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### Authors

Zhang, Liang  
Sun, Dan  
Wei, Qiulong  
[et al.](#)

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Understanding the Electrochemical Reaction Mechanism of  $VS_2$   
Nanosheets in Lithium-Ion Cells by Multimodal *in situ* and *ex situ* X-ray  
Spectroscopy

Liang Zhang,<sup>1</sup> Dan Sun,<sup>2</sup> Qiulong Wei,<sup>3</sup> Huanxin Ju,<sup>4</sup> Jun Feng,<sup>1</sup> Junfa Zhu,<sup>4</sup> Liqiang  
Mai,<sup>3</sup>

Elton J. Cairns,<sup>2,5</sup> Jinghua Guo<sup>1,6\*</sup>

1. Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
2. Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States
3. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China
4. National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China
5. Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States
6. Department of Chemistry and Biochemistry, University of California, Santa Cruz, California 95064, United States

\*Email: [jguo@lbl.gov](mailto:jguo@lbl.gov)

## Abstract

Recently two-dimensional layered transition metal dichalcogenides (TMDs) have attracted great scientific interest in electrochemical energy storage research. Vanadium disulfide ( $VS_2$ ) as an important family member of TMDs, is a promising electrode material for lithium-ion cells because of its remarkable electrical conductivity and fast  $Li^+$  diffusion rate, but its electrochemical reaction mechanism is still poorly understood. Herein, we have prepared  $VS_2$  nanosheets as the electrode and systematically investigated its structural and chemical evolution during the electrochemical processes by employing both *in situ* and *ex situ* X-ray spectroscopy. The  $VS_2$  undergoes intercalation and conversion reactions in sequence during discharge and also this process is found to be partially reversible during the subsequent charge. The decreased reversibility of the conversion reaction over extended cycles could be mainly responsible for the capacity fading of the  $VS_2$  electrode. In addition, the hybridization strength between S and V shows a strong dependence on the states of charge, as directly illustrated by the intensity change of the V-S hybridized states and pure V states. We have also found that the solid electrolyte interphase on the electrode surface is dynamically evolved during cycling, which may be a universal phenomenon for the conversion-based electrodes. This study is expected to be beneficial for the further development of high-performance  $VS_2$ -based electrodes.

**Keywords:**  $VS_2$  nanosheets, lithium ion batteries, electronic structure, solid electrolyte interphase, X-ray absorption spectroscopy, resonant inelastic X-ray scattering

Lithium-ion batteries (LIBs) have been extensively developed as the leading energy storage devices in portable electronics and electric vehicles.<sup>1-6</sup> However, the relatively low theoretical capacities of the commercial electrodes (e.g., 372 mAh/g for graphite and 170 mAh/g for LiCoO<sub>2</sub>) are insufficient for the ever-increasing demands of society.<sup>7</sup> As a consequence, enormous efforts have been devoted to the exploration of new electrode materials with lower costs and higher energy densities.

Transition metal dichalcogenides (TMDs) have attracted intensive attention in electrochemical energy storage recently owing to their unique layered structures and versatile electronic and chemical properties.<sup>8-9</sup> For example, MoS<sub>2</sub> has been largely explored as the anode material for LIBs due to its high theoretical capacity and fast lithium ion diffusion rate.<sup>10-12</sup> However, the intrinsically low electrical conductivity of MoS<sub>2</sub> seriously inhibits its electrochemical performance, especially under high current conditions. In contrast, VS<sub>2</sub>, another important member of TMDs, demonstrates an intrinsic metallic behavior and a faster lithium ion diffusion rate than that of MoS<sub>2</sub> and graphite,<sup>13-15</sup> which makes VS<sub>2</sub> a promising electrode material for LIBs. For instance, Fang *et al.* showed that a hierarchical VS<sub>2</sub>/graphene nanosheet electrode exhibited a high reversible capacity of 528 mAh/g at a specific current of 0.2 A/g after 100 cycles.<sup>16</sup> More recently, Zhou *et al.* synthesized ultrathin VS<sub>2</sub> nanosheets with a few atomic layer thickness, which delivered a remarkably high capacity up to 1000 mAh/g at a specific current of 0.1 A/g and 570 mAh/g at a specific current of 10 A/g.<sup>17</sup> These reports were mainly focused on the improvement of the electrochemical performance of VS<sub>2</sub>-based electrode materials, whereas little attention has been paid to the detailed mechanism of the redox process and the reason for the capacity fading, which can be beneficial for the better modification of the VS<sub>2</sub> structure to achieve a superior electrochemical performance.<sup>17-20</sup>

In this work, we synthesized  $\text{VS}_2$  nanosheets using a facile hydrothermal method. We then applied multimodal *in situ* and *ex situ* X-ray spectroscopies, including hard (V K-edge), tender (S K-edge), and soft (V L-edge, C and O K-edge) X-ray absorption spectroscopy (XAS) as well as resonant inelastic X-ray scattering (RIXS, V L-edge), to investigate the evolution of the structural, physical, and chemical properties of the  $\text{VS}_2$  nanosheets used as the electrode material for LIBs in order to understand the electrochemical reaction and capacity fading mechanism. The unique character of XAS and RIXS is that they are element-resolved and highly sensitive to the local chemical bonding environments, and provide a deep insight into the electronic structures of both occupied and unoccupied partial density of states (PDOS) of the investigated materials.<sup>21-22</sup> The qualitative and quantitative analysis of the *in situ* and *ex situ* X-ray spectroscopy provides valuable information about the redox process and the formation process of the solid electrolyte interphase (SEI) layer for the  $\text{VS}_2$  nanosheet electrodes.

