

A simple, experiment-based model of the initial self-discharge of lithium-sulphur batteries

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Abstract

One of the main challenges in the development of lithium-sulphur batteries is the so called “shuttle mechanism”, which involves the diffusion of sulphur and polysulphides from the sulphur electrode to the lithium electrode, where they get reduced via chemical reactions with lithium. The shuttle mechanism decreases the capacity delivered by the battery, hampers its rechargeability, and promotes battery self-discharge. We have developed a simple model of the shuttle mechanism that reproduces quantitatively the rate of the initial self discharge of lithium-sulphur batteries. The rate of sulphur and polysulphide diffusion has been quantified by studying cells with varying number of separators between the electrodes. We have found that it is essential that the model incorporates the presence of carbon additive in the sulphur electrode, which slows down the decrease of the open circuit potential with time. The model also reproduces well the rate of self-discharge of lithium-sulphur cells containing sulphur dissolved in the electrolyte. In conclusion, the present model provides a basic

understanding of the mechanism of self-discharge of lithium-sulphur cells, and allows quantifying the two main causes of sulphur loss at the sulphur electrode: sulphur diffusion across a concentration gradient and sulphur reaction with polysulphides formed at the lithium electrode.

Key words: lithium-sulphur batteries, shuttle mechanism, model, diffusion

1. Introduction

Lithium-sulphur batteries hold the potential to revolutionize the rechargeable energy storage market, since they can potentially deliver a much higher energy than lithium-ion batteries of the same weight [1-12]. However, improvements at the level of cell performance are required. In order to achieve their full potential, the discharge reaction of lithium-sulphur batteries should involve the full conversion of sulphur into Li_2S .



However, in the pathway of sulphur reduction, lithium polysulphides of variable chain length, Li_2S_n , are formed [13-21]:



Li_2S_n can diffuse to the lithium electrode, where it can be chemically reduced to shorter-chain polysulphide, Li_2S_m



It has been shown that Li_2S_m with $m > 2$ has a high solubility [22], and therefore, it could diffuse back to the sulphur electrode, where it could be further reduced to Li_2S :



An important effect of the shuttle mechanism is to decrease the capacity delivered by the battery: addition of equations (2) to (4) shows that the total number of electrons involved per mole of S_8 equals $16 \times (1 + 1/n - 1/m)$, which is lower than the 16 electrons involved in reaction (1), since $m < n$.

The shuttle mechanism is also the cause of battery self-discharge. Sulphur from the sulphur electrode will dissolve in the electrolyte and diffuse to the lithium electrode. There, sulphur will get reduced to polysulphides, which will travel back to the sulphur electrode. The increase in polysulphide concentration at the sulphur electrode produces a decrease in the potential that can be understood from the Nernst equation. For instance, if only Li_2S_8 and sulphur were present at the sulphur electrode, the potential would be given by:

$$E = E_{S_8/Li_2S_8}^0 + \frac{RT}{2F} \ln a_{S_8} - \frac{RT}{2F} \ln a_{Li_2S_8} \quad (5)$$

where a_{S_8} and $a_{Li_2S_8}$ are the activities of sulphur and Li_2S_8 . Therefore, the dissolution and reaction of sulphur via the shuttle mechanism during battery self-discharge produces a decrease in the battery voltage and capacity that resembles the effect of discharging the battery by applying a current.

In this work, we have developed a simple model of the self-discharge that is able to reproduce well experimental data under a range of conditions. We demonstrate that the rate of self-discharge is markedly affected by the distance between the sulphur and lithium electrodes, and we provide an estimation of the effective diffusion coefficient of sulphur and the polysulphide shuttle species. We also show that the rate of self discharge is markedly affected by the carbon content of the electrode, since the change of the electrode potential due to the increase in polysulphide concentration is buffered by the capacitive behaviour of carbon.

