching 14 nm, after which the thickness remains essentially constant, with slight ongoing growth during the cathodic scan. After returning to 2 V, a contraction of the interphase layer is also observed; however, it is less pronounced compared to the organic carbonate-based system.

The modeled effective roughness (d_{rough}) of the LHCE-derived SEI is determined to be roughly half as pronounced in comparison to the CCE-derived interphase, where a surface roughness of ~ 10 nm is already reached at the 1 V potential hold, indicating a more inhomogeneous SEI nanostructure with the organic carbonate electrolyte. After returning to a potential of 2 V, the interphase roughness markedly decreases, reaching 3 nm with CCE and 1 nm with LHCE (Figure 4a).

In both cases, the MSE does not exceed 16 and is below 10 for most of the time, indicating good mathematical accuracy of the used Cauchy model with the determined parameter and the measured optical data (Figure S5). In line with the SEI growth, the LHCE induces lower reductive currents compared to the organic carbonate-based electrolyte, with reduced current rises during potential sweeps and overall lower current plateaus during potentiostatic holds (Figure 4a). The total charge over the SEI formation regime (until reversal to 1 V vs. LiLi^+) yields 0.238 C (0.066 mAh) for the organic carbonate-based system vs. 0.036 C (9.7×10^{-3} mAh) for the LHCE system, corresponding to a roughly sixfold reduction in charge attributed to SEI consumption, even though only an about twice as thick interphase is formed with CCE compared to LHCE (Figure S6). This indicates that a substantial amount of the reductive current with CCE does not translate to SEI growth. Instead, the high fraction of organic reduction products reported for organic carbonate-based electrolytes is likely to be rapidly dissolved in the liquid electrolyte and not incorporated into the SEI after formation [33, 36].

Comparing the LHCE-derived SEI thickness evolution with a corresponding cyclic voltammogram, the distinct peak at 1.5 V coincides with rapid SEI growth and can be attributed to the reductive decomposition potential of the FSI^- within an anion-rich Li solvation structure, leading to the formation of an inorganic interphase (Figure 4b) [37, 38]. The sharp increase in thickness growth rate (0.34 nm min^{-1} between 2.35 and 2.80 h), combined with the subsequent drastic reduction in decomposition current and interphase growth, demonstrates the effectiveness of the often-praised anion-derived SEI in weakly coordinating LHCEs and also highlights the fast reaction kinetics during SEI formation, another crucial factor promoting dense Li deposition [39].

Incorporating a potential hold at 0.05 V for 12 h after a potential sweep from OCP further highlights the less effective interphase formation with the organic carbonate-based electrolyte compared to the LHCE counterpart (Figure 4c). After an initial rapid interphase layer growth of ~ 50 nm during the first hour, the SEI growth rate decelerates and eventually reaches 75 nm (d_{rough} , 11 nm) and then contracts again to 41 nm (d_{rough} , 3 nm) under open circuit conditions. The LHCE-based cell also exhibits rapid SEI growth, which, however, already stabilizes at an average thickness of 25 nm, showing only very moderate growth thereafter. During the subsequent 6 h OCP step, the value decreases only slightly, from a maximum of 32 nm (d_{rough} , 6 nm) to 21 nm (d_{rough} , 1 nm). Consistent with the first potential hold

experiment, a pronounced decrease in the surface roughness accompanies the contraction of the interphase layer. The reduction in SEI thickness and measured roughness at elevated potentials and under OCP highlights the dynamic nature of the SEI. This contraction and smoothening of the SEI is likely driven by partial dissolution and reorganization of organic SEI components, leading to a structural densification of the interphase. Organic SEI species, particularly prevalent with organic carbonate-based electrolytes like CCE, can redissolve into the electrolyte under non-reductive conditions, leading to a measurable decrease in effective SEI thickness [40, 41]. In addition, the SEI formed under cathodic polarization may initially be porous and solvent-swollen. Once the reductive conditions are removed, solvent expulsion and reorganization of loosely bound components result in a densification and smoothening of the SEI. The substantially smaller contraction observed for the LHCE-derived SEI indicates a chemically and mechanically more stable, inorganic-rich interphase. These findings emphasize that SEI effectiveness is not only governed by its formation but also by its structural stability under nongrowth regimes.

