Review Article

Evaluating the effectiveness of in-situ characterization techniques in overcoming mechanistic limitations in lithium-sulfur batteries

Sarish Rehman^{a,*}, Michael Pope^b, Shanwen Tao^c, and Eric McCalla^{a,*}

^aChemistry Department, McGill University, 801 Sherbrooke St. W, Montreal, Qc

^bQuantum Nano Centre, Department of Chemical Engineering, University of Waterloo, N2L 3G1, Ontario, Canada

^cSchool of Engineering, University of Warwick, Coventry, CV4 7AL, UK

* Corresponding authors: eirc.mccalla@mcgill.ca and sarish.rehman@mail.mcgill.ca

Abstract:

Advanced energy storage systems require high energy and power densities, abundant availability of raw materials, low cost, reasonable safety, and environmental benignancy. Owing to their exceptionally high theoretical gravimetric power density (2600 Wh kg⁻¹) and specific capacity (1675 mAh g⁻¹), lithium sulfur batteries (LSBs) are considered a promising candidate for nextgeneration energy storage systems. However, low sulfur loading, rapid capacity depletion, poor coulombic efficiency, and unstable cyclability have so far prevented their commercialization. These issues mainly originate from the lack of knowledge about the mechanisms taking place during the redox reactions involved in the complex conversion chemistry that LSBs rely on. Insitu characterization techniques have long been sought to help answer questions regarding these mechanisms. Herein, we review the major advancements in the field of LSBs with a particular focus on the role of in-situ methodology. In-situ methods often require adapted cell designs and significant resources to achieve useful results. It is, therefore, an opportune time to take stock as to what advancements have been made in LSBs thanks to in-situ methods, where all previous exsitu methods have failed. The important details regarding implementing the in-situ characterization techniques to properly understand the mechanistic of LSBs are discussed, as are the major challenges associated with these methods. Finally, future perspectives regarding viable commercial LSBs are presented.

Broader context:

Li-S batteries (LSBs) are one of the most promising types of secondary battery systems for high energy density applications. Having the potential to make a lighter-weight, less expensive and more sustainable battery for the widespread electrification of vehicles, they will be essential to reduce green-house emissions and fight climate change. However, challenges arise as a result of the complex "dissolution-redeposition" reaction paths. Over the last decades, considerable efforts have been made to stabilize and better understand LSB chemistry and improved cell designs. A complete understanding of the mechanisms at play in LSBs is still missing and in-situ characterization techniques are increasingly relied upon to deepen our understanding. This is also enabling us to rationally design and implement various chemical and materials strategies to overcome their current shortcomings. This same emphasis on in-situ methods is present in modern research & development of all important and emerging battery technologies and numerous other technologies where complex chemical reactions are being harnessed for application. Given the large investments already committed to such methods, it is essential to now evaluate whether or not they are paying off.

1. Introduction

Lithium sulfur batteries (LSBs) have gained significant attention due to their high theoretical specific capacity of 1672 mAh/g and theoretical gravimetric energy density of ~2500 Wh/kg. ^{1–5} In particular, the abundant availability, nontoxicity, and low cost of sulfur which is employed as the cathode active material, make LSBs an attractive alternative to lithium ion batteries (LIBs) that most often employ less abundant and expensive components such as Co and Ni.^{6–10}

Like all secondary batteries, a typical LSB is an electrochemical cell containing a cathode (where reduction occurs upon battery discharge) and anode (where oxidation occurs upon battery discharge). In a LSB, sulfur is the cathode and lithium metal is the anode. The electrodes are isolated electrically, typically using a porous polymeric separator that enables ionic conduction between the two electrodes which is facilitated by an electrolyte. The electrolyte can be liquid, solid or gel, and is used to fill the pore space within the separator and the electrode particles, thereby acting as an ionic charge transfer medium.¹¹ The difference in redox potential between the anode and cathode drives a spontaneous galvanic process during the discharge of the battery, and this turns chemical energy into electrical energy when electrons flow through the external circuit. The amount of charge that can flow via this external circuit is governed by the capacity of the electrodes, which is typically normalized by the mass of each electrode. Figure .1a shows the general configuration of a typical operational LSB cell during which the following conversion reaction occurs: $16\text{Li} + \text{S}_8 \leftrightarrow 8\text{Li}_2\text{S}$, which occurs at an average potential of $E = 2.20 \text{ V vs. Li/Li^+}$. The forward reaction corresponds to the discharging of the battery, with the reverse occurring during charge.

Though the overall reaction seems simple, the actual electrochemical mechanism is much more complicated, with intermediate steps resulting in various lithium polysulfides (LiPSs). Figure 1b represents the charging/discharging voltage profile of a LSB cell. Two voltage plateaus are seen during discharge in the range from 2.4 to 2.0 V corresponding to (1) the ring-opening reduction of octa sulfur to long-chain LiPSs (Li₂S_x, (4 < x \leq 8), which corresponds to 25% of the theoretical capacity: 419 mAh g⁻¹) and (2) further conversion of long-chain LiPSs to short-chain LiPSs (Li₂S_x, $2 < x \leq 4$, which corresponds to 75% of the theoretical capacity: 1256 mAh g⁻¹).^{12–1516–18} During

the charging process, two plateaus around 2.2 and 2.5 V can be observed. Based on the conversion reaction mechanism, the discharge process can be divided into the following two steps in the voltage curve involving a total of 5 reactions:

- Sulfur is first lithiated to form a series of long-chain LiPSs (Li₂S_x, (4 < x ≤ 8)), which are highly soluble in the conventional ether-based electrolytes used.
 S₈ + 2Li⁺ + 2e⁻ → Li₂S₈ (solid-liquid) ... (2)
 3Li₂S₈(1) + 2Li⁺ + 2e⁻ → 4Li₂S₆ (liquid-liquid) ... (3)
 Li₂S₈ + 2Li⁺ + 2e⁻ → 2Li₂S₄ (liquid-liquid) ... (4)
- II. Further lithiation leads to converting long-chain LiPSs to insoluble short-chain LiPSs such as Li₂S₂ and Li₂S, which have a low solubility and typically deposit on the electrode surface as a solid product.

$$Li_2S_4 + 2Li^+ + 2e^- \rightarrow 2Li_2S_2 \text{ (liquid-solid)} \dots$$
(5)

$$Li_2S_2 + 2Li^+ + 2e^- \rightarrow 2Li_2S \text{ (solid-solid)} \dots \tag{6}$$

Due to the sluggish kinetics of electrochemical reduction and the electrically and ionically insulating nature of the Li_2S , the final product after discharge is a mixture of Li_2S_2 and Li_2S instead of the desired pure Li_2S .^{5,19} These limitations result in relative changes to the capacity of the upper and lower discharge plateau, which is typically assessed by the voltage hysteresis.^{20,21}

Overall, the reversible conversion of S_8 undergoes a series of structural and compositional changes of complicated redox reactions, from solid to dissolved, then redeposited as a solid. These transitions make the chemistry of LSBs highly complex compared to intercalation batteries, where all electrodes remain in the solid state throughout battery operation. The term "dissolution-re-deposition" is therefore often used to illustrate the electrochemical process of LSBs.



Figure 1: Top: Schematic representation of a typical LSB. Bottom: voltage profile showing various sulfur and LiPS species at different stages of charge/discharge. Figure reproduced from²²with permission.

Despite their high energy density, various technical challenges hinder the realization of viable, high performance LSBs, including the poor electronic conductivity of the sulfur cathode, complex multi-electron reaction mechanisms and electrolyte degradation.¹¹ In this section, we will discuss the various problems associated with LSBs. The following sections will then explore to what extent in-situ methods have effectively addressed each of these issues. We identify 4 key challenges for LSB commercialization:

(1) Low electronic and ionic conductivity. One of the major challenges with LSBs is the poor electrical and ionic conductivity of sulfur $(5 \times 10^{-30} \text{ S cm}^{-1})$ and its intermediate discharge products.^{23–25} Typical sulfur cathodes have limited ability to utilize active materials and result in lower rate performance due to the poor electronic conductivity of sulfur.²⁶ For an electrochemical reaction to occur, continuous electron transfer between the two electrodes is crucial. To address this issue, various conductive materials such as carbon black,²⁷⁻³⁰ graphene,^{31–34} CNTs,^{35–38} carbon nanofibers,^{39,40} and conductive polymers^{41–45} are used in various configurations to improve the electronic conductivity of the sulfur cathode.^{46–52} These strategies aim to protect sulfur from direct contact with the electrolyte and enhance conductivity.^{51,53} The low melting point of S makes it easy to incorporate into porous carbon; however, the process is complex and expensive, which hinders its commercial application. In addition, the use of such carbon encapsulation does not increase ionic conductivity. For the commonly used aprotic organic electrolytes typically based on ethers such as the 1,3-dioxolane (DOL)/1,2-dimethoxyethane (DME) (v/v = 1/1) with 1.0 mol L^{-1} lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 2 wt % LiNO₃ the ionic conductivity is sufficient for the initial electrochemical reactions to take place.^{54,55} However, the sulfur redox reactions go through a dissolution-re-deposition pathway where significant quantities of LiPSs dissolve in the electrolyte. Exacerbated with high-sulfur loading cathodes, a high LiPSs concentration increases the electrolyte viscosity and significantly reduces its ionic conductivity.⁵⁶ As a consequence, low ionic conductivity results in sluggish reactions kinetic manifested by large polarization of the second discharge plateau and poor rate performances.

(2) Polysulfide shuttle effect. As discussed above, organic electrolytes containing lithium salts (e.g., lithium perchlorate (LiClO₄), LiPF₆, lithium trifluoromethanesulfonate $(LiCF_3SO_3)$, or lithium bistrifluoromethylsulfonyl imide $(Li(CF_3SO_2)_2N))$ are commonly used for LSBs.^{3,57} However, unlike intercalation-based chemistries, LSBs undergo complex redox reactions via several distinct steps (shown schematically in Figures 2a&2b) involving the formation of various kinds of intermediate products that possess different stabilities and solubilities for a given electrolyte (Figure 2c).⁵⁸⁻⁶⁰ The dissolved LiPS serves as an intrinsic redox mediator to increase S utilization through a chemical pathway (commonly disproportionation and comproportionation reactions). However, back-andforth diffusion of LiPSs between the two electrodes, which is mainly concentration-driven, induces other concerns, such as: i) the shuttled polysulfides react with the lithium metal anode, causing rapid corrosion of lithium;⁶¹ ii) the solubility of LiPSs in electrolytes causes severe self-discharge during both the charge/discharge and during resting states resulting in low coulombic efficiency and short cycle life.^{62–64} iii) The redistribution of S and LiPSs disturb the homogenous distribution of S in the conductive matrix materials and lead to a shuttle effect that significantly depends on the rate of LiPSdiffusion and the charging current;⁶⁵ iv) some of the LiPS formation and transformation mechanisms are irreversible and result in loss of active sulfur which ultimately leads to a more or less gradual decline in capacity.^{19,66,67} v) the higher order LiPSs tend to precipitate away from the current collector and the conductive scaffold. This results in the loss of electric contact between solid LiPS products and the cathode.^{68,69} vi) deposition of electrical insulating discharge products (Li₂S₂ and Li₂S) on both the electrodes results in a significant increase in impedance.

Many research groups have attempted to understand and solve LSB's fading issues.^{70–73} Conductive frameworks with large surface area and abundant pores are thought to adsorb LiPSs, thus physically mitigating the undesired shuttle effect.^{74–77} Furthermore, LiPS scavengers have been found to play a significant role in preventing the shuttle effect by tailoring the polarity or Lewis acidity/basicity of the electrode or adsorbate additives.^{78–81} However, there is still a long way to go before LSBs are considered a viable alternative to commercial LIBs.



Figure 2: (a) Schematic representation of polysulfide dissolution. (b) (I) Fragmentation reaction of S8, (II) reduction potentials of polysulfides and lithium polysulfides, (III) association or dissociation reactions of polysulfides, and (IV) chemical reactions between polysulfides and LiPSs with TEGDME solvent molecule. (Reproduced with permission (c) Schematic representation of reduction pathways for polysulfide anions based on the computed free energies of various reactions and reduction potentials. (i) Each row represents the mechanism of the formation of small polysulfides (Sn, n \leq 3) from longer chain sulfides (Sn, 4 \geq n \leq 8). In each row, adjacent yellow cells represent electrochemical processes; cells with Rn (green colored cells) represent chemical transformations and cells with blue color (with 2Li⁺) represent the addition of two lithium ions. (ii) Each row represents the mechanism of small chain LiPSs (Li₂Sn, n \leq 3) (last column) from LiPSs (Li₂Sn, n \leq 8). In each row, adjacent yellow cells represent electrochemical (two-electron reduction) reactions. In each row, the green cell represents reaction with 2Li⁺ ions and subsequent fragmentation to give the species shown in the red cell (second last column). The species in the red cell undergoes further reaction sequences, including reduction, the addition of

lithium-ion, and subsequent fragmentation to form the species in the final column, which are shown in the subsequent rows. Figure reproduced form⁶⁰ with permission.

