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Interaction of FeS₂ and Sulfur in Li-S Battery System

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Abstract: Many transition metal sulfides are electronically conductive, electrochemically active and reversible in reactions with lithium. However, the application of transition metal sulfides as sulfur cathode additives in lithium-sulfur (Li-S) batteries has not been fully explored. In this study, Pyrite (FeS₂) is studied as a capacity contributing conductive additive in sulfur cathode for Li-S batteries.

Electrochemically discharging the S-FeS₂ composite electrodes to 1.0V activates the FeS₂ component, contributing to the improved Li-S cell discharge energy density. However, direct activation of the FeS₂ component in a fresh S-FeS₂ cell results in a significant shuttling effect in the subsequent charging process, preventing further cell cycling. The slight FeS₂ solubility in electrolyte and its activation alone in S-FeS₂ cells are not the root causes of the severe shuttling effect. The observed severe shuttling effect is strongly correlated to the 1st charging of the activated S-FeS₂ electrode that promotes iron dissolution in electrolyte and the deposition of electronically conductive FeS on the anode SEI. Pre-cycling of the S-FeS₂ cell prior to the FeS₂ activation or the use of LiNO₃ electrolyte additive help to prevent the severe shuttling effect and allow the cell to cycle between 2.6V to 1.0V with an extra capacity contribution from the FeS₂ components. However, a more effective method of anode pre-passivation is still needed to fully protect the lithium surface from FeS deposition and allow the S-FeS₂ electrode to maintain high energy density over extended cycles. A mechanism explaining the observed phenomena based on the experimental data is proposed and discussed.

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Introduction

Over two decades of research and development, Li-ion battery technology is approaching its theoretical limit in terms of energy density and power capability with limited room for improvement. In recent years, more attention has turned into “beyond Li-ion” chemical systems in searching for the next generation energy storage power sources.(1) This has led to the revival of interest in the Li-S battery. In spite of their high theoretical energy density (2450 Wh kg^{-1}), Li-S battery systems under development still suffer from low energy utilization and low efficiency due to factors such as the insulating nature of both sulfur and lithium sulfide, active material dissolution and the well-known shuttling effect.(2)

Dissolution of polysulfide species generated in partial sulfur lithiation is one of the major contributors to the poor cycling performance and low Coulombic efficiency of the Li-S battery.(3) However, it is also recognized that the liberated polysulfide ions in liquid solution turn the system into a liquid redox cell, which also boosts the rate capability and compensates for the inefficiency of Li^+ and electron transport in the two end members, Li_2S and sulfur.(4) As a result of this paradox, although physically constraining sulfur by surface coating or encapsulating to control the redox processes in solid state can significantly improve the cycling and energy efficiency(5-8), the power capability might be compromised as well. In parallel, a different route has also been frequently taken by researchers to mitigate polysulfide dissolution chemically. A wide variety of compounds have been found or designed to show strong interactions with polysulfide through acid-base or redox processes to temporarily adsorb the polysulfide(9-14), which slows down the outward diffusion of polysulfide from porous cathode and the associated loss of active material, reducing the shuttling effect, and decelerating the capacity fade. This concept still allows the generation of polysulfide intermediates in the porous composite electrode's liquid electrolyte network to partially preserve the liquid redox cell character. Therefore, the approach with polysulfide adsorbing additive in the composite electrode can potentially provide a better compromise between cycle life and power capability than completely isolating sulfur from the liquid electrolyte.

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With the pioneering work done by Nazar et al., exciting results have been published on polysulfide adsorbing electrode additives. (12-14) However, one disadvantage of using these additives is that most of them do not contribute any capacity in the voltage range (1.6V-3.0V) used in the Li-S battery. This leads to a reduction in practical energy density at the cell level. It is desirable to develop a new additive that functions as polysulfide capturer and also provides considerable capacity within the voltage window to compensate for their added mass and volume. Electronically conductive metal sulfides, such as TiS_2 , CoS_2 , and CuS have been shown to possess significant amount of reversible capacity in the voltage window of Li-S battery(15-18), and some of them have also been shown to improve the performance of Li-S battery as additives.(15, 16, 18)

