

Understanding Battery Interfaces by Combined Characterization and Simulation Approaches: Challenges and Perspectives

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Driven by the continuous search for improving performances, understanding the phenomena at the electrode/electrolyte interfaces has become an overriding factor for the success of sustainable and efficient battery technologies for mobile and stationary applications. Toward this goal, rapid advances have been made regarding simulations/modeling techniques and characterization approaches, including high-throughput electrochemical measurements coupled with spectroscopies. Focusing on Li-ion batteries, current developments are analyzed in the field as well as future challenges in order to gain a full description of interfacial processes across multiple length/timescales; from charge transfer to migration/diffusion properties and interphases formation, up to and including their stability over the entire battery lifetime. For such complex and interrelated phenomena, developing a unified workflow intimately combining the ensemble of these techniques will be critical to unlocking their full investigative potential. For this paradigm shift in battery design to become reality, it necessitates the implementation of research standards and protocols, underlining the importance of a concerted approach across the community. With this in mind, major collaborative initiatives gathering complementary strengths and skills will be fundamental if societal and environmental imperatives in this domain are to be met.

1. Introduction

The advent of electrochemical energy storage and conversion devices in our everyday life, with the Li-ion batteries being the most obvious example, has provoked ever-increasing attention to the comprehension of complex phenomena occurring at the solid/liquid interface, where charges, ions and electrons, are exchanged. Electrochemists, chemists, and theoreticians have thus adopted in recent years an increasingly complex experimental toolbox to study battery interfaces. Owing to the redox potentials of common electrode materials, battery interfaces operate outside of the thermodynamic stability window of common carbonate-based liquid electrolytes.^[1–3] More specifically, the use of characterizations techniques with electrochemical measurements gave rise to our understanding that a mosaic-like, passivating solid interphase grows upon charge on the surface of the battery's

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negative electrodes such as graphite.^[4] While detrimental at first sight, unlocking the details of the formation of this interphase, which possesses the properties of a solid electrolyte (ionically conducting but electronically insulating) and was thus denoted as solid electrolyte interphase (SEI), was essential to comprehending its critical role in inhibiting further electrolyte degradation and ensuring high Coulombic efficiency and performances over cycling for today's Li-ion batteries (LIB).^[5–7] One should here recall that mastering the SEI formation on the surface of graphite was the key finding that enabled the commercialization of LIB as we now know them. Building on the fortuitous intrinsic character of the SEI, an intense race for finding electrode materials with increasingly improved energy densities has taken place over past decades, resulting in the emergence of novel classes of negative and positive electrodes. Although this innovative spirit gave rise to numerous fundamental discoveries, the transition into practical, commercial devices has nevertheless often lagged behind due to instabilities at the interfaces. Hence, balancing the benefits of the protective character of the interphase with its negative side effects now constitutes the main technological challenge to improve battery performances which is compounded at the positive electrode, as the high potential cathode also forms an interphase (cathode electrolyte interphase, CEI).

Despite our fundamental need for mastering the interfacial processes in battery technologies, up until now researchers still overwhelmingly rely on an array of data/information to build a posteriori a coherent picture regarding battery interfaces, where

the investigative power of each technique is largely hampered by their inherent limitations. From a chemical point of view, the identification of major species has proved difficult and has given rise to many controversies, mainly due to the low thickness of the SEI and its extreme sensitivity to air and/or impurities. Indeed, the majority of SEI studies are based on ex situ characterization protocols involving cell manipulation in an inert atmosphere (glove box), transfer vessels, and specific washing processes, all of which tend to contaminate the sample, thus limiting useful data acquisition. Additionally, most of the laboratory characterization techniques employed, either post mortem or operando, lack the time resolution necessary to study events associated with the charge transfer at the interface, and instead probe the interphase that grows upon reactivity of the electrode with the electrolyte. In contrast, electrochemistry is the technique of choice to quantify charge transfer at interfaces but by itself is chemistry blind when not associated with the use of model electrodes or coupled with complementary physical characterizations. Hence, simultaneously visualizing both electron and ion dynamics still presents a major experimental challenge. From a theoretical point of view, the advent of computational approaches, such as density functional theory (DFT) or molecular dynamics (MD), critically widened the scope of possibilities to comprehend phenomena at the atomic or electronic level. However, DFT calculations suffer from the large computing cost associated with the introduction of explicit electrolyte or interphase components, whereas classical MD simulations so far lacked the inclusion of charge transfer. Finally, the dynamics of the solid interphases under external stimuli such as cycling, temperature, etc. over prolonged operational periods is still poorly characterized, hindering our ability to predict battery performance based on our understanding of the interfacial charge transfer or the chemical/physical properties of the solid interphases. To overcome these limitations, the development of a continuum model is indispensable.

Such a brief overview underlines one general pitfall of the field: the solid interphase forming at the electrode/electrolyte interface is the most tangible of all the events occurring at battery interfaces and thus the most frequently investigated^[8,9] (helped by compatible time/length scales). However, SEI/CEI formation is preceded by the creation of a double layer and charge transfer at the interface followed by chemical reactions and precipitation of inorganic and organic components. Furthermore, complex dynamical phenomena occur after the SEI/CEI formation, with constant self-passivation followed by dissolution/precipitation equilibrium and potential cross-talking effects between both interfaces, all of these effects being dependent on external stimuli such as temperature, charging conditions or mechanical constraints associated with electrode expansion/contraction. Thus, there is no doubt that the future development of batteries, for a wide variety of applications and for which safety and efficiency will become the overriding factors, will force us to design and employ characterization techniques coupled with modeling/simulation approaches capable of identifying these highly complex and interrelated processes.

Rather than presenting an exhaustive list of experimental procedures and modeling techniques previously developed, this perspective will highlight the main tools currently used, as well as emerging approaches, in the study of solid interphase formation,

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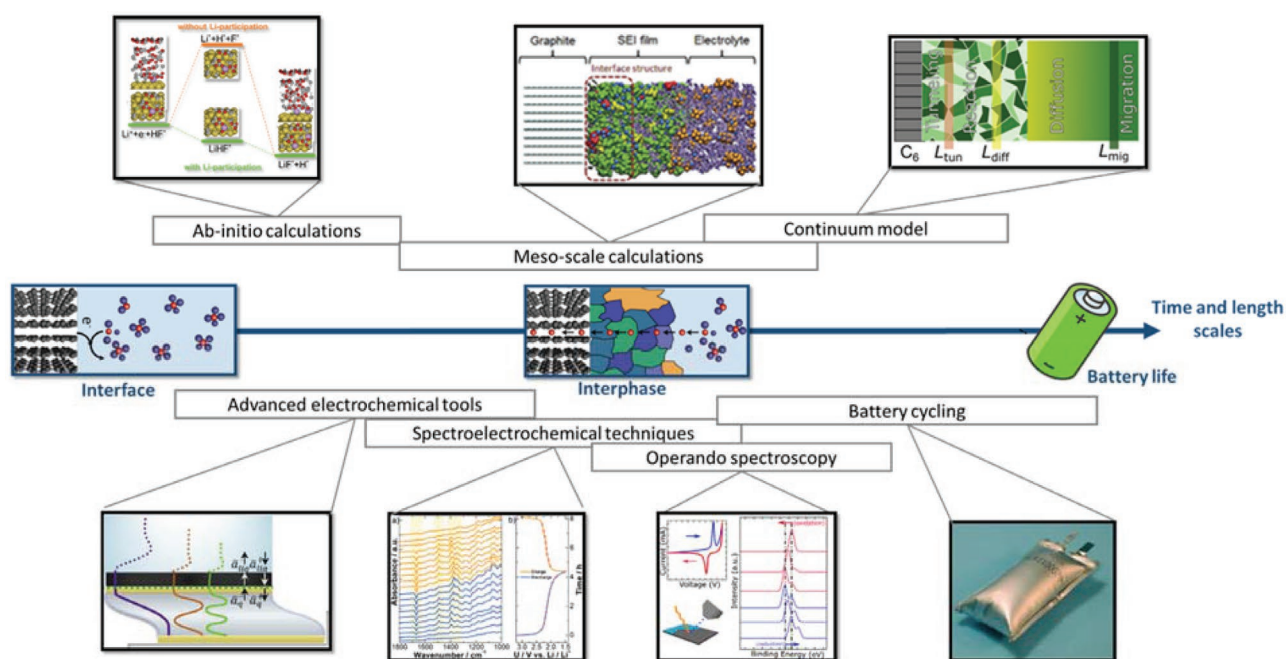


Figure 1. Schematic representation of the time- and length scales covered by different simulations/modeling techniques as well as by different characterizations to study electrode/electrolyte interfaces as well as interphases formation and the battery life. Adapted with permission.^[9] Copyright 2015, ACS. Adapted under the terms of the CC-BY license.^[10] Copyright 2020, The Authors, published by Wiley-VCH. Adapted with permission.^[11] Copyright 2019, Elsevier. Adapted with permission.^[12] Copyright 2019, Elsevier.

growth, and dynamics at electrode/electrolyte interfaces, along with the resulting effects on charge transfer—commencing with electrochemical techniques before going on to describe recent developments in the fields of characterization and simulation/modeling. In doing so, intrinsic limitations in terms of both time- and length-scales will be given (Figure 1), proceeded by the listing of several examples which provide crucial information regarding the dynamics of these phenomena, as well as the cascade of events occurring during both the formation and the lifetime of the interphase. These examples will cover novel electrochemical approaches and characterization techniques as well as calculation/simulation methods currently under development.

2. Electrochemical Characterizations of Battery Interfaces

Electrochemistry is by definition the science of interfaces. Thus, our understanding of the SEI, its chemical nature and physical properties, is closely related to advances made in the description of the electrochemical properties of battery interfaces. Following the pioneering work by Scarr in 1970 who studied the capacitance of metallic lithium in LiClO_4/PC electrolyte as well as the Tafel slopes and exchange current densities for plating/stripping extrapolated using current interrupt techniques,^[13] Peled generalized the concept of SEI in 1979 for alkali and alkali-earth metals identifying its decisive role in the operation of anode materials for non-aqueous batteries.^[4] Several years later, and following numerous studies by FTIR or XPS on the chemical compositions of the SEI, Aurbach defined the multilayer/laminar model—the combination of a dense inner layer associated with a low capacitance covered by a porous outer layer

with characteristic high capacitance^[14]—using electrochemical impedance spectroscopy (EIS). These pioneering works, using a combination of chemical/physical characterizations with EIS and cyclic voltammetry (CV) studies, defined our methodology to investigate the SEI; a practice still widely employed today. Nevertheless, the possibilities offered by electrochemistry are multiple and the future will certainly see researchers departing from this traditional approach to embark on more data driven and quantitative analysis, such as high-throughput screening.

