

Direct Observation of Li Migration into V_5S_8 : Order to Antisite Disorder Intercalation Followed by the Topotactic-Based Conversion Reaction

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Cite This: *ACS Appl. Mater. Interfaces* 2020, 12, 36320–36328

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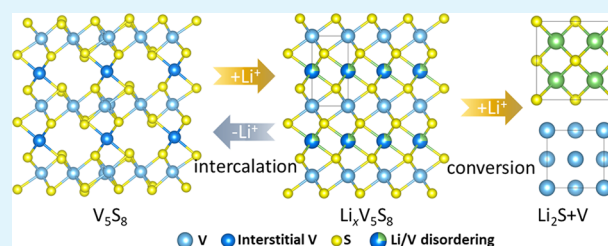
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ABSTRACT: Two-dimensional transition-metal dichalcogenides hold great potential in rechargeable lithium-ion batteries. Their electrochemical properties are closely related to the structural evolutions during lithium-ion migration. Understanding these migration/reaction mechanisms is important to help improve battery performance. Herein, we report the real-time and atomic-scale observation of phase transitions during the lithiation and delithiation for V_5S_8 via in situ electron diffraction and high-resolution transmission electron microscopy techniques. We find that the phase transformation proceeds via a sequence of order to antisite disorder intercalation and topotactic-based conversion reaction. During the intercalation reaction, the lithium ion destroys the orderings of the interstitial V with the formation of Li/V antisite. Such a reaction is found to be reversible, i.e., the extraction of lithium from $Li_xV_5S_8$ leads to the recovery of V orderings. The conversion reaction involves heterogeneous nucleation of Li_2S with 3–20 nm nanodomains, which maintain the crystallographic integrity with $Li_xV_5S_8$. These findings elucidate the complex interactions between the lithium ion and host V_5S_8 during ionic migration in solids, which should be helpful in understanding the relationship between phase transformation kinetics and battery performance.

KEYWORDS: *in situ TEM, transition-metal chalcogenide, lithium-ion migration, Li/V antisite, topotactic growth of Li_2S*



1. INTRODUCTION

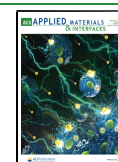
Rechargeable lithium-ion batteries (LIBs) have been used as an efficient energy storage device in portable electronics and electric vehicles.^{1–3} The ever-growing demand for unique applications such as ultrafast discharging–charging, super large capacities, and high output power necessitates searching and developing new electrode materials. Transition-metal dichalcogenides (TMDs) have been extensively explored as promising anodes^{4,5} in LIBs due to their two-dimensional (2D) layered stacking structure through weak van der Waals interactions, which facilitates the fast alkaline ions transport.⁶ These TMDs have demonstrated good Li-storage capacities via complex reactions including intercalation, conversion, and alloying reaction.^{7–10} It is reported that the inserted lithium ions trigger different phase transformations via different pathways, such as 2H to 1T transition in MoS_2 ,^{11–13} disordering transition¹⁴ and intermediate superstructure¹⁵ in SnS_2 , two-phase transition in TiS_2 ,^{16–18} metal extrusion in CuS_2 ,¹⁹ and anisotropic lithiation in ReS_2 .²⁰ These diverse lithiation pathways generate different intermediate or final products, which in turn influence the reaction reversibility, energy efficiency, and battery cyclability.^{21,22} Therefore, it is important to investigate the reaction pathway and phase transformation to improve battery performance.

Metallic VS_2 has a large interlayer spacing of 5.67 Å,²³ which processes a high energy density and good reversibility as an anode material for LIBs.^{24,25} V_5S_8 is another member of vanadium sulfides family that consists of ordered V within the interlayers, occupying one-quarter of available S–S octahedral sites and linking the two adjacent VS_2 monolayers. Such a three-dimensional structure can overcome the drawback of a 2D structure with anisotropic diffusion, which requires more engineering to align the crystal planes with the diffusional direction to achieve large insertion efficiency.²⁶ Moreover, the metallic nature of V_5S_8 is beneficial to the transport of electrons. These aspects enable V_5S_8 to be used in not only Li but Na and K ion batteries with good electrochemical performance.^{27–29} For example, V_5S_8/C delivers high discharge and charge capacity of 1245 and 1112 mAh g⁻¹ at 0.1 A g⁻¹ and the capacity is maintained at 846 mAh g⁻¹ after 700 cycles at 1 A g⁻¹ for LIBs. With the current density increased