2.4 | Ex Situ Analysis of the SEI and Li Deposition Morphology

The nanostructure and homogeneity of the SEI were further investigated via SINS, in which an atomic force microscopy (AFM) tip is illuminated by a broadband synchrotron source, thereby enhancing the electromagnetic field at the tip apex. This enables chemical mapping of a sample's surface with a spatial resolution of 20 nm [42–45]. The ex situ investigations corroborate the trends in SEI thickness and homogeneity observed during the ellipsometry experiments. The organic carbonate-induced SEI has an average roughness of 7.4 nm (Figure 5a), almost four times higher compared to the LHCE-induced interphase (roughness SEI_{LHCE} , 1.6 nm), which exhibits a comparably homogeneous surface roughness (Figure 5b). While the roughness trends are similar, deviations in the absolute values from the operando ellipsometry measurements are likely due to differences in the measurement procedures (operando vs. ex situ) and the cell setup, particularly the absence of stack pressure in the optical cell. Furthermore, these quantities are not identical by definition: via AFM, a height variation over a micrometer-scale scan area is measured, whereas with ellipsometry, the thickness of an effective roughness layer with a 50% filling fraction is extracted. In contrast to the topographical roughness, a high degree of compositional homogeneity is observed on both electrodes, as the local SINS spectra within one electrode are consistent in peak positions and relative intensities, with only subtle differences detectable (Figure 5c,d and Figure S11). In the low-wavenumber region ($<600 \text{ cm}^{-1}$), both interphases exhibit broad IR absorption bands, indicating pronounced formation of inorganic SEI components, i.e., LiF , Li_2O , and Li_2S (LHCE-only) [44]. The divergence of these absorption bands between both systems likely originates from compositional differences in the inorganic SEI layer itself, as well as from variations in nanostructure and encapsulated organic decomposition products, which can impede near-field coupling between the components and the probe. The higher wavenumber region (1750 to 600 cm^{-1}) consists mainly of vibrational modes attributed to residual electrolyte and organic decomposition products. In the case of CCE, strong signals in the $\text{C}=\text{O}$ and carbonate region (1750 to

