Vibrational Spectroscopy Insight into the Electrode|electrolyte Interface/Interphase in Lithium Batteries

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Lithium-ion batteries (LIBs) have transformed the use of mobile electronics and storage technologies. Alongside advances in materials, an in-depth understanding of the interfacial phenomena and interphase formation mechanisms in LIBs is crucial. Interphases are widely recognized as the most important and the least understood components of LIBs and play a direct role in defining cell performance, cyclability, and safety. This article presents a review of recent developments in vibrational spectroscopy techniques of Raman, infrared, and sum-frequency generation spectroscopies to probe the fundamental aspects of interphases on the anode and cathode of LIBs. First the vibrational spectroscopy techniques and their relevant technical considerations for interphase characterization are briefly introduced. In the next step, the latest studies on the fundamental properties, composition, and structure of interphases employing vibrational spectroscopy techniques are presented. This review focuses on in situ/operando investigations; however, post-mortem studies are also discussed briefly.

1. Introduction

Lithium-ion batteries (LIBs) are critically important for all modern technologies, including portable electronic devices and electrochemical energy storage systems. Several decades of intense research have resulted in the development of novel battery designs with radical improvement in theoretical capacities.[1–2] However, neither state-of-the-art nor novel cell chemistries deliver the anticipated outcomes to achieve practical capacities close to the theoretical ones.

The achievable practical capacities, performance, cycle life, and safety in LIBs are primarily limited due to the side reactions at the electrode–electrolyte interface. As shown in Figure 1a, the side reactions form a new phase known as interphase: solid electrolyte interphase (SEI) on the anode and cathode electrolyte interphase (CEI) on the cathode.[3,4]

Interphases are widely recognized as the “most important and the least understood” components of LIB cells[5] because of their determining role in LIBs function. SEI and CEI are not part of the original cell components; however, their chemical and transport characteristics determine the battery performance and cyclability. The interphase structure constitutes an active layer with mixed organic and inorganic chemistries due to the electrolytes’ smaller electrochemical stability window (ESW) than the operating potentials of LIBs (Figure 1b).

The interphase location in a LIB cell is fundamentally crucial because electrons and Li-ions combine at the SEI and CEI to be stored in the electrode via different mechanisms. Therefore, interphases are recognized as Li-ion conducting phases that are simultaneously electronically insulating to protect electrolyte components from electrochemical decomposition leading to capacity loss.[6–10]

However, the functional importance of the interphases to guarantee a long cycle life of LIBs by preventing electrolyte decomposition imposes a heavy toll on the practical capacity of LIB cells. The interphase formation evolves with the consumption of electrolyte components and loss of active Li inside the cell, which lead to irreversible capacity loss, especially in the initial cycles. Interrupting the Li-ion transport and slowing down the cell kinetics by introducing a Li-ion resistance phase is another dramatic effect of the interphase on cell performance.

1.1. Designing Interphases

A basic understanding of the mechanism of the interfacial reactions is a critical requirement for the intention of designing interphases with better performance, cycling stability, and safety feature. Unfortunately, this requirement has not been fully achieved, and our knowledge about the fundamental aspects of interphase is not sufficient to reach this goal.[3,5] As a consequence, the identification of proper materials for the interphase of LIBs remains dominated by trial-and-error approaches. These approaches include developing new electrolyte formulations, mainly through incorporating film-forming additives[11–14] and artificial interphase design by reassembling different materials on the surface of the electrodes.[15–17] In both approaches, an ideal interphase design requires considering parameters of i) high ionic conductivity, ii) low electronic...
conductivity, and iii) high chemical and mechanical stability. As a result, the formed interphases suppress the parasitic redox reactions on the electrodes by producing a homogenous and mechanically stable interphase.\cite{18,19}

Nevertheless, improving our understanding of the interfacial phenomena toward the goal of designing efficient and stable SEI and CEI has been an active field of research. Capturing the dynamic nature and complex compositions of interphases has been a permanent challenge toward this understanding.\cite{8,20-26} Significant efforts have been focused on overcoming this challenge by developing experimental spectroscopy techniques to elucidate the interfacial chemistry in LIBs.\cite{25,27-41} These efforts have led to an improved understanding of SEI and CEI by introducing models on the structure/property relation of the interphases. The current models suggest that the interphase is a two-layer mosaic structure consisting of outer organic and inner inorganic species, as schematically depicted in Figure 1.\cite{42-44} For more information on different aspects and developed models on the interphase of LIBs, we refer to the review by Tripathi et al.\cite{45} These models increased our understanding of the parameters linked to the interphase structural properties, but the state-of-the-art experimental techniques still face challenges to fully verify these models due to technical and fundamental restrictions.\cite{3,5} Fundamentally, the interphase’s inhomogeneous chemical distribution and complex behavior make detailed analysis difficult for any experimental technique. Also, an interphase is a dynamic medium that actively evolves under different electrochemical conditions. This implies prioritizing developing strategies to address the interphase functional properties under real working conditions.\cite{45-46}

Vibrational spectroscopy is a fast and reliable technique for interphase investigation by providing invaluable compositional and reactivity information about the interfacial species in LIBs. The chemical species are identified in vibrational spectroscopy based on their characteristic vibrational and energy modes.\cite{47} Furthermore, vibrational spectroscopy can be relatively easily combined with electrochemical techniques for in situ/operando investigation of different interphases. This review is focused on crucial issues of the chemical fingerprint, structural information, molecular interaction, and orientation in the interfacial region between the electrodes and electrolytes in LIBs. Many of the studies addressed in this review concentrate on experimental approaches to investigate the nanometric thin interphase and interfacial phenomena while minimizing the role of electrolytes and electrodes in the signal. This review prioritizes the in situ/operando techniques to resemble the electrochemistry in LIBs. However, post-mortem analysis studies are also covered to a certain extent. The recent developments in the experimental setups and understandings of interphases in LIBs employing infrared (IR), Raman, and sum-frequency generation (SFG), as the three most crucial vibrational spectroscopy techniques, are covered.

2. Raman Spectroscopy

2.1. Background of Raman Spectroscopy: Conventional Raman, SERS, SHINERS, and TERS

Raman spectroscopy is a well-established technique in the battery community for characterizing electrode materials or electrolytes.\cite{48-53} In addition, Raman spectroscopy has a high sensitivity under specific conditions for trace analysis and is a nondestructive technique that offers a straightforward solution to perform operando investigations of LIB’s components. Also, Raman allows quick generation of data and, compared to other techniques like X-ray photoelectron spectroscopy (XPS), sample preparation is straightforward.\cite{49} Whereas the investigation of electrode materials is a standard routine in LIBs studies, addressing interphases using classical Raman spectroscopy is a challenging task. The typical interphase thickness in LIBs is in the nanometer range containing a trace amount of different species compared to the electrodes.\cite{46,54} Moreover, combining the significantly negligible amount of the interphase species with their low Raman-scattering cross-section and inefficient Raman scattering phenomena in classical Raman, very low
peak intensities of interphase species are expected, making any reliable characterization nearly impossible.\(^{[48-49,55]}\)

However, several advanced Raman spectroscopy techniques have been developed over the last decades, which provide a promising platform for interphase investigation in LIBs. With surface-enhanced Raman spectroscopy (SERS), the detection sensitivity for surface species can be increased significantly (up to \(10^7\)), allowing even the detection of single molecules.\(^{[49]}\) As shown in Figure 2, SERS is based on plasmonic active materials like gold or silver, used as substrates for the investigated samples. Excitation of these substrates leads to the creation of a plasmonic field which significantly enhances the Raman intensities of adsorbed species.\(^{[46,56-59]}\) SERS is a powerful technique; however, due to its dependence on plasmonic active substrates, the number of applications in LIBs is limited.\(^{[55,60,61]}\)

Tip-enhanced Raman spectroscopy (TERS) technique is a SERS variant that uses a sharp tip made of SERS active metal (gold or silver) as a plasmonic antenna (referred to as hot-spot).\(^{[55,62-64]}\) In TERS, during the measurement, the tip moves to close proximity to the substrate with the help of the feedback control mechanism of a scanning probe microscope (SPM). While the tip is fixed in this position, the laser of the Raman is focused on the tip apex to create a plasmonic resonance enhancement of the species in the spatially confined area below the tip. As the created plasmonic field is nanometric confined, TERS offers a plasmonic enhancement with an excellent spatial resolution of the surface species. Furthermore, SPM allows TERS mapping, in which the SPM tip or sample moves in lateral directions to simultaneously provide semitopographical and TERS spectra of the interfacial species with nanometric resolution.\(^{[46,62,65]}\)

