**A Highly Sensitive Electrochemical Sensor of Polysulfides in Polymer Lithium-Sulfur Batteries**

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**Abstract**

A novel and highly sensitive electrochemical sensor is used here to detect polysulfides as intermediates formed during cycling of a solid polymer lithium-sulfur cell. The formation of polysulfides is found to produce dramatic changes in the shape and magnitude of the voltammetric current of the sensor. Impedance analysis is also applied to quantify electrochemical properties such as charge-transfer and Warburg resistances of the polysulfide species. This new experimental set-up enables a rigorous analysis of the electrochemical properties of polysulfides and sulfur species, and it is used here to elucidate the fundamental cause of the effect of the choice of lithium salt (LiTFSI or LiFSI) on solid polymer Li-S cell performance.

**Introduction**

Solid polymer Li-S batteries can potentially deliver a very high energy, of more than ca. 800 Wh/kg at a cell level, which is almost three times higher than current Li-ion batteries.1 Furthermore, sulfur is cheap and environmentally friendly, and solid polymer electrolytes enable a safer operation than liquid electrolytes, as well as higher gravimetric energy density.1, 2 Consequently, the interest in polymer lithium-sulfur electrolytes has grown markedly in recent years, but progress in understanding of the reaction mechanism has been limited.

Impressive performance improvements have been achieved with solid polymer Li-S batteries.2 Cairns and coworkers3 showed that poly(ethylene oxide) (PEO) Li-S cells could achieve nearly the full theoretical capacity of 1672 mAh/gS, although at very low C-rates. Major improvements in rate capability and capacity retention with cycling were later demonstrated via incorporation of inorganic particle fillers in the polymer electrolyte, which increase the polymer conductivity and the lithium metal anode interfacial stability4-10 and, also, using advanced carbon structures and metal-organic frameworks.11-13 The choice of the lithium salt contained in the polymer electrolytes has also been shown to be critical. Use of alternative lithium salts such as LiTNFSI,14{Ma, 2016 #54} LiFSI,15 LiFTFSI,16 LiN3,17 LiC(CN3),18 and LiDFTFSI19 produced remarkable improvements in cycling stability and sulfur utilisation, which were explained by the formation of more stable and protective lithium metal anode/polymer interfaces. Unfortunately, the number of techniques available to directly prove the reaction mechanism in solid polymer Li-S cells is very limited. In order to demonstrate the mechanistic origin of the improvements in performance, and more generally, to advance the fundamental understanding of the reactions required for the rational battery development, incorporation of analytical techniques able to monitor the reactions in polymer Li-S batteries is necessary.

Whilst a wide variety of techniques have been applied to elucidate the reaction mechanism of Li-S batteries with liquid electrolytes, including XAS, UV-vis, Raman, NMR, HPLC, etc., as discussed in recent reviews,20-22 the fundamental study of polymer Li-S batteries has been scarce. Zaghib and coworkers23 used operando SEM and UV-vis spectroscopy to study the transformation of solid sulfur into soluble polysulfide species, and vice versa, during discharge and charge, respectively, of a polyether polymer Li-S battery. Balsara and coworkers u{Wujcik, 2015 #20}sed XAS24-26 to characterise the various polysulfide species formed during the discharge of a polystyrene-poly(ethylene oxide) diblock copolymer (SEO) Li-S battery, and X-ray microtomography27 to monitor structural changes with cycling. Wan and coworkers28 used real-time optical microscopy, and ex-situ XPS and Raman to study the degradation of a Li-S battery with a polymer-ceramic composite electrolyte made with poly(ethylene oxide) and Li6.75La3Zr1.75Ta0.25O12. The present study demonstrates, for the first time, the development of an in-situ electrochemical sensor for the direct detection of polysulfide species that are formed in polymer Li-S batteries.

