Kinetics of sulphur dissolution in lithium–sulphur batteries

Matthew Dent*, Ewa Jakubczyk, Teng Zhang and Constantina Lekakou

Department of Mechanical Engineering Sciences, University of Surrey, Guildford, United Kingdom
* Author to whom any correspondence should be addressed.
E-mail: m.j.dent@surrey.ac.uk

Keywords: sulphur, dissolution, DOL:DME electrolyte, diffusion, Li–S batteries

Supplementary material for this article is available online

Abstract
This study investigates and determines the dissolution kinetics of solid sulphur in DOL:DME solution, a typical electrolyte solution for lithium–sulphur (Li–S) batteries, at four different temperatures, in the range of 17 °C–20 °C. The dissolution kinetics is considered as a function of the solid sulphur–solution interfacial area. The analysis yielded fast dissolution kinetics with a mass transfer coefficient of $2.3 \times 10^{-3}$ m s$^{-1}$ at 20 °C but low sulphur solubility of 0.058 S mol lt$^{-1}$, with the latter being a limiting factor in sulphur dissolution. In later stages, swelling of the solid sulphur region was also observed as a function of time from which the diffusion coefficient of the DOL:DME solution in the solid sulphur was determined. A novel model for the sulphur dissolution and electrolyte impregnation in a Li–S cathode in battery fabrication is presented taking into account the pore size distribution of the cathode host. A computer simulation was carried out and the model and the dissolution parameter values were validated by comparing the predictions with experimental data from in operando microscopy during the dissolution of sulphur and infiltration of the DOL:DME solution in a commercial sulphur-conductive carbon cathode.

1. Introduction

Energy storage remains the bottleneck for the electrification of many engineering sectors, such as electric vehicles in land, sea and air [1, 2], and portable devices, along with the wide adoption of renewable energy sources [3]. Lithium–Sulphur (Li–S) batteries have the potential of high capacity compared to the current industry standard of lithium-ion (Li-ion) batteries, in terms of both gravimetric and volumetric energy density [4], high availability of sulphur in the Earth's crust, low cost [4] and low toxicity of sulphur [5]. However, there are several problems to overcome before Li–S batteries can become the industry standard [6]. For the Li–S batteries to attain the critical metrics [7], it is imperative to achieve high sulphur loading in the cathode, minimise the amount of electrolyte and maintain high battery efficiency and cyclability.

A major issue with high sulphur loading (usually targeted above 70 wt% and 4 mg cm$^{-2}$ of cathode [7]) is to be able to dissolve all sulphur impregnated in the cathode during the time of the discharge phase [8], which becomes even more difficult in lean electrolyte battery cells [7]. Optimisation of the amount of electrolyte in Li–S battery cells is based on the solubility of the polysulphides Li$_2$S$_x$, $x = 2–8$, which has been measured to reach a maximum of 5–6 M in terms of S mol lt$^{-1}$ [9, 10]. However, atomic sulphur solubility in electrolyte solvents is much lower, $40 \times 10^{-3}$ M in terms of S mol lt$^{-1}$ in 1 M LiTFSI in DOL:DME 1:1 v/v [11], due to the large difference between the solubility parameters [12, 13] of sulphur ($\delta_{\text{sulphur}} = 33.1$ J$^{1/2}$ cm$^{-3/2}$ [14]) and the typical electrolyte solvents DOL ($\delta_{\text{DOL}} = 20.76$ J$^{1/2}$ cm$^{-3/2}$) and DME ($\delta_{\text{DME}} = 18.00$ J$^{1/2}$ cm$^{-3/2}$) [15].

Another issue related to the electrolyte is the dissociation of polysulphides and their shuttling between anode and cathode, which reduces the efficiency, capacity and usable lifetime of the cell [16]. A smaller amount of electrolyte reduces the sulphide migration but, as it can also dissolve less sulphur, an optimum needs to be determined.

Modelling and simulations of the operation of the Li–S battery could be employed for the optimisation of the amount of electrolyte and design of cathode as well as optimisation of the battery cell cycling conditions,
especially for the first ‘formation’ cycles. Several types of battery models can be used. A simple zero-dimensional model for a Li–S battery with the shuttling being represented by the rate of lost sulphur proportional to the $S_8$ concentration [16, 17], employing an empirical constant, may be useful for the simulation of Li–S battery operation but not for material and electrolyte design. One-dimensional models based on the Nernst-Plank equations are more useful to describe the shuttle effect as they include ion transport in the cell [18]. If such models are extended to multiple ion transport equations for different pore sizes [19, 20], taking into account the pore size distribution of cathode, they could be also employed for the design of the cathode materials [6].

Current research into sulphur dissolution is limited and there is a gap in data for its kinetics. While a number of recent studies focused on modelling the nucleation and growth kinetics of Li$_2$S [21–23], the only source in the literature with parameters for the dissolution kinetics of sulphur and sulphides is traced back to Kumaresan’s 2008 paper [18], in which, in fact, the authors state that their parameter values are assumed. Furthermore, the dissolution kinetics in Kumaresan’s model [18] relies on the simplifying assumption that the sulphur dissolution rate is independent of the area of the solid-liquid interface, which means that their model does not provide any accurate predictions of sulphur dissolution depending on the initial sulphur particle size [24] or the size of the pores in which the sulphur might be impregnated [25].

The present study focuses on filling this gap by investigating and determining the dissolution kinetics of solid sulphur. Furthermore, a novel model for the sulphur dissolution and electrolyte impregnation in a Li–S cathode in battery fabrication is presented and the dissolution of sulphur is investigated in a commercial sulphur-conductive carbon cathode via computer simulations and experiment. The model takes into account the pore size distribution of the cathode host.