A great advantage of TERS is that it can theoretically be used on every surface and does not rely on gold or silver substrates, making this technique suitable for battery research. However, the total Raman scattering is still weak due to its high spatial resolution, leaving only molecules with a large Raman cross-section as suitable samples for TERS experiments.\(^{[62,63]}\) Also, controlling crucial parameters like tip geometry and shape, coating, and laser-tip interaction between the confocal microscope and SPM system is necessary, making the requirements for a reliable experimental setup challenging.\(^{[60,61]}\)

A very beneficial SERS variant is shell isolated enhanced Raman spectroscopy (SHINERS). In SHINERS, nanoparticles (NPs) made of plasmonic active materials, like gold or silver, are introduced to the surface of the sample to function as plasmonic hotspots.\(^{[55,59,66]}\) To ensure the isolation of the NPs and prevent the catalysis of unwanted reactions on the NPs’ surface, a SiO\(_2\) or Al\(_2\)O\(_3\) coating with optimum thickness is applied. Similar to the substrates used for SERS measurements, the NPs create an enhancing plasmonic field in their proximity in the presence of the electric field. SHINERS offers a straightforward sample preparation compared to equivalent TERS and is not limited to certain substrate materials. The inert NPs can theoretically be added to every sample, enabling the investigation of interphases on different electrode materials.\(^{[66]}\)

In contrast to TERS, SHINERS measurements do not require complex experimental setups.\(^{[60]}\) Nevertheless, the synthesis of the NPs is challenging, as many factors have to be considered. For example, the size of the NPs to ensure maximum enhancement is of high importance. Also, the thickness of the coating must be optimized not to be too thin to guarantee the NPs’ inertness, but also not to be too thick to prevent their signal enhancement capability.\(^{[60,65]}\) Furthermore, it has to be noted that the addition of NPs may change the surface of the investigated electrodes, influencing their electrochemical behavior. Moreover, controlling the NPs distribution and their inhomogeneity on the surface is another drawback of the SHINERS technique for interphase investigation.

In general, it can be concluded that all of the discussed techniques have various advantages, making them suitable for interphase investigation, but at the same time, they represent specific drawbacks, making their application and experimental setup challenging. One of the main challenges with all these techniques is acquiring a sufficient signal-to-noise ratio. Apart from that, even with signal enhancement of the advanced Raman techniques, identifying and separating peaks of the species with trace quantities and high ionic bonding state remains a challenge. In addition, it is necessary to have multiple excitation lasers at different wavelengths to ensure proper signal enhancement, as maxima of the excitation wavelength of the plasmonic active substrates differ depending on the analyte or the size of the NPs. Different lasers also might increase the likelihood of resonance Raman scattering of the species and enhance the signal-to-noise ratio. Also, by applying these techniques to batteries, challenges arise that are worth considering. One problem is the strong fluorescence of LiPF\(_6\) species and electrolyte decomposition products, which overlap with the Raman scattering signal, complicating any analysis of the obtained data.\(^{[67]}\) Moreover, especially in situ and operando measurements suffer from challenging experimental setups, as the modified electrode configuration might lead to increased overpotential or deviation from the actual electrochemistry cell.

2.2. Raman Spectroscopy for Interphase Characterization in LIBs

As mentioned before, classical Raman spectroscopy is not widely employed to characterize the interphases in LIBs due to its intrinsic limitations of low Raman scattering process from the nanometric thin interphases. However, SERS, TERS, and SHINERS allow the characterization of the interphases in LIBs.

2.3. SERS for SEI Investigation

In 2000 and 2002, Hong Li et al.\(^{[54]}\) and Guifeng Li et al.\(^{[68]}\) for the first time, reported the characterization of the SEI on Ag electrodes in LIBs by utilizing advanced Raman spectroscopy. Employing the SERS effect of the formed Li-Ag alloy, they were able to identify LiOH and Li\(_2\)CO\(_3\), as well as organic Li-compounds (ROCO\(_2\)Li), as components of the formed interphase in a 1 M LiPF\(_6\) EC/DEC (EC: ethylene carbonate, DEC: diethyl carbonate; 1:1) and a 1 M LiClO\(_4\) PC/DMC (PC: propylene carbonate, DMC: dimethyl carbonate; 1:1) electrolyte. In more recent studies, investigations of the interphases on more relevant electrode materials using SERS were reported. To investigate the SEI on silicon anodes, Piernas-Muñoz et al. and Ha et al. employed different experimental methods to achieve signal enhancement. Piernas-Muñoz et al.\(^{[58]}\) used
electrodeposition to introduce Au NPs to the surface of a silicon electrode. This method enabled to track the presence of organic lithium compounds and other olefinic molecules as the decomposition products of the electrolyte (1.2 m LiPF$_6$ in EC/EMC (EMC: ethyl methyl carbonate; 3:7)) at the interphase. Moreover, SERS caught organophosphates on the SEI, recognized as a decomposition product of LiPF$_6$. Using the same electrolyte, the presence of organo-lithium species within the SEI on silicon electrodes was also confirmed by the study presented by Ha et al.\[59\] In their investigation, however, signal enhancement was not achieved using Au NPs as in the previous approach. Instead, a roughened Cu-mesh, topped with ≈30 nm of amorphous silicon was used as a signal amplifier (Figure 3). With their setup, Ha et al. were able to in situ track the changes in the interphase as well as the silicon electrode at different cell voltages.

In 2016, Liu et al.\[57\] reported on the preparation of SERS active graphene electrodes for Li-air batteries. To achieve the SERS signal enhancement, Au nanodots were introduced to graphene electrodes via a mask-sputtering technique. Using their experimental setup, Li$_2$O$_2$ and Li$_2$CO$_3$ were identified as the main interphase products on the investigated electrode in a 1 m LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) in dimethyl sulfoxide (DMSO). In contrast to the studies presented so far, relying on adding a SERS active material to achieve signal enhancement, Tang et al.\[56\] used the properties of lithium nanostructures, prepared by electrochemically roughening or electrodeposition on copper electrodes, to investigate the formation of interphases on lithium metal (Li-metal) electrodes in contact with different carbonate-based electrolytes. With their innovative approach, Tang et al. showed that the

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Figure 2. Presentation of the four Raman techniques’ working principles, discussed in this review in a setup. Schematic a) shows the conventional Raman approach without any additional applications to enhance Raman scattering, which results in low Raman intensities. The SERS approach is shown in schematic b). For signal enhancement, the sample/working electrode is placed on an Au-, Ag-, or Cu-substrate. Note that the working electrode is designed significantly thin to ensure proper SERS enhancement. In schematic c), the TERS approach is shown. For signal enhancement, an Au-tip is moved to the closest proximity of the investigated electrode. The displayed schematic features side-illumination and the use of a scanning probe microscope (SPM) to control the Au-tip. Schematic d) shows the SHINERS approach. For signal enhancement, coated Au- or Ag- NPs are introduced onto the surface of the sample. The use of the SERS, TERS, or SHINERS approach leads to significant signal enhancement.
addition of 50 ppm H_2O as an additive to the solution of 1 m LiPF_6 in PC and EC/DMC (2:1) leads to the formation of mostly inorganic interphase comprising of LiOH, LiF, and Li_2CO_3. In a similar approach, Schmitz et al. used lithium metal deposition on copper electrodes. They detected the formation of an interphase comprising of Li_2CO_3, Li_2C_2, and different semicarbonates as a decomposition product of the electrolyte (EC/DEC, 3:7, 1 m LiPF_6). Moreover, gas analysis by mass spectrometry was utilized to ensure that the formation of Li_2C_2 derives from electrochemical processes and not from laser-induced decomposition processes of interphase components. In a more recent study from 2020, Mozhzhukhina et al. used operando SERS to investigate double layer charging effects and the formation of an early SEI in a 1 m LiPF_6 EC/DEC (1:1) electrolyte. They observed that upon charging, the concentration of Li-ions in the proximity of the SERS-substrate surface increases, indicating the formation of a double layer. In addition, during further charging, the formation of Li_2CO_3 and LiF species were detected. While it was possible to catch Li_2CO_3 directly, the formation of the Raman inactive LiF was detected indirectly. During the charging of the cell, a decrease in the intensity of the electrolyte peaks was observed. The authors stated that this effect is due to the formation of LiF on the electrode surface, increasing the distance between the SERS substrate and the electrolyte molecules, which subsequently leads to decreased signal enhancement. Moreover, the decomposition of HF and H_2O impurities within the electrolyte were tracked using gas analysis.

2.4. SERS for CEI Investigation

CEI formation on positive electrode materials was also investigated using SERS. In 2019 Chen et al. reported an operando investigation of the CEI formed on binder-free NMC111 in a 1 m LiPF_6 in EC/DMC (1:1) electrolyte. A monolayer from Au nanocubes was added onto the investigated surface for signal enhancement. Recorded Raman signals in combination with DFT calculations indicated the formation of a mostly organic interphase and an ether-linked polymer comprising of the electrolyte solvents.

