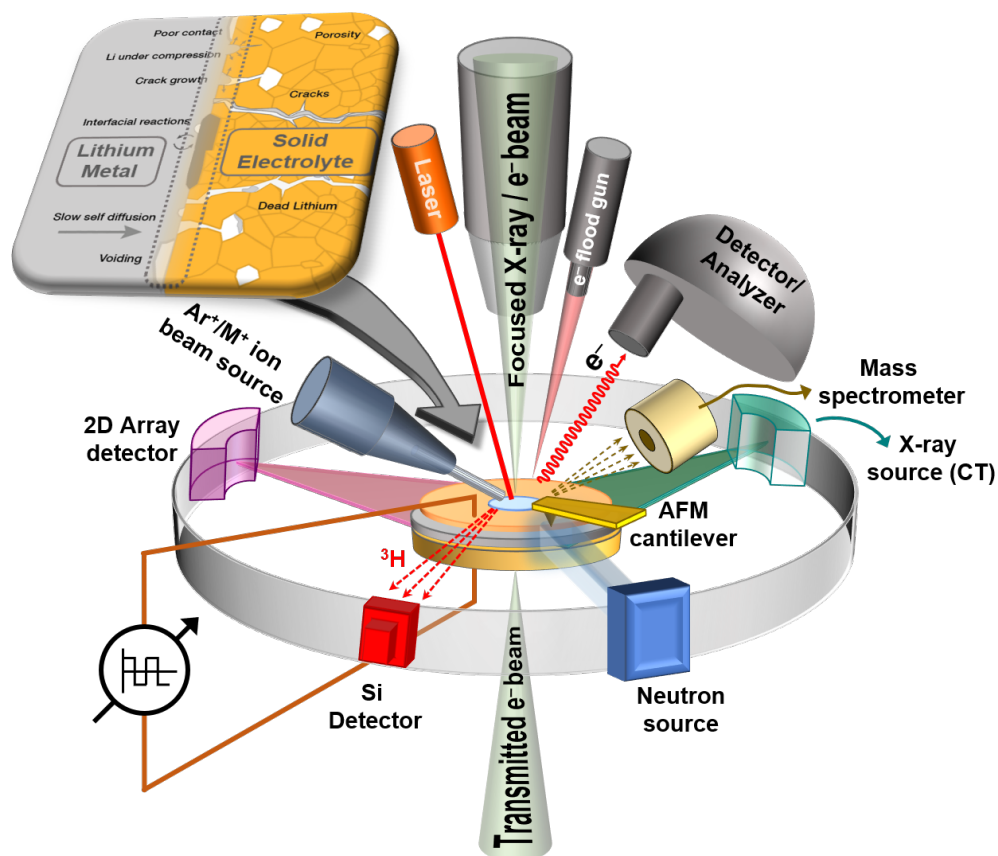


Graphical Abstract

In situ and *Operando* Characterisation of Li metal – Solid Electrolyte Interfaces

Sudarshan Narayanan, Joshua S. Gibson, Jack Aspinall, Robert S. Weatherup, Mauro Pasta



Highlights

***In situ* and *Operando* Characterisation of Li metal – Solid Electrolyte Interfaces**

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- Dynamic evolution of the interface between Li metal and solid electrolytes presents a major challenge to the advancement of solid-state batteries (SSB), warranting development of novel techniques to characterise them *in situ* or *operando*.
- While materials in SSBs can be relatively easily probed using advanced ultra-high vacuum-based techniques using *ex situ*, *in situ* or *operando* methods, accurate characterisation of interfaces with Li metal under “true” operating conditions is hindered by long acquisition times, instrumental barriers to application of pressure and temperature, extraneous contamination during handling, and limitations on resolution of instrument.
- A perspective on characterisation challenges through the lens of interfacial chemistry, chemo-mechanical degradation, morphological and structural evolution of Li metal-SE interfaces is presented.
- The advent of a host of unique adaptations to regular X-ray and neutron-based techniques, along with unconventional correlative methods using neutron and XR-CT, and also additive ones like AFM-E TEM, etc., can pave the way for more thorough electro-chemo-mechanical characterisation of Li-SE interfaces.

In situ and *Operando* Characterisation of Li metal – Solid Electrolyte Interfaces

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Abstract

The use of lithium metal as the negative electrode holds great promise for high energy density solid state batteries of the future, but at the same time presents major technical challenges in their development. Li metal, with its high reactivity, soft and ductile nature, and propensity towards mechanical deformation during electrochemical cycling, is susceptible to the formation of various defects such as voids, cracks and filamentary deposits at the Li metal – solid electrolyte interface, that eventually cause rapid degradation of electrochemical cell performance. In order to gain insights into these interfacial processes, and identify mechanisms for failure, *in situ* and *operando* characterisation approaches are essential. In this perspective, we present our opinions on the current state of such techniques, while highlighting the existing limitations and scope of these methods. We also endeavour to present opportunities for future research into developing and building on existing approaches to better evaluate the Li metal-solid electrolyte interface so as to guide the appropriate choice of materials to further enable efficient solid state battery architectures.

Keywords: Interfaces, solid state, *in situ*, *operando*, lithium metal

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1. Introduction

As electric vehicles (EVs) increasingly become mainstream, the energy and power density of batteries must continue to improve, whilst maintaining very high levels of safety. Incumbent Li-ion electrode materials based on intercalation are fast approaching their technical limits of energy density, with state-of-the-art cells achieving $700\text{-}800\text{ Wh}\cdot\text{L}^{-1}$ and $300\text{-}340\text{ Wh}\cdot\text{Kg}^{-1}$. New anode chemistries are thus needed to achieve significant improvements in battery performance.

Lithium metal negative electrodes (also referred to as anodes throughout this article) have a high theoretical capacity ($3860\text{ mAh}\cdot\text{g}^{-1}$ and $2061\text{ mAh}\cdot\text{cm}^{-3}$) owing to a high lithium packing density, combined with a very low reduction potential (-3.04V versus the standard hydrogen electrode (SHE)). In liquid electrolytes, lithium metal cycles poorly due to high reactivity and an unconstrained deposition morphology with large volume and surface-area changes associated with plating and stripping, ultimately leading to high rates of electrolyte consumption. The use of a solid-state electrolyte (SE) potentially offers a solution to these issues [1], with increased mechanical and chemical stability against lithium metal, restraining the deposition morphology and minimising capacity fade. These advancements in solid state battery (SSB) technology have been made possible by the discovery of a variety of solid electrolyte material systems, some of which have lithium ionic conductivities comparable to that of liquid electrolytes. In addition to enabling the use of Li metal, these SEs can also be paired with lithium intercalation-type and layered-oxide cathode materials like $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})\text{O}_2$ (NCM811) and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), that can operate at relatively higher voltages, and potentially provide stable capacities of $\sim 150\text{-}200\text{ mAh}\cdot\text{g}^{-1}$. [2, 3] Nevertheless, realising an all-solid-state battery with high performance and cycle life remains a challenge, where unresolved issues primarily include loss-of-contact, chemical degradation and mechanical fracture, among several others.[4] To understand and then develop strategies to suppress these processes occurring at the microscopic and macroscopic levels, appropriate characterisation is essential, and for this, a diverse toolbox of advanced techniques have been developed and employed that can shed light not only on the individual material properties, but also their mutual interactions.

