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Mixed-dimensional V₂CT_x/ Ti₃C₂T_x composite interlayer to boost electrochemical performance of Li-S batteries

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Abstract: A mixed-dimensional V₂CT_x/Ti₃C₂T_x composite interlayer was successfully prepared to tackle severe polysulfide (LiPS) shuttling and sluggish sulfur redox kinetics for high-performance lithium–sulfur batteries. In the unique nanoarchitecture, two-dimensional Ti₃C₂T_x nanosheets served as a stable skeleton with superb electronic conductivity, good mechanical strength, and high polysulfide adsorption, whereas one-dimensional V₂CT_x nanorods played a crucial role in chemisorbing LiPSs and catalyzing the conversion of LiPSs due to their high polarity and electrocatalysis. With the synergistic effect of V₂CT_x and Ti₃C₂T_x composite interlayer showed an impressive long-term cycling stability and small capacity decay rate of 0.062% per cycle over 600 cycles at 1C and exhibited an outstanding rate capability of 935.3 mAh·g⁻¹ at 2 C.

KEYWORDS

polysulfides, sulfur redox kinetics, $V_2 C T_x/Ti_3 C_2 T_x,$ separator, shuttling, lithium–sulfur batteries

Introduction

Lithium-sulfur batteries (LSBs) have been regarded as one of the most promising next-generation high-energy storage devices. This is because of their advantages of possessing high energy density (2,600 Wh·kg⁻¹) and being low cost and environmentally friendly (Chung et al., 2018; Ye et al., 2020; Xia et al., 2021). However, the notorious shuttle effect of lithium polysulfides (LiPSs) leads to the loss of active materials, the sluggish LiPS redox kinetics, and the inferior cycling performance. These could limit the specific capacity and cycling lifetime of LSBs (Chen et al., 2019; Tian et al., 2020).

It is important that the severe shuttle effect and sluggish LiPS redox kinetics are overcome to obtain high electrochemical performance of LSBs. Among the effective strategies, the high-performance interlayers between the cathode and separator are proposed. Among the various materials, the carbon-based materials are extensively applied to prepare the interlayer because they have excellent electrical conductivity (Ma et al., 2020; Wei et al., 2020; Yu et al., 2020). However, the weak interaction between nonpolar carbon materials and LiPSs is difficult to block the diffusion of LiPSs to Li metal anode. Therefore, some polar materials, such as metal oxides (Guo et al., 2019; Li et al., 2020), sulfides (Paolella et al., 2018; Yao et al., 2018), nitrides (Yao et al., 2020), and metal-organic frameworks (Wu et al., 2019), are used to prepare interlayers to further chemically anchor LiPSs. Although they can well immobilize the LiPSs and hinder the shuttle effect, their poor electrical conductivity slows down the multistep redox reactions of sulfur (S) species. Recent research studies showed that a catalyst could make the conversion of LiPSs become fast and shorten the residence time of LiPSs in an electrolyte (Song et al., 2019; Zhang et al., 2020). Therefore, if the incorporated interlayers have an excellent electrical conductivity and could anchor the LiPSs as well as catalyze the LiPS conversion, the slow LiPS redox kinetics and the notorious shuttle effect of the LiPSs could be effectively resolved. Thus, the high-performance interlayer was constructed with a rational design. As a representative, post-graphene two-dimensional (2D) black phosphorus (BP) (Hu et al., 2020) and MXenes (Naguib et al., 2011; Gao et al., 2020; Gao et al., 2021a; Gao et al., 2021b; Zhang et al., 2021; Gao et al., 2022a; Gao et al., 2022b; Cao et al., 2022) have attracted tremendous attention since 2011, due to the layered structure and excellent physicochemical properties. Ti₃C₂T_x, a typical MXene material, has been widely used as interlayer materials in LSBs (Ghidiu et al., 2014; Liang et al., 2015; Song et al., 2020). Compared with the carbon-/metalbased materials, Ti₃C₂T_x possesses good conductivity for electron transport and high mechanical properties for structure stability. Nevertheless, 2D $Ti_3C_2T_x$ nanosheets tend to aggregate, which will lead to a decrease in active sites for trapping and catalyzing LiPSs, and slow down the ion transport as well (Qiu et al., 2020). One-dimensional (1D) V₂CT_x nanostructures has been recently explored, which possesses the advantages of strong adsorption to LiPSs and catalytic properties (Wu et al., 2020; Zhang et al., 2022). Therefore, mixed-dimensional V₂CT_x/Ti₃C₂T_x nanostructures together as interlayers will achieve high electrochemical performance for LSBs.