2.5. TERS for SEI Investigation

Although TERS is a powerful technique, studies of interphases in LIBs are relatively rare. To the best of our knowledge, only Nanda et al. reported a TERS-based study on the SEI formed on silicon anodes in a carbonate-based electrolyte (1 m LiPF_6 in EC/DEC (1:1)) up to this date. Using TERS, Nanda et al. showed that the composition of the SEI undergoes ongoing changes during cycling (Figure 4). While lithium ethylene dicarbonate (LEDC) and polyethylene oxide (PEO)-like oligomers dominated the SEI after the initial cycle, mostly LEDC species were detected after the 5th cycle. Another change in the interphase composition was observed at higher cycle numbers, as carboxylate and fluorinated lithium-phosphate species were identified as the main component of the SEI after 20 performed cycles. Besides the reported changes in the interphase composition, a significant increase in the interphase thickness was observed with ongoing cycling. Based on these results and using the high spatial resolution mapping offered by TERS, the authors proposed the formation of a nanomosaic-multilayer interphase on the silicon electrode.

2.6. SHINERS for SEI Investigation

Implementation of SHINERS for interphase investigations in LIBs is gaining momentum due to the advantages in sample preparation, simplicity, and significant signal enhancement. In 2014 Hy et al. reported in situ SHINERS investigation of the SEI formation on copper and silicon electrodes in a 1 m LiPF_6 in EC/DEC (1:1) electrolyte. Due to the signal enhancement of the utilized Au NPs, Li_2CO_3 was identified as one main component of the SEI. In addition, they analyzed the effect of vinylene carbonate (VC) on the formed SEI composition. The recorded SHINER spectra showed signals assigned to R=O and C=C stretching of semicarbonates, indicating the polymerization products of VC. Also, based on the fact that these signals were observed above the reduction potential of EC, it was stated that the decomposition of VC occurs before the decomposition of the main electrolyte. Gajan et al. investigated the interphase formation on Sn-electrodes in LIBs in contact with carbonate-based electrolytes (1 m LiPF_6 in EC/DEC (1:1)). Bipyramidal Au NPs were implemented to increase the signal enhancement, and lithium ethylene monocarbonate (LEMC) and diethyl 2,5-dioxahexane dicarboxylate (DEDOHC) were found as the main decomposition products of the electrolyte solvents, while...
the formation of Li₂CO₃ was not observed. Figure 5b shows the corresponding spectra of the operando investigation performed by Gajan et al. It can be seen that new spectral features appear upon reaching a potential of 1.6 V, assigned to the formation of DEDOHC and LEMC species, highlighted by the red and black dotted lines. Moreover, the dissolution of before-formed DEDOHC into the electrolyte at low reduction currents was captured utilizing SHINERS.

Using Au-SiO₂ core-shell NPs for in situ SHINERS investigations, Cabo-Fernandez et al. reported the formation of a mostly organic SEI on carbon-coated Zn₀.₉Fe₀.₁O electrodes. ROCO₂Li, ROLi, RCO₂Li, and PEO-type species were identified as components of the investigated interphase, derived from the decomposition of the carbonate-based electrolyte (1 m LiPF₆ in EC/DMC (1:1)). Also, in agreement with the findings of Gajan et al., Li₂CO₃ could not be detected within the formed SEI.

In 2017, Galloway et al. reported the use of SHINERS to investigate the interphases on Li-metal and carbon-based electrodes in Li-O₂ batteries. To enable the use of SHINERS for the investigation of the highly reactive Li-metal, a technique was proposed by the group in which the NPs were cast on the optical window of the spectroscopy cell instead of introducing them directly to the surface of the electrodes. Using this method, they tracked the formation of Li₂CO₃ on the surface of the Li-metal electrode cycled with a carbonate-based electrolyte (1 m LiPF₆ in EC/DMC (1:1)). In contrast, electrodes cycled with
an ether-based electrolyte (0.25 M LiClO₄ in diglyme) did not show the presence of Li₂CO₃. On the surface of carbon cathodes, cycled with a DMSO-based electrolyte (0.5 M LiClO₄ in DMSO), Li₂O₂, Li₂O, Li₂CO₃, and LiOOH were identified.

2.7. SHINERS for CEI Investigation

While most of the published studies focus on SEI formation, Li et al. [73] used SHINERS for in situ investigations of the CEI on NMC811 and NMC111 cathodes in a 1 M LiPF₆ EC/EMC (3:7) electrolyte. They monitored the formation of LiF, as well as LiNiₓFᵧOz on the surface of the investigated electrodes. In addition, they showed that the higher Ni content of an NMC811 electrode results in the formation of LiF and LiNiₓFᵧOz at lower potentials compared to the NMC111 electrode. In 2014, Hy et al. [74] investigated the interphase formation on Li-rich Li[NiₓLi1−2x/3Mn2−x/3]O₂ (LLNMO) (0 ≤ x ≤ 0.5) electrodes in a carbonate-based electrolyte (EC/DEC, 1:1, 1 M LiPF₆). SiO₂-coated Au-NPs were added to the electrode to enhance the Raman signals of the formed molecules. Using this technique, the authors observed reversible peak shifting of the cathode active material upon charging and discharging. Moreover, the formation of Li₂O and Li₂CO₃ was detected during the charging of the cell. In addition, the anode was investigated, revealing the formation of LiOH·H₂O on the anode surface.

3. Infrared Spectroscopy

3.1. Background of IR Spectroscopy Techniques: ATR and Reflection Mode

Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy are similar but also complementary methods for the identification of species via vibrational excitation. Whereas Raman spectroscopy is based on inelastic scattering of the incident monochromatic light, molecular information in FTIR spectroscopy is gained via absorption of molecule-specific wavelengths in polychromatic light. This results in benefits like the prevention of fluorescence, sample heating, and sample decomposition when applying mid-IR light. [49,75,76] Both methods allow fast and relatively straightforward data generation, as described above. One advantage of FTIR spectroscopy over Raman spectroscopy is a higher sensitivity of 6 decades, [77] which allows the identification of trace amounts of analytes nondestructively. Especially the “fingerprint” range (1500–500 cm⁻¹), showing the molecule’s characteristic absorption bands, allows easy and reliable identification of the present IR-active molecules. Quantification of an analyte based on the Beer–Lambert law is also straightforward when measuring the transmission spectra of different known concentrations of a sample. Transmission measurements (Figure 6a) are universally applicable, as it allows simple sampling of gaseous, liquid, or solid-state materials. [78]

Nowadays, different methods of reflection spectroscopy have become increasingly popular for samples not suitable for conventional transmission, i.e., surface coatings. For example, specular reflection (Figure 6b) and reflection-absorption spectroscopy (RAS) are used for the identification of species and functional groups on surfaces. [79] Samples with a reflective surface can be investigated with specular reflection. Here, the IR beam focusing on the sample cannot penetrate and is reflected on the surface, thus offering exclusive identification of species on the sample’s surface. [78]

The identification of species in a thin surface film on a reflective support can be achieved with IR-RAS (Figure 6b). When focusing the IR beam onto the surface film, a fraction of the IR beam is directly reflected on the film’s surface, contributing via specular reflection. The other fraction of the IR beam is reflected by the reflective support. Thus, the incident light that penetrates through the surface film passes through it twice, leading to an increased absorbance sensitivity compared to simple transmission measurements. [79]

When rough surfaces are investigated, a variation of the specular reflection method can be applied: the so-called diffuse reflectance infrared FT spectroscopy (DRIFTS). In short, a fraction of the incident IR beam is regularly reflected (specular
reflectance) but also scattered diffusely in all directions at grain boundaries. As the spectra obtained with reflectance measurement are different compared to transmission spectra, transformation can be applied to convert reflectance measurements into absorption spectra.\[79\] However, a detailed depiction of this method is beyond the scope of this review.