Received: May 11, 2020

Accepted: July 15, 2020

Published: July 15, 2020



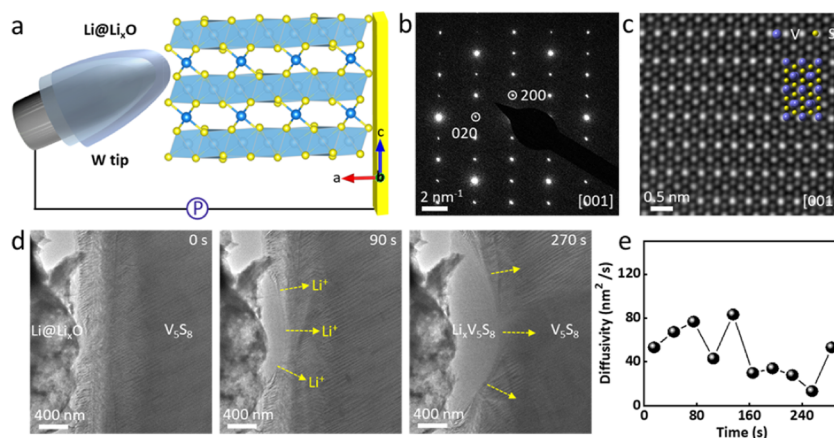


Figure 1. In situ lithiation of a V_5S_8 nanosheet. (a) In situ TEM setup, including a metallic lithium probe, a thin passivation layer of Li_xO , and a V_5S_8 nanosheet. (b) SAED pattern along the $[001]$ direction and (c) corresponding atomically resolved HAADF-STEM image. The purple balls indicate V and yellow balls represent S. (d) Time-series TEM images during the lithiation of a V_5S_8 nanosheet. A clear boundary between V_5S_8 and $Li_xV_5S_8$ can be observed. The yellow arrows roughly indicate the diffusion directions of lithium ions. (e) Estimated diffusivity of lithium ions is plotted as a function of time.