- (3) Volume expansion during cycling. In a LSB, both positive and negative electrodes undergo structural modifications. Due to the significant difference in density between Li2S and S (1.66 vs. 2.07 g cm^{-3}), a large volumetric expansion is accompanied by the complete lithiation of sulfur.⁸²⁻⁸⁴ This is exacerbated by the dissolution-re-deposition process during discharge and charge, creating an even lower packing density of these solid products as cycling proceeds.^{85–87} At the same time, the lithium anode contracts due to Li metal stripping/oxidation. During charging, the opposite processes occur: the Li anode expands as a result of the lithium plating, and solid precipitates from the cathode side are removed, causing the thickness of the cathode side to decrease. This volume deformation disturbs the electrode assembly, resulting in its pulverization and can lead to rapid capacity decay.⁸⁸ This problem of severe volume change hinders meeting the energy demands of commercial application because it is challenging to realize high sulfur loadings as the thicker films are more susceptible to the associated mechanical stresses.⁸⁹ As a result, high loading cathodes require the addition of significant amounts of carbon, or other conductive agents, and binders that can buffer the volume deformation of sulfur.⁹⁰
- (4) Challenges with Li- metal anodes. The high reactivity of Li metal results in uncontrolled growth of dendrites, leading to depletion of active Li metal and raising safety concerns. Lithium has low fermi energy and results in the reduction of electrolytes and the formation of solid electrolyte interphase (SEI).^{91,92} In addition, when dissolved LiPSs react with the Lianode, LiPSs can precipitate, resulting in loss of active material. This and the continuous electrolyte consumption in the form of SEI caused by the expansion and contraction of the

Li-anode during cycling causes severe corrosion of the Li-anode and eventual depletion of the electrolyte.^{93,94} The repeated dissolution and re-deposition of Li leads to the formation of Li dendrites which can penetrate through the separator and generate internal short circuits. Furthermore, these dendrites can become electrically disconnected from the rest of the lithium leading to so-called dead Li, which can no longer support an electrochemical reaction. To mitigate some of these problems, protective layers have been developed for the Li metal anode capable of prolonging the cell life by mechanically blocking dendrites or helping to smooth the spatial distribution of Li-ions during Li plating.^{73,95–97} In addition, 3D nanostructured electrodes with metallic Li have been proposed to alleviate the Li anode challenges by reducing the effective current density via a higher surface area and using the 3D scaffold to buffer the effectively infinite volume expansion of Li metal upon LSB charging.⁹⁸



Figure 3 Long-term cycling data plotted as percent initial capacity versus equivalent full cycles for NMC/graphite cells as described in the legend. The data from this work for 100% DOD cycling was collected to an upper cutoff potential of 4.3 V. The data from Ecker et al.,2 used 4.2 V as 100% state of charge. The purple and green data (this work) should be compared to the black data (Ecker et al.). Data for restricted range cycling (i.e. 25 - 75% SOC and 40 -60% SOC) for the cells in this work is not available but is expected to be far better than the data shown for 0 – 100% DOD cycling by analogy with the cells tested by Ecker et al.Figure reproduce from ⁹⁹with permission. (b) capacity fade of LSBs employing different amounts of electrolytes vs cycle numbers. Figure reproduce from ¹⁰⁰with permission.

The above mentioned key challenges significantly limit the cycle-life and energy density and have thus hindered the practical application of advanced LSBs. Although numerous strategies have been employed to enhance the performance of LSBs^{101–107} these challenges remain limiting. The development of high-performance batteries requires an improved understanding of the internal electrochemical processes of LSBs. Traditionally, ex-situ characterization techniques have been used to try to uncover the important processes during battery operation. In such cases, one stops the cycling at a state-of-charge of interest, leaving the cell in an open circuit where all redox reactions stop, introducing it into an argon glovebox, and sealing the battery component of interest in an air-sensitive holder characterization. However, this always leaves doubt about whether the electrode sample remained strictly in the same state while in an open circuit. As such, during the past years, a great deal of effort and investment has been devoted to developing state-of-the-art insitu and operando characterization tools. These tools represent a significant step forward because it allows researchers a more thorough understanding of the electrochemical processes under real operating conditions and helps answer the question as to whether the easier ex-situ methods are adequate or not. The in-situ characterization refers to the measurement performed under reaction conditions or similar conditions to reaction conditions. While "operando" means measurement carried out during operation without interruption.^{108,109} These techniques aim to monitor the electrochemical reaction during the charge/discharge process and study battery failure under actual operating conditions. The number of these significant discoveries has increased significantly during the past few years.

While most of the previously reported reviews have highlighted the advances achieved in the structural design of various components (e.g., sulfur electrodes, anodes, separators, electrolytes, current collector and binder) and performance improvement of LSBs,^{6,73,110–117} only a few reviews focus on the fundamental understanding of their electrochemical reaction mechanisms.^{118–120} Considering the importance of in-situ characterization techniques for a mechanistic understanding of LSBs, here we will summarize the various research reports intended to elucidate and better understand LSB reaction and kinetics process, with a focus on in-situ characterization techniques such as X-ray diffraction (XRD), X-ray microscopy (XRM), X-ray absorption spectroscopy (XAS), X-ray absorption near edge spectroscopy (XANES), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (AFM), and insitu nuclear magnetic resonance spectroscopy (NMR). In particular, the focus will be placed on how state-of-the-art in-situ characterization techniques are applied and used in combination. Case studies are used to illustrate how these advanced characterization techniques have improved upon our fundamental, mechanistic understanding of LSBs and how they have brought LSBs one step closer to commercial fruition.

2. Advanced research into mechansims

Over the past few decades, numerous researchers have attempted to reveal the fundamental science and mechanisms underlying LSB electrochemistry to overcome the challenges outlined in the next section. Various ex-situ and in-situ materials characterization approaches have proven important in this regard. Besides the aforementioned advanced characterization techniques, theoretical computations also play an essential role in promoting a mechanistic understanding of LSBs and are far less resource-intensive than in-situ experimentation such that they are in, a sense, a competitor to the advanced experiments. In the following section, we will summarize some theoretical studies and various models used to understand the chemistry of conversion reactions in

LSBs and explain why there is a need for advanced characterization techniques. Then we will present the key in-situ techniques that have been utilized in LSB batteries.

2.1. Theoretical calculations of LSBs

Theoretical calculations are an effective tool that can help to illustrate the complex multielectron reactions taking place in LSBs and the interaction of LiPSs with various functional groups. They provide us with a proper guideline for screening, identifying, and selecting potential host materials for sulfur cathodes.^{121,122} The primary purpose of screening host materials is to promote active sulfide binding to decrease the LiPS dissolution in the electrolyte and ensure a high capacity LBS.

Various methods have been developed, such as density functional theory (DFT), Hartree– Fock-based models, the post-Hartree–Fock methods (configuration interaction, coupled cluster, the Møller–Plesset perturbation theory, etc.), molecular dynamics (MD), continuum modelling, quantum mechanics/molecular mechanics (QM/MM), and other semi-empirical and empirical methods.¹²³ Among these methods, DFT, with a dramatic increase in the number of publications since 1990, has been widely used to explore the mechanisms at play within LSBs.¹²⁴ Thermodynamic quantities, including energies, enthalpy, entropy, and Gibb's free energy, can be calculated by computational approaches combined with statistical mechanics. Such basic properties are very important to assist in the understanding of electrochemical reactions.

Mikhaylik et al. established the first mechanistic model that included the shuttle effect of LSBs through the use of an empirical shuttle constant.¹²⁵ But their model lacked ion transport phenomena that would lead to concentration polarization. Hofmann et al. introduce a mechanistic model by considering ion transportation to show the polysulfide shuttle and capacity loss in LSBs.¹²⁶ However, the relationship between polysulfide solubility and the shuttle problem

remained unclear. Kumaresan et al. proposed a model for a LSB to study the complex interaction between the electrochemical reactions like lithium oxidation on the anode and reduction of various sulfides in the cathode and chemical reactions consisting of precipitation/dissolution of elemental sulfur and various LiPS.¹²⁷ Specifically, the multicomponent transport in the dilute electrolyte and simplified precipitation kinetics are taken into consideration. However, the rate-dependent capacity has not been determined. Ghaznavi modified the key parameters of this model and expanded it for sensitivity analysis. ^{128–130} However, those models lack a crucial reduction reaction of high-order polysulfides $(S_n^{2-}, n \ge 4)$ at the Li electrode, which results in overcharge and polysulfide shuttling and thus cannot be utilized for the prediction of LSB cycling performance. Yoo et al. propose a modified mathematical model based on the work of Kumaresan et al. ¹²⁷ to demonstrate the influence of solid sulfur species, LiPS solubility and diffusivity in the electrolyte, and LiPS reduction reaction rate constants at the Li electrode on the electrochemical performance characteristics of LSBs.¹³¹ Chen et al. presented DFT studies of Li_2Sx clusters, x = 1 to 8, to describe the geometries, stability, and their role in the discharge process.¹³² However, thermochemistry of chemical and electrochemical processes in solution and reaction mechanisms of expected intermediates from these reactions with non-aqueous electrolytes are still unknown.

Assary et al. calculated the energy, enthalpy, and Gibbs' free energy of various sulfur species, including sulfur molecules, LiPS, sulfur ions, and sulfur radicals, to understand various chemical and electrochemical processes.¹³³ Similarly, in another study, with the help of DFT calculations, the binding energies of various species, including a metal oxide, metal sulfide, electron-rich groups, and sulfur-rich groups with LiPSs, were calculated to help optimize materials and further investigate their interfacial interactions. For example, using DFT, it was found that binding energies of LiPS with metal oxide and sulfides $(2.6-3.5 \text{ eV})^{134-136}$ are higher compared to

doped carbon $(1.3-2.6 \text{ eV})^{137,138}$ and functional polymers $(0.5-1.3 \text{ eV})^{.139-142}$ The most potent interaction of Li₂S_x, $4 \le x$ (~1.01 to 1.26 eV) was found in the case of electron-rich groups with lone pairs of electrons such as esters, amides, ketones, and ethers. On the other hand, the most stable configuration represents the lithium atom, leading to a coordinate like the Li–O bond due to strong interaction with the lone pair of electrons on the oxygen atom.⁶⁴ Sulfur rich functional groups (such as sulfides, disulfides, and thiols) also exhibit a strong affinity towards Li₂S_x, $4 \le x$ species through a Li–S interaction. In particular, metal sulfides have better prospects than metal oxide because they possess high room temperature conductivity and serve as reaction mediators. Furthermore, metal sulfide reactions with lithium have high electrochemical activity and thus contribute to the capacity of LSBs. Non-polar carbon materials interact with Li₂S_x, $4 \le x$ via weak van der Waals forces with low binding energies (0.1–0.7 eV). Various other materials based on their binding energies with Li₂S_x, $4 \le x$ is categorized in Figure 2a-d.⁹⁰ These measurements have helped with the design of polysulfide scavengers which is one of the biggest advances in the field.



Figure 4: (a) Functional polymers interact in the form of $\text{Li}^+-\text{N/O/S}$ interactions, with *E*b ranging from 0.5 to 1.3 eV. (b) Heteroatom-doped carbons interact mainly via $\text{Li}^+-\text{N/O}$ or S–S bonding, with *E*b between 1.3 and 2.6 eV. (c) Stoichiometric metal chalcogenides interact mainly in the form of $\text{Li}^+-\text{O/S}-\text{M}$, with *E*b ranging from 2.6 to 3.5 eV (M = metal). (d) Metal-organic frameworks (MOFs) and non-stoichiometric metal chalcogenides interact in the form of Lewis acid–base bonding, exhibiting the highest *E*b values ranging from 3.5 to 7.0 eV. (Figure reproduced from⁹⁰ with the permission (e) Optimized geometries of the most stable Li₂S on CeO₂(111), Al₂O₃(110), La₂O₃(001), MgO(100), and CaO(100) surfaces. (f) Optimized geometries of most stable Li₂S₈ on the metal oxide surface. Figure reproduced from¹⁴³ with permission.

Fronczek *et al.* proposed a one-dimensional continuum model of LSBs cell to explain the voltage plateau, current density, impedance, volume fractions, and polysulfide species content under various operating conditions.¹⁴⁴ This model explained the asymmetric behavior of polysulfide species production and dissociation during the charging/discharging process. They also predicted the complex behavior of electrochemical impedance comprising of multiple impedance features.

Based on the models discussed above, it can be concluded that computational chemistry has different applications for LSB, such as geometrical and electronic structure optimization, exploring the reaction mechanisms and other kinetics and measurement of thermodynamic quantities, including energetics, enthalpy, entropy, and Gibbs' free energy. The power of computational chemistry is growing due to significant advances in artificial intelligence and powerful theoretical chemistry software. We can now track larger systems and take into account more parameters. It is increasingly being used to aid in the evaluation of experimental results, the prediction of intrinsic properties, and the exploration of new chemical phenomena. Even though theoretical methods exhibit significant advantages in these aspects, gaps remain between theoretical and experimental approaches. For example, theoretical approaches use simple single-molecule models, and phenomena that involve hundreds-thousands of atoms, such as the adsorption and the nucleation process of LiPS on conductive frameworks, are difficult to describe by simulation. Similarly, to further explore the complex and competitive bonding in LSBs, including the complicated interfacial interactions between electrolytes and electrodes, more powerful computational approaches, high-accuracy calculation methods, and large-scale models are required. ¹⁴⁵ Therefore, there remains a need to optimize theoretical models, and by taking advantage of the latest in-situ characterization techniques, we can better understand reaction thermodynamics and kinetics of LSBs.

2.2. Experimental studies of LSBs

Due to the complex reaction chemistry, the precise characterization of LSBs is quite challenging. The electrochemical mechanism is much more complex than the theoretical

explanations summarized in the last section. In this context, the techniques used to observe the electrochemical reaction pathways can play a significant role in improving our understanding of the battery performance of LSBs. So far, conventional electrochemical measurements, such as cyclic voltammetry (CV),¹⁴⁶ galvanostatic cycling at different current rates over multiple cycles, and electrochemical impedance spectroscopy (EIS),^{147,148} are standard methods for estimating the electrochemical properties of LSBs and their contributions to LSBs have been reviewed elsewhere.^{146,149} However, these methods cannot provide sufficient information regarding the electrochemical mechanisms as they focus more on the overall device performance. Low cost and easy to access ex-situ characterization techniques, such as XRD¹⁵⁰, SEM,¹⁵¹ TEM,¹⁵² XPS¹⁵³, spectroscopic techniques such as nuclear magnetic resonance spectroscopy (NMR)^{154,155} Raman spectroscopy¹⁵⁶, FT-IR spectroscopy,¹⁵⁷ etc., have been widely used to detect the chemical composition and morphological state of the electrode from disassembled cells at different state of charges (SOC) and depth of discharge (DOD). However, as discussed in the introduction, questions remain as to whether the electrodes' treatment after cycling impacts the results. Furthermore, unstable intermediate products would be difficult to detect through ex-situ characterization techniques if they exist.

Considering the complexity of the solid-dissolution-redeposition reaction mechanism of LSBs, in-situ characterization techniques are highly desirable to explore the real-time electrochemical reactions during charging/discharging. In the rest of this review article, we will discuss the various in-situ characterization techniques used to analyse the LiPS conversion reactions taking place to determine if/when in-situ experiments are vital in furthering our knowledge or if they simply serve to confirm previous ex-situ findings.

