

Methodological developments to expose and analyse buried interfaces in lithium solid-state batteries using *ex situ*, *in situ* and *operando* cycling

Julien Morey^{1*}, Jean-Bernard Ledeuil¹, L enaic Madec^{1,2*}, and Herv e Martinez^{1,2,3*}

¹ Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France

² R seau sur le Stockage Electrochimique de l'Energie, CNRS FR3459, Amiens, France

³ Ecole Centrale Casablanca, Centre de Recherche Syst mes Complexes et Interactions, Bouskoura (Maroc)

Abstract. Lithium solid-state batteries (SSBs) are a promising technology for electrochemical energy storage systems. So far, the performance of SSBs are mainly governed by the electro-chemo-mechanical properties of the diverse solid/solid interfaces and their evolution upon cycling. However, as these interfaces are buried in the battery stack, their comprehensive understanding remains a challenge. Here, we thus provide some advances in methodological developments for *ex situ*, *in situ* and *operando* cycling/analysis of these buried interfaces. It is showed that noble gaz ion milling at liquid nitrogen temperature is a suitable and reproducible method to prepare cross-section without any chemical/physical change even for polymer-based SSBs. In addition, innovative *operando* cycling using Auger analysis was proposed for the first time on a model Li/Li₆PS₅Cl stack. The interest of this approach is to be able to proceed without a dedicated electrochemical cell and to use the fully adjustable electron beam of the auger to create a surface potential difference followed by lithium migration then SEI (Solid Electrolyte Interface) formation and Li plating. Overall, this work should greatly benefits to all researchers working on buried interfaces study in lithium solid-state batteries.

1 Introduction

Lithium solid-state batteries (SSBs) are currently recognized as the most promising technology for the next generation of Li rechargeable batteries [1]–[3]. In these systems, the liquid electrolyte of common Li ion batteries is replaced by a solid electrolyte with the dual role of Li ion conductor and separator between the electrodes. Electrochemical performance of SSBs are mainly governed by (i) ionic and electronic properties of the solid electrolyte and (ii) the chemical and structural properties of the diverse solid/solid interfaces and their stability. Thus, improvement of SSBs electrochemical performance will be achieved through a comprehensive understanding of the interphases electro-chemo-mechanical properties upon cycling. [4], [5]

As illustrated in **Fig. 1**, a significant number of interfaces are identified in SSBs. For instance, the Li/solid electrolyte (SE), positive active material/SE, conductive additive/SE and current collector (CC)/SE are the main interfaces in SSBs. However, the rigorous analysis of all interfaces in SSBs is not trivial as they are buried inside the battery stack, *i.e.* two adjacent materials cannot be easily separated to probe the interphase. Moreover, separation of the two materials

can deteriorate the chemical and structural properties of the interphase, which would lead in a loss of relevant information. Suitable and reproducible approaches are thus mandatory to reveal and analyse buried interfaces in SSBs. **Fig. 1** also illustrates the *ex situ*, *in situ* and *operando* approaches used to analyse buried interfaces of SSBs. Briefly, *ex situ* analysis is the most widely used approach and consists in electrochemically cycling the SSB cell, then disassembled it w/wo specific preparation to reveal the interfaces prior to the analysis. To avoid sample pollution and possible interfaces degradation induced by the cell disassembling and sample preparation, *in situ* and *operando* approaches are very attractive. During *in situ*, the SSB cell is sequentially cycled and analysed inside an analysis chamber while during *operando*, the cycling is performed at the same time of the analysis (**Fig. 1**). Relevant examples of *operando* XPS studies on SSBs can be found in references [6]–[13].

In this paper, we will provide a model approach we recently developed to reveal and analyse buried interfaces in lithium solid-state batteries using *ex situ*, *in situ* and *operando* cycling.

* Corresponding author: julien.morey@univ-pau.fr, lenaic.madec@univ-pau.fr, herve.martinez@univ-pau.fr