2.1. High-Throughput Electrochemical Measurements

By contrast with the traditional one-shot experimental approach, high-throughput screening (HTS) methods enable the characterization of a large number of compositionally varying samples, therefore accelerating the development and optimization of battery materials and interfaces (Figure 2).^[15] HTS can be defined as the workflow of running multiple measurements in parallel. These sets of measurements are rationally designed to answer specific questions and to achieve specific goals and, in general, utilize a range of equipment and consumables, with or without the assistance of laboratory automation.^[16] Electrochemical characterization of electrode interfaces in the presence of varying electrolyte formulations has been widely employed in the search for new environmentally friendly corrosion inhibitors by using wells of a standard 12×8 plate.^[17] In a similar fashion, an array of varying metals (Al, Mg, Zn, Fe) that could be exposed to candidate corrosion inhibitors was configured by Muster et al.; this approach enabled monitoring the electrochemical current during the incremental increase of the amount of inhibitor in solution.^[18] In

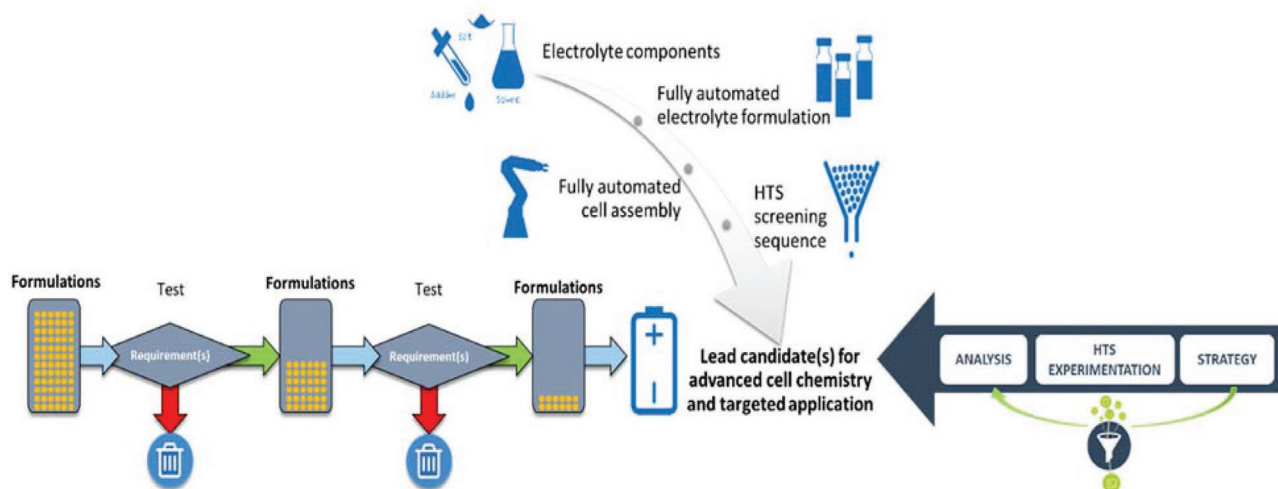


Figure 2. Schematic representation of automated high throughput workflow for battery electrolyte discovery.

addition to voltage, current, resistance and capacitance determination, high throughput electrochemical evaluation by means of voltammetry, chronoamperometry and impedance spectroscopy have been carried out^[19] by using commercial and custom-made cells.^[20] The scanning droplet cell (SDC) approach has also found application in spatially resolved investigations of conducting surfaces, allowing for surface analysis as well as preparation and structuring (galvanization, passivation, deposition) of thin-film devices. The conventional three-electrodes arrangement enables all common potentiostatic and galvanostatic techniques including among others, cyclic voltammetry, impedance spectroscopy as well as current transients of potentiostatic steps.^[21,22]

Electrochemical characterizations are in many cases well suited to HTS as they provide direct quantitative analysis of relevant properties for given chemistry and application directions. However, under certain circumstances, electrochemical measurements are complicated by additional factors including sample size, shape, and logistics, together with limitations in instrumentation. Different approaches for accelerating electrochemical characterization are under development, using commercially available instrumentation offering multichannel electrochemical data acquisition.^[20,23]

2.2. Advanced Electrochemical Analysis

In addition to HTS that allows for the fast screening of multiple chemistries and/or cell components, the correct analysis of data generated from battery testing is evidently an integral part of characterizing battery interfaces. While sharing the same technique, i.e., electrochemistry, many approaches exist across different research themes and cell formats, leading to an array of useful information. Most fundamentally, estimation of cell performance, as defined by the evolution of capacity and Coulombic efficiency upon cycling, is the principal go-to evaluation methodology. However, this conventional approach does not provide meaningful insights regarding the origins and the mechanisms for cell failure and thus only allows for a partial analysis of data accessible from electrochemical curves. The

full investigative power of electrochemistry requires the use of more advanced analysis techniques. Among them, loss of active material (LAM) due to either particle cracks, mechanical delamination and/or loss of electrical conductivity, lithium loss inventory (LLI) due to continuous parasitic reactions at interface or lithium irreversibility upon (de)lithiation, Ohmic impedance raise (ORI) due to the growth of resistive SEI/CEI, electrolyte reduction/oxidation and chemistry change indicators^[24–27] are accessible from raw measurements with further data processing such as incremental capacity analysis (ICA) and differential voltage analysis (DVA). Using both these processing techniques, additional features of the potential versus capacity galvanostatic curves can be extracted in a complementary manner from numerical differentiation.

The DVA, graphically represented by plotting the derivative of the potential with the charge (dV/dQ vs Q), takes linear contributions of positive and negative electrodes when connected in series and highlights two-phase transitions regions of the Q versus V curve.^[28] A powerful possibility of this technique is the quantification of contributions regarding electrodes and interface processes by fitting the curve of the full cell with the curves of the electrodes half cells (**Figure 3**). The alignment of the cells is obtained after horizontal displacement of the half-cell curves relative to the full-cell reference curve. This displacement is called slippage, mostly associated with LLI, and is the first fitted parameter. The analysis allows for fitting the active materials mass, which may be modified if LAM is present during the degradation of the battery. Its effects are observed by a shrinkage of the horizontal axis on both the positive and the negative curves and by an extension of the vertical axis.^[24–31] Example shown in Figure 3 shows LLI as the main degradation source, with a minor LAM detected for the anode (graphite in this example), as is commonly observed.

The ICA, given by the derivative of the capacity as a function of voltage (dQ/dV vs V), foregrounds potential regions in which phase transitions occur while peaks intensities and positions can reveal the chemical reactions occurring,^[32] as well as LLI, LAM^[33,34] and increased cell impedance.^[35] Although the contributions of each electrode are not linear, unlike in DVA, ICA brings complementary information about the cell in a fixed

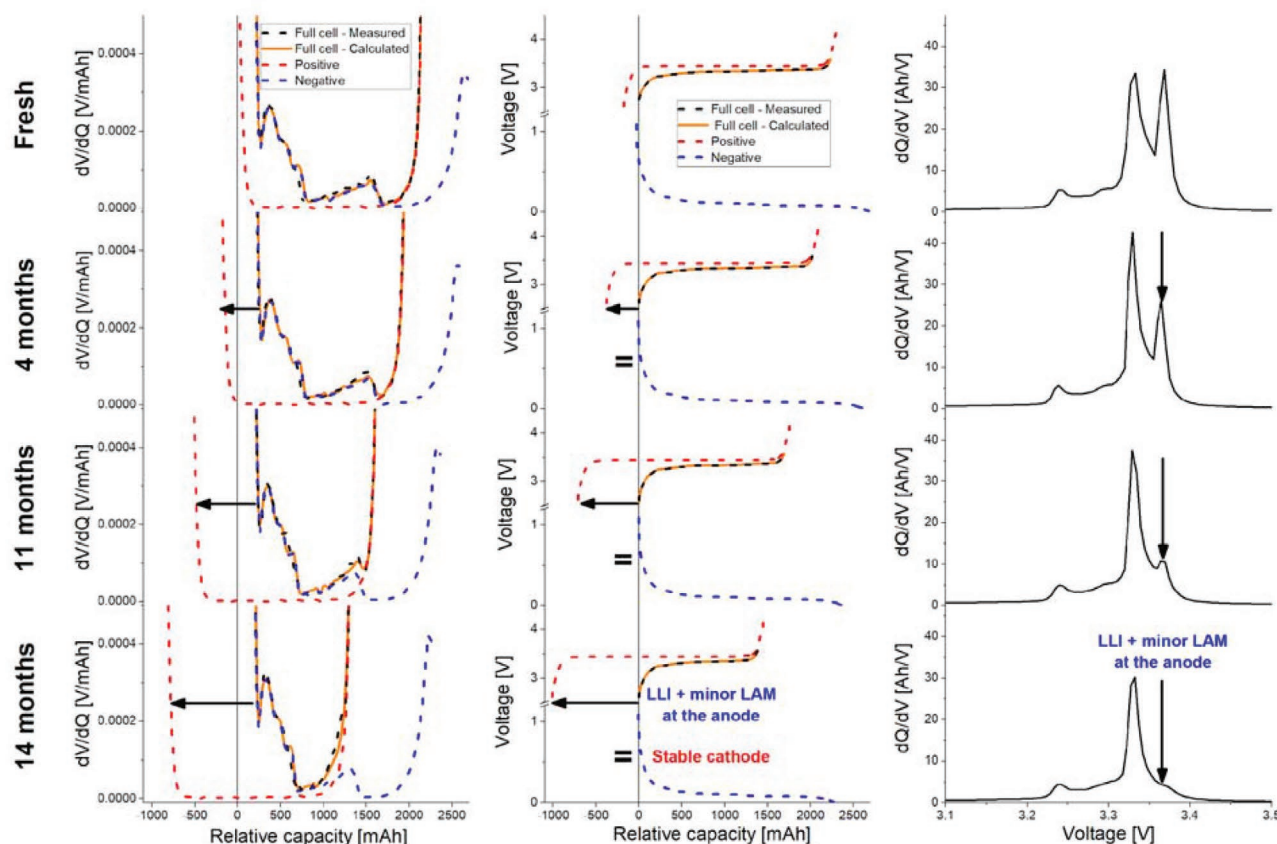


Figure 3. Differential analysis of a LiFePO_4 /graphite cell cycled at 45°C for different aging stages. Fitting of dV/dQ curves (left panel) allows rebuilding cell behavior (middle panel) during aging while dQ/dV curves complete information regarding mechanisms of battery degradation (right panel).

potential window. For instance, using a cathode material with a fixed redox potential, e.g., LiFePO_4 , degradation associated with the anode (graphite in Figure 3) is observed. As seen by comparing these two derivative plots, the LLI observed in the DVA is now tracked by the vanishing the last peak during a charge while other peaks remain mostly unaffected, indicating limited LAM and ORI. In addition to the monitoring of electrode behaviors, this approach provides crucial information regarding the SEI formation with associated reduction potentials (and CEI with associated oxidation potential) as well as information regarding the interphase stability with the LLI, two crucial parameters needed to evaluate novel electrolyte compositions and/or electrode coatings.^[36–39]

Both of these techniques reveal the thermodynamic behavior of the active materials as they rely on galvanostatic cycling with phase behavior close to equilibrium. Hence, temperature control and low currents are essential for the accuracy of the results. To add kinetic information, intermediary current regimes can be used, albeit at the cost of resolution. Different systems are readily susceptible to these analyses, although those with high LAM or drastic chemistry changes occurring upon degradation are costlier in terms of time and data treatment steps.

Numerous potentialities are thus offered by the use of advanced electrochemical analysis. Hence, these techniques can be coupled to methods like EIS and galvanostatic intermittent titration technique (GITT) to study interfaces and transport properties.^[40,41] Thus, the ever-growing importance of

controlling interfaces to enhance battery lifetime and performances will certainly be coupled with an increasing adoption of such advanced electrochemical analysis in order to obtain high-fidelity electrochemical data, representing a significant departure from the simple extraction of capacity and Coulombic efficiency as a function of cycling. This will however only be achieved through the definition and utilization of protocols accepted community-wide, as described below.