Any characterisation experiment involves a compromise between creating representative battery conditions and the practicalities of extracting high

quality data. Approaches are described as being *ex situ*, *in situ*, or *operando*, referring to an investigation conducted either post-experiment, at the site of the experiment, or during electrochemical operation, respectively. *Ex situ* characterisations are valuable in providing a broad overview of the state of the system, its function as well as failure, but they are unable to provide critical information about dynamic processes occurring within the system during operation, owing to the need for partial or complete disassembly of the electrochemical cell prior to characterisation. Furthermore, the required cell disassembly can lead to damaging of surface layers and exposure of the reactive surface species to a glovebox atmosphere, with even trace levels of contamination enough to alter the observed species. In contrast, *in situ* and *operando* techniques have the potential to capture dynamic processes occurring at very small timescales (\sim ms and lower) during operation of an electrochemical system allowing these specific processes to be well understood. The terms “*in situ*” and “*operando*” are often used interchangeably, but one distinction drawn between them is that *operando* experiments have a temporal resolution that is high enough to detect even metastable states and configurations, while *in situ* experiments involve measurement in ‘relaxed’ states. An example of this could be needing to pause electrochemical plating before data acquisition, whereas *operando* measurements occur continuously during plating. Owing to limitations on the instrument, experimental setup or the ambient conditions necessary for a stable electrochemical process, measurements are seldom conducted *operando*, at conditions that are representative of battery operation in the field, presenting the community with a significant challenge in bridging the divide between experiment and reality.[5] In the same vein, *in situ* studies too, mostly limited by tooling considerations, are often conducted in conditions that are far removed from typical operating conditions, thus probing transformations that may disregard the influence of key components, such as contaminants, operating ambient environment, applied pressure, high currents, and the likes. For instance, *in situ* experiments inside an X-ray photoemission spectroscope (XPS) or a scanning electron microscope (SEM) would typically be conducted at ultra high vacuum conditions where contamination may be at levels well below that of a battery manufacturing facility, or, taking the case of electrical currents/current densities applied to probe evolution of materials and interfaces, as in a transmission electron microscope (TEM), being in the range of \sim nA - μ A at best, orders of magnitude lower than currents/current densities experienced by a battery during standard operation.

In this article, we present a brief review of the material and characterisation challenges in the context of Li metal – SE interfaces, with a focus on critical attributes such as interfacial chemistry, chemo-mechanical degradation, morphological and structural evolution. We also highlight the opportunities and challenges that lay ahead, that will help direct the community to solve the challenges identified and move towards a more comprehensive understanding of Li metal based SSBs.

2. Current state-of-the-art

A variety of physico-chemical, mechanical and computational models and mechanisms have been proposed and discussed extensively in prior works. These provide detailed reviews of SSB characterisation techniques that can probe individual cell components and their material properties (e.g. the negative electrode, the positive electrode and SE separator) and elicit crucial information on solid-state electrochemistry, interfacial degradation, electro-chemo-mechanical evolution during and after cycling, to name a few.[4, 6–10] Furthermore, while each individual cell component presents a myriad of distinct properties that necessitate careful characterisation prior to their utilisation in a full-cell configuration, they also give rise to several critical interfaces that play a significant role in determining the functioning of the cell. In particular, the pursuit of safe, high energy density cells through the use of Li metal as the negative electrode, makes characterisation of the interface between Li and the solid electrolyte of utmost interest to the research community, as well as a significant challenge due to the reactivity, chemical instability and unique mechanical properties of Li metal. The dynamic nature of these interfaces in turn necessitates the use of *in situ* and *operando* approaches in order to better correlate the electrochemistry to the composition, structure, morphology and chemo-mechanical properties of the evolving system (Figure 1). This too, has been widely described in several recent works [5, 11–15]. Through this review we aim to highlight the issues and challenges that remain unaddressed while also indicating opportunities lying therein by broadly categorising the various electro-chemo-mechanical processes occurring at the Li metal – SE interface, within the proceeding subsections.

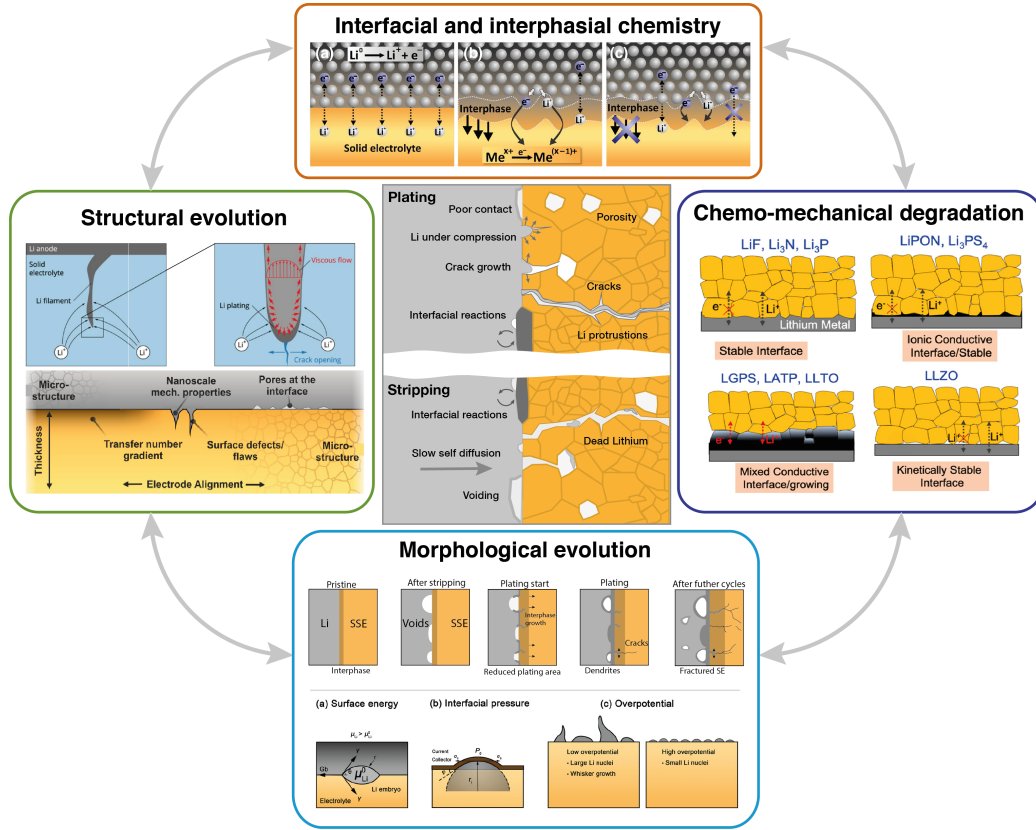


Figure 1: A representation of electro-chemo-mechanical processes occurring at the Li metal - solid electrolyte interface during plating and stripping. Schematic for chemo-mechanical degradation - Reprinted and adapted with permission from [7]; Copyright 2020 American Chemical Society. Schematic for Structural evolution - Reprinted and adapted with permission from [16], Copyright 2020 American Chemical Society and Reproduced with permission from [17]. Schematic for Morphological evolution - Reproduced and adapted with permission from ref [18] Copyright 2021 John Wiley & Sons, Inc., and ref [19] Copyright 2019 Springer Nature. Schematic for Interfacial and interphasial chemistry - Reprinted from [20], Copyright (2015), with permission from Elsevier.

