

Analysis of soluble intermediates in the lithium-sulfur battery by a simple *in situ* electrochemical probe

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Abstract

This paper describes a simple setup using a thin, insulated platinum wire as an *in situ* electrochemical probe for analysis of the soluble polysulfide intermediates formed and
10 consumed during the course of the discharge process of a lithium-sulfur cell. The probe, sharing common reference and counter electrodes with the cell, can be used to follow the changes in concentration of polysulfides in the electrolyte. The results herein both support and complement more advanced techniques studied elsewhere for understanding the dominant
15 processes occurring in the cell.

Keywords

lithium-sulfur, electrochemistry, *in situ*, mechanism, analysis

1. Introduction

20 The recent surge in interest in the lithium-sulfur (Li-S) system has resulted in considerable advances towards solving the intrinsic drawbacks of this system, especially the relatively short cycle life and high rate of self-discharge. The variety of approaches to realising the potential of this system have been detailed in several recent reviews[1–5]. In general, the advances in this field can be largely seen as a two-pronged approach: appropriate design of
25 the conductive carbon host to overcome the limitations of the poorly-conducting charge and

discharge products, and control of the production and diffusion of soluble polysulfide (PS) intermediates. The loss of the latter to the negative electrode is a major contributor to capacity fade and self-discharge.

5 However, the study of the behaviour of polysulfides in the electrolyte remains challenging: only the charge and discharge products, S_8 and Li_2S respectively, are thermodynamically stable[6]; all intermediate polysulfide compounds are unstable, making *ex situ* characterisation of the system difficult[7]. Many groups have studied this system using *in situ* techniques, for example by Raman[8], UV/Vis[9], X-ray absorption and NMR[10,11].

10 Despite this, the determination of which, if any, major intermediates exist and the major reaction mechanisms which take place in the cell remains open to discussion, especially since the chemistry of polysulfides is so highly dependent on the composition of the electrolyte, as highlighted by comparison of their electrochemistry in different solvents in a recent article by Lu *et al*[12].

15 Electrochemical analysis remains an important tool for studying the properties of polysulfides. Ordinarily, electrochemistry involves the study of analytes in dilute solution under controlled and well-defined conditions. It is of course desirable to bridge the gap between such a study and a lithium-sulfur battery, where the polysulfide concentration is higher and the electrolyte composition changes during charge/discharge. One such bridge is the construction of an
20 electrochemical cell within the battery, with small electrodes inserted between the cathode and anode of the battery. To our knowledge, such a study of the lithium-sulfur system has only been reported once, by Dominko *et al*[13]. In this work, we develop this idea further in describing a similar cell in a pouch cell configuration, using a small platinum probe -
25 referenced against Li/Li^+ - to study the changes in electrolyte composition of a lithium-sulfur

battery using the dimethoxyethane:dioxolane (DME:DOL) system. The use of such a probe as an analytical tool and the relevance of the results herein with regards to the mechanism of the overall cell reaction will be discussed.

5 **2. Experimental information**

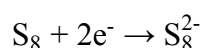
A sample of a high conductivity carbon black with a surface area of $1102 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $2.5 \text{ cm}^3 \text{ g}^{-1}$, as measured by the BET and BJH methods respectively, was kindly provided by Orion Engineered Carbons GmbH. Carbon/sulfur composite cathodes, with a composition of 58:35:7 S:C:binder were prepared by first mixing carbon black and sulfur
10 powders and heating to $155 \text{ }^\circ\text{C}$, followed by mixing the binder (a 2:3 mixture of carboxymethylcellulose sodium salt (CMC, Leclanché) and styrene-butadiene copolymer (Targray PSBR100) (CMC:SBR)) in water by planetary ball milling for 2 hours. The slurry was coated onto Al foil and cut into 20 mm diameter cathodes with a sulfur loading of approximately 1 mg cm^{-2} . After drying cathodes at $55 \text{ }^\circ\text{C}$ under vacuum overnight, vacuum-
15 sealed pouch cells were prepared in an Ar-filled glove box with $125 \text{ }\mu\text{m}$ Li foil (Cyprus Foote Mineral) used for the counter electrode, separated by two separators; a porous polyethylene separator on the positive electrode side (SOLUPOR, Lydall Performance Materials) and a glass fibre separator. The electrolyte was 1 M LiTFSI, 0.25 M LiNO_3 in 1:1 DME:DOL, and the electrolyte amount was fixed at $35 \text{ }\mu\text{L}$ per mg of sulfur in the cathode. PTFE-insulated
20 platinum wire (0.05 mm bare diameter wire, Advent Research Materials) used as the probe electrode - effectively as a $50 \text{ }\mu\text{m}$ diameter platinum disc – and a piece of Li foil were inserted between the two separators. The cell is described graphically in Fig. 1. Electrochemical experiments were performed on a VMP2 (Bio-Logic) using two synchronised channels in CE-to-ground mode in order to allow both working electrodes to share the common counter and

