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Catholyte formulations for high-energy Li-S batteries

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ABSTRACT

The sulphur electrode in LiS batteries suffers from rapid capacity loss and low efficiency due to the solubility of long chain polysulphides formed during discharge. Herein, we demonstrate the beneficial effect of original catholyte formulations containing redox active organyl disulphides (PhS₂Ph) on the capacity utilization and retention as well as the efficiency in LiS batteries. Resulting from the chemical equilibria in the electrolyte between the sulphur/polysulphides (S₈/S_x²⁻) and disulphide/thiolates (PhS₂Ph/PhS_x⁻), the polysulphide redox shuttle phenomenon is minimized due to the suppression of formation of soluble polysulphides (S_x²⁻, x > 4). Using the catholyte containing 0.4 M Ph₂S₂ as an additive in a standard base electrolyte (DOL/DME + LiTFSI/LiNO₃), a stable capacity of 1050 mAh.g⁻¹ is obtained under galvanostatic cycling at C/5 with a coulombic efficiency of >99.5%. At 45°C, it is shown that the formulated catholyte enables galvanostatic cycling at a high c-rate of 1C over 500 cycles with a capacity above 900 mAh.g⁻¹ and a high energy efficiency of 82%.

1- Introduction

Lithium-ion batteries are currently the most popularly used energy storage technology for electric vehicles and all portable electronics. The principal reason for their ubiquitous use is the relatively high energy density, which enables a long driving range for electric vehicles and increased duration of usage for portable devices on a single charge. However, the currently employed lithium ion technologies are approaching the practical limit of the achievable energy density and further improvement is only possible through the use of materials with a higher specific capacity.^{1,2} This has sparked interest of the global research community in the investigation of sulphur as a prospective cathode material.³⁻⁷ It exhibits a very high theoretical capacity of 1672 mAh.g⁻¹ which is more than eight times of the theoretical capacity of conventional cathode materials used in lithium ion batteries. However, several challenges concerning their performance need to be addressed in order enable their widespread

commercial acceptance. The main issues currently facing the sulphur cathodes are: (1) Low sulphur utilization, (2) low coulombic efficiency, (2) high self-discharge and (3) low capacity retention.^{8,9} Fundamentally, all these limitations are intrinsically linked to the high solubility of long chain polysulphides (S_{2x}²⁻; x = 3, 4) and the insulating nature of short chain species (S_x²⁻; x < 4). As a result, research efforts in the last decade have focused primarily on the intelligent design of the sulphur cathode involving creation of microscopic physical barriers to restrict the long range diffusion of the soluble polysulphides.¹⁰⁻¹⁴ Such approaches include synthesis of sulphur infused high aspect ratio microstructures and specific designed morphologies focused on effective encapsulation of the active material and discharge products. Using these approaches significant advances have been made, however, a lot of the methods remain complex, expensive and not feasible to implement on an industrial scale. Additionally a lot of this improvement

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comes at the cost of a low sulphur loading which limits the benefits of a high capacity. So far, the approaches involving electrolyte modifications to address the aforementioned challenges is relatively less explored.^{15,16} In this study, we demonstrate an original approach involving the effect of a catholyte containing diphenyl disulphide (Ph₂S₂) additive on the capacity retention, rate capability and efficiency of LiS batteries.

Using these approaches significant advances have been made, however, a lot of the methods remain complex, expensive and not feasible to implement on an industrial scale. Additionally a lot of this improvement comes at the cost of a low sulphur loading which limits the benefits of a high capacity. So far, the approaches involving electrolyte modifications to address the aforementioned challenges is relatively less explored.^{15,16} In this study, we demonstrate an original approach involving the effect of a catholyte containing diphenyl disulphide (Ph₂S₂) additive on the capacity retention, rate capability and efficiency of LiS batteries.

2- Experimental details

Electrode preparation: The sulphur electrodes were prepared by mixing powders, in a weight ratio of 2:1, sulphur (Sigma Aldrich, >99.5%) and carbon (Super C65, Timcal) respectively in a mortar and pestle. The polyvinylidene fluoride (PVDF) was dissolved in 1-methyl-2-pyrrolidone (NMP) to prepare a 2% by weight PVDF in NMP mixture. A weighed quantity of the NMP mixture was then added to the powder mixture to yield a final composition of 60:30:10 of S:C:PVDF. The prepared slurry was coated on an Aluminum foil (50 µm thickness). The coated foils were allowed to dry in air for 24 h period following which they were placed in a vacuum oven set to 30°C for 12 h. The prepared electrodes were then punched into 1 cm disks and weighed. The average sulphur loading for the electrodes was ~ 1 mg/cm². Punched lithium disks (0.75 mm thickness) of 1 cm diameter were used as the counter electrode.

Electrolytes: Prior to use, Ph₂S₂ was dried at a temperature of 30°C under vacuum for 24 hours before being stored under an argon-filled glove

box (H₂O < 5 ppm). The solvent mixture for the electrolyte was prepared by mixing equal volumes of 1,3 Dioxolane (DOL) and 1,2 Dimethoxyethane (DME). To this mixture weighed quantities of Lithium nitrate (LiNO₃) and Lithium bistrifluorosulfonylimide (LiTFSI) were added to yield a final solution of 0.25 M LiNO₃ and 0.75 M LiTFSI. From this base electrolyte different compositions which were prepared by dissolving appropriate quantities of Ph₂S₂ to yield 0.1 M, 0.2 M and 0.4 M electrolytes.

Electrochemical testing: For electrochemical testing standard 2032 type coin cells were used. While assembling the cells two separators of Whatmann (GF/C) were placed between the electrodes. The volume of electrolyte (150 µL) used was carefully measured using a calibrated pipette. All electrochemical measurements were carried out using a VMP multichannel potentiostatic/ galvanostatic system (Biologic Science Instrument, France).

