In operando Raman and optical study of lithium polysulfides dissolution in lithium–sulfur cells with carrageenan binder

Didier Blanchard* and Mark Slagter

Technical University of Denmark, Department of Energy Conversion and Storage, 2800 Kgs. Lyngby, Denmark

E-mail: didblanchard@yahoo.fr

Keywords: Li–S, lithium–sulfur battery, polysulfide, carrageenan, in operando Raman spectroscopy, optical battery study

Supplementary material for this article is available online

Abstract

In operando Raman and optical studies have been performed on lithium–sulfur (Li–S) batteries containing carrageenan binder in the sulfur cathode for chemical trapping of the polysulfides (PSs). Three different types of cells were used: coin cells, EL-cell and capillary cells to examine the PS speciation. With the coin cell we confirm the stability and cyclability of the carrageenan based Li–S cells and the improved capacity retention when compared to conventional polyvinylidene fluoride based Li–S cells. With the EL-Cell, the PS speciation at the cathode is documented but only weak evidences of the nucleophilic trapping of the PS are found. The in operando Raman and optical studies on the capillary cell revealed the dissolution and diffusion of the PS in the whole electrolyte volume. We confirm the disproportionation of S$_4^-$ into S$_3^-$ in the electrolyte. Strong inhomogeneous PS concentration in the electrolyte are found to develop in the course of the cell charge–discharge cycling which must be detrimental to the performances of the battery.

1. Introduction

During the past decade, the quest for promising next generation electricity storage systems has led significant attention to secondary batteries with high specific energy such as lithium–sulfur batteries (LSBs) (3861 mAh g$^{-1}$ lithium and 1675 mAh g$^{-1}$ sulfur at 2.15 V), [1–6] of three to five times higher energy densities than commercial state-of-art Li-ion batteries, e.g. LiNi$_{x}$Mn$_{x}$Co$_{x}$O$_2$ (NMC) and LiNi$_{1−y}$Co$_{2−y}$Al$_2$O$_2$ (NCA), 170 mAh g$^{-1}$ of active cathode material at 4.5 V and 4.1 V, respectively [7]. The inexpensive, abundant and environmentally benign nature of sulfur makes Li–S batteries even more appealing, for large-scale application purposes (e.g. transportation, portable and residential applications) than other metal-ion battery systems. However, the electrochemistry of LSBs involves complex processes and the insulating character and volumetric expansion of the active materials [8, 9], together with secondary parasitic reactions [10, 11] and polysulfide (PS) shuttling [12] impede full sulfur utilization and lead to reduce lifetime of the cells. A good understanding of the Li–S electrochemistry, PS shuttling, mechanisms of charge and discharge and degradation is still needed to find appropriate solution and improve the cells performances.

To investigate the properties of the electrolyte, PS speciation and shuttling, different spectroscopic techniques such as Raman [13–17], UV–vis [18–20], x-ray absorption [21] and x-ray photoelectron spectroscopy are used. To investigate physical changes to the electrode materials, x-ray diffraction [13, 14, 22, 23], x-ray transmission microscopy [23, 24], and x-ray tomography [25–32] are applied. Most of these techniques can be performed in operando, i.e. while the battery cell is in operation to collect real time insights into the complex chemistry and the mechanisms at play.

The inherent problem of the PS shuttling, considered as the most critical for the development of LSBs, can be mitigated by physical and chemical containment. Nano-porous functionalized cathode or separator materials, based on for example carbon materials [33–35] or metal organic framework [36, 37] have been developed. While PS physical confinement is achieved by structural designs of the cathode or separator material, the chemical trapping is obtained via surface functionalization or doping to promote polar–polar,
Lewis acid–base and catenation interactions, between the materials and the PSs [38]. Although these approaches show good improvements, they are in their early stages of development and mostly involve complicated and costly techniques in cell manufacturing. Instead, recent researches focused on alternative active binders to regulate the PS dissolution and carrageenan, mucopolysaccharides from the cell walls of the red algae [39] has been claimed to have a positive impact [40]. Each carrageenan disaccharide contains a certain number of sulfate groups highly reactive with PS species due to the fast nucleophilic substitution between the PSs and these groups. Ling et al [40] performed a straightforward PSs adsorption study demonstrating this binding properties. Furthermore, carrageenan has advantageous features compared to commonly used binders, such as high aqueous solubility due to its high concentration of hydroxyl groups providing adequate interaction with polar electrolyte solutions, high adhesiveness, and non-toxicity [40].

In the present study, the authors used three different cell geometries to investigate, in operando, the PSs speciation in LSB with carrageenan binders, at and away from the cathode surface. A regular coin cell geometry was used as reference for the electrochemical characterization of the carrageenan based LSBs. The carrageenan binder is found suitable to obtain stable cycling of the Li–S coin cells and increase the capacity retention when compared to cells with conventional binder such as polyvinylidene fluoride (PVDF) [40]. To study the electrolyte in the space between the electrodes, important to consider since PSs dissolve and diffuse throughout the entire cell, a capillary cell design [41], allowing both in operando Raman Spectroscopy and optical image analysis was developed and used. It provided insights of the mass transport mechanisms, diffusion kinetics and concentration gradient build-up of the PS in the liquid phase. Finally, to study the PS speciation at the surface of the sulfur electrode, Raman spectroscopy was performed using an ECC-Opto-Std test cell (EL-CELL) with a geometry comparable to the coin cell.

2. Method

2.1. Cathode preparation
In this work, the preparation of carbon–sulfur cathode containing either carrageenan as a bio-binder or PVDF as conventional binder, consisted of two main steps: synthesis of the carbon–sulfur powder and incorporation of binder. λ-carrageenan was used for having the highest density of sulfate groups among all the different carrageenan types. In order to improve its electrochemical activity, sulfur must be incorporated with a conductive additive e.g. carbon. A carbon–sulfur composite was prepared using a combination of ball-milling and melt-infiltration. This modified procedure was derived from a method proposed by Das et al [42]. The conductive phase consisted of Ketjen Black EC-600JD (surface area 1400 m² g⁻¹, pore volume 4.80–5.10 m³ g⁻¹, Shanghai Tengmin Industry Co., Ltd) and activated carbon Maxsorb MCS-30 (surface area 3000 m² g⁻¹, 1.7 m³ g⁻¹, Maxsorb, Japan), mixed in a 1:1 weight ratio. As Ketjen Black is more conductive than Maxsorb, it increases the overall electronic conductivity of the composite [43]. On the other hand, Maxsorb has a large surface area, which increases the sulfur–carbon interaction. Mixing these two additives is expected to increase the overall electronic conductivity and carbon–sulfur interaction, and therefore enhance the electrochemical activity of sulfur [43]. Elemental sulfur (Sigma-Aldrich, 99.9% pure) was mixed with the carbon in a 45:55 sulfur to carbon weight ratio through ball-milling for 1 h at 400 rpm in a Fritsch Pulverisette P7 milling machine under argon atmosphere. The mixture was then heated at 155 °C for 6 h in a sealed autoclave reactor. The mixture was heated and cooled down at a very slow rate (0.2 °C), so that the sulfur can effectively diffuse into the porous carbon matrices. Finally, the exact sulfur content was checked with thermogravimetric analysis—see supporting information (figure S1 (available online at stacks.iop.org/JPENERGY/3/044003/mmedia)). λ-carrageenan was provided by CP Kelco ApS. A sulfur to binder weight ratios of 8:1 was used. Carrageenan was dissolved in deionized Milli-DI water (ρ > 1 M² cm at 25 °C). Due to the high viscosity of carrageenan in water and poor wettability of carbon, an excess of water was used. Typically, the powder to solvent weight ratio was 1:25. This ensures a homogeneous carrageenan–C–S mixture. After adding an appropriate amount of C–S powder, the suspension was stirred overnight at room temperature. Next, the excess of water was evaporated in a preheated water bath at 80 °C while stirring at 1000 rpm until a 1:5 powder to water ratio was obtained. Then, the slurry was subjected to ultrasonication for 1 h. PVDF powder obtained from Sigma-Aldrich and used as received. The electrodes were made from the C–S mixtures by preparing slurries with N-methylpyrrolidinone along with 10 wt% PVDF stirred overnight.

