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Probing Titanium Disulfide - Sulfur Composite Materials for Li-S Batteries via *In-situ* X-ray Diffraction (XRD) Technique

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Abstract

Development of Li-S batteries is hindered by sluggish kinetics resulting from the intrinsic poor conductivity of sulfur and capacity degradation due to solubility of intermediate lithium polysulfides (LiPS). One strategy for overcoming these issues is to use TiS₂, which is a good electrical conductor and LiPS absorbant, as an additive to sulfur electrodes. From a structural perspective, we probed TiS₂-S composite materials during electrochemical discharge and charge reactions in propylene-oxide based glyme (DPGDME) electrolyte using *in-situ* XRD, revealing the synergistic effects of TiS₂ and S in the composites. TiS₂ was found to function effectively as a conductive additive and improve the utilization of sulfur. Intercalation of Li⁺ into TiS₂ takes place simultaneously with the sulfur-lithium reaction, and contributes to the total realized capacity.

Introduction

The growing demand for energy worldwide is spurring the pursuit of highly efficient and cost-effective energy storage systems. Rechargeable lithium-sulfur (Li-S) batteries show great potential for energy storage applications due to the high energy density (2.51 Wh·g⁻¹) and natural abundance of sulfur.(1, 2) However, practical challenges are hindering the advancement of Li-S batteries. One issue is the insulating nature of sulfur, which necessitates incorporation of a large amount of conductive additive in the composite electrode to increase conductivity with but which consequently diminishes the volumetric and gravimetric capacity. Second, the formation of intermediate lithium polysulfides (LiPS) Li₂S_x (4 ≤ x ≤ 8) which are highly soluble in liquid organic electrolyte and shuttle between the Li anode and S cathode, results in parasitic reactions on the Li anode and capacity degradation.(3)

In order to mitigate these issues, one strategy is to use TiS₂ as an additive to S electrodes. TiS₂ is a layered Li⁺ intercalation compound and a good electrical conductor (6.7*10⁴ S·m⁻¹).(4) It has a theoretical capacity of 239 mAh·g⁻¹ and a working voltage close to that of sulfur (~2.1 V vs. Li).(5, 6) These attributes make TiS₂ suitable to function as a conductive additive and a capacity contributor in sulfur battery electrodes. Prior reports have demonstrated that TiS₂ and S worked synergistically in a hybrid electrode to allow the retention of capacity from S while obtaining

high current capability.(2, 7) In addition, density functional theory predicted TiS_2 to have a stronger affinity to the soluble LiPS compared to conventional carbon, which could make TiS_2 an effective absorbent of LiPS.(7) This prediction was validated experimentally when TiS_2 was used as an encapsulation material for LiPS and was shown to effectively bind with LiPS and reduce the dissolution of active material.(8)

Solvents of the liquid electrolyte play an important role which can impact the cycling behavior of Li-S batteries.(9) Ethers are popular electrolyte solvents for Li-S batteries, as the low-viscosity of ethers is beneficial to ionic conductivity, and high viscosity can lead to passivation of sulfur electrode due to the slow diffusion of LiPS.(10) A mixture of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) has been predominantly used in recent publications on Li-S batteries motivated by the high LiPS solubility and fast LiPS reaction kinetics offered by linear DME, as well as the stabilization of the surface of Li metal with cyclic DOL.(11, 12) To understand the discharge redox reactions of sulfur, *in-situ* XRD measurements of Li-S batteries with both DOL-based and TEGDME-based electrolytes were carried out previously.(13-15) In these studies crystalline sulfur was found to be completely reduced at ~20% depth of discharge (DOD) and recrystallized at the end of charge. An *in-situ* XRD study on an X-ray transparent pouch cell with DOL/DME electrolyte showed that Li_2S was absent throughout the discharge and charge process. By varying the electrode preparation approaches, it was demonstrated that the reappearance of crystalline sulfur was dependent on the cathode preparation method, and the absence of Li_2S was due to the failure of crystallization of Li_2S from amorphous form.(14) Another *in-situ* XRD study on a Li-S pouch cell with DOL/DME electrolyte recorded the appearance of Li_2S at the beginning of the second discharge plateau (~2.1 V). This study also showed that the formation of short-chain LiPS and Li_2S at ~2.1 V are simultaneous rather than successive.(15) Further, an *in-situ* study carried out on an aluminum-cased cell with TEGDME-based electrolyte detected the formation of Li_2S at a higher DOD of 60%, during the second discharge plateau towards the end of discharge, and reversible oxidation at 75% depth of charge (DOC).(13) These studies demonstrated that formation of crystalline Li_2S was dependent on the cell construction, test conditions and crystallization of amorphous Li_2S .