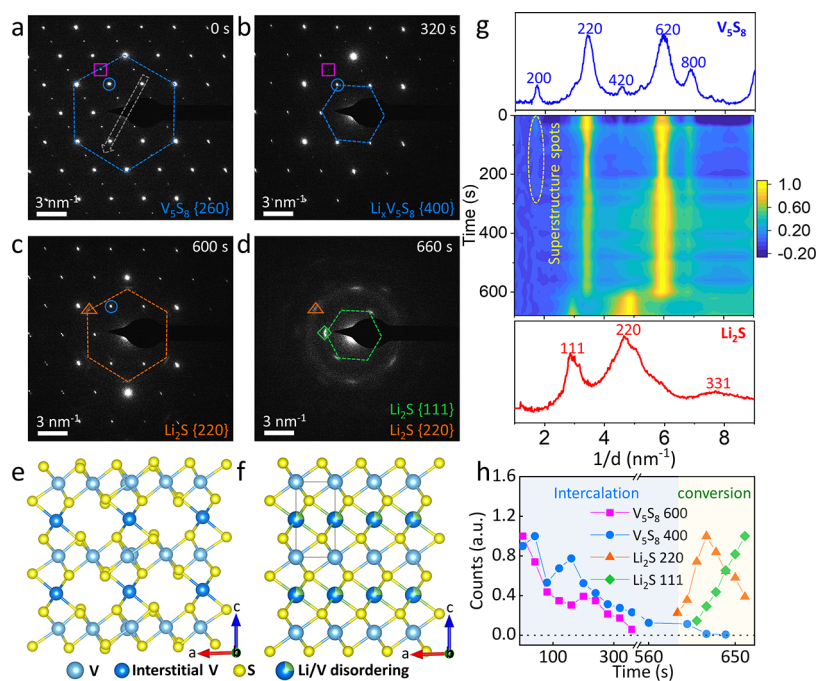


Figure 2. In situ SAED patterns tracking the structural evolution upon lithium insertion into the V_5S_8 nanosheet. (a–d) Time-lapsed SAED patterns along the $[001]$ direction of lithiated V_5S_8 . (e) Atomistic model of V_5S_8 and (f) $Li_3V_5S_8$. The gray, purple, yellow, and mixture balls indicate the V, interstitial V, S, and Li/V random arrangement. (g) Radial intensity profiles of the diffraction reflections derived from Movie S2. The top and the bottom planes show the diffraction peaks of V_5S_8 and Li_2S , respectively. (h) Extracted diffraction intensities of V_5S_8 , $Li_xV_5S_8$, and Li_2S are plotted as a function of time. The blue circles, pink squares, orange triangles, and green diamonds correspond to these label shapes in (a–d).

to 8.0 A g^{-1} , the specific charge capacity can maintain at 432 mAh g^{-1} and recovers to 821 mAh g^{-1} when the rate returns to 0.1 mAh g^{-1} . Ou et al. studied the electrochemical reaction mechanism of V_5S_8 and its reversibility during the electrochemical cycling by in/ex situ X-ray diffraction (XRD).²⁸ During the discharge, they observed an intercalation reaction to form $Li_xV_5S_8$ from open-circuit voltage to 0.45 V, followed by a conversion reaction to form Li_2S and V from 0.45 to 0.01 V. At the charge process, $Li_xV_5S_8$ is formed from 0.01 to 1.7 V and the structure is restored to V_5S_8 from 1.7 to 3.0 V. However, how the ions react with the host atoms and migrate within V_5S_8 and how the reaction interface evolves, which are

related to the electrochemical performance, have been rarely explored, thus motivating our study.

In this work, using in situ electron diffraction (ED) and high-resolution transmission electron microscopy (HRTEM) techniques, we have tracked the dynamical structural evolutions during the (de)lithiation of V_5S_8 from nanometer to an atomic scale. We find that the initial insertion of lithium ions is via an intercalation reaction, which triggers an order to antisite disorder transformation by destroying the orderings of the interstitial V. Such transition is found to be reversible, i.e., the extraction of lithium ions from $Li_xV_5S_8$ results in the recovery of the orderings of interstitial V atoms. The following

