Metal Sulfide-Blended Sulfur Cathodes in High Energy Lithium-Sulfur Cells

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Since their inception in 1991, Li-ion batteries1 have progressed at a rapid pace, with a three-fold enhancement in their performance achieved through many advances in both electrode materials and electrolytes.2−4 Current Li-ion cells from commercial vendors (e.g., Panasonic, LG and Samsung) provide an impressive specific energy of >250 Wh/kg and energy density of >600 Wh/l which are benefiting a wide range of applications including portable electronic devices, electric vehicles and aerospace needs. Yet, many of the emerging markets such as electric vehicles and renewable energy technologies place even higher demands on the battery technologies, both in terms of performance and cost. It is believed that the performance of lithium-ion technologies has reached a plateau, and any future improvements will only be marginal. Replacement of graphite anodes with Si, and conventional 4 V cathodes with the high voltage Li-rich layered-layered composite cathodes,10,11 has not yet successfully been applied to commercial batteries. Accordingly, any gains in specific energy and energy density have been modest so far after a decade of development.2,5 There is, thus, a pursuit for more energetic battery technologies beyond Li-ion batteries. This has led to a renewed interest in the lithium-sulfur system, which has the highest theoretical specific energy of all the known rechargeable systems (due to the high capacity of sulfur, 1672 mAh/g, ~6–10x of Li-ion cathodes), with the notable exception of Li-O2 which itself has several serious fundamental hurdles that are not close to being overcome.14–16 The specific energy realizable in Li-S cells is reportedly as high as 400–500 Wh/kg,17 which translates into a range exceeding 350 miles/charge for electric vehicles.2,13 Furthermore, the abundance, low-cost and non-toxicity of sulfur make such lithium-sulfur batteries appealing for widespread use in electric vehicles or in conjunction with renewable energies, such as solar and wind.

Li-S technology has been studied for a long time, but has several inherent issues that have impeded its utilization in practical devices.18 One notable problem is related to the polysulfide shuttle. The intermediate reduction products of sulfur, the higher order polysulfides (S2−4, S3−2, S4−2, S6−4), are soluble in the organic electrolyte. These polysulfides, generated at the positive electrode during discharge, diffuse to the lithium anode where they are reduced to lower-order polysulfides. These lower-order polysulfides, being also soluble in the electrolyte, diffuse back to the cathode and get re-oxidized.19 This shuttling of the polysulfide species results in self-discharge, low round-trip coulombic efficiency, and irreversible capacity loss. Additionally, the sulfur cathode tends to become passivated by the final discharge product Li2S, which is plated as a dense layer on the cathode surface. Moreover, sulfur is an insulator with a resistivity of 5 × 10−32 S cm−1 at 25 °C, resulting in poor electrochemical utilization of the active material. This can be partly mitigated by the use of conductive carbon, but the substantial proportion of this conductive diluent required reduces the specific energy and energy density of the overall cell. Further, the sulfur cathode expands by 79% upon Li uptake, causing Li2S particles to pulverize and lose electrical contact with the electrode.20 The problems with the lithium anode are equally challenging, partly due to the well-known morphological changes and poor reversibility of Li during cycling,21 further complicated by the passivation effect by the highly-reduced polysulfides Li2S2 or Li3S2.22

Several interesting strategies have been described in the literature to sequester sulfur and its reduced products within the cathode, either by modifying the cathode structure and/or electrolyte, and by fortifying the Li anode with a protective coating. Among these approaches, the improvements from cathode modifications are noteworthy as pioneered by the studies of Nazar et al.,23 with sulfur-encapsulated porous carbon scaffolds, which led to several novel carboneous nanostructures for the sulfur cathode wherein nanometer-scale pores confine the sulfur and also restrict electron transport distances.24−26 Sulfur is incorporated into the nanoporous carbon scaffolds, often by melt-inclusion, to form nanostructured carbon–sulfur composites. Several interesting structures have subsequently evolved including Hierarchical Porous Carbon (HPC) containing both micro and mesopores. The pore volume in these HPCs can be appropriately partitioned to contain the sulfur in the micropores, while the macro-pores permit electrolyte access and the overall structure is resilient to volume change. These HPC-based sulfur cathodes can have high sulfur utilization and good rate capabilities, with reduced polysulfide crossover.32 Despite these improvements, the sulfur-impregnated porous carbon cathodes cannot provide high specific energy because of their intrinsically low sulfur loadings.

An alternate design for sulfur cathode would be the use of lithium sulfide, Li2S (theoretical capacity 1166 mAh/g) as the starting material, to be paired with a non-Li containing anode such as graphite.
or Si. However, the Li$_2$S cathode is equally challenging because of its insulating nature and generation of soluble polysulfides upon oxidation, similar to issues with a normal sulfur cathode. These issues can be overcome by encapsulating Li$_2$S cathodes within electronically conductive carbon-based materials such as graphene and porous carbon. Nevertheless, the use of Li$_2$S may not be as appealing for high-energy Li-S cells, even with Si anodes, because of the loss of active Li toward passivation and also the reduced voltage (≈0.5 V) inherent to the Si anode vs. Li metal. An alternative approach to limit polysulfide issues and give improved cycle life is to use sulfurized polymers, e.g., sulfurized polyacrylonitrile (SPAN), but practical application is limited by the low electronic conductivity of the polymer, the low activity of the bound sulfur and the low specific capacity for the cathode overall. Other approaches to mitigate the polysulfide solubility are to modify the electrolyte and/or through addition of additives, amongst other methods that have been the focus of the recent research efforts.