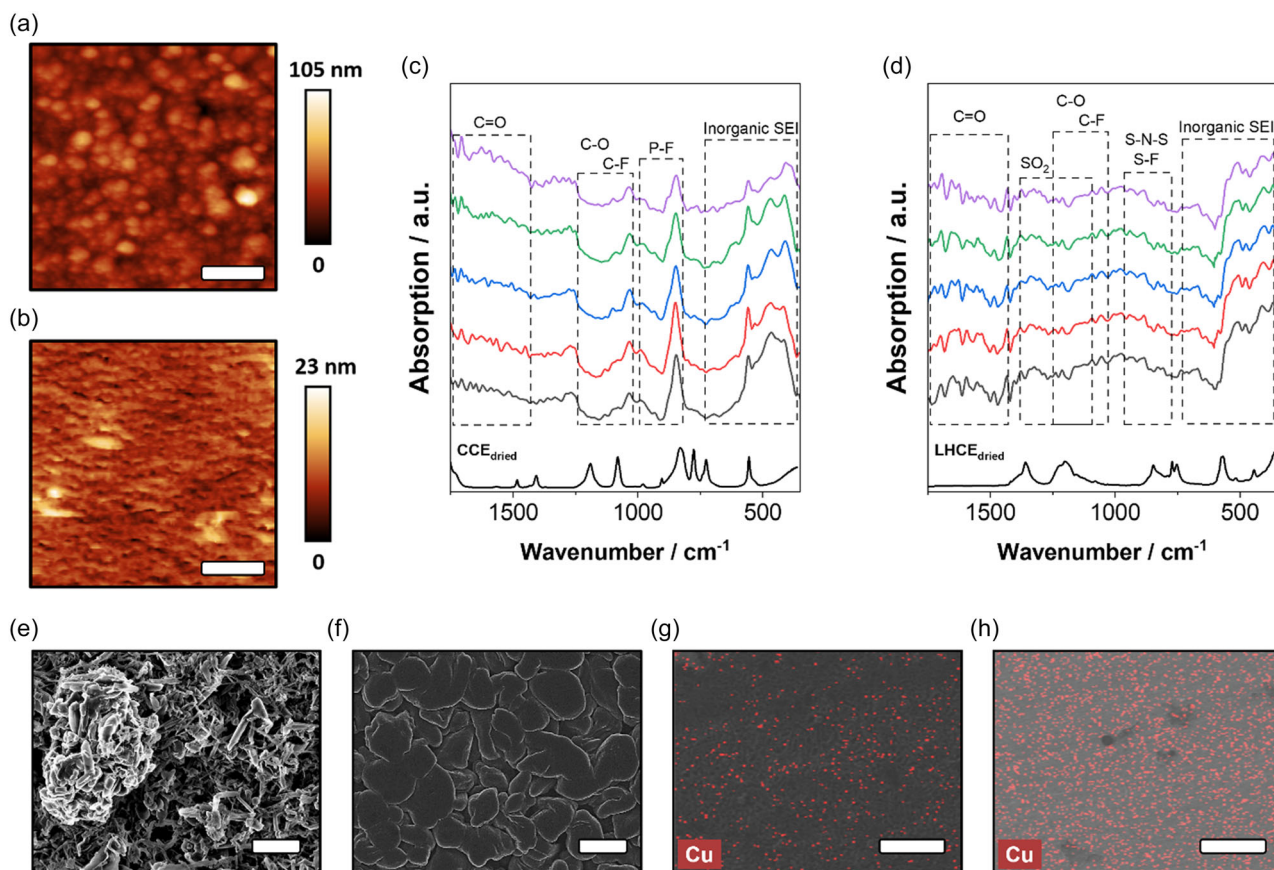


FIGURE 5 | AFM images of the SEI on a sputtered copper electrode after a 12 h potential hold at 0.05 V vs. LiLi⁺ with (a) the CCE and (b) the LHCE. SINS absorption spectra of the CCE-derived (c) and LHCE-derived SEI (d) on Cu at five different points, each with the dried electrolyte as reference (measured via ATR-FTIR), showcasing the homogeneity of the formed interphase after the potential hold. SEM images of Li deposition morphology (1 mAh cm⁻² of plated Li at 1 mA cm⁻²) with (e) the CCE and (f) the LHCE. SEM images of the Cu electrodes with included EDX measurements (Cu only) after complete Li stripping (until 1 V vs. LiLi⁺ at 1 mA cm⁻²) with (g) the CCE and (h) the LHCE. Scale sizes: 500 nm (a,b), 5 μm (e,f), 20 μm (g,h).

1400 cm⁻¹) are observed, consistent with organic carbonate decomposition products (such as LiEDC) reported in previous studies (Figure 5c) [33, 44, 46]. With the LHCE, broad bands in the range of 1400–800 cm⁻¹ are observed, which can be attributed to FSI⁻ fragments, in particular SO₂ asymmetric (1370 to 1300 cm⁻¹) and symmetric stretching (1300 to 1150 cm⁻¹) as well as S–F and S–N–S stretching features [47]. In addition, the bands between 1150 and 1000 cm⁻¹ indicate alkoxide formation and solvent decomposition (Figure 5d).

The effectiveness of the SEI in protecting Li metal, particularly the homogeneity of the layer and its formation kinetics, closely impacts the electrochemical deposition and dissolution morphology of Li metal on Cu. As a result, the observed fast anion-derived SEI formation induced by the LHCE leads to compact globular-like Li deposits on the Cu electrode (Figure 5f), while a mossy-like Li deposition morphology is observed with the organic carbonate-based electrolyte (Figure 5e). Subsequently, the inhomogeneous Li deposition morphology with the CCE leads to inefficient Li dissolution, as a considerable portion of the Cu electrode remains covered with Li agglomerates (here: dead Li), as revealed by EDX measurements (Figure 5g) [48, 49]. In contrast, almost no Li deposits remain on the Cu electrode of the LHCE-based cell after the Li electrodisolution step (Figure 5h), highlighting the high Li CE due to a substantial reduction in dead Li formation and more effective electrode protection.