Herein, we construct a mixed-dimensional V₂CT_x/ Ti₃C₂T_x composite interlayer on separators for LSBs. It can anchor LiPSs by strong chemisorption and accelerate their redox kinetics under the existence of V₂CT_x catalyst. Based on the unique structure, the LSBs achieve an excellent rate capacity of 935.3 mAh·g⁻¹ at 2 C. Also, a lowcapacity rate decay of 0.062% is obtained after 600 cycles at 1 C. These results illustrate that the incorporation of the multifunctional interlayer is a direct and effective method to achieve high electrochemical performance for LSBs.

Materials and methods

Preparation of mixed-dimensional V₂CT_x/ $Ti_3C_2T_x$ interlayers

One-dimensional V2CTx nanorods and two-dimensional Ti₃C₂T_x nanosheets were synthesized based on the previous reports (Qiu et al., 2020; Zhang et al., 2022). The suspensions of 1D V₂CT_x nanorods and 2D Ti₃C₂T_x nanosheets were mixed at a mass ratio of 2:8. Then, saturated LiCl solution was added to the resultant mixed solution and stirred, which led to the mixed V2CTx/Ti3C2Tx nanostructures settled at the bottom of the container by negatively charge-induced self-assembly (Ghidiu et al., 2014; Naguib et al., 2015). Then, the sediment was washed to remove needless salt. Finally, the V₂CT_x/Ti₃C₂T_x powder was obtained by vacuum-drying. Subsequently, V₂CT_x/Ti₃C₂T_x and PVDF were dissolved in NMP solution at a mass ratio of 9:1, and then the mixed solution was filtered on a Celgard separator (PP) under vacuum. The obtained thin film is called the mixeddimensional $V_2CT_x/Ti_3C_2T_x$ composite interlayer (the corresponding separator is labelled as V₂CT_x/Ti₃C₂T_x-PP). The V₂CT_x and Ti₃C₂T_x interlayers were prepared using the same procedure. The corresponding separators are labelled as V₂CT_x-PP and Ti₃C₂T_x-PP, respectively.

Li₂S₆ adsorption experiment

 $\rm Li_2S_6$ solution of 0.01 M was prepared by the chemical reaction of Li_2S and S at a molar ratio of 1:5 in a 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) mixture (1:1 v/v) at 60°C. A volume of 12 mg of Ti_3C_2T_x and V_2CT_x/Ti_3C_2T_x was added into 1 ml of Li_2S_6 solution, and then, the solutions were rested for adsorption.

Assembly of symmetric cells

 $Ti_3C_2T_x$ and $V_2CT_x/Ti_3C_2T_x$ (w/w 2:8) were dissolved in alcohol solution. The resulting solutions were dripped onto the carbon paper (CP) with a diameter of 15 mm (labelled as $Ti_3C_2T_x$ -CP and $V_2CT_x/Ti_3C_2T_x$ -CP). Both mass loadings were ~0.50 mg·cm⁻². The 2025-type coin cells with two $Ti_3C_2T_x$ -CP or $V_2CT_x/Ti_3C_2T_x$ -CP electrodes as the anode and cathode were assembled, using PP and 0.1 M of Li_2S_6 as the electrolyte.

Nucleation of Li_2S on $Ti_3C_2T_x$ and $V_2CT_x/Ti_3C_2T_x$

First, 0.25 M of Li_2S_8 solution was obtained by dissolving S and Li_2S at a molar ratio of 7:1 in a tetraglyme solvent at 60°C



overnight. Following this, $Ti_3C_2T_x$ and $V_2CT_x/Ti_3C_2T_x$ were dissolved in alcohol solution to obtain uniform suspensions by ultrasound, which were dripped on CPs (10 mm diameter) and dried at 60°C to obtain electrodes. The coin cell was composed of $Ti_3C_2T_x$ -CP or $V_2CT_x/Ti_3C_2T_x$ -CP cathode, lithium anode, and PP. The Li_2S_8 electrolyte of 0.25 M was used on the cathode side, and the standard electrolyte was used on the anode side. Then, the cells were galvanostatically discharged to 2.06 V at 0.112 mA and then kept at 2.05 V. Also, Li_2S nucleated and grew until the current of 10^{-2} A was reached.

