The Pitfalls and Opportunities of Impedance Spectroscopy of Lithium Sulfur Batteries

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Electrochemical impedance spectroscopy (EIS) is a valuable tool, which is frequently applied to study lithium-sulfur (Li-S) batteries. However, as shown in this perspective article, there are several pitfalls associated with the measurement parameters, impedance response interpretation, and spectra fitting, which can result in dubious or erroneous conclusions. In the first part, the available information on Li-S battery impedance response is summarized and it is critically evaluated. The authors also touch on the methodology of measurements and fitting of impedance spectra, and later on systematically overview the impedance features in sections according to characteristic peak frequencies of processes, going from the highest to lowest. Finally, specific test instructions that ensure the use of EIS’s full potential are listed and promising future directions are discussed. These range from an increase in the use of model experiments, replacement of arbitrary equivalent circuit fitting with physics-based impedance models, and coupling of the technique with other analytical tools.

1. Introduction

Lithium-sulfur (Li-S) sulfur batteries have attracted a wide-ranging appeal in the past decade, with a myriad of research published focusing on mechanism understanding and materials’ improvements. The reason for this is in the promise of technological advances due to their low cost and high theoretical performance. Despite this, this battery system still lacks the ultimate solution(s) for achieving the promised capacity and stability.

In terms of the currently accepted mechanism pathways, it is considered that sulfur is reduced to polysulfides[1–3] and eventually to Li2S.[4–6] The polysulfide species are usually soluble in the electrolyte, although the solubility varies depending on the exact electrolyte composition employed.[7–11] Short chain polysulfides, such as Li2S2 and Li2S are less soluble and precipitate from the electrolyte solution upon their formation.[12,13] Sulfur and Li2S are electronically non-conducting materials,[14] necessitating conductivity additive inclusion in the cathode and resulting in possible passivation upon redeposition from polysulfides in solution. Polysulfide solubility can also prove problematic, since it means that the species can transport through the separator, reach the anode, and are lost in unwanted side reactions.[15]

Trying to determine which of these processes is the most limiting is no easy task and requires a systematic use of selective and accurate analytical methods. When it comes to electrochemical systems, the most obvious choice is electrochemical impedance spectroscopy (EIS),[16–20] which offers a unique ability of separation of processes based on their time (frequency) scales. Although impedance spectra are relatively easy to measure, their interpretation and process decoupling often prove difficult. This perspective paper will provide a survey of the available information on EIS of Li-S batteries, critically evaluate the explanations and offer possible future research directions.

2. Impedance Spectra Measurement, Fit, and Interpretation

The measurement of an impedance spectrum consists of applying a small amplitude alternating voltage (or current) and measuring the resulting response from the system. By taking the resulting sinusoid and obtaining its amplitude and the phase shift between the input and output signal, we obtain the impedance spectrum.[21] The data are plotted as one point for each frequency of the alternating current signal used during the measurement. There are several possible representations of the data, but in the field of batteries it is usually drawn as a Nyquist plot, that is, as minus imaginary part of the impedance (−Im(Z)) versus the real part of the impedance (Re(Z)). In this case, the phase shift and the absolute impedance are the angle and length, respectively, of the vector going from the origin to the measured frequency point.[22]

The chosen input signal amplitude needs to be large enough to obtain a spectrum which is smooth and without much interference from noise, while at the same time, small enough to not change the electrochemical state of the system. A typical practical range found in battery research is between 5 and 10 mV.[22,23]
The frequency range is usually limited with the instrument’s capability in the high frequency limit (hundred kHz to several MHz is common), while the low frequency limit depends mostly on the stability of the system. Namely, a single-wave impedance spectrum measurement of each point takes at least as long as a single wave. Thus, going low in the frequency range means long measurement times. Since the system can change during this measurement (due to passive layer growth, self-discharge, and other unwanted side reactions), the spectra can be distorted and any subsequent fitting or other analysis wrong. Furthermore, in their low frequency limit the measurements are closely related to direct current measurements, which means that a system change is likely inevitable. Nevertheless, a limited frequency range also provides limited information. For example, if the direct current measurement of a quasi-linear system suggests a 1 kΩ total resistance and our limited frequency range impedance spectra provide contributions of only 100 Ω, the lower frequency contributions are not negligible, suggesting extended frequency measurements are needed to fully grasp the mechanism of operation. There exist alternative methods, such as multi-wave impedance measurement or Fourier transform EIS, which can give low-frequency information in a faster way than the conventional impedance measurements. However, it should be always considered that a shorter measurement time leads to larger errors in the obtained signal.

