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Cathode loading effect on sulfur utilization in lithium-sulfur battery

Ke Sun¹, Helen Liu², and Hong Gan^{1*}

Abstract: The Lithium-Sulfur (Li-S) battery is under intensive research in recent years due to its potential to provide higher energy density and lower cost than the current state-of-the-art lithium-ion battery technology. To meet cost target for transportation application, high sulfur loading up to 8 mAh cm⁻² is predicted by modeling. In this work, we have investigated the sulfur loading effect on the galvanostatic charge/discharge cycling performance of Li-S cells with theoretical sulfur loading ranging from 0.5 mAh cm⁻² to 7.5 mAh cm⁻². We found that the low sulfur utilization of electrodes with sulfur loading of > 3.0 mAh cm⁻² is due to their inability to deliver capacities at the 2.1V voltage plateau, which corresponds to the conversion of soluble Li₂S₄ to insoluble Li₂S₂/Li₂S. This electrochemical conversion process recovers to deliver the expected sulfur utilization after several activation cycles for electrodes with sulfur loading up to 4.5 mAh cm⁻². For electrodes with 7.0 mAh cm⁻² loading, no sulfur utilization recovery was observed for 100 cycles. The root cause of this phenomenon is elucidated by SEM/EDS and EIS investigation. Carbon interlayer cell design and low rate discharge activation are demonstrated to be effective mitigation methods.

Key words: Lithium-sulfur battery; sulfur utilization; sulfur loading; activation.

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1. Introduction

The Li-ion battery has been the dominant player in the energy storage market since its commercialization by SONY in 1991 [1]. It played a vital role during the development of portable electronics that now penetrate into every part of modern lifestyle, and also enabled the preliminary achievement of affordable electric automobiles for the average household [2]. Nonetheless, the desire for energy storage devices with even higher energy density, higher power density and lower cost is anything but vanishing, due to the increasing demand for global transformation to sustainable economics and the exponential expansion of the consumer electronics market [3]. Although significant progress has been made in research on the improvement of current Li-ion battery technology based on lithium intercalation electrodes, identification of new intercalation compounds with the combined merit of high energy density, high power capability and low cost still remains a major scientific challenge.

Meanwhile, new research horizons such as Lithium-Sulfur (Li-S), Lithium-Air, Zinc-Air batteries, etc. have attracted more attention and effort because they theoretically might be able to triple the energy density of the best Li-ion batteries today, while maintaining or even reducing the manufacturing cost [4]. Amongst these options, the Li-S battery has a theoretical energy density of 2600 Wh kg^{-1} , which is about 6 folds of Li-ion battery with LiCoO_2 and graphite electrodes. In addition, sulfur's abundance and cheap access also define Li-S battery as a low-cost system. In spite of these advantages, Li-S battery systems under development still suffer from low energy utilization and efficiency due to factors such as the insulating nature of both sulfur and lithium sulfide (Li_2S), active material dissolution and the well-known shuttling effect [4,5]. Current strategies to solve these problems generally involve the trapping of sulfur in various porous carbon nanostructures by means of surface coating, encapsulation and impregnation, which helps to enhance the electronic contact between the active sulfur component and inactive conductive network and to trap soluble polysulfide species developed during the lithiation of sulfur [6-12]. Except for a few cases [11,12], this route almost always tremendously increases the weight percentage of inactive carbon in the whole electrode and reduces the actual loading of sulfur to less than 60 wt%. If high sulfur loading is not achieved in real devices, the practical energy density of Li-S battery will be dramatically compromised. In the meantime, a recent cost analysis of Li-S battery based on the techno-economic model proposed by Eroglu et al. has demonstrated that sulfur would potentially assume only 0.1% of the total cost of the whole

system, while a majority of the materials cost goes to other components such as the lithium anode, current collectors, electrolyte, and separator, etc.[13]. This means that the final cost of future Li-S batteries greatly relies on the sulfur loading per unit mass/volume of other components, if the design-pack energy is a constant determined by application. Finally, Eroglu et al. predicted that the loading of sulfur per electrode coating must be sufficient to deliver more than 8 mAh cm^{-2} in order to make the whole system competitive enough to meet the low cost target for electric vehicle applications. This means high sulfur loading per unit area in electrode fabrication will be vital in the success of the Li-S batteries, and if sulfur percentage lower than 60% has to be used to ensure performance, then the use of a thick sulfur electrode coating is inevitable for the battery to achieve a good balance between energy and cost. Therefore, a systematic study on the effect of sulfur electrode thickness and sulfur loading per unit area on the performance of Li-S battery will be very meaningful for this territory.