To summarize, although the above strategies have shown promise in reducing the polysulfide shuttle effects, the sulfur loading in all these studies is quite low, less than 3 mg/cm$^2$. In order to achieve high specific energy for a practical Li-S battery, the sulfur proportion in the cathode should be considerably high (>60%) in a high voltage with high active material loading (>15 mg/cm$^2$), as discussed below. However, at such high loadings, the utilization of sulfur cathode is poor unless blended with sufficient carbon (>30%). To address this, we have chosen to blend sulfur with metal sulfides that are significantly more conducting (than sulfur) and are denser than carbon. Interestingly, the metal sulfides we found to be most successful (i.e., titanium disulfide and molybdenum disulfide) are also known to be electrochemically active and are hence expected to act as a ‘redox’ mediator, similar to MnO$_2$ as reported by Nazar et al. In this paper, we present the performance enhancements achieved with such metal sulfide-blended sulfur cathodes in a dense structure relevant to practical Li-S cells.

**Experimental**

Sulfur cathodes were prepared by coating Al foil substrates on one side using a mini-laboratory coater from MTI, with slurries of 55 wt% Sulfur (Aldrich), 40 wt% C black (Shawinigan), and 5 wt% poly(vinylene difluoride) (PVDF) binder (Sigma Aldrich, MW avg = 534,000) in N-methyl-2-pyrrolidinone (NMP) (Sigma Aldrich). For the cathodes with metal sulfides, TiS$_2$ (Aldrich, crystalline, hexagonal form) and MoS$_2$ (Aldrich, crystalline, hexagonal form), the composition was typically 65% S, 15% metal sulfide, 15% carbon black and 5% binder, unless specified otherwise. Cathodes were prepared by starting with bare aluminum foil and adding a coating of carbon ink (Henkel) with a doctor blade set to 100 μm. The substrate was dried under vacuum at 80–100°C. Elemental sulfur, carbon black (Super P from Alfa Aesar), PVDF and TiS$_2$ or MoS$_2$ were mixed together in the appropriate ratios for a total mass of 5 g. This solid mixture was suspended in 7–13 mL of NMP and mixed in a Flacktek SpeedMixer for 15 minutes. The suspension was coated on the dried substrate described above using a doctor blade set to 350–450 μm. Finally, the electrode was dried overnight in an 80–100°C oven with no vacuum applied (vacuum drying caused the sulfur to sublime), weighed to determine loading and cut to the desired size. TiS$_2$ coatings were applied, when used, to 1.27 cm$^2$ cathodes using a solution of 0.1 g TiS$_2$ and 0.5 g NMP. The solution was mixed with a magnetic stir bar for 18 hours prior to coating. The coating was applied to the surface of the cathode with a Pasteur pipette until the area was completely covered, followed by spin coating for approximately 15 seconds. This process was repeated five times. Samples were dried in an oven (no vacuum) and weighed to determine loading (typically 2 mg/cm$^2$). A similar procedure was followed for coating with LiTFSI that included 0.25 M lithium nitrate (Aldrich) as an additive.

The sulfur loading on these disks was about 5 mg/cm$^2$ in the pristine sulfur cathodes, but increased to ∼12 mg/cm$^2$ in metal-sulfide blended cathodes. These electrode-loading levels are much higher than what is normally reported in the literature, and were chosen to provide high areal capacity for the sulfur cathode. In our experience, cells built with lower loadings exhibit better performance, high sulfur utilization and superior cycle life, but are less applicable to real-life high-energy cell development. Multiple cell replicates (at least four cells per formulation) were used to validate the reproducibility of the cell data.

Coin cells of the 2032-type with aluminum-clad cans (MTI) were assembled using lithium foil (MTI) as the anode, two polypropylene separators (Celgard 2400) and electrolyte consisting of 0.5 M lithium bis(trifluoromethanesulfonfyl) imide (LiTFSI, Aldrich) and 1,2-dimethoxyethane/1,3-dioxolane (Aldrich), typically in a ratio of 95:5. Each cell had an electrolyte volume of 140 μL. Cells with 0.5 M LiTFSI that included 0.25 M lithium nitrate (Aldrich) as an additive were also assembled and tested for comparison. In addition, different compounds were tested as co-solvents and additives, which include VC, TFEB, FEC, BMP-TFSI and LiNO$_3$.

Charge-discharge measurements and cycling tests were performed with an Arbin battery cycler. The cycling tests were carried out at current densities of 0.25 mA/cm$^2$ (∼C/5 rate) and 0.50 mA/cm$^2$ (∼C/3 rate) for charge and discharge, respectively. The cells were charged to 3.20 V, followed by a tapered charge period at constant potential for three hours, and discharged to 1.8 V, with 15 minutes of interval between the charge/discharge steps. Electrochemical studies, including DC Tafel polarization for electrode kinetics and Potentiostatic Intermittent Titration Technique (PITT) for diffusion kinetics of Li$^+$ within the cathodes were carried out in three-electrode pouch cells. These cells were assembled with a 12 cm$^2$ sulfur cathode, a Li-wrapped Ni mesh anode and a Li reference electrode. The Li reference electrode was made with a 1 × 1 cm Ni mesh substrate spot-welded to a Ni tab and wrapped with two layers of Li foil. The electrode was sealed in an envelope made of Toner separator and placed between the cathode and anode, covering only a small portion of the anode/cathode. Tafel and PITT measurements were made using a potentiostat/galvanostat/frequency response analyzer (Bio-logic VMP2).

X-Ray Diffraction (XRD) measurements were carried out using a PANalytical PW3040-PRO, with Cu Kα radiation between 5° and 90° 2θ, scan rate 0.02° 2θ/min, at an accelerating voltage of 45 kV and tube current of 20 mA. Structural identification of was performed using Jade 9.0 software coupled to the International Centre for Diffraction Data (ICDD) database using the PDF-4+ 2014 library and the Inorganic Crystal Data Structure database (ICSD). The lattice parameters were calculated using a Rietveld refinement on a number of fitted peaks.