Conductivity measurements were performed with a multichannel conductivity meter (BioLogic, France) based on frequency response analyser (MCM 10) connected to a Peltier-based temperature control unit (WTSH 10). The viscosity measurements were carried out between 5°C and 80°C by using an Anton Parr digital rolling-ball viscometer. The temperature of the cell during measurement was controlled within ±0.02°C.

3- Results and discussion

During discharge in a LiS battery, the elemental sulphur (S₈) in the cathode reacts electrochemically with the lithium ions to produce a series of discharge products (Li₂S_x, 1 ≤ x ≤ 8). Since the sulphur exists as octatomic rings in the elemental form, this process is often visualized as a series of ‘ring opening’ and ‘ring shortening’ steps.⁸ As observed in Figure 1 (a) a typical discharge profile for a sulphur electrode consists of three distinct regions; a high potential flat region (center potential ~ 2.3 V vs. Li/Li⁺, P_{D1}), a sloping potential region (~2.2 V) and a flat potential region (~2.1 V, P_{D2}).¹⁷ Through in-situ studies on the discharge process it has been shown that the region P_{D1}

corresponds to the initial reduction of the elemental sulphur to Li_2S_8 and Li_2S_6 (long chain polysulphides as per reaction (1)) giving almost the complete theoretical capacity close to 418 mAh.g^{-1} .¹⁸ This is followed by a further reduction to medium chain length polysulphides (S_3^{2-} , S_4^{2-}) in the second region as per reaction (2). The polysulphides generated during the last stage (P_{D2}) are insoluble and deposit back on the cathode after formation according to reaction (3) and the reaction exhibits a capacity much smaller than the theoretical capacity of 836 mAh.g^{-1} . In the corresponding dQ/dV curve shown in Figure 1 (b), two pairs of peaks corresponding to the redox reaction of long chain and short chain polysulphides can be clearly seen. These are labelled as P1 and P2

For understanding the effect of addition of the diphenyl disulphide (Ph_2S_2) additive to the electrolyte, similar cells of configuration $\text{Li//catholyte//C/S}$ are compared in which the electrolyte contained either 0.0 M or 0.2 M Ph_2S_2 . In general, the diphenyl disulphide belongs to the family of diorganyl disulphides (R_2S_2) specifically distinguished by the presence of S-S linkages.^{19,20}

The diorganyl disulphides are capable of undergoing electrochemical reduction to thiolate ions (RS^-) in aprotic media and the previously reported reduction potential for Ph_2S_2 is $\sim 2.08 \text{ V}$ (vs. Li/Li^+).^{21,22} The single step reduction process to form thiolate ions is of other anions such as cyanides (CN^-), sulphites (SO_3^{2-}) or arsenites (AsO_3^{3-}) to form

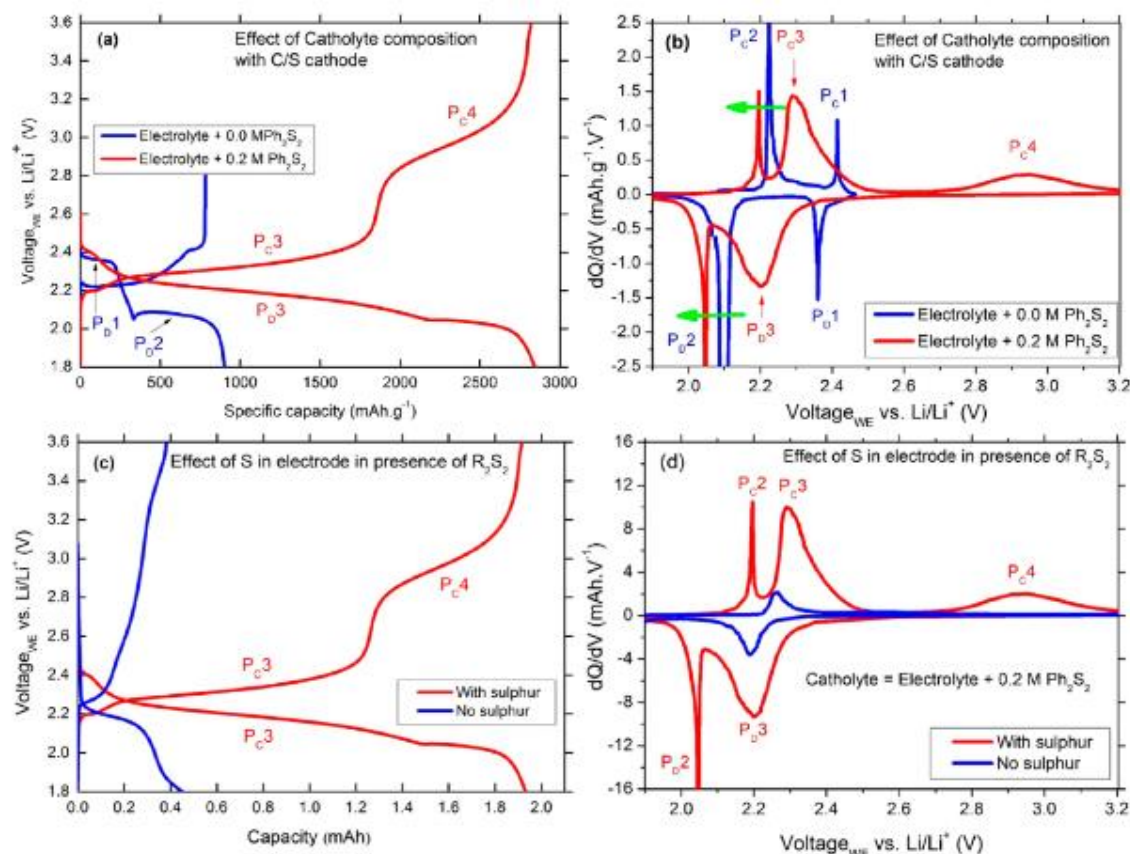


Figure 1. Effect of catholyte composition on the (a) galvanostatic voltage profiles and (b) dQ/dV curves. Effect of presence of sulfur in the electrode on the (c) galvanostatic voltage profiles and (d) dQ/dV curves for cells with catholytes containing 0.2 M Ph_2S_2 . The first cycle for cells charged and discharged at C/10 are shown.