To date, a few ultra-high areal sulfur loading electrodes have been demonstrated on a lab scale based on sophisticated surface treatments of the cathode or lithium anode [14-18]. However, the scaling-up of these processes for real applications remains a major challenge. Systematic studies of areal sulfur loading in Li-S batteries based on conventional materials and methods are also seen in limited publications [19-21]. All of these works unanimously observed poor sulfur utilization and cycling at high areal sulfur loading. However, only one of them clearly identified a mechanism for the malfunction of thick sulfur electrodes, which is the corrosion of the lithium anode induced by excess polysulfide in the cell [20]. In the present study, we observed and identified a completely different mechanism for the inefficiency of thick sulfur electrodes, which suggests that cathode engineering and cell design may play a more crucial role in limiting the utilization of thick sulfur electrodes. In this work, the mechanism will be demonstrated based on a systematic study of the areal sulfur loading on the electrode's performance, with the emphasis put on the initial capacity utilization.

2. Experimental

2.1. Material preparation and cell construction

Sulfur-mesoporous carbon (S-MC) composite with a 3:1 weight ratio of elemental sulfur (Alfa Aesar) and mesoporous carbon (Sigma Aldrich, surface area: 150-250 m²/g) was prepared by heating the mixture at 155° C for 20 hours in a glass oven (Buchi) situated in an argon filled glovebox (Mbraun). There is no weight lost during this process step. Using 0.8 g S-MC composite as a basis, the cathode slurry was prepared with a 60:30:10 target mass ratio of S:C:PVDF binder (Alfa Aesar) by adding 0.1g Super C65 carbon black (TIMCAL) and 0.1g PVDF (Alfa Aesar). The mixture was roller milled for 12hrs, while 7.5g 1-Methyl-2-pyrrolidinone (NMP) was gradually added during this process to turn the mixture into homogeneous slurry. The slurry was coated onto a piece of aluminum foil using a doctor blade. The gap of the doctor blade was set at values between 100 and 1200 μm as a measure to adjust the final sulfur loading. The casted slurry was dried in a fume hood under continuous dry air flow (dew point < -40°C) for 24 hours before it is transferred into an oven to be heated at 50°C for another 24 hours to eliminate residue solvent and moisture. 2032 coin cells were assembled using electrodes of different coating thickness prepared as described above as the working electrode (1.27 cm²) and a lithium disk as both counter and reference electrodes, with 2 layers of Celgard (2325) separator in between to prevent shorting. The electrolyte used in this study was Lithium bis(trifluoromethane)sulfonimide (LITFSI) (1 M) dissolved in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 ratio, by volume) obtained from BASF. 1wt% of LiNO₃ was dissolved into the electrolyte before use to help the lithium electrode passivation and alleviate shuttling of polysulfide species. In each coin cell, ~80μL electrolyte was added.

To improve the sulfur utilization of thick electrodes, a carbon-coated separator was introduced as a conductive interlayer during the cell assembly. This interlayer was prepared according to the procedure developed in Ref.[22]. 0.3g Super C65 carbon black (TIMCAL) and 0.1g PVDF (Alfa Aesar) were mixed in 6g of NMP to form homogeneous slurry. The slurry was then deposited onto one side of a Celgard separator with a doctor blade, the gap of which was set at 200μm. The casted slurry was dried in a fume hood under continuous dry-air flow (dew point <40°C) for 24 hours, followed by vacuum drying at 50°C for 24hrs. For cells assembled with this interlayer, the carbon-coated separator was sandwiched between the sulfur cathode and an extra Celgard separator, with the carbon-coated side facing the sulfur electrode.

2.2. Cell testing and analysis

Galvanostatic charge/discharge tests were carried out on these cells at a constant current density of 335 mA g⁻¹ sulfur (0.2 C) in the potential range of 1.8V to 2.6V at 25°C on a Biologic (VMP3) potentiostat. The charging process was always ended with a voltage-holding step at 2.6V until the current fell below 84 mA g⁻¹ sulfur (0.05C).