As DME is considered to be a hazardous component due to its high flammability and toxicity, the consideration of alternative electrolytes is valuable. Glymes (glycol ethers, G_n), with the general structure of $\text{CH}_3\text{-O-(CH}_2\text{-CH}_2\text{-O)}_n\text{-CH}_3$ ($n=1-5$) are saturated polyethers with multiple ether-type oxygens in a single molecular structure.(16) There are two major categories of glymes - ethylene oxide based- glymes (EGDME) and propylene oxide based- glymes (PGDME). Glymes can solvate Li^+ through oxygen-ion chelating and dissolve Li salts of high concentration.(17) In addition to their low flammability and low toxicity, glymes demonstrate high oxidation stability when complexing with Li^+ - ~4 V vs. Li/Li^+ .(18) Due to these advantageous properties, glymes have been studied as single solvents and in binary or ternary mixture for Li-S battery electrolytes.(19, 20) Glymes solvate the lithium salt quickly, but the relatively high viscosity results in the accumulation of LiPS in the cathode and therefore low sulfur utilization. Other solvents such as DOL can be added to the solvent to lower the viscosity and optimize the ionic conductivity. So far, the glymes studied as electrolyte solvent for Li-S batteries have been ethylene oxide-based,(9, 19, 20) and the application of propylene oxide-based glymes as electrolyte solvent has been rare. Di(propylene glycol) dimethyl ether

(DPGDME) is a non-flammable, non-toxic and electrochemically stable solvent. It has been studied as an electrolyte solvent for non-aqueous Li-O₂ batteries.(21)

In order to understand the reaction mechanism of the TiS₂-S composite electrode, it is very important to determine the individual participation of TiS₂ and S during electrochemical cycling, as well as the synergistic effects of TiS₂ and S in composite electrodes from a structural perspective. Herein, for the first we investigated the electrochemical behavior of TiS₂, S as well as TiS₂-S composite electrodes with DPGDME-based electrolyte. In the present work, we measured the *in-situ* XRD patterns of TiS₂, S and TiS₂-S composite electrodes during discharge and charge for the first time. This study provided detail regarding the Li⁺ intercalation and extraction processes in the TiS₂ structure and the reaction of sulfur with Li.

Experimental

Materials characterizations – XRD data for TiS₂, S, and TiS₂-S composite powders and *in-situ* pouch cells were collected on a Rigaku Miniflux Diffractometer. Scanning electron microscope (SEM) images and energy dispersive x-ray microscopy (EDX) were collected on a JEOL 7600F Microscope.

Cathode Preparation - TiS₂ (Sigma Aldrich), S (Alfar Aesar) and Super P Li (Timcal) in different weight ratios were pre-mixed in a Spex Mill. The mixture was then mixed with polyvinylidene fluoride (PVDF) in 1-methyl-2-pyrrolidone (NMP) solution and casted onto Al foil with a Doctor Blade. TiS₂ and S are both considered active material in this study. TiS₂ and S weight ratios used in this study were TiS₂ (100%) + S (0%), TiS₂ (75%) + S (25%), TiS₂ (50%) + S (50%), TiS₂ (25%) + S (75%) and TiS₂ (0%) + S (100%), respectively. The five samples are referred to as TiS₂, 3TiS₂/S, TiS₂/S, TiS₂/3S and S, respectively in the following text. The cathode composition is active material (60%) + Super P (30%) + PVDF (10%).

