Letter

TiS2-Polysulfide Hybrid Cathode with High Sulfur Loading and Low Electrolyte Consumption for Lithium-sulfur Batteries

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TiS$_2$-Polysulfide Hybrid Cathode with High Sulfur Loading and Low Electrolyte Consumption for Lithium-sulfur Batteries

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Abstract

Sulfur cathodes have a high theoretical capacity of 1,675 mAh g^{-1}, making the lithium-sulfur batteries a promising technology for future energy-storage devices. However, their commercial viability is faced with challenges arising from intrinsic electrochemical instabilities and inappropriate cell fabrication parameters. We report here the feasibility of employing TiS_2 as a conductive polysulfide adsorbent, which allows the use of a high amount of electrochemically active polysulfides in building a TiS_2-polysulfide hybrid cathode. The hybrid cathode exhibits long cycle stability at a C/5 rate over 200 cycles with a high areal capacity and energy density of, respectively, 10 mAh cm^{-2} and 20 mWh cm^{-2}, exceeding those of commercial $LiCoO_2$. Such an enhanced electrochemical performance is obtained in cells with a high sulfur content (65 wt.%), high sulfur loading (12 mg cm^{-2}), high sulfur mass (12 mg/cathode), and a low electrolyte/sulfur ratio of just 5 µL mg^{-1}.

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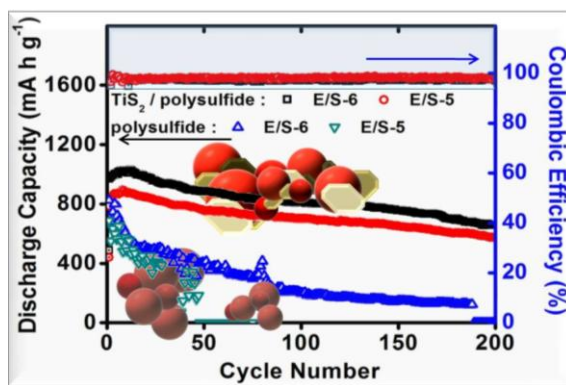
Development of next-generation rechargeable batteries with a higher energy density is crucial for applications in electric vehicles and grid-scale energy storage.[1,2] The replacement of insertion-compound electrodes currently used in commercial lithium-ion batteries with conversion-reaction electrodes offers great promise in producing rechargeable batteries with a higher charge-storage capacity and energy density. One promising example is the lithium-sulfur batteries, as sulfur offers a high theoretical charge-storage capacity of 1,675 mAh g^{-1} at a low-cost with environmental compatibility.[1-3] However, to commercialize the lithium-sulfur technology, its intrinsic limitations, such as low active-material utilization and inferior cycle stability, must be overcome.[2-4] Recently, a growing number of research articles have cautioned[4-6] that the commercial viability of lithium-sulfur cells faces multiple challenges, particularly in terms of commonly-used fabrication parameters that artificially boost the electrochemical performance, including low sulfur loading (< 4.0 mg cm^{-2}), insufficient sulfur content (< 65 wt.% in the whole cathode), and excessive use of electrolyte (electrolyte/sulfur ratios of > 11 µL mg^{-1}).[5-7] As a result, there have been greater efforts devoted to better understanding the fundamental processes involved in lithium-sulfur cells and ways to overcome such challenges. However, there are still a significant gap between the current research and viable lithium-sulfur technology for practical applications.[4-7]

In regards to improving both the electrochemical characteristics and fabrication parameters for a viable lithium-sulfur technology, recent studies have pursued different strategies,

employing novel electrode configurations and cathode materials.[4,8] Improved cathode configurations are needed for a better utilization of the unique lithium-sulfur battery chemistry. Fabricating cells with a three dimensional electrode structure involving an inner conductive matrix helps reduce the cathode resistance caused by the insulating sulfur and additionally creates a reservoir for accumulating polysulfides (Li_2S_{4-8}).[9,10] Polysulfides, which are charge/discharge intermediates formed during the redox reactions of sulfur with lithium ions, can facilitate the reaction kinetics of sulfur cathodes; however, they also have high solubility in the ether-based electrolytes commonly used in lithium-sulfur batteries and as a result tend to easily diffuse out from the cathode.[2,6,10] The irreversible polysulfide relocation causes a series of negative impacts, starting with the loss of active material from the cathode, polysulfide shuttle between the two electrodes, and surface passivation of the anode and cathode.[7-10] Thus, encapsulation of sulfur and polysulfides within a three-dimensional structure improves the electrochemical utilization and stability of the cathode. Moreover, functioning as an active-material reservoir, a three dimensional electrode can be loaded with a high amount of sulfur.[4,9,11]

