Published in final edited form as:

New J Chem. 2016 March 1; 40(3): 2935–2943. doi:10.1039/C5NJ03402G.

Insight on the Li_2S electrochemical process in a composite configuration electrode

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Abstract

A novel, low cost and environmentally sustainable lithium sulfide-carbon composite cathode, suitably prepared by combining polyethylene oxide (PEO), LiCF_3SO_3 and $\text{Li}_2\text{S-C}$ powders is here presented. The cathode is characterized in lithium-metal cell employing a solution of LiCF_3SO_3 salt in dioxolane-dimethylether (DOL-DME) as the electrolyte. Detailed NMR investigation of the diffusion properties of the electrolyte is reported in order to determine its suitability for the proposed cell. The addition of LiNO_3 to the electrolyte solution allows practical application in a lithium sulfur cell using the $\text{Li}_2\text{S-C}$ -based cathode characterized by a specific capacity of about 500 mAh g^{-1} (as referenced to the Li_2S mass). The cell holds its optimal performances for over 70 cycles at C/5 rate, with a steady state efficiency approaching 99%. X-ray diffraction patterns of the cell upon operation suggest the reversibility of the Li_2S electrochemical process, while repeated electrochemical impedance spectroscopy (EIS) measurements indicate the suitability of the electrode-electrolyte interface in terms of low and stable cell impedance. Furthermore, the EIS study clarifies the activation process occurring at the Li_2S cathode during the first charge process, leading to the decrease of the cell polarization during the following cycles. The data here reported shed light on important aspects to be considered for the efficient application of the Li_2S cathode in lithium battery.

TOC image

A novel, low cost environmentally sustainable cathode combining PEO, LiCF_3SO_3 and $\text{Li}_2\text{S-C}$ is reported for application in high-energy lithium battery

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Keywords

Li₂S; lithium battery; NMR; EIS; lithium-sulfur process

1. Introduction

Lithium battery applicative scenario has consistently broadened over the last decades and it is nowadays ranging from advanced portable electronics to electrified transport and smart energy grids. The acceptance and deployment of this appealing energy storage system over a global scale presently requires a breakthrough in performance, characterized by higher energy density, lower costs, improved safety and relevant environmental compatibility.¹ Conventional lithium ion battery (LIB) is characterized by a specific capacity intrinsically controlled by the cathode performance that is of about 150 mAh g⁻¹ for LiCoO₂, i.e., a value limiting the theoretical cell energy to about 550 Wh kg⁻¹, reflected in a practical value of 150 Wh kg⁻¹. In this respect, the exploitation new electrodes, such as of Li₂S cathode, represents one of the most convincing solutions to achieve the power and energy density targets of emerging applications.

The Li₂S electrode operates in lithium cell following the electrochemical process $\text{Li}_2\text{S} \rightarrow 2\text{Li} + \text{S}$, characterized by a theoretical specific capacity extending up to 1166 mAh g⁻¹, delivered at about 2.1V with a resulting theoretical energy density as high as 2500 Wh kg⁻¹ as referred to the cathode mass.² However, Li₂S suffers from poor electronic and ionic conductivity and consistent volume changes upon cycling that severely limit its cell performances. Moreover, the dissolution within the electrolyte of the polysulfide species, formed as reaction intermediates during the electrochemical process, leads to active material loss and shuttle reactions strongly limiting the cell cycle life. Great efforts have been devoted to the search of viable solutions for these issues over the last years and remarkable advances in Li₂S –battery chemistry have been achieved so far. The low Li₂S electronic conductivity has been addressed by the formulation of Li₂S-carbon composites electrodes with optimized morphology.^{3–7} A valid example is represented by nanostructured Li₂S-Carbon composites characterized by a specific capacity of about 410 mAh g⁻¹ stable for 50 cycles at C/10 rate.⁸ Specific capacities as high as 280 and 480 mAh g⁻¹ have been obtained by employing pitch Carbon-coated Li₂S electrodes in liquid electrolyte and solid electrolyte lithium half-cells at 30°C and 80°C, respectively.³ Average capacity of about 380 mAh g⁻¹ have been achieved by using nanostructured composite cathodes in which the Li₂S active material is incorporated within the pores of mesoporous carbon.⁹ Moreover, the exploitation