**Results and Discussion**

**Electrolyte effects.**—The electrolyte plays a crucial role in determining the performance of sulfur cathode through minimizing the polysulfide solubility and also reducing the passivation or polarization arising from the insulating nature of polysulfides. Polysulfide species generated in the sulfur cathode are very strong bases and nucleophiles, and stability against these species is a strict requirement for the electrolyte. The purpose of this study was to select a suitable electrolyte formulation for the development of the high-capacity cathodes described here and to quickly screen the effect of electrolyte additives. Numerous studies have been reported in the literature on electrolytes for Li-S cells, as summarized in recent reviews. In general, the best electrolyte for rechargeable Li-S cells is considered to be a solution of 1 M lithium bis(trifluoromethanesulfonyl) imide (Li[N(SO$_2$CF$_3$)$_2$]), LiTFSI in a binary mixture of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL), usually in a proportion of 1:1 by volume. Other solvents suitable for Li-S cells are based in high molecular weight analogues of DME and 1,3-dioxolane, where n is a number between 1 and 5. In particular, tetruglyme, also known as TEGDME, has been used in mixtures with DOL. For the DME-DOL blend, the capacity increases as the DOL content decreases, possibly due to the lower...
solubility of polysulfide in DME. Consistent with this, a DOL proportion below 20% reportedly provides better cycle life.91

Here, we tested electrolyte formulations with various ratios of DME and DOL and with different additives using a conventional sulfur cathode mixed with Super P carbon. The configuration of the sulfur cathodes used for these studies was 55% S, 40% carbon black and 5% PVDF with a loading of ∼4–5 mg/cm². Fig. 1 shows the performance of conventional sulfur cathodes with different ratios of DME and DOL: a) 1.0 M LiTFSI in 1:2 (vol.) DME+DOL, b) 1.0 M LiTFSI in 2:1 (vol.) DME+DOL, c) 1.0 M LiTFSI in 95:5 (vol.) DME+DOL and d) 1.0 M lithium triflate in 95:5 (vol.) DME+DOL. The observed capacity retention is consistently higher with increasing proportion of DME, with concomitantly superior capacity retention (Figs. 1c vs 1a). Use of lithium triflate salt results in faster capacity fade and lower coulombic efficiency compared with the imide (Fig. S1).

The VC additive provides no enhancement in the performance. The initial discharge capacity is high, almost 1200 mAh/g based on S content, but there is a steady decrease in the capacity, suggesting an increasing shuttle effect. The coulombic efficiency is also low, around 0.4. The fluorinated co-solvents TFEB and FEC appear even less suitable for this chemistry. TFEB, as well as BMP-TFSI ionic liquid, seem to alter the electrochemistry with an unusual discharge behavior, indicative of reactivity of these co-solvents with the lithium anode (Fig. S1). FEC addition is even worse, showing low initial discharge capacity and almost negligible capacity in subsequent discharges.

Lithium nitrate is known as a preferred additive to form a protective film on the Li anode, making it less susceptible to polysulfide poisoning and thus improving the cycle life of Li-S cells.92 Fig. 3 shows the comparison of performance in the 1.0 M LiTFSI/DME+DOL (95:5 vol.) solution with (0.2 M) and without LiNO₃ additive (Fig. 1c). The intention here was to establish a baseline electrolyte for the subsequent cathode development described below. The addition of lithium nitrate does enhance the performance of the sulfur cathode, i.e., cycle life and (more noticeably) coulombic efficiency are improved. However, the beneficial effect does not last long. The observed coulombic efficiency is >100% in the initial cycles (through 10 cycles), possibly due to the reduction of LiNO₃. Subsequently, the efficiency stays high (>95%) through 20 cycles, followed by a gradual decay both in the efficiency and discharge capacity, most likely due to an increased presence of polysulfides in the electrolyte. Higher coulombic efficiencies and better cycle life have been reported in the literature with LiNO₃ additive, but only in conjunction with thinner electrodes.93 With a dense sulfur cathode, the benefits are not as significant, consistent with larger absolute amounts of polysulfides in the electrolyte. Nevertheless, we selected the baseline electrolyte containing LiNO₃ additive as the electrolyte in the subsequent studies, i.e., 1.0 M LiTFSI in DME+DOL (95:5 vol.) with 0.2 M LiNO₃.

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Figure 2. Cycling performance of conventional sulfur cathode (S:C:PVDF 55:40:5, loading: 4 mg/cm²) in cells containing electrolytes with 1.0 M LiTFSI dissolved in; (a) DME + DOL (95:5 vol.) + 2% VC, (b), DME + TFEB + DOL (75:20:5 vol.), (c) DME + FEC + DOL (75:20:5 vol.), and (d) DME + BMP-TFSI + DOL (45:50:5 vol.).

Apart from modifying the cathode and electrolyte, another approach to sequester sulfur within the cathode is via insertion of a polysulfide-blocking layer between the cathode and the separator. For example, the use of a thin carbon layer was reported by Manthiram et al.96 to be effective in reducing polysulfide shuttle effects. In addition to carbon, other blocking layers have been reported to be useful, e.g., MnO2 by Nazar et al.97 and V2O5 by Li et al.98 Here, we used Toray carbon paper with 78% porosity or carbon cloth (labelled as plain carbon cloth), which is easier to punch into discs or cut into shape. Fig. 4 shows only a marginal improvement in performance with the use of a carbon blocking layer, placed between the cathode and separator, possibly due to the use of a denser sulfur cathode (6.2 mg/cm²). With denser cathodes, more polysulfides go into the electrolyte.