## **Experimental details**

### **Synthesis of $\text{VS}_2$ nanosheets**

Ammonium vanadate ( $\text{NH}_4\text{VO}_3$ , 4 mmol) was dissolved in distilled water (30 mL) after water bath at 70 °C. After the solution was cool down, the ammonium hydroxide (30%, 4 mL) and thioacetamide (TAA, 28 mmol) were added under continuous stirring. Then, the mixed solution was loaded into an autoclave and maintained at 180 °C for 20 h. After that, the obtained suspension was centrifuged and washed with distilled water and ethanol and then dried at 60°C for 12 h in a vacuum oven. Last, the products were heated at 300°C in argon atmosphere for 2 h to obtain  $\text{VS}_2$  nanosheets.

### **Cell preparation and electrochemical cycling**

The VS<sub>2</sub> electrodes were prepared by mixing active materials, super P, and PVDF binder at a weight ratio of 7:2:1. The slurries were then coated onto a commercial copper foil. CR2325 coin cells were assembled in an argon-filled glove box using lithium foil as the counter electrode and 1 M LiPF<sub>6</sub> in EC/DEC (1:1, by volume) as the electrolyte. The electrochemical performance of the cells was evaluated between 0.05 V and 3.0 V using a battery cycler (Arbin BT2000). The cyclic voltammograms were measured using a Biologic electrochemical workstation at a scan rate of 0.1 mV/s.

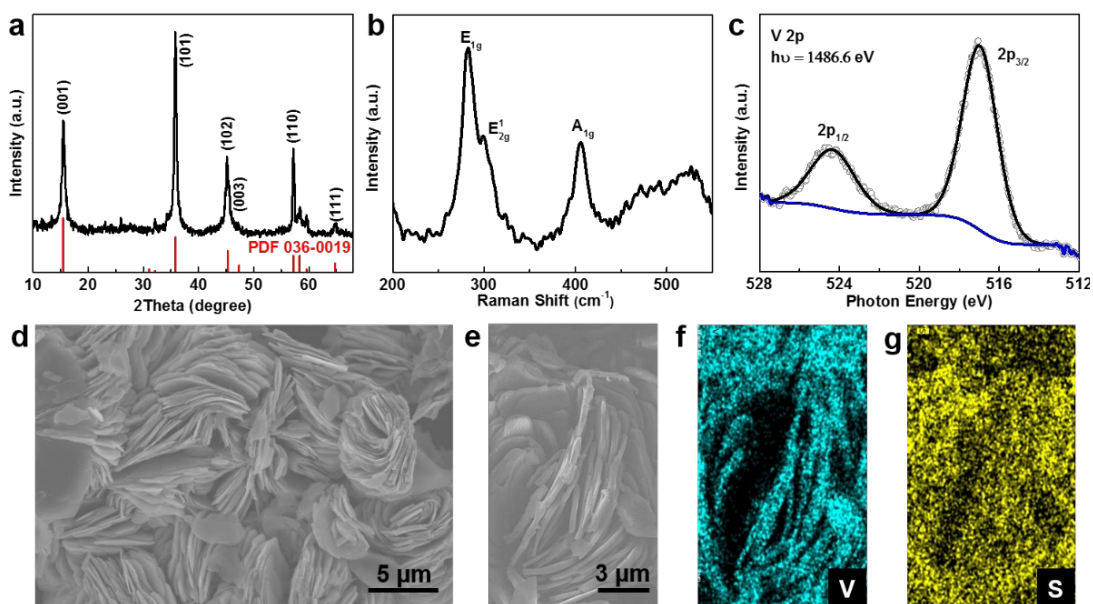
### ***In situ* and *ex situ* X-ray absorption spectroscopy measurements**

The *in situ/operando* and *ex situ* S and V K-edge XAS spectra were measured at beamline 5.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (LBNL). The *in situ* electrochemical cells were adapted from the CR2325 coin cells, as described in our previous reports.<sup>23-24</sup> The *ex situ* V L-edge, C and O K-edge XAS spectra and V L-edge RIXS maps were measured at beamline 8.0.1 at the ALS, LBNL. The photoemission spectroscopy experiments were performed at the Catalysis and Surface Science Endstation at the BL11U beamline in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China.

### **Results and discussion**

The phase of as prepared VS<sub>2</sub> nanosheets was identified by X-ray diffraction (XRD), as shown in Figure 1a. All the XRD peaks correspond to the typical diffraction peaks of hexagonal VS<sub>2</sub> with a space group of *P*-3*m*1 (PDF No. 036-0019), indicating the successful formation of VS<sub>2</sub> without any side reaction. The Raman spectrum (Figure 1b) shows three peaks located at 282, 300, 405 cm<sup>-1</sup>, which are assigned to the E<sub>1g</sub>, E<sup>1</sup><sub>2g</sub>, and A<sub>1g</sub> vibrational bands of VS<sub>2</sub>, respectively.<sup>17-18</sup> The V 2p X-ray photoemission spectroscopy (XPS) spectrum shows two peaks at 517.01 and 524.36 eV, corresponding to the V 2p<sub>3/2</sub> and V 2p<sub>1/2</sub> states due to the spin-orbital splitting effect, respectively. In addition, the V 2p peak positions are very similar to those of VO<sub>2</sub>,<sup>25</sup>