of polymeric binders has been demonstrated to be beneficial for both the Li^+ diffusivity and for the electrode mechanical stability upon cycling.^{10,11} A slurry-less, nano- Li_2S cathode-Graphene Oxide Paper cathode has been recently demonstrated to stably deliver capacities as high as 600 mAh g^{-1} even at high cycling rates (i.e. 5C), using LiNO_3 and Li_2S - added electrolyte.⁶ Polysulfide dissolution has been physically and chemically limited by confining the Li_2S active particles within carbonaceous and polymeric matrixes⁸ and by replacing conventional electrolytes with polymeric, solid state^{12,13} and polysulfide saturated solutions.^{14,15} Remarkable cycling performances (i.e. specific capacity of 550 mAh g^{-1} for 50 cycle with capacity fade of about 0.25% per cycle) have been achieved by using ball milled Li_2S cathode in lithium half-cells employing 1% LiNO_3 additive within the electrolyte.¹⁶ Although these advances toward the suitability of Li_2S -based materials for application as cathodes in next generation, high energy LIBs are encouraging,, various drawbacks still hinder its practical application, such as stability issues not fully addressed, difficulties associated with the determination of a proper electrode composition, including binder and solvent, as well as of the most suitable electrolyte.

A novel Li_2S -C composite electrode, including polyethylene oxide (PEO) binder and a lithium trifluoromethanesulfonate (LiCF_3SO_3) salt in its composition, is here originally reported. The new electrode configuration is expected to enhance the diffusivity of Li^+ ions within the insulating Li_2S active particles, thus improving the electrode mechanical stability upon cycling and limiting polysulfides dissolution during cell operation. Moreover, the electrode film here disclosed is easily prepared by using Li_2S -C-(PEO)₂₀ LiCF_3SO_3 mixed powders and 1,3 dioxolane (DOL) solvent, that is a further advantage in view of large-scale applications. The cathode is characterized in a lithium metal cell, using bare and LiNO_3 added, 1m LiCF_3SO_3 , DOL:DME electrolyte. A detailed NMR study of the electrolyte diffusion properties demonstrated the full applicability of the solution in advanced lithium battery. Furthermore, the features of the Li_2S electrochemical process, including the highly polarized first cycle and the trend leading to a polarization decrease during following cycles, are studied by combining galvanostatic cycling tests, electrochemical impedance spectroscopy and ex-situ XRD measurements. The proposed electrode/electrolyte formulation, employing economically and environmentally sustainable materials, is herein suggested as a suitable candidate for application in enhanced energy density and environmentally friendly batteries.

2. Experimental Section

2.1 Cathode and electrolyte preparation

Dry Polyethylene Oxide (PEO, Mw 600000 Da, Sigma Aldrich), LiCF_3SO_3 (>99.9% Sigma Aldrich), in a EO: LiCF_3SO_3 molecular ratio of 20:1 ($\text{PEO}_{20}\text{LiCF}_3\text{SO}_3$), Li_2S (>99.9% Sigma Aldrich) and Super P carbon (Timcal) powders were mixed under Ar atmosphere in a $\text{PEO}_{20}\text{LiCF}_3\text{SO}_3$: Li_2S :Super P weight ratio of 30:35:35. The mixture was subjected to soft, glass-ball milling under Argon atmosphere for 24 hours. The cathode, hereafter referred to as Li_2S -C-PEO was prepared by doctor-blade casting on Al foil a slurry obtained by dispersing the soft milled ($\text{PEO}_{20}\text{LiCF}_3\text{SO}_3$ - Li_2S - Super P carbon mixture in 1,3 dioxolane (DOL, Sigma Aldrich) in Ar filled glove box. The electrode mass loading was 1.5

mg cm⁻². The electrolyte solutions were prepared by dispersing LiCF₃SO₃ (>99.9% Sigma Aldrich) powder in a 1:1 wt mixture of 1,3 dioxolane (DOL, Sigma Aldrich), 1,2 dimethoxyethane (DME, Sigma Aldrich), with 1 mol/kg (1m) triflate concentration. LiNO₃ additive (1m) was subsequently added to the solution. 1–2 dimethoxyethane (DME Sigma Aldrich) and 1,3-dioxolane (DOL, Sigma Aldrich) herein reported as DOL-DME were dried under molecular sieves separately until the water content was lower than 10 ppm of water. Karl Fischer titration instrument (Metrohm) to control the water content was used. Before electrolyte preparation, both LiCF₃SO₃ and LiNO₃ salts were dried under vacuum at 100°C.