Recently, Zhang et al. reported that FeS_2 improves the cycling stability of Li-S battery as a sulfur cathode additive.(18) However, the voltage window they explored was 1.8V – 3.0V, and the extra capacity of FeS_2 was not taken advantage of since an initial discharge with lower potential limit of 1.0V has to be applied to electrochemically activate FeS_2 . Part of the concern might be that the FeS_2 could be converted to FeS and S after recharge(19), which might no longer serve similarly to FeS_2 in immobilizing polysulfide species in sulfur composite electrode. On the other hand, there has also been experimental evidence that FeS might be partially oxidized by polysulfide during the recharge and form FeS_2 surface layer on the FeS particles.(20) It can be imagined that the concentration of polysulfides and their oxidizing power should be even higher in S- FeS_2 composite electrodes than pure FeS_2 electrodes during cycling, so the chances of converting FeS to FeS_2 coated FeS should be even higher. The FeS_2 coated FeS might have a similar effect in adsorbing polysulfide in the later cycles of the S- FeS_2 electrode.

In this work we extend the work by Zhang et al. and explore the S- FeS_2 system further by using a larger potential window 1.0V-2.6V, with the hope of exploiting the benefits of both the adsorbing effect of FeS_2 and its extra capacity contribution to the sulfur electrode. Electrochemical methods and chemical analysis will be combined to elucidate the interactions between sulfur and FeS_2 in this voltage window.

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Experimental

For Li/FeS₂ batteries, electrodes were prepared by casting a slurry of FeS₂ and polyvinylidene fluoride binder (PVDF) in 1-methyl-2-pyrrolidone (NMP) with Super P carbon (85% active, 5% super P, 10% PVDF, electrode loading of 3.79 mg/cm²) and without Super P carbon (90% active, 10% PVDF, electrode loading of 5.15 mg/cm²), onto aluminum foil and dried at 50°C under vacuum. Coin cells were assembled in an Argon atmosphere glovebox using lithium metal as the counter electrode, FeS₂ composite as the working electrode, 1.0 M lithium bis(trifluoromethane)sulfonimide (LITFSI) dipropylene glycol dimethyl ether (glyme) electrolyte, and Celgard 2500 separator. The cells were galvanostatically cycled using a Maccor cycle life tester between 2.4V and 1.1V at a C/20 rate (0.2 and 0.3 mA/cm² for cells with carbon and without carbon, respectively) for both discharge and charge at 30°C with a 2 hour potential hold step at 2.4V.

For Li/S batteries, electrodes were prepared with conventional methods by mixing active materials with carbon black (TIMCAL) and PVDF (Alfa Aesar) in 1-methyl-2-pyrrolidone (Alfa Aesar) into homogeneous slurry, which was casted onto an aluminum foil using a doctor blade. The electrode was dried in a fume hood under continuous dry air flow (dew point < -40°C) for 24 hours before it was transferred into an oven to be heated at 50°C for another 24 hours to eliminate residual solvent and moisture. The composition and loading of S (Alfa Aesar), FeS₂ (Sigma-Aldrich), and S-FeS₂ composite electrodes are listed in **Table 1**. 2032 coin cells were assembled by using electrodes prepared above as working electrode and a lithium disk as both counter and reference electrode, with 2 layers of Celgard (2325) separator in between to prevent shorting. Electrolyte used for testing of the Li-ion type cells was LITFSI (1.0M) dissolved in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 ratio, by volume) obtained from BASF. For the Li-symmetrical cell, two lithium foils of the same size and thickness in S or hybrid electrode cells were placed on both sides of the separator wet with LITFSI electrolyte in a coin cell. 70mM Li₂S₈ was also dissolved into this electrolyte to mimic the environment experienced by a lithium anode in sulfur or hybrid electrode coin cells during cycling. The method for dissolving Li₂S₈ into

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electrolyte will be introduced in one of the following paragraphs. Electrochemical measurements were conducted at room temperature using a Bio-logic (VMP3) battery cycler. Cells were cycled galvanostatically at 0.2C between 1.0V and 2.6V or 1.8V and 2.6V versus lithium. Every charging also includes a constant voltage step till the current falls below 0.1C. Intermittent constant current charge (0.1C) was also applied to charge S-FeS₂ cells to different depth of discharge, and impedance data was collected following each 1 hour charging sequence and an additional 1 hour open-circuit period. During measurement frequency was varied between 500 kHz and 50 mHz and with a perturbation amplitude of 5 mV. The same impedance measurement was performed on the Li-symmetrical cell 24hrs after cell assembly.