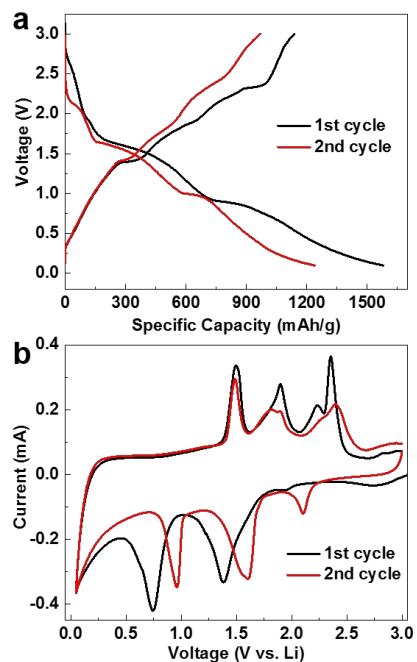
indicating that the V atoms in  $\text{VS}_2$  are mainly present as  $\text{V}^{4+}$ . To investigate the morphology of the as synthesized  $\text{VS}_2$ , we further performed scanning electron microscopy (SEM). The SEM image (Figure 1d) reveals that  $\text{VS}_2$  is composed of stacked nanosheets with a lateral size of several  $\mu\text{m}$ . The thickness of the  $\text{VS}_2$  nanosheets is estimated to be  $\sim 20$  nm. Moreover, the energy dispersive spectrometry (EDS) results exhibit a similar distribution of V and S in the  $\text{VS}_2$  nanosheets (Figure 1e-g). This unique thin nanosheet structure of  $\text{VS}_2$  could be beneficial for the rapid and durable lithium ion storage.



**Figure 1.** Structure characterization of the synthesized  $\text{VS}_2$  nanosheets. (a) XRD pattern. (b) Raman spectrum. (c) V 2p XPS spectrum. (d) SEM image. (e-g) EDS elemental mapping of V and S.

To evaluate the electrochemical performance of the  $\text{VS}_2$  nanosheets for LIBs, we paired the active materials with metallic lithium foils in standard coin cells and then cycled them in the voltage range of 0.05-3.0 V at a specific current of 0.2 A/g. Figure 2a shows the discharge-charge voltage profiles of the initial two cycles. Two plateaus near 1.4 and 0.8 V are observed in the first discharge curve, which correspond to the

intercalation and conversion reactions, respectively.<sup>17</sup> It has been predicted that the theoretical specific capacity of VS<sub>2</sub> for lithium intercalation can reach up to 466 mAh/g, which corresponds to the formation of Li<sub>2</sub>VS<sub>2</sub> (i.e.,  $0 \leq x \leq 2$ ).<sup>13,15,26</sup> In contrast, a series of plateaus are observed in the charge voltage profile. The first discharge and charge capacities are 1580 and 1138 mAh/g, respectively. The relatively low Coulombic efficiency (72%) could be related to the decomposition of electrolyte and formation of a SEI layer. The corresponding plateaus are still discernable in the second cycle, suggesting that the lithium intercalation and conversion reactions are reversible.



**Figure 2.** Electrochemical characterization of VS<sub>2</sub> nanosheets. (a) Discharge/charge voltage profiles at a scan rate of 0.2 A/g. (b) Cyclic voltammograms at a scan rate of 0.1 mV/s.

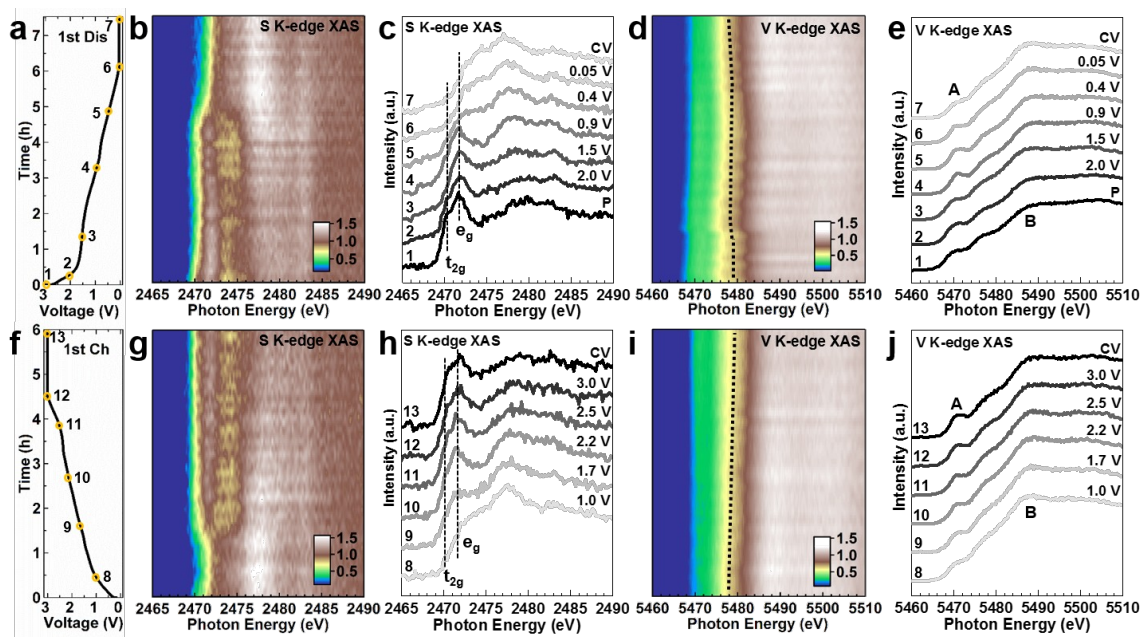
In order to better understand the lithium intercalation and conversion reaction mechanisms, we further performed cyclic voltammetry (CV) for VS<sub>2</sub> in the voltage range of 0.05-3.0 V at a scan rate of 0.1 mV/s, as depicted in Figure 2b. Consistent