To understand the behavior of sulfur electrodes with different loadings, an electrochemical impedance study (EIS) coupled with galvanostatic cycling was performed on selected electrodes. These cells were cycled with the very similar protocol introduced above. The main difference is that for each cycle, when the cell reached 2.1V, 1.8V during the discharge and after the 2.6V constant voltage charge process, it was allowed to relax for one hour. After this open-circuit period, impedance data was collected with frequency varied between 500 kHz and 50 mHz and with a perturbation amplitude of 5 mV. The galvanostatic discharge/charge resumed after the impedance spectrum was taken.

SEM and EDS mapping of the pristine and cycled sulfur electrodes were recorded with JOEL 7600F analytical SEM.

3. Results and discussion

3.1. Preparation of sulfur electrode with different loading

The average thickness of electrodes as a function of slurry coating gap is shown in Figure 1a. In total, electrodes of 7 different thicknesses were coated, including doctor blade loading gaps of 100, 200, 300, 400, 500, 850, and 1250 μm . Starting at 1250 μm , the coated layer experienced serious uneven shrinkage after air-drying, which led to electrodes with a lot of delamination and cracks, indicating the process limitation is reached with the adopted preparation method. To ensure the quality and reliability of the data, only the first 6 lower-loading electrodes (excluding 1250 μm) were tested electrochemically. From Figure 1a, it is obvious that the thickness of dried electrodes follows a linear relationship with the initial coating gap. Using a linear fitting, the coefficient of thickness shrinkage during drying is about 0.1, and the upper bound of final electrode thickness for the formulation used for this study is about 90 μm . In parallel, the sulfur mass and the theoretical capacity loading per unit area is also plotted against the initial coating gap (Figure

1a and Figure 1b). A similar linear relationship holds for these two parameters, and the coefficient of areal sulfur mass and capacity loading versus coating gap thickness is determined to be $5.4 \text{ mg cm}^{-2} \text{ mm}^{-1}$ and $9.0 \text{ mAh cm}^{-2} \text{ mm}^{-1}$, respectively. In order to achieve the 8 mAh cm^{-2} goal proposed by ref.[13], at least a $900 \mu\text{m}$ gap is needed. The $850 \mu\text{m}$ gap in this series is close to this value. Although the slurry formulation is unique in this study, the correlation between coating gap and areal sulfur loading obtained here might still serve as a helpful reference if similar work is performed in other labs with a slurry formulation in close proximity.

3.2. Cycling performance of sulfur electrode with different loading

Discharge capacities of electrodes with different loading are plotted with cycle number in Figure 1c. Three different kinds of behavior were observed, which is correlated with sulfur loading. For loading not larger than 1.40 mg cm^{-2} (2.34 mAh cm^{-2}), all cells start with an initial discharge capacity of around 800 mAh g^{-1} , which corresponds to a utilization of around 50% of sulfur's theoretical capacity, and all of them experience a continuous decay of capacity throughout the 100 cycles tested to reach around 350 mAh g^{-1} . This behavior is similar to many Li-S cells in literature without special materials processing [22-24]. When the sulfur loading is between 1.85 mg cm^{-2} (3.09 mAh cm^{-2}) and 2.38 mg cm^{-2} (3.97 mAh cm^{-2}), the initial utilization of sulfur becomes much lower than the first case, around 350 mAh g^{-1} and 200 mAh g^{-1} for the two sets of electrodes coated with $400 \mu\text{m}$ and $500 \mu\text{m}$ gap respectively. Moreover, unlike the lower-loading electrodes, initially these electrodes do not directly enter the capacity-fading regime. In contrast, the capacity starts to recover until a maximum value before the continuous decay taking-place. This suggests that there seems to be an electrode activation process for electrodes falling into this loading range, which has also been observed in some high sulfur loading prototype cells [16-18]. Finally, for the highest loading 4.18 mg cm^{-2} and 4.38 mg cm^{-2} (6.98 mAh cm^{-2} and 7.31 mAh cm^{-2}) samples, except for a few spikes where capacity experiences a temporary boost at certain cycles, for the major part of the test the cells can only deliver around 150 mAh g^{-1} . This low efficiency can be expected since when the electrode gets too thick both electronic and ionic transport naturally becomes much impeded. These 3 behaviors can be summarized in Figure 1d and Figure 1e, where actual capacity delivered per unit area is plotted as a function of theoretical capacity loading per unit area for cycle 1 and cycle 30. A clear linear relationship