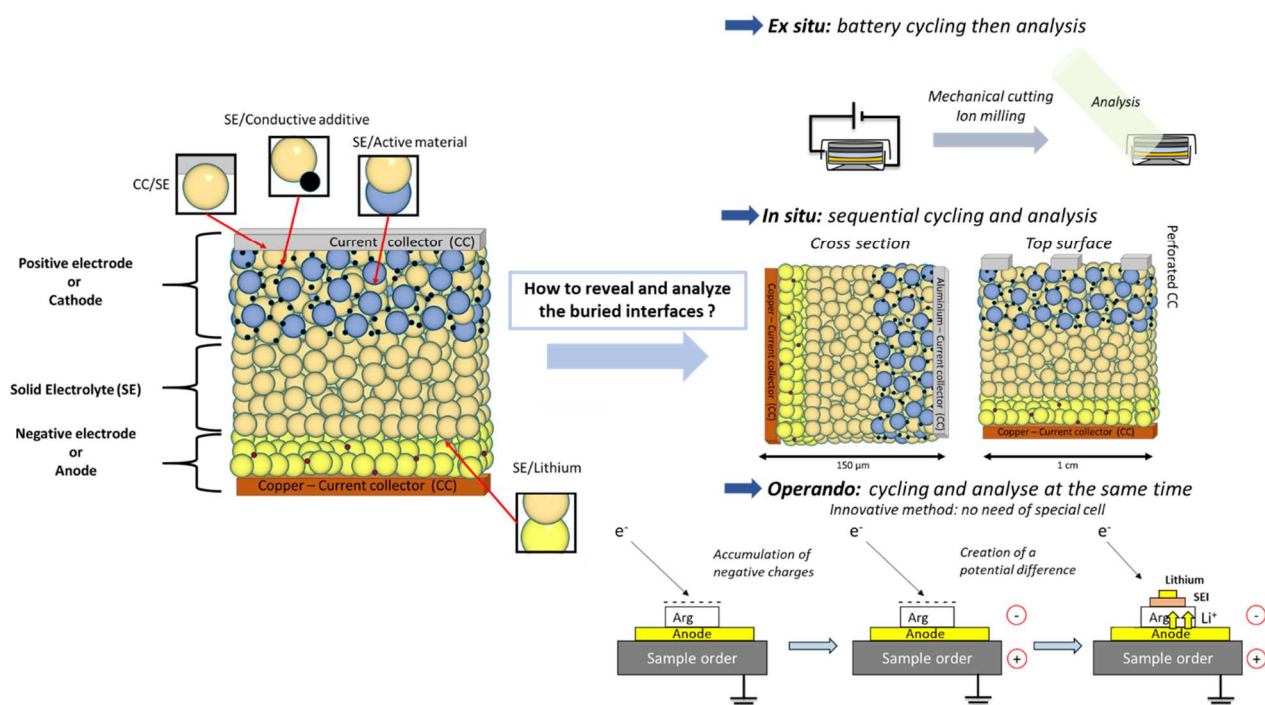


Fig. 1. Schematic illustration of buried interfaces in SSBs and the *ex situ*, *in situ* and *operando* approaches to analyse them.

2 *Ex situ* analysis of buried interfaces in SSBs

To analyse *ex situ* the buried interfaces of SSBs using surface analytical techniques, it is mandatory to reveal these interfaces in a first step. However, numerous literature reports rely on the manual ability of a researcher to separate mechanically the interfaces [5], [14]–[16]. Here, we will show that even for polymer-based SSBs, the use of Ar^+ ion milling (*i.e.* a cross-polisher, **Fig. 2a**) is a suitable method to reveal buried interfaces. In this study, the common poly(ethylene oxide) (PEO) with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was used as polymer electrolyte. Commercial graphite and NMC532 electrodes (MTI corp) were used and filled by the PEO-LiTFSI using anhydrous acetonitrile followed by its evaporation at 70°C . Preparing cross-section of such NMC/PEO-LiTFSI/graphite stack is thus a challenge. Indeed, polymers are expected to flow and/or to delaminate and/or to be simply damaged by the constraints produced by the Ar^+ beam such as the heat. Therefore, to obtain a perfectly flat cross-sectioned surface without any physical and chemical change, different parameters such as the ion beam voltage/current and working temperature were adjusted by iterative tests. Finally, an Ar^+ beam of 8 kV and 3.5 mA as anode current was used and the temperature was fixed at 133°K using liquid nitrogen cooling in a SEMPREP2 from TECHNOORG LINDA. **Fig. 2b** shows the SEM image of the obtained cross-section for the NMC/PEO-LiTFSI/graphite stack after 6h. As observed, no delamination or flowing of the polymer occurred. To further check that no chemical damage was induced during ion milling, surface analysis was carried out. Auger spectroscopy (AES) and X-ray spectroscopy (XPS) showed that no major difference was observed