2.1. Interfacial chemistry/reactions

Understanding the physical and chemical processes that occur at the interface between an electrode and an electrolyte is of fundamental importance for the development of future battery technologies. It is at this interface that lithium-ion and electron transfer occurs, as well as side reactions and interfacial layer formation, often referred to as the solid electrolyte interphase or “SEI” (analogous to the term used in conventional Li-ion batteries).

The stability of these interfaces depends on the interplay between thermodynamic driving forces and available kinetics at the reaction temperature, which is difficult to predict.[4] Electrochemical methods such as electrochemical impedance spectroscopy (EIS) allow changes in the interfacial resistance to be observed, but provide very little information on the chemical processes that are involved. Experimental techniques to observe changes in battery materials *in situ* and *operando* have been performed for liquid electrolytes, as detailed in several review articles. An attractive method employed in this regard is the use of impermeable and mechanically robust membranes to enclose the electrochemical reaction cell, that are also transparent to X-rays and electrons. As an example, Weatherup provides a variety of reaction cell designs for membrane-based XPS characterisations, one of which is schematically illustrated in Figure 2a.[21–23] Probing the buried interface between an electrode and an electrolyte, especially in the solid-state context, requires either complex experimental methods, cell designs or use of a probe that is not attenuated by the electrode or electrolyte material. [24]

One advantage of SE materials over their liquid counterparts, from an analysis perspective, is the ability to load them directly into the vacuum chambers used in many surface analysis techniques, without the electrolyte evaporating. Examples of this include X-ray photoelectron spectroscopy (XPS), a highly surface sensitive (typically <5 nm) technique, frequently utilised in *ex situ* characterisation of battery materials due to the elemental and chemically specific information available. *In situ* preparation of lithium metal films has been demonstrated by a variety of methods including Li metal sputtering [25], electron beam growth (depicted graphically in Figure 2b) [26] and thermal evaporation [27], allowing the formation of reaction species to be observed as the Li metal is deposited onto the electrolyte material. Recent work has suggested that the lithium deposition methodology affects the observed interfacial species, with interfacial damage observed for the case of lithium metal sputtering and electron beam irradiation.[28]

In the same vein, formation of electrochemical contacts to allow controlled electrochemistry and well-established methods, such as EIS, are also a necessary addition in future developments of such *operando* approaches to help collate the data collected with the wealth of existing understanding obtained with *ex situ* methods. Thus, by tracking chemical species formation and phase changes in real time, modified surface probing techniques provide valuable insights into the failure mechanisms of some systems, often understood to be associated with the electrode-electrolyte interface. Unfortunately,

there is great difficulty in obtaining highly surface sensitive information, often requiring a probe with a short attenuation length, whilst attempting to study a buried interface. To this end, many existing *operando* techniques utilise analysis probes which are less readily attenuated, such as optical and high-energy electron microscopy.[29] Consequently, these will obtain more bulk-sensitive results which may miss out on observing interfacial species. As a result, X-ray spectroscopies, which can be both surface sensitive and chemically specific are among the most promising candidates for developing *operando* methods to understand the evolution of chemical interfaces.

Alongside XPS, X-ray absorption spectroscopy (XAS) has been utilised to provide element specific information on oxidation states, providing detailed information on the electronic environment of the atomic species that are absorbing the X-ray photons. X-ray absorption near edge structure (XANES) measurements are valuable in determining the valence states of absorbing species and can consequently be used to track the reversibility of redox reactions. In contrast to XPS, XAS is most commonly performed at synchrotron sources.[21] Through careful cell design involving the use of suitable X-ray transparent windows, battery samples have been studied *in situ* and *operando* with XAS.[30] For example, polyimide films a few tens of μm in thickness are commonly incorporated into pouch or coin cells to facilitate *in situ* and *operando* measurements, especially using hard X-rays.[31] However, it should be noted that the longer attenuation lengths of X-rays (and the electrons that they liberate) that make these measurements more straightforward in the hard X-ray regime, ultimately result in less interface-sensitive information being acquired. Light elements commonly of interest (Li, C, O, F) as well as some of the frequently measured absorption edges in transition metals (Ni, Co, Mn, Fe L-edges) have absorption energies under 1 keV. However, achieving *in situ* and *operando* measurements in this range requires careful consideration of X-ray attenuation, membrane thicknesses, and detection mode (electron or fluorescent yield). Meanwhile, other techniques such as neutron reflectometry (NR) and nuclear magnetic resonance (NMR) have also been used under *in situ* and *operando* conditions by Kawaura et al. and Hope et al. respectively, to study the evolution of interfacial structure and also buried interfaces, paving the way for the adoption of a multi-pronged approach in studying Li-SE interfaces.[32, 33]

Use of destructive techniques such as secondary ion mass spectrometry (SIMS) may not be suitable for *operando* studies due to the destruction of the electrode material. It may be possible to probe different areas of the electrode

as a function of time, allowing a *quasi-operando* experiment to be performed, although sample inhomogeneity may become an issue. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in conjunction with focused ion beam (FIB) milling have been used to thin out existing electrodes and to apply biases to the milled out micro electrodes.[34, 35] Recent progress in vacuum transfer technology for atom probe tomography (APT) [36], coupled with the growing experience in cryo-FIB of battery materials [37], may soon enable the study of solid-state SEI structures with atomic resolution. These techniques are, again, time consuming and present a risk of changing the chemistry of the surface, with the etching beams increasing the likelihood of lithium vaporisation and structural changes. For these reasons, non-destructive surface probes hold the most promise for true *operando* analysis of the evolution of the electrode-electrolyte interface in SEs.

Despite the advancements in understanding that many *in situ* analysis methods have afforded, there are still limitations that these techniques will pose towards the application of *operando* studies. Development of suitable *operando* cells remains the main technological challenge for both XPS and XAS. These cells need to have suitably thin X-ray and photoelectron transparent films to allow the study of the interfacial layering, whilst also maintaining a reliable electrical connection between the electrode material, current collector and potentiostat. One approach has utilised high precision lasers to drill holes through the current collector to allow soft X-rays in and emitted X-ray fluorescence photons out (Figure 2c).[38, 39] Moreover, acquisition times for both XPS and XAS can reach over an hour for full characterisation of a single point, and often at least 10 minutes for a single element. This inevitably risks missing out on efficiently observing reactions happening on the sub-second timescale, although snapshots of particular chemical states could be recorded with much higher frequency. Clearly, technological development as well as corroboration of research efforts and techniques is required to drive the advancement of *operando* studies, to negate the shortcomings in each individual technique.