In the field of batteries, impedance is usually measured at open circuit voltage (OCV), when the cell is stable enough to ensure a reliable measurement. If we want to change the state of charge (SOC) of the cell, the cell is usually first discharged/charged to the desired SOC, the current stopped for a short period to stabilize cell’s voltage and only then the impedance spectrum is measured. Although in this case the measurement is stable, it suffers from at least two drawbacks. One is that the impedance of certain battery processes is different if under load or not. A typical example is the charge transfer impedance which is expected to drastically change with applied voltage/current as it is linked to the non-linear Butler–Volmer equation. In practice, this means that the spectra measured at OCV, although smoother, will inevitably be different than those measured under load. Furthermore, although paramount for ensuring a stable measurement, we should not disregard that the rest period can inflict some change to the cell impedance, since side-reactions do not stop under OCV conditions. A completely different option is the so-called dynamic impedance, where a small amplitude excitation signal is superimposed on the direct current used for SOC change. In this case, the impedance is measured simultaneously as the cell’s SOC is changed, avoiding the issues previously described for OCV EIS measurements. Not without disadvantages, the smoothness and the reliability of the dynamic impedance spectrum depend on the stability of the voltage in the duration of the spectrum measurement. If there were no large deviations (roughly below 10 mV), then the spectrum is considered to be dependable. The chance of voltage drift is higher if measurements are long, resulting in another handicap of the dynamic impedance—low frequency measurements are usually not possible.

A third option, which, to the best of our knowledge, has not yet been applied to Li-S batteries, is hybrid EIS. In this mode, the amplitude of the applied current input signal is continuously adjusted to ensure that voltage is not extended beyond the linear range.

Besides appropriately choosing the input parameters of the measurements, the choice of cell geometry is also significant. Measuring impedance spectra of two electrode full Li-S battery cells will always give the impedance contributions of all parts of the cell. If we are only interested in understanding the interactions between sulfur species, the non-negligible contribution of metal anode might obscure them. These cells also include the issue of self-discharge or lithium metal passivation. Measuring symmetrical cathode–cathode cells can help with that, but such geometry lacks the option of changing the cell’s SOC and suffers from the drawback of limited electrode stability, if cycled electrodes are used for symmetrical cell assembly. It is therefore advisory to measure both cell geometries, to scrutinize the acquired data and to only use that which is clearly proven to stem from the electrode we are interested in. Three electrode cells are a common way of avoiding these obstacles, but can include serious errors in the measurement that might not be detected. The usual reference electrode used in Li-S battery cells is lithium metal. Although probably the best of the simple options available, it is far from a reliable reference electrode. It certainly gets passivated itself and any side reactions of polysulfide species such as common for the lithium anode, cannot be avoided for it either. Besides Li, lithiated gold electrodes were also investigated in the Li-S battery system and applied to study Li metal impedance in Li-ion batteries. Another issue is the electrode geometry, which commonly produces spurious impedance features, such as middle frequency loops, which are not seen in two electrode measurements. With all these various aspects considered, although they take longer and require for several measurements in different cell designs, two-electrode impedance measurements of Li-S cells surpass three-electrode cell experiments in their reliability for many experimental cases. We therefore suggest that the latter be avoided in simpler studies and that their drawbacks be kept in mind and explained should they be employed. A simple reliability measure is to first record impedance spectra between the working (WE) and the counter electrode (CE) in two electrode mode and compare that to three electrode measurement of EIS of both WE and CE.