holds for these two parameters in lower-loading samples, with highest-loading samples always showing much inferior utilization than that predicted from this linear increase. Intermediate-loading samples started with poorer utilization initially, but gradually recovered their capacity and made their way back to be unified with lower-loading samples in the later cycles. Coulombic efficiency (defined as the percentage of discharge capacity of cycle “n” over the charge capacity of cycle “n-1”) of different cycles is also plotted as a function of loading in Figure 1f. For low sulfur loading cells the initial Coulombic efficiency is low most likely due to the capacity lost linked to the anode SEI formation and system equilibration. The Coulombic efficiency after the initial cycles approached 100% in later cycles. For the intermediate loading cells, the Coulombic efficiency is larger than 100% until the completion of the capacity recovery cycles, then returned to around 100% - consistent with the observed activation phenomenon. There is no trend for the high sulfur loading cells since the full reduction of sulfur to lithium sulfide was never achieved except for a few cycles with capacity spikes.

To understand these 3 different behaviors, attention was paid to the voltage profile during discharge. Figure 2a is the voltage profile against discharge capacity for the same group of electrodes in Figure 1c. In this plot, higher-loading electrodes deliver less capacity and also experience more severe voltage polarization, which is expected from Figure 1c. Something requiring more attention is the ratio between the delivered capacity of the flat region around 2.1V and the sloped region above 2.1V in each voltage-capacity curve. A simple calculation using 2.1V as the boundary finds this ratio is decreased dramatically from 1.17 to 0.07 when the loading is increased from 0.29 mg cm⁻² to 4.38 mg cm⁻². It is generally understood that the sloped region in the discharge corresponds to the initial conversion of solid sulfur into soluble Li₂S₈ and the further lithiation of S₈²⁻ into S₄²⁻. Beyond the transition point around 2.1V which corresponds to the maximum concentration of polysulfides in the electrolyte, the plateau region is correlated with reduction of soluble S₄²⁻ into solid Li₂S₂ and Li₂S, followed by a very short sloped region that probably involves solid state conversion of Li₂S₂ to Li₂S [4,5]. The gradual shrinkage of the plateau region relative to the initial sloped region with increasing sulfur loading suggests the poor sulfur utilization at high loading is mainly caused by the difficulty to undergo the liquid-solid conversion of S₄²⁻ to Li₂S₂/Li₂S. To our knowledge, this voltage profile trend has not been reported previously.

Plotting of voltage-depth of discharge curves for different cycle numbers can also help the understanding of the 3 different kinds of behavior observed in Figure 1c. Figure 2b is the voltage profile of the electrode with 1.28 mg cm^{-2} sulfur loading in 5 representative cycles. In this case, as cycle number increases, both the sloped region and the flat region shrink almost commensurately to induce the capacity fade. Figure 2c is the same evolution for the electrode with the intermediate loading of 2.23 mg cm^{-2} . According to Figure 1c, the first 4 data series in this plot correspond to the capacity recovery or activation regime where capacity increases with cycle number. It can be seen that during this recovery process the capacity contribution from the sloped region almost remains constant, while the plateau region sees a steady increase from 45 mAh g^{-1} to 342 mAh g^{-1} . This means the electrode activation process for electrodes with intermediate sulfur loading is mainly caused by the gradual recovery of the electrode's ability to sustain the S_4^{2-} to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ process. From cycle 45 to cycle 80, the overall capacity starts to decrease, and similar to the lower-loading sample, both regions lose capacity commensurately. Finally, the voltage-capacity profiles of high loading sample with 4.18 mg cm^{-2} are shown in Figure 2d. In this case, there is no obvious trend of the change of the two voltage regions. Notably for cycle 80, the capacity of the plateau region experienced a major increase, which accounts for the capacity spike observed in Figure 1c. In this case, it seems that the capacity of the sloped-voltage region does not change significantly, which means that the S_8 to S_8^{2-} and S_4^{2-} conversion process is fairly stable and reversible.