with the first discharge voltage profile, two reduction peaks centered at 1.4 and 0.75 V corresponding to the intercalation reaction and conversion reactions are observed in the first cathodic scan. The reduction peaks shift to higher potentials in the subsequent cathodic scan. This observation is probably due to the partial irreversible structure change after the first cycle.<sup>24</sup> Several oxidation peaks are observed in the anodic scans, suggesting a multistep delithiation process of  $\text{VS}_2$ . Note that a new reduction peak appears at 2.1 V in the second cathodic scan, which may be related to the phase change of  $\text{VS}_2$  during lithium intercalation or the adsorption of lithium at the defect sites of  $\text{VS}_2$ .<sup>16</sup> The exact origin of this peak is not yet fully understood at the moment and further investigation is highly recommended.

To further understand the electrochemical reaction mechanism of  $\text{VS}_2$  electrodes, we performed an *in situ/operando* S and V K-edge XAS experiment to evaluate the local structural and chemical evolution of  $\text{VS}_2$  during the discharge and charge processes. Figure 3a-e and 3f-g show the voltage profiles, the *in situ/operando* S and V K-edge XAS maps, and the representative XAS spectra of  $\text{VS}_2$  during the first discharge and charge processes in real time, respectively. Note that the voltage was held at the cutoff voltage for 1.5 h at the end of discharge and charge to ensure a full reaction of  $\text{VS}_2$  (Figure 3a and f). For S K-edge XAS spectra (Figure 3b, c, g, h), the main features located at 2470.3 and 2471.6 eV are attributed to the  $t_{2g}$  and  $e_g$  states induced by the hybridization between S 3p and V 3d states, while the broad feature at 2480 eV reflects the S 3p-V 4s, p hybridized states. As shown in Figure 3b and c, the intensity of  $t_{2g}$  and  $e_g$  states decreases continuously during lithium intercalation process. In addition, it seems that the  $t_{2g}$  state is more influenced by lithium intercalation than the  $e_g$  state. These observations indicate that the electrons are also partially transferred to the  $t_{2g}$  states of sulfur during discharge, resulting in the decreased transition probability of sulfur 1s to these levels during the X-ray absorption process. This means that the sulfur is also electrochemically active and

participated in the redox process. The involvement of anionic redox for the  $\text{VS}_2$  electrode is most likely due to the overlap between S 3p states and V 3d states.<sup>15</sup> A similar phenomenon has also been observed for  $\text{TiS}_2$  during the discharge and charge processes.<sup>27</sup> With further discharge, the  $t_{2g}$  and  $e_g$  states totally disappear, and instead, two broad features at 2473.5 and 2476.6 eV are developed. The spectrum collected at the end of discharge is very similar to that of  $\text{Li}_2\text{S}$ ,<sup>24,28</sup> indicating the conversion from  $\text{VS}_2$  to  $\text{Li}_2\text{S}$ . Upon recharging the electrode to 3.0 V (Figure 3g and h), the characteristic  $t_{2g}$  and  $e_g$  states of  $\text{VS}_2$  are gradually recovered, indicative of the reversible intercalation and conversion reactions of  $\text{VS}_2$  in the first cycle.



**Figure 3.** *In situ/operando* S and V K-edge XAS of  $\text{VS}_2$  electrodes for the first cycle. (a) Discharge voltage profile at a specific current of 0.2 A/g for the *in situ/operando* XAS measurement. (b) *Operando* S K-edge XAS map and (c) representative XAS spectra during the first discharge process. (d) *Operando* V K-edge XAS map and (e) representative XAS spectra during the first discharge process. (f) Charge voltage profile at a specific current of 0.2 A/g for the *in situ/operando* XAS measurement. (g) *Operando* S K-edge XAS map and (h) representative XAS spectra during the first