The mechanism of ion transport in solid polymer electrolytes is very different than in liquid electrolytes. Polymer electrolytes are a solid solution of a salt (for instance, a lithium salt) in a polymer (for instance, PEO). Lithium cations are complexed by ether oxygens in the PEO chain, and their transport is related to the motion of the complexing segments of the PEO chain.2, 29-32 The low dielectric constant of PEO limits the degree of dissociation of the lithium salt, producing the formation of ion aggregates, but still, reasonably high conductivities can be obtained by increasing the temperature above room temperature. In application for Li-S batteries, polymer electrolytes are expected to exhibit low solubility and diffusion of polysulfide species,29 thus they are very well suited to suppress the problem of polysulfide shuttling, which decreases the practical capacity and hampers the rechargeability of Li-S batteries.33 Polymer electrolytes made by dissolving lithium polysulfides in PEO or SEO block co-polymers showed much lower conductivity than the same polymer electrolytes made with an inert lithium salt (LiTFSI),34, 35 showing that, indeed, transport of polysulfide species in the polymers is slow. On the other hand, the low polysulfide solubility will also result from the high lithium salt concentrations used to prepare the polymer electrolytes, where typically the molar ratio of lithium cations to the ethylene oxide unit is of the order of 1:20.2, 29-32 Highly-concentrated liquid electrolytes have similarly been shown to suppress polysulfide dissolution in Li-S batteries, thus suppressing polysulfide shuttling and consequently, improving rechargeability and cycle life.36, 37

In this work, we detect, for the first time, the polysulfide species formed during the operation of polymer Li-S batteries using an electrochemical sensor. Experiments were performed using solid PEO electrolytes and PEO-sulfur composite electrodes containing either LiTFSI or LiFSI as the lithium conductive salt. The choice of lithium salts is inspired by the work by Judez et al,15 who demonstrated a dramatic improvement in performance of polymer Li-S cells containing LiFSI instead of the more popular LiTFSI salt, which was ascribed to the higher stability of the lithium metal anode/polymer interface. A glassy carbon electrode is used here as an electrochemical sensor, based on our previous work in liquid electrolytes38 that demonstrated the high sensitivity of glassy carbon, which was not found in other candidate electrode materials (aluminium, copper, stainless steel, etc.). Using voltammetric and impedance measurements, this work demonstrates the high sensitivity of the glassy carbon electrochemical sensor for the detection of the polysulfide reaction intermediates formed in the pathway of Li-S battery reactions in solid polymer electrolytes. It is also shown that the polysulfide species undergo a fast electrochemical process centred at ca. 2.45 V vs. Li+/Li, followed by a more sluggish electrochemical reaction at around 2 V vs. Li+/Li. The charge-transfer resistance of the former process is found to be 13-14 Ω cm2, based on impedance measurements. The electrochemistry of the polysulfide species is remarkably similar, regardless of the lithium salt (LiTFSI or LiFSI), thus supporting the hypothesis that the improvements in polymer Li-S cell performance with LiFSI originate at the lithium metal anode. Additional measurements were done with cells containing only the glassy carbon sensor and the PEO-sulfur composite electrodes, with no lithium electrode, in order to assess the effect of the lithium salt on the electrochemical behaviour of elemental sulfur dissolved in the polymer electrolyte, and again, the same results were obtained with the two different lithium salts. This further corroborates that the difference in performance of LiFSI and LiTFSI in polymer Li-S batteries is caused by different behaviour of the lithium metal anode/polymer interface, since the electrochemistry of sulfur and polysulfides at the cathode is the same regardless of the lithium salt. More generally, the new electrochemical sensor here developed is shown to be a powerful tool for the elucidation of the reaction mechanism of polymer Li-S batteries, since it enables the accurate and direct detection of polysulfide intermediates.

Experimental

 Cells were constructed with either two or three electrodes, i.e. without lithium or with lithium. Figure 1b shows the details of the cell design with two electrodes. As in our previous work38, 39, a glassy carbon electrode (3 mm diameter, type 2, Alfa Aesar) is embedded in a 1-inch diameter borosilicate glass disc attached to a glass tube which fits a standard 1 inch ‘Swagelok’ cell. The glassy carbon electrode serves as the working electrode. A poly(ethylene oxide) (PEO) membrane (25 mm diameter) with either LiFSI or LiTFSI is used as the polymer electrolyte. On the other side of the cell is a disc-shaped sulfur-PEO composite electrode (11 mm diameter) on top of a stainless steel current collector. The sulfur composite electrode is used as the counter-reference electrode.

Figure 1a shows the details of the cell design with three electrodes. In this case, an additional, ring-shaped lithium electrode (20 mm outer dimeter, 10 mm inner diameter), is included on the same side as the sulfur-PEO composite electrode. The sulfur and lithium electrodes are arranged concentrically on top of a special stainless steel current collector, which contains an embedded PEEK tube to maintain electrical isolation between these electrodes. The sulfur composite electrode can be discharged by connecting the cell in a 2-electrode configuration with the sulfur composite electrode as the working electrode and the lithium ring electrode as the counter-reference electrode (leaving the glassy carbon electrode unconnected). Polysulfides can be detected by, then, connecting the cell in a 3-electrode configuration, where now the glassy carbon electrode is the working electrode, the sulfur composite electrode is the counter electrode and the lithium ring electrode is the reference electrode.