3.3. SEM/EDS morphology study of cycled sulfur electrode

SEM images of electrodes with sulfur loadings lying in the neighborhood of 2.36 mg cm^{-2} in the fully discharged state after different numbers of cycles also supports that the capacity recovery phenomenon observed for intermediate-loading electrodes is caused by a gradual increase of the conversion efficiency of S_4^{2-} to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ in the initial cycles. As it is shown in Figure 2e, after the first discharge there is not much morphological change of the electrode surface relative to the pristine electrode. On the other hand, after the cell reaches its peak capacity by going through the initial 15 cycles, its surface is covered with thick and dense deposition. Another electrode with same loading shows similar surface morphology after 50 cycles, which already experiences a significant capacity fade after the activation process. If the surface deposition is mainly composed of $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$, then the delay of its heavy accumulation to the cycle with the highest

delivered capacity supports the hypothesis that cells with intermediate loading experience an activation process of the second plateau ($\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ deposition) in the initial cycles to reach a maximum capacity before capacity fade begins. The relative S/C peak signal ratio in the EDS spectrum (Figure 2f) taken at the electrodes' surfaces starts from 3.35 for the pristine electrode and drops to 0.86 after the 1st discharge, and it then rises to 3.24 after 15 cycles and declines to 1.99 after 50 cycles (see inset in Figure 2f). The positive correlation between S/C peak signal ratio and visual morphology of the deposition indicates that the deposition is likely Li_2S .

3.4. EIS study of coin cells with different sulfur loading

To understand the mechanism for these different behaviors, EIS was performed on Li-S cells assembled with two samples, one with lower sulfur loading of 0.77 mg cm^{-2} , and the other one with intermediate sulfur loading of 2.62 mg cm^{-2} . The Nyquist plots of these cells at various stages of the first cycle are shown in Figure 3a and Figure 3b. The sample with lower loading exhibits two depressed semi-circles at high and middle frequencies and an inclined line with a slope ~ 1 at low frequencies, while the intermediate loading cell only shows one high frequency semicircle and a steeply inclined line resembling a blocking interface at low frequencies. However, when the cells enter the first galvanostatic cycle, the differences between the two loadings become smaller, and the cell with intermediate loading also starts to show two semicircles and an inclined line with slope close to 1. The main difference here is that the cell with lower loading shows a semicircle with a much larger magnitude in the middle frequency in the fully discharged state (1.8V).

An equivalent circuit adopted from Ref. [25] is applied to fit each individual Nyquist plot in order to offer an easier comparison between the two cells and between different cycles and depths of discharge within the same cell. The equivalent circuit and the representative EIS data fitting are shown in Figure 3c. The R_1 corresponds to the resistance of the electrolyte. $R_2//\text{CPE}_2$ and $R_3//\text{CPE}_3$ represent the depressed semicircles at high frequency and middle frequency. According to Ref. [25], $R_2//\text{CPE}_2$ and $R_3//\text{CPE}_3$ represent the interface charge conduction from the current collector to the reaction front and the charge transfer process at the solid liquid interface, respectively. A constant phase element (CPE_4) is used to simulate the diffusion process of reactants Li^+ in solid state or $\text{Li}^+/\text{S}_n^{2-}$ in liquid electrolyte at low frequency. Warburg impedance

was not employed for the diffusion process in this study for similar reason as Ref. [25], which is the ease to lead to singularity in the fitting process.

