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Interaction of TiS_2 and Sulfur in Li-S Battery System

Ke Sun,^a Qing Zhang,^b David C. Bock,^c Xiao Tong,^d Dong Su,^d Amy C. Marschillok,^{b,e,*} Kenneth J. Takeuchi,^{b,e,*} Esther S. Takeuchi,^{b,c,e,**} and Hong Gan^{a,z}

^aSustainable Energy Technologies Department, Brookhaven National Laboratory, Upton, New York 11973, USA

^bDepartment of Materials Science and Engineering, Stony Brook University, Stony Brook, New York 11794, USA

^cEnergy Sciences Directorate, Brookhaven National Laboratory, Upton, New York 11973, USA

^dCenter for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York 11973, USA

^eDepartment of Chemistry, Stony Brook University, Stony Brook, New York 11794, USA

With the ability to adsorb polysulfide, electronically conductive and electrochemically active TiS_2 is an effective multifunctional cathode additive to improve Li-S battery cycling performance. By using X-ray Photoelectron Spectroscopy (XPS), direct evidence is obtained to demonstrate the strong interaction between Li-polysulfide and TiS_2 . The observation of Li signature on Li_2S_8 treated TiS_2 proves that the TiS_2 possesses the ability to adsorb Li-polysulfides species on its surface. An electron density transfer from Ti to Li and S is identified based on the positions of the peaks in the XPS spectrum before and after the interaction, which is consistent with the theoretically predicted polysulfide- TiS_2 interaction models in the literature. TiS_2 sample with 2.5x higher BET surface area is obtained by milling the raw TiS_2 particles and used as cathode additive in the sulfur electrode. In the presence of TiS_2 additive, long cycle life and improved sulfur utilization of Li-S cells under high rate discharge are demonstrated. In addition, we find that a uniform TiS_2 distribution in the sulfur- TiS_2 hybrid electrode is vital in determining its effectiveness in enhancing the performance of sulfur electrodes. Therefore, processing method and condition should be very important considerations in future development of sulfur electrodes with TiS_2 additive.

The Li-S battery is one of the major frontiers in energy storage research. It has been well known for its high theoretical gravimetric capacity 1675 mA g^{-1} and energy density 2600 kWh kg^{-1} , and this can hardly be matched by any of the current Li-ion battery chemistries.^{1,2} However, the tendency for partially reduced sulfur to form soluble polysulfides that lead to fast capacity fade and low coulombic efficiency, the insulating nature of sulfur and Li_2S , and the considerable volume change $\sim 80\%$ between these two end products all put inevitable constraints on electrode architecture and cell level designs in attempts to approach or achieve these appealing theoretical values.¹⁻³

Based on the discoveries in the last 10 years it has been found that cathode architecture is vital and active sulfur must be either pre-confined into a conductive host least permeable to polysulfide dissolution⁴⁻⁷ or an strongly polysulfide binding compound should be dispersed into the cathode network,⁸⁻¹³ otherwise both the utilization of sulfur and cycling performance will suffer. Furthermore, the combination of the above two approaches is also reported.^{14,15} Generally these measures increase the inactive component ratio and compromise energy density.

Recently, it has been found that inclusion of electronically conductive TiS_2 ¹⁶ into sulfur electrode helps to improve both the cycle life and high rate performance of Li-S cells.¹⁷⁻²⁰ Theoretical and indirect experimental evidences all suggest that TiS_2 potentially have surficial affinity for polysulfides, which make it an ideal mediator for active material loss. More importantly, TiS_2 distinguishes itself from other polysulfide mediators by providing an extra capacity of 239 mAh g^{-1} in the same voltage window of Li-S battery operation and it is highly reversible, which compensates for its own mass and space occupied.

However, the mechanism for polysulfide adsorption by TiS_2 is not yet fully understood, and it also has not been established how to use this compound as an additive in sulfur electrode most efficiently. This work is targeted toward these issues.

Experimental

TiS_2 powder used in this study was obtained from Sigma Aldrich. In order to achieve the highest possible surface interaction between TiS_2 and Li-polysulfides, TiS_2 powder was milled by a McCrone

Micronising Mill to reduce the particle size and increase the specific surface area. The TiS_2 was kept dry with the milling process in a dry room atmosphere with -70°C dew point. Brunauer-Emmett-Teller (BET) surface area was measured on a Quantachrome Nova e3000 Analyzer. In the following study, all TiS_2 mentioned will be the milled TiS_2 . To prepare TiS_2 samples treated with Li-polysulfides, Li_2S_8 solution in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 ratio, by volume) was prepared. 10 mM Li_2S_8 solution is prepared by mixing 4.6 mg Li_2S and 22.4 mg sulfur in DOL:DME 1:1 (v/v) mixed solvent at 55°C under magnetic stirring for 48 hours under Argon inside a glove box (O_2 , $\text{H}_2\text{O} < 0.5 \text{ ppm}$). The final volume of the solution was tuned to be 20 mL. After this preparation, 10 mg of TiS_2 was added to the polysulfide solutions and mixed at room temperature in the same argon-filled glove box for 48 hours. The treated TiS_2 was collected by filtering with a piece of quartz filter paper and remnant liquid solution was absorbed by another piece of dry quartz filter paper.