between the analysis of the cross-section and references (*i.e.* starting) materials (**Fig. 2c** and **2e**). In details, AES analysis showed that no unexpected transition appeared, and the shape line matched perfectly with the reference. Regarding the XPS, no major change was observed on the Mn 2p and Ni 2p except some peaks broadening, characteristic of a less well-defined local chemical environment following the creation of the cross-section or the possible reduction of the transition metals despite that it is not expected for such material in a lithiated environment. This is supported by the fact that no LiF formation was observed from the LiTFSI salt degradation while it would have been expected using Ar^+ milling. Furthermore, characteristic signals from the fluorine, Auger KLL transition and XPS peaks overlapping with the Ni 2p peaks could be identified. Note that the possible degradation was also investigated by ToF-SIMS, which confirmed the XPS and AES results (not shown here). Finally, scanning Auger microscopy (SAM), *i.e.* elemental 2D nano distribution images showed that PEO-LiTFSI electrolyte filled the entire electrodes thickness as deduced from the sulphur mapping attributed to the LiTFSI salt (**Fig. 2d**). Overall, AES, XPS and SAM showed that the ion milling performed at the liquid nitrogen temperature did not chemically/physically damage the revealed surface as no significant change was observed. Thus, this cross-section preparation method combined with *ex situ* cycling can easily be implemented to investigate the interfaces over cycling.

3 In situ / Operando analysis of buried interfaces in SSBs

3.1 In situ cycling

As discussed in the introduction, *in situ* cycling refers to an alternation between electrochemical cycling and XPS ; (ii) from the top surface, using a perforated current collector is a good alternative to overcome possible cross-section limitations. However, interfaces of only one electrode can be probed at once.

analysis. To do so, dedicated cells need to be design according to the analytical machine used. Importantly, two different configurations can be used (**Fig. 1**): (i) using cross-section, all the interfaces are directly exposed but the spatial resolution of the technique may limit the analysis of the Li/SE interfaces, especially in the case of

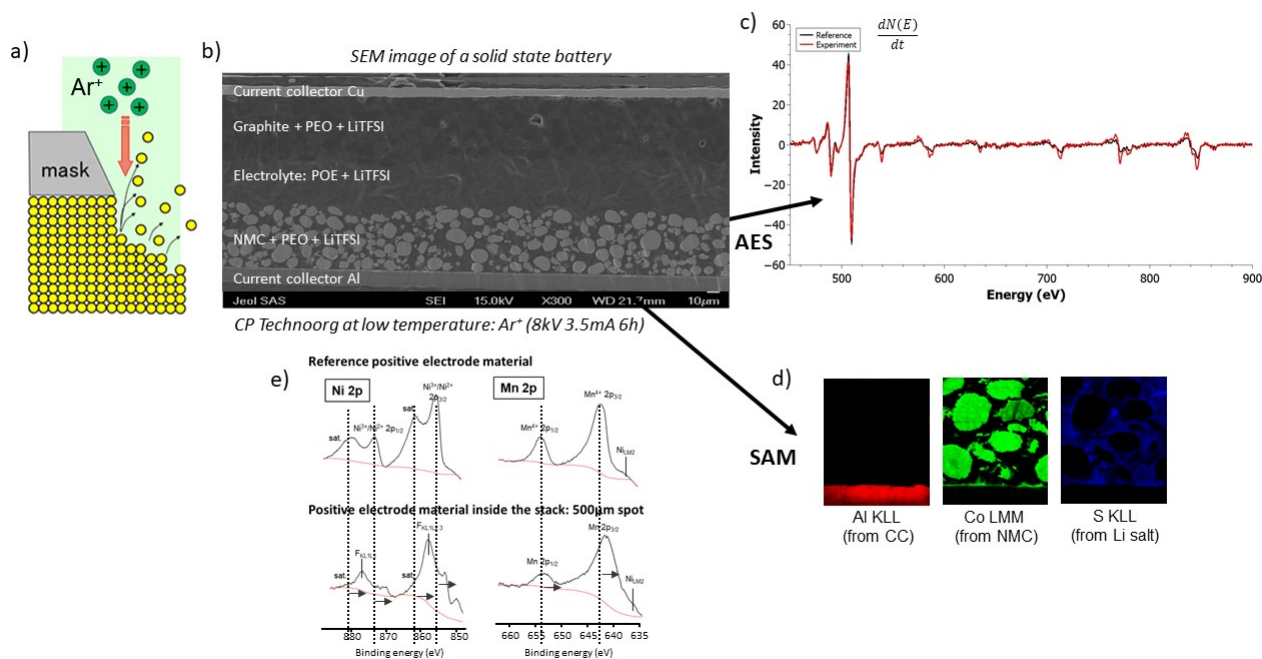


Fig. 2. a) Schematic representation of the ion milling (*i.e.* cross-polishing) principle, b) SEM image of a NMC/PEO-LiTFSI/graphite cross-section obtained after 6h at 8 kV, 3.5 mA and 133°K, c) comparison of AES spectra for the reference NMC electrode and the cross-section, d) SAM (elemental 2D nano distribution) images of the cross-section, e) comparison between XPS spectra from the reference NMC electrode and the cross-section.