The results of the fitting are plotted in Figure 3e for R_2 , Figure 3f for R_3 , and Figure 3g for R_1 . The discharge capacity evolution of the two cells per cycle number is also plotted in Figure 3d as a reference, which is consistent with the observation in Figure 1c. It can be seen that two cells also show distinct behavior in the 3 fitting parameters. Among them, Interface resistance R_2 is where the two cells share the highest similarity. Both cells started with a R_2 of around 60-70 ohm at the beginning of life, which dropped significantly after the first cycle and then rose slightly in the later 39 cycles in the fully charged state (2.6V). The huge decrease of R_2 during the first cycle is probably due to the redistribution of sulfur to more reactive sites in the conductive network from the initial as-prepared random distribution. Evolution of R_2 in the partially discharged state (2.1V) and fully discharged state (1.8V) also share similar trends between the two cells. For the partially discharged state, R_2 of both cells dropped slightly in the initial 3-5 cycles and did not experience much change in the later cycles, in spite of some fluctuations. On the other hand, R_2 was decreasing throughout the 40 cycles in the fully discharged state for both cells. It can be observed that for both cells, R_2 at the fully discharged and charged state gradually converged with each other as cycling proceeded, although a full overlap happened much earlier for the low loading cell. This gradual convergence is indicative of the possibility that as the cycling proceeds the structural difference is diminishing between the charged and discharged state. This is reasonable since the capacity fade during the cycling must be accompanied by the introduction of isolated sulfur and Li_2S in the electrode. The accumulation of these inaccessible sulfur contents will naturally reduce the compositional difference between charged and discharged states. However, one observation contradictory with this explanation is the recovery of capacity of the high loading cell in Figure 3d in the first 12 cycles, which must be associated with an initial decrease of inaccessible sulfur. Based on this, it is inferred that the consideration of dependence of contact resistance on electrode microstructure probably should involve more than just the composition.

Although qualitatively the two cells are quite similar in R_2 evolution, the quantitative difference is still prominent. The drop in R_2 from pristine to a few cycles after the cycling started is especially more

significant for the intermediate loading cell than the low loading cell, and on average R_2 is 20 ohms lower for the former than the latter. This suggests that although electrodes with higher loading are supposed to experience more resistance in operation because of the accompanied higher electronic resistance, tortuosity and diffusion lengths for Li^+ and S_n^{2-} , contact resistance is indifferent to these factors that are correlated with electrode loading. The quantitative value is probably more sensitive to the microstructure and the mechanical integrity of the electrode, which depends more on the electrode processing and cell construction conditions. In this case it is probably more useful to limit the comparison of the magnitude of different parameters to each cell but focus on the comparison of evolution trend between the cells.

As expected, the evolution of charge transfer resistance R_3 in Figure 3f is completely different between the two cells, especially at the fully discharged state. R_3 at 1.8V declined monotonically for the low loading cell throughout the test, while the other cell experienced a continuous increase till cycle 13 before entering the reduction regime. This increase/decrease transition is reminiscent of the capacity recovery behavior shown in Figure 3d for the intermediate loading cell. If observed closely, it can be seen that R_3 and 2nd region capacity in Figure 3d are strongly correlated for both cells. Since discharge capacity below 2.1V for Li-S is generally believed to be the result of S_4^{2-} to $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ conversion, it is inferred that the amount of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ in the electrode directly determines the charge transfer resistance. This is also supported by the consistently low R_3 observed at 2.1V and 2.6V for both cells, where sulfur and polysulfides are the main sulfur species in the electrode network.

The different behavior of electrolyte resistance R_1 in Figure 3g provides the same indications as R_3 . For both cells, R_1 reaches its maximum at 2.1V, corresponding to the highest viscosity of the electrolyte when polysulfides are most concentrated at the end of the first discharge region. Correspondingly, R_1 should always be at its minimum in the fully discharged or charged state because polysulfides should be least concentrated at these stages. This is the case for the low-loading cell. On the contrary, for the intermediate-loading cell, only the fully charged state showed this behavior, while at 1.8V R_1 almost started at the same level with that at 2.1V and gradually decreased to converge with that at 2.6V after 12 cycles. This also suggests that the conversion of polysulfides into $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ was initially not very effective for intermediate loading cell, but slowly recovered after 12 cycles.