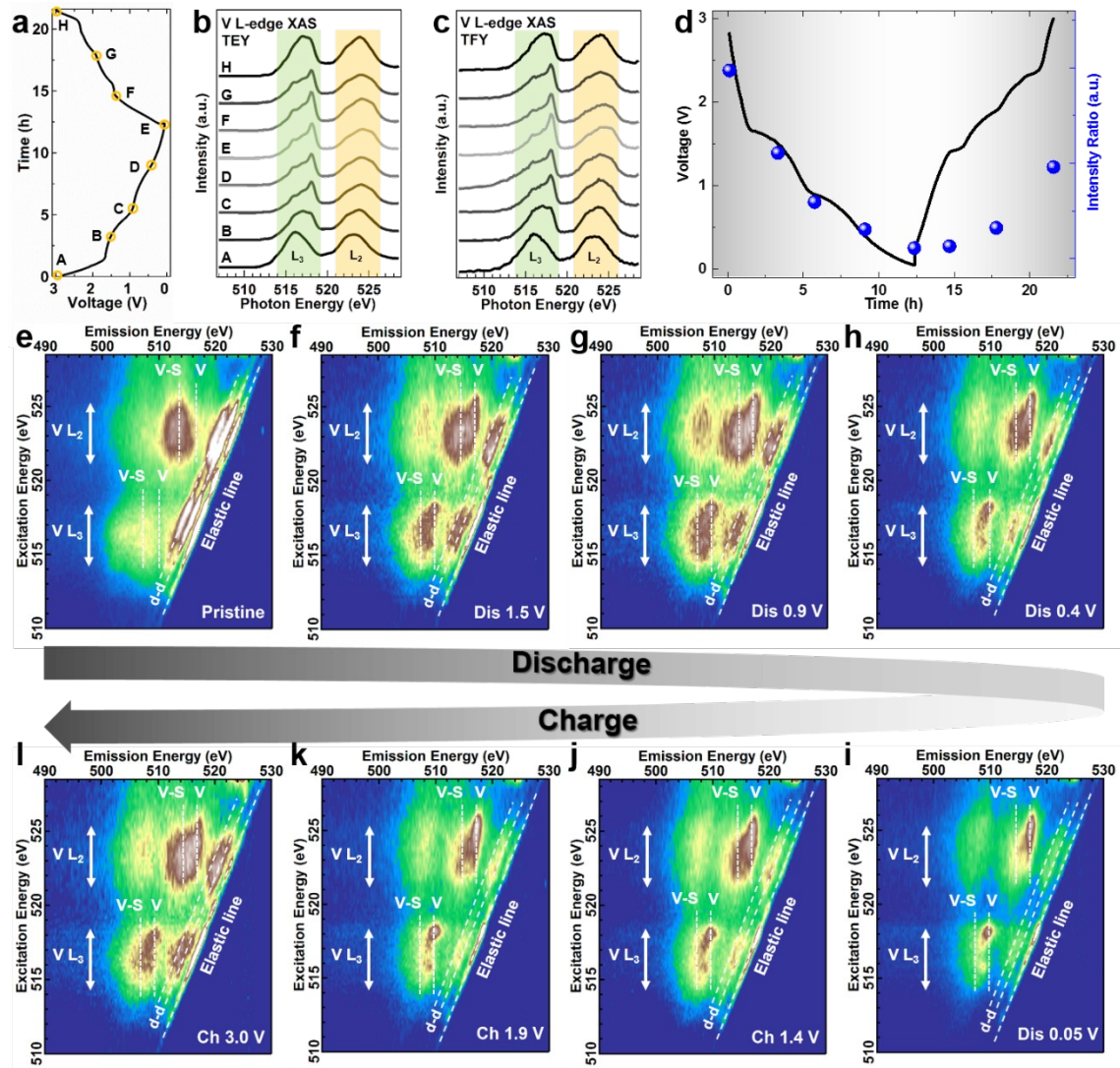
discharge process. (i) *Operando* V K-edge XAS map and (j) representative XAS spectra during the first discharge process.

The *in situ/operando* V K-edge XAS results further confirm the reversibility of the electrochemical reaction of  $\text{VS}_2$  (Figure 3d, e, i, and j). For the spectrum of pristine  $\text{VS}_2$ , the distinctive pre-edge peak A at  $\sim 5470$  eV is attributed to the dipole-forbidden V 1s to 3d transition.<sup>29</sup> The presence of this peak implies a slightly distorted octahedral symmetry of V atoms in  $\text{VS}_2$ , and the intensity of this peak is strongly dependent on the local coordination environment of V atoms.<sup>29-30</sup> The main absorption peak B at  $\sim 5490$  eV corresponds to the V 1s to 4p transition. During the discharge process, a shift of the main absorption edge to lower energies is clearly observed, reflecting the reduction of the oxidation state of V.<sup>31-32</sup> In addition, the intensity of the pre-edge peak also gradually decreases, which is induced by the symmetry change of V atoms as a result of lithiation. Actually, the lithiation induced local coordination environment change of metal atoms has also been observed for other conversion electrodes, e.g.,  $\text{NiFe}_2\text{O}_4$ ,<sup>33</sup>  $\text{TiS}_4$ ,<sup>34</sup> and  $\text{FeS}_2$ .<sup>35</sup> Note that the spectrum at the end of discharge is still different from that of V metal, which may be related to the small domain size of the as formed metal clusters and/or the interaction between formed  $\text{Li}_2\text{S}$  and V metal.<sup>36-38</sup> During the subsequent charge to 3.0 V, the intensity of the pre-edge peak increases and the main absorption edge shifts back to higher energies, indicating the recovery of the symmetry and the gradual oxidation of V atoms. Overall, the *in situ/operando* S and V K-edge XAS results clearly demonstrate that the electrochemical reaction of  $\text{VS}_2$  is reversible in the first cycle and both S and V are involved in the redox reactions during the electrochemical processes.

In order to confirm the changes observed in the *in situ/operando* results, we also measured the *ex situ* S and V K-edge XAS for the  $\text{VS}_2$  electrodes at different states of charge (Figures S1 and S2). The results show similar changes to those observed in the *in situ/operando* results, confirming the relatively high reversibility of the

intercalation and conversion reactions of  $VS_2$  during the first cycle. However, a gradual decrease of the reversibility of the reactions is observed after 2 and 10 cycles (Figures S1 and S2), which could be a main reason for the capacity fading of the  $VS_2$  electrode.