3. In-situ X-ray and neutron techniques

In-situ synchrotron-based X-ray techniques are providing some basic guidelines for researchers in the battery field. In-situ X-ray techniques, including X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), in-situ X-ray radiography and X-ray imaging (XRM), in-situ transmission X-ray microscopy with some practical tips for electrochemical cell design and their main outcomes will be discussed. Neutron diffraction will also be considered in this section as a complement to XRD.

3.1. X-ray diffraction

To enhance the performance of LSBs, the most strategic techniques are to identify the process of LiPS formation, factors affecting their production, and methods of making these processes reversible. The detection of LiPS species is challenging as they are involved in a complex equilibrium during the charging/discharging process and produce various types of complex amorphous structures when redeposited in the solid state.³⁸

Previously reported ex-situ XRD of LSBs,^{83,158–163} did not enable clear solid/soluble phase transition determination because inter-sulfur species conversions occurred upon cell disassembly and may alter the cell's overall composition after equilibrium.¹⁶⁴ The beginning of Li₂S formation was claimed to occur at the end of discharge,^{158,162,163} or somehow in the middle of the lower discharge plateau.¹⁵⁹ Its further re-oxidation to crystalline sulfur during the charging process was also debated. In-situ XRD has been used to resolve this conflict in the literature by providing insight into the exact position of Li₂S formation. Detecting the discharge products of LSBs using in-situ XRD was first reported by Nelson and co-workers.¹⁶⁵ They found the recrystallization of S at the end of the charging cycle, and they proposed that this might depend on the preparation method used to make the sulfur cathodes. However, in contrast with previous ex-situ XRD results,

where there were significant differences in the amount of Li₂S reported to be present at the end of discharge, no evidence of crystalline Li₂S was found at the end of the discharge process in any insitu study.^{159,166–169} They claimed that the appearance of crystalline Li₂S might result from sample post-treatments. However, Lowe et al. used in-situ XRD and they found that crystalline Li₂S is not detected until the cell voltage drops below 2 V, at which point the diffraction peak rapidly grows until the end of the discharge.¹⁵⁰

It is now important to review the various cell designs used for in-situ XRD to recognize any significant modifications made to battery chemistry and form factor in order to make the in-situ measurement possible. A number of such designs have been used as illustrated in Figure 5. A common approach is to adapt a traditional coin cell design as shown in Figure 5a.¹⁵⁰ In the casings, 3 mm diameter holes were drilled, and Kapton TM windows were epoxied in place. To reduce air and moisture diffusion, 100 µm thick windows were utilized on both anode and cathode casings. All KaptonTM windows used a 70 nm thick aluminium layer on both sides to prevent atmospheric contamination and serve as current collector. The cell was comprised of a sulfur cathode, lithium anode and a gel polymer electrolyte of 1 M LiClO₄ in tetra(ethylene glycol) dimethyl ether.¹⁵⁰ All cells were maintained in hermetically sealed, argon-filled vials until the experiment was performed at a synchrotron within 4 days after cell production. This study demonstrated that the abrupt appearance of crystalline Li₂S at the end of the voltage plateau suggests that its formation is due to the complex reaction mechanism than to a kinetically limited crystallization of amorphous Li_2S . However, one of the drawbacks of this study is that they are using a gel polymer electrolyte which is not a typical electrolyte for LSBs and a considerable self-discharge may occur if cells are maintained for so long at OCV.⁵ Following this, several studies used in-situ XRD and demonstrated the presence of crystalline Li₂S at the lower discharge voltage plateau. For example,

Cañas et al. Demir-Cakan et al. and Walus et al. detected the formation of Li₂S and the recrystallization of S.^{170–172} However, Cañas et al. reported the existence of crystalline Li₂S in the lower discharge plateau around ~1.8 V at a much higher state of discharge (~60%). They found broad Li₂S peaks with a full width at a high maximum (FWHM) of $0.904^{\circ} \pm 0.027^{\circ}$. The fitting results confirm that Li₂S crystallites had a size of $6.3 \pm 0.4 \,\mu\text{m}$ at 100% DOD. They claimed that due to the broad peak shape, low concentrations of Li_2S are challenging to analyse and quantify. The in-situ cell used in their study had two aluminium plates with small holes in them (the cathode and anode plates shown Figure 5b). A conductive epoxy is used to secure the aluminium window to the cathode plate. Each plate serves as a current collector and can be directly linked to the potentiometer by introducing banana jacks into the holes in the cell's plates. There is therefore no need to adapt the battery chemistry in using this cell design. Further studies such as that by Walus et al. used a pouch cell set up as shown in Figure 5c,d. In this work, it was found that the signal for Li₂S starts to appear at the beginning of the second discharge plateau and its intensity gradually increases until it reaches to maximum discharge state. The pouch cell used in-situ XRD was comprised of aluminium-laminated pouches with S cathode, lithium anode and two porous separators wetted with commonly used electrolyte (1 M LiTFSI in a 1:1 volume mixture of tetraethylene glycol dimethylether and 1,3-dioxolane, with 0.1 M LiNO₃ additive). To allow the beam to reach the electrodes, three holes of 3 mm were cut the aluminum-laminated pouches and sealed with Kapton tapes on each side. To further air tighten the pouch cell, it was sealed in a polythene bag. To ensure enough electrolyte in the cell, Viledon® was used as an additional layer of the separator. After assembling in the dry room, the cell was mounted on a movable holder so that it can be scan at the desired position.



Figure 5. Modified coin cells and scattering geometries for in-situ X-ray studies of lithium sulfur batteries. (a) Cell designed for XRD in transmission geometry reproduced from¹⁵⁰with permission. (b) Exploded illustration of the in-situ XRD cell: 1) Anode plate, 2) polymer gasket, 3) insulator plastic tube, 4) spring, 5) Al-anode collector, 6) anode, 7) separator, 8) cathode, 9) cathode plate, 10) Al-window and 11-12) holes for connecting the banana jacks. Figure reproduced from¹⁷⁰with permission. (c) In-situ XRD pouch cell (d); schematic illustration of the cell components, with indicated beam positions at which XRD of the metallic Li1 [1], total cell [2]a and the sulfur electrode [3] were recorded. Figure reproduced from¹⁷²with permission.

It is now clear that in-situ XRD has resolved the questions regarding when solid Li_2S is present during cycling. Another topic of hot debate relates to the Li_2S_2 species, sometimes considered a solid product,^{177,178} which had never been experimentally detected by ex situ XRD, leading researchers to question whether or not it actually precipitates as a solid. Paolella et al., for the first time, detected crystalline Li_2S_2 as a transient species under "solvent-in-salt" (7 M LiTFSI in DME/DOL) electrolyte condition using in-situ XRD.¹⁷³ They observed the Li_2S_2 peaks near the end of the first charge and before the end of the second discharge. Though it is universally believed that Li_2S_2 is formed close to the end of the discharge process, it did not appear again in subsequent cycles. However, in this study, re-crystallization of the Li₂S was observed at the end of each charging cycle or at the beginning of discharge, indicating that the production of Li₂S₂ in these cells is the result of chemical reactions (disproportionation) rather than electrochemical reactions. From the above observations, it was concluded that for the Li₂S₂ crystalline phase to appear, it is essential that the critical concentrations of both Li-ion and sulfur (or sulfide) have been reached. Furthermore, the authors did not see the formation of Li₂S₂ when a lower salt concentration of 1 M was used, which agrees with the result reported by Canas et al.¹⁷⁰

Though in-situ XRD studies have indirectly detected LiPSs, simultaneous investigation of all phases still constitutes a challenge due to the solubility of LiPSs in the electrolyte, leading to rapid molecular reorientation. Nonetheless, Conder et al. directly observed LiPSs in LSB using in-situ XRD.¹⁷⁴ They used a glass fiber separator where SiO₂ (fumed silica) from the separator act as an electrolyte additive and as a scavenger for long-chain polysulfide, making the observation of LiPSs clear. They identified two broad peaks, and after a systematic investigation of the evolution of these features as a function of the state of charge, it was demonstrated that the broadening of peaks corresponds to the structural changes during the conversion of sulfur into Li₂S. In addition, SiO₂ used in this study acts as a polysulfide adsorbent and enhances the efficiency of LSBs.

In-situ XRD has therefore proved extremely useful in order to probe bulk solid products present in the cell, and these studies have confirmed that ex-situ XRD reports in the past did suffer from material transformation during cell disassembly.

3.2. X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is a technique for measuring electronic transitions in atoms between the core electronic states and its excited electronic states (LUMO). Spectra fall in two regimes: measurement of the sharp absorption edge is referred to as X-ray absorption nearedge structure (XANES), while probing the continuum of absorption above the edge is referred to as extended X-ray absorption fine structure (EXAFS). In both techniques, synchrotron sources provide a range of X-ray energies to study atoms' chemical composition and surroundings in molecules. Whereas XANES can give information about the oxidation state of the atom in question (the edge shifts with oxidation state), EXAFS can be used to probe the local structure around the atom (a fourier transform yields the pair distribution function). Therefore, an important advantage of XAS over XRD is that it can extract local structural information even from disordered materials where no long range order is present (e.g. amorphous or solvated species).

Our understanding of the multi-step redox electrochemical reactions in LSBs has been dramatically improved by virtue of in-situ X-ray absorption spectroscopy (XAS). LSBs were first investigated using this technique by Cuisinier et al. to provide insight on sulfur speciation and how this governs sulfur and Li₂S dissolution and deposition. ¹⁷⁵ The cell used for this study was adapted from a 2325 coin cell, with an aluminized KaptonTM window for X-ray beam penetration as shown in Figure 6a. Other modifications were limited to the electrode design and the nature of the lithium salt. To eliminate any contribution to the S absorbance spectrum, LiTFSI electrolyte was replaced with LiClO₄ (lithium perchlorate), and the cells were assembled with the cathode material facing the KaptonTM window. This cell design limits the measurements to being done in reflection, rather than the more reliable transmission mode; nonetheless the findings obtained are important as detailed below. This study determined the cause of why the reported maximum first discharge capacities were limited to 1675 mAh g^{-1} (i.e. 75% of the theoretical capacity). They found that the disproportionation reaction $S_8^{2-} \rightarrow S_6^{2-} + \frac{1}{4} S_8^0$ shown in Figure 6c yields 25% inactive sulfur. Different from previous assumptions,^{125,176}, this study shows that unreacted sulfur results in the reduction of first discharge capacity, not Li₂S precipitation. Similarly, in contrast to previous XRD

studies that did not detect crystalline α -S₈ after one complete cycle,^{84,177} this study found the characteristic XANES spectrum of pure elemental sulfur at the end of the charge (XANES can detect amorphous S as shown in Figure 6d, top). In another study using the same experimental approach, the authors investigated the effect of sulfur radicals formed during LSB cycling.¹⁷⁸ It was observed that radical S₃⁻⁻ is not produced in electron pair donor solvents, such as dimethylacetamide, but it can only be formed in solvents, such as dimethoxyethane and 1,3-dioxolane.



Figure 6 (a) Schematic illustration of the operando cell for XAS experiment, which was adapted from a 2325 coin cell using an aluminized KaptonTM window to allow X-ray beam penetration. (b) Top view of the sulfur cathode carbon paper. (c) Evolution of sulfur K-edge XAS spectra upon electrochemical cycling based on linear combination analysis. (d) reference spectra for elemental sulfur (top), linear polysulfides (S_2^{2-} , S_4^{2-} , and S_6^{2-} ,middle) and Li₂S (bottom), together with the initial, charged state (red line in the top panel) and discharge states (red lines in the bottom panel). Figure reproduced from ¹⁷⁹ with permission.

Following this study, in-situ XAS was used to probe structural changes of both crystalline and amorphous LiPSs. By tracking the pre-peak intensity of the operando XAS spectra, in 1M LiClO₄ in TEGDME, it was found that elemental S₈ is reduced to long-chain LiPS ($S_n^{2-}, 8 \ge n \ge 7$) at the beginning of the first discharge plateau.¹⁵⁰ The dissociation of long-chain polysulfides generates intermediate LiPSs ($S_n^{2-}, 6 \ge n \ge 4$). The equilibrium between S_3^- and the reduced LiPSs lasts throughout the second plateau until the end, where Li₂S is generated. At the end of the lower voltage plateau, there is a concerted decrease in cell voltage and the peak intensities, as seen in the XANES spectra in Figure 7a-c. The same group used in-situ XAS at the S K-edge to further investigate the nature of end discharge products and conversion chemistry of S in acetonitrile (ACN)-based electrolytes.¹⁸⁰ This study demonstrated that disproportionation reactions in the LSBs are restrained due to the existence of the activation process required for de-complexation of solvent from (ACN)₂-LiTFSI, which hampers the solvation and transportation of LiPSs. Following the results of this study, it was proposed that due to the formation of complexes, all the acetonitrile molecules are efficiently bonded, preventing their reaction with Li-anode and suppressing the LiPS dissolution. Compared to reference spectra, remarkable fluorescence can be observed (Figure 7d) from the pristine and discharged phases and evident variation of the XANES spectra vs. discharge capacity can be seen (Figure 7e).



Figure 7. XAS data for a lithium-sulfur battery with a gel polymer electrolyte. (a) Waterfall plot of the dataset for a full galvanostatic cycle. b (i) Spectra selected from specific points during the cycle. (ii) Variation of the fluorescence signal and cell voltage as a function of charge. Data points correspond to the intensity of the first derivative of each spectrum at 2471.1 eV (pre-peak, black), 2472.6 eV (main peak, red), and 2473.9 eV (Li₂S, green). (Figure reproduced from¹⁵⁰ with permission) (c) Sulphur K-edge XANES showing: evolution of absorbance as a function of the electrochemical discharge at C/10. (d) Reference spectra for elemental sulfur (blue), S_2^{2-} (red) and Li₂S (black). (e) Pristine (blue) and discharge state (black). Dotted lines highlight the contribution of the difference reference species to the spectra acquired. Figure reproduced from¹⁸⁰ with permission.

Similarly, Wang et al. measured the average length of LiPs chains from the pre-edge XAS peak.¹⁸¹ By tracking the area under an XAS peak, they monitored the formation of Li₂S. In addition, they calculated the rate constant of various simple reactions of LSBs commonly reported in the literature and it was found that the relative rate constants depend on the electronic structures of the LiPSs participating in the reactions.