2.2. Coin cell fabrication
For the preparation of cathode electrodes, the slurries were tape-casted on aluminum foil (t = 0.2 mm) using a 2 MIL (50.8 µm) doctor blade and then dried at room temperature or 60 °C overnight, for the carrageenan and PVDF based cathodes respectively. The casting speed was kept constant at around 0.1 m s⁻¹. The electrodes were punched into 15 mm discs and assembled into CR2032 type coin cell batteries. All cells were
assembled in an argon filled glovebox using 16 mm freshly cut metallic lithium disks (Sigma-Aldrich, 99.9% pure, thickness 0.4 mm) as counter electrode and sealed by a press (Hohsen Corporation). The electrolyte contained 1.0 M bis(trifluoromethylsulfonyl)-amine lithium salt (LiTFSI, BASF) in a 1/1 v/v binary solvent of 1,2-dimethoxyethane (DME, Sigma-Aldrich, 99.5% pure) and 1,3-dioxolane (DOL, Alfa Aesar, 99.5% pure) with 2 wt% LiNO₃ as additive. The amount of electrolyte used is of 10 µl mg⁻¹ of sulfur. Whatman™ filter paper was used as the separator. Furthermore, polypropylene gaskets were used to ensure an airtight seal of the coin cells. Stainless steel wave springs with a diameter of 15 mm and thickness of 1.4 mm and stainless steel spacers with a diameter of 16 mm and thickness of 1.0 mm were used to provide adequate contact between the anode and the casing.

The assembled batteries were placed in a climate chamber at 25 °C connected to a potentiostat (MPG-2, Bio-Logic). Open-circuit voltage was measured for 30 min. Galvanostatic discharge–charge cycles were performed (galvanostatic cycling with potential limitation) in a voltage range from 2.6 V to 1.8 V at a constant current density corresponding to a (dis-)charge rate of 0.1 °C with respect to the theoretical specific capacity of 1675 mAh g⁻¹ sulfur.

2.3. EL-CELL® preparation
To study the cathode material during discharge and charge, an ECC-Opto-Std test cell (EL-CELL) equipped with a 0.3 mm thick sapphire glass window and a cell lid with a 2 mm diameter window opening was used to perform operando Raman measurements (see figure S2). The electrochemical cell consisted of a sulfur cathode, a glass microfiber separator, a lithium anode, a holey aluminum current collector (300 mesh), and the liquid electrolyte as describe above. The sulfur cathodes were prepared by tape-casting the slurries on Whatman™ filter paper using a 2 MIL (50.8 µm) doctor blade and subsequently dried at room temperature overnight. The electrodes were punched into 10 mm discs. The cell was assembled from bottom to top. First, a 9 mm freshly cut lithium disk was placed on top of the cell’s piston, followed by placement of the glass fiber separator and the sulfur cathode. A holey current collector was then placed in contact with the cell window. After fastening of the cell, electrolyte was added to the cell using a syringe (~50 µl mg⁻¹ of sulfur). The electrochemical measurements were carried out on a Reference 600™ potentiostat (Gamry Instruments) controlled by Gamry Framework. The cell was discharged and charged using chronopotentiometry at a constant current density corresponding to a (dis-)charge rate of 0.1 °C with respect to the theoretical specific capacity of 1675 mAh g⁻¹ sulfur. The cutoff voltages were 1.8 V for discharge and 2.6 V for charge.

Simultaneously, operando Raman measurements were performed on an InVia™ confocal Raman microscope (Renishaw) equipped with a 532 nm excitation laser using a 50× long distance objective with a 1 µm diameter spot size and an energy of less than 8 mW. The experimental setup is shown in figure S2. All data was recorded and analyzed utilizing the WiRE software v4.2 (Renishaw). Measurements were carried out in the wavenumber range of 80–1330 cm⁻¹ (static scan mode) every 5 min with 30 scan repetitions, 1 s exposure time each. The cathode material before cycling and electrolyte solution were also examined.

2.4. Capillary cell fabrication
A 316 stainless steel current collector with a diameter of 1.5 mm was dip coated in the prepared C–S-carrageenan ink (section cathode formulation). After drying at 80 °C for 30 min, the coating step was repeated twice. The rod was placed in a glass capillary with an inner diameter of 1.275 mm and wall thickness of 0.225 mm, fixed by Cyberbond U3600 UV-curable adhesive. The anode part of the cell consisted of another 316 stainless steel rod coated with metallic lithium foil. The capillary was filled with the same electrolyte used for the other battery cells (~100 µl mg⁻¹ of sulfur). The rod with lithium was then carefully inserted into the capillary under argon atmosphere. Finally, the cell was sealed by UV-curable adhesive (see figure S6). The capillary cell was used for two purposes: operando Raman investigation and optical imaging of the electrolyte system. Raman measurements were performed using the same equipment and settings as for the ECC-Opto-Std test cell (section EL-Cell fabrication). For optical imaging, the cell was placed in an insulating sample holder frame and connected to a CompactStat potentiostat (Ivium Technologies), which was used to discharge and charge the battery with a constant current corresponding to a rate of 0.1 °C with respect to the theoretical specific capacity of 1675 mAh g⁻¹ sulfur. The voltage was set to have a lower limit at 1.9 V for the discharging and an upper limit at 2.6 V for the charging. Simultaneously, images were taken every 5 min with a Dino-Lite Edge digital microscope. The capillary cell was placed against a defocused white background created using a piece of paper to ensure correct white balance. All color images were processed using Mathematica’s image processing functions (see supplementary information). Firstly, all images were spatially registered to the first image taken prior to conversion to gray scale images. To quantify the intensity gradient the region between the electrodes has been divided into 39 equally spaced domains (shown in supplementary information). The first image was then subtracted to the following images, to emphasize the
Figure 1. Electrochemical performance of Li-S coin cell batteries subjected to continuous cycles at 0.1 C in the voltage range from 2.6 V to 1.8 V. (a) Voltage profiles for a carrageenan based cell and (b) discharge capacity (circles) and coulombic efficiency (triangles) evolution for the first cycles. Black symbols—carrageenan based cell, gray symbols—PVDF based cell.

changes and in each domains the average gray scale value taken and normalized to the maximal intensity measured resulting for each point of time in normalized gray intensities (NGIs).