Material characterizations and electrochemical analyses

The morphology of mixed-dimensional $V_2 C T_x/T i_3 C_2 T_x$ composite interlayers were observed using scanning electron

microscopy (SEM) (SU70, Japan). The X-ray diffraction (XRD) measurement was recorded using a Rigaku D/ max2600 X-ray diffractometer. The cathode is a mixture of Ketjen black/sulfur, super-P, and PVDF at a mass ratio of 8:1: 1. The diameter of the cathode was about 13 mm, and the loading of S was ~1 mg·cm⁻². The coin cells were assembled with KB/S cathode, Li anode, and PP with Ti₃C₂T_x-PP, V₂CT_x/Ti₃C₂T_x-PP, or V₂CT_x-PP, respectively. The electrolyte consisted of 1.0 M lithium bis-trifluoromethane sulfonimide (LiTFSI), 2% LiNO3 additives, and a mixture of DOL/DME (volume ratio = 1:1). The galvanostatic charge-discharge (GCD) profile of the assembled cells was tested at 0.5 C in the voltage range of 1.7–2.6 V using the LAND cell testing system. The electrochemical impedance spectra (EIS) and cyclic voltammograms (CV) were carried out using an electrochemical workstation (VMP3). X-ray photoelectron spectroscopy (XPS) was conducted by applying ESCALAB 250XI.

Results and discussion

SEM images of 1D $V_2 CT_x$ nanorods and 2D $Ti_3 C_2 T_x$ nanosheets are shown in Figures 1A,B. The length of V₂CT_x nanorods is about 230 nm, while the diameter is tens of nanometers. Also, the size of irregular 2D Ti₃C₂T_x nanosheets is a few micrometers. Furthermore, the top-view SEM image of the mixed-dimensional $V_2CT_x/Ti_3C_2T_x$ composite interlayer is presented in Figure 1C. The trace amount of V₂CT_x nanorods can be seen on the top surface of the composite interlayer. On the other hand, the cross-sectional SEM image of the V2CTx/Ti3C2Tx composite interlayer shows that V_2CT_x and $Ti_3C_2T_x$ are superimposed on each other, forming a well-arranged layered stacking structure (Figure 1D). XRD of the $V_2CT_x/Ti_3C_2T_x$ composite interlayer was carried out to characterize the crystalline structure, as shown in Figure 1E. The two diffraction peaks at 6.1 and 7.45° correspond to the (002) crystal plane of 2D Ti3C2Tx nanosheets and 1D V2CTx nanorods, respectively (Li et al., 2017; Zhang et al., 2022). In contrast, the (002) diffraction peak intensity of V₂CT_x is weaker, due to the low content of V₂CT_x. The XRD pattern proves that V_2CT_x and $Ti_3C_2T_x$ were successfully synthesized. The composition of the V2CTx/Ti3C2Tx composite interlayer was further confirmed by XPS analysis (Li et al., 2017; Zhang et al., 2022). A high-resolution XPS spectrum of C 1s in the V₂CT_x/Ti₃C₂T_x composite interlayer is shown in Figure 1F. C-V and C-Ti bonds were observed. Meanwhile, the corresponding V-C and Ti-C bonds can also be found in the high-resolution XPS spectra of V 2p and Ti 2p in V_2CT_x and $Ti_3C_2T_x$ respectively, further proving that the composite interlayer is composed of V₂CT_x and Ti₃C₂T_x (Figures 1G,H). The LiPS adsorption behavior of V2CTx/Ti3C2Tx composite materials was surveyed by visualized adsorption tests, as shown in Figures 1I,J. $Ti_3C_2T_x$ was used as the control sample. Figure 1I shows the initial states of different samples placed in Li_2S_6 solutions. In Figure 1J, the solvent colors with both $Ti_3C_2T_x$ and V₂CT_x/Ti₃C₂T_x composite materials undergo a significant change after resting for 5 h. The solution including Ti₃C₂T_x materials changes only lighter in color. However, the solution including V2CTx/Ti3C2Tx composite materials become almost colorless. These findings demonstrate the strong chemical adsorption of $V_2CT_x/Ti_3C_2T_x$ composite materials to LiPSs compared with Ti₃C₂T_x.

The mixed-dimensional interlayer with more active sites and stronger catalytic capacity can facilitate the solid–liquid–solid transformations of the S species. At the first stage of LiPS conversions in LSBs, S undergoes solid–liquid phase transformation to high-order LiPSs and then liquid–liquid conversion to low-order LiPSs. Rapid liquid–liquid phase conversions will reduce LiPS accumulation in the electrolyte, which is conductive to ion transport. To investigate the effect of interlayers on the conversions of LiPSs in a liquid–liquid phase, the CV curves of $V_2CT_x/Ti_3C_2T_x$ -CP and $Ti_3C_2T_x$ -CP symmetric