For XPS measurement, 3 samples were prepared. In addition to the Li_2S_8 treated TiS_2 sample as prepared from above, the two references were solid state Li_2S_8 and TiS_2 powder. Li_2S_8 reference was obtained by removing the solvent from the 10 mM Li_2S_8 solution under vacuum and the obtained solid was then dried on a hot plate at 150°C for 5 hours in the glove box to remove the solvent residue.²¹ The TiS_2 powder reference was milled TiS_2 . The XPS collection was done at a pressure of 1×10^{-8} torr. Carbon was used to calibrate the shift due to charging. An argon-sputtering process was also applied to the 3 samples to remove their surficial layer before another XPS spectrum was collected in order to obtain information of the bulk region.

To re-investigate the additive effect of TiS_2 in sulfur electrodes, constant current discharge-charge tests were used to test electrodes of 3 different compositions, including a sulfur reference, and two S- TiS_2 hybrid electrodes with the same compositions but prepared by different mixing procedures. For the sulfur reference, the composition of the electrode is S:Super C65(carbon black):PVDF = 50:42:8, and for the two S- TiS_2 hybrid electrodes the composition is S: TiS_2 :Super C65(carbon black):PVDF = 50:17:25:8. To make the sulfur reference, sulfur and Super C65 was added to an alumina bowl filled with Al_2O_3 milling media to be ball milled for 12 minutes at 300 rpm, after which PVDF and NMP solvent (9 times the weight of powder) were added to Al_2O_3 bowl, and the mixture was milled at 200 rpm for another one hour before casting. For S- TiS_2 hybrid electrode 1, every component including the NMP solvent was added together to the Al_2O_3 milling

*Electrochemical Society Active Member.

**Electrochemical Society Fellow.

^zE-mail: hgan@bnl.gov

bowl directly to be milled at 200 rpm for 1 hour. For S-TiS₂ hybrid electrode 2, sulfur and TiS₂ were first milled together at 300 rpm for 12 minutes, and then other ingredients were added and the slurry was finally made with the 1-hour 200 rpm milling process. The ball mill machine used in this study was Pulverisette 6 (Lab Synergy). All 3 electrodes were coated with a doctor blade onto an aluminum foil. The electrodes were dried in a fume hood under continuous dry air flow (dew point < -40°C) for 24 hours before it was transferred into an oven to be heated at 50°C for another 24 hours to eliminate residual solvent and moisture. The sulfur loading for all three electrodes is ~1.2 mg cm⁻² and the TiS₂ loading is ~0.4 mg cm⁻² for the two hybrid electrodes. Scanning electron microscopy and energy dispersive spectroscopy (JOEL 7600F) were used to observe the morphology and element distribution in the electrodes before the electrochemical tests. EDS was collected at 15 kV gun bias and emission current of 110 μA. The public domain Java image processing program Image J was used to analyze the distributions of regions where S and Ti were detected in the EDS maps. After spatial calibration using the scale bar from the EDS map, a color threshold and sizing algorithm was applied, resulting in tabular data. 2032 coin cells were assembled by using electrodes prepared above as working electrode and a lithium disk as both counter and reference electrode, with 2 layers of Celgard (2325) separator in between to prevent shorting. Electrolyte used for testing of the Li-ion type cells was LITFSI (1.0 M) dissolved in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 ratio, by volume) obtained from BASF. 1 wt% LiNO₃ was added to the electrolyte to improve Coulombic efficiency. Electrochemical measurements were conducted at room temperature using a Bio-logic (VMP3) battery cycler. Cells were cycled galvanostatically between 1.8 V and 2.6 V versus lithium. The discharge current rates were 1 C and 2 C, and the charging was done at 0.2 C. Every charging also includes a constant voltage step till the current falls below 0.1 C.

Results and Discussion

Polysulfide – TiS₂ interaction.—Several papers have been published on the effectiveness of TiS₂ as a host material or an additive in sulfur or Li₂S electrode.^{17–20} Although the extent of cycle life and rate performance enhancement varies from case to case, almost all of them agree on a same proposed mechanism why TiS₂ is beneficial for high energy density sulfur electrode: the surface of TiS₂ tends to interact strongly with Li-polysulfide species in electrolyte and slows down their outwards diffusion. First principle calculations predict binding energy values of 2.6 eV¹⁸ and 2.92 eV¹⁹ between a Li₂S trimer and a single-layer slab of TiS₂. Recent modeling report also predicts the high binding strength of 1.02 eV between polysulfide Li₂S₆ and TiS₂.²² All these values are considerably higher than values from carbonaceous surface and Li₂S (~0.29 eV). Indirect evidence has also been provided by Reference 18, where in the presence of TiS₂ the dissolution kinetics of Li₂S₄ was observed to be much slower in tetraglyme solvent. However, there has been no direct evidence that polysulfide species is adsorbed onto the TiS₂ surface, and the specific mechanism has not been fully studied yet.