with subscript C or D for charge or discharge.

shown in equation (4) in Scheme 1. These thiolate anions have an affinity for sulphur atoms which has been termed as ‘S-nucleophilicity’ or ‘thiophilicity’ by Kharasch and Parker.²³ This is analogous to the tendency

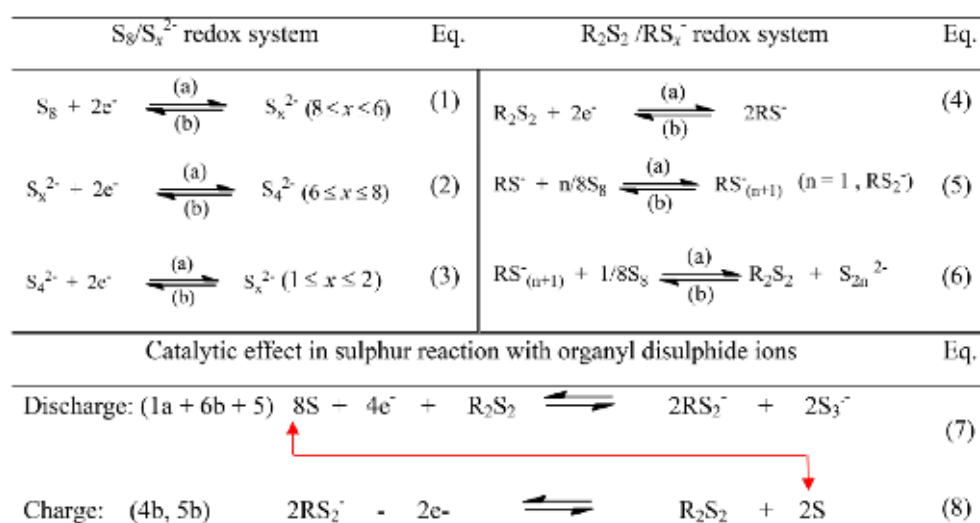
thiocyanides (SCN^-), thiosulphates ($\text{S}_2\text{O}_3^{2-}$) or

thioarsenates (AsSO_3^{3-}). For ease of interpretation, the nomenclature scheme for all sulphur containing species generated during the redox reactions is summarized in Table S1. The thiolate ions (RS^-) can thus react spontaneously

with elemental sulphur from the electrode to form a series of organyl polysulphides (RS_n^- , $n = 1, 2, 3$) as per reaction (5). It is important to remember that this is purely a chemical equilibrium between species at the electrolyte/cathode interface. The displacement of this equilibrium in the direction of longer chain organic polysulphides (RS_n^- , $n > 1$) is governed by the nature of R.^{21,24,25}

The organyl polysulphides (RS_2^-) subsequently formed can be oxidized by elemental sulphur (equation 6) to regenerate R_2S_2 and short chain polysulphides such as S_x^{2-} ($x < 4$). These equilibria have been previously studied by Anouti et. al. using spectroelectrochemistry method. Thermodynamic and kinetic equilibrium constants for the equilibria have been evaluated in aprotic media for a series of alkyl and aryl polysulphides.^{21,24,25} In essence, by considering reactions (4-6) it is

Scheme 1. Characteristic Redox Reactions of the (S_8/S_x^{2-}) and the (R_2S_2/RS_x^-) Redox Systems



obvious that the role of R_2S_2 is merely that of a catalyst which enables the direct reduction of S_8 to S_x^{2-} ($x < 4$) via an alternative route to the normally observed 'ring opening' and 'shortening' mechanism.¹⁸

From Figure 1 (a) it can be seen that in the presence of the catholyte, the voltage profiles are significantly altered. The capacity obtained is much larger than the theoretical capacity of Sulphur (1672 mAh.g⁻¹) which implies that a fraction of the capacity is also derived from the redox reaction of the dissolved disulphide in the catholyte. A new prominent peak appears during charging at a high potential (P_{D4} ~2.9 V) with no obvious analogue on the discharge. The observed peak potential is in excellent agreement with the known oxidation potentials for the thiolate (PhS^-) to Ph_2S_2 according to reaction (4).²¹ The irreversibility of the redox reaction of Ph_2S_2 is evident from the large ΔV (~600 mV) between the oxidation and reduction peaks even under slow charging conditions

(C/10). In fact, this irreversibility is quite generally observed across large number of organyl disulphides reported previously.^{26,27}

From the corresponding dQ/dV curve shown in Figure 1(b) it can be seen that a pair of analogous peaks (labelled as P3) appear with a redox potential of ~2.25 V. It is interesting to note that the appearance of the peak P3 is coincident with the absence of peak P1 during both charge and discharge. This observation can be directly explained by the thiophilicity of thiolates (RS^-) which catalyzes the reduction of elemental sulphur to short chain polysulphides while bypassing the formation of soluble long chain polysulphides completely as described earlier. Some additional equations shown (equation S11-S13) show other possible reactions leading to an equilibrium between the various organyl polysulphides.^{23,28} The S_x^{2-} ($x < 4$) thus formed can be further reversibly reduced to short chain insoluble polysulphides as evidence by the presence of the P2 pair of

peaks. These peaks are analogous to those observed in the cells not containing Ph_2S_2 but its redox reaction is slightly shifted to more reducing potentials (green arrow).