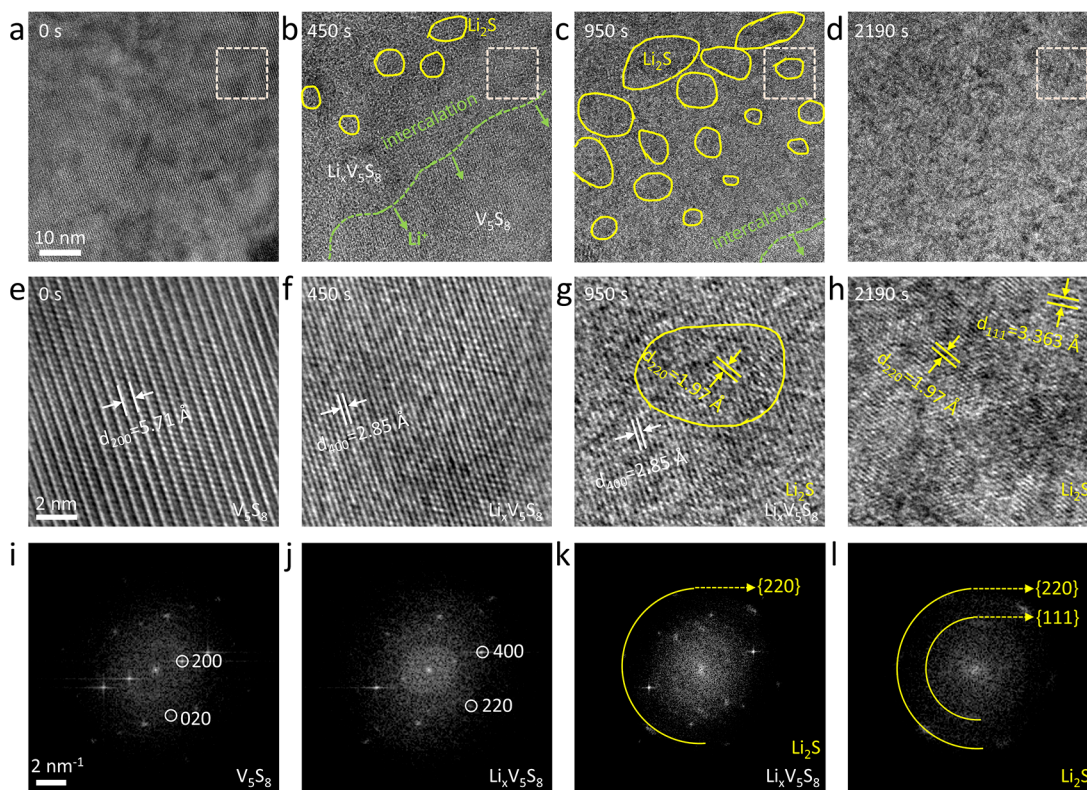


Figure 3. In situ HRTEM tracking the structural evolution during lithiation of V_5S_8 . (a–d) Consecutive HRTEM images during the insertion of lithium into V_5S_8 . The green dashed lines indicate the intercalation interface between V_5S_8 and $Li_xV_5S_8$. The yellow circles in (b) and (c) mark the nucleation of Li_2S . (e–h) Corresponding enlarged region highlighted by the white dashed squares in a–d, and (i–l) the corresponding FFT patterns.

conversion reaction involves the heterogeneous nucleation and topotactic growth of Li_2S nanodomains. These findings reveal detailed structural evolutions during lithium migration in V_5S_8 , indicating delicate and complex interactions between foreign ions and host atoms rather than a simple van der Waals interaction that may exist in TMD electrode materials.

2. RESULTS AND DISCUSSION

Figure 1a shows a typical schematic diagram of a nanosized solid battery to achieve (de)lithiation, including a Li counter electrode, a solid-state electrolyte (a passivation Li_xO layer), and a V_5S_8 nanosheet as the working electrode. The V_5S_8 nanosheet is thinned from the bulk (Figure S1), which is synthesized by a chemical vapor transport method, as we have previously reported.³⁰ V_5S_8 is composed of distorted VS_2 layers intercalated with ordered V atoms, which occupy one-quarter of the octahedra sites (Figure 1a). Such interstitial V atoms cause superstructure diffraction spots (Figure 1b), compared with that of VS_2 (Figure S2). The acquired high-angle annular dark-field-scanning TEM (HAADF-STEM) image in Figure 1c is consistent with the atomistic structure along the [001] rather than the [100] zone axis despite their ED patterns being quite similar (Figure S3). The bright and dark atom columns are identified as V and S, respectively. Upon lithium insertion, a clear phase boundary between $Li_xV_5S_8$ and V_5S_8 can be observed, as shown in Figure 1d and Movie S1. As the lithiation progresses, the reaction gradually propagates from the surface to internal. We further acquire the diffusivity of the lithium ion (Figure 1e), according to the equation $D = d^2/2t$,³¹ where D is the diffusivity, t is the diffusion time, and d is the

diffusion distance. The measured diffusivity is based on the migration of the reaction front, indicating the lithium diffusion in V_5S_8 . The calculated diffusivity is about 10^{-13} – 8×10^{-13} $cm^2 s^{-1}$, which is comparable to the electrochemically measured diffusivity (6.168×10^{-13} – 8.285×10^{-13} $cm^2 s^{-1}$).²⁸ The valley at 100 s is likely caused by the change of a worse contact between Li_2O and V_5S_8 . More accurate Li diffusion coefficients in different phases can be obtained by the galvanostatic intermittent titration technique.