Attenuated total reflection (ATR) FTIR can be utilized for liquid or solid-state samples that can be attached to an ATR crystal, making sample preparation obsolete. As shown in Figure 6c, the incident IR beam is totally reflected at the crystal-sample boundary, if the crystal's refractive index, $n_{\text{crystal}}$, is higher than $n_{\text{sample}}$ of the sample. The incident IR beam is reflected with an offset of one wavelength, resulting in the so-called evanescent wave traveling through the sample at a distinct penetration depth ($d_b$). Since the penetration depth is dependent on the wavelength of the IR light, a decrease in relative intensity with increasing wavenumbers is observed. This obliges an ATR correction when ATR and absorption spectra are to be compared. Depending on the ATR crystal geometry, the IR beam is reflected only once (i.e., in semispherical crystal) for better spatial resolution, or multiple times (i.e., trapezoid form) to enhance signal intensity. Additionally, the maximum penetration depth can be varied with the utilization of different ATR crystal materials offering a different refractive index, such as ZnSe, diamond, germanium, or silicon. Another advantage over transmission or reflection measurements is that with a variation of the incident angle $\theta$ in Figure 6c, the penetration depth of the evanescent wave can be varied, which offers the valuable opportunity to monitor deeper surface layers and thus record a depth profile of the sample.\[75–80\]

For electrochemical studies, subtractively normalized interfacial FTIR spectroscopy (SNI-FTIRS) can be used; therefore, an IR window is introduced in the cell housing where the electrode of interest is placed on the top. The reflection spectra $S$ are measured each at a base potential $E_1$ and a potential $E_2$ of interest, subtracted, and afterward displayed as a relative change in electrode reflectivity, as shown in Equation (1)\[81\]

$$\Delta S = \frac{S(E_2) - S(E_1)}{S(E_1)}$$  \hspace{1cm} (1)

An advantage of this method is that all absorption peaks that do not change with a potential change are canceled out. Furthermore, arising or decaying peaks, which are usually peaks relating to the species of the electrode–electrolyte interphase, are more pronounced in this method. Thus, background signals like bulk electrolyte signals are removed, the resulting spectrum is normalized and changes in the amount of different interphase species are highlighted. Also, this method can be used when spectra are acquired with internal or external reflection.

3.2. In Situ ATR-FTIR Spectroscopy in Battery Research

ATR-FTIR spectroscopy in battery research is already a known technique and has been applied for SEI and CEI investigations, especially in the last 25 years, as it allows low-cost instrumentation and a simple optical design. The surface sensitivity of the ATR mode enables in situ monitoring of the composition of the electrode–electrolyte interphase in a $\mu$m range as well as interfacial reactions with a time resolution down to milliseconds. However, to increase the signal-to-noise ratio, the time resolution is usually in a range of seconds to several minutes. One common cell setup for these measurements is the Kretschmann configuration (Figure 7a), where the electrode of interest is placed on the IR crystal with the electrolyte on top. This cell configuration allows interphase probing through the working electrode, while minimizing the signal from the bulk electrolyte.\[80,82\] Nevertheless, a major drawback of this cell setup is that the working electrode has to be IR transmissive, which does not apply to commonly used graphite electrodes. Also, an increased surface roughness with the cycle number of the used electrodes limits this configuration to a small number of cycles.\[80\]

There are also configurations reported with the working electrode surface facing the IR crystal to probe the SEI or CEI, which can be useful if the working electrode is not sufficiently IR permeable, as shown in Figure 7b,c. Here, the counter electrode and, if necessary, a reference electrode can be placed on top of or beside the working electrode. Thus, this cell design may not represent conventional battery cells, where the electrodes are facing each other.\[83\] Nevertheless, considering the small penetration depth ($\mu$m range), it is crucial to minimize the gap between the IR crystal and electrode surface. This is necessary to adequately probe the electrode surface instead of the electrolyte. It is also necessary to keep a certain space to ensure sufficient electrolyte contact and diffusion. The size of the IR crystal-electrode gap is of high importance since SEI/CEI species are predominantly formed by electrolyte or additive decomposition. Thus, the bulk electrolyte bands are likely to interfere.\[83–86\]

One another intrinsic challenges of the above-mentioned cell configurations is acquiring a sufficient signal-to-noise ratio, as the quantity of the arising surface species is much lower than the amount of bulk material. Also, identifying different arising surface species is very complex, as these are decomposition products of the bulk material. Hence, these are chemically very similar to the bulk material and other decomposition products. Increasing the signal-to-noise ratio can be done using, for instance, potential modulation like SNI-FTIRS or polarization modulation. When modulating the polarization, the bands of the bulk electrolyte can be filtered out, while the signal of the surface species is increased. This is done by subtracting the spectra measured at $S$ polarization from those measured at $P$ polarization, as the $P$ polarized light carries the most surface species information.\[87–89\] Additionally, as the interphase is considered a mosaic structure with organic and inorganic species, it is a mix of different materials with similar absorption bands. Consequently, separating the resulting peaks in the spectrum is worsened and distinguishing between different species is more complicated.\[82–84,86\] For instance, electrolyte solvents like EC and DMC, additives like VC, and decomposition products like polycarbonate, Li$_2$CO$_3$, LiEDC, or DEDOHC are based on the carbonate functional group, in which the characteristic bands occur very close to each other and may interfere in the obtained IR spectrum. To circumvent this issue, some studies use solvents without carbonate functional groups like THF.\[86,90,91\] Another drawback of in situ FTIR of interphases
is the lack of functional groups in some inorganic species, such as LiF, which hinders adequate detection in the probed interphase. Also, an intrinsic limit of single-reflection ATR-FTIR is the detection of interphase species in only one spot, as seen in Figure 7, whereas, for instance, multiple spots can be examined with a Raman mapping method. Unlike Raman, in situ interphase investigations LIBs with IR spectroscopy are also prone to interferences with contaminants, like atmospherical CO₂ and H₂O.

### 3.3. In Situ FTIR Spectroscopy for SEI Investigations

External reflection SNIFIRS was first introduced by Pons et al. in the early 1980s for in situ recording of adsorption of thiocyanate in an aqueous solution and tetrabutylammonium tetrafluoroborate in acetonitrile on Pt electrodes in the electrode–electrolyte interface and later in the late 1990s used by Winter et al. for investigations of the SEI in LIBs. The correlation of in situ SNIFIRS and galvanostatic charge/discharge measurements caught the reduction of the chloroethylene carbonate additive to CO₂ on graphite electrodes at 1.7 V versus Li/Li⁺. CO₂ was believed to be an intermediate product necessary for the formation of an effective protective SEI film. Indeed, in the presence of chloroethylene, the chemical decomposition of EC was prevented since no ethylene gas was detected. Furthermore, the SEI formed by chloroethylene also prevented EC cointercalation into the graphite.

In subsequent studies in the early 2000s, the SEI formation on graphite of the vinylene derivates acrylic acid nitrile, acrylonitrile, vinyl acetate, and 2-cyanofuran additives in a LiClO₄ in PC electrolyte was investigated. Since PC electrolytes are known to lead to graphite exfoliation, additives forming a polymeric SEI to protecting the graphite are of high interest. Employing SNIFIRS, the mechanism of the SEI formation via electropolymorization was confirmed and implementation of reduction products of the PC solvent molecules was suggested.

An in situ ATR-FTIR study in 1998 by Pyun et al. on the SEI on graphite anodes formed by LiPF₆ and LiAsF₆ in EC and DEC also revealed an SEI mainly composed of ROCO₂Li, Li₂CO₃, and the salt decomposition product LiₓPF₉ or LiₓAsF₉. The combination of in situ ATR-FTIR and cyclic voltammetry led to the observation that the SEI formed by the LiPF₆ containing electrolyte provides a lower passivity compared to the LiAsF₆ containing electrolyte, as the LiPF₆ reduction interferes with the compact sedimentation of ROCO₂Li.

Microscope SNIFIRS (external reflection) was also used later in 2010 by Li et al. to investigate the interfacial properties of an Sn-Co alloy anode during lithiation and delithiation, respectively. During lithiation and delithiation of the alloy electrode, the desolvation and solvation of Li-ions by EC and DMC were monitored and an SEI layer on the Sn-Co alloy electrode mainly formed by alkyl carbonate lithium (ROCO₂Li) species was determined.

A combined method of in situ Raman and FTIR microscopy was conducted by Pérez-Villar et al. for the study of interfacial...
reactions and the spectral characterization of the local structure of the electrodes on the same spot. Here, the in situ FTIR presented in Figure 8 showed the absolute intensities’ dependence of external reflection SNI-FTIRS on ion migration into and out of the thin electrolyte layer. Thus, it was successfully demonstrated that surface adsorption processes are not necessarily involved when the intensity of the absorption bands changes. Furthermore, the SEI formation on glassy carbon (GC) with VC and ethylene sulfate as electrolyte additives was investigated. It was found that ethylene sulfate forms a thicker SEI as VC, which may be responsible for a larger overall overpotential. In situ Raman spectra of the GC electrode showed slight shifts in the D-band and a significant shift in the G-band of the bulk electrode during charging. These shifts were also confirmed by in situ SNI-FTIRS spectra obtained from the exact same spot and were assigned to charge-transfer effects. However, random lithium insertion reactions were also mentioned as a plausible explanation for the observed shifts.