Only a few studies have addressed the quantitative analysis of the shuttle phenomena. In 2004, Mikhaylik and Akridge [23] developed a simple model of the polysulphide shuttle, which they used to simulate experimental data of charge and discharge voltage profiles, battery self-discharge and thermal effects. This elegant model could explain all these processes in terms of one global parameter, the shuttle constant, which reflects the rate at which long-chain polysulphides are consumed on the lithium electrode. In this work, we give a more detailed physical meaning of this “shuttle constant”, and relate it to the rate of diffusion of polysulphide between the sulphur and lithium electrodes.

More complicated models were developed later. Kumaresan et al. [24] developed a complete model of a lithium-sulphur cell that included effects of precipitation, electrode kinetics, diffusion, migration, etc. Fronczek and Bessler [25] used a similar approach and extended the analysis to simulate impedance spectra. Neidhardt et al. developed a mathematical framework that was used to model not only lithium-sulphur batteries, but also lithium-oxygen batteries, solid oxide fuel cells and polymer electrolyte membrane fuel cells [26]. More recently, Hofmann et al. [27] developed a detailed mechanistic model of the lithium-sulphur cell that was validated with experimental data. Moy et al. [28] developed an experimental method to measure the shuttle current by chronoamperometry and they simulated the experimental data with a 1-D diffusion model. Zhang et al. included a concentration dependent electrolyte resistance in the model, which provided a better agreement with the experimental data [32]. All these models involve a large number of unknown parameters (diffusion coefficient, rate constants, relative thermodynamic stability of the different polysulphide species, etc.). Ghaznavi et al. [29-31] performed a sensitivity analysis that evaluated which parameters produced a more marked effect on battery performance.

There is no doubt that all these models are very powerful, but as we will show below, our simple model is capable of reproducing quantitatively experimental data under a range of conditions and it provides a quantitative understanding of the shuttle phenomena. In order to validate our model, we measured the battery self-discharge, which is known to directly reflect the rate of sulphur and polysulphide shuttling.

In conclusion, the purpose of this work is to provide the simplest mechanistic explanation of the rate of self-discharge of lithium-sulphur batteries. We have only included in the model the essential steps that are needed in order to obtain a quantitative agreement with the experimental data. These steps are: i) diffusion of sulphur from the sulphur electrode to the lithium electrode, ii) reduction of sulphur to polysulphide at the lithium electrode, iii) back diffusion of polysulphide to the sulphur electrode, and iv) charge transfer of polysulphide to the carbon double-layer. Remarkably, only one free parameter is needed to reproduce well the variation of the open circuit potential with time during battery self-discharge. This parameter is the average diffusion coefficient of sulphur and polysulphide, and the value obtained from the fit is in agreement with independent estimations using an RDE electrode [15].

Due to the simplicity of this model, we can clearly demonstrate that charge transfer of polysulphide to the carbon double-layer is important in lithium-sulphur batteries and it significantly slows down the voltage decrease during the initial self discharge. This model also allows comparison of the rates of self-discharge of different lithium-sulphur cells while taking into account different cell characteristics such as thickness of the separator, electrode area, carbon content, etc.

2. The model

Full details of the model are described in the supporting information. Briefly, the model considers the diffusion of sulphur from the sulphur electrode to the lithium electrode, and the back diffusion of polysulphides (in particular, we consider Li_2S_8 as the main shuttle species) from lithium to the sulphur electrode. The boundary condition at the lithium electrode is that the rate of conversion of sulphur into polysulphide is limited by the rate of sulphur diffusion. The boundary condition at the sulphur electrode is set by taking into account that polysulphides will act as reducing species, and therefore, they will get oxidized at the sulphur electrode. Since the net current is zero, the oxidation of polysulphide is coupled to charge transfer to the carbon double-layer.

3. Results and discussion

Figure 1 shows the evolution of the open circuit potential (solid lines) of lithium-sulphur batteries containing a different number of separators between the lithium and sulphur electrodes (see experimental details in the supporting information). In all cases, the batteries were assembled with fresh electrolyte, lithium and sulphur-carbon composite, and the measurements of the open circuit potential started < 5 minutes after cell assembly. It is seen in figure 1 that when increasing the number of separators, the distance between the electrodes increases, and the self-discharge becomes slower. This evidences the fact that the rate of self-discharge is influenced by the rate of diffusion of sulphur and polysulphides.