To investigate the structural evolutions during lithium ions intercalation, we carried out time-series in situ electron diffraction experiments, as shown in Figure 2a–d and Movie S2. The SAED pattern (Figure 2a) indicates a good single crystalline structure of V_5S_8 . Upon the insertion of lithium ions, we observe that the superstructure diffraction spots gradually disappear (Figure 2b). The superstructure reflections are caused by ordered interstitial V atoms; thus, its disappearance suggests that such periodic interstitial V arrangement is damaged and all octahedral sites within the interlayer are randomly occupied by lithium or V,³² as illustrated in Figure 2e–f. The crystal symmetry of V_5S_8 is monoclinic (space group: $F2/1m$), while $Li_xV_5S_8$ with disordered V is hexagonal (space group: $P\bar{3}m1$).³³ The simulated ED pattern of such a Li/V random structure can match with experimental one (Figure S4). In contrast, the superstructure can be maintained for 2 h under the pure electrical field (Figure S5 and Movie S3), further suggesting that the disappearance of the superstructure is not caused by the electrical field and the electron beam irradiation at low doses but related to lithium insertion. With more lithium ions insertion, we observe the formation of Li_2S (JCPDS No. 23-

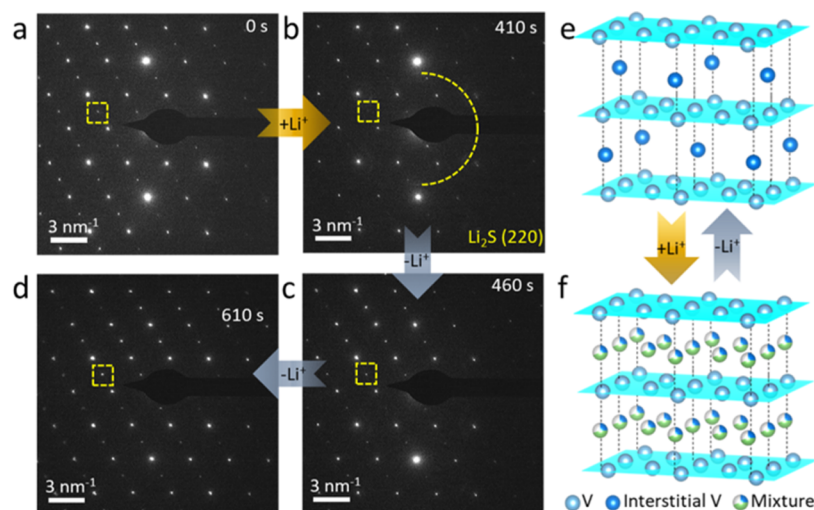
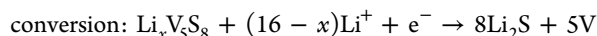
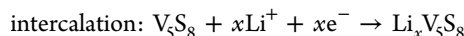


Figure 4. Reversible V ordering and disordering during lithium-ion migration in V_5S_8 . (a, b) Time-series SAED showing lithium interaction and (c, d) extraction process. Lithiation is achieved using a -2 V voltage until the appearance of Li_2S , indicated by the yellow arc at 410 s in (b). Then, the voltage is changed to be $+4$ V to extract lithium. The yellow squares highlight the gradual disappearance and reappearance of the characteristic superstructure reflection. (e, f) Atomistic models of V_5S_8 and $Li_xV_5S_8$. Sulfur atoms are omitted for a better visualization of V atoms.

0369), indicating the start of the conversion reaction (Figure 2c). The Li_2S {220} crystal planes are formed prior to {111} planes (Figure 2c,d). Interestingly, the newly formed Li_2S maintains crystallographic integrity with V_5S_8 (highlighted by the hexagons), indicating that the nucleation and growth of Li_2S are coherent to the pristine V_5S_8 structure.

The whole lithiation reaction is further examined by acquiring the radial intensity profiles (Figure 2g) of the diffraction reflections derived from Movie S2. It is observed that the superstructure peak (200) gradually disappears within ~ 320 s. Basically, the in-plane crystal parameter is almost unchanged in the intercalation process (Figure S6). The formed $Li_xV_5S_8$ shows an increased interlayer spacing ($\sim 2.6\%$) compared with V_5S_8 based on the previous XRD results.²⁸ Finally, the peaks of $Li_xV_5S_8$ disappear and then the (220) and (111) peaks of Li_2S appear sequentially. After a deep lithiation, metal V is formed (Figure S7). Based on the changes of in/out-plane crystal parameters, the volume expansion during the intercalation process is about 2.6%. The conversion reaction always shows more obvious volume expansion, as observed during the lithiation of Co_3O_4 .³⁴ However, V_5S_8 we used for in situ TEM is a large micron sheet (Figure 1d), making it difficult to identify the morphology changes caused by the volume expansion. The diffraction intensities of V_5S_8 , $Li_xV_5S_8$, and Li_2S are extracted in Figure 2h, presenting the whole reaction process that is initiated from an intercalation reaction to form interstitial-V-disordered $Li_xV_5S_8$, followed by the conversion reaction to form Li_2S and V. The corresponding reaction equations can be expressed as