Several ideal three-dimensional structures have been developed over the past five years. Tables S1 and S2 in the Supporting Information summarize their cell-fabrication parameters with regard to sulfur loading with a unit of "mg cm^{-2}," sulfur content with a unit of "wt.%," and electrolyte/sulfur ratio with a unit of "μL mg^{-1}."[4-7] The resulting sulfur cathodes demonstrate enhancement in sulfur areal loading and areal capacity simultaneously.[7,8,22] However, the lack of

intrinsic improvements in the cathode's charge-transfer capability and polysulfide adsorbent

property leads to insufficient discharge/charge efficiency and low polysulfide retention. These

negative impacts are reflected in the limited rate performance, shortened cycle life, and unstable

Coulombic efficiency. [7-9,11]

Utilizing novel cathode materials is another way of intrinsically increasing the electrode

conductivity and the cell cyclability. Normally, additional carbon is added to the sulfur cathode

as a conductive agent in the range of $10 - 40$ wt.% to realize fast electron transfer.[4,5,12] Recently,

TiS_2, a semi-metal,[13-15] has attracted increasing attention as a conductive agent due to its high

conductivity[13,16,17] as well as its ability to transport lithium ions.[16-18] Recent studies show that

TiS_2 is able to adsorb polysulfides, which benefits the electrochemical stability of the TiS_2-sulfur

hybrid cathode.[17,19] Moreover, TiS_2 is a known cathode material since its first investigation to

demonstrate the concept of rechargeable lithium cells in the 1970s;[13-15] TiS_2 reversibly

intercalates/deintercalates lithium ions at $1.7 - 2.5$ V, which matches the operating voltage range

of lithium-sulfur cells $(1.5 - 3.0$ V).[14,17] Therefore, having TiS_2 as a secondary active material in

sulfur cathodes would provide (i) high conductivity,[13,16-18] (ii) polysulfide-adsorption,[17,19] and (iii)

additional capacity,[13,16-18] suggesting its potential as a hybrid cathode material (see Tables S3 and

S4 of the Supporting Information for the electrochemical characteristics and fabrication

parameters of previous studies on TiS_2/sulfur cathodes).[16-19]