XPS is a technique able to detect most elements in the periodic table and also highly sensitive to the chemical environment and valence state of the detected elements, which can be used to distinguish the presence of the same element in different chemical species. Further, it is also a surface sensitive technique that only analyzes the very top layer of a surface (1–10 nm), which is ideal for studying adsorption phenomena. Indeed, it has been already applied in various cases to provide chemical insights in the study of the interactions between various oxides-based polysulfide mediators and Li-polysulfides.^{9,10} It is therefore again chosen here to help understand the interactions between TiS₂ and Li-polysulfides.

Figure 1a compares the appearance of 5 mM Li₂S₈ solution after 48 hours of storage with and without the presence of TiS₂. 5 mM Li₂S₈ solution is used here because the difference is more dramatic and easier to discern. It is evident that the color of the Li₂S₈ solution with TiS₂ became much lighter when compared with the pure Li₂S₈

solution. This again serves as the evidence that TiS₂ interacts with Li-polysulfides and actively anchors and immobilizes them onto its surface, leading to the reduced Li₂S₈ concentration in the solution. XPS spectrum of TiS₂ recovered from a Li₂S₈ (10 mM)–TiS₂ mixture was collected to further analyze the nature of the interaction. Pure Li₂S₈ and TiS₂ were also studied as references. In the analysis, the main focus is put on Ti2p, S2p, Li1s, and Ti3s. The XPS spectrums of Ti2p peaks of TiS₂ reference, TiS₂ reference sputtered, Li₂S₈-treated TiS₂, Li₂S₈-treated TiS₂ sputtered are shown in Figure 1b. The 4 spectrums are very similar to each other in shape, and all of them can be deconvoluted into 2 pairs of Ti2p_{3/2}/2p_{1/2} spin-orbit doublets. In all spectrums, the two pairs of Ti2p doublets are ascribed to Ti in TiS₂ at lower binding energy and in TiO₂ at higher binding energy. The presence of Ti in TiO₂ environment is probably coming from hydrolysis or oxidation process of TiS₂ when it is exposed to ambience. The peak positions are recorded in Table I. It seems that the peak values are very close to each other. One thing to be noted is that the Ti 2p_{3/2}(TiS₂) is at slightly higher binding energy in Li₂S₈-treated TiS₂ than other cases, suggesting slightly higher electron loss in this case. The XPS spectrums of S2p peaks of Li₂S₈ reference, Li₂S₈ reference sputtered, TiS₂ reference sputtered, Li₂S₈-treated TiS₂, Li₂S₈-treated TiS₂ sputtered are shown in Figure 1c. 3 pairs of S2p_{3/2}/2p_{1/2} spin-orbit doublets were used to fit the Li₂S₈ reference, and 2 pairs for Li₂S₈ reference sputtered. The peak positions are recorded in Table II. For both of them, the 2 doublets at lower binding energies are very close to terminal (S_T⁻¹) and bridging sulfur (S_B⁰) reported in literature,¹⁰ 161.7 eV for S2p_{3/2} (S_T⁻¹) and 163.1 eV for S2p_{3/2} (S_B⁰). The other doublet in Li₂S₈ reference at higher binding energy can be ascribed to SO₃²⁻ species, which might come from the short exposure to ambience during sample transfer. Sputtering process removed this oxidized layer and it was absent in Li₂S₈ reference sputtered. S2p spectrum of TiS₂ reference contains a total of 3 doublets after fitting. The detailed discussion in the literature on S2p XPS spectrum of TiS₂ is limited, and the S2p_{3/2} at 160.60 eV and S2p_{3/2} at 161.35 eV are ascribed to S²⁻ in TiS₂ and S₂²⁻ in TiS₃ environment respectively, according to literature report.²³ The other S2p_{3/2} located at higher binding energy 168.25 eV can be ascribed to SO₄²⁻ species, which should also be the result of exposure of TiS₂ to ambience. The two S2p doublets of TiS₂ reference sputtered and Li₂S₈-treated TiS₂ sputtered are both similar in shape when compared with those of TiS₂ reference at lower binding energies. Their values are recorded in Table II, and S²⁻ in TiS₂ and S₂²⁻ in TiS₃ were used to ascribe the 2 doublets as well in these 2 cases. The peak positions in 2 sputtered TiS₂ samples are very similar, so both of them could be considered to be representative of the sulfur environment in bulk TiS₂. It can be seen in Table II that the peak positions of surface S in non-sputtered TiS₂ reference all shifted to lower binding energies relative to the sputtered TiS₂. This means surface S is gaining more electrons than in the bulk in TiS₂. The fundamental mechanism for this surface effect requires more theoretical elucidation. According to the initial premise of strong interaction between TiS₂ surface and Li-polysulfides, it is naturally expected that XPS spectrum of Li₂S₈-treated TiS₂ is composed of features from S²⁻ in TiS₂, S₂²⁻ in TiS₃, and terminal (S_T⁻¹) and bridging sulfur (S_B⁰) in Li₂S₈. However, although in Figure 1c the S2p spectrum of Li₂S₈-treated TiS₂ is indeed different in shape from other 3 TiS₂ cases, it is not a simple addition of any two spectrums either. There is also some overlap between Li₂S₈-treated TiS₂ and TiS₂ reference or Li₂S₈ reference, but there is a portion of spectrum at low energy (~160 eV) that does not overlap with any other spectrums. Currently the best-fit result is still coming from the use of two doublets, and the peak positions are recorded in Table II. Apparently, there is an additional shift to lower binding energy values in this case, indicating that the surface sulfur species on TiS₂ is even gaining more electrons after TiS₂ being treated with Li₂S₈ solution.