reference electrodes. A faraday cage and a low current option on the VMP2 were used to minimise noise when using the probe electrode.

The intermediates in the electrolyte formed on the first discharge were initially studied by cyclic voltammetry. The potential on the probe electrode was swept, beginning in the cathodic direction, between 1.8 and 2.8 V vs Li/Li⁺ at a scan rate of 1 mV s⁻¹; we did not extend the scan beyond the cathodic limit of 1.8 V so as to avoid the possibility of electrode passivation by reduction of LiNO₃. At the conclusion of the single cycle, the cell was discharged by approximately 50 mAh g⁻¹ at a current density of C/10 (167.2 mA g⁻¹). The cell was kept at open circuit while the CV on the probe electrode was again measured; this sequence of CV and discharge was continued until the cell reached the cut-off voltage of 1.8 V vs Li/Li⁺.

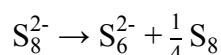
3. Results and discussion

The results of the first discharge experiment are summarised in Fig. 2 a) and b). Typical CVs of polysulfides in the electrolytes are shown in the left hand plot. The major features of all the CVs were a broad cathodic peak, $j_{p,c}$, towards the cathodic limit, and a generally sharper and larger anodic peak, $j_{p,a}$, at approximately 2.6 V vs Li/Li⁺. A second cathodic peak is seen at 2.3 V vs Li/Li⁺ at the conclusion of the scan: since this peak is not seen on the first reduction even if the initial potential for the scan is more positive than this peak, and that the major reducible species in the electrolyte at the start of the scan are polysulfides, then this peak is likely due to the reduction of sulfur generated as the potential is scanned through the anodic peak:



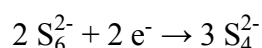
As such, following the study of sulfur speciation in DME:DOL by Cuisinier *et al*[11] and the electrochemical studies of Yamin *et al* in THF electrolytes[14] - which is similar to DME:DOL in terms of donor number and dielectric constant - it seems reasonable to suggest that in this electrolyte system, S_8^{2-} formation is followed by its disproportionation:

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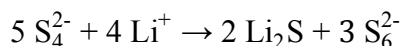
Similarly, the analysis in the aforementioned studies suggests that the major electrochemical reduction at the cathodic peak ($j_{p,c}$) on the first scan involves reduction of S_6^{2-} to S_4^{2-} , with an overall reaction of the form:

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Following refs. [12] and [14], and noting the lack of passivation of the probe electrode in this experiment, it is unlikely that S_4^{2-} is electrochemically reduced to Li_2S , since such a reaction is not observed above 1.8 V; the ultimate discharge product is likely a result of a disproportionation reaction, for example:

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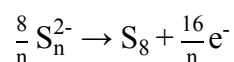
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Such a redox cycle of the electrochemically reducible S_6^{2-} is a reasonable explanation for the shape of the discharge profile in the cell, i.e., that most of the capacity is extracted at a constant potential of ~ 2.1 V. This scheme is consistent with the measured value of $j_{p,c}$ - which should be roughly proportional to $[S_6^{2-}]$ - and with the results of Cuisinier *et al*, in that the concentration of S_6^{2-} (and S_4^{2-}) is observed to be roughly constant over the duration of much

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of the lower plateau. The decrease in $j_{p,c}$ towards the end of discharge indicates depletion of PS in the electrolyte, which is again consistent with the literature[11]. The coincidence of PS depletion with an increasing cell overpotential (i.e., difference between the discharge potential and the OCV) near the end-of-discharge suggests that the end point (and hence maximum sulfur utilisation) might be determined more by PS depletion rather than passivation of the composite electrode.