After the measurements have been conducted, impedance spectra contributions are then usually evaluated and interpreted, which frequently involves fitting with an equivalent circuit. Due to possible ambiguities, it is strongly recommended that at this point one envisions which processes are taking place in the cell in question. For example, if we have a porous carbon cathode in contact with a polysulfide solution in the electrolyte, we expect a limited number of possible impedance contributions. Going in the usual direction from high to low frequencies, these are: a) electrolyte resistance, b) charge transfer resistance for the reaction of a given polysulfide on the carbon surface, b’) transport of polysulfides through the porous carbon, and d) the diffusion of polysulfides through the separator. An example of an expanded impedance spectrum, containing all of the contributions of the mentioned physical processes is shown in Figure 1a. In this representation, the time constants of various processes were adjusted so their impedance contributions in the spectra are resolved.
Figure 1. Example of expanded impedance response generated with transmission line models. Such expanded graphs are unrealistic and assume that the time constants for different processes are far apart. This representation allows for visualization of various processes that can be expected in measurements of Li-S cells impedance response: a) simulated spectrum of symmetrical porous carbon cathode with polysulfide catholyte simulated with a transmission line model from ref. [43]; b) simulated spectrum of symmetrical lithium metal anode cell simulated with a model from ref. [44]; c) spectrum of an asymmetrical Li-S battery cell simulated by combining the transmission line models from (a) and (b).

Depending on the properties of polysulfide species of different chain length, there might only be one species dominant at a given stage—producing one charge transfer contribution and two diffusional contributions, or there might be several, multiplying the impedance arcs.

Similarly, the impedance of the lithium anode can be divided into its respective contributions (expanded spectrum shown in Figure 1b). These pertain to the e) electrolyte resistance, f) migration of Li$^+$ ions through the compact solid electrolyte interphase (SEI) layer, g) diffusion of ions through the porous SEI layer, and h) the diffusion of ions through the separator.

In some more complex models, charge transfer reaction at the interface between bulk Li metal and compact SEI$^{[45]}$ or desolvation of Li$^+$ ions when entering the compact SEI$^{[46]}$ are also included.

As explained earlier, complementary symmetrical cell and full cell measurements should always be measured to get reliable basic information. One must consider, though, that the full cell impedance is not just a simple sum of cathode and anode contributions, since the presence of anode changes the cathode’s contribution and vice versa. Anode active ions (Li$^+$) contribute to the double layer on the carbon cathode and the cathode active ions (polysulfides) to the double layer on the Li metal anode. Although the Li metal is passivated through the formation of the SEI, polysulfides are still reduced at the Li interface (a process contributing to the shuttle effect), which produces a large low frequency arc. For more information, the reader is referred to ref. [47] The impedance contributions expected in a full Li-S battery cell spectrum are therefore the ones corresponding to the aforementioned processes attributed to the respective half-cells and i) an additional contribution due to the interaction of polysulfide species with the Li metal anode. All of these are included in the expanded spectrum shown in Figure 1c.