After the testing, lithium electrodes were recovered from the Li-S type coin cells and cleaned with DOL. Characterization of the reaction products on the surface of lithium anode will help to understand the interaction mechanism between sulfur and FeS₂, as it will be shown in the results. Morphology and composition of the lithium surface species were examined by scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS, JEOL 7600F) and X-ray photoelectron spectroscopy.

To measure the solubility of FeS₂ in polysulfide solutions, Li₂S₈ solution in electrolyte was prepared. 70 mM Li₂S₈ solution is prepared by mixing 32.6 mg Li₂S and 159.3 mg sulfur in 20 ml DOL:DME 1:1 (v/v) mixed solvent at 55°C under magnetic stirring for 48 hours under Argon. After this preparation, 10 mg of FeS₂ was added to the polysulfide solutions and mixed at room temperature in an argon-filled glovebox (O₂, H₂O <0.5ppm) for one week. A Thermo Scientific iCAP 6000 was used for inductively coupled plasma-optical emission spectroscopy measurements. Five iron calibration standards were prepared (0.1, 0.5, 1.0, 5.0, 10.0 ppm Fe), and the resulting linear calibration curve was used ($r > 0.99998$) with $\lambda = 324.7$ nm.

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Results and Discussion

The cycling stability of the Li/FeS₂ cells was tested between 2.4V and 1.1V at a C/20 rate. The first, 2nd and 50th cycles voltage profiles for Li/FeS₂ cells are depicted in **Figure 1a**. Upon initial discharge, the voltage quickly drops to 1.43 V where the first plateau is observed. The first discharge capacity was 849 mAh/g where 63% of that capacity was recovered during the charge process. As cycling progresses, the discharge capacity drops to 70% (597 mAh/g pyrite) of the original capacity in the second cycle. Upon full reduction, the first discharge plateau is generally ascribed to the stepwise irreversible conversion of FeS₂ into intermediate Li₂FeS₂ and the end products Fe and Li₂S. The following recharge and discharge processes start to show double plateaus, at around 1.8V and 2.45V for charge and 1.5V and 2.08V for discharge, which are retained in the following cycles. It is generally believed that at room temperature the first recharge process leads to the formation of a mixture, FeS_n (n~1) and S, instead of FeS₂,⁽²¹⁾ and that the two plateaus correspond to their separate reactions with lithium afterwards. Since the FeS₂ phase is not reformed upon the first recharge process, some inefficiency is observed as a result, consistent with prior reports.⁽²¹⁾ By the 50th cycle, 82% of the second cycle discharge capacity (58% of the capacity in the first cycle) was retained, **Figure 1b**. Additional cells were constructed using FeS₂ cathodes that were prepared without added carbon. This test was designed to probe the electrochemical performance of pure FeS₂, **Figure 1c and 1d**. In the first cycle, the Li/FeS₂ cell without carbon yielded 760 mAh/g. The discharge curve shows an immediate voltage drop to 1.4V. Upon charging, there are plateaus at 1.78V, 1.98V and 2.07V. The first charge capacity provided 477 mAh/g (63% of the first cycle discharge capacity). On the second discharge, the discharge capacity decreased to 71% of the first cycle discharge capacity 539 mAh/g, **Figure 1d**. On cycle 20, the cells delivered ~490 mAh/g. While the efficiency of the cells without carbon added to the cathode was lower than for the cells that contained carbon in the cathode formulation, the successful charge and discharge illustrates that FeS₂ has sufficient conductivity to function as a cathode material without carbon.

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Slow rate constant current charge/discharge was used to determine the gravimetric capacity and cycling performance of FeS₂ in the DOL:DME ether based electrolyte. The voltage profile of FeS₂ vs. Li at 0.05C current density is shown in **Figure S1** and was consistent with that observed in the glyme electrolyte, **Figure 1a**. The first discharge of FeS₂ delivers a gravimetric capacity of 871mAh g⁻¹, slightly lower than the theoretical value 894mAh g⁻¹. This again supports that FeS₂ is compatible with ether solvent based electrolytes, which are widely utilized for Li-S battery research.