The overall reaction mechanism is similar to previous in situ XRD results²⁸ that are initiated with intercalation and followed by a conversion reaction. However, our in situ TEM experiments provide more microscopic structural insights that the inserted lithium ions can destroy the orderings of the interstitial V and the formed Li_2S maintains the crystallographic integrity with $Li_xV_5S_8$.

To further reveal local structural evolutions, time-series HRTEM images are recorded in Figure 3a–h. Figure 3a is a typical HRTEM image of V_5S_8 viewing along the [001] direction. Due to the orderings of interstitial V atoms, the pristine V_5S_8 features superstructure stripes (Figure 3e) and diffraction spots (Figure 3i). Upon the lithium insertion, such superstructure stripes and diffraction reflections disappear and the corresponding plane distance (2.85 Å) (Figure 3b,f,j) becomes one-half of the pristine one (5.71 Å), indicating the loss of the orderings of interstitial V. We can observe the intercalation interface between V_5S_8 and $Li_xV_5S_8$ as well as the formation of Li_2S nanodomains (Figure 3b). The priority to forming the Li_2S {220} plane is again observed (Figure 3c,g,k). Interestingly, we find heterogeneous nucleation of Li_2S during the conversion reaction marked by the yellow circles in Figure 3b,c. The size of Li_2S nanodomains ranges from 3 to 9 nm near the reaction front and grows larger away from the reaction front (12–18 nm). From the enlarged view of a small Li_2S domain (Figure 3g), we can observe that the clear lattice stripes of the Li_2S (220) plane maintain a topotactic relationship with the $Li_xV_5S_8$ (400) plane. These small Li_2S domains grow larger and larger, and finally, the structure totally transforms into Li_2S (Figure 3h,l). Note that Li_2S nanodomains are formed near the interface (Figure 3b,c) between the pristine V_5S_8 and $Li_xV_5S_8$, which suggests that bulk V_5S_8 is partially inserted and then converted rather than fully intercalated and then converted. Such nonequilibrium lithiation has also been observed in Fe_3O_4 ³⁵ and Co_3O_4 ³⁴ nanoparticles, which is influenced by discharging rates. At a low rate, the conversion reaction starts after the full intercalation while the intercalation reaction can be overwhelmed by the conversion reaction at a high rate.³⁴ Accordingly, an effective controlling the degree of the lithiation can be achieved by regulating the discharging rate for these intercalation-conversion-type electrode materials.

For rechargeable LIBs, it is a prerequisite to reversibly insert lithium ions into host materials. We find that once the insertion of lithium ions into V_5S_8 is controlled within the intercalation range, the lithium ions in $Li_xV_5S_8$ can be partly extracted (Movie S4). We first insert lithium ions into V_5S_8 by