3 | Conclusion

In summary, this study demonstrates clear differences in Li metal protection ability between a standard organic carbonate-based formulation (CCE) and a baseline localized LHCE via complementary operando and ex situ techniques. In particular, ellipsometry combined with a modified electrochemical cell setup provides real-time, quantitative tracking of the SEI growth, allowing for direct correlation of growth kinetics with electrochemical features. After refining the optical parameters of the components, a potentiodynamic protocol enables the determination of distinct SEI growth modes as a function of the electrolyte chemistry. With the LHCE, a rapid SEI formation is observed at the reductive decomposition peak of FSI⁻ at 1.5 V vs. LiLi⁺, followed by a strongly suppressed growth rate down to 0.05 V vs. LiLi⁺. In contrast, the organic carbonate-based electrolyte provides ineffective protection of the sputtered Cu electrode, as an accelerated SEI growth rate is observed during the cathodic potential sweep, accompanied by a roughly sixfold higher current density than in the LHCE-based cell. A 12-h potential hold experiment at 0.05 V vs. LiLi⁺ further highlights the differences in the protecting ability of the electrolyte-derived interphases. While the thickness of the LHCE-derived SEI already stabilizes at 32 nm (d_{rough} , 6 nm) and only partially dissolves down to 21 nm (d_{rough} , 1 nm) upon OCP, the organic carbonate-based interphase grows up to a thickness of 75 nm (d_{rough} , 11 nm).

and contracts to roughly 41 nm (d_{rough} , 3 nm) under the open circuit conditions. Further discoveries include a decrease in surface roughness during nongrowth regimes (OCP or at ≥ 1 V vs. Li/Li+), highlighting SEI compaction likely due to dissolution and reorganization of organic-rich SEI components. Ex situ SINS and SEM experiments further confirm the more homogeneous, less rough nature of the SEI with the LHCE, which ultimately leads to a denser Li deposition morphology and more efficient Li stripping compared to the organic carbonate-based system. The study further highlights the effectiveness of FSI[−]-derived SEI formation in terms of reaction kinetics, protective abilities, and the promotion of efficient Li electrodeposition/dissolution and identifies operando ellipsometry as a powerful analytical tool for elucidating SEI growth modes through real-time correlation with electrochemical responses.

4 | Experimental Section

4.1 | Materials

The materials used for the electrolyte formulations in this study are summarized in Table 1.

Li metal rods (Ø13 mm), sourced from Sigma–Aldrich, were used to fabricate the Li electrodes (200 μm thickness) via an in-house built Li pretreatment method, as in our previous studies [10, 14, 31]. Cu and Al foils were cleaned with ethanol and dried together with the used separator Celgard 2325 (Coin cells) and Whatman grade GF/D (Swagelok cells) at 60°C under reduced pressure before storing them in an argon-filled glovebox. The Cu electrodes (for SINS and ellipsometry) were fabricated with sequential DC sputtering onto a fused silica substrate (University Wafer, U01-210714-1: Fused Silica JGS2). First, a thin layer of Ti (30 nm) was DC sputtered (3×3 " TORUS Mag Keeper sputter guns) as an adhesion layer at a power of 200 W for 2 min with a deposition pressure of 4 mTorr (0.53 Pa) of argon. Cu (300 nm) was then sputtered at 400 W for 5 min at a pressure of 4 mTorr (0.53 Pa) of argon. Substrate temperature during deposition was 25°C.

4.2 | Ionic Conductivity Determination Measurements

The ionic conductivity was determined by electrochemical impedance spectroscopy using a 96-channel impedance setup equipped with custom-built electrodes. Seven hundred fifty microliters of

liquid electrolyte was used for each cell, and the cells were sealed gas-tight in an argon-filled glovebox to avoid air exposure. Impedance spectra were collected at 20°C with a potentiostat connected to an 8×12 multiplexer (Metrohm Autolab). The cell constants were determined using a 0.01 KCl solution, and the spectra were recorded from 50 Hz to 20 kHz. The data was analyzed using an equivalent circuit consisting of the electrolyte's Ohmic resistance R_s in series with a parallel R_p -CPE element. The ionic conductivity was eventually calculated via the cell constant and the extracted electrolyte resistance.