Hongyou et al.[83] investigated the initial charging process of graphite with in situ ATR-FTIR. By analyzing the solvent bonds, similar to the study by Li et al.[80] they found that the quantity of solvated and desolvated solvent molecules changed toward more desolvated solvent molecules in the early stage of the charging process (3.2–0.5 V vs Li|Li⁺). This reflects Li-ion intercalation without exfoliation (intercalation of Li-ions without desolvation). With ongoing charging, the formation of ROCO₂Li occurred at a voltage plateau of 0.5 V versus Li|Li⁺; however, ROCO₂Li is dissolved in the electrolyte. Below 0.5 V versus Li|Li⁺, ROCO₂Li is then deposited onto the graphite, participating as a main component in the SEI formation. At an electrode potential of 0.0001 V versus Li|Li⁺, the solvent molecules are decomposed and form a thick SEI, preventing efficient Li-ion intercalation. An improvement of the SEI was shown with VC as an additive, as it suppresses the ROCO₂Li formation by preventing electrolyte solvent decomposition.

In another study combining scanning electron microscopy (SEM), in situ SNI-FTIR by Lanz et al.[99] the results from Hongyou et al.[83] were confirmed. The combination of these techniques proved successful in tracking lithium intercalation into graphite and changes at the electrode/electrolyte interface. This was done by correlating the G and D bands of graphite observed with Raman spectroscopy and the change of free and Li-coordinated electrolyte molecules observed with FTIR.

It is well known that the SEI formation and composition are mainly dependent on the electrolyte, including additives and lithium salt. However, reductive decomposition of cyclic carbonates EC and PC were discussed overwhelmingly in the past. Shi et al.[100] also investigated Au (noncatalytic) and Sn (catalytic) as electrode materials with EC and DEC utilizing in situ ATR-FTIR to reveal electrode surface influence. It was found that with a noncatalytic surface, the state of ion solvation determines the electrolyte decomposition, leading to LEDC formation through EC decomposition and lithium propionate. However, a catalytic surface leads to the formation of DEDOHC through the reaction of DEC and EC during reduction and lithium propionate. Thus, the electrode surface dependence in regard to selectivity and overpotential of electrolyte reduction
also plays an important role in SEI formation. These findings are also supported by a study by Haregewoin et al.,[101] where DRIFTS was utilized for an in situ analysis of EC and DEC reduction products on Pt electrodes.

### 3.4. In Situ FTIR Spectroscopy for SEI Investigations on Si-Containing Electrodes

Yang et al.[102] investigated the SEI formation on electrodes with 60% silicon powder with in situ ATR-FTIR and found a one-electron reduction pathway at low current densities for EC and DMC decomposition, leading to ROCO$_2$Li, which reacts then with HF (from LiPF$_6$) to form CO$_2$. With ongoing deeper lithiation and during subsequent delithiation, the CO$_2$ is consumed and Li$_2$CO$_3$ is formed. Moreover, with ongoing lithiation and delithiation, the silicon particles undergo a volume change leading to cracks and a continuous SEI formation on the freshly exposed Li$_x$Si surface, deteriorating the cell performance. Generally, it is stated that most of the SEI material on silicon is formed during delithiation.

Shi et al.[80] used in situ ATR-FTIR to investigate the interface chemistry of SEI formation on a silicon wafer, as shown in Figure 7a. As in their previous study, they identified DEDOHC as the main SEI reduction product. Furthermore, LEDC was found on the lithiated silicon surface, which indicates ongoing electrolyte consumption on surface cracks and the subsequent surface passivation during charge/discharge cycling. The used setup with a variable incident angle of the IR beam allowed a variation of the penetration depth to distinguish between the bulk electrolyte and the near-electrode surface region. Thus, a depth profile of the SEI was monitored, showing the formation of DEDOHC on top of the native SiO$_2$ film, a transition of the SiO$_2$ and Si layers during lithiation, and LEDC formation. A schematic drawing of the results is shown in Figure 9.

### 3.5. In Situ FTIR Study of the Electrolyte Structure at the Electrode/Electrolyte Interface

The aim of a fundamental study by Cave et al.[103] with in situ ATR-FTIR was to investigate the ion-pairing dynamics and kinetics of interfacial ion speciation during Li-ion storage in TiO$_2$, as important influencing parameters on the cell performance. For example, with PC as electrolyte solvent, exfoliation in graphite electrodes and PC decomposition occurs, whereas with EC exfoliation is mitigated and a stable SEI is formed. This demonstrates the importance of understanding ion solvation at the electrode/electrolyte interface to increase cell performance. It was revealed in this work that Li-ions extracted from contact ion pairs are faster stored in the negative electrode than Li-ions, which need to be desolvated from the electrolyte solvent. Thus, it was suggested that manipulating the contact ion pairs in the electrolyte could have a significant influence on the rate capability, as shown in Figure 10.

### 3.6. In Situ FTIR Spectroscopy for CEI Investigation

Besides the investigation of the SEI in LIBs, the cathode and the CEI were also investigated with in situ FTIR in previously conducted studies. Burba et al.[104] were able to perform in situ transmission measurement of a very thin LFP cathode. In this setup, the electrodes are arranged next to each other between
two KBr windows instead of a stacked configuration, thus, the anode is not interfering with the transmission measurement. The configuration was used to follow the two-phase mechanism for insertion of lithium into FePO₄, which was previously followed during Li-ion extraction. With in situ transmission FTIR, the transition of FePO₄ into LiFePO₄ was tracked and the general ability of in situ transmission FTIR to evaluate electrode materials was demonstrated. However, LFP delithiation could not be investigated, as it resulted in Li-metal plating starting from the lithium anode and covering the KBr windows.

Joho et al.[105] investigated the oxidative decomposition of PC and EC/DMC with in situ SNI-FTIRS to analyze the decomposition mechanism on the cathode. As cathode materials like lithium cobalt oxide (LCO), lithium nickel oxide, or lithium manganese oxide (LMO) are not reflective due to their rough surface, polished nickel was used as a compromise, as it formed oxide on the surface. As a result, it was found that the oxidation of PC-based electrolytes results in much more CO₂ evolution than EC-based electrolytes, whereas there was no CO₂ evolution during DMC oxidation. PC oxidation was also investigated via SNI-FTIRS by Kanamura et al.[106] using a thin film (<1 μm) LCO electrode. It was found in this investigation that the choice of the lithium salt has a small influence on the oxidation rate of PC on the cathode, but not on the oxidation products. In a subsequent study by Matsushita et al.[107] cobalt oxide (Co₃O₄) impurities were incorporated into the LCO electrode material and different LCO phases arising during charge/discharge or preparation were evaluated. It was found that the surface state of the cathode and the amount of impurities influence the electrochemical properties and the oxidation process, i.e., the presence of Co₃O₄ lowers the interaction of the electrode and electrolyte. The setup used by Kanamura et al. was further used by Matsui et al.[108] to study the CEI formation and decomposition on thin LCO electrodes. In this work, polarization modulation FTIR (PM-FTIR) was used to amplify the absorption spectrum of the electrode surface. With in situ PM-FTIR, the oxidation of PC or EC/DEC formed a surface film at 3.75 V versus Li/Li⁺ and higher during charge was monitored. However, due to weak interaction between electrode and CEI, the CEI is decomposed and stripped off during discharge. This is supported by XPS depth profiling and atomic force microscopy (AFM) measurements, where the CEI was determined to be thicker and rougher for charged electrodes than for discharged electrodes. In a subsequent study by Matsui et al.[109] this phenomenon with EC/DEC was reviewed on thin LMO and LNMO. Again, the arising CEI was not stable and was stripped off during cathodic polarization. Nevertheless, it was shown that highly oxidized manganese (4.0–4.3 V vs Li/Li⁺) or nickel (4.6–4.8 V vs Li/Li⁺) has a catalytic effect on CEI formation. In the previous studies by Kanamura et al.[106] Matsushita et al.[107] and Matsui et al.[88,108] LiPF₆ and LiClO₄ were used as Li salt. It was concluded from these works that the salts and their decomposition products are also incorporated into the CEI besides organic species, but, according to Matsui et al.[109] the addition or single use of LiBOB could prevent the decomposition of PF₆⁻. Employing in situ SNI-FTIRS, the adsorption of LiBOB on LCO above 4.0 V versus Li/Li⁺ was proven, which is assumed to suppress continuous LiPF₆ decomposition. However, this also results in a thermodynamically destabilized electrolyte which may lead to earlier initiation of a thermal runaway. A study by Tremolet de Villers et al.[92] on NMC622 employing in situ ATR-FTIR investigated the voltage dependency of the EC/EMC electrolyte solution structure at the electrode surface, transition metal redox chemistry, and CEI evolution. The findings of previous studies on changes in the electrolyte structure near the electrode surface due to CEI formation was confirmed in this study. Above 3.8 V versus Li/Li⁺, the EMC signal decreased, and a CEI formation by EMC decomposition is suggested. Moreover, an NMC phase change from hexagonal to monoclinic during transition metal oxidation, a partial collapse of the NMC structure above 4 V versus Li/Li⁺, and bulk

Figure 10. Schematic depiction of a fast insertion into the negative electrode of Li-ions extracted from a contact ion pair and slow insertion of Li-ions extracted from a completely electrolyte-dissolved Li-ion in 1 M LiClO₄ in acetonitrile and corresponding salt (unpaired perchlorate at 1102 cm⁻¹ and paired 1134 cm⁻¹) and solvent (free nitrile at 2253 cm⁻¹ and Li-coordinated nitrile at 2276 cm⁻¹) peaks. Reproduced with permission.[103] Copyright 2021, American Chemical Society.
electrolyte signal are observed. It is assumed that during structural change, new pores arise, which are filled by the bulk electrolyte. The phase change also causes a higher electrical conductivity as well as a decreased penetration depth of the IR light by monoclinic NMC, which is reversed after the phase transition to hexagonal during discharge. Also, a growth of carbonate species on the surface was observed, which is shown in Figure 11. However, caused by the experimental setup (Figure 7c), it has to be considered that most of the electrochemical processes and Li-ion (de)insertion may have happened on the electrode side facing the porous Al current collector and counter electrode instead of the side facing the IR crystal.

