Recent advances on characterization techniques for the composition-structure-property of solid electrolyte interphase

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Abstract The Solid Electrolyte Interphase (SEI) is a nanoscale thickness passivation layer that forms as a product of electrolyte decomposition through a combination of chemical and electrochemical reactions in the cell and evolves over time with charge/discharge cycling. The formation and stability of SEI directly determine the fundamental properties of the battery such as first coulombic efficiency (FCE), energy/power density, storage life, cycle life and safety. The dynamic nature of SEI along with the presence of spatially inhomogeneous organic and inorganic components in SEI encompassing crystalline, amorphous and polymeric nature distributed across the electrolyte to the electrolyte-electrode interface, highlights the need for advanced *in-situ*/*operando* techniques to understand the formation and structure of these materials in creating a stable interface in real-world operating conditions. This perspective discusses the recent developments in interface-sensitive *in-situ*/*operando* techniques, providing valuable insights and addressing the challenges of understanding the composition-structure-property of SEI and their correlations during the formation processes at spatio-temporal resolution across various length scales.

H.L.[1] and M.N.[1] contribute equallity to this perspective.

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List of abbreviations.

3D – Three-dimensional

ADF STEM – Annular dark-field imaging scanning transmission electron microscopy

AFM – Atomic force microscopy

APXPS – Ambient pressure X-ray photoelectron spectroscopy

Ag – Silver

Au – Gold

CEI – Cathode electrode interphase

C_2H_4 – Ethylene

C_1C_6ImFSI – 1-hexyl-3-methylimidazolium bis(fluorosulfonyl)imide

C_1C_6ImTFSI – 1-hexyl-3-methylimidazolium (bis(trifluoromethanesulfonyl)imide

CO – Carbon monoxide

CO_2 – Carbon dioxide

Cryo-TEM - Cryogenic transmission electron microscopy

Cu – Copper

CV – cyclic voltammogram

DEC – Diethyl carbonate

DMC – Dimethyl carbonate

DNP – Dynamic Nuclear Polarization

DS-PERS – Depth-sensitive plasmon-enhanced Raman spectroscopy

EC – Ethylene carbonate

EC-AFM – Electrochemical atomic force microscopy

EC-SFA – Electrochemical surface force apparatus

EDL – Electrical double layer

EELS – Electron energy loss spectroscopy

EEI – Electrolyte-electrode interface

E_g – Energy gap

EMC – Ethyl methyl carbonate

EQCM – Electrochemical quartz crystal microbalance

EQCM-D – Electrochemical quartz crystal microbalance with dissipation

FEC – Fluoroethylene carbonate

FCE – First coulombic efficiency

FTIR – Fourier transform Infrared Spectroscopy

HAXPS – Hard X-ray photoelectron spectroscopy

HOPG – Highly oriented pyrolytic graphite

HOMO – Highest occupied molecular orbital

IL – Ionic liquid

Li – Lithium

$LiClO_4$ – Lithium perchlorate

$LiCoO_2$ – Lithium cobalt oxides

Li_2CO_3 – Lithium carbonate

LiF – Lithium fluoride

LiTFSI – Lithium bis(trifluoromethanesulfonyl)imide

Li_xMoO_3 – Lithium molybdate

Li_2O – Lithium oxide

$LiPF_6$ – Lithium hexafluorophosphate

LUMO – Lowest unoccupied molecular orbital

MLLS – Multiple least squares fitting

NMR – Nuclear Magnetic Resonance

OXPS – operando X-ray photoelectron spectroscopy

PC – Propylene carbonate

QCM – Quartz crystal microbalance

SECM – Scanning electrochemical microscopy

SECCM – Scanning electrochemical cell microscopy

SEI – Solid electrolyte interface

SERS – surface-enhanced Raman spectroscopy

SFA - Surface force apparatus

SHINS – Shell-isolated nanoparticles

SXPS – Soft X-ray photoelectron spectroscopy

STEM – Scanning transmission electron microscopy

sXAS – soft X-ray absorption spectroscopy

TAG – Thermogravimetric analysis

TOF-SIMS – Time-of-Flight Secondary Ion Mass Spectrometry

UV – Ultraviolet

XPS – X-ray Photoelectron Spectroscopy

1. Introduction

1.1. What is Solid-Electrolyte Interphase (SEI)?

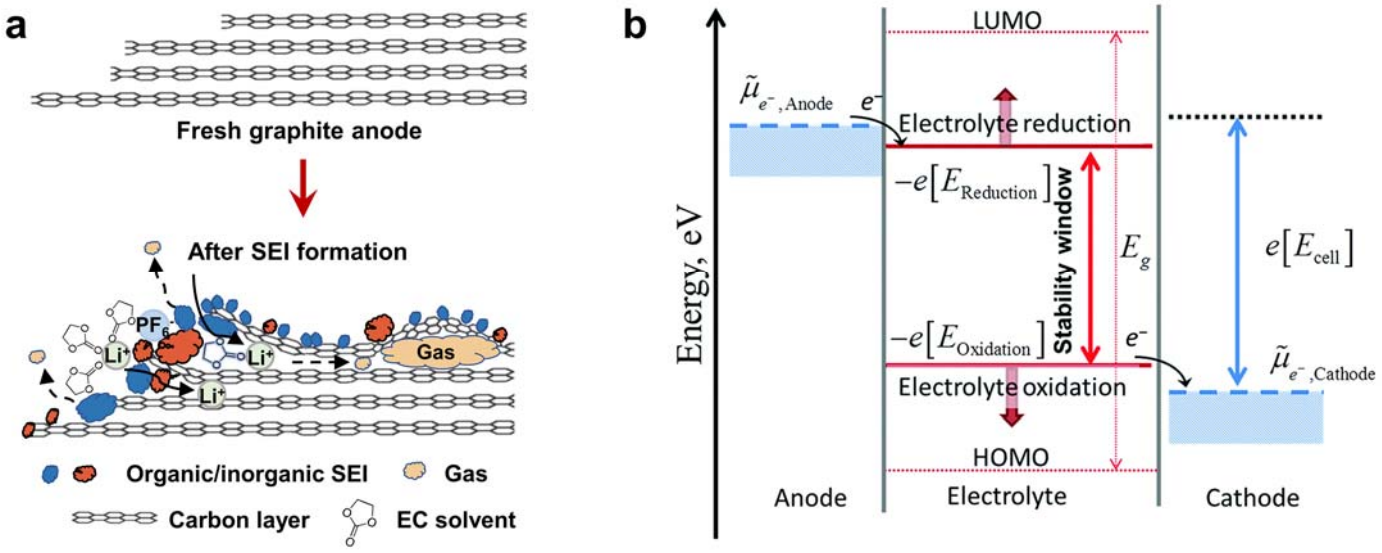

Figure 1 (a) Schematic of electrolyte decomposition and SEI formation in graphite anode. (b) The negative and positive voltage (potential) limits for the electrolyte stability, and the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), reproduced with permission. [1]Copyright 2018, RSC Publishing.

Solid-Electrolyte Interphase (SEI) is a passivation layer ~~component~~ that forms on the electrode surfaces of lithium/sodium-ion batteries during their initial electrochemical cycles and continues to evolve upon storage and charge/discharge cycling[1-3]. This SEI layer plays a critical role in stabilizing the interface between the electrode and electrolyte and in enhancing performance, longevity and safety of lithium/sodium-ion batteries. Ideally, ~~–~~SEI should be uniform, thin and chemically, electrochemically and mechanically stable.~~It is also vital for the lifespan and safety of lithium/sodium-ion batteries~~, ~~acting as a protective barrier that stabilizes the interface between the electrode and the electrolyte~~[4]. ~~By~~ Hence an ideal SEI layer, not only prevent~~s~~ing continuous electrolyte decomposition and limit~~s~~ing side reactions but also minimizes ~~,~~ further growth of SEI. This in turn, reduces ~~the SEI minimizes~~ active material loss, ~~and~~ ensures efficient ion transport, ~~,~~maintains uniform alkali metal ion flux, ~~-~~suppresses dendrite growth and mechanical stress. Further, ~~thereby preserving battery~~mitigates capacity fade and power fade ~~–~~thereby preserving the battery's performance ~~capacity~~ over time[5]. Additionally, it plays a crucial role in safety by mitigating risks such as ~~reducing the risk of~~ dendrite formation, thermal runaway, ~~mitigating thermal runaway,~~ and preventing the flammable exothermic gas generation that can lead to swelling or rupture[6-8]. Hence, it's very important to understand that, not only the basic components such as positive electrode, negative electrode, electrolyte and separator must be chemically, electrochemically and mechanically stable , but the newly formed SEI ~~a~~A ~~stable and well formed SEI~~stability is also crucial ~~is essential~~ for enhancing battery durability and reliability, making its optimization a key focus of ongoing research[9].

Taking the widely used graphite anode as an example (Figure 1a), the development of SEI layer is explained succinctly. T~~t~~he SEI layer originally derives from the sequential processes of "adsorption → decomposition → precipitation/growth" - of electrolyte components on the graphite electrode surface. This SEI layer then acts as a protective barrier that prevents further electrolyte reaction with the graphite edge and basal planes either by restricting electron tunnelling or by solvent diffusion[3], which is increasingly significant toward designing novel secondary batteries, such as graphite–graphite dual-ion battery[10]. At the same time, the formation and growth of the SEI layer result in loss

of lithium inventory during repeated insertion/extraction of Li-ion as it consumes active lithium and electrolyte leading to capacity fading, increased battery resistance and low power density. However, it also plays a role in facilitating ion de-solvation and transportation between the graphite edge plane and electrolyte, preventing the co-intercalation of the strong coordinating solvent (such as EC) which often induces graphite delamination[11]. Therefore, the formation and stability of the SEI layer have a significant impact on the overall performance of the battery, including storage life, rate capability, cycle life and safety. Although the SEI is of nanoscale thickness and is insignificant compared to the overall size of Li-ion batteries, it plays a crucial role in its operation and functionality.

1.2. Fundamental perspectives on the formation of interfacial passivation layers

The interfacial decomposition reactions of the electrolyte-electrode interface can be elucidated from the thermodynamic perspective considering electrolyte reactivity in terms of reduction and oxidation at high and low potentials, respectively. In the early stages, it has been postulated that the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy levels of the electrolyte dictate the thermodynamic stability of the battery electrolyte-electrode interface[2]. However, as shown in Figure 1b, a narrower electrochemical stable window compared to the energy gap (E_g) between the LUMO and HOMO levels is often experimentally observed in the realistic battery electrolyte. Hubert et al further proposed the optimized electrode-electrolyte thermodynamic model based on redox potentials and Fermi level of the electron in solution to explain the electrolyte decomposition and SEI formation below the LUMO and above the HOMO energy levels. When the anode chemical potential ($\tilde{\mu}_{e^-,\ Anode}$) is higher than the electrolyte reduction potential ($-e[E_{reduction}]$), the electrons from the anode side can "jump" into the electrolyte, resulting in the reductive decomposition of the electrolyte. It is worth noting that a similar oxidation reaction can occur on the cathode side, resulting in the formation of SEI on the cathode surface, also commonly referred as cathode electrolyte interphase (CEI)[1, 12].

Currently, commercial lithium-ion battery electrolytes comprise primarily cyclic (EC, FEC, PC, etc.) or linear carbonate solvents (DEC, EMC, DMC, etc.), lithium salts, and a minor quantity of functional additives. The reduction voltage ($E_{reduction}$) and oxidation voltage ($E_{oxidation}$) of commercial electrolyte is typically around 1.0 V and 4.7 V *vs*. Li^+/Li, respectively. As a result, during the initial battery formation cycle, once the surface potential of the negative electrode material gradually decreases below 1.0 V, or that of the cathode side reaches 4.7 V, the reduction/oxidation and decomposition of electrolyte occurs and the insoluble products gradually accumulate on the electrode surface, ultimately forming the SEI membrane. By introducing an additive that can undergo reduction just before the electrolyte, the reduction of the liquid electrolyte can be prevented, and the integrity and robustness of the SEI can be improved.

To date, the interphases in lithium-ion batteries with liquid electrolytes at the anode/electrolyte and cathode/electrolyte surface are referred to as SEI and CEI respectively and the distinction between this nomenclature is unclear. However, this nomenclature is a misnomer, as it is also applied in emerging technologies like all-solid-state batteries. For those reasons, Amponsah et al. proposed a nomenclature for the interphase at anode/cathode with liquid electrolyte as liquid-electrolyte/anode interphase (LEAI) and liquid-electrolyte/cathode interphase (LECI)[12]. Although we agree with this and emphasize the need for clear naming, we are aware that it has to be discussed in detail to reach a consensus on nomenclature and it's out of the scope of this paper. Hence, in this paper, SEI refers to the interphase formed at the liquid electrolyte/anode in lithium-ion or lithium-metal batteries.