3.2 Operando cycling

The aim of *operando* cycling is to follow directly the evolution of the materials and interfaces without the minimum sample preparation and concomitant possible alteration. Ultimately, it is then possible to eliminate the use of a dedicated electrochemical cell by using instead the compensation charge gun working in an only electron flooding mode for XPS and ToF-SIMS analysis or the primary electron beam for SEM/Auger analysis (**Fig. 1**) [17]. In that case, the main drawback remains the lack of pressure and voltage control, especially for inorganic SSBs. The most common use and interest of this approach is the study of the Li/SE interfaces formation that cannot be access by *ex situ* or *in situ* analysis. [18]–[20] Typically, a Li/solid electrolyte stack is positioned directly on a sample holder (being grounded) and the electron flow applied on top of the solid electrolyte will create a potential difference by charges build up which will induced Li^+ migration from the lithium electrode (**Fig. 1**). SEI formation and Li plating will then occur. Moreover, the UV gun, often present in XPS equipment, can be used to reversibly

strip the Li by removing valence band electrons. Note that is also possible to use a Li/solid electrolyte/positive electrode stack or any other desired configuration and thus charge/discharge the whole assembly by combining flood and UV guns in XPS analysis.

In this work, this innovative *operando* cycling method was performed for the first time using Auger analysis (JEOL JAMP9500F) on a model system composed of a lithium/argyrodite ($\text{Li}_6\text{PS}_5\text{Cl}$, noted Arg thereafter). **Fig. 3a** shows that after applying a current beam of $5 \cdot 10^{-8}$ A, 10 KeV (0.8 mA/cm^2) for 2h using a large area scan of $30 \times 20 \mu\text{m}$, the surface of the Arg became covered by some new compound(s) with a secondary electron black contrast. Auger spectra showed the decrease of the P LVV, S LVV and Cl LVV transition peaks from the Arg and the increase of the Li transition peak (**Fig. 3b**), indicating possible Li plating. This latter was confirmed by the peak shape and position that corresponded perfectly to the Li KVV transition of a pure Li metal reference available in the JEOL database (not shown here).

Again, by comparison with JEOL references, another component transition appeared during the experiment and is attributed to the reduction of Arg into Li_2S (not

shown here). The Li_2S area corresponds to the secondary electron white contrast area surrounding the Li metal plating in the SEM image (**Fig. 3b**). Note that Li_2S was also found to form first before Li plating (not shown here). The SAM image overlay of Li_{metal} (KVV), $\text{Li}_{\text{Li}_2\text{S}}$ (KVV) and S_{Arg} (LVV) clearly illustrates the Li_2S formation and Li plating (**Fig. 3c**). Due to the shape of the Li(KVV) analysis and the JEOL references a differentiation between Li metal and oxidized Li can be made. Note that these results were confirmed by XPS

analysis using the flood gun as electron source in a pair sample (not shown here). Overall, this experiment demonstrates that *operando* cycling in Auger analysis is a very powerful method to study the solid electrolyte reactivity in SSBs. Indeed, using Auger, the electron beam parameters (*i.e.* the current/cm² corresponding to the cycling rate) are fully adjustable compared to flood guns in XPS and ToF-SIMS. Thus, *operando* Auger analysis needs to be further develop in the future.