2. Model of sulphur dissolution and electrolyte infiltration in the cathode

Figure 1 presents the schematic of the sulphur dissolution experiment to determine the dissolution kinetics in this study. The sulphur is in solid phase as $S_8$ [25, 26] in contact with the electrolyte solution via a distinct plane solid–liquid interface of area $A$. The dissolution kinetics at the solid-liquid interface is described by the following equations [27–29]:

$$\frac{\partial m_{S_8}}{\partial t} = k_{S_8}A \left(C_{S_8\text{ - bulk}} - C_{S_8\text{ - sol}}\right)$$  \hspace{1cm} (1)

where $\frac{\partial m_{S_8}}{\partial t}$ is the rate of the dissolved $S_8$ ($S_8$-mol s$^{-1}$), $C_{S_8\text{ - bulk}}$ and $C_{S_8\text{ - sol}}$ are the saturation and bulk concentrations of $S_8$ in the solution ($S_8$-mol m$^{-3}$) and $k_{S_8}$ is the mass transfer coefficient (m s$^{-1}$) of $S_8$ in the solution.

Sulphur further diffuses in the solution according to Fick’s law:

$$\frac{\partial C_{S_8}}{\partial t} = D_{S_8\text{ - Sol}} \frac{\partial^2 C_{S_8}}{\partial y^2}$$  \hspace{1cm} (2)

where $t$ is time (s), $y$ is distance (m), $C_{S_8}$ is the $S_8$ concentration ($S_8$-mol m$^{-3}$), $D_{S_8\text{ - Sol}}$ is the diffusion coefficient of $S_8$ in the solution given by the Stokes Einstein relation [19, 20]:

$$D_{S_8\text{ - Sol}} = \frac{k_B T}{3\pi \eta d_{S_8}}$$  \hspace{1cm} (3)

where $k_B$ is the Boltzmann’s constant, $T$ is the absolute temperature (K), $\eta$ is the solution viscosity ($\eta = 0.5$ mPa s for the DOL:DME 1:1 v/v solution [30]) and $d_{S_8}$ is the size of the $S_8$ molecule in the solution [25, 31].

Fick’s law is also applied for the diffusion of solvent molecules in the solid sulphur phase:

$$\frac{\partial C_{\text{sol}}}{\partial t} = D_{\text{Sol-SS}} \frac{\partial^2 C_{\text{sol}}}{\partial y^2}$$  \hspace{1cm} (4)

where $C_{\text{sol}}$ is the solvent concentration in the solid $S_8$ (mol m$^{-3}$) and $D_{\text{Sol-SS}}$ is the diffusion coefficient of solvent(s) in the solid $S_8$ phase. Determination of $D_{\text{Sol-SS}}$ is useful for the modelling of the species transport through $S_8$ in small pores of the cathode host [32], in which, in fact, $S_8$ remains mostly undissolved during Li–S battery cycling and Li$^+$ ion transport and sulphide reactions may happen either in fully solid sulphur phase or semi-solid phase [33] where some solvent might have diffused.

A cathode in a Li–S battery consists of a porous conductive host with sulphur impregnated in the pores. The conductive host might comprise a network of conductive particles such as carbon black, SuperP carbon...
Figure 1. Diagram of S\textsubscript{8} concentration profile against distance \(y\) in the dissolution of sulphur from solid phase (yellow) to a solvents solution (light blue).

Figure 2. Diagram of the porous host plaque domain (black), impregnated with sulphur (yellow), with a crack channel surrounding the perimeter of half width \(W_{ch}\).

or carbon nanotubes \cite{24}, graphene and graphene oxide \cite{34} or activated carbon \cite{35, 36}. Many of these cathodes can be considered homogeneous in-plane, as cloth-type cathode hosts \cite{25, 37} or coatings \cite{38} but some coatings exhibit cracks surrounding polygon-shaped regions. Such coatings include high volume-low density hosts, such as graphene and graphene oxide \cite{39–41}, carbon nanotubes \cite{42, 43} or carbon black, which shrink during solvent evaporation and form cracks. Figure 2 displays the schematic of cathode used for modelling the electrolyte infiltration. It comprises a 3D domain with a circular host porous plaque (black) of diameter \(D_{host}\) and transverse thickness \(H_{c,o}\). The porous plaque is impregnated with sulphur which fills the pores and any sulphur excess forms a solid sulphur layer wrapping the plaque of thickness \(H_{S}\). A crack surrounds the composite domain of half channel width \(W_{ch}\).

When the electrolyte is added during fabrication, it fills the crack channel and the remainder lies over the composite plaque and crack channel. As time proceeds, the numerical solution of the computational model proceeds in timesteps. At each timestep, the electrolyte dissolves some of the sulphur according to equation (1) with the local bulk concentration, \(C_{S8-bulk}\), being updated to take into account the dissolved sulphur. The dissolution process starts with the solid sulphur layer of \(H_{S}\) thickness and any solid sulphur particles. If the whole \(H_{S}\) thickness is dissolved before \(C_{S8-sat}\) is reached, the electrolyte reaches the sulphur in the pores of the plaque. The plaque host has a pore size distribution (PSD) and sulphur dissolution in the pore sizes of the PSD is considered in parallel. After the porosity \(\varepsilon_{p}\) of each pore size \(p\) increases after sulphur dissolution
at the beginning of each timestep, the electrolyte infiltrates the generated pore volume in capillary flow
obeying Darcy’s law [25, 44] to determine the average velocity through each pore size $p$, in the radial
direction, $U_r$, and the transverse direction, $U_y$:

$$
U_r = \frac{K_p \, P_{c,p}}{\varepsilon_r \eta \, L_{r,r}} \quad U_y = \frac{K_p \, P_{c,p}}{\varepsilon_y \eta \, L_{r,y}}
$$

(5)

where $L_{r,r}$ and $L_{r,y}$ are the filled lengths in $r$ and $y$ directions, respectively (electrolyte filling starting from
the perimeter and top of the plaque in figure 2), $K_p$ is the permeability of porous material of pore size $d_p$ given
by Carman-Kozeny equation for flow through spherical particles [45]:

$$
K_p = \frac{\varepsilon_p d_p^2}{16 \times 7.5}
$$

(6)

and $P_{c,p}$ is the capillary pressure in pore $p$ given by the Young-Laplace equation [46]:

$$
P_{c,p} = \frac{4 \sigma \cos \gamma}{d_p}
$$

(7)

where $\sigma$ is the surface tension and $\gamma$ is the contact angle: $\sigma = 28.68$ mN m$^{-1}$ for the DOL:DME mixture
[47, 48] and $\gamma = 20^\circ$ between DOL:DME solution and a carbon-sulphur surface [49].