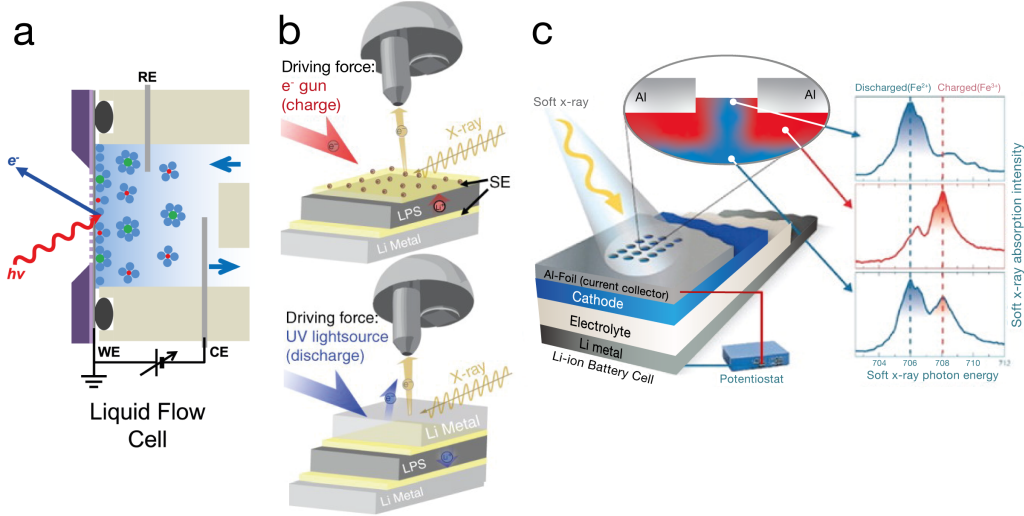


Figure 2: Suggestions for technological solutions towards *operando* X-ray spectroscopy (a) through use of a supported graphene membrane for electrochemical flow cells (Reprinted from [23], Copyright (2018), with permission from American Chemical Society), (b) through a virtual electrode approach on solid electrolyte materials (Reprinted from [26], Copyright (2018), with permission from Springer Nature), and (c) by etching through the current collector with a precision laser source (Reprinted from [39], Copyright (2014), with permission from Taylor and Francis).

2.2. Chemo-mechanical degradation

For any SE material, to be amenable to pairing with Li metal as the negative electrode, a wide electrochemical stability window is essential as decomposition of SEs at the interface can readily cause significant increase in interfacial impedance, eventually resulting in failure of the electrochemical cell. Most oxide and nitride-based SEs have reasonably wide stability windows, but this is not the case with most sulphide-based ones ($\sim 1-2$ V).[4, 40] At applied voltages beyond their stability windows, a cocktail of decomposition products are generated that can readily alter the thermodynamic and kinetic driving forces in play during electrochemical cell cycling. These have been extensively studied both computationally and experimentally in recent past.[4] Despite the reversible nature of some of these decomposition products, large volume changes associated with their formation (such as Li_2S , LiCl , Li_3PS_4 in sulphide SEs, Li_2O , La_2O_3 in garnet-type SEs, etc.), in conjunction with anodic expansion/contraction of the Li metal layer during cyclic charge-discharge processes, also effects irreversible contact loss at the

electrode-electrolyte interface.[41]

Electro-chemo-mechanical degradation of the Li metal-SE interface can occur in different ways, for which several mechanisms and models have been proposed. Krauskopf et al. succinctly summarise the current understanding of such interfaces, broadly categorising the degradation modes into either – (i) mode 1 in which initiation of failure is thought to present itself as rapid penetration of lithium metal at cracks along the SE surface, or (ii) mode 2 in which Li proceeds to gradually deposit internally within the SE (along grain boundaries, pores and cracks). The former is originally brought about by current focusing and Li flux imbalance owing to poor contact, presence of surface contamination, grain boundaries and surface defects.[8] Wu et al. and Li et al. were able to monitor the morphological dynamics of this process, as well as directly observe Li filament growth in SEs, using synchrotron radiation X-ray tomographic microscopy (SRXTM) (Figure 3a) and *in situ* neutron depth profiling (NDP) respectively.[11, 42] Davis et al. recently reported the observation of continued formation of an interphase layer even after prolonged plating of Li on an $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) SE using both *operando* XPS and *operando* video microscopy, in stark contrast to a relatively stable and finite interfacial layer in the case of an $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCl) SE (Figure 3b).[43]. Whereas, evidence for mode 1 degradation, as described above, was presented by Krauskopf et al. in another related article, using a microelectrode in contact with an $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) surface and an applied bias, while monitoring formed cracks and filling of Li in these, through an SEM (Figure 3c).[16]