cells were measured, as shown in Figure 2A. The current response of the CP symmetric cell without Li₂S₆ is almost in line. It can be seen from Figure 2A that the current response of $V_2CT_x/$ Ti₃C₂T_x-CP symmetric cells with Li₂S₆ is the largest among the $Ti_3C_2T_x$ -CP and CP cells, indicating that $V_2CT_x/Ti_3C_2T_x$ composite materials accelerate the liquid-liquid conversion of LiPSs, make the liquid phase LiPS conversion become more thorough, and boost the LiPS redox kinetics. At the same time, the accumulation of LiPSs in the electrolyte will also be greatly reduced. This is due to the rapid conversion of liquid LiPSs. It is beneficial to suppress the shuttle effect. Figure 2B shows the EIS curves of symmetric cells. The smallest semicircle diameter of the V₂CT_x/Ti₃C₂T_x-CP symmetric cell implies the smallest charge transfer resistance (R_{ct}) , thus confirming the rapid electron and ion transportation at the interface between V2CTx/Ti3C2Tx composite materials and S species. Kinetics of Li₂S precipitation in LSBs is another significant factor for highperformance LSBs. This is due to the fact that 75% of the capacity originates from the Li₂S deposition during discharge. Therefore, Li₂S nucleation tests were carried out. The constantvoltage discharge curves at 2.05 V are shown in Figures 2C,D. Obviously, the V2CTx/Ti3C2Tx-CP electrode demonstrates the earlier Li₂S deposition compared with Ti₃C₂T_x-CP electrodes, indicating that the V2CTx/Ti3C2Tx-CP electrode has the greater catalytic ability, and accelerates the conversion of LiPSs to Li₂S. The Li₂S precipitation capacity on Ti₃C₂T_x-CP and V₂CT_x/ $Ti_3C_2T_x$ -CP electrodes were calculated by the integral of current vs. time, corresponding to 540 and 595 mAh·g⁻¹, respectively. The precipitation capacity of the V₂CT_x/ Ti₃C₂T_x-CP electrode becomes higher, implying that the faster LiPS conversion is achieved. The PP, Ti₃C₂T_x-PP, and V₂CT_x/ Ti₃C₂T_x-PP cells were assembled to assess the effect of PP, $Ti_3C_2T_x\mbox{-}PP\mbox{, and }V_2CT_x\mbox{-}Ti_3C_2T_x\mbox{-}PP\mbox{ on the electrochemical}$ performance of LSBs. Figure 2E shows the CV profiles of PP, Ti₃C₂T_x-PP, and V₂CT_x/Ti₃C₂T_x-PP cells at a scan rate of 0.1 mV·s⁻¹. Two reduction peaks for three cells can be seen and be attributed to the two reduction processes of S8 to LiPSs (Li₂S_x, $4 \le x \le 8$) and Li₂S₄ to Li₂S₂/Li₂S, respectively. Two oxidation peaks correspond to the oxidation process of Li₂S to LiPSs, which are then oxidized to S8. The CV curve of the $V_2CT_x/Ti_3C_2T_x$ -PP cell shows the most intense peak, the lowest electrochemical polarization, and the highest current density, illustrating that the V₂CT_x/Ti₃C₂T_x composite interlayer makes LiPS redox reactions become the fastest among PP and Ti₃C₂T_x-PP cells. In addition, Figure 2F also reveals the excellent electrochemical kinetics of the V2CTx/Ti3C2Tx-PP cell from the EIS curve. The results show that the $\mathrm{V_2CT_x}\!/$ Ti₃C₂T_x-PP cell has the lowest R_{ct} and excellent charge transfer ability at the electrolyte/electrode interface. This is due to its high ionic and electronic conductivity.

The GCD curves of different cells were measured at 0.5 C, as shown in Figure 3A. The discharge capacities of $V_2CT_x/Ti_3C_2T_x$ -PP, $Ti_3C_2T_x$ -PP, V_2CT_x -PP, and PP cells are 1,090, 2,



977.3, 892.4, and 842.8 mAh·g⁻¹, respectively. In contrast, the V₂CT_x/Ti₃C₂T_x-PP cell has the highest specific discharge capacity due to the existence of trace amounts of V₂CT_x. In addition, the polarization overpotential of the V₂CT_x/Ti₃C₂T_x-PP cell is only 211 mV, which is significantly smaller than that of other cells and consistent with the results of CV tests. Then, the cycling performance tests of the PP, Ti₃C₂T_x-PP, and V₂CT_x/Ti₃C₂T_x-PP cells were also performed, as shown in Figure 3B. The V₂CT_x/Ti₃C₂T_x-PP cell can still remain at a high discharge capacity of 775.2 mAh·g⁻¹ and high capacity retention rate of 71% after 300 cycles. However, the capacity