In order to further decouple the contribution of the catholyte and the sulphur to the overall reversible capacity observed, the galvanostatic profiles of cells with or without sulphur in the

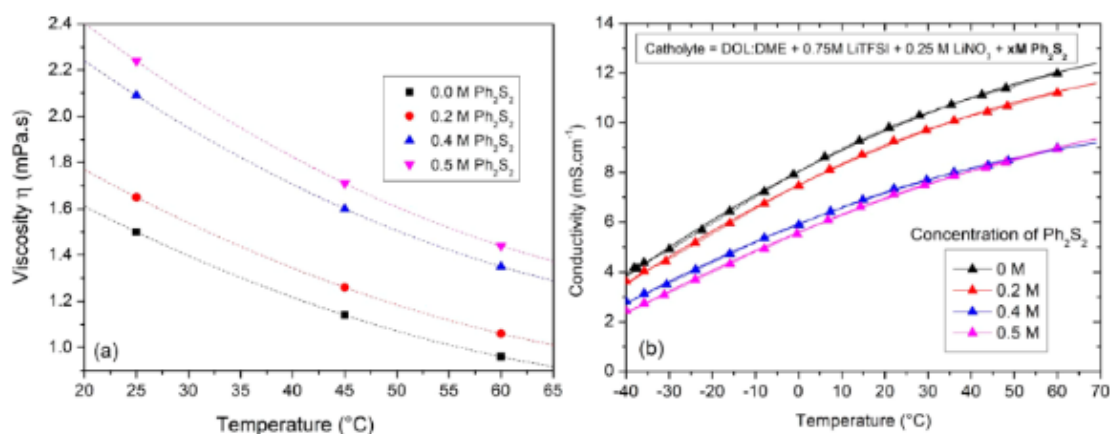


Figure 2. Measured (a) viscosity (η) and (b) conductivity (σ) of four catholyte compositions containing 0.0 M, 0.2 M, 0.4 M, and 0.5 M Ph_2S_2 .

Table 1. Conductivity ($\text{mS}\cdot\text{cm}^{-1}$), Viscosity ($\text{mPa}\cdot\text{s}^{-1}$), and Walden Product^a ($W = \Lambda\eta$) of Three Electrolyte Compositions at 25 and 60 °C

T (°C)	[Ph_2S_2]								
	0 M			0.2 M			0.5 M		
	σ	η	W	σ	η	W	σ	η	W
25	10.13	1.50	15.20	9.40	1.65	15.51	7.24	2.24	16.22
60	11.99	0.96	11.51	11.21	1.06	11.88	8.95	1.44	12.89

^aWalden product is calculated as $\Lambda\eta$ ($\text{S}\cdot\text{cm}^2\cdot\text{mPa}\cdot\text{s}^{-1}\cdot\text{mol}^{-1}$).

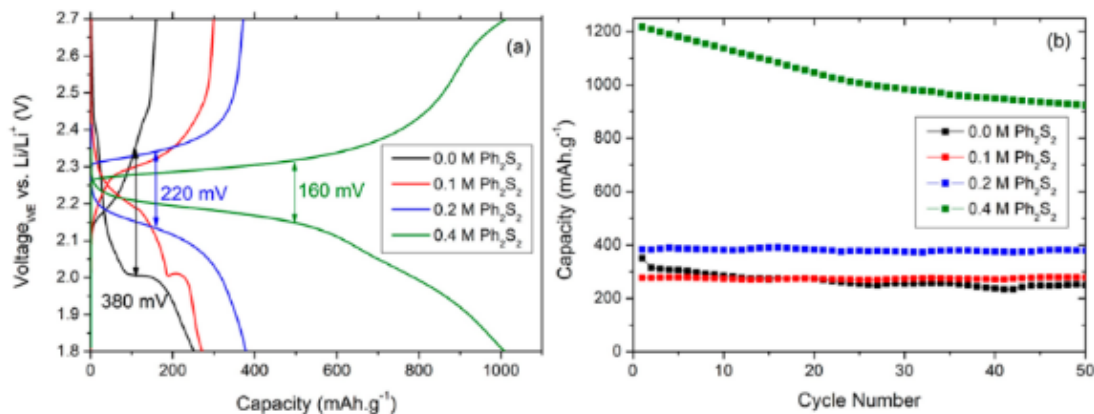


Figure 3. (a) Charge and discharge voltage profile for galvanostatic cycling at C/5 for cells with different electrolyte compositions (0.0, 0.1, 0.2, and 0.4 M Ph_2S_2). (b) Specific capacity retention ($\text{mAh}\cdot\text{g}^{-1}$) as a function of cycle number over the first 50 cycles.

cathode are compared in Figure 1 (c). The electrodes without sulphur for these experiments were prepared by mixing the conductive carbon and PVDF binder only to prepare the slurry. The electrolytes for both cells herein, contained 0.2 M Ph_2S_2 and were cycled at a C/10 current rate. In the presence of the sulphur, the observed capacity is about five times higher than in its absence, indicating that the presence of sulphur is essential for obtaining a majority of the capacity. The re-oxidation of

thiolates in the absence of sulphur is kinetically hindered and requires a high potential (> 2.7 V) as also observed in the presence of sulphur (PC_4). For applications in batteries, it is more beneficial to rely on the redox capacity of sulphur rather than the Ph_2S_2 for two reasons; the large hysteresis in the electrochemical redox reaction of Ph_2S_2 and its relatively low theoretical capacity ($245 \text{ mAh}\cdot\text{g}^{-1}$). Overall, by observing the differences in the profiles, it is clear that the electrochemical redox reaction of

mineral polysulphides (S_8/S_x^{2-}) is significantly modified due to the presence of thiolates (RS^-) in the catholyte.