4. SFG Spectroscopy

4.1. Introduction into SFG Spectroscopy

SFG is a powerful surface-specific technique that can reveal vibrational spectra of molecules and molecular structures at electrochemical interfaces. In LIBs, SFG can mainly help to reveal reaction mechanisms at the interface, which are the root cause of the SEI and CEI formation.

The selection rules in SFG spectroscopy are different from Raman and IR. A molecular vibration is active in SFG only when the center of symmetry at both macroscopic and molecular levels is broken. Considering this, the species at the electrode–electrolyte interface lack symmetry at the macroscopic level than the bulk species and are usually active in SFG. In addition, for the interfacial species to be SFG active, they must possess a net polar orientation.

SFG occurs when two femtosecond and picosecond lasers of fixed visible wavelength and tunable IR beam achieve temporal and spatial overlap to emit the SFG signal of the active molecular vibrations at the interface.

In the standard SFG measurement, the SFG intensity \( I_{\text{SFG}} \) is enhanced when the frequency \( \omega_{\text{IR}} \) from the tunable IR laser matches the vibrational mode of the interfacial species \( \omega_n \) and the interfacial species is excited

\[
I_{\text{SFG}} = \sum_n \frac{A_n}{(\omega_a - \omega_n)^2 + i\Gamma_n} + A_{\text{NR}} e^{-i\epsilon}
\]  

(2)

Where \( A_n, \Gamma_n, A_{\text{NR}}, \) and \( \epsilon \) are the strength, damping constant, nonresonant SFG signal contribution, and its phase angle, respectively. The intensity of the nonresonant component is considered largely independent from \( \omega_{\text{IR}} \) in the practical spectroscopic window of SFG. As shown in Equation (2), when \( \omega_{\text{IR}} \) matches \( \omega_n \), a large enhancement in the SFG signal is observed due to the resonant effect.

4.2. SFG for Interphase Characterization

The first SFG study on electrochemical interfaces is reported by Guyot-Sionnest and Tadjeddine. Nowadays, SFG has become a unique technique in interfacial science to probe molecular species and surface dynamics under real working conditions.

The electrochemical cells for SFG investigation of the electrode–electrolyte interface have similar configurations to IR spectroscopy cells in Figure 7 with external and internal reflection modes, as shown in Figure 12.

The external reflection mode is widely used in SFG spectroscopy and takes benefits from its design simplicity. In this mode, to minimize the solvent effect and absorption loss of the IR pulse, the substrate is placed in the close vicinity of the window. Similar to IR spectroscopy, the limitations of the external reflection mode can be overcome by employing an internal reflection element in Figure 12b.

Similar to Raman and IR techniques, SFG spectroscopy shows some challenges for interface characterization. This technique suffers mainly from weak interface signals, making any reliable peak assignment a challenge. In addition, SFG investigation of mixed structures like the ones present at the LIBs interphase is complicated due to the weak and broad resulting peaks. In this regard, most of the SFG investigations are limited to the peak evolution of the known adsorbent species at the interface against external stimuli signals such as applied potential/current. Another significant challenge of the SFG techniques arises from the selection rules that must satisfy both IR and Raman spectroscopy. This considerably decreases the number of active vibrations, especially in molecules with a certain level of structural symmetry. The presence of multiple interfaces of...
electrode|interphase, and interphase|electrolyte makes the signal analysis very complicated. The combinational use of two excitation sources also combines the challenges associated with both lasers, like local heating and alignment issues.\cite{45}

### 4.3. SFG Investigation of the Adsorption of (Carbonate) Electrolyte Components

Liu et al.\cite{117} used in situ SFG in 2009 to investigate the adsorption behavior of PC on LCO cathode. Two SFG peaks of the carbonyl group at 1830 and 1780 cm\(^{-1}\) was attributed to two different orientation of PC, one pointing toward the LCO substrate and another one in the opposite direction. Fitting the relative peak intensities results in assigning the peak at 1830 cm\(^{-1}\) to the tilted configuration with the angle of \(\approx 48 \pm 2^\circ\) from the surface, while the peak 1780 cm\(^{-1}\) is attributed to the angle of \(\approx 202 \pm 2^\circ\), as shown in Figure 13. In a later study, Yu et al.\cite{118} carried out SFG measurements to investigate the structure of the solvent molecules adlayer of EC, DMC, and DEC as pure and mixed carbonate esters on the LCO surface. It was found that the EC molecules are dominantly adsorbed on the LCO surface because of their stronger interaction with the carbonyl group orientation toward the surface. Mukherjee et al.\cite{119} employed in situ SFG as an interface-selective technique to monitor the electrode|SEI and electrolyte|SEI interface on Au and Cu electrodes in EC/THF, LiClO\(_4\) electrolyte. In the potential range of 2.0–0.2 V versus

![Figure 12. Schematic representation of in situ SFG cells with a) external and b) internal reflection modes. WE, RE, and CE stand for working, reference, and counter electrodes in these figures, respectively.](image)

![Figure 13. a) sps- and ssp-SFG spectra (circles) of LiCoO\(_2\) surface in contact with PC. SFG spectra are offset for clarity. See text for details. b) Two possible orientation structures for the CdO group of PC were observed at 1780 and 1830 cm\(^{-1}\). The y-direction is the surface normal. c) Schematic illustration of PC absorption on LiCoO\(_2\) surface. The simulated components for ssp-polarization are multiplied by a factor of 5 for clarity. Reproduced with permission.\cite{117} Copyright 2009, American Chemical Society.](image)
Li|Li+”, it was observed that SEI formation on the Au surface co-occurs with Li-ion plating and dissolution; however, no Li-ion deposition was observed on the Cu surface. In situ SFG also proved that EC molecules are present at the electrolyte interface in both Cu and Au electrodes; however, at the Au interface, LEDC, as the products of EC reduction, and epoxide peaks were observed during cycling while the Cu interface behaved differently. The SFG signal intensity during cycling on the Cu interface showed a prominent oscillation with maxima at 2.0 V versus Li|Li+ and small maxima at 0.2 V versus Li|Li+ assigned to the EC potential-driven reorientation. Similar results were obtained by Nicolau et al., who studied SEI formation on a gold surface versus Li-metal as a model system and in the presence of the EC/THF, LiClO4 electrolyte. It was seen that LEDC and lithium salts are primarily the dominant SEI components on the surface. The potential-dependent SFG results at a defined electrified interface indicate an initial hindering effect of SEI formation due to the presence of THF molecules on the surface, which was minimized at higher cycle numbers.

Peng et al. characterized the adsorption behavior of DMC and PC as well as known additives of VC and fluoroethylene carbonate (FEC) on the thin film of carbonaceous materials. In various mixtures of PC and DMC in 0.5 m LiClO4, PC is adsorbed preferentially on the surface of the electrode, realized by its different peak ratio from the bulk. For the DMC/PC 3:1 as an example, the molar ratio of PC on the surface is about 51%, higher than its 25% bulk contribution. The coadsorption structure of VC and FEC with DMC showed similar behavior as PC. Iwahashi et al. studied the effect of Li-ion on extending the electrochemical stability window of the interface of Pt in contact with the ionic liquid 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)amide (C2mim)[FSA]) at room temperature. They reported a >1.0 V extension in the ESW on the cathodic edge of Pt when Li-ion is present in the electrolyte. The in situ SFG analysis showed that [FSA]- anions desorb at potentials more negative than 1.5 V versus Ag/Ag+ if no Li-ion is present in the systems. However, [FSA]- anions strongly interact with Li-ion and stay and anchor to the Pt surface, which prevents the reduction of [C2mim][FSA] anions and results in an extended ESW.