1.3. The composition-structure-property of SEI and their correlations

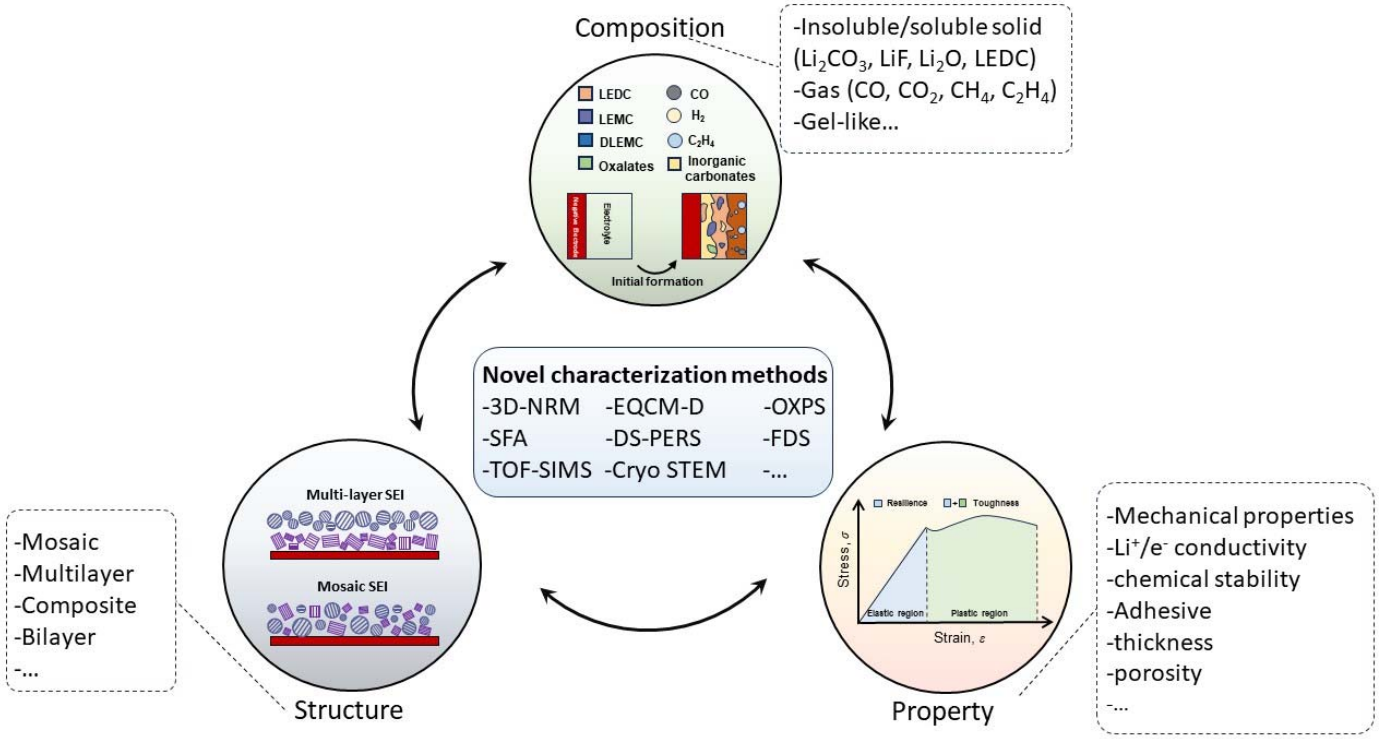

Figure 2 Schematic of the composition, structure & property of SEI.

The chemical or electrochemical reactions involved in the formation mechanism of the SEI layer are exceedingly complex due to the intricate composition of the electrolyte and driven by a diverse array of chemical and electrochemical reactions influenced by factors such as the electrolyte, composition, electrode surface chemistry includes the active sites and catalytic properties of the surface, formation process parameters, and impurities such as water and acids[3]. To fully understand the formation mechanism of SEI, one should start with the comprehensive characterization of SEI from the perspective of compositions, nanostructures, as well as physical/chemical properties.

1.3.1 Composition:

The ultimate compositions of the SEI layer result from a complex interplay of various competing reactions[3, 13, 14]. As shown in Figure 2, the decomposition products arising from electro-reduction reactions encompass soluble, partly soluble or unstable deposits (lithium carbonate (Li_2CO_3), lithium oxalate ($Li_2C_2O_4$) lithium alkoxides, lithium ethylene dicarbonate (LEDC) and lithium alkyl carbonates), insoluble deposits (lithium fluoride, LiF), lithium oxide (Li_2O), etc.) and gases like H_2, CO, CO_2, CH_4, and C_2H_4. These gases can lead to gas evolution during the battery's cycling, whereas soluble deposits may dissolve into the electrolyte itself. Only the insoluble deposits can form various deposition structures on the negative electrode surface, ultimately constituting the SEI layer[3, 13, 14]. Among them, although there still exists a controversy about the role of LiF in the SEI [5], LiF is the most commonly observed SEI component in various electrolyte-electrode combinations. Considering the formation of similar degradation products in the interface films on both negative and positive electrodes of conventional lithium-ion batteries, the existence of distinct acronyms SEI and CEI rather than the anodic SEI and cathodic SEI and only reinstates the ambiguity in the nomenclature as discussed earlier.

1.3.2 Structure:

SEI represents a region where the properties of two phases of interest, ie. electrode and electrolyte, have undergone significant changes due to the chemical or electrochemical reaction between the

two phases, eventually resulting in the formation and growth of new products or phases with modified thickness. Therefore, SEI can be conceptualized as a three-dimensional contact of two phases having different physicochemical properties consisting of several phases and interfaces unlike, classical interfaces which are typically two dimensional[15, 16]. Researchers have identified various three-dimensional morphological arrangements of these decomposed products within the SEI, including mosaic, multilayer, and mixed structures[17-19]. As sketched in Figure 2, the mosaic structure of the SEI refers to a heterogeneous and patchy distribution of different components across the surface of the electrode. It's called "mosaic" because it appears as if different materials are arranged in irregular patterns, somewhat like a mosaic artwork[17]. While the multilayer structure of the SEI refers to the formation of distinct layers of different materials on the electrode surface[18, 19]. The two-layer SEI structure, consisting outside organic-rich component layer combined with an inner inorganic layer ($LiF/LiCoO_2$), is generally considered as a stable and robust structure[5, 20]. Additionally, the mixed structure of the SEI refers to a combination of different components, including inorganic and organic species, within the same layer or region[19]. Here, one should always bear in mind that the SEI is not a uniform and static layer, it undergoes changes and transformations during the cycling of the battery. Meanwhile, the variation in the compositions and structures – the arrangements of different components of the SEI can vary depending on factors like the type of electrode material, electrolyte composition, storage and cycling conditions.

1.3.3 Properties:

Apart from the components and nano-structures, researchers have also investigated the physical/chemical properties of the SEI layer using various analytical techniques[3, 13, 14, 21]. The physical properties of SEI refer to the thickness, porosity, mechanical strength and morphology, while the chemical properties ~~contain the component~~include chemical composition, stoichiometry, electrochemical stability and ionic/electronic conductivity (ion/electron transfer characteristics). The SEI is typically a nanoscale thin layer, having a porous structure which can influence ion transport and diffusion within the layer. The mechanical properties of the SEI, such as its adhesion to the electrode surface, its ability to withstand the volume expansion, and the mechanical stress during continuous insertion/extraction of ions during charge/discharge cycles, are closely related to its chemical compositions and nanostructures. Thus, the chemical composition, stoichiometry, nano architecture and physicochemical properties of SEI are not fixed but evolve over cycling and are the determinant factors in the overall performance of batteries. The SEI should ideally allow the transport of lithium ions while preventing the passage of electrons. Managing electronic conductivity is essential to prevent continuous electron flow and maintain the electrochemical isolation of the electrodes. Comprehending the charge transfer dynamics and other physio-chemical properties of SEI is beneficial for the chemical stability of SEI. As instabilities in the SEI can lead to capacity fading, increased impedance, and safety concerns, researchers are continuously working on the development of advanced analytical techniques including spectroscopy, microscopy, and other surface science methods, to reveal the intrinsic nature of SEI in real time to provide deeper understanding between SEI and battery performance.

1.4. *Aims and scopes of this review*

Despite the crucial role of SEI in battery performance, the SEI layer has a thickness in the nanometre range, very sensitive and susceptible to change in environments and consists of a mixture of crystalline, nanocrystalline, amorphous and polymeric materials which are on the surface and buried underneath the surface. In addition to this, the structure and composition of the SEI evolve dynamically during charging and discharging. As there is a complex interplay between composition, structure and properties, understanding the physicochemical properties of this SEI presents a significant challenge. It is especially difficult to comprehend the effect of different phases from the

surface to the subsurface under dynamic conditions, which is essential for improving performance and safety. To date, there are a handful of reviews that highlight the state of development of *ex-situ*, *in situ* and *operando* studies to evaluate the battery interfaces[22-24], a fundamental understanding of the composition-structure-properties correlation of SEI across various length scales by *in situ* or *operando* is rarely discussed except in modelling studies[25]. As our main objective is to obtain a vivid portrait of SEI to understand the complexity, this perspective highlights some recent literature on *ex-situ* and focuses mainly on recent advances *in situ* and *operando* techniques, the key findings, challenges and the importance of a multimodal approach to decouple the composition-structure-property of SEI and their correlations.

In Section 2, we will briefly discuss recent advances in *ex-situ* (or post-mortem) SEI characterization techniques, highlighting the significant advancements in enhancing surface sensitivity compared to the traditionally bulk-sensitive techniques, which have been instrumental in spatially resolving the nanoscale distribution of organic and inorganic components within the SEI layer. Section 3 delves into various recently developed *in situ* (or *operando*) techniques, ~~providing a~~that allow detailed ~~examination~~ investigation of SEI ~~characteristics~~features, including nanostructures, nanomechanical properties, electrochemical activities, chemical compositions and so on. These innovative methods have unveiled new insights into the intrinsic properties, formation mechanisms, and impacts of the SEI on battery performance. Nevertheless, this article mainly explores the techniques that integrate both chemical and physical properties and offer a fresh viewpoint for examining the surface and sub-surface of the SEI at nanometer resolution. Finally, Section 4 summarizes our key perspectives on SEI characterization techniques and provides~~esents~~ an outlook on their potential future research directions.

2. *Ex situ* characterization techniques

Ex situ or post-mortem analysis methods conventionally entail subjecting the electrode to initial cycling within a standardized battery cell unit and the sample for *ex situ* measurement undergoes a series of procedures, including washing and transfer, all conducted within the confines of a glovebox. This process carries with it the inherent risk of reactions occurring between the SEI and impurities present within the glovebox environment [19]. Such reactions may lead to the partial dissolution of the SEI and the transformation of metastable SEI compounds into more stable states. However, it is imperative to acknowledge that despite these challenges, *ex situ* characterization techniques have played a pivotal role in advancing our understanding of SEI films. The *ex-situ* or post-mortem, for example, various analytical techniques, including Infrared Spectroscopy (IR), X-ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy, and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), Nuclear Magnetic Resonance (NMR) have been employed to elucidate the average chemical composition and molecular structure of the SEI layer and this has been discussed extensively in other Reviews[24, 26-30].

This section discusses briefly on *ex-situ* methods where significant efforts have been made to enhance the surface sensitivity over the traditionally bulk-sensitive techniques and played a crucial role in spatially resolving the distribution of organic and inorganic components in the SEI layer at the nanoscale. Here, we highlight the substantial advancements made through the application of NMR spectroscopy in understanding the compositions and structures of SEI. The research team of Professor Clare Grey has developed room-temperature enhanced ^{7}Li, ^{1}H, and ^{19}F NMR spectra under magic angle spinning conditions by Overhauser Dynamic Nuclear Polarization (DNP). Here, the conduction electrons of lithium metal anode have been used as a free electron source to selectively amplify the signal in the order of magnitude at room temperature[30]. Although hyper polarization of lithium metal is not surface selective on the length scale, the subsequent spin diffusion from the hyperpolarized ^{7}Li metal anode could enhance only the SEI components which

are sufficiently close to interact with the conduction electron (Figure 3). This strategy has been used to reveal that LiF exists closer to the metal compared to other lithium-containing species such as Li_2CO_3 LEDC and lithium butylene dicarbonate (LBDC) and the thickness of SEI is thinner in 1.0 M $LiPF_6$ EC/DMC (LP30) with additive fluoroethylene carbonate (FEC) compared to electrolyte without additive. The outcomes of these studies have supported that the chemical composition and structural characteristics of the SEI are profoundly influenced by the choice of electrolyte system. Also, it supports the current understanding that SEI is impermeable to PF_6^-.

In this work, DNP has been utilized to study the buried/internal metal–diamagnetic solid–solid interfaces and hence, sheds light on the spatial distribution within the SEI interface in addition to the chemical composition of SEI. However, it is worth noticing that the NMR has yet to be realized in *operando* monitoring of SEI compositions and nano-structures in real battery conditions, and the physio-chemical properties of SEI have barely been revealed by NMR.