Therefore, if S-FeS₂ composite electrode is fully discharged to 1.0V to utilize the extra capacity of FeS₂, then in principle it will be converted to a mixture of S-FeS after the first recharge. The S and FeS are generated from the decomposition of Li_{2-x}FeS₂ (x>0.8) during further delithiation, which is not reversible at room temperature.(21) However, there has been evidence that FeS coming from FeS₂ recharge is covered by FeS₂ surface layer,(20) so the polysulfide adsorption capability should still be partially retained.

The first discharge/charge voltage profile of S-FeS₂ composite electrode is shown in **Figure 2** at 0.2C discharge rate, also shown is the sulfur electrode with similar sulfur loading (0.9 mg cm⁻²) as a reference. In the first discharge, the S-FeS₂ composite electrode delivers more capacity than the sulfur electrode, if only the mass of the sulfur component (excluding FeS₂) is used as a basis for gravimetric capacity calculation. Since both electrodes have the same sulfur content (**Table 1**), the enhancement of capacity mainly comes from the extra capacity of FeS₂ as shown by the extra sloped-plateau around 1.5V that is absent in the control sulfur cell. This observation supports the initial concept of using FeS₂ as capacity-contributing polysulfide adsorbing additive. In the recharge of this composite electrode, 1.8V and 2.45V plateaus characteristic of FeS₂ recharge is evident at the beginning. However, it is then followed by an indefinite charging plateau at ~2.35V that can never be surpassed at 0.2C charging rate. The recharge of reference sulfur electrode also shows some prolonged charging at ~2.35V as we normally expected due to shuttling effect, but the behavior observed in the S-FeS₂ composite electrode has never been observed in this or other sulfur cells tested in this lab.

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The indefinite charging process is evident of severe shuttling effect in the cell with S-FeS₂ composite electrode during the recharge. The shuttling effect is not surprising since the presence of polysulfide species generated by both S and FeS₂ readily serve as the vehicle of the shuttling effect in the cell. The position of the indefinite voltage plateau is close to the second charging voltage plateau of reference sulfur electrode recharging, as it is shown in **Figure 2**. It is still not clear why neither sulfur nor FeS₂ experiences such a significant shuttling effect individually but it is observed when they are mixed and both lithiated.

In order to get a better understanding of the shuttling effect here, an intermittent constant current titration coupled with an electrochemical impedance spectroscopy was applied to probe the evolution of the S-FeS₂ system during the shuttling process. In this test, an S-FeS₂ composite electrode is first fully discharged to 1.0V at 0.1C, and then an intermittent 0.1C charging current was applied to the electrode for one hour, followed by a one hour rest, after which an impedance spectrum was taken. This charging process was repeated for 16 times to monitor the evolution. The results are shown in **Figure 3a** and **3b**. It can be seen that the S-FeS₂ electrode still start the charging process with the characteristic 1.8V and 2.45V plateaus for FeS₂ in the first one hour charging, after which the open circuit voltage almost levels off at 2.18V in one hour of rest. In the following sequences, the open circuit voltage at the end of the 1 hour rest experiences only a minor increase of 0.01V to a local maximum 2.19V after another 2 charging sequences, indicating that the shuttling probably already starts after the first hour of charging of S-FeS₂ electrode. More interestingly, after the first 3 one-hour charging sequences, the 1 hour rest open circuit voltage starts to decline steadily towards lower values. This suggests that as the shuttling is continued, self-discharging is getting more and more severe. The impedance spectrums taken after each charging sequence are overlaid in **Figure 3b**. All impedance spectrums are similar in shape and are composed of a semicircle at high and intermediate frequency with an inclined straight line at low frequency. Nonetheless, except for the increase of semicircle diameter after the 1st charge sequence, the size of the semicircle decreases almost monotonically as the number of charging sequences increases and the low frequency