3. Results and discussion

3.1. Coin cell analysis

Figure 1(a) displays the voltage profile of a carrageenan coin cell, typical of Li–S cell chemistry. It shows that the coin cell, with cathode elaborated with carrageenan as binder exhibits reasonable cycling stability. The high and low voltage discharge plateaus can be observed at ∼2.35 V and ∼2.08 V, respectively. These plateaus are associated with the formation of higher-order PS and lower-order PS species respectively. During the charging, one can observe two plateaus, at around 2.15 and 2.49 V. The shape of the voltage profile did not substantially change upon cycling. The discharge capacity decreased more rapidly during the first ten cycles than for the following and seemed even to stabilized reaching a value of 1277 mAh g⁻¹ at cycle #19 with a coulombic efficiency close to 100% over the discharge–charge cycles (figure 1(b)). This proves the feasibility of using carrageenan as binder in the sulfur electrode. Figure 1(b) also displays, for comparison, the discharge capacity evolution for the PVDF based Li–S coin cell. The voltage profiles can be found in the supplementary information (figure S9). In agreement with Ling et al [40], we found a better capacity retention for the carrageenan based cell.

3.1.1. EL-Cell operando Raman analysis

To obtain information on the carrageenan cathode S₈ conversion process, operando Raman spectroscopy was performed using the EL-Cell configuration. The Raman spectrum of the cathode material before cycling is shown in figure 2, together with the voltage profile for the first discharge/charge cycle of an exemplary Li–S EL-Cell.

The Raman spectrum shows multiple distinctive sharp peaks and a few smaller peaks which are typical for octatomic S₈. These peaks may be assigned using the normal coordination calculations for the Raman-active 2A₁ + 3E₂ + 2E₃ modes suitable for S₈ in a D₄d symmetry, as described by Scott et al [44] and supported by a more recent paper from Poleshchuk et al [45]. The peak at 85 cm⁻¹ and 152 cm⁻¹ can be assigned to the E₂ symmetry species, the sharp peak at 219 cm⁻¹ to the A₁ species, and the ones at 242 cm⁻¹ and 442 cm⁻¹ to the E₃ species. The sharp peak at 473 cm⁻¹ can most likely be ascribed to the combination of the E₂ and A₁ modes of sulfur. The last small band at 192 cm⁻¹ might be ascribed to a Raman forbidden E₃ mode. The Li–S EL-cell was cycled between 2.6 V and 1.8 V at 0.1 C rate (figure 2(b)). The discharge curve shows a higher capacity (∼1450 mAh g⁻¹) than the charge capacity (∼1000 mAh g⁻¹). This difference was also observed for the coin cell batteries during the first cycle and illustrates the presence of irreversible electrochemical reactions. The voltage profile is similar to the one obtained for the coin cells with the presence during the discharge of two plateaus, circa 2.3 and 2.1 V.

Figure 3 shows the evolution of the Raman signal during the first discharge of one carrageenan based Li–S EL-Cell. The evolution of the peak intensities can be found in the supplementary information (see figure S4). During the initial period of the first plateau, all the peaks are assigned to the different vibrational
modes of octatomic sulfur, as explained above. These peaks quickly decreased in intensity and eventually disappeared completely at the end of the high voltage plateau (figure 2(b) at ∼2.3 V, zone I). This indicates that almost all the sulfur rings were opened to form the high-order PSs, or more simply, that sulfur dissolution in the electrolyte happened. However, the quick intensity drop of the sulfur peaks suggests that electrochemical reduction is a more reasonable explanation than simple chemical dissolution. Simultaneously, a new band at 491 cm⁻¹ emerged with a blue-shift to 495 cm⁻¹ at the end of the plateau. This peak may be ascribed to $S_4^{2-}$ stretching modes [14]. Observation of only one peak at the high voltage plateau is notable since one would expect other bands to emerge originating from other $S_4^{2-}$ vibrational modes and other PS species. This may indicate that the sulfide species formed in the cathode are constrained.
as an effect of nucleophilic substitution between sulfur and carrageenan [40]. This reaction would result in new C–S bonds with stretching vibrational modes in the region between 570 and 750 cm$^{-1}$ [46]. These modes were not observed but since little is known about the exact interaction between carrageenan and sulfur under working conditions, this does not necessary exclude the nucleophilic reaction between carrageenan and sulfur during discharge. The S–S stretching modes of S$_2^{2−}$ were not observed at this stage of discharge. These peaks are expected near 398 cm$^{-1}$ [14]. This could mean that S$_2^{2−}$ is directly created from sulfur near the cathode material, or that reduction of S$_2^{2−}$ species to S$_2^{2−}$ from the sulfur ring occurs truly fast. A more likely reason for the absent of S$_2^{2−}$ stretching modes might be that S$_2^{2−}$ species are dissolved in the electrolyte, and therefore are undetectable—this later hypothesis is supported by the Raman study made on the capillary battery (see below). Finally, a broad band emerged at 491 cm$^{-1}$. It could be that this band is related to the nucleophilic substitution reaction. As discharge proceeded, new peaks started to emerge. In the region between 125 and 300 cm$^{-1}$, a peak at 233 cm$^{-1}$ and a weaker band near 205 cm$^{-1}$ appeared at the beginning of the low voltage plateau (figure 2(b) at ∼2.1 V, zone III). The 233 cm$^{-1}$ band gradually grows till the end of the plateau. An extensive Raman study of reactions between sodium sulfide and sulfur has been performed by Jaroudi et al [47]. They reported Raman spectra of mixture between Na$_2$S with a large excess of sulfur and observed similar bands at 205 cm$^{-1}$ and 233 cm$^{-1}$ which were ascribed to bending vibrational modes of S$_2^{2−}$ [48]. In the region between 300 and 600 cm$^{-1}$, a peak at 460 cm$^{-1}$ and a weaker band at 405 cm$^{-1}$ emerged. The band at 460 cm$^{-1}$ probably corresponds to the stretching mode of S$_2^{2−}$ [47]. This band decreased as the discharge proceeded and disappeared completely at the end of discharge (∼1.85 V).