Figure 3. Comparison of cycling performance for conventional sulfur cathode (S:C:PVDF 55:40:5, loading: 4 mg/cm²) in baseline cells in 1.0 M LiTFSI / DME + DOL (95:5 vol.) solution with (0.2 M) and without LiNO3 additive (shown in Fig. 1C).

Figure 4. Cycling performance of conventional sulfur cathode (S:C:PVDF 55:40:5, loading: 6.2 mg/cm²) in a cell with carbon cloth as a polysulfide blocking layer (placed between cathode and separator).
contributing to a performance loss. It may be inferred that even with a carbonaceous layer, it is a challenge to realize good cycle life in a thick sulfur cathode.

In our subsequent studies, we used the baseline electrolyte with LiNO₃ additive (1.0 M LiTFSI in DME+DOL (95:5 vol.) with 0.2 M LiNO₃ and a carbon cloth sandwiching the Tonen separator and sulfur cathode.

**Sulfur cathode with high areal capacity.**—In order to achieve high specific energy in a Li-S cell, the sulfur cathode needs to have both high loadings and a high active material proportion.

**Design of a high-energy sulfur cathode.**—We take as our basis for comparison a conventional commercial high-energy Li-ion cathode to estimate the required sulfur loadings in a high energy Li-S cell. For the lithiated nickel cobalt aluminum oxide (NCA), the reversible capacity is 170 mAh/g and the cathode loading is typically 22 mg/cm² per side. The areal capacity is 3.3 mAh/cm² per side and the areal energy is 13 mWh/cm² per side. To provide higher specific energy compared to Li-ion cells, e.g., 1.5 times (with the expectation that there will be some performance gains from the lithium metal anode over carbon), the areal energy of sulfur cathode will need to be ~19 mWh/cm² or ~9 mAh/cm² per side. Taking into account the lower discharge voltage (2.1 V) exhibited by the sulfur cathode, and assuming a reversible capacity of 800 mAh/g for this cathode with a sulfur proportion of 65% (lower proportions will require even higher loadings), the cathode material loading is required to be as high as 17 mg/cm² per side or a sulfur loading of 11 mg/cm².

In contrast to the above design considerations, all the reports of Li-S cells in the literature describe performance of cathodes with low loading of 2–3 mg/cm² (or, 1–1.5 mAh/cm²) and/or with low Li-S cells in the literature describe performance of cathodes with LiNO₃ and a carbon cloth sandwiching the Tonen separator and sulfur cathode. The lithium nickel cobalt aluminum oxide (NCA) cathode described in Ref. 99, for example, has a sulfur loading of 11 mg/cm².

In the lithium nickel cobalt aluminum oxide (NCA) cathode described in Ref. 99, for example, the areal capacity is 3.3 mAh/cm² per side and the areal energy is 13 mWh/cm² per side. To provide higher specific energy compared to Li-ion cells, e.g., 1.5 times (with the expectation that there will be some performance gains from the lithium metal anode over carbon), the areal energy of sulfur cathode will need to be ~19 mWh/cm² or ~9 mAh/cm² per side. Taking into account the lower discharge voltage (2.1 V) exhibited by the sulfur cathode, and assuming a reversible capacity of 800 mAh/g for this cathode with a sulfur proportion of 65% (lower proportions will require even higher loadings), the cathode material loading is required to be as high as 17 mg/cm² per side or a sulfur loading of 11 mg/cm².

**Sulfur cathodes with metal sulfide blends.**—Our rationale for forming a composite cathode with certain transition metal sulfides is three-fold: Firstly, some of the metal sulfides provide good mixed ionic/electronic conductivity. Replacing part of the carbon conductive diluent with the metal sulfide enables the use of thicker electrodes with higher sulfur loading and utilization compared to carbon-only electrodes, as the metal sulfides are denser than carbon. Secondly, many of these transition metal sulfides are electrochemically active and can undergo reversible reactions, thus contributing to the cathode capacity. We have selected TiS₂ and MoS₂ for this study, which are, indeed, two of the most-studied cathode materials for Li metal rechargeable cells (before the advent of Li-ion cells). Titanium disulfide is a highly reversible cathode with good electrochemical activity (specific capacity of 335 mAh/g) in Li battery electrolytes and extensively-studied in 1970’s and 80’s, pioneered by Whittingham et al. at Exxon Research Laboratories. Its voltage window is 2.4 to 1.8 V vs Li. In fact, prototype Li-TiS₂ cells were made by several laboratories, including JPL in various ether-based solutions. In contrast, molybdenum disulfide is not as reversible in the crystalline form (which is used here) and only 0.1 M of Li is reversibly intercalated at 1.8 V vs Li. Amorphous MoS₂ is, however, more reversible with higher voltage. Haering et al. modified MoS₂ by changing the molybdenum coordination from trigonal prismatic to octahedral, which was effectively used as a cathode in the Li-MoS₂ cells commercialized by MoliEnergy. Based on the fact that these cathodes undergo single-phase intercalation reaction, there would not be any morphological changes in these composite cathodes from the metal sulfide additions. Since these metal sulfides undergo redox reactions in the same voltage range as sulfur, they are expected to mediate the sulfur/polysulfide redox processes. The presence of a reversible metal sulfide material with facile kinetics (as evidenced by cycling rates demonstrated in Li-TiS₂ cells) dispersed in the sulfur cathode may, therefore, provide some catalytic effect toward the sulfur redox reactions.