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part is shifted to the left side of the real axis as a result. Based on literature, the diameter of the semicircle at high and medium frequency corresponds to the convoluted contributions of both contact resistance in the cathode composite network and charge transfer resistance experienced at all reactive interfaces in the system, including side reactions.(22) From **Figure 3b**, it is likely that one or several of these charge transfer processes is experiencing less resistance to reduce the size of the convoluted semicircle with extended shuttling processes. To help distinguish the contributions to the impedance from the lithium anode and from the cathode, a lithium-lithium symmetrical cell was built with electrolyte containing 70 mM Li_2S_8 . Li_2S_8 was added to simulate the polysulfide-containing environment in coin cell test. The impedance spectrum of this symmetrical cell was shown in **Figure 3c**, and the equivalent circuit used to simulate the spectrum is also included (22). Based on this circuit, the depressed semicircle can be deconvoluted into 2 smaller ones, and the characteristic frequencies $f_{\max}=(2\pi RC)^{-1}$ at the top of these individual semicircles are very close to each other and lie at over 1 kHz. A similar procedure was done on the spectra collected from the S- FeS_2 full cell and an example (after 7th charge sequence) is shown in **Figure 3d**. As shown in **Figure 3d**, the depressed semicircle can be deconvoluted to 2 smaller ones. In this case, the characteristic frequency 4.8 kHz of the higher frequency semicircle is very close to the two semicircles in the lithium symmetrical cell case, but the other semicircle has a much lower characteristic frequency of 73Hz. In addition, the values of R_2 and R_3 from the fitting are 12 ohm and 55 ohm respectively for lithium symmetrical cell and cannot be neglected when compared with those of S- FeS_2 coin cell in **Figure 3e**. Considering these observations together, it is inferred that the high frequency semicircle R_2 in S- FeS_2 cell is most likely related to charge transfer process associated with lithium anode and low frequency semicircle R_3 should be related with S- FeS_2 electrode processes. In **Figure 3e**, it can be seen that R_2 experiences a continuous decrease during the prolonged charging process for S- FeS_2 full cell after the sharp initial rise, indicative of a less and less resistive surface passivation layer against different charge transfer processes at the lithium surface, including the reduction of high order polysulfide into low order polysulfide, which is the main driving force for the shuttling process in the Li-S cell. The initial increase of R_2 is probably due to the enhanced deposition of $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ on the lithium anode upon

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polarization to a more negative voltage during recharge. This passivation layer is somehow damaged in the subsequent charging process, which is suggested by the continuously declining R_2 . The reduction of R_3 is probably not the cause of the shuttling behavior of the S-FeS₂ cell, as the magnitude of this R_3 has been found to be positively related to insulating Li₂S/Li₂S₂ formation and sulfur deposition on the cathode's conductive network (22), its continuous decrease during charging is likely due to the gradual dissolution of Li₂S/Li₂S₂ and the inability of regeneration of sulfur in prolonged shuttling process. The dissolution of Li₂S/Li₂S₂ alone is not enough to cause the significant shuttling process observed here.

To test the hypothesis of passivation failure of the lithium anode surface, lithium anodes from both a sulfur cell, an FeS₂ cell after 5 cycles, and from an S-FeS₂ cell that was fully discharged and experienced over 40 hours of shuttling under 0.2C recharge were recovered and observed with SEM. The SEM images are shown in **Figure 4a-c**. The surface of lithium anode from sulfur cell and FeS₂ cell is relatively compact and some roughness is present, while the surface of that from S-FeS₂ is less uniform and seems to be covered with granular deposition. The photos of the anodes as recovered from coin cells are also shown in the insets of **Figure 4a-c**. It appears that the surface of the anode from S-FeS₂ cell is much darker than the others. This darkness probably stems from the granular deposition observed in its SEM image. X-ray energy dispersive spectroscopy is performed on the regions shown in **Figure 4a-c** and the spectrum is shown in **Figure 4d**. All samples show strong x-ray emissions from O, F, and S, but apart from these peaks the lithium sample from cycled S-FeS₂ cell also has Fe's K_α and K_β lines at 6.40keV and 7.05keV, respectively. Based on this, there should be no doubt that S-FeS₂ cell experiences iron dissolution during cycling. The dissolved Fe species probably also interacts with the anode surface in parallel with polysulfides. Once Fe is reduced and co-deposited with sulfides onto the anode surface, the SEI layer on lithium surface will no longer be as effective because the potentially imbedded Fe, FeS and FeS₂ are all more electronically conductive than the naturally deposited Li₂S in sulfur cells. This is probably the root cause of the exacerbated shuttling effect observed in S-FeS₂ cell.