2.3. Implementation of Standards and Protocols

Evidently, gathering sufficient information to obtain a full picture of interfacial processes occurring in batteries is an enormous task, even with the implementation of HTS, and likely to be beyond the capacities of one single group. Only by comparing data between various chemistries and techniques will enable a sufficient leap forward in the comprehension of these complex phenomena. In that respect, the battery field, when compared to other technologies such as photovoltaics or organic chemistry applied to pharmaceuticals, suffers from a major disadvantage: the lack of standardization for cell assembly, testing protocols, data acquisition, and analysis. Hence, despite the enormous volume of scientific publications (more than 30000 currently^[42]) and internal reports on battery technologies, a scattering of results, when indeed sufficient information is provided for comparison, is widely observed

for given chemistries.^[42] This difficulty is not new, but can hardly be solved when cell format, cycling protocols, and consequent performance metrics differ for each battery chemistry and application. Mature technologies such as alkaline primary batteries and MnO₂ electrode materials were developed via the standardization of cell formats, but more recent technologies, notably Li-ion batteries, still do not benefit from the implementation of such similar standards.

In light of the possibilities offered by the use of advanced electrochemical analysis to obtain meaningful information regarding battery interfaces, the main difficulty thus lies in the quality of the data necessary to carry out such analysis. Therefore, the implementation of protocols will play a critical role in the coming years. Such protocols must cover cell assembly, with large deviations naturally existing between cell formats (18 650, pouch cell, coin cells, etc.) owing, for example, to different electrolyte volume/mass of active material ratio and the relative weight of non-active components, but also for their intrinsic formats.^[43] To demonstrate this, recent studies have highlighted the large scattering of battery cycling performances as a function of electrodes size, electrodes misalignment, the difference in stacking pressure, wettability issues, electrolyte volume, among others.^[44,45] Similarly, protocols must ensure that data sampling allows for a correct analysis, more specifically that adequate sampling is carried out to reduce the amount of filtering/smoothing preanalysis manipulations. Nevertheless, data filtering is necessary to obtain noiseless derivatives curves; crucial for accurately extracting redox potentials and/or slippages (capacity and mass).

Finally, standard cycling protocols must be agreed upon for each interfacial process of interest. In addition to the classical constant current constant voltage (CCCV) charge, constant current discharge cycling procedures commonly employed to study capacity over cycling, and EIS to study the SEI/CEI growth and stability, many cycling procedures exist to study more complex phenomena. Among them, asymmetrical charge/discharge protocols should be used to study the effect of C-rate and D-rate on the stability of battery interfaces. Slippages associated with SEI/CEI formation and stability are studied with the use of reference cycles at low discharge rate, as previously described. Similarly, the temperature dependence of the rate of capacity loss was demonstrated allowing to distinguish between SEI versus Li plating-related effects and their role in capacity loss.^[46] Activation energies can thus be extracted and may be compared with calculated theoretical values. Furthermore, coupling this temperature dependence approach with C-rate dependence studies, investigations in which the use of charges at elevated temperature (>25 °C) were demonstrated to allow for fast charging whilst avoiding Li plating have provided promising results.^[47] With these novel protocols in place, synergies with recent machine learning studies dedicated to finding the ideal fast-charging protocols can be readily envisioned in order to optimize temperature/C-rate condition, as has been very recently shown.^[48,49]

Evidently, the difficulty in agreeing upon standard protocols for cell assembly and cycling lies in the complexity and the particularities associated with different battery chemistries and applications. A large body of work now exists proposing specific protocols which accurately assess performances for Li-ion, solid-state metallic lithium, and Li-S batteries, along with many other chemistries. Only by ensuring the reproduction of such quality data will permit the automatization of electrochemical

data acquisition across different labs, which in turn is necessary to collect sufficient data analyzed in a similar fashion and extract meaningful information regarding the impact of chemistry (electrolyte, electrode, SEI/CEI) on battery interfaces and cycling performances. Initiatives were recently taken by several journals including Joule,^[50] Journal of Power Source,^[51] ACS Energy Letters,^[52] among others, to provide templates/guidelines on how to report battery results. Nevertheless, even though such initiatives will certainly promote the use of standards and protocols by researchers, they should ideally be complemented by the implementation of online laboratory notebooks in order to compile all the necessary information/metadata for battery characterizations and testing, similar to systems already widely adopted in fields such as pharmaceuticals and organic chemistry in general.^[53] Towards this goal, different initiatives have been undertaken, including within BATTERY 2030+, with the need to first develop a comprehensive and complete ontology for describing battery materials and/or phenomena.^[54]

2.4. High-Quality Data through Novel Electrochemical Characterization Techniques

As for physical and/or chemical characterizations, electrochemical characterization of battery interfaces can be categorized as follows: 1) high fidelity data, wherein the high-throughput and advanced analysis of electrochemical cycling data discussed above lie, and 2) high-quality electrochemical measurements, providing, through the use of advanced techniques, a more in-depth understanding of events at the local scale pertinent to battery interfaces. In this second category, conventional transient or stationary techniques like voltammetry, galvanostatic, or impedance spectroscopy, which are routinely used for the characterization of electrode materials, have been specifically developed for battery applications. Galvanostatic or potentiostatic intermittent transient techniques (GITT, PITT) were introduced about 35 years ago to obtain complementary information about both thermodynamic and kinetic parameters.^[55] More specifically, they offer a reliable method for measuring the diffusion coefficients in intercalation-type host electrodes as a function of their state of charge. A series of electrochemical techniques based on potentiodynamic and/or potentiostatic experiments have also been proposed during the past decade to provide further insights of reaction kinetics, i.e., decoupling surface versus bulk (diffusion-limited) processes.^[56,57] We can therefore see that our understanding of the SEI, its chemical nature and physical properties, is closely related to experimental advances directly resulting from our interest to fully describe SEI electrochemical properties.

What is more, the possibilities offered by electrochemical analysis are multiple, and researchers have already departed from conventional approaches and techniques to develop specific electrochemical tools such as scanning electrochemical microscope (SECM)^[58,59] and electrochemical quartz crystal microbalance (EQCM)^[60,61] to access further information about electron and ion transfers at the local scale.^[62] In gravimetric mode, EQCM tracks the electrode weight change during electrochemical polarization due to the variation of the resonance frequency of a quartz crystal. Although it was initially applied to analyze the double layer formation and charge storage mechanism for large surface area porous carbon electrodes,^[60] the

EQCM tool has been further employed in gravimetric mode to study the Li-ion intercalation in various electrode materials.^[61,63] The modification of the LiFePO_4 /electrolyte interface during (de)lithiation reaction was found to be highly dependent on the electrolyte solvent, and the number of solvent molecules pertaining to the solvation shell being markedly greater for water than for propylene carbonate-based electrolytes.^[61] A further refinement of EQCM consists in studying the change of the viscoelastic properties of the electrode/electrolyte interface by analyzing the change in the resonance frequency at multiple odd overtone orders. EQCM with dissipation monitoring (EQCM-D) is thus highly suited for tracking the formation/modification of SEI layers at Li batteries electrodes.^[64,65] Berg et al. combined electrochemical impedance spectroscopy and EQCM-D measurements to study the effect of electrolyte additives on SEI formation and stability.^[65] The QCM-sensor resonance frequency and dissipation changes were fitted with an acoustic multilayered viscoelastic Voigt model to obtain the change of the SEI shear storage modulus and changes of the SEI layer and electrolyte viscosity during polarization. These results shed light on the role of various electrolyte additives in the transformation of the electrode/electrolyte interface. In this context, EQCM-D offers a broad range of opportunities for the in operando study of mechanical property modifications at the electrode/electrolyte interface. However, as an advanced and highly sensitive technique, it is quite complex to analyze, and mathematical modeling is needed to get key information about the local deformation, electrolyte viscosity, amongst other parameters.^[64,65]

Scanning electrochemical microscopy (SECM) gives access to the local electrode reactivity and kinetic parameters.^[58] SECM consists of recording the current flowing through an ultramicroprobe electrode (the tip), while controlling the tip/electrode distance. The presence of the substrate (electrode) close to the microprobe affects the current at the tip. Recording the so-called approach curves by controlling the substrate/tip distance allows the construction of a current mapping of the electrode surface that can be further converted into topography images of the same surface. The resolution depends on the electrode and tip used but it is generally limited to several microns square. In feedback mode, a redox mediator is added to the electrolyte and the tip is maintained at a constant potential where the mediator is oxidized or reduced. An electrically conductive substrate will result in the increase of current at the tip due to the regeneration of the mediator at the surface, whereas an insulating substrate will block the ion diffusion resulting in a decrease in tip current. The tip current thus depends on the nature and roughness (distance) of the substrate and can therefore be used to obtain information in operando of the electrode local reactivity and conductivity. Applying a polarization to the electrode (substrate) will result in modifying the measured tip current as a function of the electrode conductivity and reactivity. SECM has been used to characterize the SEI layer formed at negative graphite electrodes at OCV and under polarization.^[59] The feedback current was found to be dependent on several factors, including the electrode substrate conductivity, the substrate driving force effect, and the lithium migration effect at the interface. SECM was also able to track modifications of the SEI layer during cycling, including some dissolution and growth mechanisms, before reaching a final stable, insulating

layer. Besides imaging, the SECM tool can be used to estimate local reaction kinetic constants by fitting the approach curves recorded during electrochemical mapping.^[66] One drawback of the SECM in feedback mode is the need for a redox mediator, which can interact—via redox coupling for instance—with the electrode (substrate). To tackle this issue, SECM can also be used in combination with electrochemical impedance spectroscopy, by adding a sinusoidal voltage bias to the dc voltage applied to the tip, in order to obtain the complex value of the impedance. This technique, called ac-SECM, allows for measuring the local conductivity of the electrode without the need for a redox mediator, enabling substrate topographic feature identification by the simple measurement of the local electrode impedance.^[67,68]

In summary, SECM and EQCM are examples of advanced electrochemical techniques that are currently under development to address the growing needs for local, in operando characterization of the electrode/electrolyte interface; there is little doubt that they and other electrochemistry and electrochemical techniques will play a key role in this context in the immediate future.

3. Physical Characterization of Battery Interfaces

3.1. Overview of Different Ex Situ and In Situ/Operando Characterization Techniques

The characterization of interfaces in the field of LIBs remains a challenging issue, specifically when several techniques have to be used. In the last decade, coupled protocols combining different characterization methods such as electrochemical and spectroscopic or microscopic techniques have paved the way to considerable progress in this domain, giving rise to our common understanding of the evolution of SEI/CEI during battery cycling. An overview of the available techniques for interface characterization is given in **Figure 4**. Access to complementary information on the same area of interest is of course highly relevant, but in the vast majority of cases, the various techniques are applied sequentially and separately, due to constraints regarding time- and length-scales of the probed phenomena (such as charge transfer and dynamic growth of the SEI). Furthermore, some techniques are extremely surface sensitive (<5 nm) while others average information over hundreds of nanometers or are chemically unspecific. This makes it difficult to access specific information on buried interfaces. Numerous techniques have been proposed to observe the reactivity of electrode materials with liquid electrolytes at electrode/electrolyte interfaces and under operando conditions. These techniques will be introduced in the following sections on laboratory-based spectroscopy and microscopy (excluding X-ray methods) as well as neutron and X-ray-based experiments.