Attracted by the multifunctionality of TiS_2 for improving the performance of sulfur cathodes, we present here a hybrid TiS_2-polysulfide cathode encapsulated within a carbon electrode shell to produce electrochemically stable lithium-sulfur cells. The TiS_2-polysulfide active-material mixture utilizes the advantages of TiS_2 (*i.e*., electronic conductivity, polysulfide-adsorption, and electrochemical activity)[13,16-19] to enable the direct use of a high amount of Li_2S_6 polysulfide catholyte as the primary active material, facilitating a fast reaction kinetics.[4,7,10] Thus, the hybrid cathode delivers high areal capacity and energy density of, respectively, 10 mAh cm^{-2} and 20 mWh cm^{-2} at a C/5 rate. With a carbon electrode shell to demonstrate the good polysulfide retention and an encapsulation of the hybrid active material,[11] the cell demonstrates a long-term cyclability over 200 cycles. Such enhanced electrochemical performances are also reflected by the ability to employ high sulfur content, loading, and mass of, respectively, 65 wt.%, 12 mg cm^{-2}, and 12 mg/cathode with a remarkably low electrolyte/sulfur ratio of just 5 µL mg^{-1}.[5,6,12]
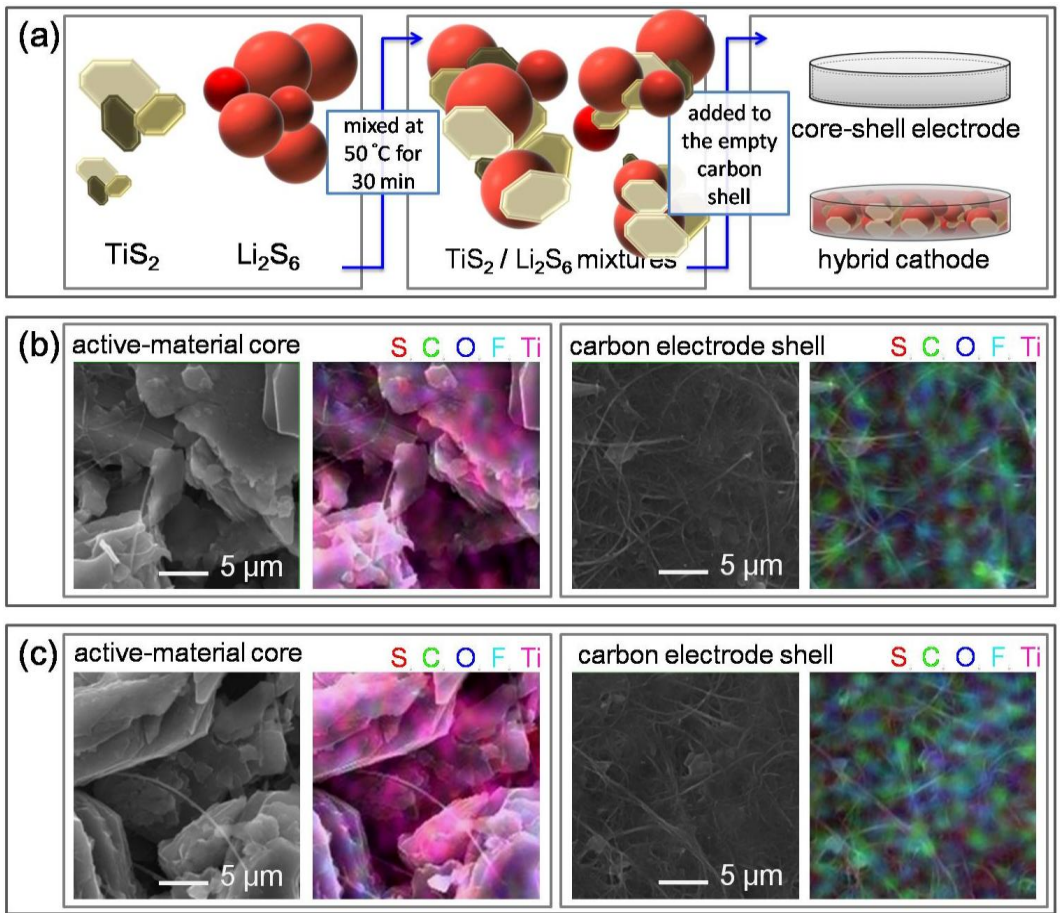
Figure 1. (a) Schematic fabrication process of the hybrid TiS_2-polysulfide cathode. Microstructural analysis with SEM and EDX of the (b) freshly-made cathode and (c) cycled cathode after 200 cycles.

Figure 1a depicts the fabrication process of the hybrid TiS_2-polysulfide cathode. The hybrid active-material mixture, different from the reported TiS_2-sulfur cathodes,[16-19] contained 1.5 mg TiS_2 and 60 μL of 1.0 M Li_2S_6 polysulfide catholyte.[7] The commercial TiS_2 powder was blended with the polysulfide solution at 50 °C for 30 min in a sealed glass vial filled with argon.

The mixture turned into a viscous paste because of the adsorption of polysulfides by TiS_2[17,19] as well as due to the low electrolyte/sulfur ratio of 4.2 μL mg^{-1} employed in the catholyte. The paste was encapsulated in a carbon electrode shell as the hybrid active-material core (Figure S1, see more details in the Supporting Information).[11] This cathode design allowed us to fix the amount of sulfur in each cathode, as well as enabled us to easily detect the appearance of polysulfide diffusion outside the porous carbon electrode shell. We also prepared a control core-shell cathode fabricated with only the polysulfide catholyte as the active-material core in order to demonstrate the effect of TiS_2 in facilitating the electrochemical reactions, stabilizing the polysulfides inside the electrode shell, and contributing additional reversible capacity.