Prior to each use, glassy carbon electrodes were polished in deionised water (Purite, 18.2 MΩ cm) with 25, 3.0 and 0.3 μm alumina powder and finally on a ‘blank’ polishing pad, and rinsed with deionised water. They were then dried, along with other cell components, under vacuum at 80 ⁰C for a minimum of 1 hour before being transferred to an argon filled-glovebox (<1 ppm water content, < 10 ppm oxygen content, MBraun).

The PEO-based solid polymer electrolytes and sulfur electrodes were prepared as in previous work.15 First, the lithium salt, either LiFSI or LiTFSI (battery grade, Solvionic, France), was dissolved in acetonitrile (ACN) (Reagent grade, Scharlau) followed by the addition of PEO (molecular weight: 5 × 106 g mol−1, Sigma-Aldrich), forming a viscous slurry that was mixed by magnetic stirring for at least 5 hours until complete homogenization. The ratio of the volume of acetonitrile to the mass of PEO was 50 mlACN gPEO−1, and the molar ratio of the Li salt to ethylene oxide units was 1:20. The slurry was then poured into a Teflon dish of 3.1 inch diameter and dried overnight at room temperature in a desiccator. After full evaporation of the solvent, a polymer electrolyte film was obtained, which was hot pressed at 100 °C and 3 tons of pressure for 1 min (using a heating plate connected to a manual hydraulic press, Speacac). After compression, the thickness of the polymer electrolyte was 70 μm (thickness gauge Mitutoyo ABSOLUTE Digimatic). The sulfur composite electrodes were prepared by mixing elemental sulfur (99.98 %, Sigma-Aldrich), conductive carbon (Ketjen Black, 600JD*,* Akzo-Nobel), and the LiX/PEO polymer electrolyte (X = FSI, TFSI) in a mass ratio of sulfur: carbon: polymer electrolyte of 40:15:45. First, dry sulfur and carbon were mixed in a mortar and the mixture was then added to a slurry made with the PEO polymer, the Li salt and acetonitrile, previously mixed by magnetic stirring. The slurry was then further mixed with a high-performance dispersing instrument (Ultra Turrax, IKA) at 16000 rpm for 20 min, followed by degassing for 30 min (roller mixer, Stuart). The slurry was then coated on a carbon-coated aluminium foil (3M) to a wet thickness of 500 μm (Micrometer adjustable film applicator, IKA), and then dried under vacuum at 50 ºC for 1 h. The final electrode had a sulfur loading of 0.9 mg cm-2. Finally, the polymer electrolytes and sulfur composite electrodes were punched by hand to the required diameter and dried for 3 days at 50 ⁰C under vacuum in a Buchi furnace, before being transferred to the glovebox. Lithium electrodes (battery grade, 100 μm thickness, Rockwood Lithium) were punched by hand to the required diameters inside the glovebox.

Cells were assembled inside the glovebox before being transferred to an oven at 70 ⁰C, and were allowed to equilibrate for 24 hours at 70 ⁰C prior to measurement. Electrochemical measurements were carried out using Bio-logic VMP2, VMP3 and SP-150 potentiostats. Cyclic voltammograms at the glassy carbon electrode were carried out at scan rates of 2-50 mV/s as indicated. EIS measurements were carried out with a voltage amplitude of 10 mV and frequencies of 200 kHz-10 Hz. All measurements were done at 70 ⁰C.