The use of TiS₂ was reported earlier by Manthiram et al. in the context of achieving additional capacity from TiS₂ in the S cathode. The cathode described featured a low sulfur proportion (about 45%) with low electrode loading. Sun et al. studied the effect of blending CuS into the sulfur cathode (CuS has the highest electronic conductivity among the transition metal sulfides), but the performance was rather poor, as also confirmed by our studies with both CuS and FeS₂. An interesting related study reported by Cui et al. described an Li/S cathode encapsulated with a TiS₂ to form Li₂S@TiS₂ core–shell material that possesses both high conductivity and strong binding with Li₂S/Li₂S₈, species because of its polar nature. Specific capacity of 503 mAh/g based on the Li₂S content was achieved at high rates as well as an areal capacity of 3.0 mAh/cm² with a cathode mass loading of 5.3 mg Li₂S/cm². Even though these values are encouraging, they are still short of the desired values in high-energy Li-S cells. Vanadium and zirconium sulfides were also studied by Cui et al. with similar benefit.

Even though metal sulfide additions were studied earlier, these were done either to demonstrate that TiS₂ can contribute to additional capacity (Manthiram et al. and to show its role in retaining sulfur products within the cathode (Cui et al.). But neither these two or any of the earlier papers, to the best of our knowledge, suggest or demonstrate the benefits of TiS₂ blends in fabricating denser sulfur cathodes with high utilization, which is the focus here for achieving high specific energy. MoS₂ is one of the many additives studied computationally (Cui et al.), but other than this, there is no report to our knowledge that demonstrated its use in a Li-S cell, prior to the current work. Recently, there have been a few studies with dense sulfur cathodes, using different approaches, including metal sulfide blends which confirmed our findings. For example, Zhao et al. employed metal–organic frameworks, specifically metal-organic polyhedra (MOP) to encapsulate sulfur nanoparticles (S@MOP) for long-life cathodes. Archer et al. showed interesting performance with S/MoS₂ composite cathode, similar to ours, except that the hybrid cathodes are formed by infusing sulfur into Ti foams. Even though conceptually all these studies are related to our approach, their electrode fabrication methods are unconventional and not relevant to large-scale manufacturing environment, for e.g., use of carbon nanotubes, use of Ti foam, layer by layer stacked sulfur-carbon electrodes, etc. In contrast, the S/metal sulfide composites cathodes in this study are fabricated using the conventional slurry-coating method, as commonly employed in today’s Li-ion industry.

Among the various metal sulfides evaluated here, both TiS₂ and MoS₂ have shown interesting results. Fig. 5A shows the charge-discharge curves of the sulfur cathode blended with TiS₂ and MoS₂ in comparison with the pristine cathode. The charge-discharge curves seem to be slightly above and to the right of the addition of the metal sulfide, especially TiS₂, with slightly higher capacities as a result of the electrochemical activity and/or ionic conductivity from the metal sulfide. In the TiS₂-blended sulfur cathode, the plateau is smoothed to some extent.
Figure 5. (A) Charge/discharge profiles and (B) differential capacity plots of conventional sulfur (S:C:PVDF 55:40:5, loading: 6 mg/cm²), sulfur blended with MoS₂ (S:MoS₂:C:PVDF 65:15:15:5, loading: 9 mg/cm²) and sulfur blended with TiS₂ cathodes for the 1st cycle. (S:TiS₂:C:PVDF 65:15:15:5, loading: 9 mg/cm²).

Figure 6. (A) Specific capacity of the MoS₂-blended sulfur cathode (based on the (1) active material and (2) overall electrode mass) as a function of the amount of MoS₂, compared with the (3) lithium nickel cobalt aluminum oxide cathode and (B) specific capacity (based on sulfur) for various amounts of MoS₂-blended cathodes.

extent both during charge and discharge. Fig. 5B shows the dQ/dV plots from the charge discharge curves of pristine sulfur, MoS₂-blended sulfur and TiS₂-blended sulfur cathodes after the first cycle. With the TiS₂-blended cathode, the peaks shift about 30–40 mV both during charge and discharge. Also, the peak height is noticeably reduced with the TiS₂-blended cathode, which is consistent with the smoothened voltage plateau during discharge and charge (Fig. 5A). With the MoS₂-blended cathode, on the other hand, the peaks are closer to the pristine sulfur cathode.

Proportion of the metal sulfide.—Building from these promising results, we screened the metal sulfide (MoS₂) content in the cathode, varying it from 20% to 5%. The proportions of both carbon diluent and PVDF binder were kept the same at 20% and 5%, respectively. The ratios of S and MoS₂ were varied from 55:20, 60:15 and 70:5. The specific cathode formulations were thus i) 55:20:20:5, ii) 60:15:20:5, iii) 65:10:20:5 and iv) 70:5:20:5 for S:MoS₂:C:PVDF at a typical loading of ~9 mg/cm². Fig. 6A shows performance data after three cycles for the MoS₂-blended sulfur cathodes with different amounts of MoS₂, which indicates that the preferred MoS₂ is between 10 to 15%. Higher amounts of MoS₂ improves the utilization of sulfur but reduces the overall capacity of the electrode. Smaller amounts will not have higher specific capacity based on the overall cathode mass, but the utilization of sulfur is not as efficient. The specific capacity based on the overall cathode mass peaks around 10–15% of MoS₂ with a value of ~570 mAh/g. This is about 3.7 times that of an NCA cathode in a Li-ion cell (151 mAh/g). Fig. 6B shows the cycle life performance of these four different cathodes through twenty cycles, which shows the cycle life is also good with the MoS₂ content of 10–15%. Based on the high initial capacity and good cycle life, a proportion of 15% for MoS₂ seemed to be beneficial and was chosen in further studies, but with a slightly higher proportion of sulfur (S:MS:C:PVDF = 65:15:15:5). We didn’t perform similar optimization for the TiS₂ blends, but used the same proportion (15%), which seems to be beneficial as well.