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Effort is also made to identify the chemical nature of Fe containing deposition on lithium anode of S-FeS₂ cell. X-ray photoelectron spectroscopy was taken on the surface of lithium anode recovered from S-FeS₂ cell that was fully discharged and experienced over 40 hours of shuttling in the 0.2C recharge. The spectrum in the neighborhood of Fe 2P emissions is shown in **Figure 4f**. After fitting, four peaks can be distinguished at 710.25, 713.34, 723.66, and 725.53 eV. 710.25 eV and 723.66eV peaks can be ascribed to 2P_{3/2} and 2P_{1/2} lines of FeS, and 713.34eV and 725.53eV can be ascribed to 2P_{3/2} and 2P_{1/2} lines of FeO. FeO is probably generated by the oxidation and hydrolysis of Fe or FeS_x species in the SEI layer during the short exposure to air in sample loading. FeS is more likely one of the major iron containing compounds in the SEI layer. The electronic conductivity of FeS is 10-1000 S cm⁻¹, higher than carbon black ~ 3 Scm⁻¹.(23, 24) Therefore it is not surprising that the SEI layer becomes a mixed conductor of electron and Li-ion, and polysulfide reduction by lithium is facilitated, which leads to the observed severe shuttle effect.

The contaminated SEI layer can probably explain the shuttling in S-FeS₂ cell recharge, and the question left is why the dissolution of iron becomes more prominent when S-FeS₂ combination is used. Based on **Figure 4e**, FeS₂ also has slight solubility by itself in ether-based electrolyte and iron can also be detected on the surface of the lithium anode in the FeS₂ cell. However, the extent of iron deposition on lithium is much smaller and also the Coulombic efficiency is always more than 95% in **Figure 1b**. Hence it can be inferred that sulfur or soluble polysulfide ion generated by sulfur lithiation might play a vital role in FeS₂ dissolution. Indeed, similar phenomenon has also been observed before in S-CuS system.(17) In order to check whether polysulfide is responsible for FeS₂ dissolution, Li₂S₈ solution was made and solubility of FeS₂ was tested with the help of inductively coupled plasma-optical emission spectroscopy (ICP-OES). Li₂S₈ was used here because the observed shuttling effect is most intensive at the higher charge plateau of Li-S system, which most likely corresponds to the generation and consumption of higher order S_n²⁻ (n>4). The solubility data is shown in **Table 2**. Based on this measurement, FeS₂ has some solubility in DME:DOL=1:1 solvent by itself and addition of 70mM S₈²⁻ did not lead to any obvious change to the

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value. To ensure that lower order polysulfide does not enhance FeS_2 dissolution, a separate electrochemical test was also performed. Based on **Figure 1a** and above discussion, FeS_2 does not start its reaction with lithium until 1.5V in the first discharge and sulfur almost finishes its reaction with lithium at 1.8V, therefore the full spectrum of polysulfides can interact with FeS_2 if 1.8V discharge cut-off voltage is used for S- FeS_2 composite electrode cycling, and this should be reflected in the voltage profile. The S- FeS_2 composite electrode's voltage profile cycled between 1.8V and 2.6V is shown in **Figure 5a**, and sulfur electrode's profile is also included in parallel. It can be seen that there is no major difference between the two voltage curves. What is more important is probably the disappeared non-stop shuttling effect here for S- FeS_2 cell. Besides, there is no significant difference in Coulombic efficiency between S cell and S- FeS_2 cell in this voltage window for the first 5 cycles, as it is shown in **Figure 5b**. EDS spectrum shown in **Figure 5c** almost detected no Fe signals on lithium anode from S- FeS_2 cell cycled for 5 times between 1.8V and 2.6V. These observations clearly indicate that Fe dissolution is not the result of the direct interaction of polysulfide and FeS_2 , which is consistent with the results of FeS_2 solubility study, **Table 2**. In combination with earlier discussion it can be speculated that certain reaction intermediates or end products of FeS_2 discharge and recharge might be the source of dissolved Fe in electrolyte. The EDS spectrum taken on lithium anode in a S- FeS_2 cell after a 1.0V discharge and 40 hours of open circuit storage is also shown in **Figure 5c**, no Fe is detected in this case. The above observation indicates that the Fe dissolution mainly happens during the recharge of S- FeS_2 after 1.0V discharge. This is also in agreement with the observation in **Figure 3b**. The magnitude of the impedance semicircle first increases in magnitude after the initial hour of charge but experiences steady declination in the subsequent anodic current titrations, which has been correlated with the resistance of the SEI on lithium and therefore also the amount of iron containing species in it. Based on this, we can further deduce that dissolution probably mainly evolves after S- FeS_2 electrode has been charged to be higher than the 2.4V activation voltage barrier observed commonly in both S and FeS_2 electrodes individually during recharge in **Figure S1** and **Figure 2**. However, isolation of the responsible compound requires a