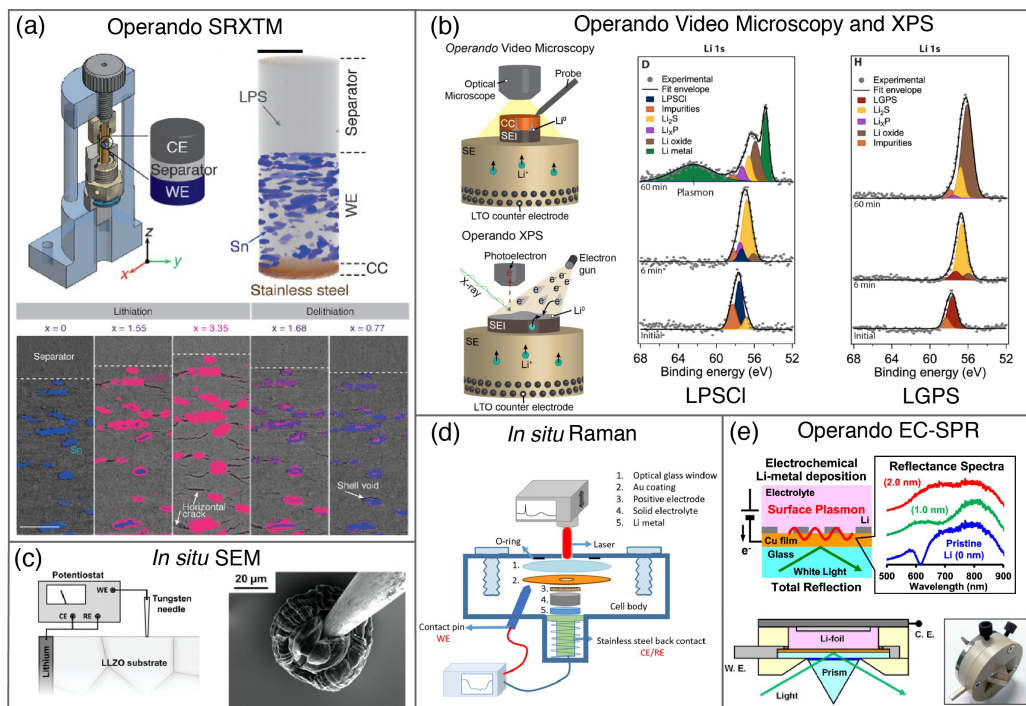


Figure 3: *In situ* and *operando* techniques to probe chemo-mechanical degradation in Li metal-SE interfaces. (a) *Operando* SRXTM to monitor and visualise anisotropic volumetric changes in anode, formation and evolution of voids, and propagation of cracks in the SE (Reproduced with permission from ref [11] Copyright 2019 John Wiley & Sons, Inc.), (b) *Operando* video microscopy and XPS to track and compare chemical degradation in different SEs during Li plating (Reproduced with permission from ref [43] Copyright 2021 IOP Publishing Limited), (c) *in situ* SEM to study charge transfer kinetics at Li metal-LLZO interface (Reproduced with permission from ref [16] Copyright 2020 WILEY-VCH Verlag GmbH & Co.), (d) *in situ* electrochemical Raman spectroscopy for the Li-Li₆PS₅Cl system to detect interfacial decomposition (Reproduced with permission from ref [44] Copyright 2020 WILEY-VCH Verlag GmbH & Co.), and (e) *operando* EC-SPR to investigate initial Li metal deposition processes (Reprinted with permission from ref [45] Copyright 2021 American Chemical Society).

The cause for such large variations in reactivity of SEs with Li metal has widely been attributed to the latter's strong reduction potential, based on which interfaces have been categorised into three types - (a) mixed ionic and electronic conducting (MCI), which is unstable both kinetically and thermodynamically resulting in continuous degradation, (b) ionically conducting but electronic insulating, where spontaneous decomposition occurs upon contact with Li metal, but not continuous, and lastly, (c) stable interfaces with

negligible decomposition.[4] While the nature of interfaces for different SEs are difficult to predict and characterise either *in situ* or *operando*, computational methods can serve as useful guides in somewhat predicting these reactions and associated interfaces. This presents tremendous opportunity for designing and engineering interfaces, promotes the idea of interlayers, and underscores the need for systematic *in situ* characterisation studies of chemo-mechanical stability using even conventional spectroscopic techniques such as XPS [26], Raman spectroscopy [44], Fourier transformed infrared spectroscopy (FTIR) [46] and also, novel ones like electrochemical surface plasmon resonance (EC-SPR) (Figure 3d-e).[45]

Moreover, *in situ* nanoindentation has been used to probe the mechanical properties of a wide range of battery materials *ex situ*, giving valuable data on the mechanical properties of the materials.[47, 48] Modern nanoindenters, operating within secondary electron microscope chambers, are capable of probing the mechanical response of exposed surfaces with nm depth resolution and micron lateral resolution giving information about elastic and plastic deformation, and failure dynamics. Some also offer electrical measurement between the indentation tip and the sample.[49] With intelligent cell design, it seems possible to probe mechanical responses at the lithium-solid electrolyte interface *in situ* akin to the work done on the lithium-silicon system by Epler and coworkers.[50] There are significant opportunities to pursue this approach, allowing the mechanical properties of chemical reaction products at the interface to be measured, as dynamic changes in stress/strain during cycling are quantified for a more comprehensive understanding of the chemo-mechanical degradation of these interfaces.

2.3. Morphological evolution of metal anodes

Another crucial feature that governs the behaviour of the Li metal SSB is the evolution of morphologies occurring at both the anode as well as the SE side. Together with the interfacial chemical reactions that occur at the interface between the two, as described in the previous section, the materials themselves undergo temporary and permanent physical transformations during cell operation.

Firstly, continuous alloying/mixing and dealloying/demixing reactions occurring at the anode-SE interface is associated with large volume changes, significant deformations and generation of stresses, that can lead to fragmentation of the anode material, fracture of the current collector and subsequent loss of contact, eventually resulting in short-circuiting of the cell.[11, 51] In

this regard, by conducting *in situ* TEM on a carbon nanofiber sandwiched between amorphous-Si (a-Si) layers, Wang et al. reported direct evidence of volume changes stemming from Li insertion into a-Si during lithiation (Figure 4a).[52] Zhang et al. and Koerver et al. were able to monitor the evolution of stress in active cells, to later visualise the effect of volume changes through electron microscopy and transmission X-ray tomography (XRT) in $\text{In} \mid \text{Li}_{10}\text{GeP}_2\text{S}_{12} \mid \text{LiCoO}_2$ cells under *ex situ* conditions to reveal volume expansion at the anode end with Li alloying into In.[53, 54] Meanwhile, Wu et al. conducted *operando* 3D and time-resolved synchrotron X-ray tomography microscopy (SRXTM) using a customised experimental setup, with Sn as an electrode in order to exacerbate the volume change occurring at the SE-electrode interface. In this manner, they demonstrate that while electrode expansion/compression processes are reversible, these cumulatively induce mechanical fracture on a soft SE like amorphous $\text{Li}_2\text{S-P}_2\text{S}_5$ (LPS) over time, thereby providing valuable insights into fracture and crack propagation at the interface, that impact Li ion migration.[11] It has been surmised that by careful design of interlayers, volume changes during lithiation/delithiation, and corresponding mechanical degradation of the Li metal-SE interfaces, can be mitigated to enable long-term cyclability in SSBs.[55] Furthermore, “anode-less” configurations are also currently being investigated to address this problem while keeping in view aspects like manufacturability and scalability, which, however, come with their own sets of challenges and limitations.[56, 57]

Secondly, Li plating and stripping processes themselves are fairly complex, where the morphology of the Li being plated or stripped depends on numerous factors such as applied stack pressure, current density, nature of the surfaces involved, and mechanical properties of the materials, to name a few.[18, 56, 58, 59] During the plating process, nucleation of Li occurs in a manner where the size of the nucleates depends on the overpotential at the interface. By studying the lithium nucleation process in lithium phosphorous oxynitride (LiPON) thin-film batteries, the dependence of nuclei size on the overpotential and Young’s modulus (E) of the current collector was derived, where increasing current collector stiffness was correlated with increased overpotentials, that in turn resulted in smaller Li nuclei. Further nucleation and growth of the Li layer can be in the form of (a) whiskers, (b) lateral dendritic growth and (c) layered, as directed by the SE surface, current collectors and the current densities.[8, 18] Using *in situ* scanning electron microscopy (SEM) at the interface between Cu and LiPON, Sagane et al. observed sparsely dis-

tributed initial lithium growth sites, whereupon further growth takes place to form whisker/needle-like precipitates.[60] Later, a more systematic study on the kinetics determining whisker-like growth on garnet-type SEs (LLZO) was presented by Krauskopf et al. using a combination of *in situ* and *ex situ* electron microscopy, where microstructural inhomogeneities on the SE surface were found to be responsible for generation of localized “hot-spots” of nucleation and differing lithium deposition morphologies arising at such sites. Herein, the authors also describe an *in situ* electrodeposition technique adaptable to an SEM using which, controlled electron injection on the SE can lead to lithium metal formation at the surface and provide valuable insights into the tendency for preferential nucleation of lithium at grain boundaries (Figure 4c).[61, 62] Upon stripping, however, the inhomogeneity of the current density distribution stemming from interfacial defects and decomposition (SEI), can lead to the formation of pores, voids and complete loss of contact as a consequence. Repeated plating and stripping across such an inhomogeneous surface eventually results in the continuous consumption of lithium at its interface with the SE, forming a variety of decomposition products along with unreacted metallic Li which remains electrically isolated, further enabling the gradual accumulation of “buried” interfaces. This unreacted Li, termed “dead Li”, deriving its nomenclature from liquid organic electrolyte analogues, renders the SSB inefficient by causing capacity loss and further exacerbating anodic volume expansion.