The main problem in the speciation of S compounds with XANES at the S K-edge is the distortion of the intensity of the main peak (the white line, WL), which is, in principle, proportional to the number of empty p states, and, as a result, to the oxidation state of S. To avoid sulfate interference Dominko et al. used K-edge XANES combined with extended X-ray absorption fine structure (EXAFS) with an electrolyte (1 MLiTDI TEGDME: DOL) that does not contain any sulfur or chlorine-based components, and a composite cathode (carbon/Mn₂O₃ doped silicate/sulfur) with the ability to absorb LiPSs.¹⁸² The mechanism of S conversion into Li₂S and their deposition/precipitation in the electrode and separator was described. It was demonstrated that at high voltage, the concentration of LiPSs reached a maximum value, while at low voltage, an equilibrium of short-chain LiPSs/Li2S is found. In another study, they used in-situ XAS in combination with in-situ UV/Vis to show Li₂S to S conversion without LiPS production.¹⁸³ The cathode consisted of carbon coated Li_2S particles prepared by the carbothermal reduction of Li₂SO₄. They claimed that applying a potential higher than 2.5 V vs. Li/Li⁺ results in the direct oxidation of Li₂S to S, suppressing the formation of parasitic LiPSs, which usually are the reason for the dramatic capacity fading of LSBs. Similarly, to reduce the distortion of main white peaks of the XANES at the S K-edge Kavčic et al., employed in-situ resonant inelastic X-ray scattering (RIXS) to provide quantitative analysis of sulfur compounds and to study the polysulfide dissolution mechanism.¹⁸⁴ The resonant excitation condition significantly enhances the sensitivity of polysulfide detection and it was found that on the high voltage plateau of the discharge curve, rapid conversion of solid sulfur into liquid phase LiPSs occurs. Furthermore, the concentration of dissolved LiPSs reaches its maximum at the end of this plateau. At the same time, the precipitation of the Li₂S from the dissolved LiPSs is observed at the start of the low voltage plateau at a constant rate, which tends to decrease toward the end of the discharge. In a recent study, they carried out a

quantitative evaluation of the evolution of the peak area ratio as a function of the LiPS chain length using in-situ XAS.¹⁸⁵ It was demonstrated that the Li_2S_x chain length could be reliably determined by the normalized area of the pre-edge, which confirm theoretical predictions by Pascal et al.¹⁸⁶

To detect the dissolved, amorphous, and crystalline solids phases of polysulfides and further investigate the mechanism of their dissolution, Gorlin *et al.* used spatially resolved in-situ XAS characterization.¹⁸⁷ They investigated the LSB cell having Li₂S as cathode during the first and second charge and spectra were collected from the cathode and the membrane separator. This study provides insights into the mechanism of Li₂S oxidation in the DOL-DME electrolyte. They also ruled out LiPS production during the first charge, whereas a constant concentration of LiPSs was recorded during the second charge. To justify the obtained results, they proposed a two-step reaction pathway to produce the final oxidation product during charging.

In-situ XAS has also been used to understand the impact of electrolyte additives such as LiNO₃ on suppressing the LiPS shuttle.¹⁸⁸ After evaluating the SEI layer on the top of the Li anode composed of Li₂SO₃ and Li₂SO₄, it was concluded that LiNO₃ could oxidize LiPS to Li₂SO₃ and Li₂SO₄. This layer was found to alleviate the polysulfide shuttle effect due to suppressing subsequent reactions between LiPS in electrolyte and lithium metal. Jia et al. recently studied the migration of LiPSs by precisely monitoring the S chemical speciation at the cathodic electrolyte-separator and electrolyte-anode interfaces by using in-situ XAS.¹⁸⁹ They used a modified separator of hybrid bismuth sulfide and bismuth oxide nanoclusters embedded in a carbon matrix (BSOC) which acts as an electrocatalytic layer. A special cell was designed for this study, as shown in Figure 8a that helped to probe different interfaces across the LSB. S speciation at the cathode electrolyte–separator interface and at the anode electrolyte-separator interface was monitored by in-situ S K-edge XAS spectra as a function of applied potential along the discharge process (Figure

8b-g). It was observed that using the modified separator helped in trapping LiPSs and catalyzing the conversion of S species which aided in suppressing the LiPS shuttling effect.



Figure 8 (a) In-situ/operando S K-edge XAS observations at the cathodic side of Li/S cells with/without BSOC layer. a) Schematic illustration of the coin cell design for CEI observation in our in-situ/operando XAS study. The operando cell was adapted from commercial 2025-type coin cell. A $2 \times 1 \text{ mm}^2$ hole was drilled at the cell shell; the hole was then sealed with a 13-µm thick kapton film to avoid electrolyte leaking and allow X-ray beam penetration through. From top to bottom: kapton film (13 µm), top (cathode) cap, sulfur cathode (with a small hole), BSOC-PP separator, gasket, lithium anode, spacer, spring, and bottom (anode) cap. b) Initial discharge voltage profile of pristine cell at 0.1 C while performing the operando XAS measurement. c) In-situ/operando S K-edge XAS map, and d) representative XAS spectra collected at different potentials (from I to VI marked by stars in b) for Li/S cell using PP separator during the first discharge process. e) Initial discharge voltage profile of SK-edge XAS measurement. f) In-situ/operando S K-edge XAS map, and g) representative XAS spectra collected at different potentials (from I to VI marked by stars in e) for Li/S cell using BSOC-PP separator during the first discharge process. Figure reproduced from ¹⁸⁹ with permission.

Though researchers have obtained the absorption spectra of many LiPSs, however, there are only two types of LiPS dianions that can be used to evaluate the operating batteries.^{175,190} It is

worth emphasizing that operando XANES research should focus on obtaining and calibrating a comprehensive absorption spectrum. In general, XAS experiments are usually relatively simple to perform and an electrochemical cell can easily be adapted for XAS. However, the penetration depth of X-rays should be carefully taken into account for the choice of window material and cell assembly. Despite this, the important insights obtained from in-situ XAS are numerous, with only minor compromises to battery chemistry.

3.3. X-ray radiography

X-ray radiography is an imaging technique that uses ionizing (X-rays, gamma rays, or similar) and non-ionizing radiation to produce images on the scale of the electrodes. This approach visualizes structures by attenuating incoming X-rays. X-ray radiography is a technique in which an X-ray generator projects an X-ray beam onto an object. Specific amounts of X-rays or other radiation are absorbed depending on the density and structural makeup of the object. A detector (either photographic film or a digital detector) catches the X-rays that pass through the item and generate an image; this technique is referred to as projectional radiography.

X-ray imaging is typically preferred for macroscopic analysis of sulfur-containing cathodes. Previously, it has been used to study the distribution of sulfur in carbon cathodes of LSBs, because sulfur has a substantially greater absorption coefficient than carbon, and it is relatively easy to monitor the deposition of sulfur crystals on the carbon. However, those studies involved post mortem analysis of the cycled cells.¹⁹¹ Risse *et al.* used in-situ X-ray radiography for the first time to get insight into the complex electrochemical reaction of LSB in combination with electrochemical impedance spectroscopy (EIS).¹⁹² Figure 9a shows the operando cell used in this study. The cell uses a carbon cloth-like material cathode (surface area= 1500m²/g) with a thickness of roughly 1 mm. The benefit of a monolithic carbon cathode for this application is its macroscopic uniformity and relatively low X-ray absorption coefficient. The anode is a lithium foil with a circular X-ray window (6 mm) cut into it. The cell can be run like a coin cell CR2032, allowing to study voltage as a function of current. The electrolyte used in this study was a mixture of 0.1 M Li_2S_8 (made of lithium sulfide and sulfur), 4 wt% lithium nitrate (LiNO₃), 8 wt% bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) and a 1 : 1 mixture of dioxolane and dimethoxy ethane (w/w). A µCT system was used to perform the X-ray radiography measurements.¹⁹³ The images were captured using a flat panel detector with approximately 10 mm per pixel resolution after every 20 seconds. After minor processing, the images can be used to determine morphological changes on the carbon cathode as shown in Figure 9.

They studied the charging/discharging of the first five cycles and found the formation of stable α -sulfur (rhombic) and metastable β -sulfur (monoclinic) at the end of the charging cycle (as shown in figure 9c).¹⁹² Characteristic signals in impedance spectroscopy accompany the appearance of these crystalline structures. In agreement with the previous in-situ XRD results,^{170,172} no Li₂S macroscopic crystals were observed upon full discharge as Li₂S is expected to be the nanoscopic size.

This in-situ method is not widely used, given the fact that the observations have to date served to confirm that which has been previously seen in XRD. Should the resolution be further improved in order to see more subtle changes in electrode morphology, this method may prove of greater use, but to date the microsocopic methods to be discussed in section 4 tend to be preferred to observe morphological changes.



Figure 9: Schematic setup of the operando cell that combines operando X-ray radiography (b) I. impedance spectroscopy and II. time dependent voltage measurement. (c) X-ray images: fully charged (I) and discharged (II) state of the Li/S cell of the 2nd cycle analysed (in Fig. 3 of the reference). A time dependent evolution of the regions of interest highlighted by the white dashed line can be found (in Fig. 4 and 5 of the reference). Fully charged state of the 1st cycle (III). Both insets (a, b) magnify the obtained macroscopic sulfur structures. The respective crystal habit of a- and b-sulfur is also inserted into the magnified images (a: rhombic; b: monoclinic). The colour legend on the right was used for all X-ray images in this work. Figure reproduced from ¹⁹² with permission.

3.4. Small-angle neutron scattering

Small-angle neutron scattering (SANS) is a technique that uses elastic neutron scattering at narrow scattering angles to study the structure of various substances on a mesoscopic scale of 1–100 nm. This, as X-ray radiograph discussed above, therefore represents a method of potential interest to study morphological changes in electrodes.

Previously, in-situ tools have been mainly used to understand the formation and dissolution of solid S_8 and Li_2S . However, no one focuses on the center of precipitation of the solid products in operational LSBs. Risse et al. used in-situ small-angle neutron scattering to provide information on the locus of solid (S_8 and Li_2S) precipitation.¹⁹⁴ Figure 10a gives a general overview of the

operando cell used in this study. The dry carbon cathode utilised in this investigation is ACN-157-15 by Kynol. The electrolyte was composed of 1:1 deuterated tetrahydrofuran and deuterated dimethoxyethane and 0.1 M Li₂S₈. Furthermore, to enhance the lithium-ion conductivity 8 wt % (0.29 M) of LiTFSI and 4 wt % (0.6 M) of LiNO₃ were added. The internal cell geometry is similar to a regular lab CR2032 coin cell. Both windows made of aluminum are neutron transparent. A Kapton foil is sandwiched between one of the aluminium windows and the metallic lithium chip to prevent undesirable alloying of the aluminium. During the experiment, the cold neutrons were employed with a 4.5 Å, and the detector distance was 1m. Every ten minutes, SANS curves were taken.

The main aim of this experiment was to detect that solid product (S₈ or Li₂S) precipitates within or outside of the micropores of the carbonaceous cathode. The deuterated electrolyte was added within the first 22 h to the cathode to monitor the wetting process during the open circuit (OCP) conditions. The micropores are filled with solvent to reduce their scattering contribution. The first and last three cycles are shown in Figure 10b. The first row depicts the time-dependent voltage variation of the cell during galvanostatic cycling. The scattering intensity around the discharged state correlates to two voltage curve locations (red dots, vertical white dashed lines). The first point is located at ~ 2.050 ± 0.01 V, at which the viscosity reaches a maximum correspond to change from long- to short-chain LiPSs, which is in agreement with in-situ XAS^{150,175,182} and XRD results.^{195,196} The second point at 2.385 ± 0.010 V indicates the end of the Li₂S dissolution process, consistent with earlier in-situ XRD results.^{170,174} The scattering intensity is shown as a heat plot in the second row. After evaluating the SANS patterns, it was demonstrated that precipitation of both solid products does not occur inside the micropores but instead it occurs on the outer surface of the micrometer-sized carbon fibers used in their study. Furthermore, the wetting process of the microporous carbon electrode was investigated. The results emphasized the importance of a certain rest time before starting the electrochemical cycling to reduce the cell's inner resistance.

SANS is typically used to probe long-range magnetic structures (e.g. ¹⁹⁷). The purely structural information extracted from SANS in the above discussed article is also accessible by small angle X-ray scattering (SAXS). Interestingly, SAXS can be performed either in a lab or at a synchrotron and to our knowledge, no one has yet applied SAXS to the study of Li-S batteries. This may represent a more accessible method to obtain the same information available from SANS.


Figure 10: (a) Scheme of the operando cell used (sectional view). The neutron beam (sample slit \bigcirc 6 mm) penetrates through two aluminum windows, one Kapton foil, the metallic lithium chip, the Celgard 2700 separator, and the carbon. (b) Summary of the operando small angle neutron scattering experiment. The upper row shows the voltage curve of cycles 1–3 and 8–10. The red points mark a characteristic point on the voltage curve that coincides with the local minima of the scattering intensity. The second row summarizes the SANS results. The periodic appearance of local maxima correlated well with the charged (S₈) and discharged state (Li₂S) of the operando cell. The precipitation of Li₂S shows, as expected the highest intensity due to its stronger contrast with the carbon matrix. Figure reproduced from¹⁹⁴ with permission.

3.5. Transmission X-ray microscopy

X-ray microscopes is a technique that can provide nondestructive, high-resolution images (tens of nanometers). Transmission X-ray microscopy (TXM) is one of the most common types of X-ray microscopy techniques. TXM enables the quick acquisition of images that are appropriate for tomographic imaging and chemical mapping. A condenser lens is used to focus a big incoherent X-ray beam onto the sample. The imaging field of view of a sample depends on the X-ray energy and it can vary from a few micrometers to tens of micrometers in diameter. More often, the objective lens of a Fresnel zone plate collects the scattered and transmitted X-rays across the sample and creates a real-space intensity image on a CCD camera. The spatial resolution for TXM is usually decided by the numerical aperture of the objective lens.¹⁹⁸

The volume deformation of sulfur cathodes during battery operation is one of the critical hurdles to implementation in commercial devices. The severe volume change (~80%) of the sulfur induces the detachment of the active materials from the electrode and ultimately causes rapid capacity decay due to loss of electrical contact. In the past, manual measurements with a micrometer have been used to determine the changes in volume by measuring the difference in the thickness of the electrodes in the fully charged and discharged state ex-situ.¹⁹⁹ The results demonstrated the direct proof of approximately 22% volume expansion during the discharging

process. Recently, significant attention has been paid to the direct observation of volume expansion in LSBs cells to apply protective measures.