Figures 1b and 1c display the scanning electron microscopy (SEM) images of the freshly-made and cycled hybrid cathodes after 200 cycles, respectively. In addition to the microstructural characterization, elemental analysis was also performed with energy dispersive X-ray spectroscopy (EDX) on the inner active-material core and the outer carbon shell of the hybrid cathode. A comparison of the cathodes before and after cycling reveals very similar microstructures. The corresponding elemental analysis also shows almost the same strong elemental sulfur signals within the electrode shell and the same weak elemental sulfur signals on the outside of the carbon shell. The corresponding EDX analyses reconfirm the almost unchanged elemental signal intensities of the sulfur as well as other elements, including carbon, oxygen, and fluorine before and after cycling (Figure S2).

As a comparison, we also inspected the outer shell before and after cycling of the control core-shell cathodes, which had been fabricated with just a polysulfide core. In contrast to the almost unchanged morphology and elemental distribution of the hybrid TiS_2-polysulfide cathode, the control cathode displayed increasing elemental sulfur intensity on the outer shell after cycling (Figure S3). The polysulfide migration out of the carbon electrode shell indicates the irreversible loss of active material and the possible polysulfide shuttle during cell cycling.[16,18] This comparison provides evidence for the strong polysulfide-adsorption capability of TiS_2,[17,19] which we anticipate will improve the electrochemical performance of the cell.
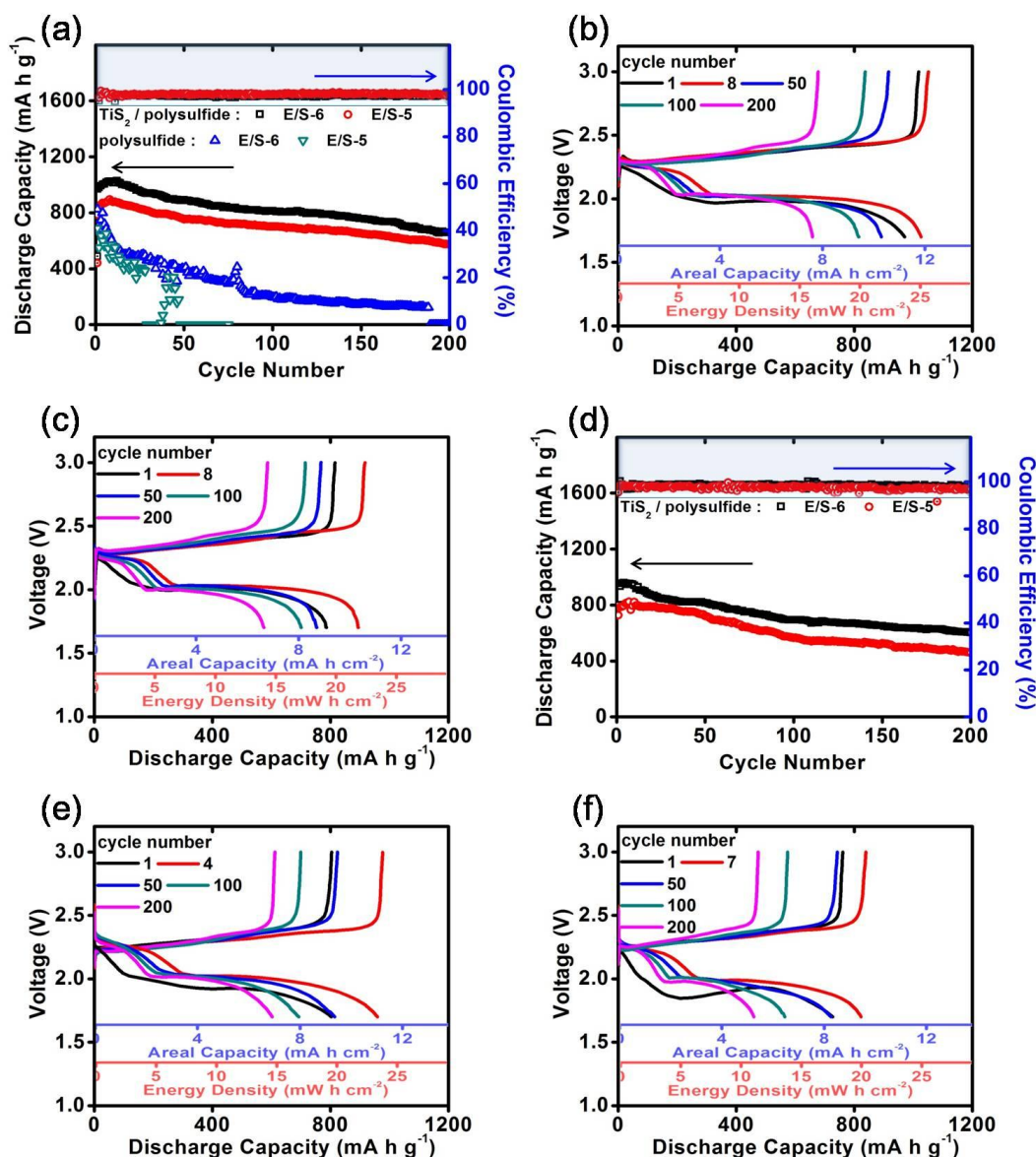
Figure 2. Cell performance of the hybrid cathodes and a control cathode with a sulfur loading of 12 mg cm^{-2}, sulfur content of 65 wt.%, and sulfur mass of 12 mg/cathode at low electrolyte/sulfur ratios of 6 and 5 μL mg^{-1}. (a) Cyclability analysis at C/10 rate and the corresponding discharge/charge curves of the hybrid cathodes with electrolyte/sulfur ratios of (b) 6 and (c) 5 μL mg^{-1}. (d) Cyclability analysis at a C/5 rate and the corresponding discharge/charge curves of the hybrid cathodes with electrolyte/sulfur ratios of (e) 6 and (f) 5 μL mg^{-1}.