A third factor governing the morphological evolution of the interface, that is mostly a consequence of the above two processes, is the generation and propagation of stresses at the Li metal – SE interface. Electrochemically generated stress during Li plating at this interface can reach a few hundred MPa up to even 1 GPa from an overpotential of ~ 135 mV.[59, 63] Thus, Li deposition under even modest overpotentials generate tensile stresses of several MPa on the solid electrolyte, driving fracture. Chen et al. studied Li diffusion mechanisms using *in situ* TEM, through plating/stripping of lithium within large parallel mixed ionic-electronic conducting tubules to suggest a Coble creep type mechanism as a means to relieve these stresses.[63] The magnitude of stresses during Li plating and dendrite/filament growth, however, was estimated by Zhang et al. using *in situ* atomic force microscope - environmental transmission electron microscopy (AFM-ETEM), a unique and emerging technique to investigate dendrite propagation as well as quantify their mechanical properties such as yield strengths and Young’s moduli (Figure 4b).[64] Independently, scanning probe techniques such as atomic

force microscopy (AFM) and scanning tunneling microscopy (STM) find increasing use in mapping topography and dynamics of morphological evolution through advanced characterisation modes built into modern AFMs, such as electrochemical atomic force microscopy (EC-AFM) and scanning electrochemical microscopy (SECM), although, most studies employing these techniques often report on Li plating/deposition on liquid electrolyte systems or on electric potential distribution within cathode-solid electrolyte interfaces, indicating untapped potential and opportunities for future scanning probe microscopy (SPM) based *in situ* characterisations.[65, 66]

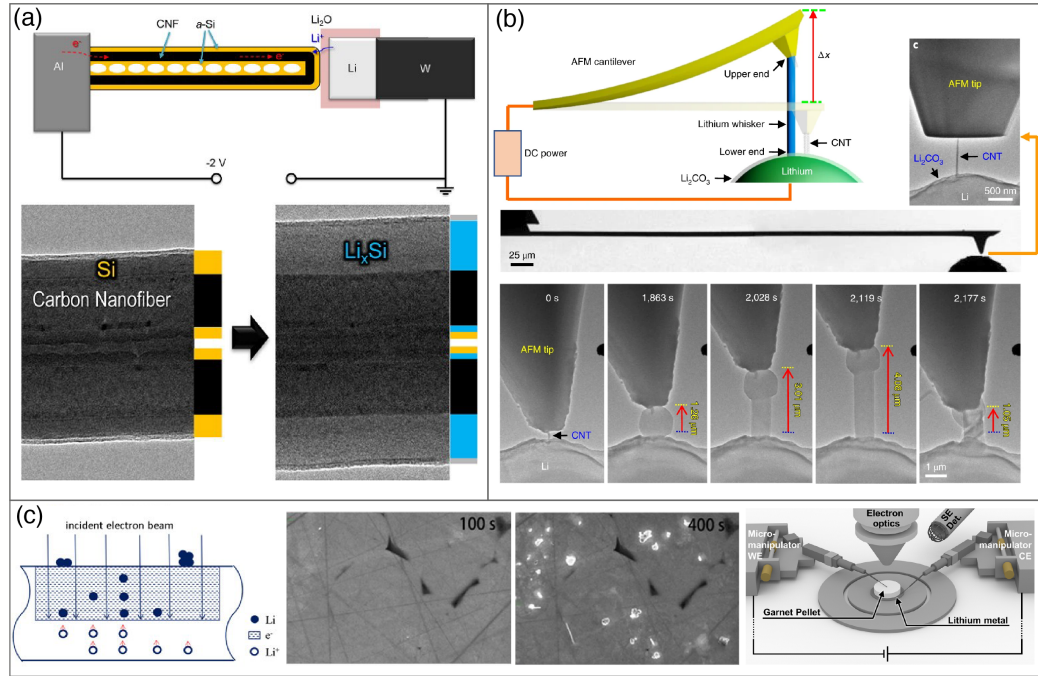


Figure 4: Characterisation methods employed to study morphological evolution at the Li-SE interface. (a) Volume changes in the anode during lithiation and delithiation processes investigated using *in situ* TEM in carbon nanofibers sandwiched between Si layers (Reprinted with permission from ref [52] Copyright 2012 American Chemical Society), (b) *In situ* AFM-ETEM technique used to measure mechanical properties of growing Li filaments (Reproduced with permission from ref [67] Copyright 2020 Springer Nature), and (c) Mapping of Li nucleates at SE surface through electron by means of electron-beam induced lithium expulsion (Reprinted with permission from ref [61] Copyright 2018 American Chemical Society) and external micromanipulators (Reproduced with permission from ref [62] Copyright 2019 Elsevier).

It is worth noting here that a systematic and quantitative study of these processes under *in situ* and dynamic conditions using electron microscopy remains a challenge, primarily due to the buried nature of these interfaces.[7, 16, 19, 59] Nonetheless, the high penetration power of synchrotron X-rays have been utilised with reasonable success in providing visual evidence of buried structures beneath Li metal anode surfaces using *in situ* X-ray microtomography.[68] Additionally, novel neutron-based techniques such as neutron reflectometry (NR) and neutron depth profiling (NDP) can provide quantitative information about changes occurring within the interfaces while “tracking” the movement of lithium, *in situ* or *operando*, as a function of depth. The interaction of neutrons with only the nuclei of the materials involved enables non-destructive depth probing, sensitivity to even light elements like lithium, as well as reasonable isotopic contrast.[13] Together, the use of X-ray tomography and neutron-based techniques, particularly using high-energy synchrotron radiation, have the potential to supplement learnings from *in situ* electron microscopy to provide a more holistic and visual understanding of the dynamic evolution of interfacial morphologies between Li metal and SEs, under more realistic cycling conditions.