Although the above V K-edge XAS results clearly reveal the structural and chemical change of  $VS_2$  during the cycling process, it would be more convincing if we can directly probe the evolution of the V 3d states.<sup>39</sup> We therefore further performed *ex situ* V L-edge XAS and RIXS on a series of  $VS_2$  electrodes at different states of charge and discharge (Figure 4a) to understand the evolution of unoccupied and occupied V 3d states. Figures 4b and c show the V L-edge XAS spectra of the  $VS_2$  electrodes cycled to different voltages in both total electron yield (TEY, ~5nm detection depth) and total fluorescence yield (TFY, ~100 nm detection depth) modes, respectively.



**Figure 4.** *Ex situ* V L-edge XAS spectra and RIXS maps of  $\text{VS}_2$  electrodes at different states of charge in the first cycle. The samples are pristine (A), 1.5 V discharge (B), 0.9 V discharge (C), 0.4 V discharge (D), 0.05 V discharge (E), 1.4 V charge (F), 1.9 V charge (G), and 3.0 V charge (H), as indicated in the corresponding voltage profile (a). The spectra were measured through the current collector side. (b) and (c) V L-edge XAS spectra collected in TEY and TFY modes, respectively. (d) Intensity ratio evolution of the V 3d-S 3p hybridized states to the pure V 3d states as a function of discharge and charge voltages. (e-i) V L-edge RIXS maps of  $\text{VS}_2$  at different states of charge throughout the first cycle.

The two main regions of the XAS spectra can be assigned to the L<sub>3</sub>-edge (2p<sub>3/2</sub> to 3d) at 514-519 eV and L<sub>2</sub>-edge (2p<sub>1/2</sub> to 3d) at 521-526 eV, originated from the spin-orbital splitting.<sup>29</sup> We mainly focus on the line shape evolution of the L<sub>3</sub>-edge because the L<sub>2</sub>-edge demonstrates broader features owing to the shorter lifetime of the 2p<sub>1/2</sub> states and the Coster-Kronig Auger decay process.<sup>22</sup> It is clear that the shape of the L<sub>3</sub>-edge shows a strong dependence on the state of charge. More specifically, the intensity of the feature located at ~516 eV continuously decreases during discharge (spectra A-E) and increases during charge (spectra E-H). Note that the evolutions of the spectra collected in TEY and TFY modes are similar, indicating that the oxidation state changes of V are similar for the surface and bulk of VS<sub>2</sub> electrodes at the current collector side. The evolution of the absorption spectra can be interpreted by the redox reaction of V in VS<sub>2</sub>. The occupancy of V 3d states is increased (decreased) during discharge (charge), resulting in the change of the oxidation state of V. The modification of the oxidation state of V and the resultant change of metal-ligand bonding strength thus lead to a distinct change of the XAS signatures. It is very likely that the electrons are mainly transferred to the low-energy d orbitals (d<sub>xy</sub>, d<sub>xz</sub>, and d<sub>yz</sub>) upon discharge, and therefore the spectral shape change mainly occurs at the low energy region of the L<sub>3</sub>-edge.<sup>40-41</sup> At the end of charge back to 3.0 V, the V L-edge line shape (spectrum H) is not fully recovered to that of pristine VS<sub>2</sub>. These observations, consistent with the V K-edge XAS results, indicate that the redox reaction of V is only partially reversible during the first cycle, which explains the low Coulombic efficiency observed in the electrochemical results. Moreover, the V L-edge XAS also demonstrates a gradually decreased reversibility of the conversion reaction of VS<sub>2</sub> (Figure S3), in good agreement with the V K-edge XAS results.

The occupied electronic structure change of V 3d states during the cycling process is further investigated by V L-edge RIXS. The RIXS results map the fluorescence intensity as a function of excitation (ordinate) and emission (abscissa) energies. For