We next studied the effect of TiS_2 in enhancing the electrochemical utilization[13,16-18] and

stability[17,19] of the hybrid cathode. **Figure 2** shows the electrochemical performance of lithium-

sulfur cells fabricated with core-shell cathodes containing the hybrid TiS_2-polysulfide core, as

well as the control polysulfide core. The testing cells had low electrolyte/sulfur ratios of 6 and 5

μL mg^{-1}, which are appropriate for demonstrating both the enhanced electrochemical

performance and practical feasibility of the cells.[6,7,12] In Figure 2a, the cells fabricated with the

hybrid cathodes attained high peak charge-storage capacities of 1,030 and 895 mAh g^{-1}

(presented as the red discharge curves in Figures 2b and 2c), respectively, with low

electrolyte/sulfur ratios of 6 and 5 μL mg^{-1}. This implies the hybrid cathodes maintain high

electrochemical utilization along with high sulfur loading, mass, and content under low

electrolyte/sulfur ratios. The cells with electrolyte/sulfur ratios of 6 and 5 μL mg^{-1} also retained

high reversible charge-storage capacities of, respectively, 659 and 575 mAh g^{-1} after 200 cycles

with high capacity-retention rates of 64% in both cases. These favorable features demonstrate the

excellent electrochemical utilization and reversibility of the hybrid TiS_2-polysulfide cathodes

during long-term cycling.

Although the control cells that are also shown in Figure 2a initially had discharge

capacities of 825 and 690 mAh g^{-1} with low electrolyte/sulfur ratios of, respectively, 6 and 5 μL

mg^{-1}, they soon suffered fast capacity fade and unstable Coulombic efficiency, even with $LiNO_3$

added as a co-salt in the electrolyte and catholyte,[20,21] implying extensive polysulfide diffusion

out of the carbon electrode shell (Figures S4 and S5). The diffusing polysulfides cause active-

material loss and polysulfide shuttle, which are reflected in the poor electrochemical reversibility

and efficiency. Furthermore, the irreversible polysulfide relocation gradually causes the

degradation of the cathode and anode, which eventually results in cell failure.[7,10] The

electrochemical inefficiency and instability became even worse as the electrolyte/sulfur ratio

decreased to 5 μL mg^{-1}. Such challenges encountered by the control cathode affirm that the

electrochemical characteristics of the lithium-sulfur cathode are vulnerable to high amounts of

sulfur[4,5,7,9] at low electrolyte/sulfur ratios.[6-9,12] However, as these cell parameters are the most

realistic for viable commercial applications, they should be considered when presenting the

resulting electrochemical characteristics and properties of the cells.[5-8,12]

The significant differences between the hybrid cathode and the control cathode show that