In this manner, a transport equation is written for the determination of the volume fraction of electrolyte
saturation, $S_{c,p}$, in pore size $p$:

$$
\frac{\partial (\varepsilon_p \rho_e S_{c,p})}{\partial t} + U_r \frac{\partial (\varepsilon_p \rho_e S_{c,p})}{\partial r} + U_y \frac{\partial (\varepsilon_p \rho_e S_{c,p})}{\partial y} = 0
$$

(8)

where $\rho_e$ is the density of the electrolyte solution.

Finally, the concentration for the local bulk concentration is given by the sulphur transport
concentration:

$$
\frac{\partial (\varepsilon_p C_{88-sbaulk,p})}{\partial t} + U_r \frac{\partial (\varepsilon_p C_{88-sbaulk,p})}{\partial r} + U_y \frac{\partial (\varepsilon_p C_{88-sbaulk,p})}{\partial y} = D_{88-sol} \frac{1}{r} \frac{\partial}{\partial r} \left[ r \frac{\partial (\varepsilon_p C_{88-sbaulk,p})}{\partial r} \right] + D_{88-sol} \frac{\partial^2 (\varepsilon_p C_{88-sbaulk,p})}{\partial y^2} + \frac{\partial m_{88}}{\partial t} \frac{\partial \delta V}{\partial \delta V}
$$

(9)

where $dV$ is the cathode volume element.

3. Materials and experimental methods

The materials used are: solvents 1,3 dioxolane (DOL) (anhydrous, 99.8% purity, Sigma Aldridge, UK),
1,2-dimethoxyethane (DME) (99+% purity, Alfa Aesar™, Europe), sulphur (Sigma Aldridge, UK), and
cathode material NANOMYTE® BE-70E (NEI Corporation, NJ, USA). This cathode consists of a 16 µm thick
carbon-coated aluminium sheet as the current collector, one-side coated by a 55 µm thick tape containing
70 wt% sublimed sulphur as the active material (3.7 mg cm$^{-2}$), 20 wt% Super P carbon black and 10 wt%
poly(vinylidene fluoride) (PVDF) as the binder.

The solvents DOL and DME were mixed at a proportion of 1:1 v/v. For the experiment to determine the
kinetics of sulphur dissolution, 0.5 g of sulphur powder was placed in a quartz glass cuvette of a square
cross-section of 1 cm$^2$. This cuvette was placed in a preheated silicon oil bath at 125 °C for the sulphur to
melt. The process required a few hours to ensure that the sulphur powder was completely melted. The
cuvette was then removed from the silicon bath and held level to ensure the sulphur solidifies and its top
surface is flat and horizontal. The cuvette was moved to a fume cupboard (with fan switched off), under
constant light conditions. 3 cm$^3$ of premixed DOL:DME 1:1 v/v solution was added. A colour video camera,
opposite one face of the cuvette, recorded the process for up to three hours. Four such experiments were
carried out at: 17 °C, 18 °C, 19 °C and 20 °C.

Another experiment was carried out to determine the corresponding saturation concentration values
of sulphur in the DOL:DME solution. Test tubes were filled with 1 ml of premixed DOL:DME 1:1 v/v solution
and different amount of sulphur powder: 0.0013 g, 0.0016 g, 0.0019 g, 0.0022 g, 0.0026 g and 0.0029 g,
(corresponding to the following concentrations if fully dissolved: 0.04 M, 0.05 M, 0.059 M, 0.069 M, 0.08 M,
and 0.09 M, all in terms of monatomic sulphur.
For the experiment of electrolyte solution infiltration in the composite sulphur-carbon cathode, a 47 mm diameter disc of NANOMYTE® BE-70E cathode material was cut and placed at the bottom of a flat glass petri dish with an internal diameter of 47 mm and the dish was placed in a fume cupboard at 21.1 °C. 1.1 ml of solution DOL: DME 1:1 v/v was added on top of the cathode coating at an electrolyte-to-sulphur ratio E/S = 17.1 µl mg⁻¹. (This amount was calculated so the subsequent battery cell would be fully flooded if all sulphur was converted to sulphides during battery operation, the sulphides would be dissolved in the electrolyte resulting in 1.986 M solution in terms of monoatomic S-mols.) A digital optical microscope was placed over the coating from the beginning of the experiment and set in recording mode to record cathode coating and electrolyte, after the electrolyte covered the composite cathode, started dissolving the sulphur and infiltrated any pores. Images were taken from the resulting video and analysed using ImageJ to determine microstructural characteristics.

The NANOMYTE® BE-70E coating was also characterised on a Thermo Scientific Apreo 2 scanning electron microscope (SEM) under a voltage of 10 kV and beam current of 0.8 nA. Quantitative elemental mapping was obtained using Thermo Scientific ColorSEM Technology for live elemental imaging based on energy dispersive X-ray spectroscopy (EDS), enhanced with Pathfinder microanalysis software.