After this mental exercise, the possible theoretical contributions need to be connected to the measured ones. This is not straightforward, since a lot of the impedance features overlap. The step of assignation of impedance features to physical processes is frequently carried out hastily, by settling for the already published hypotheses and skipping to the fitting of spectra. Nevertheless, we find it paramount to obtaining trustworthy information on the researched system, so we will devote some space for explanation of this step. For the additional analysis, some basic physics’ laws come in handy. First, the migration of ions through the separator is always seen as a resistive intercept in the high frequency part of the spectra, making it the easiest contribution to evaluate. Similarly, the peak frequency, $\nu_0$, of a diffusional connection is linked to the thickness of the layer, $L$, through which diffusion is taking place and the effective diffusion coefficient, $D$, of the ion in question ($\nu_0 = \frac{2\pi D}{L^2}$). If we have an estimate of the size order of both of those parameters, we can calculate the frequency where this contribution is expected and rule out any other, that are in an exceedingly different part of spectra. Further in-depth analysis nevertheless requires additional experiments through varying the cell geometry. If we are still unsure about which contribution is due to transport through the separator, we can measure the impedance of a cell with a varying number of separators and observe the trends in the spectrum. Only the contributions connected to the thickness of them will change, making them easier to pin-point. A similar experiment can be conducted with changing charge transfer contribution by varying polysulfide concentration, or the contributions due to transport through the carbon cathode through varying its thickness. Temperature variations are also a good idea, since different processes change differently with varying the temperature. These series of experiments are time consuming, but are probably the only means of providing an accurate interpretation of impedance spectroscopy data. They are also very rarely done in the available published research papers, which casts significant doubt whether the conclusions of the latter are to be dependent upon.
After as many contributions as possible are reliably connected to their underlying physical processes the last step is fitting of the measured spectra to an appropriate model. In most cases authors resort to fitting with an equivalent circuit which, in the best case, reflects the physical processes mentioned above. As with previous phases, this point of impedance analysis can also lead to questionable, if not misleading, results. In fact, it is very hard to fit complex spectra that contain various contributions which usually significantly overlap and additionally contain unpredictable artefacts. Besides rough surfaces producing depressed non-ideal semi-circles (i.e., arcs), the usual problem is overparameterization. An impedance spectrum of a symmetrical porous carbon cathode cell with polysulfide catholyte, for example has several expected impedance contributions but they are hardly resolved. In fact, what we observe is a resistive intercept, a small middle-frequency depressed arc and a larger lower frequency one. If we include all the expected physical processes as resistors and capacitors into an equivalent circuit, we end up with at least 12 parameters. The fit to the measured data will undoubtedly be excellent, but there is a significant possibility that at least some of the parameters will be wrongly assigned and/or evaluated.

One has to, therefore, be wary of using equivalent circuit models. In some cases, in particular in simple cell geometries, where contributions are few and the system well controlled, they in fact can be imperative to prove the origin of impedance features. An example is a symmetrical planar glassy carbon cathode cell with well-defined polysulfide catholyte. Impedance spectra of these cells have only one intercept and two arcs which can be well fitted with a Randles circuit model which offers an accurate physical description of these features: electrolyte resistance, one charge transfer reaction arc, and one Warburg element due to diffusion of active species. As the physics in such basic flat electrode configuration is rather simple, there is also a high probability that a corresponding simple circuit (Randles circuit) provides the correct description of those processes. For more complex impedance spectra that are usually obtained in the case of more realistic porous electrodes, the equivalent circuit model fits are usually a lot less useful or even entirely inappropriate. In such cases it is strongly recommended to use one of the several physics-based approaches to modeling of impedance spectra: analytical solutions (where they exist), numerical methods, or physics-based transmission line models.

Bearing in mind the advantages and drawbacks of various approaches to impedance spectroscopy analysis explained above, let us examine typical data available for Li-S battery cells.

3. Electrolyte Resistance

The resistive intercept seen in the high frequency part of the spectrum is often termed as “electrolyte resistance.” This contribution stems from the migration resistance of ions present in the electrolyte through any porous layers present in the cell (excluding migration through porous electrodes where reaction can occur). This is usually considered to be the separator, but it should be kept in mind that it can also be passive layer formations. These are usually several orders of magnitude thinner than the separator, so their contribution is close to negligible. In some cells, nevertheless, they can be thicker, in which case their effect should be considered.[45]