Figures 7A and 7B show the performance of dense sulfur cathodes blended with TiS₂ and MoS₂, respectively in the ratio (S:TiS₂:C:PVDF = 65:15:15:5). Fig. 7A shows the performance of TiS₂-blended cathodes in two different cells with loadings of 8.5 mg/cm² and 9.4 mg/cm². The initial capacities are 700–800 mAh/g, based on the sulfur mass, and stabilized at 600 mAh/g through 100 cycles. Fig. 7B shows the performance of MoS₂-blended cathodes in two different cells with loadings of 7 mg/cm² and 10 mg/cm². The initial capacities are ~1000 mAh/g and 800 mAh/g, based on the sulfur mass, and stabilized at 800 mAh/g and 600 mAh/g, respectively through 80 cycles. As may be expected with a higher loading, the sulfur utilization is reduced, possibly due to increased polysulfide effects, but the areal capacities would be higher, e.g., 3.5 and 5 mAh/cm² (per side) in these two cases. As shown above, the performances of the sulfur cathodes blended with TiS₂ and MoS₂ are noticeably improved, compared to the baseline sulfur cathodes, even with higher proportion of sulfur and loading of cathode material.
Advanced sulfur cathode with metal sulfide coating.—Based on the ability of the metal sulfides to trap the polysulfides, it may be possible that a (thin) coating of the metal sulfide on the sulfur cathode could reduce the polysulfide shuttle effects and improve the cycle life. Various oxides,115 for example, V2O596 and MnO294 were either suggested or demonstrated in the previous studies to trap the polysulfides. Here we have examined the effect of a coating of TiS2 or lithium titanate onto a sulfur cathode, either pristine sulfur or a composite sulfur cathode to provide a conformal barrier for polysulfides diffusing away from the cathode. These coatings, being good electronic/ionic conductors (both TiS2 and lithium titanate), would facilitate lithium charge transfer and may assist in re-oxidizing the insoluble precipitated Li2S while simultaneously trapping soluble polysulfides within the cathode. Fig. 8A shows performance of a pristine sulfur cathode (loading 5 mg/cm²) coated with a thin layer of TiS2. Here, the coating of TiS2 is applied over a conventional sulfur cathode, using a spin-coater from mix of TiS2 and NMP, as described in the Experimental section. The amount of TiS2 coating on the cathode is ∼1.5 mg/cm². As may be seen here, there is an improvement in the cycle life from the TiS2 coating, with ∼900 mAh/g of capacity from sulfur and with a coulombic efficiency of over 0.9, not seen with baseline sulfur earlier (see Fig. 4).

To have a synergistic effect of metal sulfide both in the bulk of the cathode and on the surface of the cathode, a coating of TiS2 is applied onto an MoS2-S composite cathode (65:15) with a loading of 9–10 mg/cm² (Fig. 8B). Here we have two different cases, one with a relatively thicker coating of 5 mg/cm² applied using a brush from slurry of TiS2+NMP. In the second case, the coating is thinner with ∼2 mg/cm², applied using a spin-coater. The specific capacity, based on the sulfur mass, is higher, i.e., about 1200 mAh/g, due to a larger contribution from TiS2 (∼330 mAh/g). The capacity is quite stable through 80 cycles, beyond which the (Li) anode cyclability might be an issue. In the second instance (slightly thicker cathode), the specific capacity stabilizes around 800 mAh/g during cycling. The areal specific capacity is between 5.5–4.5 mAh/cm² (per side), which is quite impressive. The coulombic efficiency in both cases is in excess of 0.9.

Fig. 8C shows the effect of a lithium titanate coating (1.5 mg/cm²) over a S:MoS2 (65:15) composite cathode with a loading of 10 mg/cm². This coating was mixture of titanate + NMP, applied using a spin-coater in similar fashion. Unlike TiS2, lithium titanate remains in the lithiated form, without undergoing redox process in the voltage range of sulfur (2.4 V – 1.8). The average capacity during cycling is around 700 mAh/g through 100 cycles, with an areal specific capacity of >4 mAh/cm².

It is clear from the presented results that is possible to fabricate efficient and dense sulfur cathodes by blending with suitable metal sulfides and later coating with similar materials, as evidenced by the good performance (1200 mAh/g) of a thick (12 mg/cm²) S:MoS2 cathode spin coated with TiS2. These approaches are promising and provide a pathway toward improving the specific energy, energy density and cycle life in a Li-S cell.

Structural analysis of electrodes by X-ray diffraction (XRD).—Electrodes harvested from coin cells were analyzed after cycling (1-2 cycles) using powder X-ray diffraction to understand the structural evolution during the redox processes. The XRD analysis for baseline S, MoS2-blended and TiS2-blended electrodes was carried out at the following states: a) pristine, uncycled, b) end of 1st discharge, c) end of 1st charge, d) end of 2nd discharge, and e) end of 2nd charge.

Baseline sulfur electrodes.—The XRD patterns for baseline S-electrodes at different states are presented in Fig. 9A. The pristine, uncycled electrodes show diffraction from orthorhombic sulfur (PDF #83–2285); the peaks were fit based on this reference pattern to calculate the lattice parameters listed in Table 1 (via Rietveld refinement), and the results were in agreement with previous values reported in the literature.118 Minor, weak diffractions from carbon black and PVDF were observed for all the electrode samples; similarly, peaks arising from the presence of LiNO3 (electrolyte additive) were minimal.
for these baseline S-electrodes, indicative of an effective removal of the electrolyte components by washing with DOL after harvesting. The contribution of the Al foil to the spectra was significant, as indicated by the assigned peaks in Fig. 9A. The redox processes evidently for these baseline S-electrodes, indicative of an effective removal of the electrolyte components by washing with DOL after harvesting. The contribution of the Al foil to the spectra was significant, as indicated by the assigned peaks in Fig. 9A. The redox processes evidently
differentiated by the fitted S lattice parameters were slightly modified from their standard values, indicating a minor lattice expansion most likely due to a degree of interaction between the S and MoS2 components. The MoS2 peaks were not observed to change regardless of the charge/discharge state of the electrode, indicating that MoS2 does not participate in the electrochemical lithiation process at the potentials investigated. The sulfur component behaves essentially the same as observed for the baseline S-electrodes, transforming from the orthorhombic form in the pristine electrode to the monoclinic form upon subsequent charges.