2.2 XRD and SEM characterization

Ex-situ XRD measurements were performed on the electrode at different stages of charge/discharge by using a Rigaku D-Max Ultima + diffractometer, with Cu K α source and a graphite monochromator, in 2 θ / θ scanning mode. The electrodes were collected from the cell in Ar-filled glove box, washed with DME, and sealed in plastic-bags into the XRD-sample holder in order to avoid the change of the electrode structure by contact with air. The electrode morphology was investigated by means of Scanning Electron Microscopy, using a Phenom-FEI instrument. The electrode was then transferred into the instrument under argon, and subjected to fast vacuum upon introduction into SEM-sample holder, in order to avoid excessive contact with atmosphere.

2.3 Electrolyte characterization^{14,15}

A Bruker 400 Avance III NMR spectrometer was used to measure self-diffusion coefficients with a pulse field gradient double-stimulated echo sequence. The data were acquired each 10°C from 20 to 60 C°, using a diffusion delay of 80–250 ms between the gradient pulses of strength of 0–45 G/cm and duration of 1–2.5 ms. The Nernst-Einstein equation (1) was used to calculate conductivity values from the self-diffusion coefficient following indicated by δ_{NMR} .

$$\delta_{NMR} = \frac{F^2[C]}{RT} (D_{Li} + D_{CF_3SO_3}) \quad (1)$$

where F is the Faraday constant (96485 Coulomb), [C] represents the solution concentration (mol cm⁻³), R is the ideal-gas constant (8.314472 J K⁻¹ mol⁻¹), T is the temperature value, D_{Li} and D_{CF₃SO₃} are the self-diffusion coefficients of the Li⁺ cation and CF₃SO₃⁻ anion, respectively. The lithium transference number (t^+) was calculated from the equation (2).

$$t^+ = \frac{D_{Li}}{D_{Li} + D_{CF_3SO_3}} \quad (2)$$

The electrochemical impedance spectroscopy to obtain conductivity values of the electrolyte was carried out in a 2032 coin cell, stainless steel current collectors and a Teflon ring as a separator were used to keep the cell constant fixed. The measurements were carried out with a signal amplitude of 10 mV in a frequency range from 100 mHz to 100 KHz using a biological VSP instrument. The ion association was calculated following the equation (3):

$$\alpha = \left(1 - \frac{\delta_{\text{EIS}}}{\delta_{\text{NMR}}} \right) \quad (3)$$

where δ_{EIS} and δ_{NMR} are the conductivity measured by EIS and calculated by equation (1), respectively.

2.4 Electrochemical tests

The electrochemical tests were performed on coin cells assembled in Ar filled dry box using Celgard separators. The cell were assembled using the $\text{Li}_2\text{S-C-PEO}$ cathode and a 1 m LiCF_3SO_3 , DOL:DME 1:1 v/v electrolyte, to which 1 m LiNO_3 was added as a film-forming agent, in order to avoid shuttle reaction (evidenced by a cycling test performed by using a LiNO_3 -free electrolyte). About 30 μl of electrolyte solution was used for the cell assembly. A Maccor Series 4000 Battery Test System was used for the galvanostatic cycling tests, within the voltage limits 1.4–3.7 V and 1.9–2.7 V during the first and subsequent cycles, respectively, at a C/5 C-rate ($1\text{C} = 1166 \text{ mA g}^{-1}$). Electrochemical Impedance Spectroscopy (EIS) tests were performed by applying 10mV AC amplitude signal to the cells within the 1MHz – 0.1 Hz frequency range. The equivalent circuit used for the analysis of the impedance data is $R_e(RQ)_{\text{PF}}(R_{\text{CT}}Q_{\text{DL}})Q$, where R_e is the electrolyte resistance, the $(RQ)_{\text{PF}}$ elements are associated to the passivation of the electrode surface, R_{CT} and Q_{DL} describe the charge transfer and double layer capacitance associated with the cathode lithiation/delithiation, respectively, and Q is related to Li^+ diffusion within the electrode. A VSP (Biologic) was used for the EIS measurements upon cycling. The EIS responses were analysed by using the Boukamp program.¹⁷ All the electrochemical tests were run at 40°C.