Electrochemical cell assembly and in-situ XRD measurement – The cells were built with cathode (TiS₂, S, or TiS₂-S composite), Li metal anode, polypropylene separators and liquid electrolyte in a plastic pouch under dry condition (humidity < 0.5%). The electrolyte used in this study was 1M lithium bis(trifluoromethane)sulfonimide (LiTFSI) salt in di(propylene glycol) dimethyl ether (DPGDME). For the in-situ XRD measurement, pouch cells were discharged and charged in the voltage window of 1.5-3.0 V at a current density of 24 mA·g⁻¹ by a Biologic VMP Instrument while XRD data were collected continuously.

Results and Discussion

XRD data for TiS₂, 3TiS₂/S, TiS₂/S, TiS₂/3S and S powder samples are shown in **Figure 1a**. TiS₂ and S can be indexed to reference pattern PDF# 00-015-0853 and PDF# 98-000-0420 respectively. The peaks in the three mixture samples can all be designated to TiS₂ phase or S phase, indicating the absence of other phases and that TiS₂ and S do not react with each other. The EDX maps of the 3TiS₂/S, TiS₂/S and TiS₂/3S electrodes in **Figure 1b**, indicate that the TiS₂ and S were well dispersed in the electrodes.

Figure 2 displays the voltage profiles of the TiS_2 , $3\text{TiS}_2/\text{S}$, TiS_2/S , $\text{TiS}_2/3\text{S}$ and S pouch cells discharged and charged at $24 \text{ mA} \cdot \text{g}^{-1}$ for *in-situ* XRD measurement. The discharge/charge capacity and sulfur utilization were tabulated in **Table 1**. The pure TiS_2 delivered ~92% of its theoretical capacity, and pure S delivered ~48% of its theoretical capacity. Incorporation of TiS_2 into S electrode improved the utilization of sulfur, and $\text{TiS}_2/3\text{S}$ demonstrated the highest capacity and sulfur utilization, seconded by $3\text{TiS}_2/\text{S}$.

From the discharge profiles, TiS_2 did not show well-defined plateaus, and Li^+ intercalation reaction took place from 2.4 to 1.8 V during discharge, as most capacity was gained in this voltage range. The discharge of S showed two recognizable plateaus, ~2.4 V and ~2.1 V. As already extensively reported, the 2.4 V reaction of S plateau is linked to the reduction from elemental sulfur to Li_2S_8 , which dissolves in the liquid electrolyte and becomes liquid cathode. The Li_2S_8 is subsequently reduced to lower-order Li_2S_x as the voltage drops from ~2.3 to ~2.1 V. The 2.1 V plateau corresponds to the formation of Li_2S_2 or Li_2S from lower order Li_2S_x ($4 \leq x \leq 8$).^(22, 23) A closer examination of the voltage-capacity relationship revealed that among the S containing samples, $3\text{TiS}_2/\text{S}$ showed highest utilization of sulfur in the 2.4-2.0 V reaction voltage range. As stated previously, TiS_2 has strong affinity to LiPS, which promotes the sulfur reduction. This explains why the higher TiS_2 content gave rise to higher sulfur utilization. However, $\text{TiS}_2/3\text{S}$ showed highest ~2.1 V reaction efficiency and overall highest sulfur utilization. This indicates the reaction efficiency at ~2.1 V, the reduction of lower order LiPS to Li_2S_8 or Li_2S , is not controlled by the conductivity of the electrode. It is also notable that the TiS_2 -S composite samples showed higher voltage and therefore less polarization at the 2.1 V compared to S sample.