TiS$_2$ advances the redox-reaction capability of high-loading cathodes under low electrolyte/sulfur

ratios. First, we hypothesize that this enhancement is due to the ability of TiS$_2$ to facilitate fast

electron transfer[13,16,17,19] as well as providing pathways for lithium-ion transport in high-loading

cathodes.[16,18] A result of these attributes is reflected in the low polarization and high reversibility

seen in the charge/discharge voltage profiles (Figures 2b and 2c), which enhance and maintain

the high electrochemical utilization of the hybrid cathodes during cell cycling. Second, because

of the high amount of electrochemically active polysulfides and low ratios of electrolyte/sulfur

used in the cathodes, the microstructural analysis of the cycled control cathodes shows an

increasing intensity of elemental sulfur signals detected outside of the electrode shell (Figure S3).

Such affirmative polysulfide diffusion is known to cause unstable cyclability and poor

Coulombic efficiency.[10,20,22] These negative impacts become stronger and threaten the basic cell

function at a lower electrolyte/sulfur ratio of 5 μL mg^{-1} (Figures S4 and S5). In contrast, although

the hybrid cathodes contained the same amount of polysulfides and low electrolyte/sulfur ratios

as the control cathodes, the polysulfide-adsorption capability of TiS_2 stabilizes the

electrochemically active material within the electrode shell,[16-19] resulting in an improved

electrochemical efficiency and reversibility of the hybrid high-loading cathodes (Figures 2a – 2c).

Furthermore, the TiS_2, as a conductive polysulfide adsorbent,[13,16-19] might also provide the

hybrid cathode with improved high cycling-rate performance.[15,19]

We analyzed the rate capability of the hybrid cathodes at a fast C/5 rate for 200 cycles

with the same cell parameters. Figure 2d depicts the peak charge-storage capacities of the hybrid

cathodes, attaining 959 and 823 mA hg^{-1} (presented as the red discharge curves in Figures 2e and

2f) at electrolyte/sulfur ratios of, respectively, 6 and 5 μL mg^{-1}. The capacity value of the cell

made with an electrolyte/sulfur ratio of 6 μL mg^{-1} translates into a high areal capacity and energy

density of, respectively, 11 mAh cm^{-2} and 23 mWh cm^{-2}. With a more promising

electrolyte/sulfur ratio of 5 μL mg^{-1}, both values remained high at 10 mAh cm^{-2} and 20 mWh cm^{-2}, respectively, exceeding the areal-capacity (4 mAh cm^{-2}) and energy density (10.08 mWh cm^{-2})

of commercial $LiCoO_2$ cathodes.[7,12,23] The corresponding reversible capacities after 200 cycles at

electrolyte/sulfur ratios of 6 and 5 μL mg^{-1} were, respectively, 605 and 466 mAh g^{-1}. These

results show that the capacity-retention rates stayed at as high as 63% and 57%, as the cycling

rate doubled from C/10 to C/5 rate. High capacity retention at a high cycling rate further suggests

that the conductive nature and polysulfide-adsorption capability of TiS_2 succeeds in boosting the

high-rate cyclability of the hybrid cathode. In contrast, the control cathodes failed to exhibit