On the anodic scan, it can be assumed that all polysulfides are ultimately oxidised back to elemental sulfur, i.e.,



Therefore, the anodic peak current $j_{p,a}$ can provide an indication of the total sulfur content in the electrolyte; however, it is not directly quantitative, since the current will depend on the distribution of polysulfide species. Nonetheless, as the cell transitions from the upper discharge plateau of ~2.3 V to the lower plateau at ~2.1 V, the continued increase of $j_{p,a}$ compared to $j_{p,c}$ could be an indication of the generation of S_4^{2-} (4 e⁻ oxidation to S_8) alongside S_6^{2-} (2.67 e⁻ oxidation), again as observed by Cuisinier *et al.*

To investigate further the use of polysulfide oxidation at the probe as an indicator of sulfur content in the electrolyte, the cell was charged and again discharged at a constant rate of C/10 while the probe was held at a potential of 2.65 V vs Li/Li⁺, i.e., higher than the potential of the anodic peak. The results of this experiment are presented in Fig. 2 c).

On charge, the probe current j_{probe} starts at a very low value in the deeply discharged state and rises roughly linearly over most of the charge. This is also consistent with the results of Cuisinier *et al*, who observed an approximately linear disappearance of Li_2S on charge; implying a linear increase in the sulfur-containing species in the electrolyte. The current
5 decreases again towards the end of charge, consistent with the depletion of PS to form solid S_8 inside the cathode matrix. Towards the end of charge and throughout the second discharge, the probe current fluctuates randomly; this is probably the result of nucleation of sulfur particles on the electrode surface, followed soon after by either detachment or dissolution.

10 On the second discharge, the probe current largely follows the trend observed on the first charge in the CV measurement; an increase in sulfur content peaking during the discharge at the lower plateau, followed by depletion at the end of discharge. The probe still measures a considerable ($\sim 70 \mu\text{A cm}^{-2}$) current at the end of the second discharge, implying a considerable quantity of sulfur remaining in the electrolyte. This observation, combined with
15 the large capacity drop from the 1st to 2nd cycles (1100 mAh g^{-1} to 800 mAh g^{-1}) is further evidence that a drop in initial capacity is explained by a loss of sulfur from the cathode to the electrolyte[15].

In summary, our results support previous reports that the discharge reaction is probably
20 determined mainly by the reduction of S_8 at $\sim 2.3 \text{ V}$ and S_6^{2-} at $\sim 2.1 \text{ V}$. Since Li_2S is probably not formed electrochemically, it does not necessarily have to precipitate on the electrode surface. Though we have not demonstrated so in this work, this mechanism may imply that the charge reaction operates through a similar redox cycle by similar chemical reactions of Li_2S and PS. In this case, it should be considered that there may be a *mass transport*
25 limitation, not just slow electron transfer kinetics, which may influence the rate capability of

the cell. This may be true of the discharge reaction as well, since we did not observe significant passivation of the probe electrode on oxidation to S₈.

As touched on by Lu *et al*[12], consideration of the intrinsic redox cycle mechanisms may be interesting for future developments, e.g., in optimisation of electrolytes for maximizing rates of reaction, or optimisation of the design of the cathode structure. Indeed, the exploration of redox mediated charge and discharge reactions to improve efficiency and rate capability has recently become a topic of interest in the related Li-air system[16,17], and more recently the idea has been extended to Li-S cells employing Li₂S as the starting cathode material[18].

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4. Conclusions

In conclusion, we have demonstrated a simple experiment to monitor the changes in polysulfide content in the electrolyte of a Li-S cell in operation, using a small *in situ* electrochemical probe. We believe that the results obtained by this approach support and are, in turn, supported by more sophisticated experiments conducted elsewhere, especially with regard to highlighting the important role of PS in the cell reaction. This technique is therefore a versatile complement to other techniques, electrochemical or otherwise, in the study of the electrolyte in the Li-S system.

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