4. Results and discussion

4.1. Sulphur dissolution kinetics

Figure 3 displays an example of a sequence of snapshots from the video of the sulphur dissolution in the DOL:DME solution. Five lines were selected around the centreline of the cuvette (red lines in last image of figure 3). The focus on the central part of the cuvette was undertaken so that wall effects on the initial sulphur melting, solidification and subsequent dissolution are minimised in the data analysis. A Matlab program was written to read the RGB colour values of every pixel along that line for all the video. The values were normalised by the average value of the top of the cuvette (red cross region on each line in last image of figure 3) to take into account any change in light conditions during the duration of the experiment. The normalisation method included a substration and division procedure. The values of Red, Green, Blue, their fractional values, and also values of luminance, hue and saturation were examined, especially in the regions of solid sulphur, initial solvent solution, and profiles along the central line from solid sulphur to the top of the solution. The fraction of Red and Green values (RG fraction) seemed to be the most consistent in changing between low (in the solvent), medium and high sulphur concentration (in the solid), which is as expected as the yellow sulphur colour is a composite colour between red and green. For certain species, a linear relation between a suitable RGB parameter and species molar concentration has been found [27] and assumed in this study.

Figure 4 displays the RG fraction profiles against Y-position from the bottom of the cuvette (solid sulphur) towards the top solution surface. There are examples of graphs for two experiments at two different temperatures: (a) 17 °C and (b) 20 °C. From the left to the right of each profile, the RG fraction is high indicating high intensity of the yellow colour where the solid sulphur is. The large dip shows the interface between the solid and solution. As the sulphur dissolves the interface moves left at least initially, although after long time it might move towards the right due to swelling of the solid sulphur by the diffusing solvents into the solid sulphur bulk. In general, the area under the RG fraction profile in the solid sulphur part is reduced as sulphur dissolves, and this area reduction was used to calculate the mass transfer coefficient kSB.

Figures SI-1, SI-3, SI-5 and SI-7 (available online at stacks.iop.org/JPEnergy/4/024001/mmedia) present cuvette screenshots at different times during the sulphur dissolution experiment, at the different temperatures of 17 °C, 18 °C, 19 °C and 20 °C, respectively whereas figures SI-2, SI-4, SI-6 and SI-8 present the corresponding RG profiles along the five lines in the central part of the cuvette. These RG profiles were converted to sulphur concentration profiles that were used in the data analysis for the determination of the values of kSB according to equation (1) and DSol-S8 according to equation (4). A discussion of these data is presented in the SI file for each temperature. In general, sulphur melting and solidification seem to lead to polycrystalline sulphur [50] as indicated from the vertical and lateral variation of the RG values representing different grains and porosity in the solid sulphur also observed in the literature along the grain boundaries [50], with further voids entrapped at the bottom of the cuvette and originating from the gaps between the initial sulphur powder particles.

Table 1 presents the sulphur dissolution kinetics parameters calculated from the analysis of the experimental results in this study. This includes the sulphur saturation concentration, 0.059 M at 21 °C in terms of monoatomic sulphur (S-mol), in agreement with the literature [9, 10]. A lower value of 0.04 M was reported in [11] but in their case they had considered a highly concentrated electrolyte of 1 M LiTFSI and 2 wt% LiNO₃ in DOL:DME.
Figure 3. A sequence of snapshots from the video of the sulphur dissolution experiment at 17 °C, with the video time in minutes and seconds under each image. The five red lines in the last image indicate the lines along which the RGB values were read for all pixels in the whole video, and the red X on each line indicates the line segment used to normalise the RGB values of all pixels for each line.

Figure 4. Normalised RG value profiles against Y-position at different times, for experiments at two different temperatures: (a) 17 °C and (b) 20 °C.

Table 1. Parameters of the sulphur dissolution kinetics in DOL:DME 1:1 v/v solution, as determined in this study.

| Temperature (°C) | Saturation concentration (S mol lt⁻¹) | kₐ₈ (m s⁻¹)       | Dₑ₈₅₈ (m² s⁻¹)       |
|-----------------|--------------------------------------|--------------------|-----------------------|
| 17              | 0.040                                | 7.2 × 10⁻⁴ ± 0.7 × 10⁻⁴ | 1.6 × 10⁻¹⁰ ± 1 × 10⁻¹⁰ |
| 18              | 0.050                                | 8.8 × 10⁻⁴ ± 0.5 × 10⁻⁴ | 1.8 × 10⁻¹⁰ ± 1 × 10⁻¹⁰ |
| 19              | 0.055                                | 1.5 × 10⁻³ ± 0.2 × 10⁻³ | 2.2 × 10⁻¹⁰ ± 1 × 10⁻¹⁰ |
| 20              | 0.058                                | 2.3 × 10⁻³ ± 0.3 × 10⁻³ | 3.3 × 10⁻¹⁰ ± 2 × 10⁻¹⁰ |
Table 1 displays the values of the mass transfer coefficient $k_{S8}$ determined in this study at the four different temperatures, in the range of 17 °C–20 °C, as an average between the $k_{S8}$ values determined from the solid sulphur part of each line for the five lines analysed at each temperature presented in figures SI-2, SI-4, SI-6 and SI-8 and the standard error derived from the standard deviation of the data of all five lines. As expected, the $k_{S8}$ value rises with temperature and fits well with an Arrhenius temperature dependence as presented in figure SI-9.