In Li-ion batteries, the value of electrolyte resistance remains similar throughout their discharge and charge, changing mostly due to passivation reactions consuming the salt or the solvent and changing the electrolyte’s properties. With Li-S battery, on the other hand, polysulfide formation significantly alters the electrolyte properties. Namely, through their dissolution, the conductivity and viscosity of the electrolyte significantly change. This is seen as an increase in electrolyte resistance at the beginning of discharge, reaching a peak in the transition phase between the upper and lower voltage plateau (Figure 2). That is where the concentration of polysulfides reaches a maximum, before Li₂S deposition begins.[40,42,48,49] Through the low voltage plateau the resistance decreases, although it never reaches the initial value, suggesting that some dissolved polysulfides are permanently lost in the electrolyte, that is, stored in the separator pores. The electrolyte resistance trend continues with this middle of discharge (or charge) peak trend throughout cycling.

4. Anode Impedance

Lithium metal is usually used as an anode in Li-S battery cells. Due to its low weight, low standard potential, and a resulting very high specific capacity, lithium metal anode has been researched for decades for use in various battery systems. In general, the anode’s mechanism of operation in Li-S batteries is similar to that known from other battery types. The metal passivates due to contact with the electrolyte, consuming salt(s) and solvent(s) to form a Li⁺ ion conducting layer on its surface called the SEI.[50–52] The composition of this layer is complex and not fully resolved, with most hypotheses explaining it as of double nature—a thin (only up to a few nm) compact layer directly on the surface of bulk Li and a thicker (up to several hundred nm) porous layer on top.[44] The first one only allows for migration of Li⁺ ions through the means of solid conduction. By contrast, the porous part of SEI strongly favors the transport via diffusion through electrolyte in pores. The impedance mirrors these processes well. Non-cycled Li metal anode usually exhibits a depressed arc with up to several hundred Ωcm² size and a peak frequency of 1 kHz, attributed to migration of ions in the compact layer. Additionally, non-cycled lithium also features several smaller arcs at lower frequencies associated with the diffusional processes through any porous layers present (primarily porous SEI and separator, Figure 3a).[44]

Upon stripping and subsequent plating, lithium metal anode forms non-homogenous depositions, in the worst case dendrites, which increase the electrode’s surface area and cause possible short circuiting. Due to its passivation, further consumption of the electrolyte takes place.[53–56] Because these formations can be very thin, they can also get completely passivated, forming the so called “dead lithium,” which can cut off the contact between the bulk Li and remaining metal further toward the separator. When dendritic formations cover the surface, the impedance of the lithium metal anode changes in order to account for the differences in the transport of ions through the newly formed porous structures. “Dead lithium”
layer, if present, can be imagined as an additional separator with generally different properties (porosity, tortuosity, diffusivity, transport number etc.), while “active lithium” dendrites essentially mean that the metallic part of the electrode is not planar anymore, but rather porous. This changes the impedance response by adding additional low frequency arcs corresponding to diffusion in the dendrite structures. The characteristic frequency of these is mainly dependent on the thickness of the layer and its porosity although other features such as pore size, pore size distribution, and tortuosity also affect this characteristic frequency to some extent. Due to similar thickness and porosity of various porous phases (active and dead dendrites, separator) their corresponding Warburg features tend to blend into one complex depressed low frequency arc. The porous nature of the electrode also shows in impedance as the high frequency contribution attributed to interactions with the active lithium pores starting with a 45° angle (Figure 3b,c).[44]

The same situation in terms of the impedance response of non-cycled and cycled lithium metal anode generally holds for Li-S battery cells. One significant difference is in the interaction of dissolved polysulfides with the metal anode surface. Upon contact with Li, polysulfides are reduced and precipitate in the form of Li2S on its surface.[57–60] Lithium sulfide is incorporated in the passive layer, slightly changing its properties. If the concentration of polysulfides is high, the metal surface is consequently covered with a rather thick layer of the sulfide deposit. Albeit electronically non-conductive, the antifluorite structure of Li2S allows for sufficient Li+ ion conductance. The sulfur species in the passive layer also positively influence the process of redeposition of Li+ ions and carbon cathode redox interaction with sulfur species. When full cell impedance is considered, one must consider that the cathode active ions (polysulfides) also interact with the Li metal anode and the anode active ions (Li+) interact with the carbon cathode. This can be graphically shown as different elements on terminals of a transmission line model. Since both rails (i.e., one for polysulfide ions and one for Li+ ions) of a transmission line circuit for the full Li-S cell end with a blocking element, the resulting impedance spectrum is also blocking in nature.