Ex situ/postmortem analysis, during which the electrochemical cell operation is halted at a given time to remove the electrodes from the battery and perform the measurement, still remains powerful investigative methods for battery materials and interphases. For instance, various properties such as thickness, chemical structure, or morphology of the SEI have been extensively probed by Fourier-transform infrared spectroscopy

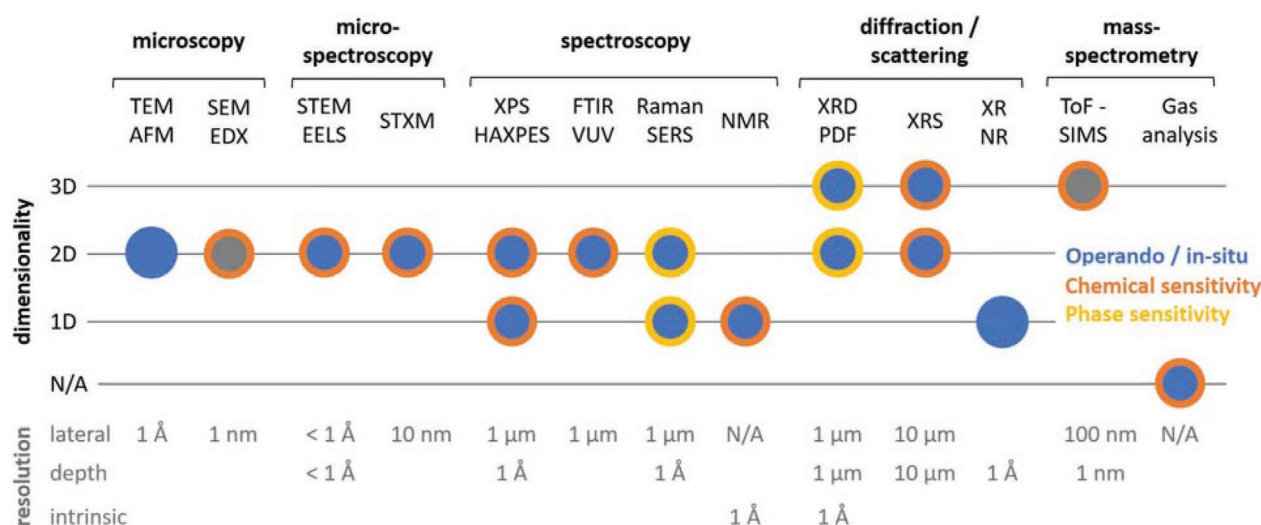


Figure 4. Overview of the different characterization techniques currently available to study battery interfaces and interphases formation. A more complete picture of all the characterizations accessible to study battery materials, not only interfaces, is available elsewhere.^[69]

(FTIR),^[70] X-ray photoelectron spectroscopy (XPS),^[71,72] Raman and Auger spectroscopies (AES)^[73] and nuclear magnetic resonance (NMR).^[74,75] Most of our up-to-date understanding of SEIs is based on ex-situ characterization protocols, which by their very nature, have the risk of spoiling the coveted information. Potential sources of artifacts may originate from excessive use of the ionic etching, including for the recently introduced low-interaction ion-sputtering technologies (gas-cluster ion-beams) used to perform depth profiling, e.g., for XPS or ToF-SIMS,^[76,77] for focused ion beam (FIB), and electron-gun exposure when using scanning electron microscopy (SEM) or transmission electron microscopy (TEM). Also, contamination of highly reactive SEI species with atmospheric constituents and relaxation of metastable SEI species are other possible sources of errors. Ex situ XPS and FTIR still remain the most popular direct and non-destructive tools to probe the SEI/CEI.

The development of in situ/operando techniques to probe interface evolution under electrochemical stimuli continues to present challenges vis à vis electrochemical cell design and experimental environments (Section 3.5.). While the term in situ implies measurements performed without altering the original conditions of the chemical environment of the test cell, operando refers to performing analysis in a dynamic mode where both sample environment and operating conditions are controlled.^[78] In situ/operando characterization opens new perspectives on combining spectroscopic and electrochemical characterization techniques—an approach which can be termed as being spectroelectrochemical.

3.2. Laboratory-Based Spectroscopy and Microscopy

The wide diversity of electrochemical techniques provides data on the dynamic processes at different time scales and dimensionalities. However, the anisotropy of the bulk electrode and the overlapping domains at electrode/electrolyte interfaces makes the interpretation of the data complex.^[79] Fundamentally,

spectroelectrochemistry techniques are ideal for time-dependent studies under controlled electrochemical conditions, thus enabling for example a precise picture of morphological changes at the interface of electrodes with the liquid electrolyte during battery operation.

Compared with the usual chemical redox methods, spectroelectrochemistry can provide information on intermediate electrochemical responses during subsequent surface redox processes. Monitoring the optical properties of molecules at interfaces through induced electrochemical perturbations leads to the gain of qualitative and quantitative structural information necessary for studying organic and/or ionic adsorbed species at the interfaces. One such example is the investigation of the electrochemical double layer under electron transfer processes.^[80,81] Careful cell design, allowing the light beam to pass through the bulk electrolyte as well as subsequent secondary signals from the interface to be collected, both without perturbations arising from interaction with the media traversed, is the minimum requirement for spectro-electrochemistry techniques. To meet these criteria, and in order to track electrolyte/electrode interface evolutions, hermetic cells have been designed for optical microscopy,^[82–84] in situ Raman,^[70,85] and in situ FT-IR.^[71,72] Because of the sensitivity of a battery's chemistry to oxygen and water, strict protocols and smart cell designs are required for minimizing contamination.^[86,87]

Due to equipment availability and the nondestructive nature of the radiative primary beam, in situ vibrational (Raman, FT-IR, UV/Vis/NIR) spectroelectrochemical techniques are powerful analytical methods for acquiring real-time information of adsorbed species on the interface of the electrode, and revealing the reaction mechanism on the interface of the electrode/electrolyte in detail. IR spectroelectrochemical experiments are mainly used for monitoring of soluble products, intermediates, and reactants of electrochemical reactions.^[88–91] The in situ spectroelectrochemical Raman technique allows monitoring intermediate species and reaction products generated during battery operation and offers unique access to the (de)lithiation

dynamics of individual oxide particles in the Li-ion composite cathodes.^[85,92] Due to their intrinsic surface selectivity, a combination of surface-enhanced Raman spectroscopy (SERS) and FT-IR spectroscopy may, in addition, offer great advantages for probing the structures of reaction intermediates, products, and solvents on the electrode surface.^[93] Nonetheless, the extensive use of this coupled approach requires meticulous experimental work accompanied by appropriate modeling in order to gain the necessary experience and reliability for its mature adoption.

The generation of gas, whether through normal or under abusive conditions, occurs at different interfaces in LIBs. This is intrinsic to the LIB chemistry and is subject to many parameters such as the electrolyte and its interaction with electrode materials, as well as operating conditions. Gas generation is deleterious and leads to an increase in the internal pressure of the battery with associated safety risks. Using gas chromatography (GC) with mass spectrometry (MS) and FTIR allowed the detection of molecules resulting from the degradation of electrolyte by-products at the electrode interfaces.^[94] The gas analysis combined with spectroelectrochemical characterization can offer valuable insights into the reactivity of active materials in LIB technology.

The dynamic evolution of interfaces induces significant morphological changes which may be observed by in situ SEM and TEM on battery systems with low vapor pressure-based electrolytes—for instance, ionic liquid, polymer, and ceramic-based electrolytes. However, induced electron beam damage, even at low voltages, constitutes a drawback for probing the SEI morphology. Nevertheless, new strategies using cryo-TEM combined with cryo-FIB (Focused Ion beam) are envisioned to reduce induced beam damage of the SEI during the operando measurement.^[95–103]

Local techniques using scanning-probe-based methods such as atomic force microscopy (AFM),^[104] scanning electrochemical strain microscopy (CESM),^[105,106] and scanning ion conductance microscopy (SICM)^[107,108] offer new perspectives for the investigation of local SEI properties and SEI evolution upon cycling.

3.3. Neutron Experiments

Neutron techniques, being complementary to X-ray methods discussed in the next section, have become an important tool in the battery domain to obtain insights into electrode and electrolyte evolution in situ or in operando. Their intrinsic sensitivity to certain elements, due to the neutron's interaction with the nucleus (instead of the electron cloud for X-rays), results in high scattering/absorption contrasts for specific elements; crucially lithium and hydrogen. Conversely, their weak interaction with heavier elements commonly used in battery casings mean that neutrons can readily probe batteries under real operational conditions, with non-significant irradiation perturbation to the material under study. Additionally, the nuclear sensitivity of neutrons can be exploited using selective isotopic substitution to modify scattering and/or absorption cross-sections of certain isotopes (notably $^6\text{Li}/^7\text{Li}$ and H/D). Beam brilliance and energy are important factors for temporal resolutions—for high

flux reactors or spallation sources producing intense thermal or cold beams, acquisition time scales are compatible with internal processes of the battery. Quasi-elastic scattering, neutron (powder) diffraction, small-angle neutron scattering, and neutron imaging (2D or tomography) have been successfully applied to elucidate bulk mechanisms from sub-nanometer to μm length scales. However, investigating the complex phenomena at interfaces, particularly for LIBs, is challenging for neutrons, with neutron reflectometry (NR) being the most suitable technique. Researchers, applying this nondestructive technique to unravel lithium kinetics at the solid/liquid interface at a single crystal silicon electrode in operando, provided key insights on SEI formation and lithiation/delithiation processes.^[109–112] They were able to give precise mappings of Li concentrations during the first charge/discharge cycles up to a depth of around 60 nm in the electrode with spatial resolutions up to several angstroms.

3.4. Structural and Morphological Insights Using X-Ray Methods

The advent of new, higher performance synchrotron sources with very low emittance, such as the Extremely Brilliant Sources (EBS) commissioned and operational at ESRF in Grenoble (France) is envisaged to lead to a change of paradigm in the domain of battery and material science in general. These so-called fourth generation sources have three advantages, respectively at the lower and higher energy end of the spectrum. The first is a higher flux for all experiments with monochromatic beams, with corresponding gains in instrument throughput and detection limits. The second improvement is an increase by a factor 100 to 200 of the brilliance. This helps to improve beam focusing, thus leading to higher spatial resolutions for imaging and mapping techniques, with a particular impact when using multimodal methodologies. The third resulting advantage is the increase in coherence flux—between 30 and 40 times. This has a strong impact on lens-less imaging exploiting the coherence to obtain images with ultimate resolution. These techniques are today not fully adopted and still remain in the domain of pioneering developers. Nonetheless, with parallel advances in adapted instruments, appropriate data analysis tools and hardware, coherent diffraction-based techniques are certain to become among the most important tools available to the community of synchrotron users.