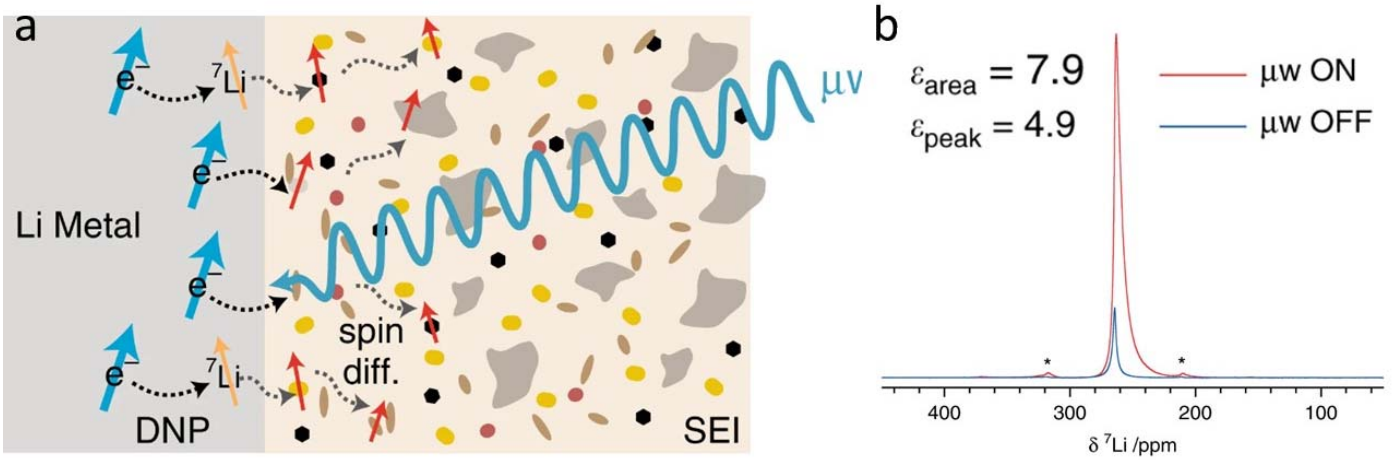

Figure 3 (a) Pictorial representation of the effect of microwave application and the resultant hyperpolarization of Li metal (DNP, black dashed arrows) and spin diffusion in the heterogeneous mixed organic/inorganic SEI (gray dashed arrows). (b) ^{7}Li NMR spectrum of microstructural lithium metal (sample A), with and without 15.6 W of microwave irradiation at 395.29 GHz (μw ON/OFF), recorded at 14.1045 T, 12.5 kHz MAS and a sample temperature of ~300 K, using a Hahn echo pulse sequence showing the enhancement. Spinning sidebands are marked with an asterisk. Reproduced with permission. [30] Copyright 2020, Nature Publishing Group.

The employment of low-temperature conditions during sample preparation has proven beneficial in stabilizing sensitive battery materials and interfaces and highlights the importance of preserving the liquid and solid phases. This approach facilitates high-resolution characterization via cryogenic transmission electron microscopy (cryo-TEM, Figure 4), revealing amorphous nanoscale structures within diverse electrolyte systems, thus contributing valuable insights into the significance of SEI in different electrochemical contexts[31, 32].

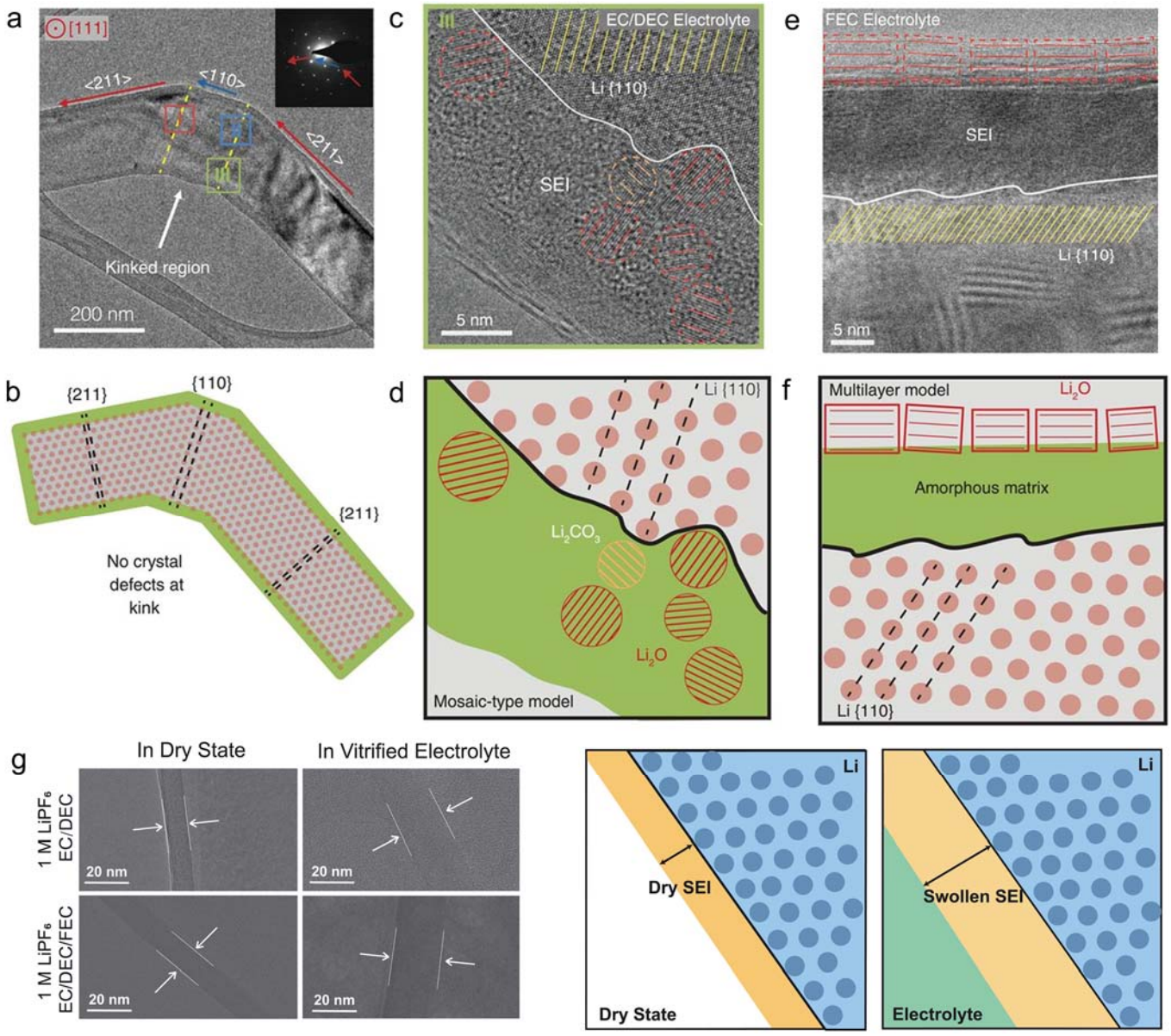

Figure 4 (a) TEM and (b) scheme of the single-crystalline nature of the kinked Li; (c) TEM and (d) scheme of the mosaic-type SEI layer; (e) TEM and (f) scheme of the multilayer-type SEI layer; (g) Comparison TEM and the scheme of the SEI in the dry and vitrified electrolyte. Reproduced with permission [19, 31]. Copyright 2017, AMERICAN ASSOCIATION FOR THE ADVANCEMENTOF SCIENCE. Copyright 2022, AMERICAN ASSOCIATION FOR THE ADVANCEMENTOF SCIENCE.

The first study of cryo-TEM from Cui et al. reveals the detailed nanostructure of the lithium metal dendritic growth within carbonate-based electrolytes, occurring primarily along <111> (preferably), <110>, or <211> crystallographic directions, resulting in the formation of multi-faceted single-crystalline nanowires (Figures 4a, b)[19]. However, it is essential to note that this structural pattern is susceptible to environmental influences. The mosaic structure of the SEI layer in standard 1M $NaPF_6$ in EC: DEC electrolyte and layered structures in electrolyte with 10 % FEC additive (Figure 4c-f), and the structure change of the SEI when exposed to the electrolyte (Figure 4g) are displayed in Cryo-TEM. For example, when the SEI is not wetted, it primarily comprises alkyl carbonates originating from the carbonate-based electrolyte. The SEI exhibits swelling behaviour when exposed to wet conditions within the electrolyte, leading to an increased presence of carbonate-based organic molecules within the wetted SEI layer (Figure 4g)[31]. Further study indicates various components within the SEI assume differing roles. Amorphous organic constituents possess mechanical elasticity, allowing them to endure the volumetric expansion experienced during the charge and discharge processes of the negative electrode[32, 33]. In contrast, crystalline lithium

carbonate exhibits instability and susceptibility to decomposition upon interaction with lithium metal. Moreover, atomic-scale images from cryo-TEM studies by Bing et. al., confirm that Li_2O or the over-lithiated amorphous phase such as LiO_x, LiC^+ always buffer the Li_2CO_3 from directly contacting the Li metal and also reveal the instability of lithium carbonate dispersed within the outer SEI which engages in continuous interactions with the electrolyte, leading to gas generation and, consequently, the formation of an evolving and porous SEI[27, 33].

Interestingly, a recent study has provided additional insights into why FEC additives can improve the cycling life when running at the carbonate-based electrolyte[28, 34]. Within the mosaic-like SEI structure, there is an uneven distribution of inorganic nanoparticles, resulting in regions with a higher concentration of these nanoparticles exhibiting expedited lithium-ion conduction and faster lithium deintercalation rates. However, once the metallic lithium within these regions is exhausted, the remaining metallic lithium is unable to sustain a conductive pathway to the electrode, rendering it inactive, often referred to as "dead lithium." In contrast, within the layered SEI structure, the density of inorganic nanoparticles is relatively uniform, leading to comparable lithium-ion conduction rates across different regions [28, 34]. This uniformity facilitates a more even lithium deintercalation process throughout the SEI, thereby promoting a more homogeneous cycling behaviour.

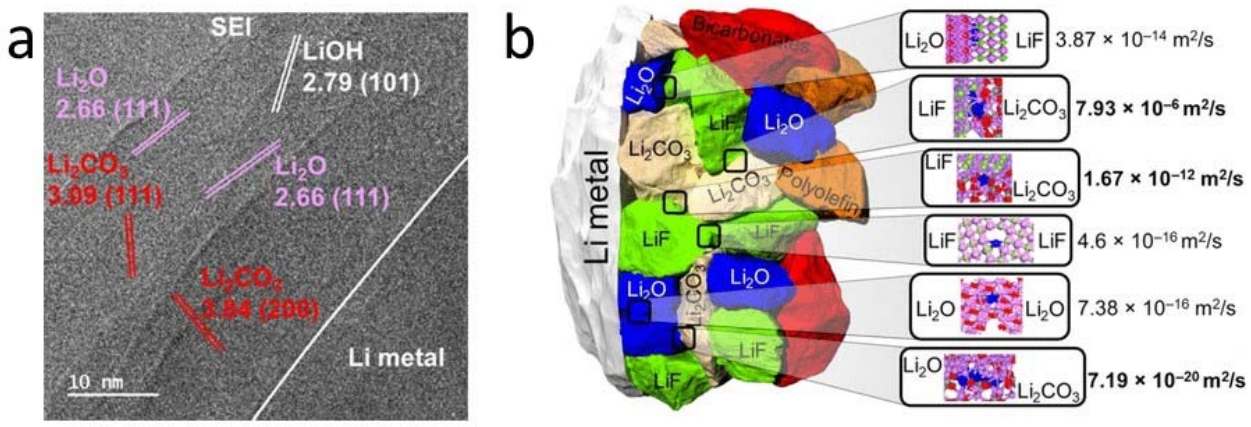

Figure 5 (a) Cryo-TEM image of the SEI layer formed on Li metal; (b) Pictorial representation of the nano structure of SEI identified from cryo-TEM and the diffusion coefficient in different grain boundaries using DFT simulations. Reproduced with permission [35] Copyright 2023, ACS Publications.

These cryo-TEM results have provided valuable information on the determination of SEI composition and structure in atomic scale/nanoscale resolution. However, the bulk inorganic components of SEI such as Li_2CO_3, Li_2O and LiF, are rather poor Li^+ conductors compared to the nanocrystalline phases of Li_2O and have moderate Li^+ ion conductivities. It's also reported that Li^+ ions are transported along grain boundaries between the different inorganic phases. This reveals that understanding the distribution of crystalline domains and the grain boundaries (GB) within the SEI is crucial for the uniform transport of lithium ions and underscores the importance of cryo-TEM in evaluating the failure modes of batteries. Hence, the impact of GBs in the SEI was investigated using cryo-HRTEM along with computational methods such as first principle calculations on the thermodynamic, kinetic, and electronic properties of the interface between the components[35].

From cryo-HRTEM, a distinct SEI layer with an approximately 25-30 nm thickness composed of Li_2O, Li_2CO_3 and LiOH crystals with d-spacing 2.66, 3.09, 2.84, and 2.79 Å and lattices orientations along (110), (111) and (200) and (101) respectively are identified as grains (Figure 5a). Although, six grain boundaries were able to identify using cryo-TEM, only three stable configurations were found theoretically (LiF(111)/Li_2CO_3(200), LiF(111)/Li_2CO_3(002), and Li_2O(111)/Li_2CO_3(111)). Among these, the LiF(111)/Li_2CO_3(200) GB showed the highest rate of Li diffusion attributed to the favourable Li

multiatom coordination within the GB that facilitates the multiatom hopping mechanism, which is more advantageous compared to other diffusion mechanisms. Furthermore, analysis and comparison of the electronic structures of the GBs revealed that the $Li_2O(111)/Li_2CO_3(111)$ GB is particularly prone to Li dendrite formation despite a relatively small diffusion coefficient. This combination of experiment and simulation suggests that the presence of this GB configuration may increase the likelihood of dendritic growth, which can pose safety risks and negatively impact the performance of Li-ion batteries. These results also reveal the importance of investigating the complex cooperative transport mechanisms of multi-components in the SEI layer compared to the single SEI components. Here, the advances in Cryo-TEM not only provided insight into the spatial distribution and the nanostructure of the SEI components, but it also been used to evaluate the transport properties of SEI. Despite all these significances, the practical application and equitable/fair access is limited due to the high cost and technical challenges associated with conducting cryogenic experiments and vast/fast data collection.