5. Polysulfide Charge Transfer Reaction

The charge transfer reaction of polysulfides on the carbon cathode has been identified through simplified planar cathode cell experiments (Figure 4)[62,63] and temperature variations.[49] The contribution has a peak frequency in the range of a few tens of Hz and a size order of 1 to 10 kΩ cm2 of available active carbon cathode surface area, depending on which polysulfide solution where no side reactions, for example, self-discharge or lithium passivation, take place. The size of the arc increases or decreases or even oscillates, owing to complex redox reactions between polysulfides in solution. Namely, since all of them are active redox species, they co-proportionate and disproportionate, changing the cell’s impedance. Although the exchange current density of various polysulfides is not identical to each other, the range isn’t broad, spanning roughly an order of magnitude. In other words, the difficulty of the redox reaction of different polysulfide species is similar to one another, suggesting none is the prevailing limiting step.[62]

The most common carbon material in Li-S batteries is mesoporous carbon, which has a high surface area, producing electrodes with 1000–10 000 cm2 of active electrode surface per areal electrode surface. If we consider this together with the previous determination of the size of the charge transfer contribution, we can deduce that it is in fact very small. Since it is only a few Ω in size, it is far from being considered a process constricting the performance.[13,43]

Figure 2. Evolution of electrolyte resistance through first discharge in various studies of Li-S battery cell impedance: a) dependence of the $R_0$ (electrolyte resistance) and $R_1$ (first arc resistance). Reproduced with permission.[42] Copyright 2013, Elsevier, and b) evolution of $R_1$ resistance values as a function of SOC and galvanostatic potential curve. Reproduced with permission.[40] Copyright 2020, Elsevier.
During discharge of Li-S cells, the reduction of polysulfides results in the deposition of Li$_2$S. This process has been commonly blamed for limiting the performance of the cells through passivation.$^{[64–72]}$ In light of recent research, the mechanism is a lot more complicated. Deposition of Li$_2$S both depletes the concentration of polysulfide reservoir in the electrolyte and covers the cathode surface with an electronically non-conductive substance. Both of these processes change the charge transfer resistance. The polysulfide depletion increases the resistance and decreases the peak frequency, while passivation increases the resistance while keeping the peak frequency the same, since the capacitance also changes due to a change in the electrode surface area.$^{[13]}$

If Li$_2$S precipitates directly through electrochemical deposition, one would expect it to form a thin (only a few nm) quasi-1D layer due to its electronically insulating properties.$^{[73,74]}$ Scanning electron microscopy (SEM) images on the other hand, show that the precipitate is several orders of magnitude thicker (up to µm in size) and porous.$^{[70,75,76]}$ Furthermore, extensive experiments on model cells done through addition of fresh polysulfides and in cells with severely limited cathode surface area, have shown that it is in fact the depletion of polysulfide species that accounts for most of the increase in the charge transfer resistance and not the passivation process (Figure 5). The reason for this is in the mechanism of deposition of Li$_2$S. Due to its structure, the electrode surface is not passivated, since pores allow for the transport of active species toward the electrode.$^{[13]}$

6. Polysulfide Diffusion

Before the last dip in operating voltage signaling the end of discharge, the diffusional contribution of polysulfides is
somewhere on the order of $1 \text{k} \Omega \text{cm}^2$ of electrode area in size with a peak frequency of around a mHz (depending on the electrolyte employed and separator properties), making it the largest contribution and the bottle-neck process.\cite{43}

We have already pointed out that toward the end of discharge, the charge transfer impedance contribution grows, mostly due to depletion of polysulfide species precipitating in the form of Li$_2$S. The decrease in the concentration of the redox active species toward the end of discharge also increases the diffusional contributions. Furthermore, Li$_2$S precipitates in a thick, porous layer, adding additional, different diffusional impedance contribution due to polysulfide species transporting through its thickness to reach the carbon cathode. The question at hand is whether the charge transfer resistance grows so much in size during the final parts of discharge that it increases in size beyond that of the diffusional contributions, or do these still prevail?