Results and Discussion

 Figure 2a illustrates the electrode arrangement design use here for the detection of polysulfide reaction intermediates with the electrochemical sensor. A disc-shaped PEO-sulfur composite electrode (containing either LiTFSI or LiFSI) is surrounded by a ring-shaped lithium metal counter electrode. Both electrodes are covered with a solid PEO electrolyte (with LiTFSI or LiFSI) and the glassy carbon electrochemical sensor is placed on the other side of the solid electrolyte. This electrode configuration is designed in order to detect the polysulfide species that diffuse away from the sulfur electrode, towards the sensor, during the electrochemical cycling of the sulfur electrode against the lithium electrode. Distances in Figure 2 are not to scale: the distance between the sulfur electrode and the sensor is the thickness of the solid PEO electrolyte, which is around 70 μm, while the gap between the sulfur and lithium electrodes is around 1.5 mm. Therefore, diffusion of polysulfides to the sensor is faster than to the lithium electrode, and as a result, the polysulfide reaction intermediates can be easily detected by the sensor (note that the time, *t*, required for species with diffusion coefficient *D* to diffuse over a distance *L* is of the order of *t* ≈ *L2/D*).40 This cell design clearly facilitates the loss of polysulfides via lateral diffusion, thus a low utilisation of the sulfur electrode is expected. Since the primary goal of this study was to study the polysulfide reaction intermediates, this unusual arrangement of the sulfur and lithium electrodes was employed, and different cells designs will be explored in further work.

Cycling of a Li-S cell was mimicked by measuring a very slow cyclic voltammogram of the sulfur electrode against the lithium electrode (that is, using the lithium metal electrode as counter and reference electrode, as is usually done in lithium-sulfur cells). Two voltammetric cycles of the sulfur against the lithium electrodes were taken (Figure S1), corresponding to a measurement time of ca. 13 hours, after which the cell was allowed to rest for 12 hours. For simplicity, the application of a cyclic voltammogram to the sulfur electrode against the lithium electrode will be referred to as “cycling the Li-S cell” in all that follows. Voltammograms at the glassy carbon electrochemical sensor (measured using the sulfur electrode as counter electrode and the lithium as reference electrode) were recorded before and after this Li-S cell cycling, and the results are shown in Figure 3. The voltammogram at the sensor measured before cycling the Li-S cells (Figure 3a) reflects the electrochemistry of elemental sulfur dissolved in the polymer electrolyte (note that, before the measurements, the cells were allowed to equilibrate for 24 hours at 70 °C; during this period, sulfur from the PEO-sulfur composite electrode dissolves in the polymer electrolyte reaching the saturation concentration). Interestingly, after cycling the Li-S cell, a dramatic increase in the current measured at the glassy carbon sensor is observed (ca. 10x increase in current), and the shape of the voltammogram also changes dramatically, with the voltammetric peaks becoming much narrower and well defined (Figure 3b). A clear difference between the first and second cycle voltammograms also appears after cycling the Li-S cells, which is characteristic of the fact that a mixture of oxidised and reduced species are present in the electrolyte.40 All these signs demonstrate the formation of polysulfide reaction intermediates upon the Li-S cell cycling, which accumulate in the polymer electrolyte and are thus detected at the sensor.

Figure 4 shows the voltammogram of the sensor after the Li-S cell cycling, but measured at a slower scan rate of 5 mV/s. At least two electrochemical processes are clearly observable: a fast electrochemical process centred at ca. 2.45 V vs. Li+/Li and a more sluggish electrochemical process at around 2 V vs. Li+/Li. The latter process exhibits clear kinetic limitations; no oxidation peak is observed at low scan rates, suggesting that the reaction involves slow chemical steps as reported in previous studies in liquid electrolytes.41 In contrast, the first process exhibits the characteristic behaviour of a fast electron-transfer reaction limited by diffusion: peak potentials are (almost) independent of the scan rate (Figure S2) and peak currents scale with the square root of the scan rate (Figure S3).

The shape of the 2nd cycle voltammograms in Figures 3b and 4 is remarkably similar to that observed for the electrochemistry of dissolved elemental sulfur in liquid, ether-based electrolytes (DME,42, 43 diglyme,42 tetraglyme43 and DOL:DME41, 43, 44) at a glassy carbon electrode. This can be ascribed to the fact that these solvents have a similar chemical formula, CH3-[O-CH2-CH2-]n-O-CH3, although with very different chain lengths (n=1 in DME, n=2 in diglyme, n=4 in tetraglyme and n≈139000 for the PEO with molecular weight of 5x10-6 g/mol used here). However, this similarity is somewhat surprising, since the voltammograms of dissolved elemental sulfur in the PEO electrolyte (Figure 3a) are much broader, indicating slower reaction kinetics, whereas the electrochemical reactions of polysulfides in the PEO electrolyte (Figures 3b and 4) appear to be as fast as those of dissolved elemental sulfur in liquid, ether-based electrolytes.