3. Recent advances in novel *operando* characterization techniques

Although the above post-mortem experiments effectively represent the formed SEI, they only reveal the static structure and composition information and there is a lack of insight into the intermediate states and the dynamic evolution of SEI during cycling. This limitation can lead to artefacts and encourages the researchers to focus on *in situ* or *operando* conditions for a more comprehensive understanding.

Operando SEI characterization techniques involve studying the SEI layer under realistic operating conditions, offering advantages over traditional *ex situ* (offline) characterization techniques when it comes to understanding battery performance. *Operando* techniques can capture the transient electrochemical reactions and directly link these processes to the electrochemical response of the battery which is often missed by *ex situ* techniques without altering the chemical and structural integrity of the interface regions. As mentioned above, more comprehensive reviews on the traditional characterization techniques that were used or modified as *operando* characterization techniques for SEI studies can be found in Refs[13, 14, 36]. In this article, we specifically focus on techniques and methodologies that amalgamate chemical or physical properties to provide a new perspective toward understanding the surface and sub-surface of SEI at nanometre resolution. Correlating the properties with the structural characteristics of the SEI from different perspectives is expected to offer unprecedented insights into its composition, structure, properties and electrochemical behaviour.

3.1 Advanced scanning probe microscopy

Traditional *operando* electrochemical atomic force microscopy (EC-AFM) has been used to study SEI formation through the real-time monitoring of electrode surface topography with nano-scale resolution[36]. However, some key information about SEI, such as the mechanical moduli, fine nanoarchitecture, electrochemical activity and ionic transportation properties, are generally inaccessible by traditional EC-AFM techniques.

Recent studies focus specifically on obtaining these key SEI properties such as elasticity and viscosity to generate the nanoscale distribution of SEI organic/inorganic components, so-called SEI fine nanoarchitecture. For example, targeting the nanomechanical properties and nanostructure of SEI, Chen et al proposed the first three-dimensional nano-rheology microscopy[11] based on the shear modulation[37] mode EC-AFM (Figure 6a) which revealed the three-dimensional nanostructure of the SEI layer formed on graphite basal and edge planes in the real operational battery. Interestingly, the key information used to differentiate and reconstruct the three-dimensional structure of SEI is the viscosity, which was less noticed but had very distinct properties for the organic and inorganic parts

of SEI. Therefore, this new technique shows good spatial resolution and mechanical sensitivity toward the different components inside the SEI layer (Figure 6b). Moreover, the electrical double layer (EDL) structure is often considered to be a key part of initial SEI, in this work, the novel AFM-based force distance spectroscopy[38-41] has also contributed significantly to the understanding of this very initial EDL structure. Nevertheless, one should note that the contrast of force curves is still under debate[42], cautions need to be taken by researchers when studying the EDL structure by 3D AFM force-distance curves. Although the correlations between EDL structure and SEI structures need further systematic characterization studies, there is no doubt that nanostructures of SEI which dominate their mechanical properties can be tuned by the EDL structures.

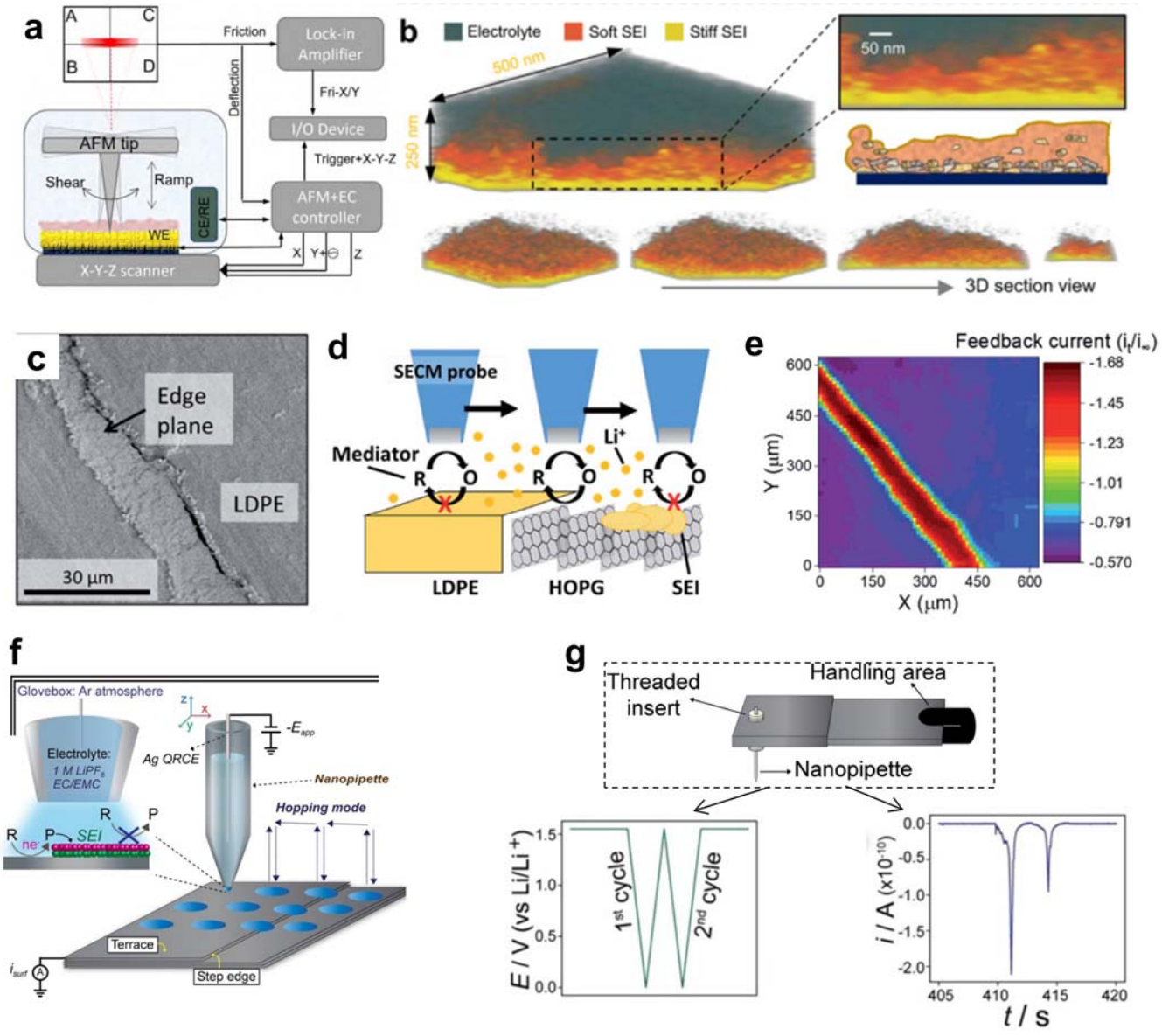

Figure 6 (a) Schematic of three-dimensional nano-rheology microscopy and (b) the observed three-dimensional nanostructure of graphite edge plane SEI layer. (c) Scanning electron microscopy of an unused region of HOPG edge for SECM measurements. (d) Illustration of SECM experimental setup and procedure for SECM imaging and positioning. (e) SECM feedback image of the HOPG substrate. (f) Schematic of SECCM operated in a hopping mode to study the formation of the solid-electrolyte interphase (SEI) at HOPG electrodes. (g) The applied potential and the measured current as a function of time during a typical SECCM experiment consisting of two voltammetric cycles at a pixel (spot on the surface). Reproduced with permission. [11, 43, 44]. Copyright 2023, Nature Publishing Group. Copyright 2019, The Royal Society of Chemistry. Copyright 2021, John Wiley and Sons.

Apart from the nanostructure and nanomechanical properties of SEI, the electrochemical activity and charge transfer dynamics such as lithium-ion transportation kinetics and electron conductivity have been explored by scanning electrochemical microscopy (SECM)[43, 45] and scanning electrochemical cell microscopy (SECCM)[44, 46, 47] with a high spatial resolution. SECM and SECCM derive from AFM and are based on a similar piezo scanner system of AFM but with distinct tips or feedback signals. Zachary et al used Li^+-sensitive probes to achieve *in situ* and localized tracking of Li^+ ions during the formation of the SEI and their subsequent intercalation processes. As shown in Figures 6c-e, by monitoring the potential-dependent reactivity of the graphite's edge planes, they investigated how the consumption of Li^+ ions at the interface led to competing reactions. Through cycling within the SEI formation potential range, their SECM measurements visualized both reversible ionic processes related to surface redox reactions and irreversible SEI formation, enabling the separation of charge-transfer steps at intricate battery interfaces. Prof. Patrick R. Unwin et al are the pioneers of introducing SECCM to study ion transportation in an electrochemical environment, including proton transportation through 2D materials[48] and lithium-ion diffusion through SEI layers[44]. As shown in the schematic diagram (Figure 6f) of SECCM proposed by Unwin et al, a mobile localized electrochemical probe operating in a hopping-mode protocol involved employing a single-barrel pipette. This pipette was loaded with electrolyte and an integrated Ag quasi-reference counter electrode. The procedure commenced by bringing the pipette in proximity to the sample surface. Upon establishing contact and forming a liquid meniscus, a cyclic voltammogram (CV) was recorded, as illustrated in Figure 6g. The most significant point of the SECCM set-up is to study the underlying local electrochemistry (spatially-resolved current-voltage relationship) of the SEI layer, which is essential for understanding the nanoscale lithium-ion transportation properties through the SEI layer and has not yet been revealed directly by other scanning probe microscopies.

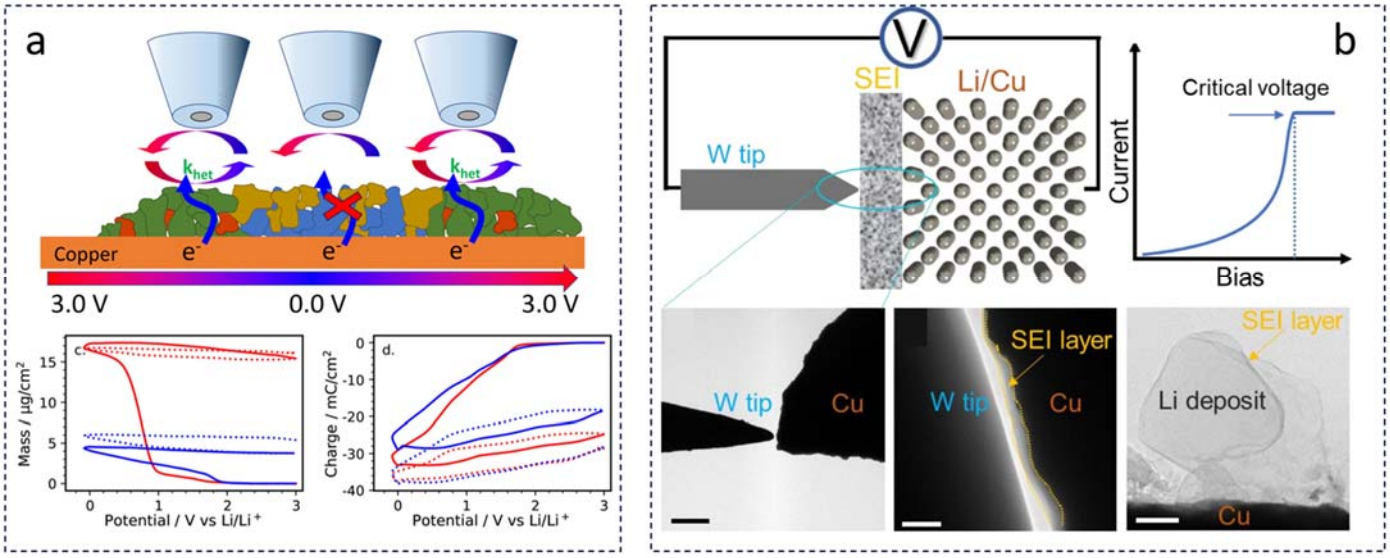

Figure 7 (a) Schematic diagram of the combination of an SECM and electrochemical quartz crystal microbalance for studying the SEI formation on Cu surface. (b) The combination of using TEM and AFM for studying the SEI conductivity. Reproduced with permission. [47, 49].Copyright 2023, ACS Publications. Copyright 2023, Nature Publishing Group.

The combination of SPM techniques and other *in situ* characterization techniques can provide an additional degree of freedom for understanding SEI composition-structure-property correlations. Krumov et al. visualized the SEI formation using SECM in feedback mode and showed that the electronic conductivity of Cu decreases at 1.0 V indicating the incipient interphase formation and kinetically limited SEI formation occurs at lower potentials[47] (Figure 7a). The observation of significant current during lithium plating 100 μV, indicates that the SEI undergoes rupture in the region where there is a development of lithium nucleation leading to positive feedback and tailing of

the distribution while regions that do not undergo lithium nucleation retain an intact SEI and maintains constant median. The subsequent lithium stripping studies reveal that the SEI is fully ruptured. The authors further validated the size and composition of the complex interfacial by complementary techniques such as *operando* electrochemical quartz crystal microbalance and *ex-situ* X-ray photoelectron spectroscopy (XPS). This observation of dynamically resolved SEI and the components by comprehending the key features such as mechanical and charge transfer properties provides solutions and insights to enhance the rational design of electrolytes and interphases in achieving better performance and safety[47, 50]. Xue et al. quantified the electrical properties of the SEI layer and battery performance by integrating *in situ* bias transmission electron microscopy (TEM) with scanning tunnelling microscopy (STM). As shown in Figure 7b, the measurement reveals that I-V characteristics of SEIs resemble certain electrical conductance rather than electrical insulators as conceived in other studies. This study also confirmed that the SEI with a higher rate differential conductance tends to exhibit a greater thickness and more complex topographic features leading to an inferior electrochemical performance[49].