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systematic study by combining electrochemical measurement and materials characterization, which is still under way and will be reported in the future.

Although the dissolution mechanism of FeS_2 is not fully understood at this point, a critical role of anode SEI on the shuttling phenomenon is uncovered. If the anode surface can be effectively passivated, it may still be viable to cycle the S- FeS_2 cell while utilizing FeS_2 as a capacity contributing cathode additive. To pre-form the anode SEI, a S- FeS_2 cell is preconditioned by being cycled between 1.8V and 2.6V for 10 times without FeS_2 activation. Start from 11th cycle (or 1st activation cycle), the discharge cut-off voltage was lowered to 1.0V to activate FeS_2 . The 1st and 10th discharge and charge profiles of 1.8V discharge cut-off cycling and the 1st activation discharge and charge profiles of 1.0V discharge cut-off cycling are shown in **Figure 6a**. It is evident that after the 10 cycles of preconditioning between 1.8V and 2.6V, the S- FeS_2 electrode can now be discharged to 1.0V to utilize the capacity of FeS_2 without leading to disastrous shuttling in the recharge. The role of preconditioning of the first 10 cycles should be the formation of a passivation SEI layer on lithium anode surface, which should be mainly composed of the electronic insulating lithium sulfide and organic species. Any further SEI must be built upon this pre-formed one. In this sense, even if the newly deposited SEI layer after the start of 1.0V-2.6V cycling might also be contaminated by FeS inclusions, the lithium anode will still be protected by the preformed SEI to slow down the polysulfide redox kinetics and mediate the shuttling effect. Unfortunately, this still only solves the problem partially, in the 1.0V cycling the capacity of S- FeS_2 hybrid cathode cell still fades fast and also the Coulombic efficiency is gradually deteriorating and becomes inferior to that of 1.8V-2.6V cycling, **Figure 6b**. This suggests that the SEI layer on lithium surface is a dynamic system that experiences dissolution and reformation, and FeS and other Fe containing compounds start to redistribute to the inner layer in the SEI to reduce its electronic resistance. This might be thermodynamically more favorable than forming an SEI layer with a fully hierarchical structure.

With the above experiment, it is realized that effectively pre-passivating the surface of lithium anode and preventing FeS deposition might be able to make the S- FeS_2 concept feasible. Attempts have also been

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made in using LiNO_3 as an electrolyte additive to control the shuttling effect. However, although LiNO_3 has been very effective in preventing shuttling within 1.6V to 2.6V voltage window for Li-S batteries, it has been known to be unstable and decomposes at lower voltages on the cathode surface to cause cell internal resistance growth.(25, 26) Similar observation is seen in our experiment as shown in **Figure S2a**, where 1wt% LiNO_3 is added to the electrolyte for an S- FeS_2 cell that is directly cycled between 1.0V to 2.6V at a C/5 rate. Although the shuttling is partially remediated in the first recharge, huge voltage hysteresis between charge and discharge starts to evolve and the cell capacity also starts to fade promptly, **Figure S2b**. This is probably the result of LiNO_3 decomposition on cathode surface that eventually starts to hinder its normal lithiation-delithiation processes.(25, 26)