In this regard, in-situ microscopic techniques have proven essential to determine the volume deformation of sulfur during the cycling process. For example, Lin and co-workers used in-situ transmission X-ray microscopy (TXM) to investigate the volume expansion of a single sulfur particle during the lithium insertion/extraction process.²⁰⁰ Due to the migration of LiPSs upon dissolution, the process of re-deposition of the same particle was not possible to monitor as it has been completely dissolved. As a result, the re-deposition of a particle subjected to a series of lithiation/de-lithiation cycles was investigated. They studied three particles and it was found that large particle grows at the expense of small particle. They observed an increase of ~116% in the size of the sulfur particle during cell cycling. This volumetric expansion far exceeds the theoretical value (% 80). A continuous reduction in the total number of particles and an increase in average particle size was observed after repeated cycles. This deformation results from the shuttle process, during which breakdown and re-deposition of polysulfides occur. Following this finding of significant volume deformation, the use of bare sulfur particles was avoided. The idea of sulfur encapsulation in carbon or other conductive coating was proposed to enhance the conductivity and eliminate the problem of volume deformation.²⁰¹

Some researchers reported that the formation of an insulating Li_2S layer rather than the polysulfide dissolution is responsible for faster capacity fading. Although various ex-situ techniques strongly provide evidence that LiPSs are mainly responsible for capacity fading, in all these cases, the electrolyte was used for analysis after washing, which suggests that some active materials may be lost – causing uncertainty in the measurements. Nelson *et al.* employed the insitu transmission x-ray microscopic (TXM) study to investigate the reason for rapid capacity decay.

²⁰² They did not observe any significant dissolution of the sulfur/super-P composite, further suggesting that the insulating Li₂S layer is responsible for rapid capacity decay. These results were supported by a recent report in which in-situ TXM was employed to quantitatively evaluate conversion/dissolution processes as well as diffusion of LiPSs from the cathode and into the bulk electrolyte.²⁰³ In contrast to previous reports where field-of-view was less than the full cathode, this study used a customized micro-tomography transparent capillary cell geometry (as shown in Figure 11a) allowing access to the full field of view tomography and thus achieving a micrometer spatial resolution. Figure 11b shows tomogram slices through the cathode of the operando cell during the later stages of discharge. The 2D tomographic slices show that Li₂S is deposited continuously across the 2.1 V plateau and is evenly distributed over the cathode structure and result in the formation of the Li₂S insulator layer. In agreement with the previous report,²⁰⁴ this Li₂S layer has previously been described as porous, thus hindering the diffusion of LiPSs and Li⁺ and limiting their access to the carbon surface for electron transfer.



Figure 11. (a) Schematic of the capillary cell used for operando measurements with the cathode on the bottom and Li-metal anode on top of the cell. (b). a-k) 2D tomographic slices of the cathode in the operando cell after the initial stage and up to full discharge. Figure reproduced from ²⁰³ with permission.

Compared to X-ray radiography, TXM provides informational on a more useful lengths scales and still readily allows in-situ measurements to be performed. This approach to probing morphological changes seems to warrant continued attention and use.

3.6 Tomogrpahy

X-ray diffraction computed tomography which is technically being produced from multiple onventional radiographs has been demonstrated as a excellent tool for producing time resolved 3D images of the structural state of electrochemical systems such as batterie.^{205,206} In this regard the Shearing group for the first time reported a multi-scale, 3D X-ray imaging approach to examine the micorsturutural evolution of a sulfur cathode at different states of charge.²⁰⁷ The in-situ 'tomography cell' consisted of 1/8" PFA Swagelok unions (PFA-220-6, Swagelok) with the Al foil cast S-composite as a cathode (10 mm diameter discs), lithium foil as an anode (3.175 mm) and glass fiber (Whatman GF/D) 3.175 mm) as the separator. In-situ X-ray micro-tomography was performed with a lab micro-CT instrument (Xradia Versa 520, Carl Zeiss Inc.) using a 50 kV polychromatic micro-focus source and a low energy filter. This demonstrated the limitations of high mass loading electrodes and re-deposition of sulfur away from its original location with cycling was observed which was linked with the agglomeration of elemental sulfur. In addition, they reported that intraparticle conductivity might be responsible for capacity issues in LSBs, rather than bulk electrode conductivity and thickness. Following this seminal report in another study, they claimed to be the first who use a 4D imaging approach to provide a mechanistic understanding of LSBs.²⁰⁸ They analyzed the sulfur particles, carbon binder domain, and the electrolyte-filled bulk pore phase as a function of state of charge using the full spatial and temporal resolution capabilities of synchrotron X-ray micro-CT. The modified cell used in this study was adapted from above is shown in Figure 12. Though it has been reported in the literature that

disproportionation processes are responsible for the reduction of S_8^{2-} to $S_6^{2-,209}$ but this work claims that both electrochemical and disproportionation reactions might be involved. They also observed that at low C-rates, sulfur utilization might not be a significant factor determining capacity. However, the kinetics and processes of multistep reactions within the LBSs are dependent on many variables, including electrolyte choice and cell temperature. Despite the fact that this work has provided insight into its microstructural evolution, it has been unable to properly describe the highly complex multiphase reaction that underpin LSBs chemistry.



Figure 12. (a) Schematic of tomography cell (not to scale) with (b) electrochemical data for the first cycle, (c) volume rendering of a cropped region of interest within the uncycled cell, and (d)

virtual slice of tomogram showing layers within the cell. Scale bar for the volume rendering and virtual slice represents 200 μ m. Figure reproduced from ²⁰⁸ with permission.

4. In-situ microscopic techniques.

Electron and atomic force microscopes have emerged as a powerful tool for the characterization of a wide range of materials. Their versatility and exceptionally high spatial resolution render them a precious tool for many applications. Microscopic techniques such as TEM, SEM and AFM have been employed to monitor the electrochemistry and volume expansion of LSBs. They are discussed below.

4.1. Transmission electron microscopy

In-situ TEM electrochemistry technique is an effective instrument to investigate the dynamic kinetics of electrochemical reactions of battery materials at high spatial resolution.²¹⁰ However, sulfur is sensitive to the high energy electron beam and high vacuum and sublimation, making the imaging of sulfur with TEM very challenging.²¹¹ The setup for in-situ TEM is the same in most of the studies, with some minor variations. It generally consists of a holder with a working electrode normally sulfur coated with a conductive coating to prevent sulfur sublimation under high vacuum and high energy electron beam conditions. The tip of the holder contains metal lithium, which acts as the anode. While the holder is transferred into the TEM, Li₂O layer formed on the surface of Li metal. Although this alters the battery chemistry, it very conveniently also serves as a solid-state electrolyte allowing Li⁺ transport and thereby making the otherwise extremely challenging in-situ TEM experiment possible.

Kim et al., for the first time, used in-situ TEM to observe the lithiation of sulfur confined within cylindrical porous carbon nanotubes (CNT) in LSB as shown in Figure 13a.²¹² CNT nanoreactors helped in dissipating heat and retaining the sulfur under the electron beam and

vacuum within the TEM. This study proposed that, in the absence of a liquid electrolyte, the direct transformation from sulfur to Li_2S is energetically (or kinetically) favorable during sulfur lithiation reactions. Similar results were obtained by Zhang and co-workers, who designed solid-state LSBs nano-batteries for in-situ TEM observation.²¹³ The electrochemical lithiation process of carbon-coated sulfur materials was studied using a solid-state LSB nanobattery. The design of an in-situ device is depicted in Figure 13b. For the first time, the S/Li₂S phase separation phenomenon is observed, which lowers the diffusion distance and creates a S/Li₂S interfaces network that is beneficial for the Li⁺ and electron diffusion during the lithiation process. Instead of the two-step reaction that occurs at the S cathode during the electrochemical lithiation process in liquid LBSs, a direct transformation of S into Li₂S (with no intermediate product of LiPSs (Li₂S_x, 4x = 8) is observed here in solid LSB with the help of in-situ TEM.

In-situ TEM has also been used to observe the structural stability and volume variation during lithiation in LSBs.²¹⁴ For example, a unique architecture featuring crystalline Li₂S nanoparticles wrapped by a few layers of graphene was prepared to maximize the function of encapsulation. It was found that the initial diameter of 430 nm was reduced to 395 nm during discharge while the size varied from 390 to 405 nm during following cycles with small volume change. By contrast, bare Li₂S exhibited severe structural degradation. After direct observation of volume changes using in-situ TEM it was demonstrated that graphene encapsulation prevents volume expansion. In another report, in-situ TEM was used to provide evidence for the correlation between electrochemical performance and volume expansion and to examine the lithiation behavior of porous carbon nanofibers/S electrodes in real-time.²¹⁵ It was observed that the expansion and overflowing of lithiation products are closely related to the microstructure and mechanical stability

of the carbon host. In addition, it was found that micropores are more favorable than mesopores, which can facilitate ionic transportation and alleviate the volume expansion.

In another study, the same authors used in-situ TEM to understand the working mechanisms and lithiation behavior of sulfur cathode (graphene nanocage structure composited with sulfur, S-GNC).²¹⁶ In-situ TEM was carried out employing the same Nanofactory in-situ TEM setup used for the above studies. The only difference is that the working electrode was attached to the gold rod with the help of conductive glue, while Li metal was scratched from one Li foil and attached to one tungsten rod that served as the counter electrode. It was found that the nanocage structure not only guarantees good structural stability against volumetric variation during the lithiation but it also provides an electronically conductive environment for loaded active sulfur species. Similarly, Xu et al. used in-situ TEM to track the reaction mechanism of LSBs. ²¹⁷A special TEM holder was designed for this study to study the morphological and structural evolution of LSBs (as shown in Figure 13e). It was observed that the diffusion of lithium mostly takes place at the surface of the sulfur particles, while an insulating Li₂S crust prevents diffusion into the bulk of the materials (Figure 13f). The insulating Li₂S layer resists the radial diffusion of Li⁺ ions and results in rapid capacity decay.



Figure13 (a) Schematic illustration of the electrochemical device set up for a real-time TEM observation of an electrochemical lithiation of nanoconfined S cathodes. Figure reproduce from²¹² with permission. (b) Schematic diagram of the electrochemical device set for in-situ TEM observation of the solid-state LSB nanobattery. Typical TEM images of sulfur sample c) before and d) after lithiation. Figure reproduce from²¹³ with permission.(e) Schematic of the Li–S cell setup for in-situ TEM study, (f) TEM images of the Li–S cell during discharge (1–60 s). Figure reproduce from²¹⁷ with permission.

In-situ TEM also provides the capability to study the electrochemical decomposition of Li₂S during charge.²¹⁸ The nanobattery design for this study consists of a microelectromechanical system (MEMS) heating device that was integrated into the TEM sample holder to examine the influence of temperature on lithiation/delithiation of LSBs (as shown in Figure 14a-b). The MEMS heating chip has an electric (blue) and a heating (red) circuit (yellow). It was demonstrated that Li₂S nucleated at the reaction interface in the amorphous and nanocrystalline states and transformed to the polycrystalline state during the lithiation process. Furthermore, it has been observed that the electrochemical decomposition of Li₂S is controlled by diffusion.

Though the above studies provide insights into the electrochemistry of LSBs with the help of in-situ TEM, however, the lithiation process is investigated in solid-state using Li₂O as the solid

electrolyte, which is remarkably different from the lithiation reaction in traditional liquid LSBs. The investigation of sulfur electrodes in a liquid electrolyte is challenging due the formation and diffusion of LiPSs. In recent decades, aberration-corrected TEM (AC-TEM) has achieved atomic resolution even in some battery materials that are somewhat beam sensitive (e.g. cathodes for Liion batteries). This has allowed for significant advances in research and development of batteries. In this regard, Zhang et al. recently developed aberration-corrected environmental in-situ TEM to visualize the sulfur-electrolyte interface evolution in an ionic liquid (IL) electrolyte.²¹⁹ The electrochemical cell used for in-situ measurements was in the form of nanotubule (S-CNT) comprised of tip flattened aluminium rod attached with a Li metal anode and partial sulfur-filled carbon nanotubule (S-CNT) as a cathode as shown in Figure 14c. It was observed that in the IL electrolyte, both with and without Li salt, sulfur is electrochemically reduced to soluble LiPSs and the in-situ generated long-chain polysulfides dissolved into the IL electrolyte quickly and were stabilized by the organic ammonium (Py_{14}^+) cation solvation (Figure 14d-g). The Py_{14}^+ cation solvation stabilized the LiPSs and the precipitation of S_8 was detected on the CNT inner wall and on the fiber separator which are acting as a surface-mediated disproportionation of long-chain LiPSs. Addition of low polarized solvents such as DOL and DME into IL weaken the interaction between the Py₁₄⁺ and the long chain LiPS, thus allowing the further electrochemical reduction of long-chain LiPS to short chain LiPS resulting in high discharge capacity.

Clearly in-situ TEM represents a challenging experiment to perform systematically on state-of-the-art LSB chemistries. To date, experiments have been limited to electrolytes that perform very differently from the state-of-the-art (Li₂O is not a competitive solid electrolyte, and IL do not perform nearly as well as the best liquid electrolytes). Nonetheless, the insights into all-solid batteries and IL batteries may prove important should either of those chemistries be further

developed to become competitive, or if methods can be developed to perform in-situ TEM on batteries with competitive solid electrolytes.