Equation (4) together with the profiles in figure 4 in the solid region were used to determine the diffusion coefficient of the solvents in the solid sulphur, $D_{Sol-S8}$, also presented in table 1. The five lines solid part in figures SI-2, SI-4, SI-6 and SI-8 were tracked to fit the diffusion kinetics with average and standard error values for $D_{Sol-S8}$ at each temperature reported in table 1. Large standard error values are reported for $D_{Sol-S8}$, which is attributed to the mesoscopic microstructure of solid sulphur resulting in the diffusion proceeding along the grain boundaries of the polycrystalline sulphur. The high region of RG profiles in the solid sulphur part in figure 4 is not smooth, even before any solution was added, but shows several fluctuations with $Y$-position, which is attributed to the grain microstructure in the solid, expected to affect the diffusion mechanism and determined values of diffusion coefficient [51]. Such RG profile fluctuations are also encountered in the lateral directions, seen as differences between the five lines in each of the figures SI-2, SI-4, SI-6 and SI-8 reinforcing the fact that diffusion really takes place at mesoscopic scale, in the amorphous region of grain boundaries, enhanced by possible micropores there. A further problem in determining $D_{Sol-S8}$ is solvent-induced annealing of solid sulphur resulting in increased crystallinity and increasing RG fraction values at some positions and temperatures in figures SI-2, SI-4, SI-6 and SI-8. This sometimes resulted in the annealing effect masking the diffusion effect in the RG profiles, in which cases the line in question was excluded from the $D_{Sol-S8}$ calculation, as it is detailed at the end the text section for each temperature in the SI-file. The diffusion coefficient value in table 1 rises with temperature which is fortunate as it is expected to follow Arrhenius temperature dependence [52]. Figure SI-10 presents the so determined $D_{Sol-S8}$ values with respect to an Arrhenius temperature fit, exhibiting considerable scatter from the fit-line, due to the large errors in the $D_{Sol-S8}$ values of table 1, attributed to the effects of the grain structure of the polycrystalline sulphur. Seager et al [29] considered a model of fragmentation of solid sulphur into grains in the presence of solvents. This has been observed in the videos of sulphur dissolution in our study as well but we have not included any modelling of sulphur fragmentation in this work apart from its effect on the RG profiles as shown in figure 4.

4.2. Sulphur dissolution and electrolyte infiltration in a composite cathode

4.2.1. Microstructural analysis of cathode

Figure 5(a) displays a low magnification SEM image of the cathode, where it can be seen that the coating has a network of cracks, each crack through the full coating thickness. Figure 5(b) displays the same image after analysis using ImageJ: macrochannels of about 30 µm wide on average and thinner macrochannels about 1–2 wide were identified occupying 13% and 6.6% of the image, respectively. Figure 5(c) presents a higher magnification image together with the EDS element maps for carbon (C) (figure 5(d)) and sulphur (S) (figure 5(f)). It can be seen that the sulphur has impregnated the free volume between carbon nanoparticles and has also formed a shell around the agglomerates, so the sulphur domains in figure 5(d) extend more in the macrochannels than the carbon domains in figure 6(e), with an average solid sulphur shell thickness of 2 µm from the S and C EDS element maps in the high magnification images in figures 5(g) and (h). The EDS sulphur maps in figures 5(e) and (g) also present high concentration S regions indicating sulphur particles that occupy about 8.3% of the image area in figure 5(e) from the processed image in figure 5(f). Image analysis of figure 5(f) yields the sulphur particle size distribution presented in figure 6(a), with particle diameters (assuming spherical particles) in the range of 7.5–29 µm. The model in the computer simulations in section 4.2.2 assumes that these sulphur particles are encountered only on the surface of the coating and are not embedded through its thickness.

The high resolution SEM image in figure 6(b) presents the Super P carbon black particles of the coating, with an average particle size of about 40 nm, which is in agreement with the usual particle size reported for Super P carbon in the literature [53, 54]. Figures 6(c) and (d) present the pore size distribution of Super P carbon black with experimental data from Olivares-Marín et al [53], which was further discretised in this study and the so discretised data used as input in the computer simulations of the electrolyte infiltration and dissolution of sulphur in NANOMYTE® BE-70E in this study.

4.2.2. Experiment of sulphur dissolution and electrolyte infiltration in composite cathode

Figure 7 depicts the NANOMYTE® BE-70E coating before and after DOL:DME solution was poured onto its surface. A slight yellowish hue of the dry coating in figure 7(a) disappears to black in 66 s after the solution was poured, indicating dissolution of the sulphur surface shell and solution infiltration and good wetting of
the porous cathode. Swimming of light-colour, elongated particles in the video indicated the detachment of the sulphur particles from the coating surface and reduction of their dimensions, especially their smaller axis, due to sulphur dissolution.

The higher magnification snapshots in figures 7(c) and (d) depict that after 66 s of sulphur dissolution the macrochannels in the coating have lost detail in their boundary and the initial sulphur originally impregnated in the microstructure of the carbon black aggregates has started dissolving from the channel walls to an in-plane distance of about 100–150 µm, where the black carbon surface is revealed in figure 7(d). More specifically, image analysis was carried out in the images of figures 7(a) and (b) using ImageJ for 25 large macrochannels: the large macrochannels in the dry coating had an average width of 84 ± 4 µm (range: 45–133 µm) and the sulphur dissolution distance from the crack edge had progressed to 133 ± 9 µm on average after 66 s in the presence of the DOL:DME solution.

4.2.3. Computer simulations of sulphur dissolution and electrolyte infiltration in composite cathode

A representative cathode domain of disc shape of diameter of 500 µm and height of 55 µm has been modelled (figure 2) surrounded by a macrochannel of a half width of 15 µm. The host disc consists of Super P carbon black of a discretised pore size distribution according to figures 6(c) and (d) (red line). The porous host is impregnated with 70 wt% solid sulphur, representing the NANOMYTE® BE-70E coating. This amount of solid sulphur has been distributed to completely fill all host pores and the excess is considered as a homogeneous layer 25 nm thick, surrounding the host disc. 0.0634 ml cm⁻² of solution DOL:DME 1:1 v/v is placed on the top surface of the disc domain as in the corresponding experiment in section 3. The numerical algorithm for the solution of the sulphur dissolution and electrolyte infiltration includes equations (1) and (5)–(9) and uses the implicit finite difference/finite volume method [55, 56]. The simulation was executed with a grid of equally distanced 65 and 15 points in the r- and y- directions, respectively, and a timestep
Figure 7. Video snapshots of the sulphur dissolution in DOL:DME solution: (a) and (c) time = 0, dry NANOMYTE® BE-70E coating; (b) and (d) time = 66 s after DOL:DME solution was poured onto the coating. Scale bars: (a) and (b): 1 mm, (c) and (d): 400 µm.

$\Delta t = 0.1$ s. A discrete pore size distribution of 8 pore sizes in the pore host domain, i.e. the discrete points of the red line in figures 6(c) and (d) was used in the simulation.