Li1s spectra of the un-sputtered and sputtered Li₂S₈ references are very similar, where both of them show a single peak at 55.5 eV, very similar to one of the few prior results reported on Li1s XPS spectrum in Li-polysulfides.²⁴ Li1s is not detected on TiS₂ reference, TiS₂ reference sputtered, Li₂S₈-treated TiS₂ sputtered. However,

Figure 1. (a) Photographs of 5 mM Li_2S_8 solution with and without treatment of TiS_2 after 48 hours of storage. (b)-(d) $\text{Ti}2p$, $\text{S}2p$, and $\text{Li}1s$ ($\text{Ti}2s$) XPS spectra and fitting of Li_2S_8 reference, TiS_2 reference, and Li_2S_8 treated TiS_2 sample. The spectra from sputtered samples are also shown. Color scheme: Red, original data; green, blue and purple, fitted individual peak or $2p_{3/2}/2p_{1/2}$ spin-orbit doublets; black, sum of all fitted peaks; yellow, fitted background.

Table I. XPS binding energy (eV) of $\text{Ti}2p$.

	Peak1	Peak2	Peak3	Peak4
TiS_2 reference	456.27 $\text{Ti}(\text{TiS}_2)$ $2p_{3/2}$	458.85 $\text{Ti}(\text{TiO}_2)$ $2p_{3/2}$	462.07 $\text{Ti}(\text{TiS}_2)$ $2p_{1/2}$	464.66 $\text{Ti}(\text{TiO}_2)$ $2p_{1/2}$
TiS_2 reference Sputtered	456.27 $\text{Ti}(\text{TiS}_2)$ $2p_{3/2}$	458.71 $\text{Ti}(\text{TiO}_2)$ $2p_{3/2}$	462.07 $\text{Ti}(\text{TiS}_2)$ $2p_{1/2}$	464.51 $\text{Ti}(\text{TiO}_2)$ $2p_{1/2}$
Li_2S_8 -treated TiS_2	456.32 $\text{Ti}(\text{TiS}_2)$ $2p_{3/2}$	458.74 $\text{Ti}(\text{TiO}_2)$ $2p_{3/2}$	462.12 $\text{Ti}(\text{TiS}_2)$ $2p_{1/2}$	464.54 $\text{Ti}(\text{TiO}_2)$ $2p_{1/2}$
Li_2S_8 -treated TiS_2 sputtered	456.24 $\text{Ti}(\text{TiS}_2)$ $2p_{3/2}$	458.50 $\text{Ti}(\text{TiO}_2)$ $2p_{3/2}$	462.00 $\text{Ti}(\text{TiS}_2)$ $2p_{1/2}$	464.30 $\text{Ti}(\text{TiO}_2)$ $2p_{1/2}$

Table II. XPS binding energy (eV) of S2p.

	Peak1	Peak2	Peak3	Peak4	Peak5	Peak6
Li ₂ S ₈ reference	161.85	163.05	163.3	164.45	167.25	168.45
Li ₂ S ₈ reference Sputtered	S _{terminal} 2p _{3/2} 161.55	S _{terminal} 2p _{1/2} 162.75	S _{Bridging} 2p _{3/2} 163.3	S _{Bridging} 2p _{1/2} 164.5	S(SO ₃ ²⁻) 2p _{3/2}	S(SO ₃ ²⁻) 2p _{1/2}
TiS ₂ reference	S _{terminal} 2p _{3/2} 160.60	S _{terminal} 2p _{1/2} 161.35	S _{Bridging} 2p _{3/2} 161.80	S _{Bridging} 2p _{1/2} 162.60	168.25	169.45
TiS ₂ reference Sputtered	S(TiS ₂) 2p _{3/2} 160.90	S(TiS ₃) 2p _{3/2} 161.80	S(TiS ₂) 2p _{1/2} 162.10	S(TiS ₃) 2p _{1/2} 163.00	S(SO ₄ ²⁻) 2p _{3/2}	S(SO ₄ ²⁻) 2p _{1/2}
Li ₂ S ₈ -treated TiS ₂	S(TiS ₂) 2p _{3/2} 160.47	S(TiS ₃) 2p _{3/2} 160.95	S(TiS ₂) 2p _{1/2} 161.65	S(TiS ₃) 2p _{1/2} 162.20	168.55	169.75
Li ₂ S ₈ -treated TiS ₂ sputtered	S 2p _{3/2} 160.90	S 2p _{3/2} 162.00	S 2p _{1/2} 162.10	S 2p _{1/2} 163.20	S(SO ₄ ²⁻) 2p _{3/2}	S(SO ₄ ²⁻) 2p _{1/2}
	S(TiS ₂) 2p _{3/2}	S(TiS ₃) 2p _{3/2}	S(TiS ₂) 2p _{1/2}	S(TiS ₃) 2p _{1/2}		