By using a rotating ring disc electrode (RRDE), Gasteiger and coworkers showed that ca. 5.5 electrons are involved in the first step of the reduction of dissolved elemental sulfur in 1 M LiTFSI in DOL:DME,41 and suggested that the reaction could proceed via the following simplified mechanism:

S8 + 4e- → S84- → ↓S2- + S42- + (3/8)S8

(3/8)S8 +(3/2)e- → (3/8)S84-→ (3/4)S42-

Overall: S8 + (11/2)e- → ↓S2- + (7/4)S42-

The thus-formed S42- (generated at the rotating disc glassy carbon electrode) could be easily oxidized to S8 at the ring electrode:

 (7/4)S42-→ (7/8)S8 +(7/2)e-

which would result in a ring-current current ratio of (7/2)/(11/2)\*100= 64%, in reasonably close agreement with the experimental result of 70%.41 Interestingly, the ratio of the charges due to oxidation and reduction in the voltammograms in Figure 3b is also 70% (on 2nd cycle). However, the reacting species are polysulfides, rather than elemental sulfur, and therefore, despite the similarity in shape and oxidation/reduction charge ratio, the mechanism of the reactions should be different. Since the nature of polysulfides involved is unknown, we can only suggest a general reaction of reduction of long-chain polysulfides to short-chain polysulfides:

Sn2- + (2n/m-2)e- → Sm2- (with m<n)

that could be coupled with polysulfide chemical reactions such as:

Sm2- + Sn2-→ Sm-x2- + Sn+x2-

Another important conclusion from the results in Figures 3 and 4 is that, in all cases, very similar results are obtained with the two different lithium salts (LiTFSI or LiFSI). This is true for the electrochemistry of dissolved elemental sulfur (Figure 3a) and polysulfides (Figures 3b and 4), and the difference in the results is within the reproducibility of the measurements (Figures S5 and S6). Whereas further work is required to improve the cell-to-cell reproducibility, the objective of the present study was to demonstrate the sensitivity of the electrochemical sensor for in-situ polysulfide detection. On the other hand, the similarity of the results obtained with the two lithium salts indicates that the reaction mechanism, polysulfide solubilities, elemental sulfur solubilities and diffusion coefficients are all very similar, regardless of the type of lithium salt (LiTFSI or LiFSI) added to the cell. This supports the hypothesis given by Judez et al.15 that the effect of lithium salt on Li-S cell performance originates from differences in the reactivity of the lithium metal anode/polymer interface. Reactions of the lithium salt at the lithium metal anode might produce a difference in surface composition, thus leading to different reactivity. The cell configuration used here (see Figures 1a and 2a) was designed to detect the polysulfides formed as reaction intermediates before they could reach and react at the lithium electrode. Consequently, the measurements here presented are not sensitive to the differences in the surface reactivity of the lithium metal anode.

In order to further corroborate that the lithium salt (LiTFSI or LiFSI) does not affect the reactions of the sulfur electrode, further experiments were done using a different electrode configuration that did not include the use of a lithium metal electrode (see Figures 1b and 2b). After equilibration of the cell for 24h at 70 °C, the PEO electrolyte (contained between the two electrodes) was saturated with elemental sulfur from the sulfur electrode. Then a cyclic voltammogram of the sensor was recorded using the sulfur electrode as both counter and reference electrode, as shown in Figure 5. Again it is shown that the nature of the lithium salt produces a negligible effect on the results (the differences are within the reproducibility of the measurements, see Figure S4). Unfortunately, the use of a sulfur composite electrode as both counter and reference electrode does not allow an accurate evaluation of the true voltammogram of dissolved elemental sulfur in the PEO electrolyte, since during the measurements, the potential of the sulfur electrode can shift with time. The experiments done in the three-electrode cell (Figures 1a and 2a, with the glassy carbon working electrode, Li reference electrode and sulfur counter electrode), show that the potential of the sulfur counter electrode slowly shifts from ca. 3.0 to ca. 3.2 V vs. Li+/Li during the cyclic voltammogram measurements shown in Figure 3a, with the polymer electrolyte saturated with elemental sulfur (Figure S7). However, the experiments shown in Figure 5 in two-electrode cells (Figures 1b and 2b) are useful to investigate whether or not the lithium salt produces an effect on the electrochemistry of dissolved elemental sulfur in the polymer electrolyte, since the simpler cell design produces a better cell-to-cell reproducibility. The fact that the same electrochemical results are obtained regardless of salt confirms again that the nature of the salt does not affect the solubility, diffusion coefficient or electrochemical reactions of elemental sulfur in the PEO electrolyte.