analyzable high-rate performances (Figures S6).
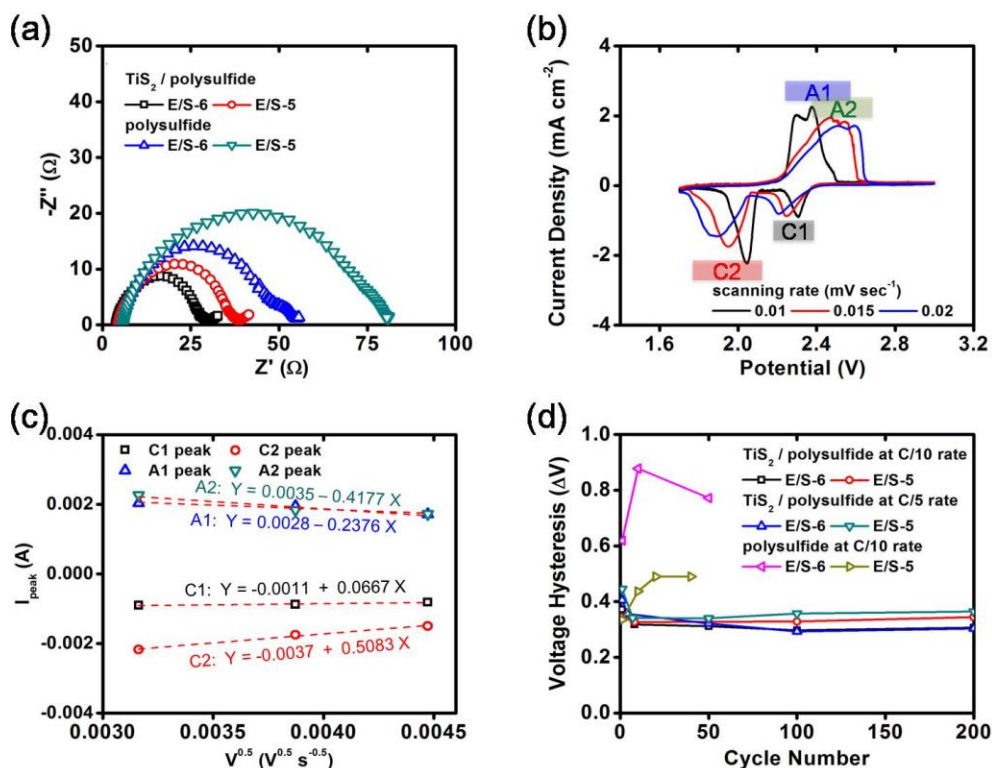
Figure 3. Electrochemical characterization of the hybrid cathodes and control cathodes with a

sulfur loading of 12 mg cm^{-2}, sulfur content of 65 wt.%, and sulfur mass of 12 mg/cathode at low

electrolyte/sulfur ratios of 6 and 5 µL mg^{-1}, including (a) impedance of the freshly-made

cathodes, (b) CV curves, and (c) $D_{(Li+)}$, and (d) Δ V.

Figure 3a compares the impedances of the hybrid cathodes and controls, illustrating that

the incorporation of conductive TiS_2 reduces the impedance of the high-loading sulfur cathode

by about half. Figure 3b displays the cyclic voltammograms (CV) of these cells, scanned at

$0.01 - 0.02$ mV sec^{-1}. The CV plot illustrates the typical two-step lithiation/delithiation reactions

of sulfur.[10,22,23] The two cathodic peaks depict the reduction reactions of sulfur to polysulfides

(C1) and polysulfides to sulfides (C2). The overlapping anodic peaks (A1, A2) represent the

oxidation reactions from sulfides to polysulfides and sulfur. The scanning peaks obtained by the

rate-dependent CVs were calculated *via* the Randles-Sevick equation, $I_{peak} = 268600 \times e^{1.5} \times$

$A \times D_{Li^+}^{0.5} \times Concn._{Li} \times rate^{0.5}$, which is used for studying the lithium-ion diffusion

coefficient (D_{Li}^+, Figure 3c).[24,25] The parameters in the calculation include the peak current

(I_{peak}), the number of electrons (e), the cathode area (A), the concentration of lithium ions in the

electrolyte ($Concn._{Li}$), and the scanning rate (rate).[24,25] In our system, the calculated lithium-ion

diffusion coefficient (D_{Li}^+) values were 2.3×10^{-9} cm^2 s^{-1} (C1), 1.3×10^{-7} cm^2 s^{-1} (C2), 2.9×10^{-9}

cm^2 s^{-1} (A1), and 8.8×10^{-8} cm^2 s^{-1} (A2), which are in the range reported in the literature ($10^{-8} -$

10^{-9} cm^2 s^{-1}).[15,24,25] This suggests that TiS$_2$ enables the high-loading cathode to maintain smooth

lithium-ion diffusion with a low electrolyte/sulfur ratio.[15,18,19]

However, as shown in Figure S7, the control cells had difficulty in achieving the

corresponding comparison due to poor reversibility and sluggish redox kinetics that were

attributed to the severe polysulfide diffusion and low conductivity of the high-loading

polysulfide control cathodes. The incomplete charge reactions become severe as the scanning

rates increase from 0.01 to 0.02 mV s^{-1}. The results evidence that the unwanted polysulfide

shuttle occurred in the control cells.[7,10] The sharp differences in the rate-dependent CV analyses

affirm the significant improvements of the electrochemical efficiency and reversibility brought about by the inclusion of TiS_2 in the polysulfide catholyte. The enhanced ion-/electron-transfer capabilities of the hybrid cathodes improve the reaction kinetics of the cells and also their electrochemical stability.[10,22,23,25] Thus, the hybrid cathodes display a reasonable low voltage hysteresis (Δ V) at C/10 and C/5 rates for 200 cycles (Figure 3d); while the control cells suffer from high polarization initially and rapid polarization after just 50 cycles (Figure S5).