Since each glass fibre separator is around 0.3 mm thick, we have run simulations where the distance between the electrodes is set to 0.3 mm times the number of separators. The results of the simulations are included in figure 1 (dashed lines). A good agreement between the experiment and simulation is observed, despite the simplicity of

the model employed here. The only free parameters of this model are the diffusion coefficients of sulphur and polysulphides shuttle species, and for simplicity, we have considered that both diffusion coefficients have the same values, $3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. These values are comparable to the diffusion coefficient of sulphur, $2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, as measured with a rotating ring-disc electrode in DOL:DME with 1 M LiTFSI [15]. These diffusion coefficients also compare well with the values used in more detailed models of Li-S cells, which were assumed to vary between 10^{-6} and $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [24, 25, 27, 28-31].

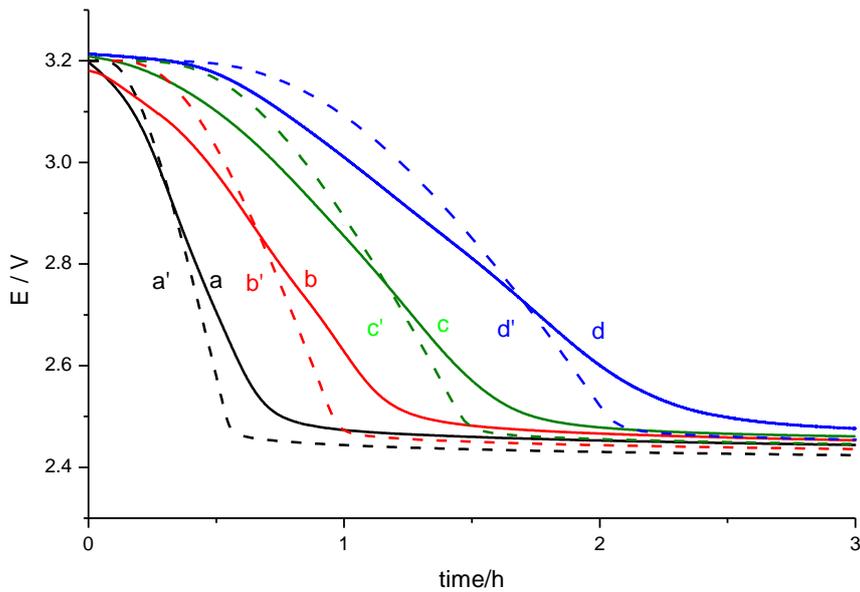


Figure 1. Evolution of the open circuit potential of lithium-sulphur cells containing 2 (a), 3 (b), 4 (c) and 5 (d) glass fibre separators (solid lines). Electrolyte: 1 M LiTFSI in DOL:TEGDME. The corresponding simulations (dashed lines) are done with a distance between the two electrodes equal to 0.6 (a'), 0.9 (b), 1.2 (c') and 1.5 mm (d'), and including the effect of the total capacitance of the sulphur and carbon composite electrode, which is 0.05 F. Full details of the experiments and simulations are given in the supporting information.