4.3 | Electrochemical Measurements

Galvanostatic cycling experiments were conducted in a two-electrode coin cell (CR2032). One-layer Celgard 2325 separator (16 mm) soaked with 16 μL of liquid electrolyte was sandwiched between two lithium metal electrodes or between a Li metal electrode and a copper foil. Galvanostatic cycling was performed on a Maccor Series 4000 battery cycler at 20°C using the specified current densities and cycle durations. To determine the average CE, the following lithium reservoir method was used: As a preconditioning step, 5 mAh cm^{-2} of Li metal was plated onto the Cu electrode and stripped (until 1 V) at 0.5 mA cm^{-2} . Subsequently, a 5 mAh cm^{-2} reservoir of Li metal was established on the Cu electrode. For 10 iterations, 1 mAh cm^{-2} of Li metal was plated and stripped at 0.5 mA cm^{-2} after which the remaining Li metal reservoir was stripped from the Cu electrode until 1 V [27]. For the ex situ SINS, single-layer pouch cells were assembled (sputtered Cu/Li) in laminated poly-foil pouches (5.5×6.0 cm) and fitted with Ni tabs [44]. The Celgard 2325 separator was soaked with 10 μL of liquid electrolyte. The voltage was swept from the open circuit voltage (OCV) to 0.05 V and held at that voltage overnight at 20°C using a Bio-Logic VMP3 workstation. Cyclic voltammetry (CV) was performed in a three-electrode Swagelok cell with an additional Li metal electrode serving as the reference electrode and two Whatman glass fiber separators soaked with a total of 200 μL electrolyte. The reference CV measurement was carried out using a Bio-Logic VMP3 workstation with a scan rate of 0.025 mV s^{-1} at 20°C.

4.4 | Operando Ellipsometry

An ellipsometer by J. A. Woollam (M2000VI) was utilized for the ellipsometry measurements.

For the operando experiments, a three-electrode electrochemical cell provided by J. A. Woollam was modified as follows (Figure 6): For the bottom of the cell, a rigid polyether ether ketone (PEEK) cover with an aluminum foil was added, which could be screwed to the cell to allow for better portability of the cell between the glovebox and the ellipsometer. The aluminum foil toward the working electrode served as a current collector during the electrochemical measurements. In addition, the tube attachments (Figure 6) were replaced with screws, from which two were punctured with a stainless steel wire to connect the Li counter and reference electrodes.

1. After drying of the cell components at 60°C, the windows and the cell mount were attached to the casing, and the cell components were introduced to the glovebox.

TABLE 1 | Chemicals used in this study.

Chemical	Purity, %	Manufacturer
LiFSI	>99.9 ^a	E-Lyte
DME	>99.9 ^a	E-Lyte
TTE	>99.9 ^a	E-Lyte
LiPF ₆	>99.9 ^b	Solvionic Co.
EC	>99.9 ^b	Solvionic Co.
EMC	>99.9 ^b	Solvionic Co.

^a(H₂O < 10 ppm).

^b(H₂O < 20 ppm).

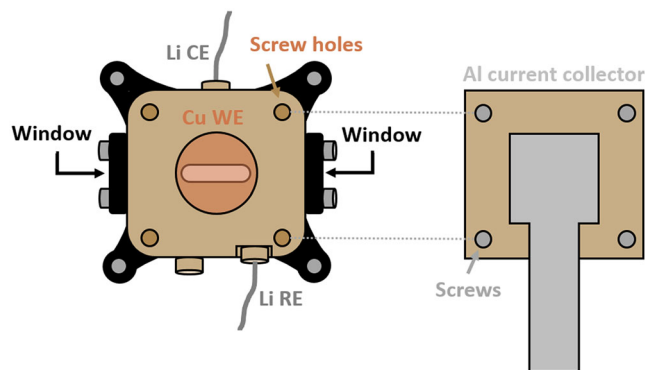


FIGURE 6 | Schematic of the modified optical cell for the operando ellipsometry experiments with CE, counter electrode; RE, reference electrode; and WE, working electrode.