The complete *in-situ* XRD scans of TiS_2 and S are shown in **Figure 3** as examples of *in-situ* XRD data. All the peaks that resulted from the cell components other than the cathode (polymer separator, lithium anode, nickel tabs) are marked on the graph. Major peaks of TiS_2 and S peaks are indexed on the plots. The peak shifting of TiS_2 peaks and disappearance and appearance of S peaks is clearly visible. The TiS_2 and S composite samples showed peaks contributed from by both phases. Based on identifiable peak positions and intensities, TiS_2 (001) and (004) peaks in TiS_2 -containing samples and S (222), (026) and (311) peaks in S-containing samples were selected to track the evolution of TiS_2 and S, respectively.

As shown in **Figure 4a**, TiS_2 is a layered material where S-Ti-S sheets are held together by weak van der Waals forces, and Li^+ can intercalate into the interlayer space.⁽²⁴⁾ The (001) plane for Li^+ intercalation is highlighted in the TiS_2 crystal structure. The evolution of TiS_2 (001) and (004) peak of the TiS_2 cell during discharge and charge are expanded in **Figure 4b**. The (001) peak shifted from $2\theta=15.6^\circ$ to 14.3° toward the end of discharge, indicating an expansion in interlayer spacing from 5.68 Å to 6.17 Å. Both the (001) and (004) peak shifted back to its original position after charge. Consistent with the changes on the (001) planes, the change on the (004) planes is 25% of the (001) planes, 0.12 Å. **Figure 4c** shows the TiS_2 d-spacing change of the TiS_2 and TiS_2 -S composite samples with respect to capacity during discharge and charge. For the S-containing samples, the TiS_2 (001) and (004) expanded to the same extent as pure TiS_2 toward the end of discharge, and contracted the same amount toward the end of charge, indicating that the Li^+ intercalation and extraction in TiS_2 was not hampered by the presence of S. With S in the electrode, TiS_2 (001) and (004) planes started to expand in a similar trend as pure TiS_2 . The more capacity gain from 2.4 to 2.1 V suggests that S is discharging simultaneously

with TiS_2 in this voltage range. The expansion of TiS_2 (001) planes reached its maximum amount at the voltage of ~ 2.05 V for all TiS_2 -containing samples, and additional capacity was attributed to the reaction of LiPS with lithium. The d-spacing change during charge was a reverse process. The S-containing samples showed a reaction plateau at 2.25 V where lower order LiPS oxidizes, and the d-spacing of TiS_2 did not change for all the S-containing samples at this reaction voltage. The TiS_2 (001) planes of all four samples contracted to the original status after charging.

Figure 5 presents the evolution of sulfur peaks in S-containing samples. No Li_2S peaks were found at the end of discharge in any of the S-containing samples, showing no formation of crystalline Li_2S . As described before, this could be due to the incomplete reaction of sulfur or incomplete crystallization of liquid Li_2S . **Figure 5b** showed the evolution of sulfur (222), (026) and (311) peaks during discharge and charge of the pure S sample. The crystalline sulfur gradually disappeared during discharge and reappeared toward the end of charge. **Figure 5c** showed the sulfur peak intensity change with respect to discharge and charge capacity of the S-containing samples. The sulfur peaks of the $3\text{TiS}_2/\text{S}$ sample were difficult to resolve due to the relatively low S content, and only TiS_2/S , $\text{TiS}_2/3\text{S}$ and S are shown in the figure. The crystalline sulfur disappeared at ~ 2.3 V for both TiS_2/S and $\text{TiS}_2/3\text{S}$, indicating the reaction of sulfur with lithium at ~ 2.4 V was complete for these two samples. However, the crystalline sulfur in the pure S electrode did not disappear until the 2.05 V plateau started, indicating crystalline sulfur did not fully dissolve and form LiPS until this stage, which accounts for the lower utilization of sulfur in pure S electrode. Thus, the data indicates that TiS_2 enhances the reaction efficiency of sulfur at 2.4 V. Also according to **Figure 5c**, the capacity gain after the crystalline sulfur is completely reacted was more with TiS_2 present, meaning that TiS_2 also facilitates the reaction for liquid cathode Li_2S_8 to lower order Li_2S_x . The recrystallization of sulfur took place at ~ 2.5 V for all the three samples. For the $\text{TiS}_2/3\text{S}$, the only detectable peak from sulfur toward the end of charge is the (026) peak, and the change of relative peak intensity could be due to change of particle orientation during recrystallization. Incorporation of TiS_2 into S electrodes can alleviate electrode polarization and improve the utilization sulfur. As reported previously,^(7, 8) TiS_2 could chemically bind with and physically entrap the LiPS species.^(7, 8) The affinity of TiS_2 to LiPS species encourages the reduction of sulfur in the earlier stages of discharge and promotes the initiation of the liquid LiPS reduction.