3. Results and Discussion

3.1 The $\text{Li}_2\text{S-C-PEO}$ electrode

A $\text{Li}_2\text{S-C-(PEO)}_{20}\text{LiCF}_3\text{SO}_3$ composite electrode ($\text{Li}_2\text{S-C-PEO}$) easily prepared by doctor-blade casting a dispersion of soft milled $(\text{PEO})_{20}\text{LiCF}_3\text{SO}_3$ - Li_2S - Super P carbon mixture in 1,3 dioxolane (DOL) and in Ar filled glove box is herein characterized as an alternative and low cost cathode material for application in Li/S batteries. Polyethylene oxide (PEO) is to date one of the most widely used binder materials in sulfur and Li_2S -based electrodes.¹ PEO is employed as ionic conductor in the composite electrode presented in this work in order to ensure intimate contact between the insulating Li_2S active materials and the carbonaceous electronic conductors. Moreover, this binder provides a connection between the electrode components and the current collector upon cycling. Chain entangled PEO binder provides a conductive network for Li^+ diffusion within the electrode and ensures electrode integrity upon cycling by minimizing Li_2S or S phase segregation and stabilizing the carbon network. As reported in literature¹⁰, high viscosity PEO binder may reasonably suppress active material loss upon cycling and reduce the dissolution rate of polysulfides within the electrode-electrolyte interphase, thus enhancing the electrode cycling efficiency and stability.¹⁹ Furthermore, the use of PEO binders enhances the electrode mechanical properties in terms of homogeneity and surface porosity, which translate into high electrode

kinetics. Super P carbon is employed as conductive agent within the insulating Li_2S active particles.²⁰

3.2 Structural and morphological study

The morphology of the Li_2S -C-PEO (Figure 1) is probed by scanning electron microscopy (SEM). The micrographs, collected at increasing magnification, demonstrate the dispersion of Li_2S active material (crystals) within the $(\text{PEO})_{20}\text{LiCF}_3\text{SO}_3$ -carbon amorphous matrix. The figure reveals the formation of micrometric Li_2S aggregates exhibiting a characteristic high active surface and lamellar morphology. The good dispersion of the insulating Li_2S active material within carbon and binder is expected to enhance the electrode electronic conductivity and Li^+ diffusivity, and to improve the mechanical stability by buffering the electrode structural changes upon charge and discharge.

3.3 NMR characteristics of DOL-DME- LiF_3SO_3 electrolyte

The DOL-DME- LiF_3SO_3 electrolyte suitability for application in battery has been investigated by NMR. Accordingly, Figure 2 reports the characteristics of the electrolyte in terms of self-diffusion coefficient (A), lithium transference number (B), conductivity (C) and ionic association degree (D), obtained at various temperatures. Fig. 2A reveals a diffusivity of the Li^+ cation and CF_3SO_3^- anion of about $10^{-9} \text{ m}^2 \text{ s}^{-1}$ while, at the same conditions, the DOL and DME solvents show a higher mobility, i.e., of about $3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, due to the hindrance effect of the ionic solvation shell. Moreover, Fig. 2A shows lower self-diffusion coefficient for DME compared to DOL, thus suggesting a higher interaction of the DME with the charged species that may be ascribed also to viscosity effects. The lithium transference number reported in Fig. 2B (calculated following equation (2) in experimental section) represents an important parameter to evaluate the electrolyte.

This parameter shows a value of about 0.5, sufficiently high for battery application, in the whole investigated temperature range. Fig. 2C displays the conductivity values calculated by using the self-diffusion coefficients (following the Nernst-Einstein equation (1) reported in experimental section) and, for comparison, the values measured by electrochemical impedance spectroscopy. The conductivities determined by the two techniques exhibit similar trend, a value higher than $10^{-3} \text{ S cm}^{-1}$ in the explored temperature range, however, a different order of magnitude. This discrepancy is attributed to a substantial difference between the two techniques. Indeed, EIS determines the transport of only the charged species, while NMR is sensitive to the movement both of charged species and to associated, neutral couples or multiple aggregation of ions.^{14,15} Accordingly, the ion association degree (α) determined by the comparison of the conductivity values determined using EIS and NMR, following equation (3) reported in the experimental section, results of about 0.95 (Fig. 2D).