Conclusion

In this work, we studied FeS_2 as a capacity-contributing additive for sulfur electrodes in the Li-S battery system by using a 1.0V to 2.6V voltage window. Using a 1.0V discharge cut-off voltage can indeed increase the overall capacity output of S- FeS_2 composite electrode, but in the ensuing recharge a severe shuttling process starts to evolve. Characterization of the lithium anode surface indicates the presence of FeS after an S- FeS_2 cell undergoes normal galvanostatic 1.0V discharge and the subsequent shuttling process in recharge. It is proposed that the FeS_2 component in the S- FeS_2 electrode experiences dissolution when FeS_2 is cycled along with S component. The dissolved Fe is incorporated into the SEI layer on the lithium anode, potentially as electronic conductor FeS, and this makes the SEI layer much less effective in slowing down the redox reactions of polysulfides on the lithium surface and thus enhances the shuttling effect. The dissolution mechanism of FeS_2 is not fully understood, but experimental evidence indicates that it is not the result of direct interaction between polysulfide and FeS_2 and more likely the interaction between polysulfides and reaction intermediates generated from FeS_2 's own cycling. The dissolution happens primarily during the recharge of the fully discharged S- FeS_2 electrode. Notably, cycling of the sulfur component in S- FeS_2 electrode between 1.8V to 2.6V for a few cycles can help to surpass the indefinite shuttling in its recharge after 1.0V discharge. However, a more effective method of

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anode pre-passivation is still needed to fully protect the lithium surface from FeS deposition and make the capacity of FeS₂ available in S-FeS₂ hybrid electrode.

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Table Captions:

Table 1. Composition and loading of Sulfur, FeS₂ and S-FeS₂ electrodes used in the interaction study

Table 2. Effect of polysulfide on FeS₂ solubility

Figure Captions:

Figure 1. Li/FeS₂ cells cycled at C/20 rate between 2.4V and 1.1V (a), (b), with carbon in cathode and (c), (d) with no carbon in cathode.

Figure 2 First cycle voltage profiles of S electrode and S-FeS₂ electrode.

Figure 3. (a) Voltage as a function of time when a S-FeS₂ cell already fully discharged to 1.0V was charged by an intermittent current titration process; (b) Nyquist plots of impedance measured at the end of each 1-hour open-circuit period shown in (a); (c) Nyquist plot of symmetric Li/Li cell impedance in the presence of polysulfide and the equivalent circuit fitting; (d) Equivalent circuit fitting of the impedance after 7th charge sequence for S-FeS₂ hybrid cell; (e) Resistance evolution of S-FeS₂ coin cell vs. the charge number.

Figure 4. (a), (b) and (c) SEM images of lithium anodes cycled in Sulfur, FeS₂ and S-FeS₂ cells respectively, insets are the photos taken before SEM, scale bar=20μm; (d) EDS spectrum taken on (a), (b) and (c); (e) Expanded EDS of (d) to show the detection of Fe on anode from FeS₂ cell; (f) XPS spectrum taken on (c).

Figure 5. (a) Voltage profiles of the first discharge and charge of both sulfur and S-FeS₂ electrodes, with 1.8V-2.6V voltage window; (b) Discharge capacity and Coulombic efficiency vs. cycle number of both sulfur and S-FeS₂ electrodes, Coulombic efficiency of nth cycle is defined as the discharge capacity of n cycle over charge capacity of (n-1) cycle; (c) EDS spectrum taken on lithium anodes obtained from an S-

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FeS₂ cell cycled between 1.8-2.6V for 5 cycles, an S-FeS₂ cell discharged to 1.0V and charged (shuttling) for 40 hours, and an S-FeS₂ cell discharged to 1.0V without recharge.

Figure 6. (a) Voltage profiles of 1st and 10th discharge and recharge of an S-FeS₂ cell cycled between 1.8-2.6V, 1st discharge and recharge and of the same cell which started to be cycled between 1.0-2.6V after the 10th cycle between 1.8-2.6V; (b) Discharge capacity and Coulombic efficiency vs. cycle number of the S-FeS₂ cell in (a).

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Table 1.

Electrode label	Sulfur	FeS ₂	Carbon black	PVDF	Electrode Loading
Sulfur	0.6g		0.5g	0.1g	1.8±0.2 mg cm ⁻²
FeS ₂		0.6g	0.3g	0.1g	1.8±0.2 mg cm ⁻²
S-FeS ₂	0.6g	0.2g	0.3g	0.1g	1.8±0.2 mg cm ⁻²

Table 2.

Sample	Corrected Fe Concentration (ppm)
FeS ₂ in 1:1 DME:DOL	2.6
FeS ₂ + 0.07 M Li ₂ S ₈ in 1:1 DME:DOL	1.8
1:1 DME:DOL only	0.0

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