2.4. Structural evolution

From the preceding sections, it is quite evident that several technical challenges need to be addressed before lithium metal can be considered a commercially viable anode for EV batteries. In addition to the chemical, mechanical and morphological aspects described as before, from a structural point of view, the first issue apparent with Li metal, is the associated slow self-diffusion kinetics, ($D_{Li} \sim 10^{-12} \text{ cm}^2\text{s}^{-1}$ at 0°C), leading to void formation at the lithium-solid electrolyte interface on stripping [19, 69], followed by growth of dendrites/filaments at local deposition “hotspots” during plating. These plating defects cause rapid degeneration of electrochemical cells followed by short-circuiting, as discussed already. In the laboratory, this issue can be partially resolved by applying stack pressures close to, or in excess of, lithium’s yield stress, with the resultant creep or plastic flow filling voids and suppressing dendrites.[67] The application of excessive stack pressures seems impractical in a multi-layer working battery, so increasing diffusivity permanently is desirable. The second issue is that the overpotential associated with the deposition of lithium under high compressive stresses, sufficient to initiate and propagate a crack in a solid electrolyte, is relatively small (135 mV/GPa) [63], therefore, the fracture toughness of the electrolyte needs to

be high, and the overpotentials associated with transport and charge transfer need to be minimised to guarantee homogeneous plating. Thirdly, as previously highlighted, lithium readily reduces solid electrolyte materials to form an interfacial layer, whose composition and structure has a significant impact on battery performance.[20, 70]

It has been demonstrated electrochemically that the self-diffusion of lithium is too slow to sustain practical stripping currents [69, 71] and that the stripping is heterogeneous, leading to voids, that have been observed at the interface between the SE and lithium metal in cross-sectional SEM [19] and *operando* X-ray computed tomography (XR-CT) (Figure 5b).[72] These studies provide visual insights into understanding the role of void formation, interphasial growth and volumetric changes on the behaviour of the electrochemical cell.

Given the fundamental insufficiency of lithium metal diffusion kinetics, recent research has focused on introducing fast diffusion pathways into the anode – which remain even after stripping. Lithium containing intermetallics [73], carbon hosts [57], de-lithiated lithium-magnesium alloys [74], micro- and nano-structured Si [75] and surface alloying [76] are all promising examples of this approach (Figure 5c). Likewise, it may be that improved diffusion kinetics, resulting from an increased dislocation density, explain much of the improved anode performance with stack pressure. With the discovery of anode materials without significant diffusion limits, there is substantial scope to characterise full cells with these superior anodes, separating the anode-linked and electrolyte-linked issues.

Lastly, Li growth into SEs, a phenomenon that arises from the issues indicated above, has been observed via SEM (Figure 5a) [77], optical microscopy [78], synchrotron X-ray CT [79–81] and NMR [82] under both *in situ* and *ex situ* conditions. A dense web of wide cracks observed during such measurements clearly indicate further propagation of the stress from lithium plating within the cracks. Other related studies using electron microscopy show that grain boundaries offer preferential paths for lithium deposition.[77] The large stresses from the plating process lead to further growth of the crack network well ahead of the plating, with the final portion of the network only around 20% full of lithium.[80] The observation of total mechanical breakdown of widely used electrolytes has driven experimental work including the development of sintering additives [83], single-crystal electrolytes [84], and blocking layers [85] all enabling an increase in the critical current density of solid-state cells. Looking forward, there’s an opportunity to conduct system-

atic characterisation experiments around the best-performing modified solid electrolytes, to accelerate their improvement. However, the initiation and first stages of propagation of the network of cracks remain to be properly characterised and understood, owing to the requirement of more advanced techniques with nanometre resolution to image sharp crack tips and initiation of dendrite/filaments.[86]

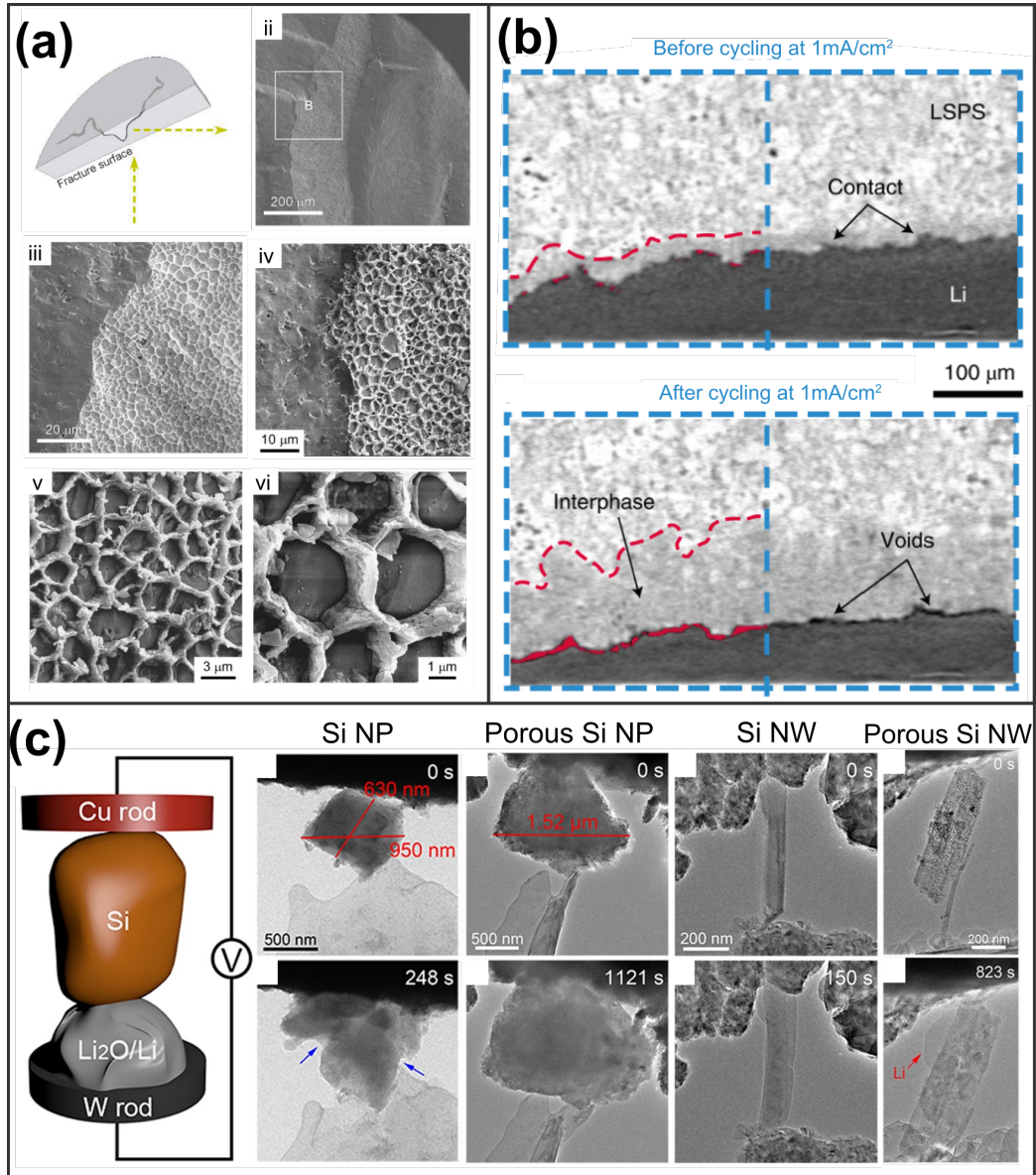


Figure 5: Evidences of structural evolution of Li metal anode, SE and Li filaments as seen using (a) SEM confirming preferential propagation of Li through LLZO grain boundaries (Reproduced with permission from ref [77] Copyright 2017 Elsevier), (b) *operando* XR-CT revealing void formation during lithium stripping in symmetric cells of Li—Li₁₀SnP₂S₁₂—Li leading to electrode-electrolyte contact loss (Reproduced with permission from ref [72] Copyright 2021 Springer Nature), and (c) *in situ* TEM correlating microstructure of host material to lithium diffusion pathways during lithiation/delithiation processes (Reproduced with permission from ref [75] Copyright 2016 Springer Nature).