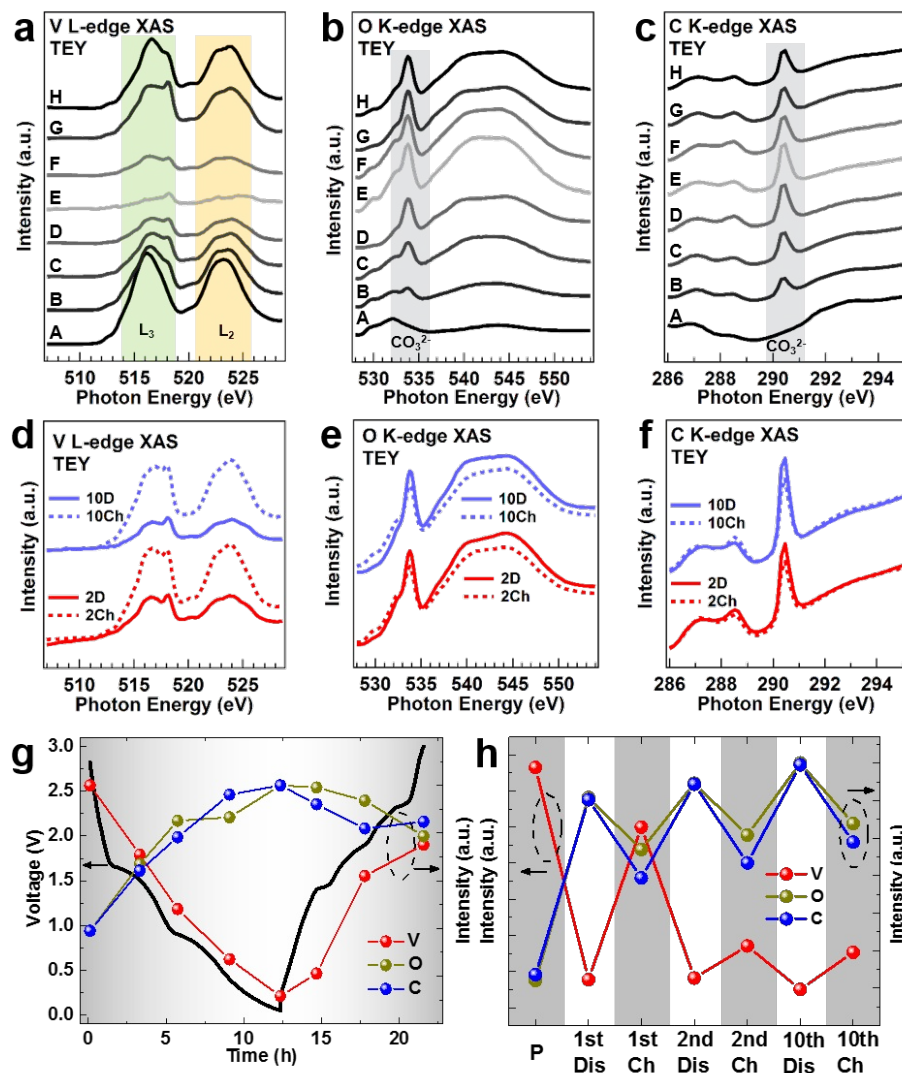
the pristine electrode, the RIXS map consists of the energy-loss features (d-d orbital excitations) that are parallel to the elastic line and the normal fluorescence features that have fixed emission energies (vertical stripes in the map). The occurrence of the strong d-d excitations is an indication of the heavily correlated nature of the electronic structure of  $VS_2$ .<sup>42</sup> The emission features located at 504-512 eV and 512-520 eV are assigned to the  $V L_\alpha$  and  $V L_\beta$  bands, respectively.<sup>29,42-43</sup> The intensity of the d-d excitations gradually decreases during discharging to 0.05 V, and then increases after charging back to 3.0 V. As the d-d excitations are highly sensitive to hybridization strength of the metal d states and ligand p states (the higher the strength, the stronger the d-d excitations),<sup>44-45</sup> the evolution of the d-d excitations observed in the RIXS maps provides direct evidence that the hybridization strength between V 3d states and S 3p states is depressed during discharge and enhanced during charge.

This scenario is further verified by the change of the fluorescence features of  $V L_\alpha$  and  $V L_\beta$  bands. The emission features at 514.5 eV (507.0 eV) and 517 eV (509.5 eV) of the  $V L_\beta$  ( $L_\alpha$ ) band originate from the V 3d states strongly hybridized with S 3p states (marked as V-S in the RIXS maps) and the pure V 3d states (marked as V in the RIXS maps), respectively, according to the calculated density of states of  $VS_2$ .<sup>13,15</sup> The weight of hybridized states is dominant for pristine  $VS_2$ . In contrast, the weight of pure V states becomes dominant with increasing lithiation, while it is greatly decreased during the subsequent delithiation. To quantitatively understand the evolution of these states, we have plotted the intensity ratio of the hybridized states and pure V states as a function of state of charge, as shown in Figure 4d. The intensity values were derived from the RIXS spectra excited at the  $L_2$  edge maximum of the corresponding XAS spectra (Figure S4). The intensity ratio evolution clearly reflects the transformation of the hybridized states to the pure V states during discharge due to the conversion from  $VS_2$  to metallic V, which is consistent with the

change of d-d excitations. However, the intensity ratio is not fully recovered to the pristine one at the end of charge, implying that the lithium is not fully extracted, consistent with the V L-edge XAS results. A similar intensity ratio evolution is also observed after 2 and 10 cycles (Figure S4 and S5). However, the intensity ratio change weakens progressively, indicating a gradual decrease of the reversibility of the lithium intercalation and conversion reactions of VS<sub>2</sub>. Again, this could be the main reason for the capacity degradation of VS<sub>2</sub> electrode with increasing cycle number.

Another important issue associated with the electrode material is the surface reaction during the cycling process. To understand this, we measured *ex situ* V L-edge, C and O K-edge XAS of the electrodes at different states of charge through the electrolyte side by both TEY (Figure 5) and TFY modes (Figure S6). The intensity of V L-edge XAS is dynamically changed as a function of the state of charge. As demonstrated in Figure 5a and Figure S6, the V L-edge XAS signal is gradually quenched during discharge (spectra A-E) and partially recovered during charge (spectra E-H). This observation suggests the formation of a SEI layer on the electrode surface, whose thickness swells during discharge and shrinks during charge. The breathing behavior of the SEI layer is also observed throughout the 2nd and 10th cycles, as verified by the intensity change of the V L-edge XAS feature (Figure 5d and Figure S6d). These results indicate that the formation of the SEI layer on the surface of VS<sub>2</sub> electrode is a highly dynamic process, in contrast to the conventional wisdom that the SEI layer is stable once it is formed.<sup>31,37,46-50</sup>