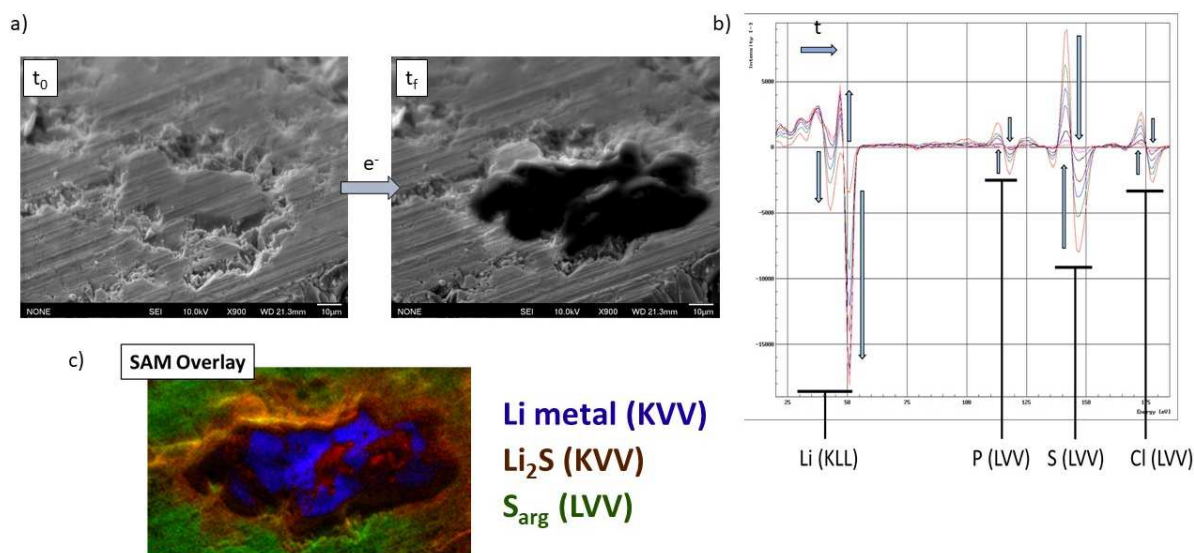


Fig. 3. a) SEM image of Arg deposited on Li metal before and after application of an electron beam using an area scan mode for 2h, b) corresponding AES spectra of the area scan recorded during the *operando* cycling of the Li/Arg stack c) SAM image overlay of Li_{metal} (KVV), $\text{Li}_{\text{Li}_2\text{S}}$ (KVV) and S_{Arg} (LVV) after 2h of acquisition.

4 Conclusions

This work provided latest advances in methodological developments for *ex situ*, *in situ* and *operando* cycling/analysis of buried interfaces in lithium solid-state batteries (SSBs).

Ion milling at liquid nitrogen temperature was proved highly efficient to prepare clean and perfectly flat cross-section of a NMC/PEO-LiTFSI/graphite without any chemical/physical change as observed by XPS, AES, SAM and ToF-SIMS analysis. This result thus highlights that ion milling, with appropriate and controlled parameters, should be preferred to manual cutting as a suitable and reproducible method to reveal buried interfaces even for polymer-based SSBs.

References

- [1] R. Chen, Q. Li, X. Yu, L. Chen, and H. Li, "Approaching Practically Accessible Solid-State Batteries: Stability Issues Related to Solid Electrolytes and Interfaces," *Chem. Rev.*, vol. 120, no. 14, pp. 6820–6877, 2020.
- [2] J. Janek and W. G. Zeier, "A solid future for battery development," *Nat. Energy*, vol. 1, no. 9, 2016.

Regarding *in situ* cycling, it is believed that top surface analysis using a perforated current collector should be preferred for XPS while cross-section analysis are more appropriate for high lateral resolution techniques as ToF-SIMS and Auger.

Finally, an innovative *operando* cycling using Auger analysis was proposed for the first time. Using a model Li/Li₆PS₅Cl stack, the SEI formation (Li_2S) and Li plating were observed by applying the Auger electron beam in area scan mode on top of this stack. In other words, that the charges build up which leads to the creation of a potential difference then the migration of lithium through the Li₆PS₅Cl solid electrolyte. Overall, this work should greatly benefits to all researchers working on buried interfaces study in lithium solid-state batteries.

- [3] Y. Ding, Z. P. Cano, A. Yu, J. Lu, and Z. Chen, "Automotive Li-Ion Batteries: Current Status and Future Perspectives," *Electrochem. Energy Rev.*, vol. 2, no. 1, pp. 1–28, 2019.
- [4] A. Banerjee, X. Wang, C. Fang, E. A. Wu, and Y. S. Meng, "Interfaces and Interphases in All-Solid-State Batteries with Inorganic Solid Electrolytes," *Chem. Rev.*, vol. 120, no. 14, pp. 6878–6933, 2020.