The solid sulphur layer of 25 nm surrounding the cathode disc domain was dissolved within the first timestep of 0.1 s. In the porous domain, the sulphur dissolution was the controlling process. Once the pores had an opening, the capillary flow of the electrolyte was rapid and completely filled the pores to $S_{e,p} = 1$.

Figure 8 depicts predictions of the relative remaining solid sulphur volume fraction contours at four different positions through the cathode coating domain thickness, against the radius of the cathode domain for different host pore diameters, at four different times of sulphur dissolution and solution infiltration. It can be seen that sulphur dissolution proceeds from the domain edge ($r = 250 \mu m$) inwards, as also evidenced in figure 7(d), and from the top surface of coating in contact with the electrolyte solution downwards to the bottom of coating in contact with the current collector foil. The top surface (visible under the microscope in figure 7) is predicted to have its sulphur dissolved faster in the large rather than in the small pores, which is attributed to the greater surface area of the solid sulphur/electrolyte solution in the large pores.

At $t = 66$ s (same time as the video snapshots in the experiment in figure 7) at the distance of 135 µm from the porous domain edge (the distance of the experimental infiltration front in figure 7(d)), surface pores greater than 150 nm are predicted (figure 8) to have a remaining sulphur solid fraction $V_{fS} = 0.60$, and pores between 50 and 150 nm are predicted to have a remaining sulphur solid fraction $V_{fS} = 0.65$, reduced from the original $V_{fS,o} = 0.707$: this reduction in the solid sulphur content at the top surface of the porous host is expected to have increased the black carbon black visibility shown in figure 7(d). Figure 8 depicts that it is predicted that at $t = 66$ s there is no sulphur dissolution in the porous coating domain below 57% of the domain thickness below the top surface and no electrolyte solution has infiltrated this region. After 2 min of infiltration time, the electrolyte solution infiltration front is predicted to have ingressed through the whole top surface of the porous domain, always proceeding radially from the edge inwards and dissolving sulphur faster in the large pores. After 5 min of infiltration time, the electrolyte solution is predicted to have reached the depth of 57% from the top surface (figure 8) with the infiltration and sulphur dissolution also proceeding radially from the porous domain edge inwards. Figure 8 illustrates that it is predicted that after 1 h the solid sulphur is fully dissolved at the top surface; at a depth of 57% from the top surface, sulphur is fully dissolved in pores greater than 40 nm and undissolved for pores smaller than 25 nm; at a depth of 86% from the top surface, sulphur is fully dissolved in pores greater than 140 nm and undissolved for pores smaller than 110 nm; finally, after 1 h sulphur is predicted to be undissolved at the bottom surface of the porous coating (in contact with the current collector) and no electrolyte has reached this depth. Figure 9 depicts little
Figure 8. Predicted contour map of the relative solid sulphur volume fraction, $V_{fS}$, relative to the initial solid sulphur volume fraction, $V_{fS,0} = 0.707$, against cathode domain radius, $r$, and cathode host pore diameter, $d_{p,host}$, at four positions through the cathode thickness $H_{c,o}$: $H_{c}/H_{c,o} = 0$ (top surface of coating), 0.57, 0.86 and 1 (bottom of coating, by the current collector foil) and four different times of solution infiltration: $t = 66$ s, 2 min, 5 min and 1 h.

Figure 9. Predicted contour map of the relative solid sulphur volume fraction, $V_{fS}$, relative to the initial solid sulphur volume fraction, $V_{fS,0} = 0.707$, against cathode domain radius, $r$, and cathode host pore diameter, $d_{p,host}$, at four positions through the cathode thickness $H_{c,o}$: $H_{c}/H_{c,o} = 0$ (top surface of coating), 0.57, 0.86 and 1 (bottom of coating, by the current collector foil) after $t = 2$ h of solution infiltration time.

difference in the predicted sulphur dissolution and electrolyte solution infiltration after 2 h, compared to that of 1 h in figure 8.

5. Conclusion

The present investigation provided the values for the parameters of the sulphur dissolution kinetics in the typical electrolyte solution DOL:DME 1:1 v/v for Li–S batteries. Such parameters have been studied and determined for the first time as a function of the solid-liquid interfacial area and will be of great use for the physical modelling of Li–S batteries. The dissolution kinetics parameters were derived from dissolution experiments at four different temperatures, the range of 17 °C–20 °C. Our work proved that whereas the
mass transfer coefficient is high at high temperatures leading to fast dissolution kinetics, the dissolution process is limited by the low solubility of sulphur in DOL:DME.

The low sulphur solubility in the electrolyte solution benefits the Li–S battery as it allows a sulphur-rich cathode after battery fabrication with high initial voltage near 2.8 V, provided that the dissolved sulphur is not converted to sulphide Li₂S₈, which has a much higher solubility of 5–6 S mol⁻¹l⁻¹ in DOL:DME [9, 10]. The S₈ to S²⁻ conversion has an equilibrium potential above 2.3 V, at about 2.4 V according to Kumaresan [18], which makes possible the start of this conversion at high potentials. Hence, a dense cathode microstructure that does not facilitate electrolyte infiltration before the start of discharging may protect the battery from self-discharging.

A further experimental study and accompanying computer simulation of the sulphur dissolution in DOL:DME solution and the solution infiltration in composite sulphur–carbon black NANOMYTE® BE-70E coating as cathode for Li–S batteries allowed us to parameter values and model as there was good agreement in the trends between experiment and predictions. It showed that after 1 or 2 h of the cathode coating being in the presence of the electrolyte solution added on the top, the top sulphur layer was fully dissolved but no electrolyte had reached the bottom surface of the cathode coating (the surface in contact with the current collector foil).

Data availability statement

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

Acknowledgments

The authors would like to gratefully acknowledge funding by the University of Surrey, Faraday Institute in association with the LiSTAR project (FIRG014) and EPSRC via the CoA grant in association with the HiPoBat project.