3.4 Lithium metal passivation by LiNO_3 -addition to the electrolyte

Despite the full suitability of the DOL:DME- LiCF_3SO_3 for battery in terms of ion transport properties and conductivity, previous papers^{14,15} demonstrated that sulfur electrode suffers from a severe shuttle effect in this electrolyte that may be prevented only by adding a sacrificial film forming agent, i.e., LiNO_3 . This issue affects also the cell using the electrode

here prepared, as indeed demonstrated by Figure 3, reporting in comparison the voltage profile of the first galvanostatic charge-discharge cycle of the Li_2S -C-PEO cathode in lithium half-cell using LiNO_3 -free (red line) and LiNO_3 -added (black line) electrolytes. The figure evidences for the cell using LiNO_3 -free electrolyte (red line) the typical profile of Li/S process affected by severe shuttle reaction resulting in a noisy, decomposition-like charge and very limited discharge. Instead, the cell using the LiNO_3 -added electrolyte (black line) reveals the charge-discharge curve typically observed during the first cycle of Li_2S electrode in lithium cells using liquid electrolyte,¹⁶ with reversible capacity of about 1000 mAh g^{-1} , without significant signs of shuttle reaction.

3.5 Characteristics of the electrochemical process of Li_2S -C-PEO electrode

Further insights into the Li_2S -C-PEO electrochemical process using the selected, LiNO_3 -added electrolyte are given by combining cycling test, X-Ray Diffraction (XRD) and Electrochemical Impedance Spectroscopy (EIS) measurements, displayed in Figures 4A, B and 4C–H, respectively. The first de-lithiation (charge) step of the Li_2S -C-PEO cathode (dark-red line in Fig. 4A) proceeds by an activation process characterized by high polarization extending up to about 3.5 V that is ascribed to the Li_{2-x}S polysulfide phase nucleation, according to the reaction: $\text{Li}_2\text{S} \rightarrow \text{Li}_{2-x}\text{S} + x\text{Li}^+ + x\text{e}^-$.

The barrier extension is not only due to the high charge transference activation energy of the lithium at the Li_2S surface, but also to contributions from other kinetic factors, including limited Li-ion diffusivity and low electronic conductivity of the electrode.¹⁶ The series of sequential steps between 3.27 V and 3.5 V during first charge are ascribed to the formation of short chain (Li_2S_y , $2 \leq y \leq 4$) and long chain (Li_2S_y , $4 \leq y \leq 8$) polysulfide intermediates.^{21,22}

The plateau centred at about 3.6 V in the Li_2S composite cathode voltage signature may be reasonably ascribed to oxidative parasitic reactions of species formed from reductive processes of the LiNO_3 additive in contact with metallic lithium during the cell assembly, i.e. before starting the cycling test. This process represents a chemical reduction of LiNO_3 . In particular, when the cell is discharged down to low voltages (below 1.6 V), the electrochemical reduction of LiNO_3 occurs and a passivation film is formed on the electrode surface which suppresses polysulfides shuttle phenomena. Moreover, as reported by Cui et al.¹⁶, the extra capacity gained at voltages higher than 3.5 V may be reasonably ascribed to poor contact between the Li_2S active material and the carbon electronic conductor. The first discharge profile (dark-blue line in Fig. 4A) reveals the two main plateaus centered at about 2.37 and 2.12 V, typical of sulfur lithiation process, as well as an additional plateau between 1.8V and 1.4 V due to the electrochemical reductive decomposition of LiNO_3 additive, precipitation at the lithium surface of the formed species and final consolidation of the passivation film that is expected to enhance the cell Coulombic efficiency.^{14,15} Following the first cycle, the reaction proceeds with very low polarization, thus suggesting a decrease of the resistivity of the active material by the ongoing electrochemical process. The evolution of the XRD patterns of the Li_2S -C-PEO electrode performed at different cycling stages of the lithium cell (i.e., corresponding to the circle marks P1-P5 in Fig. 4A) is reported in Fig. 4B. The figure reveals that the characteristic signals of Li_2S phase (JCPDS#772145),

centered at about 27, 3, 44 and 53 degrees, disappear upon full charge and then reappear, even if with lower intensity due to electrode amorphization, after full discharge, thus confirming the reversibility of the Li_2S redox process.