Since not all peak disappeared at this stage of discharge, it is unlikely that this observation is due to signal loss, but rather due to the reduction of Li$_2$S$_2$ to Li$_2$S. Most likely, the weak band at 405 cm$^{-1}$ was created by S$_4^{2−}$ species. The sudden apparition of this mode, at this stage of discharge, could be due to its back diffusion from the electrolyte to the cathode surface where it may finally react forming lower order PSs. The S$_4^{2−}$ vibrational mode at 495 cm$^{-1}$ increased in intensity, reaching its highest intensity around the end of the low voltage plateau. Then, it quickly loses intensity. This must be due to the formation of shorter chain Li$_2$S$_2$ and Li$_2$S species. Since the Li$_2$S$_2$ band also decreases at this stage of discharge, the formation of solid Li$_2$S is more likely. However, the peak associated with Li$_2$S, expected at 375 cm$^{-1}$, was not observed. Several in situ and ex situ Raman studies have shown that the intensity of Li$_2$S peaks is low and hard to identify [17]. Finally, in the higher energy region above 1000 cm$^{-1}$ a sharp peak emerged at 1069 cm$^{-1}$. Wu et al also observed a peak near this wavenumber during Li–S cell discharge, which they ascribed to the S–O stretching mode of thiosulfate (S$_2$O$_3^{2−}$). Irreversible sulfur oxidation or the reaction between the cathode and solvent was suggested as a possible reason for the formation of S–O species [17]. In our case, the formation of crystalline LiNaSO$_4$ as a product of the nucleophilic reaction between carrageenan and sulfur deposited on the cathode surface could be another explanation.

The major electrochemical reactions at the cathode surface during discharge are proposed based on the above discussed observations:

\[ S_8 + 4e^− + 4Li^+ \rightarrow 2Li_2S_4 \]  \hspace{1cm} (1)

\[ Li_2S_4 + 2e^− + 2Li^+ \rightarrow Li_2S_2 \text{insoluble} \]  \hspace{1cm} (2)

\[ Li_2S_2 + 2e^− + 2Li^+ \rightarrow Li_2S \text{ insoluble} \]  \hspace{1cm} (3)

where carrageenan might contribute to reaction $S_8 + 4e^− + 4Li^+ \rightarrow 2Li_2S_4$ (equation (1)). Formation of a strong covalent C–S bond due to the nucleophilic reaction between carrageenan and sulfur could also partially explain why $S_4^{2−}$ vibrational modes are still observed at the end of discharge.

The evolution of the Raman signal during the first charge of the carrageenan Li–S EL-Cell is shown in figure 4. The $S_2^{2−}$ and S–O bands gradually decreased in intensity. The decrease of S–O associated peak intensity could correspond to the reverse reaction of crystalline sulfate species with ‘sulfated’ carrageenan, resulting in the release of attached PS species. However, it is unlikely for this reaction to happen, since the nucleophilic substitution reaction is considered irreversible due to the formation of strong covalent C–S bonds [40]. A more reasonable explanation for the decrease in intensity could be the dissolution of LiNaSO$_4$. The decrease of the $S_4^{2−}$ bands indicates that short chain PSs were reduced towards higher order PSs, explaining the overall rapid voltage increase. Nevertheless, these species were not observed. It could be that fast dissolution and migration of high-order PSs occurred during charge. Interestingly, the distinctive peaks of elemental sulfur were also not observed. This could mean that PSs do not transform back to sulfur, but
Figure 4. Operando Raman measurement of the carrageenan EL-cell charge at 0.1 \text{C} \text{ rate} (from red to black). The green spectra represent the boundary from a plateau/slope to the next plateau/slope of figure 2(b).

remain in the electrolyte system. However, this does not explain the sharp voltage increase at the end of charge, which is believed to be due to the formation of solid sulfur. Therefore, it seems to be likely that sulfur was formed at certain electrode hotspots which have a good electrolyte accessibility, high surface area, and low resistance [15]. Post measurements at different spots directly after charge should be carried out to support this statement. Note that the signal to noise ratio decreased towards the end of charge. It is therefore difficult to discern bands related to the cathode material at this stage of charge.

The presence of carrageenan do not alter the expected electrochemical Li–S conversion as observed, at the surface of the cathode, with the operando Raman spectroscopy measurements. Some Raman features could be attributed, however not unambiguously, to the PS anchoring via the nucleophilic reaction with the carrageenan sulfate groups.

3.1.2. Capillary carrageenan cell configuration—operando Raman and optical analysis

Capillary cells were used, to monitor via Raman spectroscopy and optical imaging, during separated measurements, the PS species in the electrolyte space between the electrodes.

3.1.3. Capillary carrageenan cell operando Raman analysis

Figure 5 shows (a) the evolution of the Raman signal in the region from between 125 cm\(^{-1}\) and 600 cm\(^{-1}\) together with (b) the voltage profile during the first discharge until 2.03 V. The discharge could not be conducted any further because of the drying of the electrolyte into the cell. The Raman spectra were obtained for the electrolyte in the inter electrode volume close but not at the cathode surface. Since the first spectrum only showed peaks originating from the electrolyte system (figure S3), this first spectrum was subtracted from the following to remove the contribution form the electrolyte system. No peaks were observed in the higher wavenumber region (>600 cm\(^{-1}\)) therefore not shown. The evolution of the peak intensities can be found in the supporting information (figure S5). During the initial period of discharge (region I in figure 5(b)), no change was observed. At the beginning of the high voltage plateau (2.37 V), bands at 395 cm\(^{-1}\), 446 cm\(^{-1}\), 510 cm\(^{-1}\), and 534 cm\(^{-1}\) started to appear, showing maximum intensities at the end of the plateau (2.30 V) (region II in figure 5(b)). The band at 395 cm\(^{-1}\) quickly decreases in intensity after this.
plateau and eventually completely disappears at 2.03 V. This band can be attributed to the formation of \( \text{S}_8^{2-} \) from elemental \( \text{S}_8 \) \[14\]. The presence of \( \text{S}_4^{2-} \) species on the slope between the high- and low-voltage plateaus confirms the presence of these species at the cathode surface, as discussed above for the carrageenan \( \text{Li–S EL-Cell} \). The band at 446 cm\(^{-1}\) shows a similar progression, however did not completely disappear at 2.03 V. This band can be assigned to the S–S stretching mode of \( \text{S}_4^{2-} \) \[14\]. The simultaneous emergence of these peaks suggest a fast reduction of \( \text{S}_8^{2-} \) to \( \text{S}_4^{2-} \). The small band at \( \sim 200 \text{ cm}^{-1} \), originating from the bending mode of \( \text{S}_4^{2-} \), emerged halfway the first plateau, reaching its highest intensity on the slope between the high- and low-voltage plateau. At the cathode surface (EL-Cell) this mode was accompanied with a bending mode at 233 cm\(^{-1}\), not observed for the capillary cell. This would support the fact that this species is closely related to the reaction between carrageenan and PS species. Interpretation of the peak at 534 cm\(^{-1}\) is difficult, as many anionic PS peaks can be observed in this range. Yeon et al \[13\] also observed this peak in discharged state by \textit{ex-situ} Raman spectroscopy, and attributed it to the radical anion \( \text{S}_3^{\bullet^{-}} \) species, created through the disproportionation of \( \text{S}_4^{2-} \):

\[
2\text{S}_4^{2-} \rightarrow 2\text{S}_3^{\bullet^{-}} + \text{S}_2^{2-}.
\]