ORCID iDs

Matthew Dent @ https://orcid.org/0000-0002-1862-3877
Teng Zhang @ https://orcid.org/0000-0002-3657-5151
Constantina Lekakou @ https://orcid.org/0000-0003-4494-1761

References

[1] Masias A, Marcicki J and Paxton W A 2021 Opportunities and challenges of lithium ion batteries in automotive applications ACS Energy Lett. 6 621–30
[2] Saleh A, Lekakou C and Doherty J 2021 An investigation into energy harvesting and storage to power a more electric regional aircraft Adv. Aircr. Spacecr. Sci. 8 17–30
[3] Chen T, Jin Y, Lv H, Yang A, Liu M, Chen B, Xie Y and Chen Q 2020 Applications of lithium-ion batteries in grid-scale energy storage systems Trans. Tianjin Univ. 26 208–17
[4] Seh W, Sun Y, Zhang Q and Cui Y 2016 Designing high-energy lithium–sulfur batteries Chem. Soc. Rev. 45 5605–34
[5] Angulakshmi N and Stephan A M 2015 Efficient electrolytes for lithium–sulfur batteries Front. Energy Res. 3 17/1–8
[6] Robinson J B et al 2021 2021 roadmap on lithium sulfur batteries J. Phys. Energy 3 031501
[7] Bhargav A, He J, Gupta A and Manthiram A 2020 Lithium-sulfur batteries: attaining the critical metrics Joule 4 278–91
[8] 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 5990–100
[9] Dibden J W, Smith J W, Zhou N, Garcia-Araez N and Owen J R 2016 Predicting the composition and formation of solid products in lithium–sulfur batteries by using an experimental phase diagram Chem. Commun. 52 12885–8
[10] Gupta A, Bhargav A and Manthiram A 2019 Highly solvating electrolytes for lithium-sulfur batteries Adv Energy Mater. 9 1803096/1–9
[11] Harks P R R M L, Robledo C B, Verhallen T W, Notten P H L and Mulder F M 2017 The significance of elemental sulfur dissolution in liquid electrolyte lithium sulfur batteries Adv. Energy Mater. 7 1601635/1–5
[12] Kampouris E M, Papaspyrides C D and Lekakou C N 1987 A model recovery process for scrap polystyrene foam by means of solvent systems Conserv. Recycl. 10 315–9
[13] Kampouris E M, Papaspyrides C D and Lekakou C N 1988 A model process for the solvent recycling of polystyrene Polym. Eng. Sci. 28 534–7
[14] Guo R, Talma A G, Datta R N, Dierkes W K and Noordermeer J W M 2009 A theoretical and experimental study on solubility of curatives in rubbers Macromol. Mater. Eng. 294 330–5
[15] Mes E P C, Kok W T and Tijssen R 2003 Prediction of polymer thermal diffusion coefficients from polymer–solvent interaction parameters: comparison with thermal field flow fractionation and thermal diffusion forced Rayleigh scattering experiments J. Polym. Anal. Charact. 8 133–53.
[16] Mikhaylik V V and Akridge J R 2004 Polysulfide shuttle study in the Li/S battery system J. Electrochem. Soc. 151 A1969–76
[17] Marinescu M, O’Neill L, Zhang T, Walus S, Wilson T E and Offer G J 2017 Irreversible vs reversible capacity fade of lithium-sulfur batteries during cycling: the effects of precipitation and shuttle J. Electrochem. Soc. 165 A6107
[18] Kumaresan K, Mikhailik Y and White R E 2008 A mathematical model for a lithium–sulfur cell J. Electrochem. Soc. 155 A576–83
[19] Markoulidou F, Bates J, Lekakou C, Slade R and Laudone G M 2020 Supercapacitors with lithium-ion electrolyte: an experimental study and design of the activated carbon electrodes via modelling and simulations Carbon 164 422–34
[20] Bates J, Markoulidou F, Lekakou C and Laudone G M 2021 Design of porous carbons for supercapacitor applications for different organic solvent-electrolytes C. 7 151–17
[21] Fan F Y, Carter W C and Chiang Y-M 2015 Mechanism and kinetics of Li2S precipitation in lithium-sulfur batteries Adv. Mater. 27 5203–9
[22] Andrei P, Shen C and Zheng J P 2018 Theoretical and experimental analysis of precipitation and solubility effects in lithium-sulfur batteries Electrochim. Acta 284 469–84
[23] Danner T and Latt A 2019 On the influence of nucleation and growth of S8 and Li2S in lithium-sulfur batteries Electrochim. Acta 322 134719/1–16
[24] Di Lecce D, Marangoz V, Du W, Brett D J L, Shearing P R and Hassoun M 2020 The role of synthesis pathway on the microstructural characteristics of sulfur-carbon composites: x-ray imaging and electrochemistry in lithium battery J. Power Sources 472 22842/1–13
[25] Lasetta K, Baboo J P and Lekakou C 2021 Modeling and simulations of the sulfur infiltration in activated carbon fabrics during composite cathode fabrication for lithium-sulfur batteries J. Compos. Sci. 5 65
[26] Meyer B 1976 Elemental sulfur Chem. Rev. 76 367–88
[27] Elsayed Y, Lekakou C and Tomlins P 2014 Monitoring and modelling of oxygen transport through un-crosslinked and crosslinked gelatine gels Polym. Test. 40, 106–15
[28] Frikha N, Hmercha A and Gabsi S 2014 Modelling of a solid dissolution in liquid with chemical reaction: application to the attack reaction of phosphate by sulphuric acid Can. J. Chem. Eng. 92 1829–38
[29] Seager R J, Acevedo A J, Spill F and Zaman M H 2018 Solid dissolution in a fluid solvent is characterized by the interplay of surface area-dependent diffusion and physical fragmentation Sci. Rep. 8 7711