It is worth mentioning that another microscopic technique is emerging as a powerful tool to unveil mechanisms in Li-S batteries: cryogenic electron microscopy (cryo-EM). Although no in-situ techniques have yet been realized, the information gained from ex-situ approaches has been and is likely to continue to be very significant and thus warrants attention here. Cryo-EM represents a challenging experiment that has significant advantages over room temperature microscopy. In particular, lithium, sulfur and liquid electrolytes are all beam sensitive at room temperature such that the question of whether the observed images are solely a product of beam damage can never be dismissed. By contrast, at cryogenic temperatures the samples can be cut thin by cryo-FIB and subjected to TEM without beam damage. The progress made in cryo-EM of battery materials has been reviewed elsewhere recently.²²⁰ The introduction of cryo-EM has also provided valuable insights about sulfur distribution in different host materials and guided the design of advanced cathodes in LSBs.^{221–223} However, the atomic details and structure changes of S and intermediate LiPSs during charge and discharge processes have not been visualized by cryo-EM yet. More such studies are expected and should prove very insightful in the context of understanding mechanisms at play in LSBs. In-situ cryo-EM is not yet a reality, nonetheless exsitu cryo-EM is proving very powerful when sample preparation is performed carefully.^{224,225} Further visualization of the chemical and structure information at the nanoscale should be performed. Should in-situ TEM of LSBs with liquid electrolytes never be a reality, cryo-EM may well fill the gap in knowledge.

Electron energy loss spectroscopy (EELS), which is now extensively equipped inside TEM to provide useful atomic-level information, has been found to be an effective tool in studying the

battery materials.^{226,227} Advanced TEM configuration (e.g., as in-situ bias, in-situ heating, and cryo-TEM)^{228,229} have made it possible to achieve TEM imaging and corresponding EELS spectra of battery materials under different thermodynamics conditions and dynamic environments (e.g., electrochemical solid/liquid or solid/solid systems, heating, cryogenic, etc.).

Ex-situ and in-situ EELS, coupled with solid-state open cells, have been able to detect intermediate products in Li-ion batteries,²³⁰ but in-situ EELS experiments in a liquid cell are still a major challenge. There is only one report of an in-situ EELS study in a liquid cell that we are aware of.²³¹ Cryo-EELS has opened a new door to analyzing the beam-sensitive components in the electrode/electrolyte. If developed, then it will be very helpful to analyze the intermediate LiPSs and electrode/electrolyte interfaces and will help to evaluate the complex multielectron mechanism of LSBs. More efforts are required for the development of advanced configurations for EELS, e.g., in-situ (e.g., electrochemical) cryo-holders, high-resolution liquid close cells, etc., to facilitate the battery studies.



Figure 14. A scheme showing the setup of the solid cell implemented with a MEMS heating device for in-situ TEM observation. a) A sample holder equipped with the MEMS heating accessory for in-situ TEM observation: (i) A MEMS heating chip, (ii) the nanobattery design, (iii) TEM image showing the practical working environment of the nanobattery. (b) Schematic representation of the reaction mechanism of the lithiation/delithiation of a S@CNT cathode: (i) lithiation at 30 °C, (ii)

lithiation at 100 °C, (iii) delithiation at 30 °C, and (iv) delithiation at 300 °C. Figure reproduce from ²¹⁸ with permission. (c) Schematic of the experimental setup used in ref. ²¹⁹. (d-g) Time-lapse structure evolution of the S-CNT cathode in an IL electrolyte. The red arrows point to the IL/S interface. During the discharge (d,e) reaction, sulfur reacted with Li to form polysulfides, which dissolved into the electrolyte instantaneously. During subsequent charge (f,g), some semicircular particles precipitated out on the inner wall of the CNT. Figure reproduced from ²¹⁹ with permission.

4.2. Scanning electron microscopy

A scanning electron microscope (SEM) produces images of material by scanning it with a focused beam of electrons. When electrons contact atoms in a sample, they produce signals that tell us about the sample's surface topography and composition. An image is created by combining the position of the electron beam with the intensity of the detected signal.

In-situ SEM is an important analyzing technique that can provide insights into the preferred reaction sites of the electrode during charge/discharge. Qiu et al. used in-situ SEM to analyze structural changes in sulfur cathode during delithiation for the first time.²³² The cell used for insitu SEM is shown in Figure 15a-c. With the use of low-pressure chemical vapour deposition, a Si-rich layer (50 nm) of SiNx was deposited onto a thick silicon wafer. The windows were created using photolithography and reactive ion etching techniques. After transferring the graphene electrode and depositing Al on top of it, a transparent SiNx/graphene window was produced. After placing one drop of Li₂S solution in 100% ethanol on the chip with the SiNx/graphene layer, the chip was heated at 80 °C for 30 minutes. The Cu metal on the other side of the chips was directly deposited by evaporation. Li metal was used to hold the chip together in the middle. A sandwich structure was constructed by layering the two distinct chips together in an argon-filled glove box with the middle filled with electrolyte (1 M LiTFSI in DOL/DME solvent). It was observed that Li₂S particles encapsulated in the graphene sheets become smaller and eventually disappear upon charging to 3.5 V (Figure 15d-e). This observation led the authors to postulate that the generated

lithium polysulfides may be gradually dissolved in the ionic liquid electrolyte. The aggregation of graphene sheets was also found due to the high-viscosity electrolyte. It was concluded that to enhance the performance of the Li_2S cathode, it is necessary to create a conductive matrix with functional groups that have a high affinity for the redeposition of intermediate lithium polysulfides.



Figure 15. In-situ electronic microscopy set-ups and the characterization results during delithiation of Li₂S. a,b) A newly developed electrochemical microcell for in-situ SEM. c) An insitu TEM electrochemical characterization set-up. d) Time-lapse SEM images of the activation process of Li₂S on a single-layered graphene electrode in a standard LiTFSIDOL/DME electrolyte. Red color shows a relatively thicker Li₂S layer on graphene. The Li₂S particles on graphene became smaller and smaller during the delithiation activation process, which was due to the continuous dissolution of the intermediate lithium polusulfides into the electrolyte (see schematic diagram below). Scale bar: 20 μ m. e) Time-lapse TEM images of the activation process of HNG–Li₂S in an ionic liquid based electrolyte. Similarly, the generated intermediate lithium polysulfi des during the aggregation of

the HNG sheets and the remaining lithium sulfide or polysulfides. Scale bar: 50 nm. Figure reproduce from 232 with permission.

In-situ SEM has been coupled with other characterization techniques such as operando UV-Vis to track the degradation mechanisms of LSBs. ²³³ Similarly, Zhang et al. used in-situ SEM, combined with energy dispersive spectroscopy (EDS) and XRD to measure the volume expansion and stress evolution in composite sulfur cathodes during cycling.²³⁴ They observed that significant stresses created during the first cycle are due to nucleation and growth of solid lithium-sulfur phases and form structural rearrangements. However, subsequent cycles exhibit highly reversible elastic mechanics. In-situ SEM, particularly when coupled with other techniques, is proving to be an effective tool in probing electrode morphology changes in commercially relevant LSB chemistries. We expect its usage to continue to be important in the further development of LSBs.

4.3. Atomic force microscopy

Atomic force microscopy is the most diverse and efficient nanoscale microscopy method. it can scan three-dimensional topography and offer surface measurements to scientists and engineers. With minimal sample preparation, AFM may create atomic resolution pictures of a material's surface with angstrom scale resolution height information.

The in-situ TEM technique mainly highlights the direct observation of the morphology evolution, whereas in-situ AFM analysis can readily incorporate environmental conditions that mimic the cell environment at the nanoscale and can be used to track the evolution of the surface topography under such conditions. Furthermore, in-situ AFM can provide access to probing the formation of the solid electrolyte interface (SEI) layers during battery cycling.¹⁹⁸ In this regard, Lang et al. employed the in-situ AFM technique to study the morphology of the products and kinetic processes of LBS redox on highly oriented pyrolytic graphite (HOPG) at various charge

and discharge states under potentiostatic condition .²³⁵ In-situ electrochemical AFM studies were carried out using a potentiostat/galvanostat with a commercial AFM system. The CVs were recorded at a sweep rate of 1 mV s⁻¹ in the range 1.5 V - 3.0 V. The working electrode (HOPG) was mounted on the scanner and the electrochemical unit was integrated into the cantilever holder. The HOPG surface was scanned using EC-AFM in tapping mode using an insulated triangular silicon nitride AFM tip. Each image in this study requires 3 minutes 15 seconds to process. The cell was sealed with an O ring with a diameter of 0.8 cm and all experiments were conducted in an argon-filled glovebox to avoid contamination of the air, It was found that upon discharge, the nuclei of nanoparticles began to develop at 2 V, while lamella sediment deposition began at 1.83 V. During charging, lamella sediments were reversibly oxidized but nanoparticles (NPs) accumulated during cycling. X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy were used to examine the solid reduction products on the HOPG cathode, and the results showed that the NPs and lamella sediments were both Li2S2 and Li2S. Their findings shed light on the nucleation, growth, and decomposition processes of intermediate Li₂S₂ and final Li₂S, establishing a structure-reactivity relationship for LSBs.

Atomic-force-microscopy-based scanning electrochemical microscopy (AFM–SECM) has been employed for the first time to study the LSB cathode surface at a nanoscale spatial resolution in real-time.²³⁶ The interdependence of Li₂S morphology on its electrochemical activity during oxidation was studied with the help of SECM mode current mapping. The obtained results were further corroborated by in-situ AFM topography. The cell designed for this study is a fourelectrode electrochemical cell (Figure 16). The tip of AFM-SECM was used as a working electrode and, a glassy carbon circular disk was used as a working electrode while a lithium strip acted as a reference counter electrode. The electrolyte was comprised of 0.1 M LiTFSI with 0.1M LiNO₃ as an additive and TEGDME as the solvent. The cell was assembled inside an Argon filled glove box (oxygen and moisture levels maintained below 0.1 ppm) using a specially designed transfer chamber equipped with a provision to drain or fill the cell with electrolyte outside the glovebox without exposing it to the outer atmosphere. The chamber was thoroughly sealed inside the glove box and was then transferred to the AFM-SECM workstation. A continuous flow of Argon gas was maintained in the chamber throughout the experiments to preserve a controlled atmosphere. Electrochemically active (conducting) and inactive (insulating) regions were observed, and their contribution to the overall electrochemical activity during the oxidation process was monitored. It was observed that the discharge product contains both Li₂S₂ and Li₂S, with Li₂S₂ oxidizing faster than Li₂S. Intermediate LiPS was found to react with Li₂S and pave the way for insulating solid product deposition, limiting active materials' usage. Overall, this study provides insight into the morphological and structural changes that occur on the cathode surface due to the LSBs charging mechanism.

In-situ AFM has played important roles in understanding morphological changes in a number of battery chemistries, and though the experiment is not trivial to perform as described above, it is certainly becoming more routine and is far more widely applicable than in-situ TEM and SEM. This method should continue to play an important role in monitoring morphological changes in LSB electrolytes with a wider variety of cell chemistries than explored up to now.



Figure 16: AFM–SECM Pt tip performance: (a) cyclic voltammogram of cobaltocene redox mediator on AFM–SECM Pt tip (diameter = 100 nm), far away from the substrate (iT, ∞), SEM image of the Pt tip (inset); (b) steady state approach curve. Tip biased at reduction potential of 2.1 V, and substrate biased at oxidation potential of 2.4 V. Tip Approach performed using a stepper motor at a speed of 0.0003 µm/msec. (c) Schematic representation of SECM electrochemical cell setup and zoom-in part depicts the competitive SECM mode used for imaging of Li-S cathode surface where the substrate was biased between 2.5 to 2.7 V, and tip was biased at a constant potential of 2.6 V vs Li/Li⁺. Figure reproduce from ²³⁶ with permission.

4.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a powerful tool to investigate properties of materials and electrode reactions by applying an AC potential to an electrochemical cell and then measuring the current through the cell. The EIS response can reveal key electrochemical processes and their evolution as it allows separation of electrical processes in an electrochemical cell based on relaxation frequencies.

In order to evaluate the electrochemical mechanism of LSBs, previously ex-situ EIS has been used in different cell configurations where asymmetry between two electrodes produces distortion of EIS spectra. The two-electrode full cell is a better representative of a real system. However, the total impedance response makes it very difficult to separate the specific contributions from both electrodes. To overcome this issue Walus et al. carried out ESI measurement on symmetrical cells consisting of two pre-cycled electrodes of the same type assembled into a coin cell.²³⁷ Symmetric coin cells for in-situ EIS were prepared by stacking positive electrode, Celgard[®]2400 separator and with thick layer (240 μ m, Viledon[®], from Freudenberg) of polyolefin non-woven felt which serves as an electrolyte reservoir. The separators was soaked with 100 μ L of electrolyte and then covered by a disk of either cathode for (S8||S8) or anodes (Li||Li). This study didn't provide any new insight but has confirm the already observed phenomenon of high LiPSs dissolution at the beginning of discharge while a reverse process was observed during charge where a progressive oxidation of Li₂S accompanied with the formation of low-to-mid order LiPSs. Various other studies also confirmed the same mechanism during the charge/discharge of LSBs using in-situ EIS.^{238,239}

In a recent report the electrode/electrolyte interfacial processes were studied using in-situ EIS.²⁴⁰ The measurement were carried out under lean electrolyte (low electrolyte/sulfur (E/S) ratio) condition. In-situ EIS experiments were performed hourly during cell discharging using a Gamry Interface 1000 with a sinusoidal perturbation voltage of 5 mV RMS using coin cells. The frequency range for the potentiostatic EIS was set in the range that could be completed within 1 min to minimize the interference to the discharge process. During the transition from high-order to low-order LiPSs with a low E/S ratio, a rapid rise in charge-transfer resistance was observed which caused by a kinetic bottleneck due to Li-ion mass transfer constraint. This study also demonstrated that the sluggish kinetics of LSBs under the lean electrolyte conditions can be improved by increasing the adsorption of dissolved high-order polysulfides, which is a key step in the interfacial processes.

5. In-situ spectroscopic techniques

Understanding LiPS nature and the mechanisms at play is necessary in order to design reliable high-capacity LSBs. As some of these solid LiPS are hard to observe with the in-situ techniques discussed up to now, various in-situ spectroscopic techniques have been developed and used to quantify the dissolution of polysulfide species and control their diffusion in the electrolyte. Each of these spectroscopic techniques are detailed below.