The reflection of Li_2S centered at about 44 degrees is not taken into account because of the overlapping electrode current collector (support) signal. Figs. 4(C–G) report the impedance Nyquist plots of the lithium cell using the Li_2S -C-PEO electrode at various states of charge (corresponding to the circle marks P1 to P5 in the voltage profile of Fig. 4A), while Fig. 4H reveals the evolution of the impedance plots of the same cell, collected at the discharged states, during the subsequent cycles (following the two reported in Fig. 4A). It can be noticed that the electrolyte resistance R_e , i.e., the highest frequency intercept of the Nyquist plots in Fig. 5, is about $8\ \Omega$, without significant variation upon cycling. At the OCV (Fig. 4C, corresponding to P1 in the voltage profile of Fig. 4A), two well defined, high and low frequency semi-circles are detectable, corresponding to the formation of a passivation film on the electrode surface and to the charge transfer at the electrode/electrolyte interface, respectively. Upon de-lithiation by charge (Fig. 4D, corresponding to P2), the EIS response shows a broad and depressed semicircle, most likely from convolution of the two semicircles discussed above, while at the fully discharged states (Fig. 4E, corresponding to P3) two distinct semicircles are again detected. Following, Fig. 4 F, G and H show the same EIS trend previously illustrated, characterized by two semicircles at the discharged state merged into one during charge. This trend is ascribed to the different electrode kinetics for S (charged state) and Li_2S (discharged state). In particular, the charge transference (represented by the second semicircles) is favored by the presence of S (charged states) compared to the more insulating Li_2S (discharged state), thus allowing the second, low frequency semicircle to shift to higher frequencies (faster kinetics) and overlap the first semicircle corresponding to the passivation film.

The NLLSQ analysis of the impedance responses reported in Table 1 (see experimental section for details) reveals changes, i.e. decrease and increase, of the passivation film resistance and capacitance values upon charge and discharge that can be reasonably associated to progressive dissolution and re-formation with final consolidation of the film. Similar behavior is observed by the charge transfer process, however with a decreasing resistance trend. Indeed, Table 1 shows that the cell has OCV resistance values of about $54\ \Omega$ and $108\ \Omega$, for passivation film (R_{PF}) and charge transfer (R_{CT}), and final values of about $53\ \Omega$ and $66\ \Omega$, respectively. These data indicate a stable SEI film and an enhanced charge transference in subsequent cycles, thus accounting for the decrease of the cell polarization upon charge-discharge process and confirming the optimized electrode configuration. The suitability of the system is further suggested by the Nyquist plots during the first ten cycles reported in Fig. 5H, again suggesting stable electrode kinetics and electrode/electrolyte interface for the Li_2S -C-PEO cathode in lithium cell. Furthermore, the ex-situ SEM images of the electrode at various states of charge, shown and discussed in Figures S1 (A) and (B) in Supplementary Information section, confirm the reversibility of the redox process upon cycling.

3.6 Cycling performances of Li₂S-C-PEO electrode in lithium cell

Figure 5 reports the galvanostatic performances at C/5 rate at 40 °C, in terms of voltage profile (A) and cycling behavior (B), of the lithium cell using the Li₂S-C-PEO electrode. The electrode is reversibly charged and discharged to about 70 cycles and shows, after the first activation cycle, two main characteristic redox plateaus at about 2.25 and 2.42 V in charge and at 2.37 and 2.10 V in discharge (Fig. 5A). The voltage hysteresis rapidly decreases from about 1.4 V during the first cycle to a stable value of 0.2 V in the following ones, due to the kinetic improvement upon cycling discussed in Fig. 4. The cell shows specific capacity values ranging from about 550 to about 450 mAh g⁻¹ (referenced to the Li₂S mass) upon 70 cycles (Fig. 5B), with a Coulombic efficiency approaching 99% after the first few stabilization cycles. The slight capacity decay during cycling can be attributed to minor electrode dissolution during charge-discharge process. The operating temperature (40 °C) has been selected as suitable value for proper operation due to optimized characteristics in terms of electrode-electrolyte interface. Indeed, cycling tests conducted, for comparison, at lower temperature, i.e., at 25 °C, and reported in Figure S2 in Supplementary Information section, revealed lower capacity of the cell compared to the higher temperature value. Within the proposed cell configurations, some major problems of Li₂S-based batteries, including polysulphide dissolutions, redox shuttle effects, phase segregation and electrode mechanical instability etc., may be controlled and contained, however not completely avoided, by the use of PEO₂₀(LiCF₃SO₃). This aspect is clearly demonstrated by the poor response of the cycling test performed using binder-free, Li₂S-C electrode (Figure S3 in Supplementary Information section). Even to a minor extent, unreacted long and short chain polysulphides may be dissolved within the employed electrolyte and therefore be responsible for active material loss upon cycling and redox shuttle effect between anode and cathode.