Disproportionation of \( \text{S}_4^{2-} \) would be surprising at this stage of discharge, as \( \text{S}_2^{2-} \) species are expected to form near the end of discharge. Nevertheless, this hypothesis can be confirmed by the observation of a low intensity peak at around 510 cm\(^{-1}\) from probable \( \text{Li}_2\text{S}_2 \) formation. This band emerged almost simultaneously with the \( \text{S}_3^{\bullet^{-}} \) band and disappeared near the end of the high-order voltage plateau, which could indicate that the disproportionation reaction was terminated at low voltage level. The \( \text{S}_3^{\bullet^{-}} \) band decreased more gradually, implying that this radical species is relatively stable. Another possible reason for the formation of \( \text{S}_3^{\bullet^{-}} \) species is through \( \text{S}_6^{2-} \). Hannauer et al reported the presence of these species at discharge between 2.3 V and 2.1 V \[16\]. However, their study was performed in a cell with a mixture of tetraethylene glycol dimethyl ether (TEGDME) and DOL as electrolyte, it is therefore difficult to compare the results. Indeed, the influences of solvents' properties on the sulfur redox reaction have been studied by different groups using DOL-DME as a low dielectric and low donor solvent system and dimethyl sulfoxide (DMSO) as a high dielectric and high donor solvent system. \( \text{S}_6^{2-} \) was not involved in the discharge process in DOL-DME due to the fast reduction of \( \text{S}_8^{2-} \) to \( \text{S}_4^{2-} \) whereas \( \text{S}_6^{2-} \) and \( \text{S}_3^{\bullet^{-}} \) were observed in DMSO because of the relative slower disproportionation of \( \text{S}_8^{2-} \) to \( \text{S}_6^{2-} \) \[18, 49\]. The differences were attributed to the solvent's ability to solvate PS anions. Here, the spectra obtained from the cathode material as well as from the electrolyte system show a possible rapid reduction of \( \text{S}_4^{2-} \) from elemental sulfur during the initial period.
of discharge, suggesting that the formation of $S_3^{2−}$ through the disproportionation of $S_4^{2−}$ is more probable.

In conclusion, the major (electro)chemical reactions at the electrolyte system during discharge are proposed:

$$S_8 + 2e^- + 2Li^+ \rightarrow Li_2S_8$$  (4)

$$Li_2S_8 + 2e^- + 2Li^+ \rightarrow 2Li_2S_4$$  (5)

$$2Li_2S_4 \rightarrow 2LiS_8^{•−} + Li_2S_{precipitate}.$$  (6)

As for the Raman in operando measurement at the cathode surface, it can be concluded that the presence of carrageenan do not alter the electrochemical Li–S conversion as the expected PS species were observed in the electrolyte.

### 3.2. Operando optical imaging

Figure 6 exemplifies the color variation of the electrolyte during the first discharge–charge cycle of a carrageenan Li–S capillary cell. Note that in the first picture, before any discharge, the electrolyte already exhibits a light orange color illustrating the purely chemical dissolution of sulfur in the electrolyte [50].

During the discharge (figure 6(a)), the color changed from orange to dark red and then light yellow-green at the end of the discharge. These are typical catholyte colors when $Li_2S_4$ (dark red), $Li_2S_2$ (orange) and $Li_2S_2$ (yellow-green) PS species are dissolved in 1 M LiTFSI–DOL/TEGDME [19]. The voltage profile followed the same trend seen for the coin and El-Cells, except that the high voltage plateau is split into two plateaus at 2.32 V and 2.27 V. This split was not visible for the following discharges of this capillary cell (see figure 7). The observed color changes are in agreement with the Raman spectroscopy data. Presence of solvated $S_8^{2−}$ and $S_4^{2−}$ species before the discharge started (orange color). Increase in their concentration until a maximum dark red color at around 2.25 V, suggesting that the dominant solvated species is $S_8^{2−}$. A slight lightning of the color until the end of the first plateau, orange at 2.16 V, suggesting that the dominant solvated species is $S_4^{2−}$, followed by their reduction to shorter solvated PSs such as $S_2^{2−}$ at the end of the discharge, yellow-green color. This persistent color prove that not all the sulfur is reduced and this loss of active material explains why the reported discharge capacities of sulfur cathodes are most of the time less than the theoretical limit. During the charge (figure 6(b)), the color changed from light yellow-green to dark red with presence of a strong gradient. The charge voltage profile followed the same trend seen for charging coin and El-Cells. The same conclusion can be drawn for the charge of the cell, starting with solvated shorter PSs such as $S_2^{2−}$ and ending with $S_4^{2−}: S_8^{2−}$ solvated species (dark red). The color at the end of the discharge never return to very light color, as expected from precipitation of sulfur back into the cathode. Close to the cathode surface this might be true but strong color gradient exist in between the cathode and the anode (see below). It indicates that long chain PSs remain in the electrolyte, confirming the incomplete conversion from $Li_2S$ to $S_8$, another source of capacity loss. All these observation are in agreement with the ones reported by Sun et al [51] for a cell with a glass microfiber filter soak with the electrolyte in between the electrodes.

Herein, the geometry of our capillary cell allows however a more detailed analysis and we report the evolution of the PS concentration for several discharge–charge cycles.

To obtain quantitative information about the visual changes of the electrolyte, the average NGIs of different domains of the electrolyte were calculated for each images. The resulting evolution of the NGI, for different domain locations, are shown in figure 7(b) while the top graph (figure 7(a)) shows the discharge–charge voltage profiles.

Although the NGIs only quantifies the changes from weakest to strongest intensities, a relationship between the NGIs, the concentration of solvated PS and to some extent the typical color of dissolved PS, i.e. the composition of the solution can be postulated. The first NGI maximum in figure 7(b) corresponds to the darkest red image displayed in figure 6(a), at the voltage of 2.23 V, while the first NGI minimum corresponds to the yellow-green light image at the end of the first discharge ($\sim$1.9 V). For these two extrema, and in agreement with the Raman analysis, we can state that the dominant species in solution are $S_8^{2−}$ and $S_2^{2−}$ respectively. During cycling, the local discharge minima are increasing in values while the local maxima are decreasing with the cycle number. It illustrates that less and less solvated PSs are electrochemically converted.
as an evidence of the capacity fading. Indeed the concentration of solvated PSs, in the discharged state increases with cycling number.

Figure 8 displays the NGI gradients across the cell at various points in time during cycling. At the end of the first discharge plateau, the NGI value is at its maximum (green curve). At this point of cycling most of the sulfur has been reduced to S$_8^{2-}$ and S$_4^{2-}$, at the cathode, and therefore the PSs concentration in the electrolyte is high. Almost no gradient exists when moving away from the cathode. It shows that during discharge the diffusion of PSs species within the full electrolyte volume is fast (the NGIs curves are almost superimposed, up to NGI = 0.8 in figure 7(b)). Sun et al reported gradients during the discharge but it is difficult to compare their results since no unit was used on their graphs [51]. At the end of discharges (∼1.9 V) the intensities are low and with again, almost no gradient across the cell (see all bottom curves in figure 8, except the red one). The high order PSs have been converted into low order ones and may have precipitated into the cathode. It is to note that with increasing number of cycles, a zone of slightly higher PS concentration and situated in the middle of the interspace between the electrodes develops. This is clearly visible in figure 7(b), with the orange curve passing more and more over the blue curve during the discharge. During the charge strong gradient develop with a higher PSs concentration close to the cathode (middle curves in figure 8). It is the strongest slightly before the end of the charge (∼2.47 V) where the NGIs at the
Figure 7. Optical analysis of the capillary carrageenan cell’s electrolyte. (a) Voltage profile during cycling of the cell. (b) Normalized gray values intensity (NGI) overtime at fixed positions (blue = cathode, orange = middle, green = anode). Right: the green rectangles represents the domains where the normalized gray values intensities were evaluated.