Future advancements in electrochemical SPM for SEI studies must emphasize the importance of high-speed image capturing capability, which is crucial for observing the sub-second-scale dynamic evolution of SEI during electrochemical processes, providing valuable insights into its formation mechanisms and a more precise understanding of its morphological and mechanical properties. Under high scanning speed, the ability to maintain low-force interactions, which minimizes tip-induced damage or alteration of the delicate SEI layer, becoming more an important factor. Moreover, real-time *operando* capabilities that can capture SEI evolution under varying cycling conditions, temperatures, and chemistries are essential to bridge the gap between fundamental insights and practical battery performance optimization. By improving both these aspects, SPM-based techniques can enable more reliable and detailed investigations of the SEI, advancing our understanding of its role in battery performance and stability.

3.2 Optical methods

Optical characterization methods combined with electrochemical measurements offer several advantages, such as non-destructive, easy implementation, and multi-modal capabilities, when studying the electrode-electrolyte interface in batteries. Many optical methods[51-57] including Raman/FTIR/UV-visible light spectroscopy, ellipsometry, and embedded optical fibre sensor, have been used to study the battery electrode-electrolyte interface and provided quantitative information about the electrode phase and SEI composition changes, as well as the charge storage mechanisms.

Visible light has the advantage of studying the optical band gap changed by lithium-ion intercalation, and therefore *operando* optical microscopy has been used to study the lithiation/de-lithiation induced electronic structure changes of electrode materials, such graphite anode[52], $LiCoO_2$ cathode[54, 56] $Li_4Ti_5O_{12}$[58] and $Nb_{14}W_3O_{44}$ anode[53]. Although the thickness of SEI is at a range of a few to hundred nano metres that is typically out of the resolution limit of visible optical methods, optical microscopy with reflection interference geometry has been introduced to reveal the evolution of SEI formed on electrode surfaces. As shown in Figure 8a, Shan et al proposed a non-intrusive, real-time reflection interference microscope to capture the dynamic processes of formation and evolution of SEI with exceptional sensitivity[55]. The key optical properties used to differentiate the SEI component are the reflective index of different SEI components and their thickness. By recording the reflectance of the Cu electrode-electrolyte interface (Figure 8b), they observed the emergence of a lasting inner inorganic layer primarily composed of LiF, a brief establishment of an electrochemically charged double layer at the interface, and the subsequent appearance of a temporary outer layer rich in organic compounds. Moreover, it is worth noting that, visible light spectroscopy techniques can often be combined with other characterization methods, such as electrochemical impedance

measurements, to provide a more comprehensive understanding of SEI formation and interface dielectric properties[59]. This multi-modal approach allows researchers to correlate the optical and dielectric properties of SEI with the overall electrochemical behaviour of the electrodes.

Raman and FTIR techniques can further provide the chemical composition information of SEI with molecule structure resolution[60]. The limited sensitivity of vibrational spectroscopy, in terms of the requisite analyte concentration, renders the distinction of complex SEI species from the vibrational spectra of the electrolyte virtually unattainable. For example, in the context of *in situ* infrared research, it has been discerned that the spectral response is primarily dictated by changes in lithium coordination within the electrolyte. Notably, signals stemming from the final SEI species are essentially absent[22, 61]. Therefore, to access information predominantly from the nanoscale SEI structure by employing infrared and visible light, it is theoretically imperative to transcend the diffraction constraints[51]. Recently, a novel depth-sensitive plasmon-enhanced Raman spectroscopy (DS-PERS)[51] facilitates the non-destructive and *in situ* analysis of the nanostructure and chemical properties of the SEI with single molecule detection sensitive and sub-nanometre scale spatial resolution. This is achieved through the cooperative amplification of localized surface plasmons utilizing nanostructured copper, shell-isolated gold nanoparticles, and lithium deposits positioned at varying depths (Figure 8c). The proposed DS-PERS investigation yields detailed molecular-level insights that uncover the significant impact of lithium on altering the formation of the SEI, shedding light on the functions of SEI in controlling the de-solvation of lithium ions and the subsequent deposition of lithium at interfaces associated with the SEI.

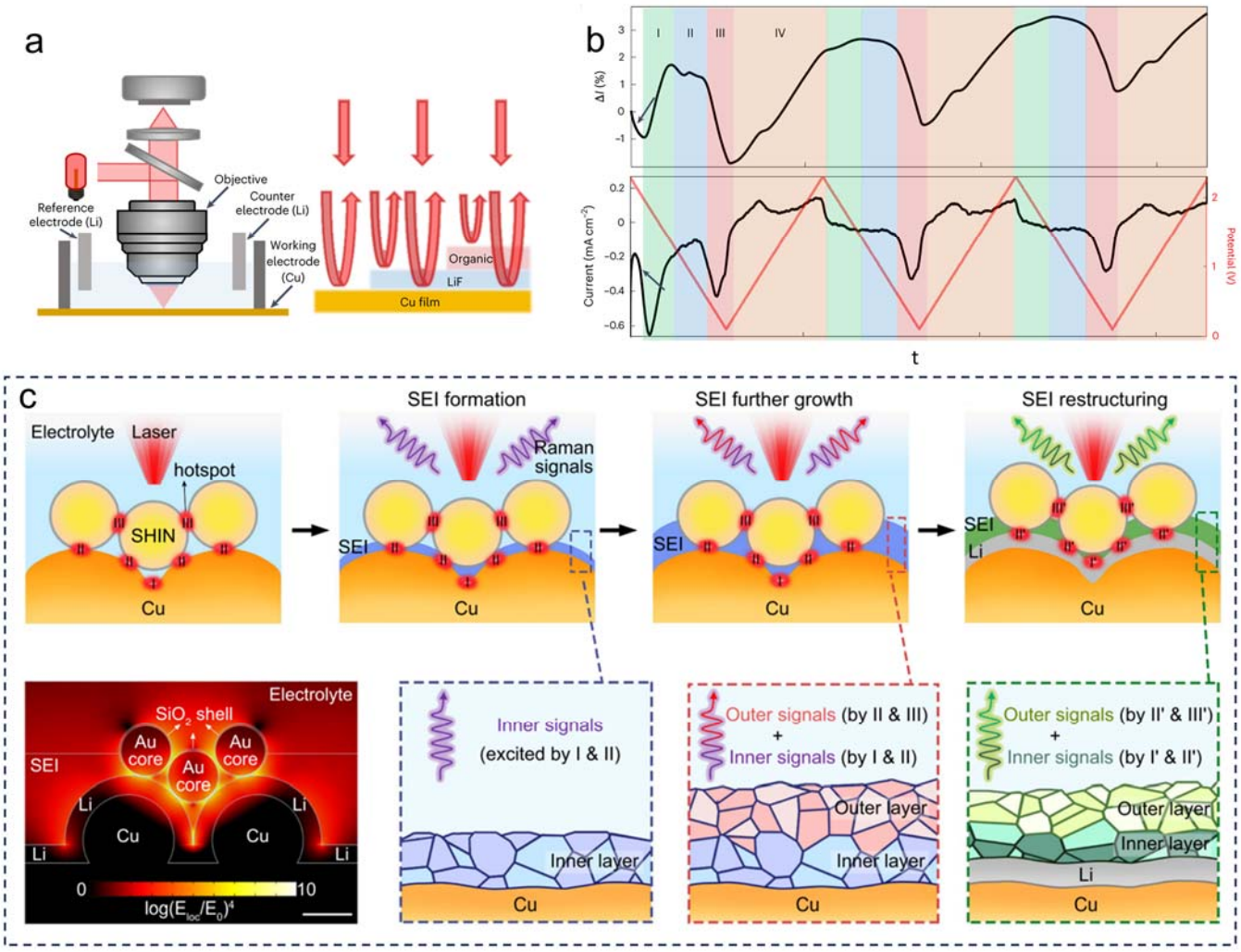

Figure 8 (a) Schematic diagram of using RIM to image the SEI formation dynamics. (b) The optical reflection signal (RIM signal) during the first three CV cycles. (c) Schematics of the DS-PERS that enable detection of

the signals from different depths in the SEI. The plasmonic structure of nanostructured Cu, SHINs and deposited Li generates a strong electromagnetic field to enhance the Raman signals from SEIs. Reproduced with permission. [51, 55] Copyright 2023, Nature Publishing Group. Copyright 2023, Nature Publishing Group.

In summary, these novel optical methods have been versatile and powerful toolkits for studying SEI formation in batteries, providing insights into dynamic processes, chemical composition, and structural changes, as well as contributing to a deeper understanding of battery performance and degradation mechanisms. The surface-enhanced Raman spectroscopy (SERS) techniques[57, 62, 63,] were also employed to investigate the stepwise SEI formation process on Au substrates immersed in a model electrolyte comprising $LiClO_4$ dissolved in EC solvent[63]. This approach facilitated the differentiation of effects associated with electrode/electrolyte bilayer charging, electrode adsorption polarization (the Stark effect), and SEI dissolution. The principal products formed at *ca*. 2 V *vs*. Li^+/Li were identified as Li_2CO_3 and Li_2O. Furthermore, under the catalytic influence of the Au interface, the reduction of EC was determined to be a two-electron process, yielding Li_2CO_3 and C_2H_4 gas. Notably, CO_2 plays a pivotal role in both chemical and electrochemical reduction pathways. The authors emphasized the significance of gas diffusion at the interface and the potential presence of contaminants during sample preparation, both of which could introduce misleading factors into the final test results within the context of interface processes[63]. In the future, the integration of high-resolution techniques, such as tip-enhanced Raman spectroscopy, could enable nanoscale chemical mapping of SEI components with unprecedented detail. Meanwhile, the development of advanced optical probes and tailored substrates that enhance sensitivity to weakly scattering species in the SEI can reveal subtle chemical changes. Lastly, leveraging machine learning algorithms to analyze large spectroscopy datasets could provide deeper insights into the complex correlations between SEI composition, structure, and battery performance.

3.3 Electrochemical quartz crystal microbalance (EQCM)

Electrochemical quartz crystal microbalance, often abbreviated as "EQCM", is a specialized analytical instrument used in electrochemistry and materials science. The basic function of a quartz crystal microbalance is to measure changes in the resonance frequency of a quartz crystal electrode as a result of mass changes occurring on its surface. When used in an electrochemical context, the EQCM can provide valuable information about processes such as electrodeposition, corrosion, and the formation of thin films or coatings. Recently, EQCM with the added ability to monitor changes in dissipation during electrochemical processes (EQCM-D)[64, 65] has driven much research attention. EQCM-D enables measuring changes in crystal oscillation energy loss or damping during electrochemical processes[66], providing information about mass changes (frequency) and viscoelastic properties (dissipation) of the SEI layer as it forms and evolves. This information can be used to understand the SEI layer's growth rate, thickness, and viscoelastic properties, as well as the mechanical properties and stability of the SEI.

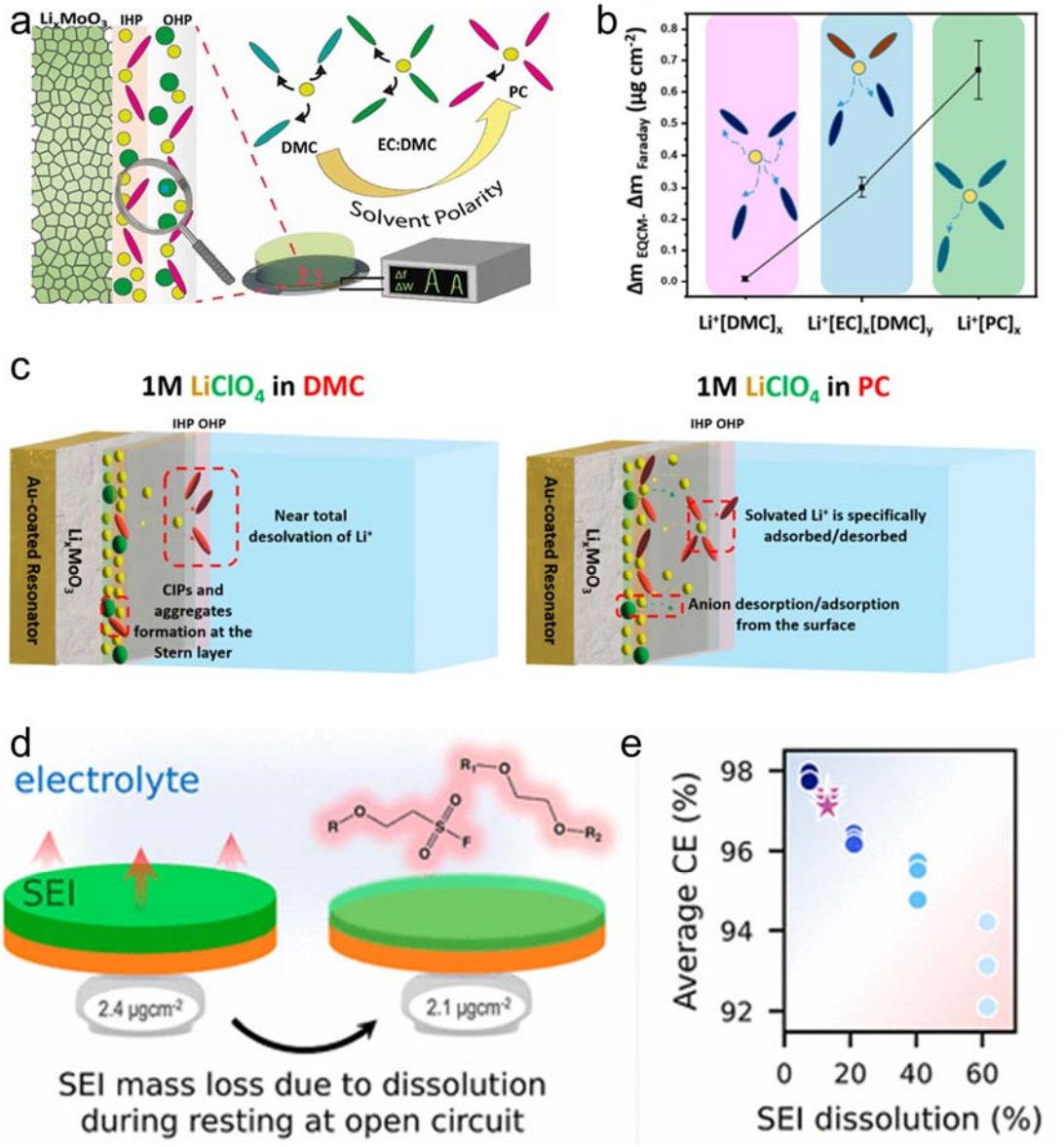

Figure 9. (a) Schematic illustration of studying solvation structure inside EDL by EQCM. (b) The tendency of the difference between both masses ($\Delta m_{EQCM} - \Delta m_{Faraday}$) following the binding energy of solvated Li^+ species in each solvent. (c) Schematic illustration of the EDL structure evolution related to solvent polarity. (d) Schematic diagram of SEI dissolution revealed by the mass changes recorded by EQCM. (e) The relation between the coulombic efficiency and the mass percentage of SEI dissolution. Reproduced with permission. [67, 68]. Copyright 2023, ACS Publications. Copyright 2022, ACS Publications.