240 presence of Li1s on Li₂S₈-treated TiS₂ is very clear. This directly
 241 proves that TiS₂ surface does have a strong interaction with Li-
 242 polysulfides and adsorb lithium-containing species. After sputtering,
 243 the Li1s peak disappeared due to the surface species removing. Ti3s
 244 peaks are very close to Li1s in energy and they are also shown in Fig-
 245 ure 1d. All of them can be fitted with two peaks, one corresponding to
 246 TiS₂ and the other to TiO₂, in a manner similar to the way Ti2p was
 247 fitted. Li1s and Ti3s peak positions are listed in Table III, it can be seen
 248 that Li1s experiences a shift to lower binding energy in Li₂S₈-treated
 249 TiS₂ compared to Li₂S₈ reference samples but Ti3s shift to a higher
 250 value compared to all the other 3 TiS₂ samples. The shift in Ti3s is
 251 in the same direction with Ti2p observed in Table I, but the extent of
 252 shifting is much more significant.

253 Based on the overall observation, the presence of Li on Li₂S₈
 254 treated TiS₂ is the only direct evidence that TiS₂ actually adsorb
 255 Li-polysulfides. However, the adsorbed Li-polysulfides is no longer
 256 in the form of original Li₂S₈. Because of the lack of existed XPS
 257 data base or literature results it is still difficult to fully identify the
 258 form of Li-polysulfides. Nonetheless, the above results can give a
 259 preliminary picture of what is happening in this system. From 1d,
 260 Li1s peak is shifted toward lower binding energy levels compared
 261 with Li₂S₈ references, indicating Li is gaining electron density after
 262 the interaction; both Ti2p and Ti3s corresponding to TiS₂ in TiS₂
 263 sample, especially Ti3s, are shifted toward higher binding energies
 264 after Li₂S₈ treatment, which suggests that Ti goes to higher oxidation
 265 state after the interaction with Li₂S₈; S2p signal of Li₂S₈ treated
 266 TiS₂ is difficult to fully deconvolute because of the interference of
 267 TiS₂'s own S2p peaks, but globally the S2p peaks are shifted toward
 268 lower binding energy levels in Li₂S₈ treated TiS₂ than the references,
 269 indicating electron gain by sulfur species in this sample, which can be
 270 S from TiS₂ itself or more likely from adsorbed polysulfide species.
 271 The sputtering experiment provides additional insight of the adsorbed
 272 species. For the polysulfide treated TiS₂ sample, sputtering removes
 273 Li1s signal. Spontaneously the S2p signal intensity near 160.9 eV is
 274 also reduced, resulting in the S2p peak shape similar to the untreated
 275 TiS₂ reference sample – indicating the removed surface species is
 276 composed of lithium and sulfur element. By removing the surface
 277 species, the Ti2p peak intensity near 459.2 eV and the Ti3s peak
 278 intensity near 61.7 eV also decrease and the overall shape of the Ti2p
 279 and Ti3s signals become very similar to the TiS₂ reference sample –
 280 suggesting the absence of the surface species interaction. Therefore,

the net effect of TiS₂-Li-polysulfide interactions is that there is a
 certain amount electron transfer from Ti on TiS₂ toward Li of adsorbed
 Li-polysulfides and S of TiS₂ itself or adsorbed Li-polysulfides. In the
 ab initio simulations,¹⁹ the reason for the enthalpy reduction (positive
 binding energy) from Li₂S-TiS₂ interaction is mainly ascribed to the
 Li-S interaction (between the Li atoms in Li₂S and S atoms in TiS₂)
 and S-S interaction (between the S atoms in Li₂S and S atoms in
 TiS₂). Reference 22 provides similar interaction model between TiS₂
 and polysulfide Li₂S₆, except that the sulfur in the polysulfide chain
 does not directly interact with the sulfur on the TiS₂ surface – therefore
 the polysulfide chain will have net gain of electrons due to the strong
 interaction between lithium ion and the sulfur in TiS₂ from the TiS₂
 surface. The difference in the predicted behavior between Li₂S and
 Li₂S₆ is probably associated with the ability of charge delocalization
 in long chain polysulfide, S₆²⁻ vs. a single-atom sulfide S²⁻. Our
 XPS study is in good agreement with the theoretical prediction and
 supports the theorem that Li and S species are actively participating
 in the interaction, besides it further marks out the critical role Ti in
 TiS₂ plays in the process.