Figure 8. Normalized gray values intensity (NGI) gradient, from the cathode to the anode, at various point of cycling. The color of the line refers to the time at which the gradients have been calculated and correspond to the color of the points (circles and triangles) in figure 7. The dashed lines are the gradients just before the end of the second plateau during the charge (triangles in figure 7).

cathode show maxima (triangles in figure 7). During the charge solid Li$_2$S is oxidized into solvable PSs up to S$_8^{2-}$ which ultimately may precipitate back in the cathode as elemental sulfur. This explains the NGI peaks seen during the charge, attributed to dark red color region (S$_8^{2-}$). The large concentration gradients indicates that at this stage of the battery charge, the diffusion of the PSs does control the concentration opposite to the observation during the discharge. Furthermore, with increasing cycling number, there is an evident splitting of the NGIs charge peaks, from the cathode to the anode position, with an increasing gradient of the PS concentration. At the end of the discharge, the concentration maximum is found in the middle of the electrodes for the second and third charges. Not all the PSs find their way back to the cathode. At the end of the last presented charge, followed by a shallow discharge (not presented here), the PS concentration at the anode is the highest while at the cathode and at the middle position the concentration have very similar evolution than for the previous charge. This could be the extreme evidence of the PSs shuttle and their reaction at the anode surface where Li$_2$S$_8$ are reduced to Li$_2$S$_4$, locally increasing the PSs concentration.
Several Li–S models have been published in the literature, some of them present the average evolution of the concentration of the different PSs during the discharge within the cathode \cite{52, 53} and in the electrolyte \cite{54} and at least one, also during the charge, at the anode and cathode \cite{55}. In all the studies, the model results are compared with the voltages results but never with experimental results on the PSs evolution. The scope of the present study was not to develop a complex model and compare the simulated results with the optical data presented here in. However, to get more insight on the optical results, we analyze further our data in the light of a very simple model.

An one-dimensional model based on the Fick’s laws (equation (7)), was developed to simulate the diffusion of the PS in the electrolyte space between the electrodes

\[ J = -D \frac{dC}{dx} \text{ and } \frac{dC}{dt} = D \frac{d^2C}{dx^2} \]

where the diffusion flux \( J \) depends on the concentration gradient \( C \) and the diffusion coefficient \( D \). Here we assume common coefficient for all the PSs. A detailed description of the model can be found in the supplementary information.

The simulations were run using, as PS source–sink term, the NGI values at the cathode surface obtained from the optical image analysis (blue curve in figure 7(b)). A diffusion coefficient, of \( D = 7.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \) was found to give good agreement of the simulated NGIs with the experimental data during the first discharge of the cell (figure 9). This value of \( D \) is of the same order of magnitude than the reported diffusion coefficient of PSs in the same electrolyte type \cite{52}.

These results show that in a first approximation, the concentration gradient mainly governs the PSs diffusion in the electrolyte during the discharge. However, with a close look at the curves in figure 9(a), after the maxima one can observe the development of a slight gradient in the concentration, with more PSs close to the cathode surface than at the anode, which is not captured by the model. This is emphasized by the relative error plots, with the error becoming larger with time and increasing distance from the cathode (figure 9(b)). This is consistent with the Raman analysis where a back flow of the \( \text{Li}_2\text{S}_8 \) is observed which at the surface of the cathode are reduced to \( \text{Li}_2\text{S}_4 \), i.e. locally increasing the PSs concentration because of the 1–2 stoichiometric ratio and ultimately precipitate as \( \text{Li}_2\text{S} \).

This simple Fick model fails to reproduce the experimental data during the charges, showing that the PS concentration evolution is not solely driven by concentration gradients during that process. Here, a more complex model must be used, integrating the migration imposed by the electric field, the localized space charge at the electrode surface from the reduction reaction including the reaction occurring at the anode resulting from the PS shuttle. This should be the content of further study.

3.2.1. From capillary to coin cell

Figure 10 displays the voltage profile evolution during the second discharge–charge cycle for carrageenan coin cell and capillary cell. Different cutting voltage were used during the discharge, 1.8 V for the coin cell and 1.9 V for the capillary cell. For the ease of comparison and discussion, normalized time is used. As already mentioned, the two cells exhibits the expected two plateaus voltage during discharge. However, the
Figure 10. Voltage profile evolution during second discharge–charge cycle for typical carrageenan coin cell (black lines) and capillary carrageenan cell red line. For ease of comparison the voltage is plotted versus normalized time.

high voltage plateau for the capillary cell is shorter, half the duration of the plateau of the coin cell. It suggests that while for the coin cell, most of the solvation of the PSs is electrochemically driven, in the case of the capillary cell concurrent chemical solvation of the PS may also occur. The solution saturation may not be reach in the case of the capillary cell due to the larger volume of electrolyte, \(\sim 100 \mu l \text{mg}^{-1}\) of sulfur vs \(10 \mu l \text{mg}^{-1}\) for the coin cell. While the second plateau is practically flat for the coin cell, for the capillary cell it is sloppy and starting at higher value. It suggests that while for the coin cell, mainly the same reduction reactions occur during the second plateau, with the precipitation of Li\(_2\)S and Li\(_2\)S\(_2\) (equations (2) and (3)), concurrent reactions starting from the reduction of S\(_8\)\(^-\) (equation (1)) and followed by the reaction of equations (2) and (3) are occurring in the case of the capillary cell. This is supported by the Raman capillary cell study with all the sulfides species, including S\(_2\)\(^-\) observed just after the first voltage plateau. The voltage dip between the two plateaus, is not observed for the capillary cell. It is common to attribute this voltage local minimum to the slow rate of precipitation and nucleation of the first seeds of solid Li\(_2\)S and the resulting critical supersaturation of S\(_2\)\(^-\)\([52]\). Our results however confirm the findings from Zhang et al\([56]\). They found that the voltage dip is also a consequence of the electrolyte resistance peaking at the transition between the two voltage plateaus, due to the high PSs concentration at this stage of discharge. This resistance peaking must be reduced when a large volume of electrolyte is used, as it is the case for the capillary cell. Note also that the voltage dip was also not observed for the EL-Cell for which the amount of electrolyte is also about 3 time larger than for the coin cell. This sheds light on the origin of the different voltage profiles one may encounter in the literature.

The charge voltage profile also exhibits a sloppier behavior for the capillary cell than for the coin cell. During the charge the over potential is larger for the capillary cell and the shallow plateaus, in principle attributed to the precipitation of elemental sulfur, appear at two very different state of charge, 0.3 and 0.75 of the normalized time for the capillary and coin cell respectively. We have no experimental evidence to understand and explain these difference. It appears more difficult to convert the lithium sulfide back to sulfur in the case of the capillary cell. The geometry of the cell is certainly having an impact here but it is difficult to assess whether it is the distance between electrode, the volume of the electrolyte, the solvation and PSs concentration gradient, different Li\(_2\)S deposition mechanisms or others mechanisms which lead to the observed difference.