Since the initial SEI formation is closely related to the electrical double layer (EDL) structure, an emerging novel application of EQCM in battery interface research is the deciphering of the EDL structures, observation of EDL charging and initial SEI formation[68-70]. As shown in Figure 9a, Ozlem et al. conducted an EQCM investigation into the impact of different combinations of solvents and salts, each varying in dipole moment and size/weight, on the structural characteristics of the EDL forming at the electrolyte-electrode interface (EEI) of Li_xMoO_3. The research highlights the substantial involvement of solvated lithium ions and anions in charge compensation at EEI. By altering the solvent type, and distinguishing between cyclic and noncyclic solvents, they provide compelling experimental evidence for the direct correlation between ion solvation and solvent polarity (Figure 9b). Figure 9c illustrates that EQCM-D detected an anionic response characterized by (electro)adsorption/desorption in electrolytes containing highly polar solvents like PC or EC: DMC mixtures. This is in contrast to less polar solvents like DMC, where there is a greater possibility of

CIP formation and aggregate formation. This observation using EQCM-D signifies the profound influence of solvent choice on EDL behaviour and later formed SEI. This further revealed that, by utilizing EQCM, the *in situ*/*operando* chemical stability of SEI can be quantified by evaluating the SEI dissolution and growth at ng/cm^2 scale. It has been demonstrated that over half of the SEI mass is lost during battery rest[71]. Further, by comparing the EQCM results with the coulometric experiments (Figures 9d and 9e), Sayawong et al corroborated that SEI dissolution is the major contributor toward SEI evolutions and established a correlation among solubility, passivity and cyclability, therefore, they added that physical and chemical properties of SEI plays a major role in minimizing the capacity loss[67]. Due to the limited volume expansion of graphite-based anode during cycling, this dissolution of SEI is not that detrimental compared to lithium metal batteries which undergo high volume expansion[67, 72, 73].

Although EQCM can provide direct results from the obtained molecular mass, qualitative and quantitative characterization of EQCM response changes during SEI formation and automatically generate atomistic models of SEI components that are compatible with EQCM data remain challenging. ALC-EQCM – a software developed for post-processing EQCM data attempts to link EQCM data with simulation capabilities[74]. The post-process of EQCM data using ALC-EQCM may offer an effective strategy to explore reaction configurations only compatible with experiments and support the research of complex reactions that generate unexplored SEI components in a new electrolyte system. In the future, integration of EQCM with other complementary techniques, such as spectroscopic or electrochemical impedance methods, could provide a more holistic understanding of the dynamic interplay between SEI mass changes, composition, and electrochemical activity. Developing *operando* EQCM setups that can operate under realistic battery conditions, including high current densities and extreme temperatures, will be essential for studying SEI behaviours in practical environments. Lastly, but most importantly, innovations in interpreting EQCM data, such as advanced modelling techniques, could improve the resolution of solvent, ion, and other species' contributions to SEI dynamics, offering deeper insights into its formation mechanisms and long-term stability.

3.4 Surface force apparatus

Electrochemical surface force apparatus (EC-SFA) is a novel SEI characterization technique that combines the principles of a surface force apparatus with electrochemical techniques, specifically good at studying the molecular interaction forces on the battery interface[75, 76]. The proposed methodology has served as a unique and valuable new tool for analysing and ultimately tuning the mechanical properties of SEI layers. As shown in Figure 10a, it consists of two parallel surfaces or mica sheets that can be brought into proximity and separated, allowing for precise measurements of forces (e.g., van der Waals, electrostatic, capillary) as a function of the distance between the surfaces. In an EC-SFA setup, the SFA apparatus is modified to include an electrochemical cell or chamber. This allows researchers to control the electrochemical environment, including the composition of the electrolyte solution and applied potential, while simultaneously measuring forces between the surfaces. Renner et al used *in situ* SFA to observe the surface force-distance curves on a gold working electrode surface during the SEI formation cycles[76]. A clear signature for a new compressible film can be recognized in the force-distance characteristic upon electrode discharge (Figure 10b), and the increased force slope was observed at the low discharge voltage region, indicating a compressible nature of SEI. Their SFA results demonstrate that SEIs are to a large volume fraction polymeric and potentially flexible. Therefore, tuning of polymeric structures in the SEI layer will hence provide a viable strategy for optimizing performance during large volume expansion and contraction cycles. Future developments should focus on integrating SFA with complementary spectroscopic techniques, which could reveal the relationship between SEI composition and its interfacial mechanics. Developing more sophisticated models to interpret SFA

data in the context of complex, dynamic SEI environments will further strengthen its role in advancing our understanding of SEI behaviour.

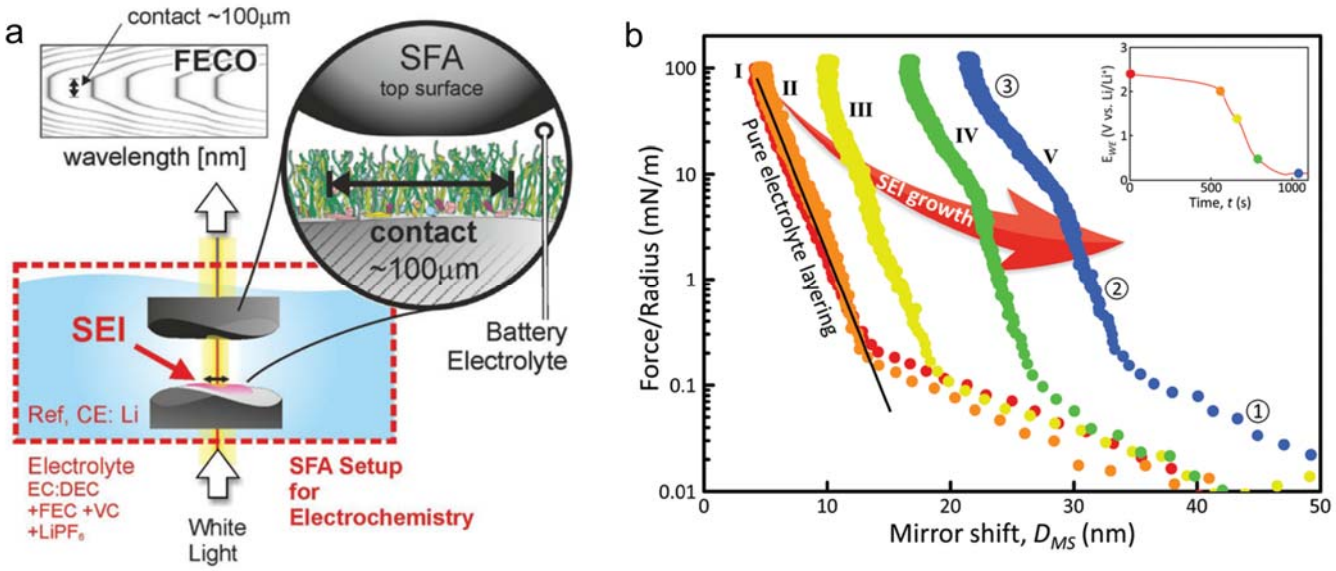

Figure 10 (a) Experimental setup of the electrochemical surface forces apparatus (SFA), modified for lithium-ion battery testing (battery-SFA). (b) Force run curves on the SEI on gold-coated mica, taken on different depths of discharge, indicated by voltage-time curve (inset). Reproduced with permission. [75, 76] . Copyright 2019, John Wiley and Sons. Copyright 2016, Nature Publishing Group.

3.5 Operando XPS

It's well known that, XPS is an indispensable technique to determine the qualitative and quantitative chemical composition, oxidation states and chemical environment of the probed elements in SEI and has opened new avenues to understand the redox processes and surface reactions that occur at the battery interfaces under post-mortem conditions[22, 77]. Since, high-energy X-ray beams are expected to damage the nanometer-thick SEI, hard and soft X-ray photoelectron spectroscopy (HAXPS and SXPS) have been used to understand the interface of solid-electrolyte interphase. However, the limitations such as ultra-high vacuum environment (UHV), shallow depth analysis (~ 5 nm) and the lateral resolution imposed by the X-ray beam of conventional XPS hindered their ability to study the chemical composition, charge transfer and the nature of chemical bonds of SEI in real battery environments. Therefore, to fully understand the complex solid-liquid interfaces in a battery, measurements at high pressure or ultra-low vacuum are required to analyse the interfaces, including the liquid phase.

The major challenge experienced with this technique is the scattering of photoelectrons before detection. To maximise the gain of photoelectrons under the desired pressure in the chamber, the aperture and the beam spot were kept at the same size[78]. To measure the nanometer thickness SEI, ambient pressure XPS (APXPS) measurement was developed, in which the electrodes are immersed in the electrolyte and then slowly retracted from the beaker to create a thin liquid meniscus. These techniques are becoming increasingly common and various electrolytes have been investigated using static droplets and liquid jet setups. These studies show that APXPS not only provides information on oxidation state and surface layer formation but also offers unique capabilities to provide information on electrode potential differences[79, 80].

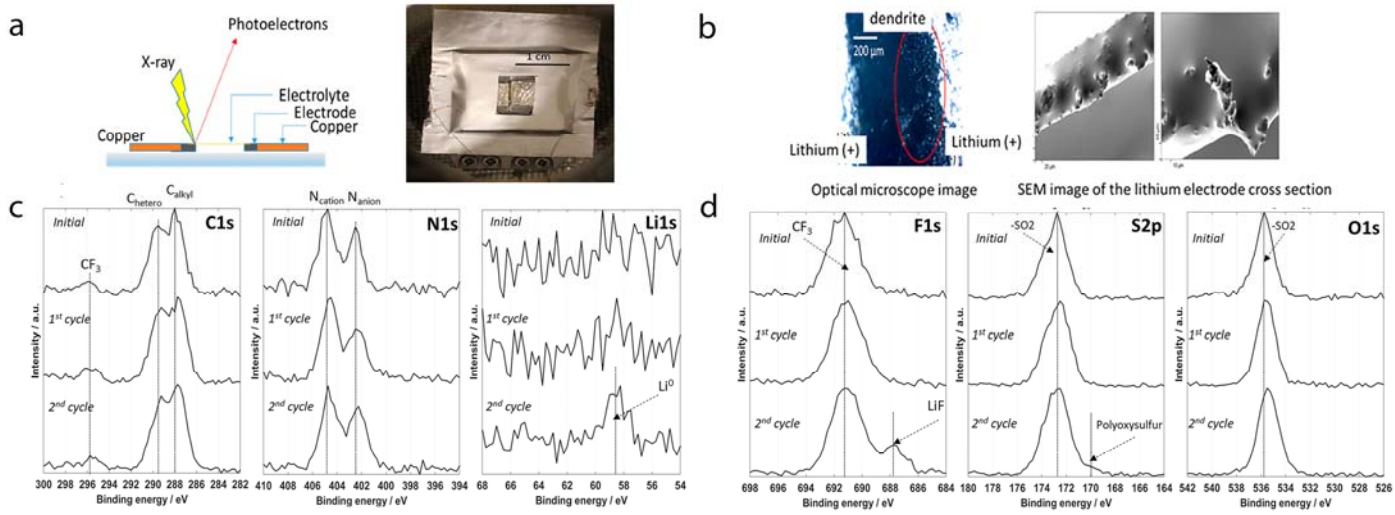

Figure 11 (a) Design of planar-like cell and the OXPS pouch cell (b) Optical and SEM images recorded after polarization, demonstrating the formation of lithium dendrites with needle-like shape. (c-d) C 1s, N 1s, Li 1s, F 1s, S 2p, and O 1s were recorded at the interface Li/C_1C_6ImTFSI-LiTFSI during the polarization at the current density of 200 µA cm^{-2} in the OXPS cell. The spectra were recorded after GEIS measurement. Reproduced with permission. [81]. Copyright 2021, ACS Publications.