**TiS2-blended sulfur electrode.**—The XRD behavior for the TiS2-blended sulfur cathodes is shown in Fig. 9B. The XRD behavior for the TiS2-blended sulfur cathodes is shown in Fig. 9B. With MoS2, the monoclinic crystalline modification of elemental sulfur is observed (orthorhombic and monoclinic modifications of sulfur (orthorhombic and MoS2 (PDF#77-0341, indicative of the dashed lines in the Figure). The fitted S lattice parameters were slightly modified from their standard values, indicating a minor lattice expansion most likely due to a degree of interaction between the S and MoS2 components. The MoS2 peaks were not observed to change regardless of the charge/discharge state of the electrode, indicating that MoS2 does not participate in the electrochemical lithiation process at the potentials investigated. The sulfur component behaves essentially the same as observed for the baseline S-electrodes, transforming from the orthorhombic form in the pristine electrode to the monoclinic form upon subsequent charges.

**TiS2-blended sulfur electrode.**—The XRD patterns for TiS2-blended sulfur electrodes are shown in Fig. 9C. As before, the pristine, uncycled electrode exhibits peaks from crystalline, orthorhombic sulfur and Al foil, with minimal contributions from carbon black, PVDF and LiNO3. Most interestingly, reversible oxidation and reduction of titanium sulfide species via lithiation can be identified from the XRD patterns observed after the charge/discharge processes performed. In Fig. 9D, the appearance of peaks from TiS2 can clearly be observed after charging the cells, with concomitant growth of peaks arising from Li2TiS3 (PDF#75-1768), and this was found to be reversible,120,121 Such behavior is consistent with TiS2 participating in the redox process along the reduction/oxidation of sulfur during cycling. In addition, sulfur most likely re-forms in the orthorhombic crystalline modification upon charging these electrodes, as evidenced through the strong (222) diffraction observed (although this phase appears to be of lower crystallinity the monoclinic form found upon charge of the baseline-S and MoS2 electrodes). This may potentially reflect a greater degree of interaction between TiS2 and S (consistent with reported calculations),199 resulting in preferential growth of sulfur in a phase more compatible with the hexagonal TiS2 crystals. Hence, we tentatively conclude that TiS2 lithiation may mediate the electrochemical cycling of sulfur in these cells, in contrast to the direct reduction and re-oxidation as observed for the baseline-S and MoS2 electrodes (as MoS2 does not exhibit such a redox transition). Nevertheless, there appears to be similar empirical benefit with the addition of MoS2 to the sulfur cathode as with TiS2.

**Electrochemical kinetics.**—Tafel polarization.—Tafel polarization studies were carried out in three-electrode pouch cells to see if the metal sulfide blends have an effect on the electrochemical kinetics of sulfur reduction. All studies were carried out at fully-charged state (100% SOC) at 25 °C. These measurements were made under potentiodynamic conditions at slow scan rates of 0.5 mV/s, approximating steady-state conditions. Fig. 10A shows the Tafel polarization curves of the baseline sulfur cathode and of the sulfur cathodes blended with 15% of TiS2 and MoS2. The Tafel polarization plots are nearly identical in all the three cathodes, with similar overpotentials vs. current densities. There is noticeable interference of mass transfer process on charge transfer kinetics, with currents assuming limiting values at high overpotentials. These data were corrected for these mass-transfer effects (Fig. 10B) and exchange current densities were extracted from the corrected Tafel plots. The exchange current density of pristine sulfur cathode is 0.19 mA/cm2 at 25 °C. In contrast, the exchange current densities of the composite cathodes with TiS2 and MoS2 blends are 0.21 mA/cm2 and 0.23 mA/cm2, respectively. In the composite cathodes, especially with the TiS2-blended S cathode, the above exchange current density may be an average of sulfur and TiS2 processes.
**Figure 9.** X-ray powder diffraction patterns of A) Baseline sulfur cathode (S:C:PVDF 55:40:5, loading: 5 mg/cm²), B) MoS₂-blended sulfur cathode (S:MoS₂:C:PVDF 65:15:15:5, loading: 9 mg/cm²) and C) TiS₂-blended sulfur cathode (S:TiS₂:C:PVDF 65:15:15:5, loading: 9 mg/cm²) at various stages of charge and discharge. Fig. 9D is an expanded section for the TiS₂-blended sulfur cathode showing the transition from TiS₂ to LiTiS₂. Major peaks of interest are identified in the figure or in the text; for the uncycled electrodes the remainder of the non-specified peaks correspond to orthorhombic sulfur (PDF#83-2285).

is clear from these kinetic data that the charge-transfer kinetics for sulfur reduction remain unchanged after blending with metal sulfide, TiS₂ or MoS₂.