**Optimization of TiS₂ additive for sulfur-TiS₂ hybrid cell
 performance.**—The above experiment and discussion provide further
 evidence to the Li-polysulfide adsorption effect of TiS₂ additive. Since
 it is clear now that this is completely a surface phenomenon, it is ex-
 pected that the total TiS₂ surface available for polysulfide adsorption
 will determine the effectiveness of TiS₂ additive in enhancing the rate
 capability and cycle life of sulfur electrode. The apparent indication
 from this is that high specific area TiS₂ should be always preferred
 when it is chosen to be the additive for sulfur electrode. It is found
 that grinding can be used to effectively decrease the particle size of
 TiS₂ and increase its specific surface area. Micronizing milling effec-
 tively breaks the TiS₂ particles (Figure 2) and increases the surface
 area of the material. According to BET surface area measurements,
 the surface area of the milled TiS₂ is 9.4 m² · g⁻¹, while the raw TiS₂
 material has a surface area of 3.7 m² · g⁻¹.

In the effort to apply the milled TiS₂ as additive to sulfur elec-
 trode, it was found that uniform distribution of the TiS₂ particles in
 the electrode network and the breakup of the TiS₂ agglomerations are
 of the same significance in order to fully utilize its potential as an ad-
 sorptive agent. Figures 3a–3c shows the SEM micrographs of a sulfur
 electrode, sulfur-TiS₂ electrode 1 made by method 1, and sulfur-TiS₂

Table III. XPS binding energy (eV) of Li1s and Ti3s.

	Peak 1	Peak 2	Peak 3
Li ₂ S ₈ reference	55.55 Li 1s		
Li ₂ S ₈ reference Sputtered	55.55 Li 1s		
TiS ₂ reference		59.31 Ti(TiS ₂) 3s	61.61 Ti(TiO ₂) 3s
TiS ₂ reference Sputtered		59.38 Ti(TiS ₂) 3s	61.56 Ti(TiO ₂) 3s
Li ₂ S ₈ -treated TiS ₂	55.10 Li 1s	59.75 Ti(TiS ₂) 3s	61.95 Ti(TiO ₂) 3s
Li ₂ S ₈ -treated TiS ₂ sputtered		59.45 Ti(TiS ₂) 3s	61.70 Ti(TiO ₂) 3s

Figure 2. SEM image of raw TiS_2 (a) and (b), and Micronized-milled TiS_2 (c) and (d).

electrode 2 made by method 2, along with the corresponding sulfur and Ti EDS mapping. Visual inspection of the EDS maps suggests that the distribution is more uniform in sulfur- TiS_2 electrode 2 than in sulfur- TiS_2 electrode 1. As a means of quantifying the uniformity of the electrode components, the area distributions of S and Ti regions detected in the EDS maps were calculated using Image J software.²⁵ The entire EDS map was analyzed in each case. A color threshold was applied in order to distinguish regions where S or Ti was detected, and a sizing algorithm was used to generate tabular data. To illustrate the differences between the samples, the data for regions where S or Ti was detected were sorted by size and compartmentalized in bins of $0.01-1 \mu\text{m}^2$, $1-10 \mu\text{m}^2$, $10-100 \mu\text{m}^2$, and $100-1000 \mu\text{m}^2$. The histograms indicate that for S EDS maps, the S control electrode has the most uniform distribution of S in the electrode, with most S detected in regions $1-100 \mu\text{m}^2$ in area. Between the two TiS_2 electrodes, preparation method 2 resulted in a more even distribution of S to a small extent (Figure 4a). Ti signal is a better indicator of TiS_2 distribution since it is the only Ti containing compound in the electrode, and as expected the differences in TiS_2 distribution are more apparent from analysis of the Ti EDS maps (Figure 4b). For electrodes prepared using method 1, a significant fraction of Ti detected (23%) was contained in regions $100-1000 \mu\text{m}^2$ in area. In contrast, 100% of Ti regions in the electrode prepared using method 2 were below $100 \mu\text{m}^2$ in area,

Figure 3. (a)-(c) SEM images and corresponding EDS mapping (S, Ti) of sulfur electrodes, S- TiS_2 electrode 1 and S- TiS_2 electrode 2, respectively. Scale bar = $10 \mu\text{m}$.

Figure 4. Area distributions of (a) S regions and (b) Ti regions detected in EDS maps from Figure 3.

Figure 5. (a) 1st discharge and charge voltage profiles of sulfur and two different S-TiS₂ electrodes at 1 C. (b) Discharge and charge voltage profiles of sulfur and two different S-TiS₂ electrodes at 2 C, corresponding to cycle 3 in (c). (c) Cycling performance of 3 different electrodes at 2 C for 200 cycles. (d) Long-term cycling performance of sulfur electrode and S-TiS₂ electrode 2 cycled at 1 C for 500 cycles, 0.2 C discharge was applied every 50 cycles starting from 51st cycle, corresponding to the intermittent capacity spikes.

with the majority (45%) between 1–10 μm^2 . Accordingly, the EDS maps indicate a more evenly distributed and uniform distribution of TiS₂ for electrodes prepared using method 2. Method 2 utilized a high speed ballmilling step of sulfur and TiS₂ before the other ingredients were added for slurry mixing, whereas in method 1 everything was added together for a single-step slurry mixing. Thus, the processing condition does have a great impact on the final distribution of TiS₂ in the composite electrodes.