In order to investigate further the mechanism of polysulfide redox reactions in solid polymer electrolytes Li-S cells, impedance measurements were performed with the PEO electrolyte containing polysulfide species, as obtained after cycling the Li-S cell (see associated voltammograms in Figure 3b). Figure 6 shows that, for both lithium salts, the impedance spectra exhibit a truncated semicircle, followed by a depressed semicircle, and followed by a 45-degree line. The results were fitted to the equivalent circuit shown in the figure. The truncated semicircle, observed at high frequencies, is associated to the transport of current through the polymer electrolyte,45, 46 which is usually described as a constant phase element coupled to a resistor in parallel. For the sake of simplicity, the electrolyte response was fitted here with a simple resistor, *Rm*, and the impedance data points at the highest frequencies were not included in the fit. The depressed semicircle corresponds to the combination of charge-transfer electrochemical reactions of polysulfides at the glassy carbon electrode, *Rct*, coupled to the double layer charging of the polymer electrolyte - glassy carbon interface, where the latter is fitted with a constant phase element (CPE) that has an associated capacitance *Cdl*. Finally, the 45-degree line is ascribed to the diffusion of polysulfides to the glassy carbon electrode, and is fitted with a Warburg element. The slow diffusion of polysulfides has been shown to limit the capacity of Li-S cells in liquid electrolytes.47-51 Table 1 summarises the results of the fit.

Table 1 demonstrates again that the two different lithium salts produce very similar results, and within the reproducibility of the present measurements. From the value of the electrolyte resistance, and taking into account the geometric factors of the electrolyte thickness (70 μm) and electrode geometric area (0.0707 cm2), conductivity values of the PEO electrolyte of ca. 0.5-0.8 mS/cm (at 70 °C) are found, in good agreement with the literature.15 Using the fitted parameters of the CPE element, the double-layer capacitance of the glassy carbon electrode is found to be around 15-20 μF/cm2 (when normalized to the geometric area of the electrode), which is as expected for a planar electrode. Finally, the charge-transfer resistance of the polysulfide redox reactions is found to be around 13-14 Ω cm2 (when normalized to the geometric area of the electrode). This value of the charge-transfer resistance is much smaller than that reported for different polysulfide redox reactions in a liquid electrolyte (1 M LiTFSI in TEGDME:DOL) by Dravaric Talian et al.52, 53 in an elegant impedance study using symmetrical cells with glassy carbon electrodes. The lower charge-transfer resistances found here are consistent with the higher temperature used in this work using polymer electrolytes (70 °C, vs. room temperature for the liquid electrolytes in refs.52, 53). The difference in magnitude of charge-transfer resistance values can also be explained by the fact that a variety of polysulfide species were formed during cycling of the Li-S cells, and the present impedance measurements are dominated by the fastest polysulfide redox reactions, which produce highly reversible voltammetric processes limited by diffusion (redox peaks around 2.45 V vs. Li+/Li in the voltammograms in Figures 3b and 4). Fast electrochemical reactions were also reported for the first step of the reduction of dissolved elemental sulfur in 1 M LiTFSI in DOL:DME up to the transfer of ca. 5.5 electrons, whereas the kinetics of the following electron transfer and chemical reactions to form Li2S as final product were found to be much slower.41

Conclusions

 The formation of polysulfide reaction intermediates in solid polymer Li-S batteries was studied here using a highly sensitive electrochemical sensor made of glassy carbon. A concentric arrangement of the sulfur and lithium electrodes was employed to promote the detection of polysulfide intermediates reaction products, which quickly reach the glassy carbon sensor by diffusion away from the sulfur and lithium electrodes. Signatures of polysulfide formation were very obvious: dramatic changes in the shape and magnitude of the current measured in cyclic voltammogram experiments of the sensor were observed. Impedance measurements were also performed to characterise the polysulfide redox reactions, obtaining results that fitted well to the classical Randles circuit, thus providing values of the PEO electrolyte conductivity, capacitance of the glassy carbon electrode, and charge-transfer and Warburg resistances of the polysulfide redox reactions. All experiments were performed using two different lithium salts (LiTFSI and LiFSI), and minor differences were within the reproducibility of the measurements, thus confirming the hypothesis given by Judez et al.15 that the only effect of the salt was to change the reactivity of the lithium-polymer interface. More generally, this new approach can be applied to study the electrochemical properties of the polysulfide species formed in-situ in any type of Li-S battery, with either liquid, polymer or polymer-gel electrolytes, providing a powerful complement to other possible in-situ (e.g. spectroscopic) techniques. Polysulfide species have been shown to act as redox mediators in Li-S cell reactions, thus enabling faster reactions, higher sulfur utilisation and more efficient charging.51, 54-58 The experimental set-up here developed is especially well suited to identify the polysulfide intermediates that exhibit fast redox reactions, which are then most likely to contribute to redox mediation. Due to their reactivity, such intermediates may be difficult to detect using ex-situ techniques. In further work, this newly developed set-up will be used to elucidate the fundamental mechanistic causes leading to different Li-S reaction kinetics in different electrolytes.