Tomographic X-ray microscopy is an advanced form of transmission X-ray microscopy (TXM). The in situ cell is rotated by 180° to obtain a series of 2D projections, 3D microstructure representations can then be reconstructed. Changes in attenuation coefficient are related to changes in density, often associated with different compositions. When operated at synchrotron facilities, TXM can reach performances that are not possible in laboratory-based systems. In particular, the possibility to exploit the coherence of the X-ray beam can enable phase-contrast methodologies, which allow, for instance, a better contrast of two adjacent phases with similar densities along with higher spatial resolution. Two approaches are commonly adopted: parallel beam microtomography and conical beam nanotomography. The first method allows fast acquisition

of relatively large samples and operando experiments with sub-micron resolution allowing the visualization of the growth of the SEI on a particle or the particle cracking.^[113] The second method is more demanding and more time-consuming but can provide up to two orders of magnitude higher lateral resolution. In situ nanotomography has been employed to characterize SEI growth and particle cracking of Si electrodes during lithiation.^[114]

X-ray diffraction (XRD), performed in laboratory and synchrotron facilities, is the most established operando technique for studying the reaction mechanisms in electrode materials. However, the structural information is averaged over the probed volume and extracting information on the SEI layer is still a challenging task because of its extremely low thickness.^[115,116] Coupling operando XRD with TXM facilitates the interpretation of the morphological information collected by TXM. If TXM serves to identify the growth mechanisms of the SEI, XRD can map the stress induced by those interfacial mechanisms, thus contributing to give the overall picture. Looking ahead, novel instruments at synchrotron facilities may pave the way to directly address some aspects of the SEI. An interesting pioneering work^[117] demonstrated the possibility of using synchrotron-based XRD, pair distribution function (PDF) analysis, and DFT calculations to study the SEI. In this perspective, it is worth mentioning beamline ID15A at the ESRF. This instrument has been designed for high-speed TXM and total scattering (XRD/PDF) tomography^[118] enabling combined operando experiments. The implementation of 3D mapping (tomographic) methods adapted to XRD and PDF will allow for studying both crystalline and amorphous phases of battery systems, including light elements.^[119,120]

3.5. Chemical Insights Using X-Ray Methods and Operando XPS

The probing of soft edges using photoemission electron methodologies can provide sensitivity to their chemical environment. In this respect, the possibility of adopting spectroscopy techniques capable of looking at embedded interfaces in their working environment is appreciated. This can in particular be useful when anodic and cathodic charge compensation contribution has to be evaluated. X-ray Raman scattering spectroscopy (XRS) represents an elegant and reliable method that can offer unique information for battery systems. This technique uses a hard X-ray incident beam to probe the sample in depth and by analyzing the energy loss of the secondary beam we can reconstruct, by differential analysis, the low energy edge under investigation. This technique is particularly attractive since it allows circumventing surface limitations and also avoiding limitations in terms of sample preparation, environment, and experimental setups. Moreover, due to its non-resonant nature, it is practically free of self-absorption. Operando soft edges of both oxygen and iron (transition) were probed in the cathode material $\text{Li}_2\text{FeSiO}_4$.^[121] The results elucidated the different contributions of iron and oxygen to the redox mechanism, primarily related to the iron, but with the oxygen playing an active role as a charge compensator. The experimental observations were supported with ab initio-based simulation.

Studying the formation of SEI in LIBs proved to be a difficult task because of its broad range of chemical compounds based on

light elements as well as their heterogeneous distribution within the small dimensions of this up to a few tens of nanometers thick layers. While, within these strong constraints, most characterization techniques provide either morphological or chemical insights, a combination of soft and hard XPS offers great possibilities for chemical speciation with nm depth profiling capabilities.^[122] However, the development of in situ/operando XPS for probing the liquid–solid interfaces/interphases in LIBs is faced with complex technological issues, typically associated with concise photoelectron escape depth due to their strong interaction with matter, and ultrahigh vacuum (UHV) causing evaporation of liquid electrolytes. While operando XPS characterization was demonstrated for low vapor pressure electrolytes (e.g., ionic liquids) or all-solid-state batteries,^[123–125] these issues constitute strong limitations to the design of functional electrochemical cells adapted to this purpose.

To overcome the difficulties related to operando characterization of liquid–solid interfaces/interphases in LIBs several solutions have been proposed. These are illustrated in **Figure 5** and include near-ambient pressure (NAP) XPS, using the dip-and-pull approach and electrochemical cells equipped with nm thick membranes. In addition, performing resonant XPS or increasing the kinetic energy of electrons with high energy photoemission (HAXPES) also helps to enhance bulk sensitivity and access interfacial chemistry in a non-destructive manner.

Open electrochemical cells can be used to probe the SEI, from the liquid electrolyte to the solid electrode. In this respect, they are complementary to the membrane cells for probing the SEI/CEI. Open cells require near ambient or ambient pressure XPS (AP-XPS) usable for in situ and operando characterization of solid/liquid interfaces.^[126,127] Accessible pressures range from mbar with soft X-ray XPS up to several bars

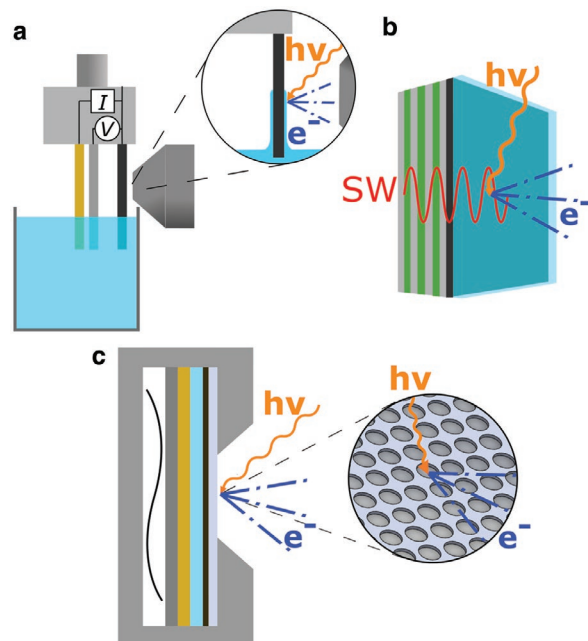


Figure 5. Schematic representation of the novel cell geometry for probing the solid/liquid interface upon battery operation using X-ray photoelectron spectroscopy with a) the dip-and-pull, b) the standing waves, and c) the membrane cell approaches.

with HAXPES.^[128] Performing XPS at high pressures requires differential pumping and adapted electron-focusing that reduces the photoelectrons' effective travel length through the gas. For studying solid/liquid interfaces, the vapor pressure of the liquid is a significant constraint. Other challenges are stabilization of a sufficiently thin liquid layer on top of the solid substrate, and adequate apparatus design.^[129]

Thin films of liquid can be obtained by condensation of, e.g., water vapor on solid surfaces.^[130] However, an electrolyte (i.e., having a multicomponent p–T phase diagram) requires other methods. For example, one can first perform a preparation step where electrolyte components are deposited on the electrode and afterward use the solvent's vapor for stabilizing the environment.^[131–133] In another methodology, the electrode is partially submerged in an electrolyte reservoir (watch glass) inside the analysis chamber. This allowed probing the gas, liquid, solid phases, and the solid/liquid interface at 2–10 mbar (but without applied potential).^[134] The latter technique was also applied to an open horizontally arranged electrochemical cell under reaction conditions.^[135]

Another in situ approach is the dip-and-pull technique (Figure 5a), in which a thin meniscus/overlayer of a liquid electrolyte is used.^[136] This meniscus forms on the electrode when it is vertically dipped into an electrolyte reservoir and slowly pulled out for placing in front of the analyzer. It is applicable to a great variety of electrodes: thin films of metals, metal oxides on various substrates such as silicon wafers, glass, and HOPG. The dip-and-pull technique may be better suited to study the outermost region of the SEI in contact with the electrolyte rather than ex situ/postmortem characterization, being sensitive to the rinsing process during sample preparation. On the other hand, there is a significant excess of electrolyte compared to the surface of the electrode, especially compared to commercial battery formats like 18 650 or pouch cells. This might enhance the dissolution rate and effects related to the shuttling of dissolved species.

Considering the layered nature of the SEI, the possibility to investigate the composition with an excellent spatial and energy resolution would permit a clearer understanding of the SEI. In this regard, the depth sensitivity of XPS measurements, including NAP-/AP-XPS or dip-and-pull methods, could be enhanced when combined with standing waves (SW), as first demonstrated for buried solid/solid interfaces in UHV (Figure 5b).^[137–139] Here, the electrode material is deposited on top of a multilayer mirror. When the mirror angle is tuned to a Bragg peak, SW are generated. By changing the angle or photon energy, thereby moving the SW through the structure, it is possible to record XPS spectra at specific depths with a high spatial resolution (<1 nm). Recently, Nemšák et al. demonstrated the feasibility of such an experiment in a NAP XPS setup to probe liquid-solid interface.^[140,141] This method could be applied for both in- and ex situ characterization, such as studying the SEI composition in relation to its closeness to the electrode.

With a sufficient electron escape depth, it is possible to investigate the SEI on the electrode using a membrane-type electrochemical cell (Figure 5c). Here, the thickness restriction is transferred from the liquid to the solid phase. An electron escape depth of several tens of nanometers can be obtained with HAXPES.^[142] The electrode materials need to be thin films or nanoparticles decorating the thin membrane.

The membrane of only a few nanometers separates liquid and vacuum and is a window for both, X-rays and photoelectrons, and acts as an electrode/current collector. Contrary to the dip-and-pull approach, it allows for an electrolyte-to-electrode ratio much closer to realistic LIBs and comparable to the conditions in coin cells. Despite these advantages, the membrane-cell approach still remains challenging.

In a pioneering work, Matsuda et al. used a cell based on 15 nm thick silicon for in situ monitoring of silicon oxide growth at the silicon/water interface during electrochemical oxidation.^[143] The photon energy was 6 keV corresponding to an electron escape depth of 30 nm; corresponding to merely 20% of the photoelectrons from the solid/liquid (the signal being dominated by the outermost material due to the exponential attenuation). Transferring this method to LIBs, the outermost material, could be probed, mainly the conditions near the electrode. For LIBs, therefore, the aim is to reduce the thickness of the membrane, while maintaining high mechanical stability and desired electrochemical functionality. Examples include 5 nm thick SiN,^[144] and 2D-materials like graphene-oxide,^[145] graphene,^[146,147] or h-BN.^[148]

3.6. Addressing Experimental Challenges

Yet, despite the arrival of all these promising techniques, significant obstacles to a routine operando characterization still remain:

- Specific cell and sample holder design for an accurate electrochemical response.
- Minimizing the effect of primary beam (electron, X-ray beam, and etc...) excitation, such as electrochemical potential change during the operando measurement.
- Improving the spatial and temporal resolutions of the excitation beam and secondary emission detectors respectively, in order to adjust the spectral response to the dynamic time scale of ionic diffusion at the interfaces.^[101]

Overcoming these instrumental challenges, the operando characterization would allow us to answer some of the following central (at least partly) open questions:^[9,149] How does the SEI form? What is it made of? How does it evolve during cycling? How do the solvated lithium ions escape from the solvation shell, pass through the SEI layer and intercalate into the electrode materials? How to control and rationally design the key features of the SEI layer such as ion conductivity, structure, density, thickness, and etc.?

Abundant data exist in the literature permitting the compilation of large databases in order to construct SEI/CEI models. However, only the combination of high-fidelity data gleaned from various characterization techniques, coupled with progress in correlative analyses applied to universally accepted ex situ, in situ and operando protocols, will provide better understandings of the SEI/CEI and thus form opportunities for major breakthroughs in the field of LIB. In this context, the application of local scanning techniques combined with correlative data treatment methods—baptized as the correlative characterization workflow approach—promises a significant

amelioration in the characterization of local electrical, mechanical, and structural dynamic evolutions probed at the same area of interest; as described in detail in another Perspective article from this special issue (Lyonnard et al). Such a workflow is intimately reliant on the use of common standards and protocols—concerning both cell morphology and cycling conditions—but also the application of on-the-fly analysis of generated data to automatically control experimental parameters in real time. Coupling these new advances with innovations in data storage/sharing/treatment and in particular the application of machine learning algorithms will, it is envisaged, fundamentally revolutionize the characterization of the SEI/CEI and LIBs in general, leading to an accelerated development of new generations of high performance, environmentally sustainable batteries.