4. Conclusion

In the present work we have confirmed that carrageenan can be used as binder for the cathode of LSB and would help to reduce the capacity fading during charge–discharge cycling. The Raman spectroscopy studies revealed that the typical electro chemistry of the Li–S is not modified and we confirmed the disproportionation of the S\(_4\)\(^-\) species in the electrolyte, not visible directly at the cathode surface. No strong evidences of the nucleophilic substitution support the functionality of the carrageenan and the Raman and optical analysis demonstrate PSs diffusion within the electrolyte volume. So even though carrageenan may trapped some of the PSs, complementary solution must be apply to limit the PSs shuttle. Slightly increasing
the amount of carrageenan in the cathode may help to increase the number of trapping site but would be detrimental for the overall electrode performances. An advantage, over conventional binder, is that carrageenan is water soluble—no need to use expensive, hazardous solvent—this would reduce the batteries manufacturing costs and should be considered for any battery technology not only for the Li–S chemistry. We observed that difference in the electrolyte volume influence strongly the voltage profiles. We report evidence of non-homogeneous PSs concentration building up along with the cycling number for the capillary cell. Whether or not this detrimental behavior occurs in cells of lower electrolyte volume should be addressed experimentally and by elaborated simulation studies.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Acknowledgment

We are thankful to CP Kelco ApS providing the carrageenan materials.

ORCID ID

Didier Blanchard  https://orcid.org/0000-0001-7777-2891

References

[1] Kim J, Lee D-J, Jung H-G, Sun Y-K, Hassoun J and Scrosati B 2013 An advanced lithium–sulfur battery Adv. Funct. Mater. 23 1076–80
[2] Song M-K, Cairns E J and Zhang Y 2013 Lithium/sulfur batteries with high specific energy: old challenges and new opportunities Nanoscale 5 2186–204
[3] Kobayashi T, Imade Y, Shishihara D, Homma K, Nagao M, Watanabe R, Yokoi T, Yamada A, Kanno R and Tatsumi T 2008 All solid-state battery with sulfur electrode and thio-LISICON electrolyte J. Power Sources 182 621–5
[4] Manthiram A, Chung S-H and Zu C 2015 Lithium–sulfur batteries: progress and prospects Adv. Mater. 27 1980–2006
[5] Lin Z and Liang L C 2015 Lithium–sulfur batteries: from liquid to solid cells J. Mater. Chem. A 3 936–58
[6] Manthiram A, Fu Y and Su Y-S 2013 Challenges and prospects of lithium–sulfur batteries Acc. Chem. Res. 46 1125–34
[7] Kim T-H, Park J-S, Chang S K, Choi S, Ryu J H and Song H-K 2012 The current move of lithium ion batteries towards the next phase Adv. Energy Mater. 2 860–72
[8] Xiong S, Xie K, Diao Y and Hong X 2014 Characterization of the solid electrolyte interphase on lithium anode for preventing the shuttle mechanism in lithium–sulfur batteries J. Power Sources 246 840–5
[9] Chan C K, Peng H, Liu G, Mellarwha K, Zhang X F, Huggins R A and Cui Y 2008 High-performance lithium battery anodes using silicon nanowires Nat. Nanotechnol. 3 31–5
[10] Li X and Nazar L F 2010 Advances in Li–S batteries J. Mater. Chem. 20 9821–6
[11] Wild M, O’Neill L, Zhang T, Purkayastha R, Minton G, Marinescu M and Offer G J 2015 Lithium sulfur batteries, a mechanistic review Energy Environ. Sci. 8 3477–94
[12] Mikhaylik Y V and Akridge J R 2004 Polysulfide shuttle study in the Li/S battery system J. Electrochem. Soc. 151 A1969
[13] Yeon J-T, Iang I-Y, Han J-G, Cho J, Lee K T and Choi N-S 2012 Raman spectroscopic and x-ray diffraction studies of sulfur composite electrodes during discharge and charge J. Electrochem. Soc. 159 A1308–14
[14] Zha W et al 2017 Investigation of the reaction mechanism of lithium sulfur batteries in different electrolyte systems by in situ Raman spectroscopy and in situ x-ray diffraction Sustain. Energy Fuels 1 737–47
[15] Hagen M, Schillfels P, Hammer M, Dörfler S, Tübke J, Hoffmann M J, Althues H and Kaskel S 2013 In-situ Raman investigation of polysulfide formation in Li–S cells J. Electrochem. Soc. 160 A1205–14
[16] Hannan A, Scheers J, Fullemarth J, Fraisse B, Stevano L and Johansson P 2015 The quest for polysulfides in lithium–sulfur battery electrolytes: an operando confocal Raman spectroscopy study ChemPhysChem 16 2755–9
[17] Wu H L, Huff L A and Gewirth A A 2015 In situ Raman spectroscopy of sulfur speciation in lithium–sulfur batteries ACS Appl. Mater. Interfaces 7 1709–19
[18] Zou Q and Lu Y-C 2016 Solvent-dictated sulfur redox reactions: an operando UV–vis spectroscopic study J. Phys. Chem. Lett. 7 1518–25
[19] Patel M U M, Demir-Cakan R, Morcrrette M, Tarascon J-M, Gaborseck M and Dominko R 2013 Li–S battery analyzed by UV/vis in operando mode ChemSusChem 6 1177–81
[20] Cañas N A, Fronczek D N, Wagner N, Latz A and Friedrich K A 2014 Experimental and theoretical analysis of products and reaction intermediates of lithium–sulfur batteries J. Phys. Chem. C 118 12106–14
[21] Cuisinier M, Cabelguen P-E, Evers S, He G, Kolbeck M, Garsuch A, Bolin T, Balasubramanian M and Nazar L F 2013 Sulfur speciation in Li–S batteries determined by operando x-ray absorption spectroscopy J. Phys. Chem. Lett. 4 3227–32
[22] Walus S, Barchass C, Colin J-F, Martin J-F, Elkaïm E, Leprêtre J-C and Alloin F 2013 New insight into the working mechanism of lithium–sulfur batteries: in situ and operando x-ray diffraction characterization Chem. Commun. 49 7899–901
[23] Nelson J, Misra S, Yang Y, Jackson A, Liu Y, Wang H, Dai H, Andrews J G, Cui Y and Toney M F 2012 In operando x-ray diffraction and transmission x-ray microscopy of lithium sulfur batteries J. Am. Chem. Soc. 134 6537–43
[24] Cheng J-H, Assiege A A, Huang C-J, Lin M-H, Tripathi A M, Wang C-C, Tang M-T, Song Y-F, Su W-N and Hwang B J 2017 Visualization of lithium plating and stripping via in operando transmission x-ray microscopy J. Phys. Chem. C 121 7761–6
[25] Tan C, Heenan T M M, Ziesche R F, Daemi S R, Hack J, Maier M, Marathe S, Rau C, Brett D J L and Shearing P R 2018 Four-dimensional studies of morphology evolution in lithium–sulfur batteries ACS Appl. Energy Mater. 1 5090–100
Taiwo O O, Loveridge M, Beattie S D, Finegan D P, Bhagat R, Brett D J L and Shearing P R 2017 Investigation of cycling-induced microstructural degradation in silicon-based electrodes in lithium-ion batteries using x-ray nanotomography J. Phys. Chem. C 121 11391–9