Recently, *operando* XPS (OXPS) was performed with a 2D-planar-like cell made of transparent glass containing two parallel lithium foils connected to a copper current collector[81]. They are separated by a cavity (0.02-0.03 cm) containing ionic liquid-based electrolyte and encapsulated in a pouch cell configuration to fix the position of the two-lithium foil and improve the electrical contact of the cell (Figures 11a and 11b). Here, the instrument is equipped with a micro-focused *X*-ray beam and a dual beam charge neutraliser. The use of electron and ion charge neutralization guns modifies the Fermi level of the electrode and was investigated to explore the dynamic chemical structure, as well as the change in surface potential at the interface between lithium and electrolyte. Using IL-based electrolytes Li/C_1C_6ImTFSI-LiTFSI/Li and Li/C_1C_6ImFSI-LiTFSI/Li, the SEI compositions were studied by OXPS and compared with post-mortem results of coin cells by Benayard et al.[81]. As shown in Figures 11c and 11d, the OXPS core level assignment (C 1s, F 1s, Li 1s, N 1s, O 1s and S 2p) confirms the formation of LiF and the lithiated electrolyte degradation products or plated lithium and N-heterocyclic carbenes. Although this study is still at the proof-of-concept level, this gives hope that XPS can be applied to study the real-time dynamics of the battery electrodes and the interfaces. Apart from the chemical component of SEI, understanding the thermal stability of SEI can be achieved through *in situ* heating XPS. During the heating treatment, the evolution of the SEI composition, nanostructure and the released gases can be further studied by XPS, cryo-TEM and gas chromatography respectively, which provides deep insights for designing an ideal SEI with enhanced stability.

In the future, further enhancing the temporal resolution of *operando* XPS is critical for capturing the dynamic chemical evolution of the SEI. Developing advanced cell designs that maintain realistic electrochemical conditions while ensuring compatibility with XPS requirements will further improve the reliability of *operando* XPS measurements. Additionally, improving the depth-profiling capabilities of *operando* XPS, such as through synchrotron-based techniques or angle-resolved methods, can provide more precise insights into the spatial distribution of SEI components.

3.6 Operando Mass Spectrometry Techniques

The recent application of TOF-SIMs in understanding the molecular signature of the interphase under dynamic conditions through chemical mapping of the SEI at nanometre scale[82, 83]. As shown

in Figures 12a and 12b, Cheng et al. designed a dedicated high vacuum compatible microfluidic device and used it to monitor the dynamic formation of SEI layer in Cu||$LiCoO_2$ micro-cell with 1.0 M $LiPF_6$/EC-DMC using TOF-SIMS. Comparing the TOF-SIMS data with the fresh cell data at 1.0 V, depth profiles of the positive ions indicate the formation of an electric double layer at 1.0 V (Figure 12c) and the onset of electrolyte decomposition at 2.0 V (Figure 12d) and the formation of SEI at 3.0 V (Figure 12e). The formation of an SEI is irreversible, i.e. the SEI layer can still be observed even after discharging to 0.5 V. This means that after charging to a stable voltage of 3.8 V, it becomes difficult to penetrate the Li-enriched solid layer to expose the electrolyte. The SEI thickness is estimated to be 30-60 nm, which is consistent with the literature-reported value based on *ex situ* measurements. Additionally, the *in situ* TOF-SIMS study also confirmed that the components of electrolytes may significantly influence the thickness and homogeneity of the SEI. Future prospects include the development of highly sensitive MS systems capable of detecting trace gaseous and volatile products associated with SEI formation and decomposition in real time. Integrating *operando* MS with advanced electrochemical setups will allow simultaneous correlation of mass spectrometric data with electrochemical performance, providing deeper insights into SEI-related reactions. Innovations in isotope labelling could enhance the capability to track specific reaction pathways and identify the origins of SEI components.

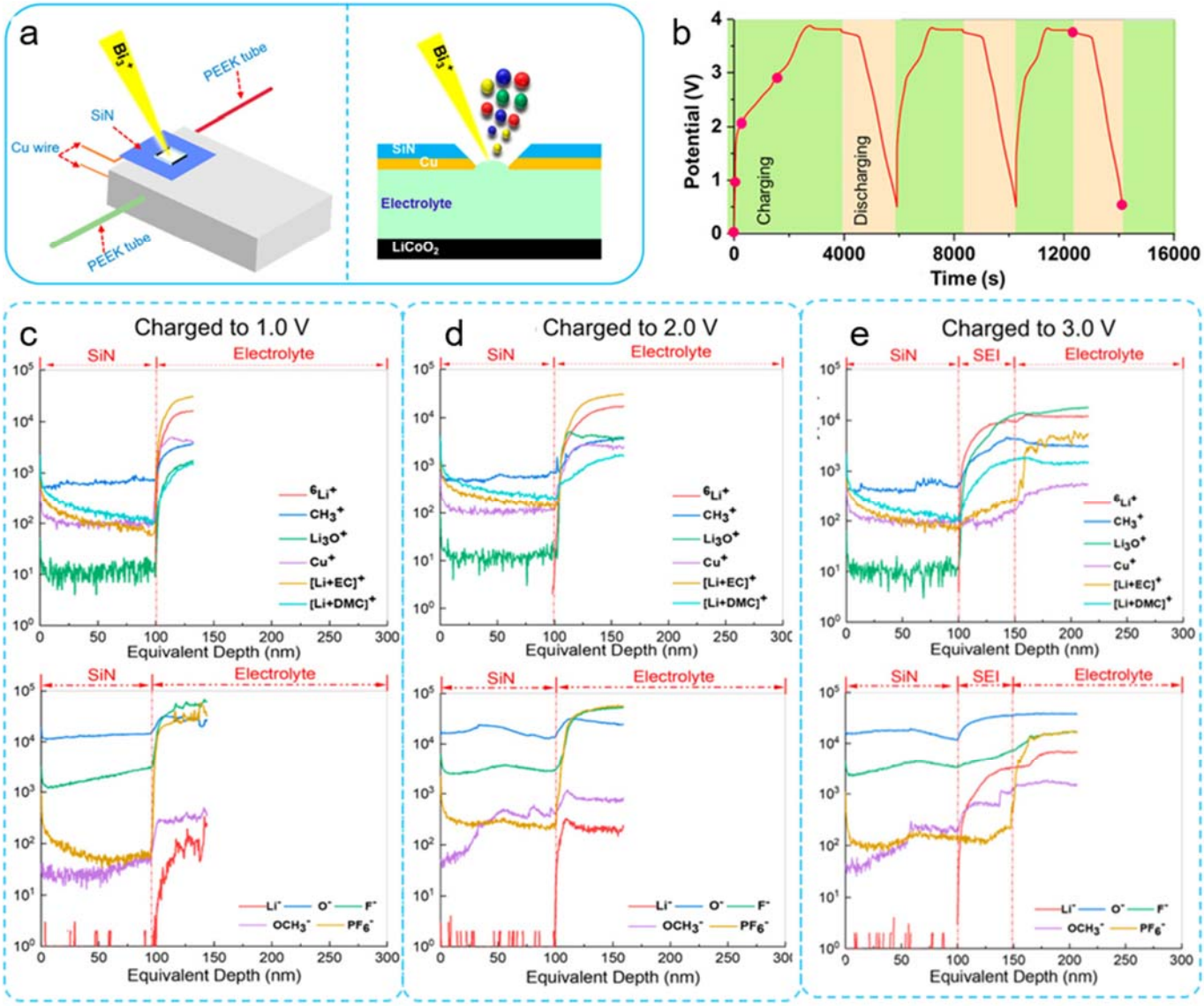

Figure 12 (a) Schematic illustration of the microfluidic cell and the *in situ* liquid SIMS analysis of SEI. (b) Diagram of the charge-discharge process of the battery and the first three cycles (red dots represent different stages of charging and discharging). (c-e) TOF-SIMS depth profiles of representative ions measured on the interface of a Cu anode and 1.0 M $LiPF_6$/EC-DMC electrolyte using the microcell at the fresh and different stages of charge/discharge as depicted in Figure 12b. Reproduced with permission. [82]. Copyright 2023, ACS

Publications.

3.7 Other novel techniques

Molecular structural characterization techniques are crucial for understanding the composition of the SEI. For example, an ultra-thin mechanically peeled graphite was selected as the working electrode and the *in situ* setup was fabricated in a controlled argon gas environment to mitigate the influence of external factors such as water and oxygen for scanning transmission electron microscopy (STEM) study (Figures 13a and 13b). It worth noticing that, this novel *in situ* STEM technique minimized the pressure differential that develops across the Si_3N_4 membrane windows when the fluid cell is placed in the electron microscope's high vacuum[84], significantly improving the resolution and EELS signal quality. While this advanced approach offers enhanced spatial resolution and analytical capabilities, it may introduce trade-offs such as reduced liquid volume, which could limit the inventory lithium in electrolytes during the SEI formation, and increased complexity in experimental setup.

The electron energy loss spectroscopy (EELS) was then employed in conjunction with STEM to obtain molecule information for various constituents of the SEI layer[84]. These "chemical fingerprints" were subsequently applied to enable high-resolution, real-space mapping of corresponding physical structures, thus yielding nanoscale spatial resolution images depicting the SEI formation process (Figure 13c). This methodology's application served to validate previously acquired information from characterization techniques, confirming the chemically heterogeneous nature of the SEI, which primarily comprises inorganic Li compounds. Notably, no evidence indicative of a "grain boundary" akin to the typical mosaic structure of the SEI was discerned. Therefore, the authors proposed an SEI model resembling the consistency of fermenting dough, wherein distinct components do not fully mix but also do not manifest delineated boundaries.

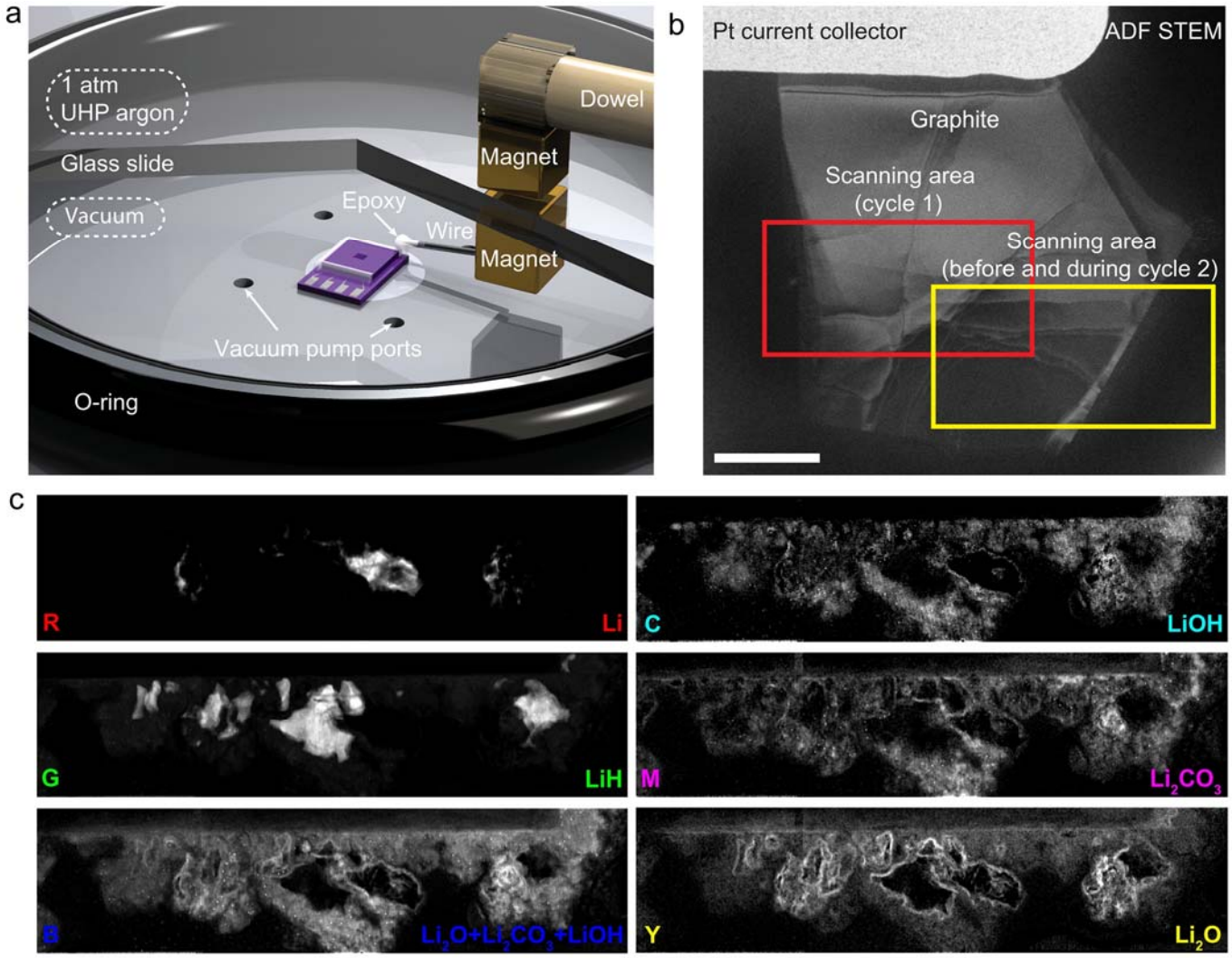

Figure 13 (a) scheme of the liquid cell imaging platform for STEM-EELS; (b) ADF STEM image of the graphite flake within a sealed fluid cell with the scale bar, 2 μm; (c) corresponding grayscale MLLS images with individual components of the graphite anode during cycling. Reproduced with permission. [84]Copyright 2023, American Association for the Advancement of Science.