4. Modeling/Simulations of Battery Interfaces

The impressive array of experimental techniques to characterize battery interfaces must thus be complemented by a wide variety of theoretical methodologies that are applied for modeling battery interfaces and interphases on various length- and time scales. Comprehensively addressing the details and capabilities of the numerous methods available by far exceeds the scope of this perspective; instead, we will focus on the interplay of complementary theoretical techniques and their application to the understanding of experimental data on interfaces/interphases currently found in LIB. Of particular importance is of course the SEI—arguably the most complex and dynamic component of a battery. The SEI, which is between 30 and 100 nm thick and can be comprised of both inorganic and organic parts, initially forms in a timescale of hours, plays a crucial role during charging and discharging cycles with a timescale of minutes and degrades on the timescale of years; all of these functional aspects being controlled by sub-microsecond processes at the nanometer scale. In spanning the ensemble of these temporal length scales therein lies one of the fundamental challenges for both experiment and modeling (Figure 1). A second challenge arises from the fact that most modeling techniques require an accurate representation of the morphology of the system they are designed to describe. As we have seen in previous sections, obtaining this complex morphology of the dynamic SEI remains a significant challenge. Owing to the lack of methods capable of describing SEI formation and functionality on the macroscale with sufficient resolution, most simulations focus on model systems that address specific aspects of the observed phenomena. Piecing together this information, particularly for a systematic scale-spanning approach, presents formidable difficulties.

In the last decades, thanks to both improvements in methodology and the increase in computational power, we have witnessed a continuous increase in computer simulations successfully applied to materials (and battery) research.^[150] Simulations usually follow two approaches: the descriptive approach, where properties are calculated for given crystal structure and composition, and the predictive approach, whereby calculations identify which structure and composition fulfill a target property. The former approach is customarily used to support and clarify experimental findings while the latter predicts properties and

suggests new chemistries for testing. While these two routes have been equally followed for studying battery materials, e.g., electrolytes or electrodes in their bulk form, few cases exist where the predictive approach has been applied to interface models.

Electronic and atomistic simulations are often used to explain experimental evidence and decouple the various effects that happen at the interface. The latter, in addition to be a strength of the method, is also one of its main weaknesses. Simulations cannot cover the whole plethora of phenomena happening at the interface, and thus they cannot provide an overall description of the electrochemical properties of the interface. Therefore, simulations require experiments on model surfaces, where the complexity is increased step by step. On the other side, simulations need to be as realistic as possible, which often includes the modeling of the solid/electrolyte interface, i.e., with implicit or explicit solvents. If this is done correctly, results of the simulations such as total energies, interface structures, diffusion, and reaction barriers, can be correlated with the outputs of experiments, such as cyclic voltammetry, XPS analysis, etc.

At the continuum scale, experimental electrochemical techniques are used to characterize different phenomena taking place inside LIBs to gain added insight into its behavior and to provide useful data for modeling parameterization. Regarding the latter, models can contribute to accelerating the parameterization or, at least, in reducing the required experimental work to estimate the physicochemical parameters. Moreover, such models can also unlock the realization of model-based ageing predictions where parameters such as remaining useful lifetime (RUL) or battery state of health (SOH) can be anticipated, and also best battery/testing conditions can be identified in advance, minimizing the number of the required experimental load.

4.1. Modeling the Electronic Structure and at the Atomic Scale

Extensive efforts have been devoted to the modeling of various aspects of the SEI/CEI at microscopic scales: ab initio simulations, such as DFT and ab initio molecular dynamics (AIMD), have been extensively used to understand the thermodynamics and kinetics of the reduction reactions of various electrolyte systems on the electrode surface and/or in an electrolyte solution, as well as the transfer mechanism of Li ion in SEI phase. To extend the simulation range of ab initio methods, MD with reactive force field was developed to study electrolyte reductions. However, it is still difficult to generate a comprehensive network of the reactions by these methods since they are strongly influenced by composition, voltage, temperature, the chemistry of the electrode surface and reaction byproducts, not to mention the role of various impurities.

Starting at the shortest time and length scales, DFT^[151] is one of the most powerful tools to investigate an interface at the atomistic level. Bulk calculations, despite their approximate nature, can already provide valuable information regarding interface properties and are achievable at reasonable computational costs. Some examples are the computational Pourbaix diagrams, which describe the material stability/corrosion in an

electrochemical environment^[152] or the band edge positions, indicating the band alignment of two materials at their interface.^[153] The main limitation of this approach can also paradoxically be considered as a strength: all quantities are calculated at the bulk level, which although not capturing the complexity of the interface nevertheless makes the simulations inexpensive. The most straightforward improvement to the bulk model is to consider slabs of material to describe its different surfaces (still without considering any electrolyte). The complexity of this slab model lies in the variety of surface orientations and reconstructions to be considered. In addition, surface calculations require larger supercells than their bulk counterparts, resulting in longer simulation times. Notwithstanding, this approach allows us to access surface energy states which may be critical for electrolyte stability, and also the ionic diffusivity on the surface—necessary to the understanding of dendritic nucleation.

A step forward is to consider both interface components (electrode and electrolyte) explicitly at the interface. In the case of solid/solid interface, DFT is a good starting point to study the morphology of the interface, the ionic diffusion, and charge transfer between the two solids. DFT can also be combined with the non-equilibrium Green's function (NEGF) formalism^[154] to evaluate charge transfer through tunnel effect and contact resistances. For the solid/liquid interface, the electrolyte can be modeled either explicitly or implicitly. In the implicit model, the solid is represented by a slab (in a similar fashion as described above), while the liquid electrolyte is characterized by a polarizable continuum model in which the main parameter is the dielectric constant of the solvent. This type of calculation is very rapid although incapable of capturing important aspects such as the adsorption of molecules at the interface, which is only accessible through explicit models.

An explicit model of the solid/liquid interface at the DFT level can be coupled to MD to evaluate forces and energies at every time step in the so-called AIMD technique.^[148] AIMD calculations can give an accurate picture of the electrochemical reactions and charge transfer at ps and ns scales, although accompanied by the pay-off of higher computational cost. Nevertheless, thanks to this methodology,^[155] the important initial

formation step of the SEI can be studied^[156,157] as can the ionic diffusion^[158] in SEI components, and in turn we may correlate these results with experimental evidence. However, a predictive approach with AIMD is not yet feasible and the complexity of the interface puts severe constraints on the effects that can currently be investigated.

Very often, a plethora of phenomena happens simultaneously at the electrochemical interface, rendering it crucial to decouple these effects in order to trace back their origins, and subsequently to control them *a posteriori*. A solution to this is to simplify the initial electrolyte model, then to increase its complexity in a piecemeal fashion. An example is to introduce, one by one, the effects of impurities in the electrolyte, which together contribute to the formation of the SEI interface. Moreover, it might not be feasible to consider a realistic electrode because of its polycrystalline nature and, very often, model systems are instead used. However, by employing these two approximations—model electrolytes and model systems—important phenomena taking place at the interface can be decoupled and we can get one step closer not only to understanding the complex origin of the SEI, but also to ultimately control its formation mechanisms (Figure 6).

Although conventional AIMD simulations are considered state-of-the-art in terms of accuracy, they are still limited by their intrinsic approximations. For instance, the adiabatic approximation makes AIMD simulations unsuitable for studying charge transfer reactions with a heavy nonadiabatic component.^[159] In principle, this could be done through Ehrenfest dynamics.^[160] However, if AIMD calculations are expensive, Ehrenfest dynamics are, presently, simply unaffordable. Another example is the thermodynamic ensemble used in AIMD simulations in which the total number of electrons in the system is typically fixed. Most of the electrochemical experiments operate at a given electrostatic potential in which the number of electrons can vary. In this case, fixed electrostatic potentials can be mimicked by using grand canonical DFT,^[161] but an efficient implementation of this method is still absent.

As previously mentioned, AIMD simulations can only address atomic-scale phenomena limited to a few nanometers

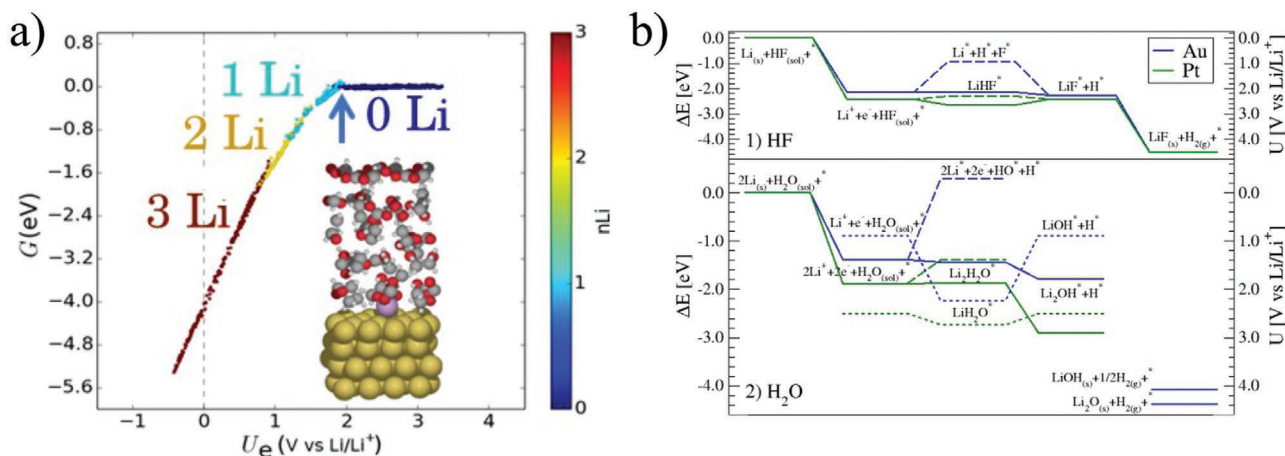


Figure 6. a) Phase diagram of Li in EC:EMC on a model surface, Au(111), calculated using AIMD. b) The structure of the interface at different electrochemical potential is used to investigate the reduction reactions of impurities responsible for the initial formation of SEI grains. Adapted with permission.^[157] Copyright 2020, The Authors, published by RSC.

or hundreds of picoseconds. Molecular dynamics simulations using classical potentials, or ReaxFF methods,^[162] have been applied to extend the time- and length-scales compared to AIMD, although at the cost of reduced accuracy. An efficient and accurate parameterization of the underlying force field is crucial to these methods and the description of changes in bonding remains challenging. However, achieving such a precise parameterization for a specific system may, in turn, render it invalid for another. This lack of transferability between systems and the omission of the electronic structure by classic potentials often prevents its use in a predictive fashion. Moreover, although much faster than AIMD, classical MD simulations are still time limited. A possible solution to this problem is to use modern machine learning approaches, which in theory can accurately calculate properties by first principles at a fraction of the computational cost required by conventional electronic structure methods. The machine learning method conventionally used is based on the neural networks (NN) approach devised by Behler and Parrinello,^[163] where a set of NNs serves as interpolation functions for fitting the solid/liquid interface's complicated potential energy surface of the solid/liquid interface.