Conclusion

We studied the structural evolution of TiS_2 and S, and TiS_2 -S composites during discharge and charge in DPGDME-based electrolyte using *in-situ* XRD. TiS_2 was able to undergo reversible Li^+ intercalation and extraction in this electrolyte. Pure S was able to deliver ~ 48 % of its theoretical capacity discharging at $24 \text{ mA}\cdot\text{g}^{-1}$. Incorporation of TiS_2 into the S electrode significantly improved the utilization of sulfur, as well as contributed to the overall capacity. *In-situ* XRD data suggest that TiS_2 and S discharge and charge simultaneously in the composite electrode, and TiS_2 facilitates the reaction of crystalline sulfur with lithium and initiation of reduction of liquid lithium polysulfides (LiPS) to solid Li_2S_2 or Li_2S .

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Figure 1 (a) XRD data for TiS_2 , $3\text{TiS}_2/\text{S}$, TiS_2/S , $\text{TiS}_2/3\text{S}$ and S powder samples; (b) SEM and EDX mapping of $3\text{TiS}_2/\text{S}$, TiS_2/S and $\text{TiS}_2/3\text{S}$ electrodes.

Figure 2 Voltage versus capacity plots of TiS_2 , $3\text{TiS}_2/\text{S}$, TiS_2/S , $\text{TiS}_2/3\text{S}$ and S pouch cells discharged and charged at $24 \text{ mA}\cdot\text{g}^{-1}$ for *in-situ* XRD measurement.

Table 1 Discharge and charge capacity of TiS_2 , $3\text{TiS}_2/\text{S}$, TiS_2/S , $\text{TiS}_2/3\text{S}$ and S pouch cells

Cell	Discharge capacity ($\text{mAh}\cdot\text{g}^{-1} \text{TiS}_2+\text{S}$)	Charge capacity ($\text{mAh}\cdot\text{g}^{-1} \text{TiS}_2+\text{S}$)	Discharge capacity ($\text{mAh}\cdot\text{g}^{-1} \text{S}$)	Charge capacity ($\text{mAh}\cdot\text{g}^{-1} \text{S}$)
TiS_2	221	209	N/A	N/A
$3\text{TiS}_2/\text{S}$	376	351	845	777
TiS_2/S	505	489	791	770
$\text{TiS}_2/3\text{S}$	792	782	981	968

S	780	725	780	725
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Figure 3 Complete *in-situ* XRD scans of (a) TiS₂ and (b) S during discharge and charge. TiS₂ (001), (002), (003) and (004) peaks are indexed in (a), and S (222), (026) and (311) peaks are indexed in (b).

Figure 4 (a) Crystal structure of TiS_2 with (001) plane highlighted. Ti atoms are represented in blue, and S atoms are represented in yellow. (b) (001) and (004) peak evolution during TiS_2 discharge and charge; (c) D-spacing change of TiS_2 (001) and (004) planes of TiS_2 , $3\text{TiS}_2/\text{S}$, TiS_2/S and $\text{TiS}_2/3\text{S}$ with respect to capacity

Figure 5 (a) Crystal structure of S_8 with (222) plane highlighted. S atoms are represented in yellow; (b) sulfur (222), (026) and (311) peak evolution during S discharge and charge; (c) sulfur peak intensity change with respect to discharge/charge capacity of TiS_2/S , $TiS_2/3S$ and S sample.