### 4.4. SFG Spectroscopy for SEI Formation on Silicon Anodes

Olson et al. proved by operando SFG that carbon monoxide-associated species are formed at distinct potentials on nano-Si anodes depending on the electrolyte formulations. It was observed that carbon monoxide evolution occurs at the highly lithiated state of the Si anode in the presence of EC, while FEC reduction shows less sensitivity to the lithiation state. The authors suggested that oligomers with low molecular weights diffuse into the electrolyte from the interface during cycling leading to interphase instability. A more stable interphase is observed upon prolonged EC reduction at 10 mV versus Li|Li+ due to the formation of higher molecular weight species like polyethylene carbonate. Equivalent operando SFG results in the presence of FEC show its reduction to Li2CO3, LiF, and CF-containing components, stabilizing the interphase irrespective of the time scale.

Horowitz et al. investigated the SEI formation mechanism on crystalline Si anode versus Li-metal in EC/DEC, 1 m LiPF6 by in situ SFG. A Si-ethoxy surface intermediate was formed from a hydrogen-terminated Si crystal due to DEC decomposition. Also, Horowitz et al. employed in situ SFG to study the reduction of 1,2-dithoxy ethane and the fluorinated version, bis(2,2,2-trifluoroethoxy) ethane, with LiTFSI on amorphous Si surface. It was observed that the =CF2 end groups of the fluorinated ether components change their orientation on the surface resulting in a more efficient and smoother SEI. Furthermore, Horowitz et al. investigated the molecular structure of EC and FEC on Si surface using SFG combined with ab initio molecular dynamics at open circuit potential. Both EC and FEC are adsorbed on the Si surface through the carbonyl bond. The detailed investigations reveal that EC is the dominant compound at the Si surface when FEC concentration is below 20 wt%. Also, the presence of FEC induces an upright ordered orientation of the electrolyte molecules on the surface. In another work, Horowitz et al. studied the SEI formation steps on a p-doped Si(100)-hydrogen-terminated wafer and in EC/DEC, 1 m LiPF6 solution in a cell with Li-metal as the anode. In situ SFG results show that Si-OCH2CH2 forms even at open circuit potential due to DEC dissociation. A stronger dissociation of DEC is observed at a potential of 1.0 V versus Li|Li+ associated with a shift in the =OCH2− group SFG peak. The vibrational modes are more redshifted at 0.8 V versus Li|Li+ and remain constant when the cell is cycled between 0.8 and 1.1 V versus Li|Li+. Horowitz et al. also addressed the SEI of Si anodes using a combined SFG and X-ray reflectivity (XRR) approaches. The SFG study shows that EC and FEC molecules on the surface of the Si anode and in the presence of 1 m LiClO4 in EC/FEC 7:3, are rearranged perpendicular to the surface. However, the X-ray reflectivity technique that probes several layers of electrolyte components on the surface represents the molecules’ surface-parallel arrangement in the next molecular layers. Figure 14b left shows the SFG spectra of Low (tight packing) and High (loose packing) of the carbonyl bond in EC at perpendicular (SSP) and parallel (SPP) polarizations. The addition of FEC to EC creates new peaks in SFG at SSP due to the re-orientation of EC molecules, while the SPS polarized SFG component vanishes with increasing the FEC content. This implies a negligible dipole moment parallel to the surface with an increased amount of FEC. The authors suggested that upon FEC addition, the primary C=O orientation of EC toward the surface changes to a more up-right position.

### 4.5. SFG on Single-Layer Graphene SEI in Li–O2 Batteries

Ge et al. investigated the influence of dissolved oxygen in the electrolyte on the SEI formation employing SFG. It has been proven that the SEI structure on single-layer graphene and EC-based electrolytes is significantly affected by the dissolved oxygen by increasing the content of polymeric species in the SEI. SFG also proves that the generation of superoxide radical anion from the oxygen reduction reaction induces a radical initiated polymerization of EC toward polymeric species. In another work, Ge et al. employed a set of vibrational spectroscopy techniques to investigate the role of superoxide
formation \((\text{O}_2^-)\) in lithium–oxygen (Li–O\(_2\)) batteries during oxygen reduction reaction (ORR). The SFG measurements in an \(\text{O}_2\)-saturated Li-ion free tetraglyme solvent show that the ORR reaction is involved with a structural change in the tetraglyme molecules on the surface. A more reversible structural change of tetraglyme molecules is observed when Li-ions are present in the electrolyte. The SFG results were confirmed with SERS and FTIR measurements, indicating the crucial role of the superoxides for solvent decomposition during the ORR reaction.

5. Overview and Summary

In this review, different in situ and operando vibrational spectroscopy methods for the characterization of interphase fundamental properties, structure, and composition were discussed. Various studies with advanced methods of Raman, FTIR, and SFG were applied on a wide range of electrodes and electrolytes.

In the case of Raman, it was found that conventional Raman spectroscopy was not suitable for investigating the evolving interphases. Nevertheless, with the implementation of SERS and its variants TERS and SHINERS, Raman spectroscopy proved to be a potent tool for interphase investigation. Many different components of the SEI and CEI on various electrodes were identified employing SERS and its variants. Initial SERS measurements of the SEI in LIBs showed that the probed interphases mostly consist of inorganic species like LiOH and Li\(_2\)CO\(_3\) and organic Li-compounds, such as ROCO\(_2\)Li, deriving from the decomposition of the electrolyte on the electrode surface. In later studies, other inorganic molecules like Li\(_2\)O\(_2\) and organo-phosphates, decomposition products of LiPF\(_6\), were detected. Combination of SERS investigations with other analysis techniques, like mass spectrometry, enabled the detection of Li\(_2\)C\(_2\) as electrochemical decomposition product of the electrolyte. Moreover, it was possible to prove the formation of LiF, despite its low Raman activity, using SERS. The implementation of TERS for interphase investigation revealed interesting insights on the mosaic structure of the SEI, and proved that changes of the surface decomposition occur with ongoing cycling. The implementation of SHINERS especially allowed the investigation of the organic components of the SEI. Different molecules, like DEDOHC, LEMC, ROLi, and PEO-type species were detected. In addition, information on the effect of film-forming additives like VC was gained by assigning semicarbonates to the polymerization of VC on the electrode.

In contrast to the number of studies published on SEI, studies concerning the CEI are rather scarce, which reflects the focus of interphase research on LIBs. However, with surging implementation of high-voltage cathodes, a better understanding of CEI properties is necessary. The mentioned advanced Raman spectroscopies are potential tools for overcoming these challenges and gain a deeper understanding of the CEI. Nevertheless, some SERS and SHINERS investigations have already been applied to investigate the CEI. While for the SERS investigation of the CEI mostly organic polymer species were discovered, the SHINERS investigations revealed additionally inorganic species, like LiF, Li\(_2\)CO\(_3\), and Li\(_2\)O, as components of the interphase.

Similar to the development in Raman spectroscopy, different methods were developed to improve interphase investigation for FTIR spectroscopy. For in situ FTIR spectroscopy, custom-build cells for transmission, SNI-FTIRS, and ATR-FTIR measurements were developed. After SNI-FTIRS was introduced for in situ monitoring of the interphase on Pt electrodes, it was adapted for interphase characterization in LIBs. In the presented studies, SEI formation by electropolymerization of EC and VC-based additives was confirmed in the late 1990s to early 2000s. It was shown that graphite exfoliation in PC electrolytes was prevented by employing the above-mentioned additives. Using in situ ATR-FTIR, the SEI on graphite was determined to be mainly composed of ROCO\(_2\)Li, Li\(_2\)CO\(_3\), and

Figure 14. a) The measurement techniques and EC/FEC orientations on the surface are depicted schematically. b) SFG spectra of pure EC and EC/FEC mixtures of perpendicular (open circles) and parallel (open diamonds) aligned adsorbates. The Low and High peaks are assigned to the EC carbonyl group vibration. The presence of FEC produces two more peaks. b top right) C=O vector and its angle \((\Theta)\) from the normal to the surface \((Z)\). b bottom right) The \(\Theta\) angle as a function of FEC wt% content. Reproduced with permission.\(^{[128]}\) Copyright 2018, American Chemical Society.
the conductive salt decomposition product, like Li$_5$PF$_6$. Additionally, it was found that, contrary to LiAsF$_6$, the reduction products of LiPF$_6$ interfere with the compact sedimentation of ROCO$_2$Li on the graphite surface. Also, it was demonstrated that the catalytic activity of the electrode surface determines the electrolyte decomposition products in an EC/DEC-based electrolyte; a noncatalytic surface leads to a rich LiEDC interphase, whereas a catalytic surface forms largely DEDOH$_C$. On silicon-containing electrodes, a one-electron reduction pathway for EC and DMC decomposition results in the formation of ROCO$_2$Li species, which are subsequently decomposed to CO$_2$ and Li$_2$CO$_3$. Furthermore, the volume changes during cycling, which cause particle and interphase cracks along with renewed LiEDC formation inside the created pores, were tracked using different penetration depths of the ATR setup.