In the experimental results shown in the following sections we reduce the voltage limits for galvanostatic cycling to a much smaller

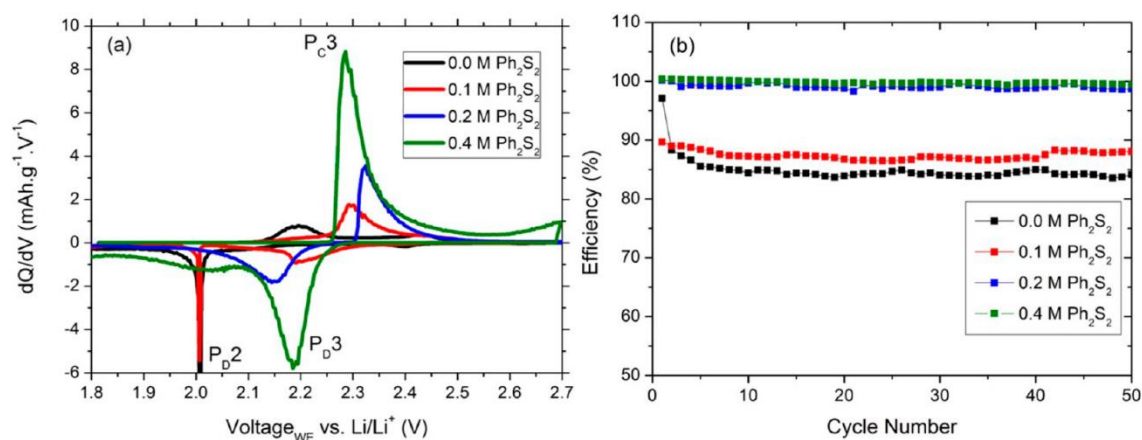


Figure 4. (a) Comparison of typical dQ/dV curves for cells with 0.0, 0.1, 0.2, and 0.4 M Ph_2S_2 containing electrolytes charged and discharged galvanostatically at C/5. (b) Measured Coulombic efficiency (%) as a function of the cycle number for the first 50 cycles.

range (1.8 – 2.7 V vs. Li/Li^+) while increasing the current rate to C/5 to focus primarily on the S_8/S_x^{2-} redox. At the higher current rate of C/5 the oxidation peak of PhS^- to Ph_2S_2 is shifted to much higher potentials (> 3.4 V vs. Li/Li^+). The effect of the concentration of Ph_2S_2 in the electrolyte on the discharge capacity ($mAh.g^{-1}$), coulombic and energy efficiency (%), rate capability and capacity retention in LiS batteries is explored.

Table 2. Calculated Charge Energy Density, Discharge Energy Density ($kWh.kg^{-1}$), and Energy Efficiency (%) from Voltage Profiles for Cells with the Respective Catholytes

catholyte	E_{Dch} ($kWh.kg^{-1}$)	E_{Ch} ($kWh.kg^{-1}$)	E_{EN} (%)
0.4 M Ph_2S_2	2.12	2.40	88.2
0.2 M Ph_2S_2	0.79	0.91	87.0
0.1 M Ph_2S_2	0.58	0.73	78.5
0.0 M Ph_2S_2	0.51	0.82	62.4
Gr//NMC	0.65	0.65	90.0
Gr//LFP	0.54	0.54	90.0

^a E_{EN} is the energy efficiency calculated as E_{Dch}/E_{Ch} expressed as percentage. Estimated nominal discharge voltage for Gr//NMC and Gr//LFP devices were 3.8 and 3.4 V respectively.

Physical characterization of Catholytes

The transport properties (viscosity and conductivity) of four electrolytes of interest was measured and is shown in Figure 2 (a) and (b) respectively. The base standard electrolyte was composed of a mixture of DOL:DME (1:1 by vol.) in which 0.75 M LiTFSI and 0.25 M $LiNO_3$ were dissolved. The inclusion of $LiNO_3$ has been shown to improve the stability of Li/electrolyte interface by the formation of an oxide layer on the surface. To this solution,

appropriate quantities of Ph_2S_2 were added to produce four different compositions (0.0 M, 0.2 M, 0.4 M, 0.5 M).

Table 3. Charge and Discharge Capacity and Coulombic Efficiency for Cells with Different Additive Concentration

composition	C_{Ch} ($mAh.g^{-1}$)	C_{Dch} ($mAh.g^{-1}$)	E_C^a (%)
0.4 M Ph_2S_2	1032.2	1030.1	99.79
0.2 M Ph_2S_2	384.0	380.7	99.12
0.1 M Ph_2S_2	314.2	274.6	87.39
0.0 M Ph_2S_2	314.9	267.1	84.79

^a E_C is the Coulombic efficiency calculated at C_{Ch}/C_{Dch} expressed as percentage.

In the rest of the paper the electrolytes will be referred to simply by the concentration of dissolved Ph_2S_2 . The conductivity measured from $-40^\circ C$ to $60^\circ C$ increases monotonically over the entire temperature range. As the concentration of dissolved Ph_2S_2 is increased from 0.0 M to 0.5 M, the conductivity at $25^\circ C$ decreases from $10.13 mS.cm^{-1}$ to $7.24 mS.cm^{-1}$. Thus, it retains a sufficiently high conductivity even when the dissolved content of Ph_2S_2 is as high as 0.5 M. As expected, the viscosity exhibits an opposite trend. When the dissolved Ph_2S_2 concentration is increased from 0.0 M to 0.5 M, the viscosity at $25^\circ C$ increases from $1.50 mPa.s^{-1}$ to $2.24 mPa.s^{-1}$. In an electrolyte where complete dissociation of the oppositely charged species of the salt occurs and ion pairing is absent, the variation of conductivity is compensated by the reciprocal variation of viscosity and can be observed as invariance of the Walden Product (W). The calculated

Walden Product ($\sigma\eta$) at the two temperatures for different electrolyte compositions shown in Table 1 are very similar indicating that although the dissolved Ph_2S_2 serves to increase the viscosity of the solution it does not have any appreciable effect on the dissociation of lithium salts or ion-ion pairing.