All the chronopotentiograms in figure 1 were simulated with the same diffusion coefficient, $3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; the only parameter that was varied was the number of separators, i.e. the distance between the sulphur and lithium electrodes. It is worth mentioning that using slightly different values of the diffusion coefficient leads to much worse agreement with the experiment. In the supporting information, we compare the experimental data with simulations done with values of diffusion coefficient equal to $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (figure S1) or $4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (figure S2). It is clear that for all the experimental conditions, the rate of self-discharge is underestimated when simulating with $D=2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, and overestimated with $D=4 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The small disagreement between the simulations and the experiments in figure 1 could be attributed to the simplifications assumed in the present model. First, the model only considers one “polysulphide shuttle species”, with a single value of the diffusion coefficient. The simulation results in figure 1 were obtained considering that the polysulphide shuttle species is S_8^{2-} with a diffusion coefficient of $3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Similar results can be obtained considering that the polysulphide shuttle species is S_4^{2-} with a diffusion coefficient of $2.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (supporting information, figure S3). In reality, a range of polysulphides with different chain lengths are involved in the shuttle mechanism, and polysulphides with different lengths (and charge) are expected to have different values of diffusion coefficient. Another simplification of the present model is that we have considered that the reaction of sulphur on the lithium electrode is mass-transport controlled. This assumption was also used in previous modelling studies, but this would need to be tested, since if the reaction of sulphur on the lithium electrode was

limited by the reaction kinetics, the present approach would lead to an overestimation of the values of the diffusion coefficient.

Figure 2 illustrates the effect of the conductive carbon additive on the rate of self-discharge. Curve a in figure 2 shows the experimental data. Curve b shows the results of the simulations that take into account the specific capacitance of the acetylene black conductive additive (the value of capacitance has been estimated from voltammetric measurements of composite electrodes containing only acetylene black and binder, which is around 0.05 F for electrodes containing 5 mg of carbon). Curve c shows the results of the simulations that do not include the effect of carbon additive.

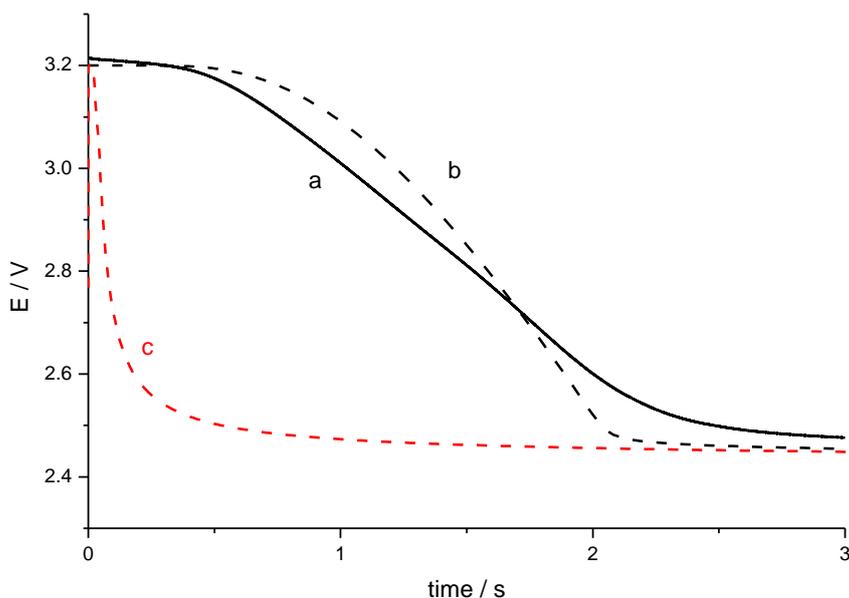


Figure 2. Evolution of the open circuit potential of a lithium-sulphur cell with 5 glass fibre separators (curve a, solid line). Electrolyte: 1 M LiTFSI in DOL:TEGDME. The dashed curve b shows the results of the simulations including the total capacitance of the sulphur and carbon composite electrode, which is 0.05 F. The dashed curve c shows the results of the simulations when the electrode had no carbon. The distance between the two electrodes in the simulations equals 1.5 mm. Full details of the experiments and simulations are given in the supporting information.

The effect of the carbon content on the rate of self-discharge has been incorporated as follows. Once polysulphides reach the sulphur electrode, they undergo a partial oxidation that is coupled to the capacitive charge of the carbon-electrolyte interphase. In this process, polysulphides transfer electrons to the carbon surface:



As a result of the reaction above, the concentration of polysulphide at the sulphur electrode is smaller than if the electrode had no carbon. Consequently, the presence of carbon buffers the increase in the polysulphide concentration, which is thus much slower than if the electrode had no carbon.