3. Challenges and future opportunities

In lieu of the inherent limitations in conventional microscopic and spectroscopic techniques in providing a more accurate understanding of interfacial evolution in SSBs via *in situ* or *operando* modes, a host of new tools and techniques are continuously being developed that serve to address these drawbacks. The primary challenges and opportunities to tackle them can be summarised as below:

- For chemical information on the processes occurring at buried interfaces existing in SSBs, novel experimental techniques are required often utilising thin film preparation. The associated risk is that these thin films are not fully representative of real-world batteries. However, an understanding of the fundamental chemistries is essential for development of solutions to many of the existing problems highlighted here.
- True *operando* measurements require detection probes that can be collected on a short timescale, in order to detect short lived chemical species. For some experimental techniques full characterisation requires at least 30 minutes (XPS, XAS, AFM, NR, etc.). In order to perform true *operando* measurements either the detection method must change, focussing on a few chemical species of interest, or reaction dynamics must be reduced, possibly through surface cooling. Such cooling may drastically alter the observed electrochemistry, rendering such an approach unsuitable for some systems.
- Application of stack pressure during cycling has been noted as being key to achieving good electrochemical performance. Most conventional microscopy or spectroscopy techniques are limited in probing interfacial dynamics with an added constraint of stack pressure. Studying variations as a function of temperature too, presents a significant challenge. Nevertheless, custom cell setups are increasingly being adopted to circumvent this issue through use of radiation-transparent windows and alternative stack designs.
- Many of the properties associated with Li metal – SE interfaces highlighted in this review are quite inter-related, as a consequence of which no one technique can adequately characterise and probe mechanisms underlying electro-chemo-mechanical evolution of the interfaces involved.

The community is increasingly starting to employ “correlative” approaches by combining multiple techniques either within the same instrument or using connected setups, to more comprehensively study target features. Correlative neutron and XR-CT, and correlative electrochemical microscopy are two such examples that have been successfully used to understand lithiation/delithiation processes.[87, 88]

- The advanced characterisation needs discussed here also present a unique opportunity for the development of central integrated ultra-high vacuum (UHV) cluster tool facilities, which can accommodate equipment capable of handling both material deposition (sputtering, evaporation, pulsed laser deposition) as well as *in situ* characterisation (XPS, UV-photoemission, Auger and Raman spectroscopies, SEM, TEM, etc.), under controlled environments, all connected to each other with easy navigability between the various instruments. This would pave the way for probing interfaces that are pristine and largely devoid of extraneous contamination. However, owing to prohibitive capital costs associated with setting up and maintaining such a facility, it may be necessary to do so under a consortium/institutional funding, with support from local or national governmental organisations, where access can be provided through proposal-grant avenues, as in the case of synchrotron facilities around the world. The DArmstadt’s Integrated SYstem for BATtery research (DAISY-BAT) is an example of such a facility set up at TU Darmstadt, Germany.
- In addition to the timescales for measurements, length-scales associated with each technique, both in terms of sample geometry and instrument resolution, are important considerations as well, when conducting *in situ* and *operando* studies. To this end, a graphical chart (Figure 6) depicts the various electro-chemo-mechanical evolutionary processes along with typical tools and techniques used to study them, collated together with achievable resolutions for each, to serve as a useful guide while considering studying these systems.

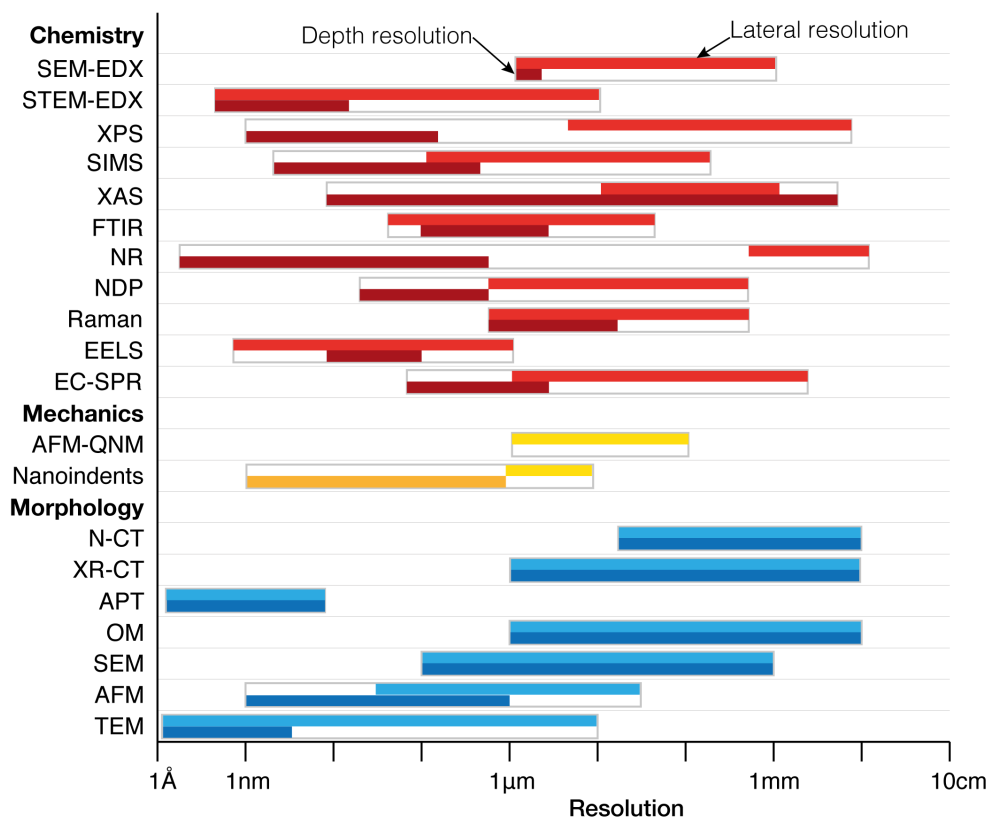


Figure 6: Chart displaying the typical resolution (depth and lateral) of techniques discussed in this perspective.[89]

4. Acknowledgements

The authors would like to acknowledge the support of The Faraday Institution (grant numbers FIRG026 and FIRG011) as well as the Henry Royce Institute (through UK Engineering and Physical Science Research Council grant EP/R010145/1) for capital equipment. MP and SN acknowledge support from Innovate UK (project number 98841) and Nissan Motors Ltd., Japan, Nissan Technical Centre Europe, U.K. RSW acknowledges funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 950598)

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