- [5] I. López, J. Morey, J. B. Ledeuil, L. Madec, and H. Martinez, “A critical discussion on the analysis of buried interfaces in Li solid-state batteries.: Ex situ and in situ / operando studies,” *J. Mater. Chem. A*, vol. 9, no. 45, pp. 25341–25368, Dec. 2021.
- [6] X. Wu, C. Villevieille, P. Novák, and M. El Kazzi, “Monitoring the chemical and electronic properties of electrolyte-electrode interfaces in all-solid-state batteries using: Operando X-ray photoelectron spectroscopy,” *Phys. Chem. Chem. Phys.*, vol. 20, no. 16, pp. 11123–11129, 2018.
- [7] X. Wu, C. Villevieille, P. Novák, and M. El Kazzi, “Insights into the chemical and electronic interface evolution of Li₄Ti₅O₁₂ cycled in Li₂S-P₂S₅ enabled by: Operando X-ray photoelectron spectroscopy,” *J. Mater. Chem. A*, vol. 8, no. 10, pp. 5138–5146, 2020.
- [8] M. Mirolo, X. Wu, C. A. F. Vaz, P. Novák, and M. El Kazzi, “Unveiling the Complex Redox Reactions of SnO₂ in Li-Ion Batteries Using Operando X-ray Photoelectron Spectroscopy and in Situ X-ray Absorption Spectroscopy,” *ACS Appl. Mater. Interfaces*, vol. 13, no. 2, pp. 2547–2557, 2021.
- [9] R. Koerver *et al.*, “Redox-active cathode interphases in solid-state batteries,” *J. Mater. Chem. A*, vol. 5, no. 43, pp. 22750–22760, 2017.
- [10] Y. C. Lu *et al.*, “In situ ambient pressure X-ray photoelectron spectroscopy studies of lithium-oxygen redox reactions,” *Sci. Rep.*, vol. 2, pp. 1–6, 2012.
- [11] M. Favaro *et al.*, “Unravelling the electrochemical double layer by direct probing of the solid/liquid interface,” *Nat. Commun.*, vol. 7, no. May, pp. 1–8, 2016.
- [12] X. Wu, M. El Kazzi, and C. Villevieille, “Surface and morphological investigation of the electrode/electrolyte properties in an all-solid-state battery using a Li₂S-P₂S₅ solid electrolyte,” *J. Electroceramics*, vol. 38, no. 2–4, pp. 207–214, 2017.
- [13] D. Weingarth, A. Foelske-Schmitz, A. Wokaun, and R. Kötz, “In situ electrochemical XPS study of the Pt/[EMIM][BF₄] system,” *Electrochem. Commun.*, vol. 13, no. 6, pp. 619–622, 2011.
- [14] J. Liang *et al.*, “Stabilizing and understanding the interface between nickel-rich cathode and PEO-based electrolyte by lithium niobium oxide coating for high-performance all-solid-state batteries,” *Nano Energy*, vol. 78, no. August, p. 105107, 2020.
- [15] R. Schlenker *et al.*, “Understanding the Lifetime of Battery Cells Based on Solid-State Li₆PS₅Cl Electrolyte Paired with Lithium Metal Electrode,” *ACS Appl. Mater. Interfaces*, vol. 12, no. 17, pp. 20012–20025, 2020.
- [16] L. Wang, D. Liu, T. Huang, Z. Geng, and A. Yu, “Reducing interfacial resistance of a Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ solid electrolyte/electrode interface by polymer interlayer protection,” *RSC Adv.*, vol. 10, no. 17, pp. 10038–10045, 2020.
- [17] A. L. Davis *et al.*, “Operando X-ray photoelectron spectroscopy of solid electrolyte interphase formation and evolution in Li₂S-P₂S₅ solid-state electrolytes,” *Nat. Commun.*, vol. 8, no. 1, pp. 6291–6302, 2020.
- [18] M. G. Boebinger, J. A. Lewis, S. E. Sandoval, and M. T. McDowell, “Understanding Transformations in Battery Materials Using in Situ and Operando Experiments: Progress and Outlook,” *ACS Energy Lett.*, vol. 5, pp. 335–345, 2020.
- [19] L. Yang *et al.*, “Dynamic visualization of the phase transformation path in LiFePO₄ during delithiation,” *Nanoscale*, vol. 11, no. 38, pp. 17557–17562, 2019.
- [20] X. Liu *et al.*, “Distinct charge dynamics in battery electrodes revealed by in situ and operando soft X-ray spectroscopy,” *Nat. Commun.*, vol. 4, no. May, pp. 1–8, 2013.