After demonstrating the importance of the fast charge-transfer and polysulfide-adsorption capabilities of TiS_2, we investigated how it could contribute an additional 240 mAh g^{-1} (the theoretical charge-storage capacity of TiS_2)[15-19,26] to the resulting hybrid cathode. The comparison of the initial capacities of the cells fabricated with the hybrid and control cathodes at C/10 rate indicates that the hybrid cathodes offer an additional 145 mAh g^{-1} and 97 mAh g^{-1} charge-storage capacities at electrolyte/sulfur ratios of, respectively, 6 and 5 μL mg^{-1}. This finding suggests that the electrochemical activity of TiS_2 increases the total capacity,[15-19,26] though the conductivity and polysulfide-adsorption capability of TiS_2 might also be involved in the capacity increase by way of providing fast reaction kinetics.[7,18,23]

In order to clarify this mechanism, we compared the capacities of the hybrid cathodes obtained when the cycling rates were increased from C/10 to C/5 and observed an 8% capacity decrease. The slight capacity decrease might result from the high active-material loading and content used in the cathodes,[5,11,12] which inevitably increases the polarization at a high cycling rate.[7,11,16,18] Another reason causing the decreased capacity might be the insufficient utilization of

TiS_2 because a C/5 rate based on sulfur is equal to a much faster cycling rate of 1.4C for TiS_2 with the same active-material masses.[15,17] At such a high rate, TiS_2 offers less than half of its theoretical capacity (Figures S8), which has been previously observed.[15,17,26] As we further consider the relatively high amounts of sulfur used in the cathodes with optimized fabrication parameters, the cycling rate for TiS_2 effectively becomes even faster and the resistance brought about by the polysulfides also increases.[17,19] This result may imply possible challenges in fully realizing the third advantage of TiS_2 in terms of gaining additional charge-storage capacity at high cycling rates.[15,17,19] Overall, even though the electrochemical activity of TiS_2 may not be obvious in our high-loading hybrid cathodes, the fast charge-transfer and strong polysulfide-adsorption capability of TiS_2[16-19] allows the hybrid cathodes to operate for long cycle numbers in parallel with high sulfur loading, content, and mass at low electrolyte/sulfur ratios.

In conclusion, the hybrid TiS_2-polysulfide cathode provides a facile and practical solution for ameliorating the intrinsic electrochemical instability/inefficiency of lithium-sulfur cells, as well as circumventing the inappropriate fabrication parameters, such as low amounts of sulfur and excessive electrolyte, used in Li-S cells. The TiS_2-polysulfide hybrid cathode features TiS_2 functioning as a conductive polysulfide adsorbent in the electrochemically active polysulfide catholyte so as to enhance the electrochemical efficiency and stability of the primary active material. The electrochemically stable TiS_2-polysulfide hybrid is encapsulated within a carbon electrode shell to demonstrate its superior polysulfide stabilization and high-loading capacity. The resulting TiS_2-polysulfide hybrid cathodes exhibit a high areal capacity of 10 mAh cm^{-2} and

energy density of 20 mWh cm^{-2} and demonstrate a long-term cyclability of 200 cycles while also realizing a high sulfur loading (12 mg cm^{-2}), content (65 wt.%), and mass (12 mg/cathode) with a low electrolyte/sulfur ratio of 5 μL mg^{-1}.

ASSOCIATED CONTENT

Supporting Information.

Experimental methods, SEM/EDX inspection methods, EDX spectra, electrochemical analysis of control cells, and electrochemical analysis of TiS$_2$. Tables summarizing all three-dimensional cathode research articles reporting a high amount of sulfur and low electrolyte volume and tables summarizing all Li-S research articles reporting TiS$_2$-sulfur cathode.

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Notes

The authors declare no competing financial interest.

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