[30] Park C, Kanduc M, Choulbros R, Ronneburg A, Risse S, Balluff M and Dzubiella J 2018 Molecular simulations of electrolyte structure and dynamics in lithium–sulfur battery solvents J. Power Sources 373 70–78
[31] Babar S and Lekakou C 2021 Molecular modeling of electrolyte and polysulfide ions for lithium-sulfur batteries Ionics 27 635–42
[32] Liu T, Hu H, Ding X, Yuan H, Jin C, Nai J, Liu Y, Wang Y, Wan Y and Tao X 2020 12 years roadmap of the sulfur cathode for lithium sulfur batteries (2009–2020) Energy Storage Mater. 30 346–66
[33] Helen M, Diemant T, Schindler S, Behm R J, Danzer M, Kaiser U, Fichtner M and Reddy M A 2018 Insight into sulfur confined in ultramicroporous carbon ACS Omega 3 11290–9
[34] Reece R, Lekakou C, Smith P A, Grilli R and Trapalis C 2019 Sulphur-linked graphitic and graphene oxide platelet-based electrodes for electrochemical double layer capacitors J. Alloys Compd. 792 582–93
[35] Li X, Lee K T and Nazer I. F 2009 A highly ordered nanostructured carbon–sulphur cathode for lithium–sulphur batteries Nat. Mater. 8 500–6
[36] Xu G, Ding B, Nie P, Shen L, Dou H and Zhang X 2014 Hierarchically porous carbon encapsulating sulfur as a superior cathode material for high performance lithium—sulfur batteries ACS Appl. Mater. Interfaces 6 194–9
[37] Elzari R, Salitra G, Garsuch A, Panchenko A and Aurbach D 2011 Sulfur-impregnated activated carbon fiber cloth as a binder-free cathode for rechargeable Li-S batteries Adv. Mater. 23 3641–4
[38] Lei C and Lekakou C 2013 Activated carbon–carbon nanotube nanocomposite coatings for supercapacitor applications Surf. Coat. Technol. 232 326–30
[39] Vermisoglou E C, Giannakopoulou T, Romanos G, Giannouri M, Boukos N, Lei C, Lekakou C and Trapalis C 2015 Effect of hydrothermal reaction time and alkaline conditions on the electrochemical properties of reduced graphene oxide Appl. Surf. Sci. 358 100–9
[40] Vermisoglou E C, Giannakopoulou T, Romanos G E, Boukos N, Giannouri M, Lei C, Lekakou C and Trapalis C 2015 Non-activated high surface area expanded graphite oxide for supercapacitors Appl. Surf. Sci. 358 110–21
[41] Vermisoglou E C, Giannakopoulou T, Romanos G, Boukos N, Psycharis V, Lei C, Lekakou C, Petridis D and Trapalis C 2017 Graphene-based materials via benzidine-assisted exfoliation and reduction of graphite oxide and their electrochemical properties Appl. Surf. Sci. 392 244–55
[42] Lekakou C, Moumad O, Markoulidou F, Andrews T, Watts J F and Reed G T 2011 2011 Toward a rational design of the activated carbon electrodes via modelling and simulations J. Compos. Sci. 11290–9
[43] Markoulidou F, Todorova N, Grilli R, Lekakou C and Trapalis C 2019 Composite electrodes of activated carbon and multiwall carbon nanotubes decorated with silver nanoparticles for high power energy storage J. Compos. Sci. 3 97
[44] Amico S and Lekakou C 2004 Flow through a two-scale porearity, orientated fibre porous medium Trans. Porous Media 54 35–53
[45] Ozgumus T, Mobedi M and Özkol U 2014 Determination of Kozeny constant based on porosity and pore to throat size ratio in porous medium with rectangular rods Appl. Comput. Fluid Mech. 8 308–18
[46] Rutt M, Lekakou C, Smith P A, Sordon A, Santoni C, Meeks G and Hamerton I 2019 Methods for process-related resin selection and optimisation in high-pressure resin transfer moulding Mater. Sci. Technol. 35 367–37
[47] Wang P, Anderko A and Young R D 2011 Modeling surface tension of concentrated and mixed-solvent electrolyte systems Ind. Eng. Chem. Res. 50 4086–98
[48] Amanchukwu C V, Kong X, Qin J, Liu Y and Bao Z 2019 Nonpolar alkanes modify lithium-ion solvation for improved lithium deposition and stripping Adv. Energy Mater. 9 1902116
[49] Hwang J Y, Kim H M and Sun Y K 2018 Controlling the wettabillity between freestanding electrode and electrolyte for high energy density lithium-sulfur batteries J. Electrochem. Soc. 165 A5006–A5013
[50] Scafe E, Nardella A and De Filippis D 2005 Elastic properties of polycrystalline elemental sulphur J. Mater. Sci. 40 3813–6
[51] Pope J and Lekakou C 2019 Thermoelectric polymer composite yarns and an energy harvesting wearable textile Smart Mater. Struct. 28 095004
[52] Fleshman A M, Forsythe G E, Petrowsky M and Frech R 2016 Describing temperature-dependent self-diffusion coefficients and fluidity of 1- and 3-alcohols with the compensated Arrhenius formalism J. Phys. Chem. B 120 9959–68
[53] Olivares-Marín M, Aklalouch M and Tonti D 2019 Combined influence of meso- and macroporosity of soft-hard templated carbon electrodes on the performance of Li2O2 cells with different configurations Nanomaterials 9 810
[54] Yoo K, Banerjee S, Kim J and Dutta P 2017 A review of lithium-air battery modeling studies Energies 10 1–41
[55] Lekakou C N and Richardson S M 1986 Simulation of reacting flow during filling in reaction injection molding (RIM) Polym. Eng. Sci. 26 1264–75
[56] Elsayed Y, Lekakou C and Tomlins P 2019 Modeling, simulations, and optimization of smooth muscle cell tissue engineering for the production of vascular grafts Biotechnol. Bioeng. 116 1509–22