2. The Li metal reference electrode (10 mm) was added, and the stainless steel wires were tightly screwed to the cell housing.
3. The cell was turned upside down, and the sputtered Cu electrode was placed on the bottom of the cell and fixed with the rigid PEEK sheet and four screws.
4. After rotating the cell back, the liquid electrolyte was added (~1 mL), and the Li counter electrode with a PEEK spacer was placed on top. The upper window was added, the cover tightly screwed to the cell case, and the cell transferred to the ellipsometer with the liquid cell-specific mounting plate.

The angles of the light source and detector were fixed at 70° , and optical data were collected every 5 s. The beam diameter was 2 mm, resulting in a projected footprint diameter (ellipse) of ~ 5.8 mm on the sample (at 70°). The Complete EASE software by J. A. Woollam was used to record and analyze data. The surface roughness was modeled as an effective roughness layer consisting of a bulk layer and the liquid electrolyte (50% filling ratio), with the thickness d_{rough} . The potential control and recording of the current response were done with a Bio-Logic VMP3 workstation. Between the stated potential holds, the potential was swept at a scan rate of 1 mV s^{-1} .

4.5 | Infrared Spectroscopy

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded inside a N_2 -filled glovebox (818GBB/Plaslabs). The measurements were performed on a Shimadzu IRTracer-100 spectrophotometer equipped with a single-reflection ATR sampling accessory (PIKE Technologies) and an extended-range diamond ATR. The FTIR spectra were recorded in a range of $4000\text{--}375 \text{ cm}^{-1}$ with a spectral resolution of 4 cm^{-1} and averaged over 40 scans. SINS measurements were conducted with a Neaspec neaSCOPE microscope housed at the Advanced Light Source (ALS) at beamline 2.4 using PtIr-coated AFM probes from Neaspec. The sputtered Cu was harvested by cutting the single-layer pouch cells in an argon-filled glovebox. The electrodes were not washed to avoid removing the organic part of the SEI. The microscope was housed in an environmental chamber continuously purged with N_2 , and measurements were performed at $\text{O}_2 < 20 \text{ ppm}$ (PureAire, Trace Oxygen Analyzer 0–1000 ppm). The data were recorded in tapping mode, with a tapping amplitude of 50–60 nm, in the range of $2000\text{--}250 \text{ cm}^{-1}$, at a spectral resolution of 8 cm^{-1} .

Near-field IR nano-images, “white light images,” were collected simultaneously with the AFM topography measurements by fixing the interferometer mirror position to the most intense feature of the interferogram and recording the resulting second harmonic of the optical amplitude value at each spatial pixel. Reference spectra were taken on an Au electrode. The second harmonic of the imaginary component of the complex-valued nano-FTIR spectra normalized to Au was chosen as the nano-FTIR absorption. This is because, in these strong resonant cases, the imaginary part most closely matches FTIR absorption databases. Spectra were processed using neaPLOT (neaspec), and the AFM images were processed using Gwyddion.

4.6 | Li Deposition Morphology Characterization

SEM and EDX measurements were performed on a Zeiss Crossbeam 550 workstation using a Schottky field emission gun with a Gemini column as the electron source. Prior to the investigations, the harvested Cu electrodes were gently washed with 1 mL of DME (LHCE) and EMC (CCE) and dried for 30 min under vacuum. The electrodes were transferred to the device in a vacuum-sealed container to avoid contact with the atmosphere. Images were taken at accelerating voltages of 3 kV (SEM) and 4 kV (EDX) using an in-lens secondary electron detector. The lens' aperture was $20 \mu\text{m}$ and the working distance 3.0 mm (SEM) and 4.0 mm (EDX).

Author Contributions

Dominik Weintz: conceptualization, methodology, investigation, data curation, writing – original draft, writing – review and editing. **Andrew Dopilka:** investigation, methodology. **Austin D. Ready:** investigation, methodology. **Monica J. Theibault:** investigation. **Robert T. Hinz:** investigation. **Robert Kostecki:** supervision, writing – review and editing. **Martin Winter:** supervision, writing – review and editing, funding acquisition. **Isidora Cekic-Laskovic:** funding acquisition, project administration, resources, writing – review and editing.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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