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**Tables**

|  |  |  |  |
| --- | --- | --- | --- |
| Parameter | Units | LiTFSI | LiFSI |
|  | Ω | 189.5 | 127.9 |
|  | Ω cm2 | 9.0 | 13.4 |
|  | Ω | 196.3 | 179.2 |
|  | Ω cm2 | 13.9 | 12.7 |
|  | F s(n-1) | 5.17 ∙ 10-6 | 4.6 ∙ 10-6 |
|  |  | 0.81 | 0.84 |
|  | F cm-2 | 13.9 ∙ 10-6 | 17.2 ∙ 10-6 |
|  | kOhm s-1/2 | 137 | 154 |

**Table 1**. Parameters obtained from equivalent circuit model fitting of the impedance spectra in Figure 6. Notes: The geometric area of the glassy carbon electrode (0.0707 cm2) was used to normalise resistance and capacitance values. The effective, non-complex double layer capacitance of the glassy carbon electrode,  is derived from the fitted parameters for ,  and  using.59 A CPE with P-value fixed to 0.5 was used for the Warburg impedance, since ZView does not include a semi-infinite Warburg element. The Warburg resistance,, is calculated from the fitted  value using . All measurements were done at 70 °C.

**Figures and Figure Captions**



Figure 1. Schematic of cell designs with (a) three electrodes (with lithium) and (b) two electrodes (no lithium).



Figure 2. Sketch of the electrode configurations employed in the present study. (a) Three-electrode configuration with a glassy carbon electrochemical sensor (grey), a sulfur electrode (blue), and a lithium electrode (yellow). (b) Two electrode configuration with a glassy carbon electrochemical sensor (grey) and a sulfur electrode (blue).



Figure 3. First and second-cycle voltammograms recorded at the glassy carbon sensor (a) before and (b) 12 hours after cycling of a Li-S cell containing a polymer electrolyte with either LiTFSI (black) or LiFSI (red). See cell sketch in Figure 1a. The voltammograms were measured in a three-electrode configuration using the sulfur electrode as the counter electrode and the lithium as the reference electrode, at a scan rate of 50 mV/s, and have been corrected for IR drop using values of the electrolyte resistance obtained from electrochemical impedance spectroscopy. Arrows indicate the start of cycling.



Figure 4. Voltammograms recorded at the glassy carbon sensor at a scan rate of 5 mV/s, after cycling of the Li-S cell containing a polymer electrolyte with either LiTFSI (black) or LiFSI (red). All other experimental details as in Figure 3.



Figure 5. Voltammograms recorded at the glassy carbon sensor in contact with a sulfur-saturated polymer electrolyte containing either (a) LiTFSI or (b) LiFSI. The voltammograms were measured in the cell shown in Figure 1b, using the sulfur electrode as the counter-reference electrode, at a scan rate of 50 mV/s, and have been corrected for IR drop using values of the electrolyte resistance obtained from electrochemical impedance spectroscopy. Arrows show the start of cycling.



Figure 6. Impedance spectra recorded at a glassy carbon electrode in contact with a polysulfide-containing polymer electrolyte containing (a) LiTFSI or (b) LiFSI. The spectra were recorded using the cell sketched in Figure 1a, in a three-electrode configuration with sensor as the working electrode, the sulfur electrode as the counter electrode and the lithium as the reference electrode, immediately before the voltammograms shown in Figure 3b. Black lines and points are the experimental data, red lines are the results from the fit to the equivalent circuit shown in the figure.