5.1. Nuclear magnetic resonance spectroscopy

To explain the LSB discharge mechanism, See et al. used a computational approach to study the LSB phase diagram, which is then supplemented by an in-situ ⁷Li NMR investigation during discharge. In-situ nuclear magnetic resonance (NMR) was then employed to investigate the nature of different LiPS and the possible cause for the lower performance of LSBs.²⁴¹ It is worth mentioning that ex-situ ⁷Li NMR had already detected the presence of both dissolved and solid Li⁺ species during charge/discharge.²⁴² However, in-situ NMR was employed to get insight into the soluble and solid intermediates LiPSs during real battery operation. The bag cells were prepared 45 min prior to the in-situ NMR experiments. For electrolyte, a standard 1 M LiTFSI in DOL/DME (1:1, v/v) was utilized such that no compromise is made in this case. In-situ NMR measurements were performed on a 7T OXFORD instruments magnet, at a 7 Li Larmor frequency of 117.2 MHz. It was demonstrated that the production rate of Li⁺ containing solid (Li₂S and Li₂S₂) remains steady during the discharge and appears not to reduce the polysulfides in solution. In-situ NMR facilitated the visualization of various phases during the discharge process. To explains the appearance of different LiPSs phases, a ternary diagram was proposed (as shown in Figure 17a). The diagram represents a single-phase region that can be assigned to Li⁺ and polysulfide species in the electrolyte. This region then drops into the ternary phase, corresponding to the dissolution of longchain LiPS. This ternary diagram thoroughly explains the phases observed in the in-situ NMR (Figure 17b). This study provides pertinent information on the phases forming in the electrolyte during discharge (Figure 17c-e) and provides real time monitoring of the dissolution of the polysulfide. Given that polysulfide dissolution continues to be the major hurdle to commercialization, this ability to monitor their formation in-situ will undoubtedly prove essential in realizing LSBs with its full potential for commercial application.

Following this study, Xiao et al. used situ ⁷Li NMR spectroscopy to monitor the transient electrochemical and chemical reactions initiated on the cathode, anode and electrolyte.²⁴³ In-situ NMR measurements were carried out in plastic capsule cell, polytetrafluoroethylene (PTFE) was used as the binder, and the cathode composite was in the form of a freestanding about 175 mm thick file, which was laminated onto an aluminum mesh.²⁴⁴ Once the dry battery gets ready, it is sealed with epoxy into the capsule case, which was filled with electrolyte (1 M LiPF6 in ethylene carbonate/dimethyl carbonate with a 1:1 volume ratio). This study provided semiquantitative information related to the LiPS reactions and the Li anode microstructural evolution during the charge/discharge processes.



Figure 17: (a) Proposed ternary diagram describing the pathway of the Li–S discharge. The system can only be explained using a ternary phase diagram as the electrolyte is actively involved in the discharge pathway. The approximate discharge profile would exhibit a plateau when passing through the three-phase region, a voltage drops upon exiting the three-phase region, and another plateau when passing through the two-phase regions thereafter. This would result in two plateaus, as seen in the experiment (b) In-situ 7Li NMR signal overlaid on the electrochemical discharge

curve for a Li–S bag cell discharged galvanostatically at a rate corresponding to C/20, using a 1 M LiTFSI in DOL/DME electrolyte. A spectrum is recorded every 14.6 min. The cell is held at an open circuit for 15 min before discharge. The Li metal resonance at +250 ppm₁₂ is not shown (b)The lowest energy solid-state structures in the Li_xS_{1-x} phase diagram, identified for Li_2S_8 , Li_2S_6 , Li₂S₄, and Li₂S₂, i.e., with stoichiometry Li₂Sy, all contain S chains of length y. These are all metastable phases, with respect to S and Li₂S. (c) Formation energies of several possible stoichiometries of Li with S normalized per atom (pa) using two different methods: ab initio structure searching, AIRSS (Method 1) and structures obtained by Li⁺ insertion into enumerated vacancy sites in fcc or hcp S_8 (Method 2). All intermediate structures lie above the convex hull indicated by the dashed line indicating that Li₂S is the only favored solid-state phase in this system. (e) The convex hull suggests that the discharge of an all solid-state Li-S battery would exhibit a single plateau at 2V (vs. Li) corresponding to one two-phase region and direct conversion to Li₂S. Figure reproduced from ²⁴¹ with permission (f) Demonstration of the four-step soluble speciesbased Li-S electrochemistry. Figure reproduced from ²⁴³ with permission. (g) current JSATS transmitter design. (h) a newly proposed downsized design. (i) cross-sectional view. (j) weight distribution of PNNL-made MB306. Figure reproduced from ²⁴⁴ with permission.

To quantitatively monitor the electrochemical process in LSBs batteries, Wang et al. used in-situ NMR.²⁴³ In order to allow sufficient time for NMR spectra acquisition, the cells were cycled at a very slow rate (C/30). All LiPS intermediates were identified by desummation and quantification of NMR spectra. In addition, due to the shuttling effect, the Li_2S accumulation on the Li anode side was clearly detected after four cycles.

In-situ NMR is another method that is proving extremely powerful in the study of LSBs and is filling in some of the final gaps in our understanding of the mechanisms at play. The fact the measurements can be performed without compromise on the cell chemistry is extremely important also. This method will undoubtedly continue to play an important role in developing the understanding needed to design a better LSB.

5.2. Infrared spectroscopy

Infrared (IR) spectroscopy is widely used to differentiate compounds with various functional groups. Specifically, the measured IR spectra could be transformed to FTIR spectra by combining an interferometer and the mathematical Fourier transform. Significantly, FTIR can identify LiPS

compounds using S-S vibrational modes.²⁴⁵ To investigate the evolution of polysulfides during charge/discharge cycles, Saqib et al. used in-situ infrared (IR) spectroscopy.²⁴⁶ The same group used ex-situ IR to develop an optical diagnostic tool that can help to determine the LiPS equilibrium order and concentration in a LSBs cell in-situ.²⁴⁷ Though the LiPS solutions were prepared by reacting lithium sulfide with sulfur instead of studying the LSBs cell in real time, the developed diagnostic tool has provided a base for in-situ optical spectroscopy. Therefore, in their subsequent study, they used in-situ IR spectroscopy to get an insight into the in operando functioning of LSBs cell. The spectro-electrochemical cell employed for in-situ IR is shown in Figure 18a. To accommodate the raised diamond crystal a 5µm thick PTFE disc and a 50 Cu foil disc were added to the cell. A 2 mm hole cut in the center of both discs is needed to transmit the IR radiation. The Cu foil acts as the current collector. The CR2032 LSBs coin cell was then assembled on top of these layers. The cell was sealed by applying pressure from above using the Smart iTX sample anvil. The spectro-electrochemical cell mounted on top of Smart iTX, was installed on a Nicolet iS50 (Thermo Fisher Scientific) FT-IR spectrometer for in-situ spectroscopy. After evaluating the spectrum collected, it was found that sulfur convert to Li₂S₈ and was further reduced to smaller polysulfides as discharging occurs. It was also demonstrated that sulfur could be recovered from the electrolyte at the end of the first charge cycle. However, crystalline sulfur is not recovered over multiple cycles during charging and capacity fading can be observed in terms of LiPS order and concentration.

One of the most influential aspects in LiPS development and redox kinetics is the electrolyte system. The commonly used 1,2-dimethoxyethane and 1,3-dioxolane (DME:DOL) binary electrolyte solvent has low viscosity and excellent lithium-ion mobility but also has significant LiPS solubility and cause LiPS shuttling. Unfortunately, few researchers have explored the

molecular interactions between electrolytes and electrodes under different electrochemical operating conditions. In this regard, Kalra and their group used in-situ FT-IR ATR to probe both the production of LiPS and electrolyte interaction.²⁴⁸ The cell was similar to that discussed above (Figure 18c). In this study, the concentration of various LiPS species was determined as a function of voltage during cell discharge. In particular, molecular-level changes were observed in the electrolyte salt anion in response to LiPSs speciation. This level of monitoring is quite useful, and given the relative ease of performing IR-spectroscopy, this method may become more popular.



Figure 18: (a) Schematic representation of the operando ATR FTIR spectro-electrochemical cell. (b) Illustration of the IR beam reflected through the ATR crystal, absorbed by the electrolyte in a porous cathode Figure reproduce from²⁴⁶ with permission(c) Schematic of the in-situ infrared

spectro-electrochemical experiment with a lithium–sulfur cell on the ATR crystal of the FT-IR spectrometer. Figure reproduced from ²⁴⁸ with permission.

5.3. Raman spectroscopy

Raman spectroscopy is a powerful optical technique for examining vibrational, rotational, and other low-frequency modes. It can identify qualitatively or semiquantitatively observe the soluble LiPS in the ether-based electrolyte during cycling.^{249,250} Hagen et al. design the first setup for in-situ electrochemical Raman for LSBs.¹⁵⁶ The cell design for this study is shown in Figure 19a,b. The cell was a rectangular chamber made of stainless steel. To protect the electrode stack from the housing four glass slides were placed at the bottom of the chamber. The electrodes and separator that were also rectangular in shape were placed in the chamber on the top of the glass slides. Although the cell design is quite complex, various useful information has been obtained during real-time LSBs operation. For example, it was found that various LiPS exist depending on the state of charge and discharge. In addition, fast self-discharge and rapid dissolution of sulfur and other discharge products was reported. It was also demonstrated that an equilibrium between long-chain and short-chain LiPS occurs, moving from shorter to longer chains during discharge and charge, respectively. At the same time, the appearance of S_8 during charging was proved as well. They have used the same cell design for in-situ Raman and the DFT calculation to explore the mechanism of Li₂S₂ and Li₂S formation mechanisms. ¹⁵⁶ The existence of mono-anions polysulfide next to di-anions were detected. Additionally, various LiPS with different chain lengths were also observed. These in-situ experiments provided valuable information about the reaction mechanism of LSB cells. However, the peak intensity was too low and hard to identify all the different phases present.

Subsequently, research was continued to simplify the cell design for in-situ Raman to investigate the electrochemistry of LSBs. Finally, a modified coin cell or punch cell was designed that was used in different studies.²⁴⁹⁻²⁵² In such cells, a transparent window is installed on the anode side, while a perforated lithium metal anode and separator is used to ensure the access of the laser radiation to the sulfur cathode surface (Figure 19c,d). This type of cell was employed for studying changes within the sulfur cathode during cycling. For example, Sun et al. employed it to study the LiPS absorbance efficiency by black phosphorus modified separator for LSBs.²⁵⁰ Raman spectra was recorded at five different states of charge and it shows the typical transition from S₈ to Li₂S during cycling. On the other hand, to investigate the intermediate discharge products a hole was punch on S cathode side and the laser beam was inserted with the aid of an auxiliary microscope as shown in Figure 18e. This in-situ Raman cell was used to prove the previous density functional theory calculations which proposed that amide groups possess strong affinity (0.95-1.23 eV) to Li₂S_n species.²⁵³ In this study, the interactions between the c-PAM binder and soluble Li₂S_n species were measured.²⁵⁴ The evaluation of Raman spectrum indicates that the majority of soluble polysulfides have been effectively trapped, providing direct evidence for the strong capability of the c-PAM binder with polysulfides.



Figure 19. Development of an in-situ Raman electrochemical cell for Li–S battery investigation. (a) Raman in-situ cell. Left panel: Photo on cell window with the electrode stack; right panel (b) drawing and assembly. Figure reproduced from¹⁵⁶ with permission (c, d) Simply modified coin cell-based in-situ Raman cells. Figure reproduced from^{249,253} with permission (e) Photograph of the in-situ scanning Raman setup. Figure reproduced from²⁵⁰ with permission (f) A simple sealed bottle-type in-situ Raman cell. Figure reproduced from²⁵¹ with permission.

To further explore the reduction mechanism of LSBs, in-situ Raman spectroscopy with cyclic voltammetry has been employed.²⁵⁵ The long-chain polysulfides were stabilized *via* using the CS₂ additive to inhibit the formation of insulating Li₂S and Li₂S₂ layers. This study demonstrated the re-appearance of S₈ during the charging process. They claimed that S₈ disappearance and LiPS appearance occurs at approximately the same rate, a rate that is similar

whether the electrode is being charged or discharged. The cell design was in fact further simplyfied by Wang et al., who used a seal bottled type cell to measure the polysulfide mediators in the absence of the separator (Figure 19f).²⁵¹ This is now helping to improve the accessibility to this technique. Despite the usefulness of the technique, the Raman signal from most polysulfides is intrinsically low, such that widespread use of this approach in LSBs requires an improvement in the sensitivity of the instruments to achieve both higher spatial and temporal resolutions. Two interesting options for future in-situ Raman spectroscopy are surface-enhanced Raman spectroscopy and shell-isolated nanoparticle-enhanced Raman spectroscopy to investigate the mechanism of LSBs. Although further developments are anticipated, more widespread use of this technique across cell chemistries should prove valuable.

5.4. Ultraviolet-visible spectroscopy

In contrast to Raman spectroscopy, UV-Vis is a type of absorption spectroscopy utilizing the sequence of absorption bands in the ultraviolet-visible range of the spectrum. Dominko and co-workers used in-situ UV-Vis spectroscopy for the first time to obtain information about LSBs.²⁵⁶ They presented a quantitative and qualitative determination of LiPS species formation. The cell used for this study had a pouch cell configuration with a sealed glass cover. The cathode was placed opposite the glass and covered with a separator and lithium anode with a 16 mm hole in it, as shown in Figure 20a. The measurement was made in the reflection mode by placing the cell in the beam of the incident light. No compromise on battery chemistry is required. Follow up work involved using in-situ UV-Vis spectroscopy to study the mechanistic cause for capacity fading in two different electrolytes (1 M LiTFSI in sulfolane and 1 M LiTFSI in TEGDME:DOL).²⁵⁷ They determined that the former electrolyte showed a much higher concentration of polysulfide shuttling species than the latter, suggesting a larger amount of

irreversible reactions and this correlated to poorer capacity retention. This represents an important example of where an in-situ method uncovered a change in mechanism leading to improved battery performance in LSB chemistries of relevance for potential commercialization.