Effect of concentration of Ph_2S_2 in catholyte on performance of LiS cell

The charge and discharge voltage profiles for cells with different concentrations of Ph_2S_2 under galvanostatic cycling at a current rate of C/5 are compared in Figure 3 (a). The corresponding dQ/dV curves are shown in Figure 4 (a). It can be seen that the overpotential gap (difference between charge and discharge voltage at half capacity) decreases with the increase of concentration of dissolved Ph_2S_2 . The presence of the additive leads to a significant decrease in the overpotential from 380 mV in absence of additive, 220 mV for 0.2 M Ph_2S_2 to 160 mV for 0.4 M Ph_2S_2 cells. For the 0.1 M Ph_2S_2 cells it is estimated to be 160 mV at half capacity although this number is not representative of the entire cycle since the overpotential-gap is much higher for the last 30% of the discharge. From the viewpoint of reaction kinetics an additive concentration of 0.4 M seems to be optimal among the tested compositions. The lowered overpotential-gap directly affects the energy efficiency (%) which is a parameter that is often overlooked when evaluating the performance of LiS batteries. The calculated efficiency ($E_{\text{DCh}}/E_{\text{Ch}}$) is listed in Table 2 for all compositions. For the cells without Ph_2S_2 the energy efficiency is only 62%, which is a cumulative effect of the high overpotential gap and low coulombic efficiency. For cells with 0.2 and 0.4 M additives it is 87% and 88% respectively making it quite comparable to commercial lithium ion batteries (90 - 95%).²⁹ It is anticipated that by replacing the thick glass fiber separators used in this study by commercial grade separators further improvement is possible. It is also pointed out that the measured density of the base electrolyte is increased by <1% when 0.2 M Ph_2S_2 is added and thus should not have any significant impact on the weight of the battery.

The evolution of observed discharge capacity for the cells for the first 50 cycles at C/5 is shown in Figure 3 (b). The average charge and discharge capacity for the shown cycles are summarized in Table 3. There is only a marginal improvement in capacity when increasing the Ph_2S_2 concentration 0.0 M to 0.1 M (267 and 275 mAh.g^{-1} respectively). However, in the cells containing 0.2 M additive concentration, an average capacity of 381 mAh.g^{-1} is observed while in cells containing 0.4 M Ph_2S_2 an average capacity of 1030 mAh.g^{-1} can be seen. The initial capacity in cells with 0.4 M Ph_2S_2 is 1224 mAh.g^{-1} which reduces to 911 mAh.g^{-1} after 30 cycles and thereafter becomes more stable. It appears that, to avail the benefits of the equilibrium between the $\text{S}_8/\text{S}_x^{2-}$ and the PhS^- ions in solution a certain threshold concentration of the dissolved organyl disulphide is required. This equilibrium is also controlled thermodynamically (reaction rate constant K, nature of 'R') and kinetically (temperature T, charge rate) and it is directly related to the amount of reactive sulphur from the electrode. In some of the other cells tested (results not shown here) we found that increasing the Ph_2S_2 content beyond 0.5 M provides only marginal improvements in sulphur utilization and efficiency leading us to believe that this may be the optimal concentration.

The modification of the sulphur redox pathway is also evident from the charge/discharge potential profiles and dQ/dV curves. At a concentration of 0.4 M Ph_2S_2 it appears as though the electrochemical reaction is completely reversible. The calculated capacity corresponding to peaks P_{C3} and P_{D3} are shown in Table S3 for five consecutive cycles. The calculated coulombic efficiency on the basis of these values is 99.77% while the difference in peak potentials is ~100 mV which is quite different from the behavior typical observed for a sulphur cathode. For sulphur electrodes, it is generally observed that only the P1 redox reaction at high voltage ~2.3 V (shown in Figure 1 (b)) is electrochemically reversible and this reaction accounts for a relatively small fraction of the discharge capacity.³⁰

The coulombic efficiency for the same cycles are shown in Figure 4 (b) and the average values are summarized in Table 3. Low coulombic efficiency is caused by the well known ‘polysulphide shuttle effect’ which is one of the fundamental challenges concerning the sulphur cathode. It can be seen that there is a marginal improvement in efficiency upon increasing the additive concentration from 0.0 M to 0.1 M (84.79 to 87.39%). However, in the cells with 0.2 M Ph₂S₂ and 0.4 M Ph₂S₂ the coulombic efficiency is significantly higher. The average values obtained are 99.12% and 99.79% respectively, which a tremendous improvement considering that the electrode does not employ any microstructural modifications to encapsulate the sulphur. The increase in coulombic efficiency is directly indicative of suppression of the formation soluble long chain polysulphides (Li₂S_n, 4 ≤ n ≤ 8) responsible for self-discharge and low coulombic efficiency.

The overall result is an equilibrium between thiolates, organyl disulphides, organyl polysulphides, elemental sulphur and mineral polysulphides which is governed by the activity of the individual species (Eq 5 and Eq 6). It is evident that the chemical equilibria of the redox species S₈/S_x²⁻ are significantly modified in the presence of another redox species R₂S₂/RS⁻ due to which an alternative route is available for the direct electrochemically reversible reduction of elemental sulphur to lower order polysulphides (S_x²⁻, x < 4), in which the generation of soluble long chain polysulphides are suppressed.

Stability of Lithium/catholyte interface

A lithium stripping/plating test was performed using a symmetric Lithium cell to establish the stability of the Lithium/catholyte interface over multiple charge/discharge cycles.^{31,32} The catholyte chosen was (DOL:DME (1:1 by vol.) + 0.75 M LiTFSI + 0.25 M LiNO₃ + 0.5 M Ph₂S₂) keeping in mind that the effect of a chemical reaction between Ph₂S₂ and lithium, if any, would be most easily observable at a higher concentration of the former (Ph₂S₂). The galvanostatic regime consisted of alternate application of current densities of ± 0.4 mA.cm⁻² during 10-minute steps for over 100 h. The evolution of the overpotential measured between the two lithium electrodes over time is presented in Figure 5. The existence of an unstable SEI layer is characterized by periodic fluctuations in the voltage polarisation which is directly related to the formation and degradation of the interface with cycling and the existence of continued side reactions. The voltage profiles initially show unsymmetrical polarisation which indicates some differences in the surface preparation of the lithium electrodes which are eliminated as the cycling continues. The average voltage polarisation of ~ 50 mV is quite low indicating that the SEI layer formed is not highly resistive and will not contribute significantly to the cell hysteresis even under fast cycling conditions. Compared to the voltage polarisation values observed in similar ether based electrolytes the currently obtained values are ~10 mV higher which can be readily explained by the electrolyte conductivity