**Diffusion coefficients using potentiostatic intermittent titration technique (PITT).**—The PITT technique was used to measure the diffusion constant of Li⁺ in all three cathode materials, i.e., baseline sulfur and sulfur blended with TiS₂ and MoS₂ to compare their initial values and evolutions over cycle life. All studies were carried out at 2.3–2.4 V at 100% SOC at 25°C and the potential was stepped in increments of 10 mV. A plot of ln(I) vs. t during these steps was found to be linear. It was thus possible to treat the data by solving Fick’s law for a semi-infinite system with a surface concentration perturbation, as outlined in Wen et al.¹²²

\[
I(t) = \frac{2Fa}{a} \frac{(C_S - C_0)D}{L} \exp\left(-\frac{\pi^2Dt}{4L^2}\right) \tag{1}
\]

where \(I(t)\) is current as a function of time, \(F\) is Faraday’s constant, ‘a’ is the electrode surface area, \((C_S-C_0)\) is the concentration change during the step, and \(L\) is the diffusion length, taken to be the particle radius. The lithium diffusion coefficient \(D\) for each sample/cycle was then calculated using the long-time approximation \((t \gg L^2/D)\):

\[
D = \frac{d\ln(I)}{dt} \frac{4L^2}{\pi^2} \tag{2}
\]

where \(d\ln(I)/dt\) is the slope of \(\ln I\) vs. \(t\) plot and \(L\) is again the particle radius. The initial diffusion constants for the baseline sulfur, TiS₂ and MoS₂ were calculated and are presented in Table I.

**Table I.** Lattice parameters of S-baseline, MoS₂-blended and TiS₂-blended electrodes.

| Electrode    | ‘a’ (Å) | ‘b’ (Å) | ‘c’ (Å) |
|--------------|---------|---------|---------|
| Literature [1] | 10.46   | 12.87   | 24.89   |
| S-baseline   | 10.23   | 12.87   | 25.95   |
| MoS₂-doped   | 9.81    | 13.89   | 26.05   |
| TiS₂-doped   | 10.31   | 12.71   | 24.45   |

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Figure 10. (A) Tafel polarization curves of 1) baseline sulfur cathode (S:C:PVDF 55:40:5, loading: 5 mg/cm²) and sulfur cathode blended with 2) TiS₂ (S:TiS₂:C:PVDF 65:15:15:5, loading: 9 mg/cm²) and 3) MoS₂ (S:MoS₂:C:PVDF 65:15:15:5, loading: 9 mg/cm²). Fig. 10B shows the corresponding plots corrected for mass-transfer effects.

TiS₂-blended sulfur and MoS₂-blended sulfur cathode are in the same range, i.e., $2 \times 10^{-9}$ cm²/s, $0.5 \times 10^{-9}$ and $1.3 \times 10^{-9}$ cm²/s respectively (Figure 11). The diffusion coefficients are slightly higher for the pristine sulfur cathode, possibly due to the higher surface area of carbon, which is replaced with a denser metal sulfide. These diffusion coefficients are consistent with the values reported in the literature. These values rose slightly for the pristine material during cycling, especially with the pristine sulfur and TiS₂-blended sulfur cathodes, possibly due to morphological changes resulting from the dissolution of polysulfides from the cathode. In short, the PITT studies suggest that the diffusional kinetics for lithium ions inside the sulfur cathodes are relatively unchanged upon blending it with metal sulfides.

Figure 11. Lithium diffusion coefficients in baseline sulfur cathode (S:C:PVDF 55:40:5, loading: 5 mg/cm²) and sulfur cathodes blended with TiS₂ (S:TiS₂:C:PVDF 65:15:15:5, loading: 9 mg/cm²) and MoS₂ (S:MoS₂:C:PVDF 65:15:15:5, loading: 9 mg/cm²), from Potentiostatic Intermittent Titration Techniques (PITT).

Conclusions

One of the life-limiting processes for the sulfur cathode is the dissolution of sulfur reduction products, polysulfides, in organic electrolytes, which form redox shuttles causing reduced coulombic efficiency, build up insulating layers on the Li anode and cause a rapid capacity fade during cycling. Several strategies, including use of complex cathode structures with porous carbon nanostructures, ionic liquids and solid electrolytes and selective electrolyte additives are being examined to minimize the shuttle effects. Promising results were obtained with some of these approaches, but only with cathode with low sulfur loading (1–2 mg/cm²). With dense electrodes, i.e., with high sulfur loadings that are essential for high energy cells, the polysulfide effects are more serious, with poor sulfur utilization and cycling. Here, we have demonstrated that by blending sulfur with a transition metal sulfide, in particular TiS₂ and MoS₂, we can achieve enhanced performance even in dense sulfur cathodes yielding >4 mAh/g (per side). There is an improvement in both the initial capacity from increased sulfur utilization (∼800 mAh/g based on sulfur content) and the coulombic efficiency (>96%). These improvements may be attributed to the increased ionic conductivity and the additional capacity from the metal sulfide. Additionally, the cycle life is found to be superior in the metal sulfide-blended cathodes even with high loadings, with >75% retained through 80 cycles of 100% depth of discharge at C/3. The improvement in the coulombic efficiency and cycle life may be understood in terms of stronger interactions between the metal sulfide and sulfur, which sequesters the discharge products within the cathode. XRD studies indicate that TiS₂ undergoes redox transitions during charge/discharge cycling of sulfur cathode, while no such transitions are evident with MoS₂; nevertheless, both materials afford similar performance benefits. Both charge transfer and lithium diffusion kinetics have been found to be nearly the same in the metal sulfide blended S cathode as with pristine sulfur cathode. Significant from a technological perspective, high sulfur loadings (>12 mg/cm² or >6 mAh/cm² per side) were demonstrated in Li-S cells containing the composite cathodes with good utilization. Finally, these approaches of metal sulfide composite cathodes with suitable sulfide/oxide coatings are promising and provide a pathway toward improving the specific energy, energy density and cycle life in a Li-S cell.

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