These phenomena may reasonably account for the reduced cycling efficiency observed during the first cycles. Indeed, the presence of polysulphide species dissolved within the electrolyte would be expected to slow down further decomposition processes, thus inducing a stabilization of the cell efficiency after few cycles. Moreover, electrode structural rearrangements, particularly pronounced during the first cycles, would also contribute to the cell cycling inefficiency. Further technological optimization of the electrode morphology and surface properties is expected to overcome these issues and to translate into higher cycling performance in terms of efficiency. The specific capacity exhibited by the cathode here presented largely exceeds the ones of conventional LIB cathode materials, such as LiCoO₂ and LiNi_{0.5}Mn_{1.5}O₄, with the additional advantages of very low cost and reduced environmental impact. The average specific capacity of 470 mAh g⁻¹(Li₂S) delivered by the cathode at about 2.1 V translates into theoretical specific energy content that is significantly higher than that ascribed to the conventional LiCoO₂ electrode. However, the electrode composition here reported, in terms of carbon and binder content, lowers the practical energy to levels comparable to the common battery. This aspect suggests the need for further optimization of the electrode by lowering the carbon and binder contents to enhance the performances of this very promising, low cost system.

4. Conclusions

This paper describes the characterization of a Li_2S -Carbon composite cathode, containing polyethylene oxide and salt, (PEO)- LiCF_3SO_3 , in its formulation for application in lithium-ion batteries. Remarkable advantages of the cathode are the facile preparation technique, the low cost and the modest environmental impact of the materials. The SEM micrographs of the electrode evidenced Li_2S active particles well dispersed within Carbon and binder. The electrochemical behavior of the cathode was investigated in lithium cells, using LiCF_3SO_3 -DOL-DME electrolyte solution. The NMR and EIS characterization of the electrolyte revealed values of Li^+ transference number of about 0.5, conductivity higher than $10^{-3} \text{ S cm}^{-1}$ and ionic association of 0.95 over the investigated 20–60°C temperature range. The applicability of the electrolyte in lithium sulfur cell has been assured by the addition of LiNO_3 to the electrolyte as sacrificial film forming agent to mitigate the polysulfide shuttle process. The reversibility of the Li_2S electrochemical process was demonstrated by ex-situ XRD measurements on the electrode at different states of charge/discharge. The cell showed an activation barrier up to 3.4V during the first charge process, attributed to kinetic limits as confirmed by EIS measurements during cycling. The EIS study revealed the enhancement of the electrode kinetics reflected into a reduction of cell polarization upon cycling. Indeed, after few stabilization cycles, the Li_2S -C-PEO cathode stably delivered at an average voltage of about 2.1 V, specific capacities ranging from 550 to 450 mAh g^{-1} for 70 cycles, with a coulombic efficiency approaching 99%. The obtained results are in line with those previously reported for Li_2S -based cathodes, both in terms of delivered capacity and cycling stability.^{3,8,16,23,2} Further work is still needed in order to address the inefficiencies affecting the first few charge-discharge cycles and to improve the overall cell performance. However the results here presented provide new insight on the suitability of the Li_2S -C cathode for application in advanced, environmentally friendly, and low cost battery systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

The work at Hunter College was supported by a grant from the U.S. Office of Naval Research, and the Hunter NMR facility is funded by a National Institutes of Health RCMI infrastructure grant (RR 003037).

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Figure 1.
SEM micrographs of the pristine $\text{Li}_2\text{S-C-PEO}$ electrode.

Figure 2. Self-diffusion coefficient (a), transference number (b), conductivity (c) and ionic association (d) of 1m LiCF_3SO_3 , DOL:DME 1:1 v liquid electrolyte at increasing temperatures as determined by NMR measurements (see experimental section for details). Temperature range: 293 K – 333 K.