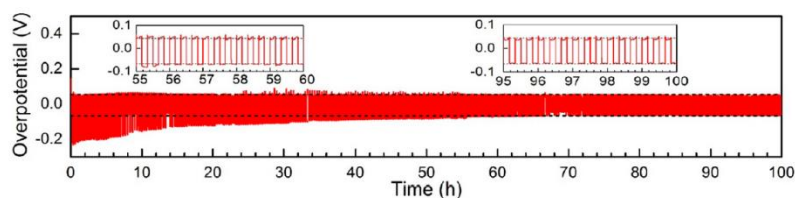


Figure 5. Lithium stripping/plating voltage profiles obtained with the (DOL/DME + 0.75 M LiTFSI + 0.25 M LiNO₃ + 0.5 M Ph₂S₂) electrolyte at current density of 0.4 mA.cm⁻² for 100 h. (Inset) Expanded view of select cycles.

reduction due to high concentration of Ph₂S₂.³³ The stable voltage polarisation can be observed majority of the test which indicates that the SEI layer formed is uniform and invariant under subsequent cycling. The inset shows an expanded view of several cycles between 55-60 h and 95-100 h where no appreciable difference

in the voltage polarisation can be observed. This result confirms that the current catholyte containing the organyl disulphide is stable at the highly reductive surface and any metal thiolates (Li—SR), if formed at the lithium surface are sufficiently soluble allowing good cycling stability of the lithium electrode.

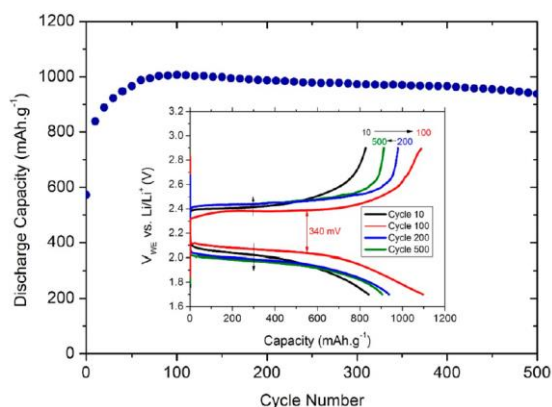


Figure 6. Capacity retention as a function of cycle life in cells with electrolyte containing 0.5 M Ph_2S_2 at 45 °C cycled at a current rate of 1C. Charge and discharge voltage profiles of select cycles (10, 100, 200, and 500) shown in inset.

Long term cycling: Effect of temperature on the $\text{R}_2\text{S}_2/\text{S}_x^{2-}$ redox equilibrium

The electrochemical redox of thiolate ions RS^- (4) and their equilibrium with sulphur (5) are temperature sensitive. In order to demonstrate the beneficial effect of temperature, we investigated the long-term capacity retention of the sulphur cathode under galvanostatic cycling using a 0.5 M Ph_2S_2 catholyte and the obtained results are shown in Figure 6. The cells were maintained at 45°C and cycled at a higher current rate of 1C, compared to results presented in the previous sections. It can be seen that the capacity increases over the first hundred cycles to attain a maximum value of 1046 mAh.g^{-1} . Thereafter the capacity remains stable gradually decreasing to about 911 mAh.g^{-1} at the end of 500 cycles (87% capacity retention).

This corresponds to a very small capacity fade rate of 0.028 % per cycle. It is hereby pointed out that at current rates as high as 1C, sulphur cathodes with active material loading of ~60 % and in the absence of any electrode modifications, exhibit a much lower specific capacity.³⁴ In our results shown in Figure 4 (b), even at a lower current rate of C/5, < 300 mAh.g^{-1} could be obtained. Estimating a nominal discharge voltage of 2.05 V, the energy density of the cell in the current configuration is 2050 Wh.kg^{-1} considering the active weight of the sulphur. The calculated energy efficiency ($E_{\text{Dch}}/E_{\text{Ch}}$) at 1C is very high (82.33%), which is in agreement with the observance of a small ΔV (340 mV) between the charge and discharge voltage curves in the inset in Figure 6. It can be

seen that the ΔV decreases for the first 100 cycles, which can be explained by the reformulation of the surface of Lithium electrode during the initial cycles, as observed in the stripping/deposition test shown in Figure 5. Between the 200th and the 500th cycles there is no observable change in the ΔV which indicates excellent stability of the Lithium interface and reversibility of the sulphur electrode in the presence of the organyl disulphide catholyte.

4- Conclusion

These initial promising results of catholyte formulations for LiS batteries show that we can enhance the electrode sulphur utilization through the control of the reactions of polysulphide ions in solution while effectively limiting their undesirable migration towards the anode. The interaction of the organyl disulphide with the sulphur can be further fine-tuned by choosing the substituent on R_2S_2 (R = alkyl or aryl) which opens the way for exploration of a wide range of electrolyte formulations. The enhanced high rate capability along with a good cycle life demonstrated herein through simple electrolyte modification may be used in conjunction with any of the promising composite electrodes reported in literature. Furthermore, the demonstration of the ability of the proposed catholyte to participate in charge storage, opens the door for it to be used in alternative cell formats such as semi-liquid batteries.³⁵

5- Perspectives of future collaborations with the host laboratory

There are several possibilities for future collaborations with the host laboratory considering the technical expertise and knowledge and extensive electrochemical characterization infrastructure available. The PCM2E laboratory has about 35 people including 14 teacher researchers, three professors, a professor emeritus and a lecturer Excellence recruited in September 2012 (as part of an LRC partnership since 2010 with CEA le Ripault). The overall project of the laboratory is built around competences in electrochemistry,

thermodynamics and chemistry of materials. The laboratory has three priority themes:

- Electrolytes, membranes and electrode materials for energy storage
- Organic semiconductors and nanostructured materials
- Ionic Liquids and applications

In addition to the above mentioned directions of research, this laboratory is a unique research organization owing to its in-depth focus on the design and development of novel electrolyte compositions. Such capability is indispensable for the research and development of any supercapacitor or battery technology globally and we envision active ongoing collaboration specifically on high energy and high power density storage devices for many years to come.