In another study, in-situ UV-vis spectroscopy was employed to investigate the electrolytedependent redox reaction pathways.²⁵⁸ The cell used for this study was a classic three-electrode system where 1.0 mm micro cuvette was used a cell body and comprised of gold mesh as a working electrode, Li metal foil as a counter electrode and Ag/Ag⁺ as a reference electrode (Figure 20b). This study found that electrolytes (e.g. dimethyl sulfoxide) that facilitate the formation of redoxactive polysulfides can accelerate the sluggish redox reactions in LSBs. Unfortunately, the traditional classic three-electrode cell design and expensive gold electrode used are inappropriate to investigate the conventional galvanostatic cycling that is a better representation of battery performance. Specifically, the voltage profile is difficult to achieve in this open system due to the large diffusion distances of soluble S-species in such cells, resulting in charge/discharge characteristics very different from conventional thin-layer configurations. In this regard, Yan et al. used in-situ UV-Vis spectroscopy using a coin cell configuration.²⁵⁹ The intermediate LiPSs were monitored during the discharge of LSBs in the presence of a new type of amino functional group binder. The modified coin cell used for in-situ UV-Vis spectra measurement is shown in Figure 20c. A hole was created both in the anode and cathode casing to allow the beam entrance. A transparent window was placed on the negative casing as well a perforated Li-anode was used. The in-situ UV-Vis spectroscopy measurement suggested the presence of characteristic long-chain LiPSs at higher voltage and short-chain LiPS at lower voltage plateau. Furthermore, a strong interaction of the binder with LiPS during discharge was reported, resulting in the enhanced performance of LSBs.

In some studies, the in-situ and ex-situ technique have been coupled to analyze the redox reaction in LSBs. For example, ex-situ SEM has been coupled with in-situ UV-Vis spectroscopy to identify soluble polysulfide species and investigate their diffusion process in the solid polymer electrolyte (Figure 20d).²³³ The electrolyte was a solid polyether-based polymer (SPE) containing LiTFSI salt. With the aid of a resistive film heater, the cells were cycled at 70 °C. This study provides insight into the formation of a sulfur passivating film on the surface of Li anodes. In addition, the occurrence of polysulfide shuttle and a high concentration of S_4 -² was found, which led to the conclusion that polymer electrolytes are not suitable in preventing the loss of sulfur compared to liquid electrolytes.



Figure 20. (a)A photograph of the in-situ UV-Vis punch cell. Figure reproduced from²⁵⁶with permission. (b)Structure of three electrode operando UV cell. Figure reproduced from ²⁵⁸ with permission. (c)Schematic view of each assembly unit of the Li–S cell used in in-situ UV-Vis spectroscopy. Figure reproduced from²⁵⁹with permission. (d) Simply modified coin cell-based in-situ UV-Vis cells. Figure reproduced from²³³with permission.

The above studies have used in-situ UV-Vis spectroscopy in reflectance mode. Since the absorption shift in reflectance mode is influenced both by the type of LiPS and their concentration that is why it is challenging to identify LiPS in this mode. While in the transmission mode, the absorption shift is dependent only on the chromophores (LiPS) and the absorption intensity represent the LiPS concentration. Therefore, in-situ UV–Vis spectroscopy in transmission mode has received the attention of the researcher in the last two decades. Recently, Het et al. used insitu UV-Vis spectroscopy in transmission mode to investigate polysulfides' electrochemical and chemical behavior.²⁶⁰ A pouch cell design with two quartz windows on front and back sides was sealed so that the beam could pass through the cell. The incident beam was transmitted through a slit (1.0 mm \times 5.0 mm) that was installed in the both working electrode and separator as well as through a larger slit (2.5 mm \times 8.0 mm) in the counter electrode to facilitate alignment and diffusion of the soluble LiPS in the slit so that it can absorb UV-Vis light of their characteristic wavelength. These studies clearly demonstrate that UV-Vis certainly represents another costefficient in-situ method that provides a great deal of insights into LSB chemistry and do not require compromise to battery chemistry.

5.5. X-ray photoemission spectroscopy

In order to gain an integrated understanding and molecular level insight of the sulfur redox reactions and subsequent evolution mechanism of the SEI layer at the Li-metal anode in LSBs batteries, Murugesan and co-workers reported the first application of in-situ XPS for a Li–S battery. The objective was to provide not only the spatially resolved chemical imaging but also elucidate

lithium polysulfides speciation via high-resolution core-level spectroscopy of the critical elements.²⁶¹ The key challenges in using in-situ XPS for LSBs are the high vapour pressures of sulfur (S₈) and the aprotic electrolyte solvents (DOL and DME). In order to overcome these issues, the authors utilized an ultrahigh vacuum compatible 1-butyl-1-methylpyrrolidinium bis(trifloromethylsulfonyl)imide ([bmpyr]+[TFSI]–) ionic liquid (IL) as a cosolvent in the electrolyte. Moreover, this kind of ionic liquid with high electrochemical stability has been reported as an electrolyte solution for LSBs that are electrochemically stable in the voltage range ($\pm 2.2 \text{ V}$).^{262,263} Ultimately, the authors claimed that it was crucial for controlling the role of the SEI layer in SBs during cycling processes. Although the experiment can be performed, being a strictly surface measurement (a few nm) greatly limits what regions of the cell can be observed such that questions will always remain as to how representative the results are of the entire battery.

6. Summary and outlook

In-situ electrochemical techniques are gaining considerable interest in secondary battery research and development due to the depended understanding they can provide, particularly when it comes to distinguishing all of the complex mechanisms competing during battery operation. Combining in-situ cells with advanced analytical instruments to acquire real-time information allows us to address a range of problems arising as a result of growing practical needs and is helping develop a thorough understanding of the electrochemical reactions in numerous battery types including Li-S batteries (LSBs). Table 1 summarizes the methods discussed herein, along with their limitations and prospects for further development of LSBs. Clearly, in-situ techniques have greatly aided the optimization and creation of more efficient battery electrodes and electrolyte materials, which has resulted in a further improvement in the overall performance of LSBs. Especially with the recent development of a third-generation synchrotron source, in-situ studies of

a cell during discharge and charge using X-ray techniques provide insight into structural changes all the way from the atomic length scales up to the macroscopic.²⁶⁴ These techniques can help track the electrochemical reaction processes by eliminating the influence and uncertainty of the post-treatment processes of the electrode materials that can occur when simpler ex-situ techniques are utilized instead.

Here, we give a detailed summary of in-situ techniques that have been applied to study LSBs and monitor the principal mechanisms involved in the complex conversion chemistry on which LSBs rely. The latest progress in many advanced in-situ techniques were highlighted. This review provides guidelines for the development of future integral electrode materials and battery architectures and the design of compatible cells within modern facilities to get insight into the performance limitations of LSBs. Despite the significant progress made in mechanism analysis by in-situ electrochemical characterizations, there are still many concerns that remain unanswered in this field. This area still faces many challenges that need to be addressed:

 In-situ characterization approaches often demand expensive facilities and sophisticated experimental setups, imposing an unacceptably high expense and inconvenience on the researchers.
The construction of an in-situ cell is a critical step in the process of in-situ characterisation. Some of the current in-situ cells are incapable of completely mimicking real battery-operating conditions. For example, in-situ TEM cells have been fabricated into a nano-battery configuration using a Li₂O layer as a solid electrolyte, but electrode/electrolyte interface information can not be accurately obtained for such systems.

3. Generally, modifying an electrochemical cell for in-situ studies limits operation to relatively low charging or discharging rates due to suboptimal geometries for optical access, large electrolyte volumes (as in pouch cells), or very long sampling times (as in NMR). The extreme example of a compromise required to perform in-situ is with TEM where in-situ methods have not been possible with the liquid electrolytes that are leading contenders for commercialization. In-situ TEM with liquid electrolytes needs to be developed. However, efforts to achieve in-situ TEM with liquid electrolytes may well prove unsuccessful (certainly in the near future), we therefore speculate than an ex-situ technique (cryo-EM) discussed herein may prove to be the way forward in terms of performing electrolytes and sulfur electrodes with CEI). The successes seen in Li metal batteries gives us optimism for this technique, even though it appears that ex-situ will be the mode to use in the foreseeable future.

4. In-situ XRD is only capable of detecting crystalline materials but is unable to identify amorphous or ultrafine particles. Thus, in-situ XRD has been normally used to monitor sulfur phase transformations in Li–S batteries (α -S₈ and β -S₈) before and after discharge and the production of crystalline Li₂S after discharge.

5. In-situ XRD studies often require synchrotron radiation and a customized cell design that enables both application and detection of the X-ray beam at a different incident beam angle. Cells are cycled at a low C rate, and XRD scans are then performed at predetermined intervals with a short enough beam angle step time to ensure that the structures do not change throughout the scan. 6. In-situ ATR FTIR is always preferable owing to its low cost, short acquisition time, and no need of a synchrotron source for monitoring the individual LiPS on the basis of the S-S vibration. However, all polysulfides show vibration peaks in a narrow range from 470 to 510 cm⁻¹, making it hard to detect a mixture of LiPS from the overlapped spectrum. 6. In-situ NMR is capable of detecting soluble polysulfides and tracking lithium dendrite stripping/plating however, it normally operates under high vacuum and is limited to nonvolatile electrolytes.

7. Though in-situ XAS provides valuable information to understand the LSBs chemistry, this technique is limited to the soft X-ray regime because of the low penetration depth of X-rays with energy below 1 keV and the severe vacuum limitations. The development of in-situ cells for soft X-ray investigations is therefore highly desirable for monitoring valence levels of most battery materials.

8. The excess electrolyte normally required for in-situ characterization techniques can significantly alter the electrochemical reaction mechanism of LSB, resulting in different characterization results. Therefore, it is important to take into account of the characterization conditions when using in-situ techniques for investigating the mechanism of LSBs.

Overall, there are certainly some compromises on battery chemistry that are required to perform in-situ experiments, but these are becoming greatly mitigated in many cases such that some of the in-situ techniques discussed herein are expected to play an ever increasing role in developing better batteries, rather than simply being satisfied with demonstrating the ability to perform the in-situ experiment at any cost. Thus, although there are many challenges, we optimistically anticipate that LSBs will realize practical application in the near future, enabled by a better understanding of the mechanisms involved. We believe that certain in-situ/operando characterization techniques will keep playing an important role towards this goal. We speculate that the path to reaching this critical goal will require the widespread use of the more accessible in-situ techniques. Whereas very challenging experiments such as cryo-EM and in-situ TEM may give important scientific understanding, it is unlikely that they will be implemented across sufficient variations in cell chemistry to make meaningful innovations to bring LSBs to commercialization. Therefore, the more accessible and complementary in-situ techniques may well be utilized more widely in such a way to bring innovations to light. For instance, Table 1 demonstrates the complimentarity of insitu XRD (long-range structures), UV-Vis spectroscopy (short range structure), and SEM (morphology) to uncover a great deal information about mechanisms in particular LSB chemistries. These methods can be implemented quite widely, such that a greater number of systematic studies looking at the fundamental impact of additives in the electrolytes may prove to lead to the final innovations required for widespread LSB implementation.

| In-situ | Function/application | Limitations | Phenomena | Prospects for |
|---------|---|--|--|--|
| techniq | | | discovered by | new |
| ue | | | technique | developments |
| XRD | Structural analysis: Monitor the long-range structure of both electrodes during cycling | Limited to detection of bulk solid phases, cannot be used to detect amorphose phases | Identified the exact position of Li ₂ S formation in the voltage curve, and the presence of solid polysulfides | This technique is mature, it is primed to be used on varied chemistries in LSBs |
| XPS | Compositional analysis, electronic structure, oxidation state | A high-vacuum testing environment; it is a surface technique such that observing all cell components is very difficult | Found the production of Li_2S at the start of the lower voltage plateau, and detection of the evolution of SEI on the Li anode surface | This remains a challenging/ex pensive system, and is likely to continue to be utilized by only a few research groups |
| XAS | Monitoring electronic structure during cycling (XANES), and structural analysis over | Limited to the use of low sulfur loading, high loading led to self- absorption | Relative rate constants of LSBs electrochemical reactions | Requires the development of in-situ cells for soft X-ray investigations |

Table 1: Summary of in-situ/operando techniques for LSBs investigations and their functions, limitations, new phenomena discovered, and prospects for new developments
| | short length scales (EXAFS) | and results in systematic errors; need access to a synchrotron | depend on the electronic structures of the LiPSs participating in the reactions | and is becoming more routine, with many synchrotrons equipped to do it. We expect wider use in LSBs |
|------------|--|---|---|--|
| Raman | Structural analysis: detect the sulfur and polysulfides by their vibrational frequencies | The signal is weak for most of the polysulfides | Carbon matrix not only support electrical conductivity but also influenced the electrochemical reactions | Cell designs are becoming simpler, wider use is expected |
| FTIR | Structural analysis: Detect the polysulfides by monitoring the S-S vibration mode | It is difficult to differentiate polysulfides from the spectra from other components | Molecular-level changes in the electrolyte salt anion in response to LiPSs speciation were observed | Wider use of this method is recommended, it is applicable to wide chemistries |
| UV– Vis | Structural analysis: Determination of soluble polysulfides both qualitatively and quantitatively during electrochemical cycling | Unable to detect Li_2S and S due to their low solubility in the electrolyte, and failed to be applied in solid-state battery system | Solvents with high donor numbers (such as DMSO) are the preferred choice as they can significantly reduce the polarization compared with low-donor numbers solvent | This is a relatively easy/affordable in-situ experiment, we expect this to be more systematically applied across LSB chemistries |
| NMR | Structural analysis: Detection of soluble polysulfides and lithium microstructures monitoring | Expensive setup and long sampling time | Investigated the evolution of sulfur species, redox reactions, and the effect of electrolyte on | A simple setup feasible with a variety of electrolytes is required |

| | | | LiPSs | |
|-----|--|---|--|--|
| | | | dissolution | |
| TEM | Morphology/structure: High-resolution morphological evolution of the solid phase sulfur and Li2S | Currently limited to the use of solid electrolyte (Li ₂ O) or ionic liquid electrolytes; beam damage is a constant concern | Formation of solid Li ₂ S in a nanoscale cell, and the morphology and degradation of Li anode | TEM with liquid electrolyte is direly needed to investigate the mechanism of promising LSBs |
| SEM | Morphology of electrodes | Large amounts of electrolyte needed | Measure the morphology of Li anode surface and its degradation during the electrochemical cycling | The cell design could be simplified, but the experiment can and should be performed on wide chemistries |
| AFM | Morphology/structure: Formation of SEI Exploring the cathode/electrolyte interfaces | The information is primarily limited to bulk volume expansion | Lithium salt in the electrolyte mediates the interfacial reactions and determines the kinetics of the LiPSs | AFM yields limited information about mechanisms, it is not expected to be utilized dramatically more than it is now |

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