This EIS study again supports the hypothesis that the gradual recovery of the electrode's ability to reduce S_4^{2-} to solid Li_2S_2/Li_2S in the initial cycles is the main mechanism behind the capacity activation process of intermediate-loading electrode. However, the impedance analysis failed to point out the factor that limits the electrode's capability to initiate the second plateau region. One factor to consider for testing with different sulfur loading is the difference in discharge current density. Since all cells were cycled under the same C-rate, the high-sulfur loading cells will experience higher current density ($mA\ cm^{-2}$) than the low-sulfur loading cells. The discharge current density ranges from 0.1 to 1.5 $mAcm^{-2}$ for loadings of 0.3 to 4.5 $mg\ cm^{-2}$ in our experiment – a factor of 15 times. According to the R_1 obtained from the impedance study, this current density difference will only induce ~18 mV IR drop when the 2.1V R_1 (Figure 3g) being used for this calculation. This IR drop is not sufficient to cause the performance difference as observed in this study (Figure 2a), especially when the electrode is at non-equilibrated state. In addition, although the reduction of electrolyte resistance R_1 and contact resistance R_2 at 1.8V with cycle number can be correlated with the initial enhancement of 2nd region capacity in intermediate loading sample, the magnitude of these parameters and the extent of the changes they experienced in the first 13 cycles are completely dwarfed by the increase of the charge transfer resistance R_3 . In other words, it is completely counterintuitive why cycle 13 should have the highest sulfur utilization if the 3 resistances in series are also the greatest through the whole test. This contradiction can be probably understood by acknowledging the fact that EIS measures the response of an electrochemical system close to equilibrium, which can be completely different when a considerable DC current is applied to the system that drives it to be far from equilibrium. For instance, the distribution of polysulfides during the discharge of the intermediate loading cell can be drastically different from the case when it was allowed to rest for one hour. From this point of view, an electrochemical method that combines the use of dynamic stimulus to the Li-S system and easiness of the decomposition of the response into system parameters that have clear physical meanings is required to understand the limiting factor for Li_2S_2/Li_2S deposition.

3.5. Utilization enhancement for high sulfur loading cells

Although the full understanding of the capacity activation process for higher loading sulfur electrode is not achieved yet, two strategies were found to boost the utilization of high-loading sulfur electrodes in the initial cycles and shorten or eliminate the time required for the capacity recovery.

As it is shown in Figure 4a, it is found that by performing a slow rate discharge of high-loading sulfur electrodes before cycling with higher rate, the high utilization of sulfur capacity in the electrode can be activated much earlier. For electrodes with capacity loading around $2.09\text{-}2.36\text{ mg cm}^{-2}$, the activation process took only 1 cycle after the 0.05C activation process. For the electrodes with similar loading without the low-rate discharge treatment, this process was carried on for more than 20 cycles. The electrodes with high loadings of $4.27\text{-}4.60\text{ mg cm}^{-2}$ experienced an activation process for 15 and 29 cycles to reach a peak capacity of 511 mAh g^{-1} and 440 mAh g^{-1} . In contrast, the two cells with $4.18\text{-}4.38\text{ mg cm}^{-2}$ loadings were not be able to get activated in the first 100 cycles when they were directly cycled at 0.2C (Figure 1c). Figure 4c and 4d updated Figure 1d and Figure 1e by including per area delivered capacity of the 3rd cycle (Figure 4c) and 30th cycle (Figure 4d) from this slow discharge activation test. The intermediate loading cells already recovered to deliver the expected capacity after just 2 cycles. Even for the high loading cells, near full capacity recovery is realized after 30th cycle. Apparently, the 1st low rate discharge helps to enhance the sulfur utilization for the high-sulfur loading electrodes.

The other strategy is to place a conductive interlayer on the sulfur electrode, which has been introduced by Yao et al [22] for Li-S cells with relatively low sulfur loading ($1.5\text{-}2.0\text{ mg cm}^{-2}$). The carbon-coated separator is incorporated in the Li-S cells with sulfur loading higher than 2.36 mg cm^{-2} in our study. The result is shown in Figure 4b. It can be seen in this case the electrodes with intermediate loading actually surpassed the activation process, and both intermediate-loading ($2.36\text{-}2.61\text{ mg cm}^{-2}$) and high-loading ($3.78\text{-}4.07\text{ mg cm}^{-2}$) electrodes achieved much higher maximum sulfur utilization, and even better than the case with 0.05C activation process in Figure 4a. In addition, the cell discharge capacity is recovered and maintained at higher level than the cells without the carbon-interlayer cell design as indicated in Figure 4d. The linear relationship follows a new slope with increased sulfur utilization for all sulfur loading samples, suggesting the possible altering the cell reaction mechanism. The sulfur utilization is further improved from $\sim 25\%$ (with activation) to $\sim 45\%$ at 30th cycle (Figure 3d). This result indicates that cell design factors

can have profound impact on sulfur cell performance and sulfur utilization. More detailed studies in this area are warranted.