The influence of the TiS₂ distribution on the performance of sulfur-TiS₂ hybrid electrode can be clearly seen in Figures 5a–5c. Figure 5a and Figure 5b are representative discharge and charge profiles of the 3 different electrodes at 1 C and 2 C rates in initial cycles, respectively. At these two rates, sulfur-TiS₂ electrode 2 exhibits clear advantage over sulfur control electrodes by showing a less voltage polarization and a higher total capacity delivered, especially at 2 C rate. However, the advantage of sulfur-TiS₂ electrode 1 over sulfur control electrode is not very clear in the initial cycles. The charging in Figures 5a and 5b were performed at the lower rate 0.2 C to ensure full recharge for all cells, and no obvious difference in polarization was observed. Based on the cycling performance shown in Figure 5c, both sulfur-TiS₂ electrodes show better capacity retention than the sulfur control electrodes in the 200 cycles at 2 C. However, the difference between the two sulfur-TiS₂ electrodes is still significant. Sulfur-TiS₂ electrode 2 always delivers at least 50 mAh g⁻¹ S more capacity than sulfur-TiS₂ electrode 1. In addition, it also takes over 30 cycles for sulfur-TiS₂ electrode 1 to develop obvious advantage in delivered capacity over the sulfur control electrodes. It is noticed that the delivered capacity reaches a maximum point for both sulfur control and sulfur-TiS₂ electrode 1 after a few cycles. The capacity recovery process might be related to electrolyte and polysulfide distribution process, which is commonly observed in Li-S cells at higher rates.^{26–28} However, long-term cycling performance should still be reliable in the comparison between different sulfur electrode architectures because of the traverse of the initial electrolyte wetting process. The above data demonstrate the importance of uniform TiS₂ distribution within

the sulfur electrode. Additional long term cycling test using sulfur control and sulfur-TiS₂ electrode 2 is shown in Figure 5d. Sulfur-TiS₂ electrode 2 and sulfur electrode are both discharged at 1C rate with intermittent 0.2C rate at every 51st cycle to check the reversible capacity retention for up to 500 cycles. The composite maintains its capacity at $\sim 500 \text{ mAh g}^{-1}$ sulfur in long term cycling while the value is maintained at $\sim 350 \text{ mAh g}^{-1}$ for sulfur control electrode. Over the 500 cycles, the average cell capacity fade under 1C rate discharge is only 0.039% per cycle for the sulfur-TiS₂ cell, which represents only 20% capacity lost from the initial cycle. In addition, about 600 mAh g⁻¹ sulfur is still maintained after 500 cycles at 0.2C rate discharge. The coulombic efficiency curves are also shown in Figure 5c and Figure 5d, all cells showed stable coulombic efficiency above 97% in long term cycling because of the addition of LiNO₃. The cycling performance supports the observations from earlier published results that TiS₂ additive is beneficial for capacity retention of sulfur electrodes. The direct correlation between TiS₂ in hybrid electrode and electrode cyclability, as well as rate performance indicates that a uniform distribution of TiS₂ in hybrid electrode is also critical in fully utilizing TiS₂'s capability to enhance sulfur electrodes' cycling performance and power.

Conclusions

In summary, this work investigated the interaction mechanism between TiS₂ and Li-polysulfides with the help of XPS. The observation of Li signature on Li₂S₈ treated TiS₂ directly proves that the TiS₂ possesses the ability of adsorbing Li-polysulfides species. Although currently it is not possible to fully identify the species formed on TiS₂ surface as a result of this interaction due to the lack of relevant spectrum documented, an electron density transfer from Ti to Li and S was identified based on the positions of the peaks in the XPS spectrum before and after the interaction. Finally, it is also found that a uniform TiS₂ distribution in the S-TiS₂ hybrid electrode is vital in determining its effectiveness in enhancing the performance of sulfur elec-

trodes. Therefore, processing method and condition should be a very important consideration in future development of sulfur electrodes with TiS_2 additive.