Figure 3.

Voltage profile of the first galvanostatic charge-discharge cycle of the $\text{Li}_2\text{S-C-PEO}$ cathode in lithium half-cell, cycled at $C/5$ ($1C=1166 \text{ mA g}^{-1}$ referred to Li_2S mass) using LiNO_3 -free (red line) and LiNO_3 -added (black line), $1 \text{ m LiCF}_3\text{SO}_3$, DOL:DME 1:1v electrolyte. Voltage range $1.4 \text{ V} - 3.7 \text{ V}$. Temperature: 40°C . The specific capacity.

Figure 4.

First and second cycles voltage profiles of the $\text{Li}_2\text{S-C-PEO}$ cathode cycled in lithium half-cell using 1 m LiCF_3SO_3 , 1 m LiNO_3 , DOL:DME 1:1 v electrolyte (A). Corresponding ex-situ electrode XRD patterns (marked by circles in the voltage profile) at various charge and discharge steps (B). Corresponding Nyquist plots of the cell (marked by circles in the voltage profile) at the OCV (C) and after full charge and discharge in the first two cycles (D, F and E, G, respectively). The evolution of the cell EIS response upon 50 cycles (H). Temperature: 40°C. Voltage ranges: 1.4 V – 3.7 V (first cycle) and 1.9 V – 2.7 V (subsequent cycles). Cycling rate C/5 (1C=1166 mA g^{-1} referred to Li_2S mass).

Figure 5.

Galvanostatic cycling voltage profiles (A) and specific capacity versus cycle number plot (B) of the Li/1m LiCF₃SO₃, 1m LiNO₃, DOL:DME 1:1 v:v/Li₂S-C-PEO cell. The Coulombic efficiency versus cycle number plot is displayed in blue. Temperature: 40°C. Voltage ranges: 1.4 V – 3.7 V (first cycle) and 1.9 V – 2.7 V (subsequent cycles). Cycling rate C/5 (1C=1166 mA g⁻¹ referred to Li₂S mass)

Table 1

Electrolyte resistance R_e , Passivation film resistance R_{PF} and capacitance Q_{PF} , Charge Transfer resistance R_{CT} , Double Layer capacitance Q_{DL} and Li^+ diffusion capacitance Q values obtained by NNLSQ fitting of the impedance responses of the lithium cell reported in Figure 5, using the Li_2S -C-PEO electrode at the OCV (P1) and upon the first two charge-discharge cycles (P2–P5).

	R_e/Ω	R_{PF}/Ω	Q_{PF}/Ω	R_{CT}/Ω	Q_{DL}/F	Q/F
OCV	7.98 ± 0.05	54.13 ± 0.51	$(2.13 \pm 0.1) * 10^{-5}$	108.17 ± 3.81	$(6.70 \pm 0.27) * 10^{-4}$	$(7.19 \pm 1.43) * 10^{-2}$
P1	7.86 ± 0.02	36.61 ± 5.91	$(8.21 \pm 0.27) * 10^{-5}$	135.51 ± 8.61	$(10.54 \pm 0.03) * 10^{-4}$	$(2.25 \pm 0.07) * 10^{-3}$
P2	8.33 ± 0.07	39.49 ± 0.61	$(3.05 \pm 0.2) * 10^{-5}$	84.44 ± 2.91	$(2.46 \pm 0.14) * 10^{-4}$	$(3.98 \pm 0.03) * 10^{-3}$
P3	8.30 ± 0.09	90.29 ± 12.50	$(6.83 \pm 0.38) * 10^{-5}$	61.09 ± 13.60	$(2.21 \pm 0.3) * 10^{-4}$	$(2.35 \pm 0.01) * 10^{-3}$
P4	7.95 ± 0.06	52.62 ± 1.03	$(3.67 \pm 0.15) * 10^{-5}$	75.41 ± 3.32	$(4.62 \pm 0.27) * 10^{-4}$	$(2.85 \pm 0.01) * 10^{-3}$
P5	8.12 ± 0.10	53.52 ± 1.49	$(3.63 \pm 0.27) * 10^{-5}$	66.21 ± 4.46	$(4.13 \pm 0.43) * 10^{-4}$	$(2.85 \pm 0.02) * 10^{-3}$