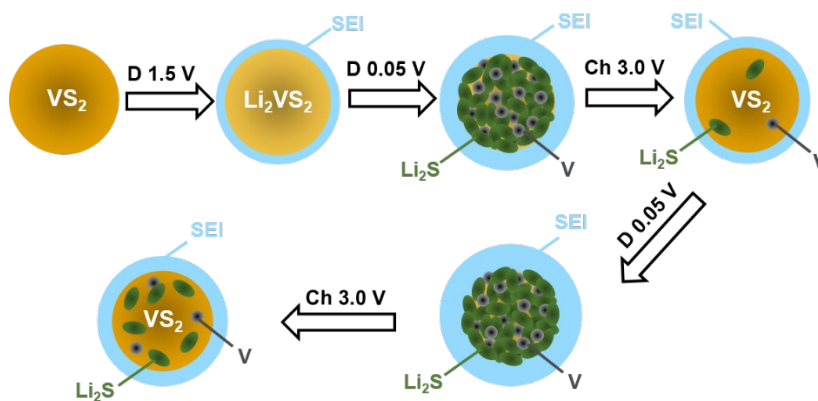
**Figure 5.** Characterization of the formation process of the SEI layer on the electrode surface. *Ex situ* V L-edge (a, d), O K-edge (b, e), and C K-edge (c, f) XAS spectra throughout the first, second and tenth cycles, respectively. The XAS spectra were collected on the same samples as the RIXS results through the electrolyte side. Intensity evolution of V  $L_{3}$ -edge feature and carbonate species as a function of discharge/charge states in the first cycle (g) and cycle numbers (h).

The dynamic evolution of the SEI layer is further confirmed by the O K-edge XAS results measured from the same samples, as shown in Figure 5b and Figure S6b. The main feature at 533.8 eV corresponds to the  $\pi^*$  peak of carbonate ( $\text{CO}_3^{2-}$ ) groups,<sup>31,46</sup>

and its intensity is greatly enhanced during discharge and partially suppressed during charge. A similar phenomenon is also observed with further cycling (Figure 5e and Figure S6e), suggesting the repeated development and decomposition of carbonate species during the electrochemical processes over extended cycles. The same evolution of the carbonate species is also observed in the C K-edge XAS results (Figure 5c, f and Figure S7c, f). The formation of carbonate species is most likely due to the decomposition of the non-aqueous electrolyte (EC and DEC in our case) at the electrode surface, which is the main component of the formed SEI layer.<sup>37,46</sup> In addition, the intensity variation of the carbonate species is similar for the TEY and TFY spectra (Figure 5 versus Figure S7), strongly indicating that the chemical composition changes throughout the SEI layer during the discharge and charge processes.

To quantitatively understand the development of the SEI layer, we plotted the intensity evolution of the V L<sub>3</sub>-edge feature and the carbonate species as a function of states of charge (Figure 5g) and cycle number (Figure 5h). Because the absolute intensity of the TFY signal contains a self-absorption effect, we only use the TEY spectra for this quantitative analysis. It can be clearly seen that the carbonate species are gradually formed during discharge and decomposed during charge, corresponding the increase and decrease of the thickness of the SEI layer, respectively. As a consequence, the intensity of the V L<sub>3</sub>-edge feature demonstrates an opposite trend to that of the carbonate species. Note that the remarkably decreased intensity change of V L<sub>3</sub>-edge feature from the second cycle is probably related to the decreased reversibility of the electrochemical reaction of VS<sub>2</sub>. In addition, it is notable that only a part of the carbonate species is degraded during charge, resulting in a steady increase of the overall amount of the carbonate species with cycling. This indicates that the formation of the SEI layer on the electrode surface is a dynamic process and the SEI layer with a large amount of carbonate species

gradually becomes more extensive over extended cycles, as illustrated in Figure 6. Actually, the dynamic behavior of the SEI layer was also observed for other conversion electrodes in LIBs, e.g., NiO,<sup>37</sup> ZnFe<sub>2</sub>O<sub>4</sub>,<sup>51</sup> and TiS<sub>2</sub>,<sup>52</sup> which may suggest that this is a universal behavior for the SEI formation process of conversion-based electrodes.



**Figure 6.** Schematic illustration for the proposed reaction mechanism and formation process of the SEI layer for the VS<sub>2</sub> electrode. The VS<sub>2</sub> electrode experiences intercalation and conversion reactions sequentially during discharge, and the reversibility of the reactions is gradually decreased over extended cycles. The formation process of the SEI layer is highly dynamic during the discharge and charge processes.

## Conclusions

We have performed a systematic investigation of the electrochemical reaction mechanism and formation process of the SEI layer from the VS<sub>2</sub> nanosheets used as the electrode material for LIBs using multimodal *in situ* and *ex situ* X-ray spectroscopy. As summarized in Figure 6, the VS<sub>2</sub> electrodes experience lithium intercalation and conversion reactions consecutively during the discharge process and the structure is partially recovered during the subsequent charge process. Both V and S are involved in the redox process during cycling and the reversibility of these reactions gradually decreases over extended cycles. In addition, we find that the

electrochemical processes can influence both the oxidation states of V and the hybridization strength between V and S, as directly evidenced by the intensity change of the V-S hybridized states and pure V states as well as the d-d excitations as a function of the state of charge shown in the RIXS results. Furthermore, we have obtained unambiguous evidence that the formation of the SEI layer on the VS<sub>2</sub> electrode surface is a highly dynamic process, in which the carbonate species in the SEI layer is developed and partially decomposed during discharge and charge, respectively, with a gradual increase of the overall amount of the carbonate species with cycling. This dynamic formation process of the SEI layer could be a universal phenomenon for conversion-based electrodes. The present study delivers deeper insights into the electrochemical reaction mechanism of TMD based electrodes for LIBs and sheds light on the formation process of the SEI layer, which could be useful for guiding the rational design of other TMD electrode materials to achieve high power and long cycling LIBs.

## Supporting information

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

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