retention rate of Ti₃C₂T_x-PP and PP cells are only 69 and 52% after 300 cycles, respectively. Under the rate performance test shown in Figure 3C, the V₂CT_x/Ti₃C₂T_x cell shows excellent rate performance as the current density changes due to the good ionic and electronic conductivity of the V₂CT_x/Ti₃C₂T_x composite interlayer. In Figure 3C, the discharge capacity of the V₂CT_x/Ti₃C₂T_x of the V₂CT_x/Ti₃C₂T_x composite interlayer. In Figure 3C, the discharge capacity of the V₂CT_x/Ti₃C₂T_x of the V₂CT_x/Ti₃C₂T_x and 935.3 mAh·g⁻¹ at 0.1, 0.2, 0.5, 1, and 2 C, respectively. Subsequently, the discharge capacity can be restored to the high reversible capacity of 1,151.8 mAh·g⁻¹ by reducing to 0.1 C. However, the discharge capacity of Ti₃C₂T_x-PP and PP



cells is 753.9 and 469.2 mAh·g⁻¹ at 2 C, respectively, indicating that the capacity decays faster with the increase in current density. Their reversible capacities correspond to 993 and 647.1 mAh·g⁻¹ at 0.1 C, respectively. Figure 3D shows the GCD profiles of the V₂CT_x/Ti₃C₂T_x-PP cell. The polarization of the V₂CT_x/Ti₃C₂T_x-PP cell is only 123.4 mV at 0.1 C. The excellent rate performance and low polarization of the V₂CT_x/Ti₃C₂T_x-PP cell can be attributed to the important role of the mixed-dimensional V₂CT_x/Ti₃C₂T_x composite interlayer in electrical conductivity and chemical anchoring. The cycle stability at a high current density is an important factor to evaluate the performance of LSBs. Therefore, the long cycling stability of different batteries were tested at 1 C. In Figure 3E, the V₂CT_x/Ti₃C₂T_x-PP cell has an excellent long-term cycling

stability with a high initial capacity of 969.9 mAh·g⁻¹ and low capacity decay rate of 0.062% after 600 cycles. In contrast, the $Ti_3C_2T_x$ -PP cell has a capacity decay rate of 0.074%. The PP cell is out of service after less than 400 cycles. The $V_2CT_x/Ti_3C_2T_x$ cell demonstrates excellent electrochemical performance and cycle stability. It is also worth noting that the electrochemical performance of the mixed-dimensional $V_2CT_x/Ti_3C_2T_x$ composite interlayer is highly competitive compared with that of the other materials reported (Table 1). In a word, the adsorbed LiPSs on the composite interlayer can quickly obtain electrons and ions at the adsorption sites to continue the redox reactions based on the high conductivity and abundant active sites of $V_2CT_x/Ti_3C_2T_x$. Meanwhile, the catalytic effect of V_2CT_x accelerates the LiPS redox kinetics.

Nanostructure	S loading (mg cm ²)	Discharge rate (C)	Final capacity (mAh g ⁻¹)	Cycle number	Capacity decay per cycle (%)	Reference
V ₂ CT _x /Ti ₃ C ₂ T _x -PP	1.0	0.5	775.2	300	0.096	This work
$S/Ti_3C_2T_x$ -N	_	0.5	1,104.3	100	0.138	Qi and Zhang, (2022)
Bi-PP	2.5	0.5	650	200	_	Huang et al. (2020a)
V ₂ CT _x /CNT-PP	1.0	0.5	1008.3	100	0.204	Zhang et al. (2022)
KB/V ₂ CT _X -PP	1.0	0.2	942	150	0.158	Han et al. (2022)

TABLE 1 Comparison of the electrochemical performance between this work and other previously reported works.

Conclusion

In conclusion, we construct a mixed-dimensional V₂CT_x/ Ti₃C₂T_x composite interlayer to suppress LiPS shuttling and accelerate LiPS redox kinetics. Profiting from the advantages of strong chemisorption of the composite interlayer to LiPSs and catalysis of V₂CT_x, the V₂CT_x/Ti₃C₂T_x cell achieves an excellent rate capacity of 935.3 mAh·g⁻¹ at 2 C and low capacity rate decay of 0.062% after 600 cycles at 1 C. Meanwhile, designing a mixeddimensional composite interlayer can provide a route to develop high-performance LSBs.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author/s.

Author contributions

WiZ, WcZ, and JY contributed to the material preparation and characterization. HL contributed to the TEM measurement. XZ and LW conceived the idea and designed the experiments.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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