The simulations in figure 2 demonstrate that the capacitive behaviour of carbon leads to a slower decrease of the open circuit potential with time (compare curves b and c in figure 2), and that omitting the effect of carbon produces a marked disagreement with the experiment (compare curves a and c in figure 2). The simulations that do not include the capacitance of carbon (curve c in figure 2) have been performed by considering that there is no reaction of polysulphides formed at the lithium electrode once they reach the sulphur electrode. Thus, the flux of polysulphides at the sulphur electrode was set to zero.

The oxidation of polysulphides once they react with carbon can be understood as follows. Initially, the sulphur-carbon electrode is at 3.2 V vs. Li^+/Li , and only trace amount of polysulphides are present. We assume that the electrode is in (quasi) equilibrium so that the electrode potential is determined by the Nernst equation (equation 5), and increasing polysulphide concentration would decrease the electrode potential. Therefore, polysulphides act as reducing species, because an increase in polysulphide concentration is associated to a decrease in potential. But such decrease in

potential requires charging the double-layer capacity of the carbon electrode, by an amount: $\Delta E = \Delta Q/C$, where C is the carbon capacitance and ΔQ is the charge involved in reaction (6), which is given by the number of electrons transferred from polysulphides to the carbon-sulphur electrode. Since in the present case, C is quite large (because high surface area carbon is employed here), the change in potential is buffered.

Figure 3 shows the concentration profile of sulphur and polysulphide for the simulation including the capacitive behaviour of carbon. Initially ($t < 1h$), essentially all the polysulphides that reach the sulphur electrode react with carbon, and that is why there is an initial plateau in potential, at around 3.2 V. The concentration of polysulphide is thus kept nearly constant, but at a trace level. The amount of polysulphide that reacts with carbon is small, because only trace amount of polysulphide reach the electrode (i.e. the polysulphide flux at the sulphur electrode is small). Therefore, ΔQ is small and ΔE is also small.

At longer times, $1h < t < 2h$, as the accumulated amount of polysulphide that reacts with carbon increases, ΔQ increases and consequently, the decrease in the potential ΔE is also more significant. As the potential of the sulphur electrode becomes closer to the equilibrium potential of sulphur/polysulphide species $E_{S_8/Li_2S_8}^0 = 2.45$ V vs. Li^+/Li , the driving force for reaction (6) decreases. As a result, polysulphides start to accumulate near the sulphur electrode, and the concentration profile at the surface of the sulphur electrode becomes more and more flat, i.e., the polysulphide flux decreases. This is the origin of the second voltage plateau at around 2.45 V. In this region, the extent of reaction (6) is small: ΔQ is small and ΔE is also small. The polysulphide concentration at the sulphur electrode continuously increases in this region, but since the effect of the concentration on potential is via a logarithmic function (Nernst equation), this does not produce a big change in the electrode potential.