Using impedance spectroscopy for that determination proves difficult. Namely, using OCV EIS measurements in points of charge, where the cell is under large strain is unreliable, since leaving it for a few minutes to relax will result in a completely different cell state. Furthermore, dynamic impedance cannot be used due to rapidly changing potential, which quickly drops around half a volt in size beyond that of the diffusional contributions, or do these still prevail?

7. Perspective and Conclusions

Impedance spectroscopy measurements are a paramount element in developing and studying novel types of battery systems. Their application to Li-S batteries has proven to provide a wealth of information on the processes taking place in the cell. Dissolution of polysulfides was shown through the change of electrolyte resistance while their inherent complex equilibria through disproportionation and co-proportionation reactions became evident in simplified geometry cell’s impedance response. Impedance analysis enabled the determination of the limiting process, the diffusion of polysulfide species in the separator pores. The impedance spectroscopy experiments also shed light on the complex mechanism of the deposition of the final discharge product, Li$_2$S, proving that the material does not, in fact, passivate the electrode surface.

Importantly, this power of impedance spectroscopy is only possible when the measurements and the interpretation of the data are done exceedingly carefully while taking fully into account the underlying physical–chemical processes. Far too many studies use impedance measurements only to embellish a paper with another added technique. Performance experiments usually conducted in such studies are not well suited for non-trivial impedance interpretation, since little attention is paid to possible artefacts in data acquisition and the proper process of connection of impedance contributions with physical processes behind them. This can, and often does, result in erroneous conclusions, which can spiral into a search of system improvements due to a supposed limiting process, while in fact, the bottle neck of system operation is something else entirely. As discussed in this paper, in Li-S batteries an example of such a misinterpretation was the increase in impedance during discharge which had been connected to non-conductive material deposition and blocking of available cathode surface area. On the contrary, in depth impedance analysis of various model experiments showed that the increase in impedance size was actually due to depletion of active polysulfide species and increasing difficulty in their transport from the bulk of the separator to the electrode.

Throughout this manuscript, pitfalls of impedance measurements and interpretation of acquired data were continuously
emphasized. Of course, it is equally important to showcase good practices and propose possible future directions. Let us therefore systematically summarize specific test instructions. Symmetrical electrodes (or to a lesser extent reference electrodes, see the discussion in the last paragraph) should be employed to determine impedance contributions of different electrodes. Studied system should first be simplified as much as possible to reduce the complexity of the response. Here the main goal is to collect reproducible data that prove unambiguously the main processes occurring in the measured system which are then captured into a reliable physics based model. Only then it is reasonably to change the system (gradually, if necessary) toward the actual practical system of interest. An example is using planar electrodes before measuring realistic

Figure 5. Determination of the effects of passivation and depletion upon deposition of Li$_2$S in Li-S batteries. a–c) Reproduced under the terms of CC-BY 4.0 license.[13] Copyright 2019, The Authors, published by American Chemical Society. Schematic representation of the conducted experiment with shown conditions at the surface of GC electrode and the corresponding measured impedance spectrum of: a) pristine GC|catholyte|Li cell; b) GC(Li$_2$S)||Li cell after prolonged discharge with Li$_2$S deposit and depleted electrolyte; c) the same discharged GC(Li$_2$S)||Li cell with a Li$_2$S deposit, where fresh catholyte was added.
porous electrodes, or employing polysulfide catholyte with controlled concentration rather than starting with elemental sulfur and discharging the cell. Other parameters that can be systematically controlled/varied in order to understand the physical processes all the way from the simple to complex realistic cells are: cell geometry, nature and concentration of active species, thicknesses of various layers, temperature, etc.