Yu S-H, Huang X, Schwarz K, Huang R, Arias T A, Brock J D and Abrau H D 2018 Direct visualization of sulfur cathodes: new insights into Li–S batteries via operando x-ray based methods Energy Environ. Sci. 11 202–10

Tan C, Kok M D R, Daemi S R, Brett D J L and Shearing P R 2019 Three-dimensional imaging of sulfur battery parameters in lithium–sulfur batteries Phys. Chem. Chem. Phys. 21 4145–54

Sun F et al 2018 Visualizing the morphological and compositional evolution of the Li/S cathode in a Li–S battery by operando x-ray tomography Science 360 681–4

Zielke L, Ragupathy P, Ahad S A, Kumar P R, Lee H-W and Kim D K 2017 A flexible glass fiber based freestanding composite electrode for lithium–sulfur batteries J. Mater. Chem. A 5 22489–96

Zielke L et al 2015 Degradation of Li/S battery electrodes on 3D current collectors studied using x-ray phase contrast tomography Sci. Rep. 5 1–12

Sun F, Olsenberg M, Dong K, Zhou D, Hilger A, Jaffa C J, Risse S, Lu Y, Markötter H and Manke I 2018 Correlating morphological evolution of Li/S electrodes with electrochemical performance of Li/LiCoO2 and Li/S battery systems: investigated by synchrotron x-ray phase contrast tomography ACS Energy Lett. 3 536–45

Sermukhambetova A, Tan C, Daemi S R, Bakenov Z, Darr J A, Brett D J L and Shearing P R 2016 Exploring 3D microstructural evolution in Li–sulfur battery electrodes using in-situ x-ray tomography Sci. Rep. 6 1–9

Li Z, Zhang J T, Chen Y M, Li J and Lou X W 2015 Pie-lead electrode design for high-energy density lithium–sulfur batteries Nat. Commun. 6 1–8

Fang R, Zhao S, Hou P, Cheng M, Wang S, Cheng H-M, Liu C and Li F 2016 3D interconnected electrode materials with ultrahigh areal sulfur loading for Li–S batteries Adv. Mater. 28 3374–82

Ragupathy P, Ahad S A, Kumar P R, Lee H-W and Kim D K 2017 A flexible glass fiber based freestanding composite electrode for high-performance lithium polysulfide batteries Adv. Mater. 29 4350–57

He J, Chen Y and Mantlimath A 2017 Vertical CaO@Co3O4 hollow nanowall arrays grown on a Celgard separator as a multifunctional polysulfide barrier for high-performance Li–S batteries Energy Environ. Sci. 10 3560–68

Rana M et al 2020 Impact of micropores and dopants to mitigate lithium polysulfides shuttle over high surface area of ZIF-8 derived nanoporous carbons ACS Appl. Energy Mater. 3 5523–32

Rana M, Ahad S A, Li M, Luo B, Wang L, Gentle I and Knibbe R 2019 Review on areal capacities and long-term cycling performances of lithium sulfur batteries at high sulfur loading Energy Storage Mater. 18 289–310

di Rosa M 1972 Biological properties of carrageenan J. Pharm. Pharmacol. 24 89–102

Ling M, Zhang L, Zheng T, Feng J, Guo J, Mai L and Liu G 2017 Nucleophilic substitution between polysulfides and binders unexpectedly stabilizing lithium sulfur battery Nano Energy 38 82–90

Johnsen R E and Norby P 2013 Capillary-based micro-battery cell for investigating polysulfides in lithium–sulfur batteries on a nanoscale basis Electrochim. Acta 100 300–8

Das S, Ngene P, Norby P, Vegge T, de Jongh P F E and Blanchard D 2016 All-solid-state lithium–sulfur battery based on a nanoconfined LiBH4 electrolyte J. Electrochem. Soc. 163 A2029–34

Unemoto A, Yasaku S, Nogami G, Tazawa M, Taniguchi M, Matsu M, Ikeshoji T and Orimo S-I 2014 Development of bulk-type all-solid-state lithium–sulfur battery using LiBH4 electrolyte Appl. Phys. Lett. 105 083901

Scott D W and McCullough J P 1961 Vibrational assignment and force constants of S8 from a normal-coordinate treatment J. Mol. Spectrosc. 6 372–8

Poleshchuk O K, Egorov N R, Akimov D V, Zherin I I and Zhuravlev N A 2016 Study of sulfur isotopes by vibrational spectroscopy and quantum chemistry IOP Conf. Ser. Mater. Sci. Eng. 112 012005

Socrates G 2004 Infrared and Raman Characteristic Group Frequencies: Tables and Charts (New York: Wiley)

El Jaroudi O, Piquenard E, Gobeltz N, Demortier A and Corset J 1999 Raman spectroscopy study of the reaction between sodium sulfide or disulfide and sulfur: identity of the species formed in solid and liquid phases Inorg. Chem. 38 2917–23

Inaj T G, Downey J R, Roduner E, Wasilczuk G J, Coutts J W and Eluard A 1976 Raman studies of sulfur-containing anions in inorganic polysulfides. Sodium polysulfides Inorg. Chem. 15 1759–63

Lu Y-C, He Q and Gasteiger H A 2014 Probing the lithium–sulfur redox reactions: a rotating-ring disk electrode study J. Phys. Chem. C 118 5753–41

Sciannma S F and Linn S 1988 Sulfur solubility in pure and mixed organic solvents Ind. Eng. Chem. Res. 27 485–91

Sun Y, Seh Z W, Li W, Yao H, Zheng G and Cui C Y 2015 In-operando optical imaging of temporal and spatial distribution of polysulfides in lithium–sulfur batteries Nano Energy 11 579–86

Kumaresan K, Mikhaylik Y and White R E 2008 A mathematical model for a lithium–sulfur cell J. Electrochem. Soc. 155 A576

Danner T, Zhu G, Hofmann A F and Latz A 2015 Modeling of nano-structured cathodes for improved lithium–sulfur batteries Electrochim. Acta 184 124–33

Ren Y, Zhao T S, Liu M, Tan P and Zeng Y K 2016 Modeling of lithium–sulfur batteries incorporating the effect of Li2S precipitation J. Power Sources 336 115–25

Hofmann A F, Fronczek D N and Bessler W G 2014 Mechanistic modeling of polysulfide shuttle and capacity loss in lithium–sulfur batteries J. Power Sources 259 300–10

Zhang T, Marinuesc M, O’Neill L, Wild M and Offer G 2015 Modeling the voltage loss mechanisms in lithium–sulfur cells: the importance of electrolyte resistance and precipitation kinetics Phys. Chem. Chem. Phys. 17 22581–6