The method relies on symmetrizing the atomic structures (of the interface) through the use of the so-called atom-centered symmetry functions. These symmetrized structures, along with their energies and forces, are then fed into a set of NNs, which fit a conservative force field for each chemical species. This force field is then used to run NN-MD simulations for the interface with speed-ups of several orders of magnitude compared to AIMD calculations. This allows simulating not only dynamics at much longer time scales (in the order of ns) but also for physically larger systems—both of which are crucial for a realistic description of the interface. One common issue with this approach is that the MD may diverge, i.e., forces and energies are unrealistic. This divergence often occurs because the model loses precision by, for example, visiting states for which it has not been trained. Adding an error estimation analysis and an on-the-fly training of the NN models, which includes new electrolyte structures when the precision drops below a certain threshold, helps solve this issue.

In addition to SEI growth, dendrite formation at the electrode/electrolyte interface is another mesoscale effect of great importance for the stability of batteries, especially for the LIB cells charged at high C-rate. Mayers et al. employed coarse-grained (CG) lattice models coupled with molecular dynamics (MD) to simulate the nucleation and growth of dendrites on nanoparticle surfaces via the non-equilibrium electrodeposition of Li.^[164] Their model indicated that the propensity of dendrite growth is augmented with the increase in applied overpotential, but, conversely, the application of pulse overpotential suppressed dendrite formation. Unfortunately, some interfacial processes, such as the degradation of the interface or growth mechanisms, cannot be tackled by the abovementioned methods. With an atomistic model, we can investigate only the initial phases of the relevant phenomena, for instance, the initial formation of the SEI layer or the outset of degradation on SEI components. Some of these limitations can, however, be addressed using mesoscopic and continuum simulations, as described below.

Increasingly, experiment and theory work hand in hand to model and improve batteries: The formation of a smooth SEI film is desirable for long-lasting batteries. Efficient electrolyte additives can improve the SEI film formation which was shown using different experimental tools SEM, TEM, XPS, and FT-IR.^[165] Complementary to these experiments the mechanisms behind the formation of such smooth films have been described successfully using hybrid Monte Carlo/molecular dynamics simulations. The hybrid MC/MD simulations can be used as guiding principles in designing the most suitable electrolytes for controlling the SEI formation.^[166] Further, the model was confirmed by an experimental study with SOXPES measurement.^[167] The influence of additives on electrolytes was investigated by combinations of classical MD simulations and FTIR experiments to understand the solvation structure^[168] and coordination. Here the experiment and theory corroborate information to improve understanding of the SEI formation and its dependence on the intermolecular interactions and solvation structure during the charging–discharging of the rechargeable battery. SEI formation in aqueous electrolytes was studied using in situ/operando techniques and MD simulations.^[169] A detailed mechanistic study of the formation of SEI has been performed using experimental techniques and MD simulations. Also, a model for durable SEI was proposed and guiding principles could be established to tailor the SEI for high-voltage batteries. In MD simulations, the COMPASS force field was used to accurately describe the elastic properties of the organic and polymeric materials formed in the SEI layer.^[170] MD simulations can accurately describe the composition and structure-dependent elasticity of the SEI layer via comparing the measurement obtained from the AFM coupled with XPS. So, by understanding the mechanical stability of the SEI layer via MD, the damage of the SEI layer can be minimized. These examples demonstrate that experiment and theory increasingly complement one another in the understanding and development of batteries, but there is much room for further improvement.

4.2. Modeling at the Mesoscale

Mesoscale methods, which include (kinetic-) Monte Carlo (kMC)^[171–173] and phase-field models (PFM)^[174,175] are used to simulate the formation and dynamic development of the SEI at the crucial mesoscopic scale; where atomistic scale methods struggle because of computational cost and continuum level models have difficulty to represent the microscopic details of the underlying processes. At the present time, there is little overlap in the length and time scales that can be addressed with either atomistic and continuum level methods, therefore the development of accurate and reliable mesoscale methods is one of the most outstanding challenges in the field, in particular when it comes to SEI formation.

kMC methods simulate the time evolution of nonequilibrium discrete systems. The system spends most of its time in locally defined states and migrates between those according to the rules of statistical mechanics. As a result, simulations reach time scales much larger than a microsecond while maintaining molecular though usually not atomistic resolution. In

heterogeneous catalysis, kMC is often applied to problems of surface chemistry. This method combines an accurate description of the elementary processes by accounting for their statistical interplay in order to properly evaluate chemical kinetics. Applied to SEI formation, Takenaka et al.^[176] coupled kMC (reaction energetics computed with DFT) and MD (with classical force field) to model the growth of a few nanometer-thick SEI on a graphite electrode. However, the reaction rates were not based on microscopic input—limiting the predictive power of this approach. Röder et al.^[171] employed a kMC algorithm with barrier inputs from ab initio simulations to understand the formation of SEI by ethylene carbonate (EC) decomposition on graphite electrodes, and the growth of a dense layer of SEI with a thickness of over 30 nm was observed (Figure 7a). While these methods still require a number of assumptions to make them computationally feasible, they open exciting opportunities to close the mesoscale gap in the method spectrum. Currently, kMC methods struggle with the complexity of the reaction network involved in SEI formation and its dependency on various parameters (described previously). Furthermore, SEI formation is not only limited to reactions, but also various transfer phenomena (Figure 7b), such as the “near-shore aggregation mechanism.”^[177] kMC faces a general problem when reaction rates occur on vastly different time scales (normally diffusion barriers are much smaller than reaction barriers) because most of the computational time is spent on very fast reactions that do not significantly participate in system evolution.

Phase-field models (PFM) are, on the other hand, an alternative approach to modeling growth processes on the mesoscopic continuum scale. Here, the state of the system is represented by one or several phase-field variables that represent the local fraction of the system in a specific thermodynamic state. The interface between phases evolves according to the phase-field equations, such that the free energy gradient, including interface contributions, controls the progression of species concentrations. The first PFM application in SEI formation attempted to take into account the non-zero charge density and the double-layer structure during SEI growth.^[178] The free energy functional of the system included the bulk energy of SEI and electrolyte phases, the interface energy, and the electric energy, respectively. The evolution equations of SEI species took the form of a Cahn-Hilliard equation. However, such a model represented neither the detailed chemistry/chemical constituents nor the porosity of the SEI. Guan et al. improved the model and focused on SEI morphology evolution and growth by minimization of the total free energy density of each component of the SEI. Combined with experiments, they modeled several important SEI species, including inorganic LiF and Li₂O as well as organic ROLi and ROCO₂Li.^[174] Later, Liu and Guan studied the SEI evolution using PFM, including cracking and dissolution, by monitoring the evolution of artificially designed cracks.^[179] Generally speaking, because the number of phase fields is limited, the complicated network of reactions involved in the SEI is difficult to represent in PFM. Also, since PFM does not support the generation of pores, additional techniques are required to reproduce the porous nature of SEI layers.

Overall, mesoscale models, by their very nature, aim to describe processes at the level of individual particles above and beyond the microscopic atomistic details but well below the

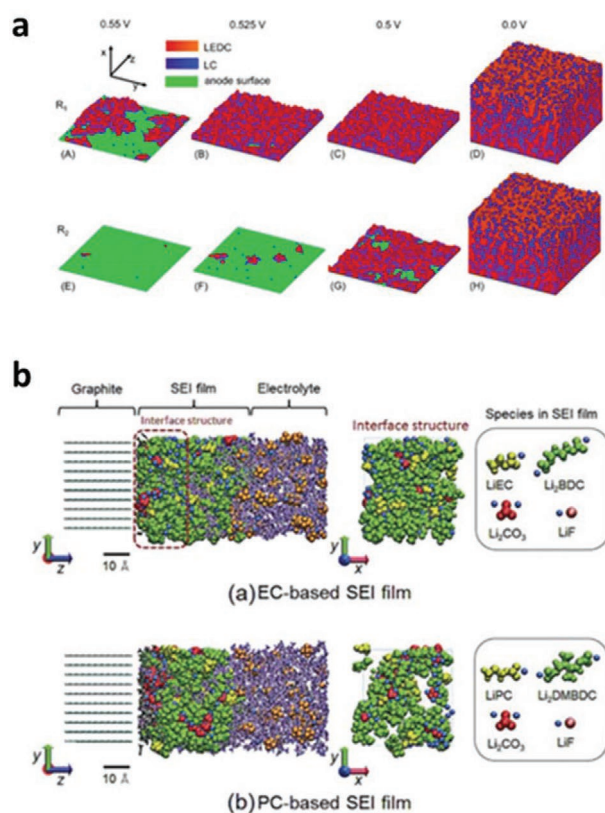


Figure 7. a) KMC configurations of the dense surface film for electrode with particle radius [WW3] $R_1 = 3 \times 10^{-6}$ m (A–D) and $R_2 = 10 \times 10^{-6}$ m (E–H) at different electrode potentials with 0.55 V (A,E), 0.525 V (B,F), 0.5 V (C,G), and 0.0 V (D,H) for the formation process due to initial charging. Reproduced with permission.^[171] b) Snapshots of the SEI films and electrolytes. Color scheme: SEI film green, Li⁺ blue, PF₃ (C₂H₄, or C₃H₆) gray, EC (PC) purple, PF₆[−] orange. The left panels show the side views while the middle and right ones show the front views of the interface structures in the SEI films (visualized in the depth $0 \leq z \leq 20$ Å of the view from the side of bulk electrolyte). Reproduced with permission.^[176] Copyright 2014, ACS.

device scale. Since many extremely important processes occur on this scale, the further development of such models remains an important step towards the adoption of predictive models for battery interfaces (including the SEI). As things stand today, the gap between microscopic models and continuum models (treated in the next section), is too large to directly transfer parameters from the atomistic to the continuum scale. This pertains in particular to the uncertain chemical composition of many interfaces, including the SEI.

4.3. Modeling at the Continuum Scale

In general, continuum battery models are based on the porous electrode theory published by Newman and Tiedemann,^[180] and are widely used to simulate characteristics and performance of Li-ion and other battery cells.^[181] The pseudo-2D (P2D) model and the single particle model (SPM) are among the most popular continuum scale tools. The P2D model builds on the porous electrode theory, the concentrated solution theory, and the

kinetics equations, respectively^[182,183] and is extensively used in Li-ion battery investigations^[184]—its predictions being relatively accurate and showing, in general, good agreement with experimental data.^[185,186] The latter motivates the inclusion of degradation models in the continuum scale to provide more realistic simulations and to test underlying mechanisms hypotheses.

Regarding degradation mechanisms, it is worth mentioning that the SEI layer formation and electrochemical stability over long-term operation should be a primary topic of investigation in further development of LIB technology, as the gradual thickening of the SEI layer further consumes Li ions, solvents, and salts, thus lowering cell capacity and coulombic efficiency and increasing cell resistance.^[187,188] Several continuum scale models have been proposed to describe the totality of the transport and reaction mechanisms involved.^[189,190] However, due to the lack of accessible experimental data and the large number of parameters needed to accurately describe the mechanisms represented in these models, uncertainty in predictions remains high and, as a consequence, insights into the nature of the processes provided by the models remains limited (**Figure 8**).