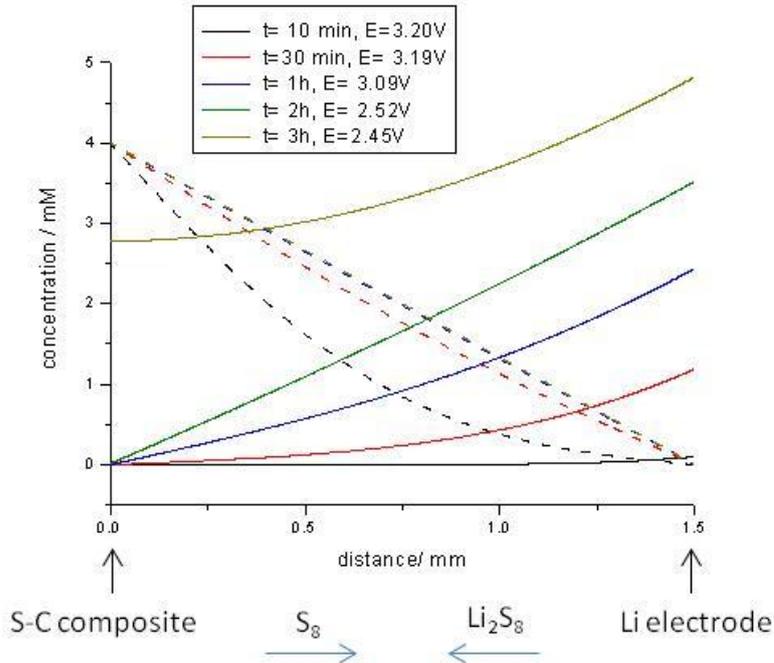


Figure 3. Calculated concentrations of sulphur (dashed lines) and polysulphide (solid lines), as obtained in the simulation where the distance between the two electrodes equals 1.5 mm and total capacitance of the sulphur and carbon composite electrode is 0.05 F. $x=0$ is the location of the sulphur electrode, $x=1.5$ mm is the lithium electrode. The corresponding variation of potential with time is represented in curve d' in fig.1 and curve a in fig. 2.

To finish, we studied the effect of using a sulphur-saturated electrolyte in the cell (Figure 4, solid line, curve b). It is observed that the self-discharge is faster than in a cell with the same electrolyte but without sulphur dissolved (Figure 4, solid line, curve a). The simulations (dashed line, curve b') also show a faster self-discharge when sulphur is dissolved in the electrolyte, which is due to the fact that the step of sulphur diffusion from the sulphur electrode to the lithium electrode is no longer involved. Some disagreement between the experiment and the simulations is observed, which could be attributed to the simplicity of the model. Better agreement between the

experiments and the simulations can be achieved by considering that the diffusion coefficient the polysulphide shuttle species is smaller than that of sulphur. However, other factors come into play when sulphur is dissolved in the electrolyte. It is reasonable to propose that, with sulphur dissolved in the electrolyte, a spontaneous SEI protective layer will form on the lithium electrode, and as a result, the rate of reaction of sulphur on the lithium electrode will be lower, leading to slower self-discharge.

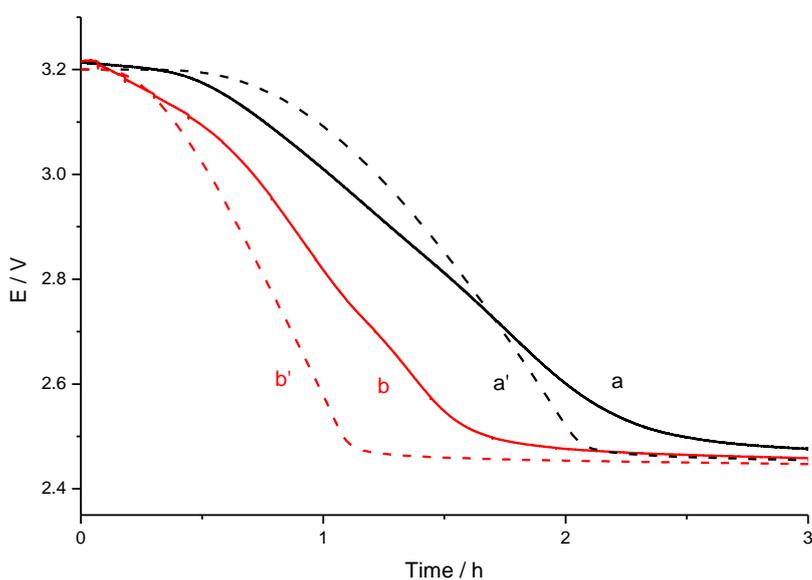


Figure 4. Evolution of the open circuit potential of lithium-sulphur cells, with 5 glass fibre separators, without (a) and with (b) sulphur dissolved in the electrolyte at saturation (solid lines). Electrolyte: 1 M LiTFSI in DOL:TEGDME. Simulations (dashed lines) were done considering that the sulphur concentration in the electrolyte is negligible (a') or the 4 mM saturation concentration reported in ref. [33] (b'). Full details of the experiments and simulations are given in the supporting information.