6- Articles published in the framework of the fellowship

1. Phadke, S., & Anouti, M. (2017). Effect of lithium salt concentration on the capacity retention of Lithium rich NMC cathodes. *Electrochimica Acta*, 223, 31-38. IMPACT FACTOR: 4.81
2. Characterization of novel LiFSI-FMD electrolytes for supercapacitors: Measuring in-situ gas formation, *Chem Phys Chem*, Satyajit Phadke, Samia Amara, Meriem Anouti, 2017, 18, 2364 – 2373 IMPACT FACTOR: 3.08
3. Catholyte formulations for high energy Li-S batteries, Satyajit Phadke, Erwann Cadaou, Meriem Anouti, *Journal of Physical Chemistry Letters*, November 2017, IMPACT FACTOR: 9.35
4. Approaches to electrolyte solvent selection for Poly-anthraquinone sulphide (PAQS) organic electrode material, Satyajit Phadke, Mingli Cao, Meriem Anouti, *CHEM SUS CHEM*, October 2017, IMPACT FACTOR: 7.23

Conference Presentations:

1. Oral presentation : Self-healing high temperature batteries for high cycle life, *Journées de la Section Régionale Centre* –

Ouest, Société Chimique de France, 2–3rd Février 2017

2. Poster presentation: Measurement of oxygen and hydrogen solubilities in electrolytes for lithium-ion batteries, BK. Xiong, S. Phadke, Michel Uldemolinsb, Cécile Tessierb, M.Anouti, 20th Topical Meeting of the International Society of Electrochemistry, Buenos Aires, Argentina 19-22 March 2017

3. Invited speaker: Organic electrode materials for energy storage applications, *Energy Storage India (ESI) 2017*, New Delhi (India), 9th-11th January 2017.

3. Oral Presentation: Evolution of energy storage technologies for stationary and portable applications, *Energy Storage India (ESI) 2018*, New Delhi (India), 10th-12th January 2018

4. Poster presentation: Effect of electrode and electrolyte composition on the gas generation in lithium-ion batteries, BK. Xiong, S. Phadke, Michel Uldemolinsb, Cécile Tessierb, M.Anouti, 68th Annual Meeting of the International Society of Electrochemistry, 27 August – 1 September 2017, Providence, Rhode Island

5. **PhD (Jury Member):** Quantification des gaz générés lors du fonctionnement d'une batterie Li-ion: Effet des conditions opératoires et rôle de l'électrolyte, Thesis Director: Mme ANOUTI Mériem, Jury Members: M. CHAGNES Alexandre, M. KOKOH Boniface, M. COASNE Benoit, M. ROSSO Michel, M. PHADKE Satyajit, Mme VIDAL Virginie. February, 2018.

6. Workshop Attended: 2nd Industrial On-Site Lithium-Ion Cell Production Technology Seminar, Itzehoe, Germany, April 4-5th 2018

7. Oral Presentation: Approaches to Electrolyte Solvent Selection for Poly-Anthraquinone Sulfide Organic Electrode Material, Satyajit Phadke, Mingli Cao, Meriem Anouti, *International Symposium on Solubility Phenomena (ISSP 18)*, 15-20th July, 2018 (Tours, France)

8. Oral Presentation: Catholyte formulations for high energy Li-S batteries,

Meriem Anouti, Satyajit Phadke, Erwann Cadaou, International Symposium on Solubility Phenomena (ISSP 18), 15-20th July, 2018 (Tours, France)

9. **Masters Thesis (co-Supervisor):** Optimisation d'électrolytes pour les batteries lithium soufre, Sirine Layouni, Matériaux Multifonctionnels et Nouvelles Technologies pour l'Energie (MM/NTE), 2017-18

10. **Masters Thesis (co-Supervisor):** Conception d'une batterie lithium-soufre, travail des techniques, et études électrochimiques de l'ensemble, Marc Dietrich, Matériaux Multifonctionnels et Nouvelles Technologies pour l'Energie (MM/NTE), 2017-18

11. Manuscript preparation: Effect of alkali cation on the electrochemical redox reaction of Prussian blue analogue electrodes, Satyajit Phadke, Roman Mysyk, Meriem Anouti, Material Horizons.

12. Manuscript preparation: Effect of Disulphides in Catholyte for Lithium-sulphur batteries: Comparison of Thiol, Dithiol and Disulphide, Satyajit Phadke, Meriem Anouti, ChemSusChem

13. Manuscript preparation: Effect of temperature, electrode and electrolyte composition on gas evolution in pouch cells, Baokou Xiong, Satyajit Phadke, Meriem Anouti

14. Manuscript preparation: Solvent effect on transport properties in CsTFSI based electrolytes, Mariam El Yagoubi, Satyajit Phadke, Meriem Anouti, ChemPhysChem

15. Patent preparation: Organic disulphide additives to enhance cycle life and longevity of Lithium sulphur batteries, Meriem Anouti, Satyajit Phadke, Alexander Kozhenko, Paul Guillaume Schmitt, ARKEMA

Written Communications for General Public:

1. Title: Pouch, Prismatic or Cylindrical Lithium-ion Batteries: What's your pick?
Authors: Satyajit Phadke, Urvi Mehta
Emerging Technology News (ETN), July 2018

2. Title: So many variations of Li-ion batteries: But what difference does it make?

Authors: Satyajit Phadke, Urvi Mehta
Emerging Technology News (ETN), November 2018

3. Title: Flow Batteries and their variations

Authors: Satyajit Phadke, Urvi Mehta
Emerging Technology News (ETN), November 2018.

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