Studies addressing cathode materials found that the oxidation of PC-based electrolytes results in much more CO$_2$ evolution than EC-based electrolytes, while DMC oxidation is free of CO$_2$ evolution. It was also shown that the CEI is decomposed and stripped off during discharge due to weak interactions between the electrode and CEI. Furthermore, during the investigation of NMC, the phase change from hexagonal to monoclinic during transition metal oxidation was observed, which caused a partial collapse of the NMC structure above 4 V versus Li/Li$^+$. Thus, in situ FTIR spectroscopy helped to elucidate the properties of the interphase in LIBs, starting with decomposition products of additives and electrolyte components in earlier studies. Later on, it was further adapted to shed light on the associated mechanisms and in-depth investigation of the interfacial reactions. However, in situ FTIR has proven to be more suitable for detecting organic species with polar functional groups, which highlights the need for combined studies with other complementary techniques such as SEM, Raman, XPS, or AFM. This approach is considered powerful in drawing a complete structural picture on a molecular (organic and inorganic) and elemental level of the interphases in LIBs.

While Raman and FTIR spectroscopies are more suited to investigate the composition during the formation and aging of the interphase, the utilization of in situ SFG spectroscopy proved successful to determine the interfacial properties of molecular vibrations rather than compositional information. Resolving the underlying interfacial structures results in a fundamental understanding of the SEI and CEI formation mechanisms. Generally, with SFG spectroscopy, it is possible to determine the ratio of different adsorbed molecules on the surface. It was also shown how the molecules adsorb on the surface, for instance, that EC and FEC adsorb on a Si surface with the carbonyl bond. Furthermore, it was found that the generation of superoxide radical anions in Li-O$_2$ batteries induces a radical-initiated polymerization of EC toward polymeric species.

6. Perspective and Future Outlook

The exploration of ongoing reactions and the elucidation of their mechanisms on the electrode–electrolyte phase boundary is necessary to gain a fundamental understanding of the evolving interphases. With this fundamental understanding, tailoring the properties and performance of SEI and CEI in LIBs can be facilitated, and durable high-performing LIBs can be developed. Here, vibrational spectroscopy plays a key role as it is a powerful tool to monitor electrolyte, interphase, and electrode compounds. Especially developing in situ vibrational spectroscopy methods is of high importance, as the interphases are formed and changed during cell operation.

With in situ vibrational spectroscopy methods, changes in binding state, composition, and phase transformation dependent on cell potential and aging can be probed. Furthermore, an in situ method also guarantees representable and reliable results during cell operation as atmospheric interferences or sample preparation is impeded. In situ Raman, IR, and SFG were already proven reliable methods in regards to LIB investigations in the previously reviewed studies and helped to understand ongoing mechanisms on a molecular level on one electrode. Nevertheless, these studies were, in large, conducted with electrode materials and electrolytes which are not fully representing the current or next generation of LIBs. Also, studies on the interphase investigations were mainly focused on the SEI with underestimating the effect of the CEI contribution. The overall increased recognition of the CEI led to an increase on CEI studies; however, the wide range of cathode materials creates a need for further in-depth studies of the CEI. Thus, it is necessary to further investigate SEI and CEI on the latest and upcoming anode and cathode materials with state-of-the-art electrolytes in the future.

The intrinsic properties of Raman, IR, and SFG also limit their application to different cathode and anode materials. While Raman and IR techniques can provide a spectroscopic fingerprint of the formed species at the interphase, SFG is primarily implemented for molecular insight at the interface of mainly model surfaces. In this perspective, SFG spectroscopy can be mainly applied to the electrode potentials within the ESW of the electrolytes, providing data on the molecular adsorption, orientation, and inter- and intra-bonding at the electrochemical double-layer region. Yet, IR and Raman spectroscopy are largely implemented for the potential regions where the electrolyte components are decomposed to form the SEI and CEI.

Another key element for performing a reliable in situ/operando vibrational spectroscopy characterization is about the electrode’s geometry and cell configuration. Unfortunately, the studies of the cell design influence on electrochemical and spectroscopic measurements are rare. Also, in these studies, the cell design for different methods varies significantly in housing, electrode arrangement, size, amount of electrolyte, and cell chemistry, which can make comparability between different studies difficult.

To perform a reliable in situ/operando vibrational spectroscopy measurement, at first, a clear relation between the cell configuration for the electrochemical and spectroscopic characterization should be established. The parameters that affect the diffusion patterns, polarizations, and rates in the spectroscopic cell need to be addressed. These parameters are two-folded: first, the electrode arrangement in the spectroscopic cell. In this regard, the size of the electrodes, their distance to each other and to the optical window, and the electrodes orientation are major factors playing key roles in the electrochemistry of the
cell and, as a result, the interphase dynamics and structure. Also, it is highly suggested to use in situ/operando optical cells with three-electrode configurations. In this case, the effect of the above-mentioned electrode parameters will be minimized. However, care must be taken in three-electrode cell systems with the effect of the reference electrode on the cell chemistry during the cell operation. Second, the electrolyte influence should be optimized for the optical cell to have comparable results with the electrochemistry characterization. One very important parameter affecting the actual applied potential/current in the optical cell is the ohmic drop and polarization due to the electrolyte resistance. It is necessary to perform ohmic drop correction before any spectroscopic characterization to avoid this pitfall caused by wrong applied electrochemical parameters. The diffusion patterns of the Li-ion in the electrolyte also need to be simulated as close as possible to the actual electrochemical cell. The amount of the electrolyte needs to be optimized in the spectroscopic cell to guarantee a facile path for Li-ion and proper wetting of the electrodes.

Furthermore, for the in situ/operando characterization of interphases in solid-state batteries with vibrational spectroscopy, new suitable cell designs have to be developed. Here, the ability to monitor and control the stack pressure and temperature during the measurement should be implemented, which gives new insights into the mechanisms at the interphase. Besides, the technical limitations of vibrational spectroscopy have hampered any in situ/operando investigation of the interphase in solid-state batteries. It is suggested by the authors of this review to prepare a cross-section of the electrode–electrolyte interface to prepare samples for spectroscopic characterization. Another strategy can include implementing electrodes, which are very thin or transparent to the excitation waves as well as the collected signals. Hence, Si electrodes with high transparency to the IR wave can be considered a good choice for inter-phase investigation, though studies of Si anodes for solid-state batteries are rare. Also, a combination of IR and Raman spectroscopy with an anode-free solid-state lithium metal battery is another configuration that can provide essential insights into the interphase of the plated lithium during the cell operation.

Also, the potential of the TERS technique for interphase characterization needs to be further explored. The advantage of TERS for high-resolution spectroscopic investigation of the spatially confined area on the interphase can assist greatly in examining the developed models of the interphase. The multi-component structural model presented in the introduction part of this review consists of organic and inorganic domains with sizes smaller than any conventional spectroscopy techniques. Hence, TERS can easily overcome this limitation for individual domain analysis and high-resolution structural mapping of the interphase. Furthermore, one of the main challenges with the interphase characterization in LIBs is peak overlapping due to the presence of compounds with similar vibrational frequencies, leading to difficulties in peak assignment and proper analysis. TERS has the advantage of resolving these vibrations by taking advantage of its high spatial resolution.

The characterization in full cells is also of importance to untangle the cross-talk phenomenon between the electrodes and the influence on SEI formation, i.e., by transition metal dissolution or interphase dissolution and migration. Moreover, recent in situ combinations of vibrational spectroscopy methods and utilization of other methods, like scanning electron microscopy (SEM), were proven successful in understanding interphase formation and getting spatial resolution. The new insights gained on a molecular level could even be deepened further to an elementary level when combined with other spectroscopic techniques like XPS. Generally speaking, vibrational spectroscopy techniques cannot solely present a comprehensive approach for understanding the interfacial phenomenon, specifically in complex systems like LIBs interphase/interface. Therefore, a combination of several analytical approaches is needed to gain comprehensive information on the interphase composition, dynamics and kinetics, electric transport properties, and in the end, the relation of all these parameters with the overall performance of a LIB cell.

Vibrational spectroscopy represents a promising analytical approach and contributes to the process of gaining in-depth fundamental understanding of interphases/interfaces in LIBs.

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Conflict of Interest

The authors declare no conflict of interest.

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