In terms of fitting and simulations aiding the interpretation of impedance spectra, physics-based impedance models have been meticulously developed in the last years, showing superior output in regards to the acquired impedance knowledge when used. This suggests that their application needs to be expanded. The use of equivalent circuit fitting as a means of impedance spectra analysis should therefore be limited only for cases where identification of physical processes behind impedance features has already been completed. As suggested, specially dedicated model experiments are needed for this purpose, where systematic variation of cell components and measurement parameters is employed.

In Li-S battery research, there are still several missing pieces of information in regards to their mechanism of operation. These are mainly connected to what happens during recharge and through prolonged cell usage. Furthermore, the mode of operation of particular Li-S battery designs, such as those employing specific electrolytes, is not well understood. Examples of such systems are those that use electrolytes where polysulfides are sparingly soluble (e.g., fluorinated solvent electrolytes) or a combination of ultra-microporous carbon cathodes with carbonate-based electrolytes, which supposedly work on a quasi-solid-state principle. Application of in-depth impedance spectroscopy studies aided with simulation of spectra with physics-based models would doubtlessly advance the know-how and help to resolve the challenges presented.

There are also other challenges associated with lithium metal anode operation or its improvement through various protective surface coatings. A typical example where EIS can be of significant help is an improvement of understanding how a particular modification of the separator structure changes the transport of species. Similarly, one could use the impedance technique for determining how the morphological features of cathode surface and pores affect the transport and reaction of polysulfides. All of these issues can even better be solved by coupling the impedance spectroscopy with other analyses. Namely, many parameters used in impedance analysis but can only be provided by other techniques. Examples are data related to morphology, particle size distribution and thickness (scanning electron microscopy,[44] focused ion beam–scanning electron microscopy[13]), atomic scale structures (transmission electron microscopy), surface roughness and conductivity (atomic force microscopy[42]), chemical composition and structure (X-ray photoelectron spectroscopy,[27] X-ray diffraction,[78] X-ray absorption spectroscopy, nuclear magnetic resonance,[79] infrared spectroscopy, and Raman spectroscopy–combined with EIS to study Mg-S batteries[88], weight (electrochemical quartz crystal microbalance), or electrolyte properties and species (viscosity measurements,[81] liquid chromatography, and ultraviolet and visible light spectroscopy[63]). Either ex situ, in situ, or operando, combining impedance spectroscopy measurement with different chemical or morphological investigations both helps to validate the impedance model and gives further insight into the mechanism of operation.

In terms of advancements of the impedance technique itself, the first important research topic needing further scientific progress is the reference electrode development. There have been some recent advances using lithiated gold electrodes,[97,38] while we would wish for more dedicated research on improving and defining systems for use with one or more reference electrodes. Second, more emphasis should be put on dynamic impedance measurements, which have the unique ability of probing the impedance during the actual charging/discharging process, that is, during change of SOC. For this, two existing problems necessitate solutions: i) the experimental issue of a continuous change in composition during charge/discharge process which means that the system is not stationary during the measurement itself and ii) further development of theoretical tools that will be able to capture the non-stationarity in combination with non-linearity of battery cells during charge/discharge. Other future directions we foresee are related to implementation of hybrid EIS,[13,34] Fourier transform EIS[25–27] and automation/high-throughput[82] impedance measurements. Each of these approaches could contribute either more accurate or additional information about the electrochemical processes taking place in lithium sulfur batteries, a battery system that is particularly challenging due to the presence of unusually large number of active redox species (polysulfides) the nature and concentration of which is difficult to control due to their extreme tendency to disproportionate.

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Conflict of Interest

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