Experimental evidence of long-term storage and cycling shows that the SEI growth rate is proportional to the square root of time, suggesting a transport limitation. Due to the SEI structure, with an inner compact layer thin enough to allow for electron tunneling and an outer, thick porous layer acting as an obstacle for solvents to reach the inner layer,^[5,192–195] several mechanisms have been considered to explain this parabolic growth behavior: electron tunneling, conduction or diffusion across SEI layer, solvent diffusion through porous SEI layer and diffusion of neutral radicals such as lithium interstitials. Qualitatively, all the models agree with the square root of time growth, except for the electron tunneling model, which shows logarithmic growth but can still be fitted to the

expected parabolic growth for certain datasets.^[192,196] However, as available experimental data show strong dependency of SEI growth on state of charge and current density^[194,197,198] several authors have argued to discard solvent diffusion as the limiting mechanism.^[191,195,199]

Both electron and lithium interstitial transport models have been reported to agree with the asymmetry of SEI growth during lithiation and delithiation of first cycles.^[10,199] However, it has been recently reported that the SEI could be a single ion-conducting material instead of a semiconductor,^[10] meaning that electron transport through the SEI can only be possible when linked with lithium ions in the form of neutral radicals or hopping between available lithium ions. With these insights on the dominant mechanisms at play, new models focused on the different growth regimes as a function of operating conditions, SEI thickness and SEI properties have been recently reported.^[10] For instance, it has been argued that during the initial stages of the SEI growth, decomposition reactions and electron tunneling are the rate-limiting mechanisms. However, at later stages and after prolonged testing of the cell, firstly lithium diffusion and later electron migration become the dominating transport mechanism.

The uncertainty of SEI properties and its evolution is, of course, one of the main obstacles to obtaining quantitative results in continuum scale modeling. Additionally, the small amount of long-term capacity loss evidenced by experimental data, together with the uncertainty related to the competition between other typical degradation mechanisms in LIBs—CEI growth, lithium plating, SEI cracking, loss of active material, cross-talking (transition metal migration), & etc.—renders validation of SEI growth models for all types of operating conditions difficult. In this regard, some of these variants have been explored up to a certain degree of detail.^[200–205] However, complex interactions between these mechanisms and feedback effects remain unknown. Despite this problem, models were recently developed allowing insights into the rate-limiting transport mechanism as a function of SEI thickness and porosity.^[193] Furthermore, Pinson and Bazant explored the influence of particle expansion leading to SEI cracking and the generation of fresh surface areas, as well as the effect of SEI delamination; both mechanisms leading to an accelerated capacity loss.^[206] Yang incorporated effects of both SEI and lithium plating in their continuum model leading to an accelerated nonlinear aging effect after a sufficient number of cycles,^[207] and Reniers modeled the interplay among several degradation mechanisms and models.^[208] However, the small amount of long-cycling experimental data available prevents researchers from discerning which model best describes certain conditions, as most of the models and combinations thereof are able to fit available experimental datasets to a certain extent.

To investigate and gain more understanding on battery degradation, the calibration of continuum scale models concomitant with parameter identification plays a pivotal role in improving predictive models' capability and accuracy. Currently, experimental and modeling efforts to achieve model parameterization generally occur independently. In the experimental approach, for example, the cell and its components' physicochemical properties are measured by performing cell teardown and conducting combined electrochemical (GITT,

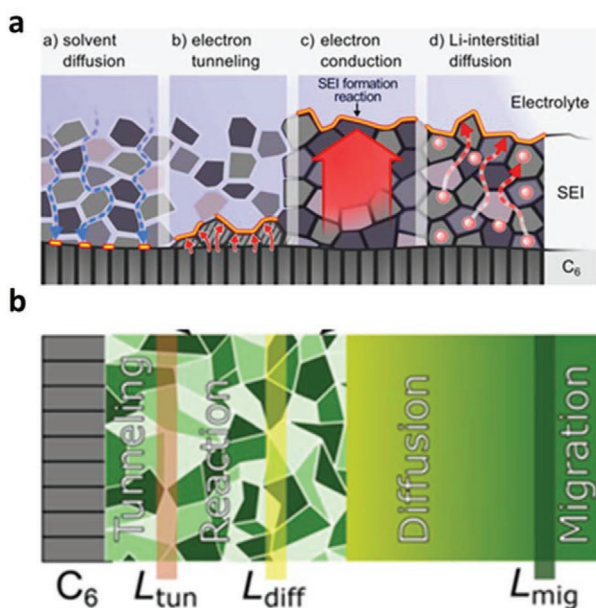


Figure 8. a) SEI growth mechanisms schemes. Adapted with permission.^[191] Copyright 2018, Wiley-VCH. b) SEI characteristic length scales. Adapted under the terms of the CC-BY license.^[10] Copyright 2020, The Authors, published by Wiley-VCH.

EIS, PITT) and physicochemical characterizations.^[209,210] For theoretical calculations, mathematical and optimization techniques for model calibration are used.^[211,212] To improve this situation, we postulate that model-based parameterization, where analytical equations are substituted by continuum scale models and optimization algorithms, may have significant potential. This approach may be particularly promising in situations where competition between several participating mechanisms hinders the applicability of assumptions in reducing model complexity.^[10,213]

The main drawbacks to SEI continuum models are that they necessarily assume a certain degree of homogeneity of the SEI, coupled with their requirement for information on transport properties and SEI characteristics. The latter has two possible solutions: either by characterizing SEI properties experimentally—which has proven to be difficult—or obtaining the properties from *ab initio* simulations at lower scales, as discussed above. Already at present, many of the SEI parameters in continuum models originate from atomistic and molecular dynamics calculations.^[214,215] It is expected that, with the evolution of simulation and experimental techniques, more information about these parameters and new insights about the SEI nature will permit us to refine and modify the models' parameters, thus enabling advances in the modeling approach at the continuum scale.

In order to overcome the problem of SEI homogeneity in continuum models, some authors proposed coupling lower scale models, such as kMC or phase-field models, with continuum models to incorporate details in the SEI simulation, whilst at the same time benefiting from continuum simulation.^[206,216] In order to explore inhomogeneous effects such as mechanical degradation, multiscale simulations are needed because only such techniques have the capability of incorporating the best characteristics of all the simulation scales involved.

It becomes increasingly clear that when these high-fidelity continuum scale models are calibrated by primary data and validated *a posteriori*, they can provide a better fundamental understanding of the main mechanisms such as the SEI growth, as well as the interaction and impact of other degradation processes to the SEI layer. In addition, these continuum scale models can be used to accelerate the analysis of certain electrochemical tests mentioned in Section 2, such as IC curves, as they are capable of differentiating the individual potentials and stoichiometry, as performed in this kind of analysis, and permit the evaluation of the EIS spectra by adapting the continuum scale model to the frequency domain and deconvoluting individual resistance contributions by fitting the experimental spectra to simulation results.

4.4. Modeling Summary

This overview of modeling methods demonstrates that significant progress has been made to elucidate various aspects of battery interfaces and interphases by simulation. However, it is clear that a number of challenges still remain. One of the most pertinent is what we would call the “mesoscale morphology challenge,” as many aspects of SEI formation and functionality can only be understood on a length scale of 10 nm and beyond,

while essentially all underlying chemistry-dependent processes operate on a length scale of less than 1 nm. This generates a circular problem, since models to describe the morphology of the system are elected on the basis of molecule-specific information, yet without this morphology, it remains difficult to characterize SEI composition. One of the most promising ways forward to overcome this problem is the development of systematic multi-scale methods which pass parameters, possibly in a circular fashion, from one scale to the other. A transferable implementation of such multiscale models calls for the development and use of workflow methodologies that encapsulate the complexity of the simulation, while permitting the user to control the system parameters.

In addition to developing improved methods to link simulations at various scales, work must also progress in the modeling of individual scales, which remains a nonbanal task. At the *ab initio* scale, we typically employ highly simplified models for surfaces and bulk systems alike, which struggle to capture defects, surface reconstruction, and disorder phenomena. Mesoscale methods in turn have problems with morphology representation, while continuum models have difficulties with moving interfaces. Above and beyond these aspects, all simulation methods share an underlying computational complexity, requiring the exploitation of high-performance computing.

In the battery domain, the development of improved analytical methods requires parallel advances in many fields such as computational chemistry, physics, and materials science, which in part explains its relatively slow progress. The use of machine learning and artificial intelligence may help to close the gap in the available method spectrum both at individual scales and also in passing parameters between scales. In particular, concerning this latter aspect, ML holds significant promise because methods at larger scales typically aggregate information, in such a way that the straightforward passing of parameters from lower scales remains challenging. However, the use of machine learning remains at a preliminary stage and only continued efforts in this direction will provide proof of its fulfilled potential. Generally speaking, large data sets are required to parameterize these methods, which are less costly to generate for simulations than for experiments. The coordinated pursuit of the ensemble of these aspects by the battery research community promises to bring experimental results and simulation into increasingly better agreement.

5. Conclusions and Perspectives

As we have described, battery interface research is a particularly complex domain but has nevertheless seen major progress in the past few years regarding advanced characterizations techniques, simulations/modeling capabilities as well as the application of robotic, high-throughput screening. However, only by intimately meshing these diverse fields will we be able to stimulate the cross-fertilization needed to generate new insights. Towards the goal of combining techniques to unleash the creativity of chemists and engineers in order to solve technology-relevant interfacial phenomena, large-scale research initiatives such as BATTERY 2030+ are uniquely positioned.^[217] Indeed, they offer an unprecedented opportunity to bring together

battery specialists with physicists, data scientists, and engineers, with the common objective of fostering novel approaches fundamental to mastering battery interfaces. Evidently, no single research entity currently gathers all the required competencies at the highest level and, rather than competing in a sterile manner, large research consortiums allow for the consolidation of previously disparate knowledge, thus providing shared tools needed for researchers to thrive and express their creativity. To develop such a transformative approach, an initial maturation step is crucially required, during which the scientific infrastructure is created and benchmarked on the next generation of Li-ion batteries, for which the bottlenecks have been clearly identified (e.g., stabilization of Si-containing anode materials and high-potential/high-capacity Ni-rich and/or Mn-rich layered oxides). More problematic and challenging chemistries such as Na-ion, multivalent chemistries, Li-S, solid state or aqueous batteries will then benefit from the development of chemistry-agnostic tools and their integration into a systematic, combinatorial approach. Toward this end, community-wide efforts in which data-driven science serves as a guideline for chemists to develop novel electrolytes or active materials are critical. However, the development of these tools and their inter-communications through an automated workflow can only be achieved by the use of an agreed, community-wide lexicon. The definition and adoption of this so-called ontology—extensively described in a parallel perspective^[54]—will thus hold the key to unlocking a fully efficient data transfer synergy between electrochemical testing, characterization, and simulations groups. In conclusion, we foresee a leap forward in our understanding and control over battery interfaces through the use of approaches and techniques such as those described in this perspective, which together represents a necessary departure from our traditional way to approach such complex issues.

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Conflict of Interest

The authors declare no conflict of interest.

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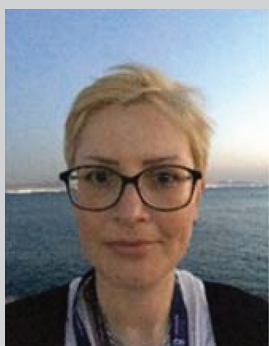
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