5. Discussion

We have proposed a new, simple model that provides a basic understanding of the rate at which the sulphur and polysulphide shuttling in lithium-sulphur batteries leads to battery self-discharge. The model explains quantitatively why increasing the distance between the sulphur and lithium electrodes decreases the rate of self-discharge, since sulphur and polysulphides have to travel over a longer distance. The model also explains why the presence of carbon in the sulphur electrode slows down the decrease of the open circuit potential with time. Finally, the model is also able to reproduce experimental data of the rate of self-discharge of cell containing sulphur dissolved in the electrolyte, where the self-discharge is faster, because the step of diffusion of sulphur from the sulphur electrode to the lithium electrode is no longer required.

By comparing simulation results with experimental data, we have been able to evaluate the effective diffusion coefficient of sulphur and the main polysulphide species. However, this parameter is not the classical physical diffusion coefficient that characterizes the diffusion across a concentration gradient. First of all, this is an apparent diffusion coefficient which reflects the tortuosity of the separators. Second of all, we have considered a single “polysulphide shuttle species”, whereas in Li-S cells a distribution of polysulphide species with different chain lengths will be formed. Most importantly, the diffusion of sulphur and polysulphides across the Li-S cell most likely involves a complex set of comproportionation and disproportionation reactions, rather than only physical diffusion (*vide infra*).

We believe that the mechanism of self-discharge of Li-S cells is as follows. Sulphur dissolves in the electrolyte and it diffuses towards the lithium electrode, where it is reduced to the thermodynamically more favourable species, Li_2S . As more sulphur reaches the lithium electrode, polysulphides are generated by comproportionation

reactions between sulphur and Li_2S . These polysulphides diffuse back to the sulphur electrode, and on their way, they react with dissolved sulphur, forming longer-length polysulphide species. Therefore, a front of sulphur concentration diffuses towards the lithium electrode, whereas a front of short-chain polysulphides diffuses towards the sulphur electrode; comproportionation and disproportionation reactions occur in parallel to physical diffusion.

In conclusion, the physical interpretation of the apparent diffusion coefficient obtained from the present model is not simple. However, we believe that these values of diffusion coefficient are, in a way, more relevant than the actual physical diffusion coefficients of all polysulphide species, since our result provides a direct measurement of the overall mass transport rate of the main shuttle species generated in lithium-sulphur batteries.

One important simplification of the present model is that it assumes that the rate of reaction of sulphur on the lithium electrode is diffusion controlled. This assumption was also used in previous modelling studies of lithium-sulphur cells [24-31], but it will only hold if the reaction of sulphur at the lithium surface is faster than the rate of diffusion. In future work, we plan to improve the model in order to incorporate experiment-based data on the reaction of sulphur and polysulphide on the lithium electrode.

A clear benefit of the present model is to bring a quantitative understanding of the origin of the “shuttle constant” introduced by the model of Mikhaylik and Akridge [23]. The shuttle constant measures the rate of loss of sulphur atoms (either in the form of molecular sulphur or polysulphides) at the sulphur electrode via the shuttle mechanism. The present model shows that there are two contributions to this loss of sulphur:

- 1) diffusion of sulphur across a concentration gradient, from the sulphur electrode towards the lithium electrode
- 2) conversion of sulphur into polysulphides via the reaction with short-chain polysulphides that have been formed on the lithium electrode