Although this method provides elements and spatial chemical mapping of the SEI, it lacks information on crystal structure. Besides STEM-EELS requires more doses to obtain a decent spectrum, which is unfriendly for beam-sensitive dendrite samples. Thus, Wang et al introduced an effective four-dimensional electron microscopy analysis to reveal the spatial distribution of compounds in lithium dendrites in a large field of view. Here, the illumination beam scans across the sample and the camera records a 2D diffraction pattern at each scanning position. This results in the acquisition of a four-dimensional (4D) data set with two dimensions corresponding to real space-scanning axes and the other two dimensions representing the reciprocal axis. Hence these 4D data sets are capable of carrying abundant information about the nanostructure and its spatial distribution in the dendrite samples at low electron dose, which however not apparent and requires further extraction. A non-negative matrix factorization (NMF) algorithm was employed to decompose SEND and SCBED data sets. The SEND/SCBED-NMF scheme can provide a larger field-of-view than HRTEM and more precise composition identification with less sample damage than STEM-EELS [85]. Recently, Walid Dachraoui et al. employed the *operando* electrochemical liquid cell scanning transmission electron microscopy (ec-LC-STEM) to understand the structure and composition evolutions of SEI during charge/discharge cycling. The real-time observations by ADF-STEM reveal the formation of mosaic structure via two main steps as expected, ie: initial SEI nucleation where the electrolyte is reduced to form an island-like layer of LiF and then on further decomposition

transforms to dispersed SEI layer composed of other inorganic and organic components. This further evolves though the densification process and once the densification prevents further electrolyte decomposition, this results in an outer layer covered by organic components[86].

Robert Whetherup and colleagues have developed an advanced *operando* soft X-ray absorption spectroscopy (sXAS) technique with nanoscale interface sensitive total electron yield mode (TEY) to monitor the crystalline, amorphous and small nanoparticles developed during the formation of the SEI layer[87]. This innovative approach employs a configuration reminiscent of the *in situ* liquid sXAS cell, utilizing a suspended Si_3N_4 membrane, approximately 100 nm thick, acting as both an X-ray transparent and pressure-resistant window (Figures 14a and 14b). Through a meticulous analysis of O, F, and Si K-edge spectra, they revealed the temporal evolution of critical reactions taking place within the amorphous silicon anode when immersed in EC and DMC electrolytes (Figure 14c). Their findings highlighted the formation of LiF phases at *ca.* 0.6 V, with organic compounds, primarily composed of carbonyl groups (e.g., -(C=O)OCH_x), emerging at potentials below 0.4 V. These results are supplemented with bulk sensitive fluorescent yield (FY) XAS measurements and density functional theory (DFT) calculated spectra. This observation is consistent with the stratified behaviour typically associated with the SEI, where LiF tends to accumulate near the anode surface, while organic components predominate in the upper layer. Additionally, the introduction of the electrolyte additive FEC was observed to enhance the generation of LiF at higher potentials, approximately 1 V. This additive played a pivotal role in passivating SEI defects, ultimately resulting in the extension of the battery's cycling lifespan. If the dynamic chemical mapping of SEI is amalgamated with this structure and component study, it will be of more significance.

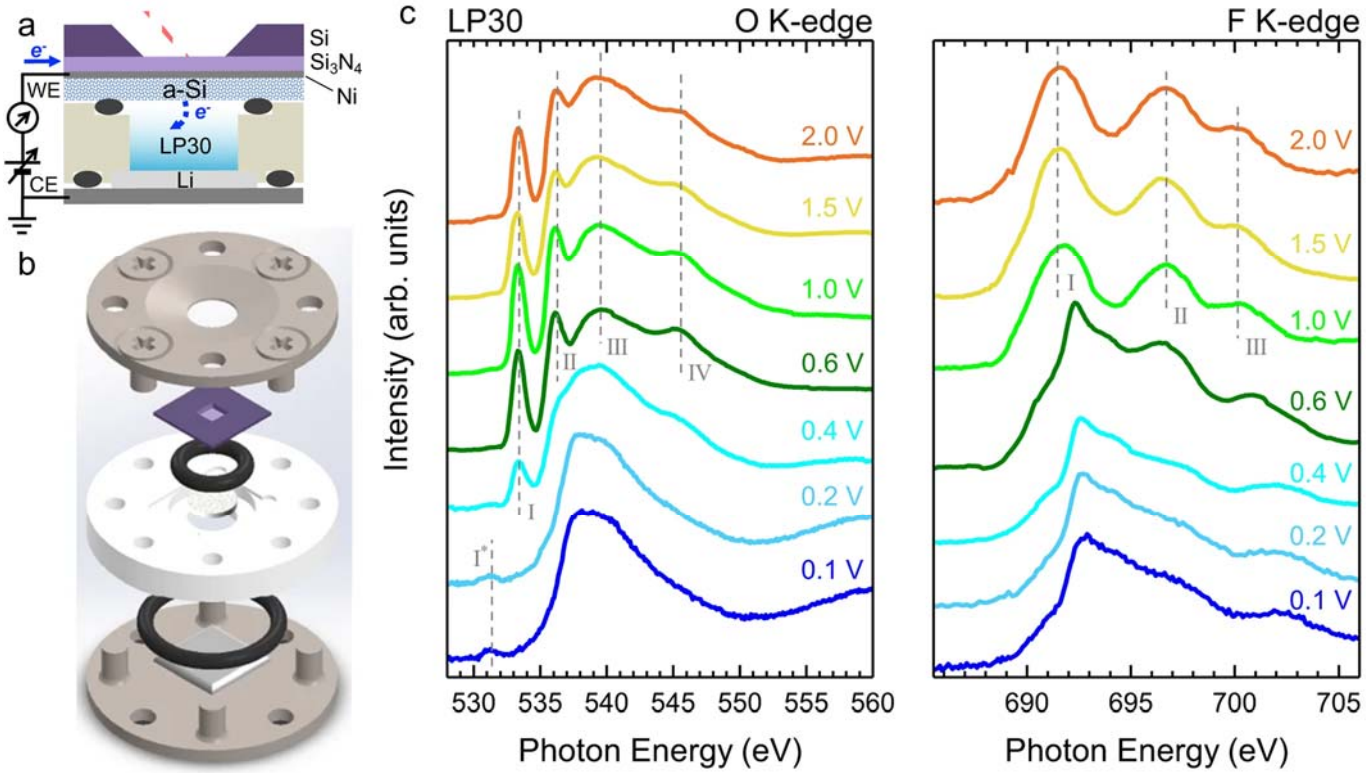

Figure 14 (a) Schematic of the operando XAS electrochemical cell; (b) cell structure including O-rings, flanges, membrane, Li electrode and separator; (c) XAS spectra of the O K-edge and the F K-edge taken during cycling in LP30 electrolyte without FEC additives. Reproduced with permission. [87]Copyright 2022, Nature Publishing Group.

4. Summary and Perspectives

The formation of the SEI layer is a complex process influenced by multiple factors, and its nanoscale thickness makes it highly sensitive when exposed to air, underscoring the necessity of advanced *in*

situ/*operando* techniques to investigate its structural evolution and impact on battery performance. Within this review, we have outlined a series of emerging *in situ*/*operando* characterization techniques and summarized the newfound insights into the SEI layer garnered from the outcomes of these *in situ* tests. Nonetheless, it is paramount to acknowledge that our understanding of SEI remains far from complete. This challenge stems in part from the noticeable gap between the atomic/molecular level and the real batteries, the continual emergence of novel rechargeable battery technologies and the intricate nature of overall battery design. Consequently, we assert that forthcoming research on SEI should be directed towards reinforcing several key areas.

1. At present, *in situ* techniques primarily rely on the feedback principles from test technologies, leading to the development of *in situ* setups that are conducive for practical implementation. However, it is important to note that these techniques often exhibit a discernible disparity compared to the actual performance observed in batteries. This highlights the need for a dynamic and precise technology to monitor the growth and evolution of SEI that can be seamlessly integrated into real battery operations. Such a monitoring technique would not only facilitate an in-depth exploration of the influence exerted by various electrolyte additives and solvent compositions on SEI membranes but would also empower the rapid selection of suitable additives and electrolytes for commercial battery production. Although, the techniques cannot currently be scaled directly to large and real battery systems, it's quite feasible to extrapolate the results to larger cells through the application of AI and machine learning for predictive modelling. This, in turn, is poised to expedite the progression of battery technology, bolster battery performance, fortify reliability and safety aspects, and ultimately address the ever-growing demands within the realm of energy storage.
2. The nanoscale physical properties of the SEI layer, such as nanomechanical, thermal and electrical characteristics, are far more complex and less understood than its chemical composition, and nanostructure. At the same time, the understanding of charge transfer dynamics, porosity and the thermal stability of the SEI remains limited. Hence, gaining deeper insights into the composition-structure-property relationships of the SEI will require a detailed investigation of the physicochemical properties with a focus on the connection between its physical properties and chemical compositions. For example, the exothermic decomposition of the SEI can trigger thermal runaway in LIBs, but the thermal properties of SEI have been rarely studied[88]. The results from *in situ* heating XPS show that the organic components of SEI are readily decomposed even at room temperature, releasing some flammable gases (e.g., H_2, CO, C_2H_4, etc.). The residual SEI after heat treatment is rich in inorganic components (e.g., Li_2O, LiF, and Li_2CO_3), and provides a nanostructure model for a beneficial SEI with enhanced stability. Other techniques need to be introduced to address the knowledge gap regarding the real-time compositional evolution and gas release of SEI during heating elucidates the underlying origin for the SEI instability, and highlights its non-negligible role in regulating the thermal runway of batteries[89, 90].
3. The role of theoretical simulations is pivotal in understanding the structure and composition of the SEI.[64-67] Through computational analyses of SEI materials, encompassing electronic structure, lattice parameters, atomic interactions, and other fundamental attributes, an in-depth comprehension of key properties such as ion transport is attainable. Furthermore, theoretical simulations aid in the identification of potential destabilizing factors that may lead to a decline in battery performance. The outcomes of theoretical simulations enable the design and optimization of novel SEI materials, ultimately contributing to enhanced battery performance. This entails the judicious selection of material constituents, structural configurations, and additives to achieve a more stable and high-performing SEI. This approach holds substantial promise within the domains of battery material design and the augmentation of battery performance. Theoretical simulations empower the prediction of SEI

stability and electrochemical performance under varying material combinations, thereby facilitating the identification of the most promising SEI materials. Additionally, they will serve as a guiding framework for experimental investigations, providing a theoretical underpinning of mechanisms governing the formation and evolution of SEI.

4. While the trajectory of understanding the atomic/molecular level changes in real battery electrodes through *in situ/operando* characterization techniques and the macro level of the real batteries by non-invasive electrochemical characterization has seen exponential growth, there exists/remains a substantial gap ~~remains~~ between these two levels. Currently, the main process to validate the non-invasive electrochemical processing is through post-mortem characterization. Similarly, the results obtained from atomic/molecular level investigations are validated by integrating theoretical models, and simulations and projecting these results to the battery level. Although the new techniques for the non-invasive characterization of SEI in real cells is underway, the complete implementation of these methodologies alongside advanced *operando/in-situ* characterization techniques has not yet been achieved. Rather than solely projecting the atomic level/molecular level changes observed in the *operando* techniques onto real battery systems, it's crucial to integrate the non-invasive electrochemical characterization methods to better rationalize the SEI evolution and degradation modes. This bottom-up or reverse engineering approach would provide a more comprehensive understanding of SEI behaviour across different scales, helping to bridge the gap between laboratory scale insights and real-world battery performance.
5. The development of multi-technique coupled *in situ* characterization platforms, such as the integration of AFM with Raman spectroscopy and SECM, as well as the combination of STEM with EELS, have offered a powerful approach to acquiring diverse information about the SEI layer, including structural, compositional, and electrochemical properties, among others. This multi-technique coupled platforms with theoretical simulations offer valuable tools for addressing the complexities associated with the SEI layer. They empower researchers to delve deeper into the distribution, interactions, and alterations of different components within the SEI, thereby facilitating a more profound understanding of its formation mechanisms and properties. We believed further integrating various non-invasive characterization techniques could enable a more precise description of SEI properties and a better comprehension of their correlation with battery performance. The development of such platforms not only deepens our understanding of SEI behaviour but also holds significant potential for advancing battery research and enhancing overall performance and safety.

Overall, a more comprehensive understanding of SEI structure-composition-property correlations informed by these advanced techniques not only addresses current characterization challenges in battery technology, but also supports the SEI optimization and revolutionize battery design. By elucidating the structural, chemical, and electrochemical properties of the SEI layer, researchers can identify key factors that influence its stability, ionic conductivity, and mechanical integrity. These insights pave the way for tailoring electrolyte compositions and additives that promote the formation of a thin, robust, homogeneous SEI with minimal side reactions, which are critical for improving battery safety and extending cycle life.

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