The success of these strategies to enhance the sulfur utilization in higher-loading sulfur electrodes probably can give some indications on the mechanism behind their low initial sulfur utilization and the capacity activation process. The carbon-coated separator cell result suggests that the contact resistance or the electron conduction from the current collector to the reaction front is probably not a crucial factor in limiting $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ deposition in the initial cycles. This can be understood by noting that electrons also have to traverse the electrode itself before it can induce $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ deposition on the carbon network coated on the separator. Indeed, a separate experiment was done where the carbon-coated interlayer is prevented from directly contacting the bottom stainless steel current collector of the coin cell, but there is no difference in the enhancement effect from the case when the direct contact was allowed. It is probably more reasonable that charge transfer resistance is more important since the extra carbon network on the carbon-coated separator naturally introduces more reaction sites for $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ deposition. The success of the low-rate discharge indicates the activation mechanism is related to sulfur dissolution, re-deposition and redistribution during the cycling. A large scale sulfur “breathing” induced by the slow-rate discharge probably can profoundly facilitate the recovery process.

Conclusion

In this work, we revisited the sulfur loading effect on Li-S battery performance by using galvanostatic charge and discharge of sulfur electrodes in the capacity loading range of 0.5-7.5 mAh cm^{-2} . It is shown that sulfur loading has a major impact on the initial utilization of loaded capacity and the evolution of capacity in extended cycling. As sulfur loading is increased to beyond 3 mAh cm^{-2} , the sulfur utilization of the 1st discharge starts to decrease significantly. However, this initial low efficiency can gradually recover to be in line with lower loading electrodes as cycling proceeds until the loading reaches $\sim 7 \text{ mAh cm}^{-2}$, in which case low sulfur utilization is maintained throughout the 100 cycles (with the exception of a few spikes). Based on a scrutiny of the voltage-capacity profile, ex-situ SEM, and EIS study, it has been

demonstrated that the difficulty to initiate the deposition of $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ is the main reason for the low initial utilization of higher loading sulfur electrodes, although this problem can be partially alleviated with extended cycling for electrodes with lower loading in this category. Because of the limitation of EIS study, it is still not fully understood which step of the reaction process is the main limiting factor for higher loading electrodes and why this rate determining step can be gradually accelerated with cycling for certain loadings. However, the boost of sulfur utilization brought about by the use of a carbon-coated interlayer indicates charge transfer resistance is more likely the rate-determining step. In addition, the use of a slow initial discharge was also found to be helpful in enhancing the sulfur utilization in heavily loaded sulfur electrodes, which suggests sulfur redistribution during cycling is probably the reason behind the capacity recovery for electrodes with intermediate loadings.

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Captions:

Fig. 1. (a) Electrode thickness and sulfur loading, (b) loading capacity as a function of coating gap, (c) cycling performance of sulfur electrodes with different loading, (d) 1st cycle areal discharge capacity as a function of sulfur loading, (e) 30th cycle areal discharge capacity as a function of sulfur loading, and (f) Coulombic efficiency as a function of sulfur loading for selected cycles.

Fig. 2. (a) First discharge voltage profile of sulfur electrodes with different loading, (b), (c) and (d) discharge voltage profile of selected cycles of sulfur electrodes with 1.28, 2.23 and 4.18 mg cm⁻² loading, (e) SEM micrographs of sulfur electrodes with loading ~2.36 mg cm⁻² at different stages of cycling, and (f) EDS spectrum of samples in (e), inset is the S/C peak maximum ratio plotted with cycle number.

Fig. 3. (a) and (b) Nyquist plots of sulfur electrode with loading 0.77 and 2.62 mg cm⁻² respectively during the first cycle, (c) equivalent circuit used for fitting and comparison between fitted results and original data for a specific curve, and (d)-(g) capacity, contact resistance R_2 , charge transfer resistance R_1 , electrolyte resistance R_3 as a function of cycle number for the two cells in (a) and (b).

Fig. 4. (a) Capacity evolution for electrodes with higher sulfur loading with low rate 1st discharge activation, (b) capacity evolution for electrodes with higher sulfur loading with a carbon interlayer cell design, (c) initial areal discharge as a function of sulfur loading and (d) 30th cycle areal discharge capacity as a function of sulfur loading.

Figures 1a to 1f

Figures 2a to 2f

Figures 3a to 3g

c)

d)

Figures 4a to 4d