If all reactions are limited by diffusion, the concentration gradient of sulphur species quickly reaches the steady state, where the concentration at the sulphur electrode is the saturation concentration, and at the lithium electrode it is zero. Therefore, the rate of diffusion of sulphur will be given by:

$$\frac{1}{A} \frac{dn_{S_8}}{dt} = D_{S_8} \frac{\partial c_{S_8}}{\partial x} = \frac{D_{S_8} c_{S_8}^{sat}}{L} \quad (7)$$

where A is the sulphur electrode area, n_{S_8} is the number of moles of sulphur at the sulphur electrode, D_{S_8} is the diffusion coefficient of sulphur, $c_{S_8}^{sat}$ is the sulphur saturation concentration, and L is the distance between the sulphur and lithium electrodes. Considering $D_{S_8} = 3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (as found in the present work), $c_{S_8}^{sat} = 4 \text{ mM}$ (saturation concentration reported in ref. [33]), and $L = 25 \text{ }\mu\text{m}$ (typical thickness of a porous polyolefin separator, as used by Mikhaylik and Akridge [23]), it is obtained that the rate of diffusion of sulphur is around $4.4 \text{ mg h}^{-1} \text{ cm}^{-2}$. For a sulphur loading of ca. 1 mg cm^{-2} , this would correspond to a shuttle constant of $k_s = 4.4 \text{ mg h}^{-1} \text{ cm}^{-2} / 1 \text{ mg cm}^{-2} = 4.4 \text{ h}^{-1}$. In the work of Mikhaylik and Akridge [23], the values found for the shuttle constant are lower than 0.5 h^{-1} , which suggests that, in their experiments, the reduction of sulphur at the lithium electrode is not limited by diffusion, but limited by the kinetics of the surface reaction at the lithium electrode. On the other hand, when the shuttle constant is higher than the value calculated by using equation (7), the most likely cause is the consumption of sulphur via comproportionation reactions with short-chain polysulphides generated at the lithium electrode:



Note that this reaction could take place not only on the sulphur electrode but also as a homogenous reaction in solution.

There are two possible ways to extend the present model to incorporate comproportionation and disproportionation reactions of polysulphides. Several polysulphide species could be incorporated in the model, and specific equations for the rates of comproportionation and disproportionation reactions could be proposed, as well as Butler-Volmer equations to describe the kinetics of electron transfer. This approach has been used in previous work [24-31], and while it is closer to the complexity of the real system, it has the disadvantage that many of the required parameters (equilibrium and rate constants, etc.) are not known. An alternative approach would be to acknowledge that the oxidation state of sulphur changes as it travels from the sulphur electrode to the lithium electrode, since sulphur is transformed into long chain polysulphides first, and then into short chain polysulphides, and ends at as Li_2S at the lithium electrode. Therefore, physical diffusion is coupled to electrochemical reactions, but it is difficult to separate these processes. A more advantageous model can be made by considering the diffusion of a single species with an apparent diffusion coefficient that reflects this mixed physical diffusion and electrochemical transformation. This second approach has been taken in the present model, and in further work we will study in more detail how it relates to the first approach with specific equations for multiple species.

6. Conclusions

In conclusion, we have developed a simple model that provides a basic understanding of the rate of self-discharge of lithium-sulphur batteries. This model allows quantifying the two mechanisms of sulphur loss from the sulphur electrode: diffusion across a concentration gradient and reaction with polysulphides formed at the lithium electrode. The maximum rate of sulphur loss by diffusion can be easily calculated by considering steady state diffusion. If the reactivity of lithium towards sulphur reduction is suppressed by, for example, formation of a stable SEI layer, it is expected that the rate of sulphur loss will be smaller than the diffusion-limited value. On the other hand, rates of sulphur loss higher than the diffusion-limited value can be achieved via comproportionation reactions of sulphur and short-chain polysulphides. The equations derived in this work allow comparing the rate of self-discharge of lithium-sulphur cells with different geometries (electrode areas, distance between the electrodes, etc.) and discussing the differences in terms of the shuttle constant or the rate of loss of sulphur.

Acknowledgements:

Saddam M. Al-Mahmoud acknowledges the Higher Committee for Education Development in Iraq (HCED) for a PhD studentship. James W. Diben acknowledges Oxis Energy Ltd. and the University of Southampton for a CASE studentship.

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