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References

1. P. G. Bruce, S. A. Freunberger, L. J. Hardwick, and J. -M. Tarascon, *Nat. Mater.*, **11**, 19 (2012).
2. A. Manthiram, Y. Fu, S. -H. Chung, C. Zu, and Y. -S. Su, *Chem. Rev.*, **114**, 11751 (2014).
3. S. S. Zhang, *J. Power Sources*, **231**, 153 (2013).
4. N. Jayaprakash, J. Shen, S. S. Moganty, A. Corona, and L. A. Archer, *Angew. Chem.*, **123**, 6026 (2011).
5. B. Zhang, X. Qin, G. R. Li, and X. P. Gao, *Energy Environ. Sci.*, **3**, 1531 (2010).
6. R. Elazari, G. Salitra, A. Garsuch, A. Panchenko, and D. Aurbach, *Adv. Mater.*, **23**, 5641 (2011).
7. Y. -S. Su and A. Manthiram, *Electrochim. Acta*, **77**, 272 (2012).
8. X. Ji, S. Evers, R. Black, and L. F. Nazar, *Nat. Commun.*, **2**, 325 (2011).
9. Q. Pang, D. Kundu, M. Cuisinier, and L. F. Nazar, *Nat. Commun.*, **5**, 4759 (2014).
10. X. Liang, C. Hart, Q. Pang, A. Garsuch, T. Weiss, and L. F. Nazar, *Nat. Commun.*, **6**, 5682 (2015).
11. X. Liang, C. Y. Kwok, F. Lodi-Marzano, Q. Pang, M. Cuisinier, H. Huang, C. J. Hart, D. Houtarde, K. Kaup, H. Sommer, T. Brezesinski, J. Janek, and L. F. Nazar, *Adv. Energy Mater.*, **6**, 1501636 (2016).
12. Z. Yuan, H. -J. Peng, T. -Z. Hou, J. -Q. Huang, C. -M. Chen, D. -W. Wang, X. -B. Cheng, F. Wei, and Q. Zhang, *Nano Lett.*, **16**, 519 (2016).
13. S. S. Zhang and D. T. Tran, *J. Mater. Chem. A*, **4**, 4371 (2016).
14. L. Ma, H. Zhuang, Y. Lu, S. S. Moganty, R. G. Hennig, and L. A. Archer, *Adv. Energy Mater.*, **4**, 1400390 (2014).
15. L. Ma, H. L. Zhuang, S. Y. Wei, K. E. Hendrickson, M. S. Kim, G. Cohn, R. G. Henning, and L. A. Archer, *ACS Nano*, **10**, 1050 (2016).
16. E. J. Frazer and S. Phang, *J. Power Sources*, **6**, 307 (1981).
17. Y. -S. Su and A. Manthiram, *J. Power Sources*, **270**, 101 (2014).
18. L. Ma, S. Wei, H. L. Zhuang, K. E. Hendrickson, R. G. Hennig, and L. A. Archer, *J. Mater. Chem. A*, **3**, 19857 (2015).
19. Z. W. Seh, J. H. Yu, W. Li, P. C. Hsu, H. Wang, Y. Sun, H. Yao, Q. Zhang, and Y. Cui, *Nat. Commun.*, **5**, 5017 (2014).
20. R. V. Bugga, S. C. Jones, J. Pasalic, C. S. Seu, J. P. Jones, and L. Torres, *J. Electrochem. Soc.*, **164**, A265 (2017).
21. J. Song, S. J. Lee, Y. Kim, S.-S. Kim, K. T. Lee, and N.-S. Choi, *ECS Electrochem. Lett.*, **3**, A26 (2014).
22. <http://bmr.lbl.gov/wp-content/uploads/sites/3/2015/01/BMR-3Q-Report-2016.pdf>; Fiscal Year 2016: Third Quarter Progress Report, Advanced Battery Materials Research (BMR) Program, Task 8.6, 134.
23. J. C. Dupin, D. Gonbeau, I. Martin-Litas, P. Vinatier, and A. Levasseur, *Appl. Surf. Sci.*, **173**, 140 (2001).
24. H. Yao, G. Zheng, P. -C. Hsu, D. Kong, J. J. Cha, W. Li, Z. W. Seh, M. T. McDowell, K. Yan, Z. Liang, V. K. Narasimhan, and Y. Cui, *Nature Commun.*, **5**, 3943 (2014).
25. C. A. Schneider, W. S. Rasband, and Eliceiri K. W., *Nat. Methods*, **9**, 671 (2012).
26. L. Miao, W. Wang, K. Yuan, Y. Yang, and A. Wang, *Chem. Commun.*, **50**, 13231 (2014).
27. S. Lu, Y. Chen, X. Wu, Z. Wang, and Y. Li, *Sci. Rep.*, **4**, 4629 (2013).
28. J. S. Kim, T. H. Hwang, B. G. Kim, J. Min, and J. W. Choi, *Adv. Funct. Mater.*, **24**, 5359 (2014).

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Reference 24: doi: 10.1038/ncomms4943

Reference 27: doi: 10.1038/srep04629

The following corrections are made:

- 1) On line 3 the author list, Hong Gan is an active member of Electrochemical Society. "*" is added.
- 2) On line 259, "From 1d" should be "From Figure 1d". Please insert "Figure" into the text (when I did it, it screw up the text format).
- 3) In the title of Tables I, II and III, the unit of (eV) is added.
- 4) The order of the data label in Figure 5a was wrong. The label is switched between "Sulfur Control" and "S-TiS₂ method 2" - I already made the correction.