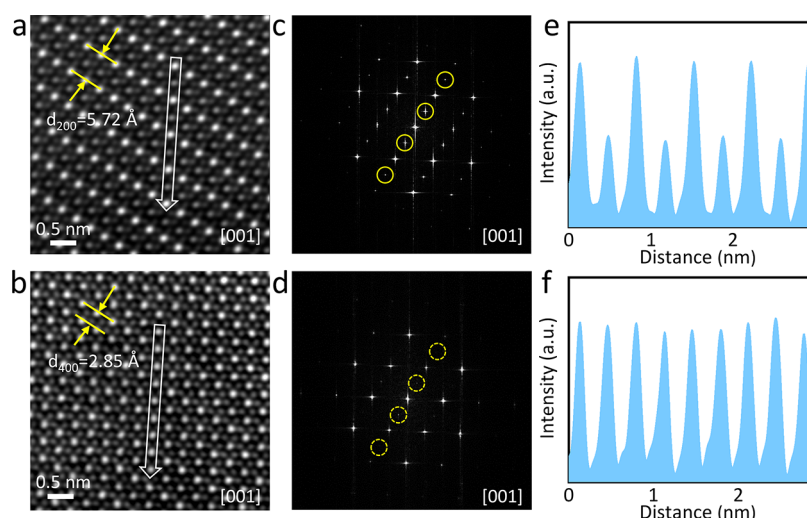


Figure 5. Atomic-scale observation of the superstructure-to-nonsuperstructure transition. (a, b) HAADF-STEM images of the pristine V_5S_8 and the structure after electron beam irradiation. The raw pristine images are shown in Figure S11. (c, d) Corresponding FFT patterns. The yellow circles highlight the superstructure diffraction spots. (e, f) Atom columns contrast extracted from the line profiles in (a) and (b), as shown by white arrows.

applying a -2 V voltage. Upon lithium insertion, the superstructure diffraction spots gradually disappear (Figure 4a,b). Though the zone axis has changed a little (Figure 4a,b), the zone axis tilting effect on the disappearance of superstructure spots can be eliminated, as explained in Figure S8. Once the diffraction spots of Li_2S appear (Figure 4b), indicating the conversion reaction starts, the applied voltage is changed to be $+4 \text{ V}$ to extract the lithium ions in $Li_xV_5S_8$. It is found that the disappeared superstructure reflections gradually reappear (Figure 4c,d), suggesting that the random V becomes ordered due to the extraction of lithium ions. Such reversible intercalation reaction, as illustrated in Figure 4e,f, can promise good cycling performance when lithiation is controlled within the intercalation range, which has been used to improve the cycling performance of VS_2 .³⁶

It is known that the battery performance is largely determined by the structural evolutions during the reaction for LIBs. By in situ TEM, we investigate the reaction pathways and phase transformations of V_5S_8 . During the lithiation of V_5S_8 , we find the orderings of the interstitial V is destroyed since the inserted lithium can take up the position of interstitial V and pull V to the neighboring octahedral sites due to Coulomb repulsion,³⁷ enabling Li and V to occupy the octahedral sites randomly. Indeed, the interstitial V in V_5S_8 can migrate to the near octahedral sites above $800 \text{ }^\circ\text{C}$, transforming into a CdI_2 -type structure.³² Then, the octahedral sites within S–V–S layers become equivalent and vacancies and cations become randomly distributed, leading to a symmetry change from $F2/m$ to $P3m1$.³³ The previous work reported that the ordered Na/vacancy superstructure within the interlayers in $NaCoO_2$ lowers Na diffusion coefficient even up to two orders of magnitude.³⁸ Based on the first-principles calculations, we also compare the diffusion barriers of lithium diffusing in the bulk VS_2 (without ordered V within the interlayers) and V_5S_8 (existing ordered V within the interlayers). The lithium diffusion barriers are about 0.26 eV in VS_2 and 0.42 eV in V_5S_8 , as shown in Figure S9. The lower diffusion barrier in VS_2 suggests a fast lithium-ion diffusion, which is consistent with the electrochemical measurements that the lithium-ion diffusion coefficient in V_5S_8 ($6\text{--}8 \times 10^{-13}$

$\text{cm}^2 \text{ s}^{-1}$)²⁸ is 2–3 magnitude lower than that for VS_2 (10^{-10} – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$).³⁹ Accordingly, the ordered V might generate a higher diffusion barrier that blocks the diffusion of lithium, and such a V disordered structure is likely beneficial to the diffusion of lithium.

To further confirm such disordering behavior at an atomic scale, we have mimicked the superstructure-nonsuperstructure transition under the high-energy electron beam, which has been widely used to track the dynamics of the phase transition.^{40,41} Figure 5a is an atomically resolved HAADF-STEM image of the pristine V_5S_8 . After beam illumination (see the Experimental Section for details), the superstructure lattices disappear with the plane distance becoming half of the pristine value (Figure 5a,b), accompanying with the disappearance of the superstructure reflections (Figure 5c,d). It is found that the uneven contrast of each atom column (Figure 5e) becomes more uniform (Figure 5f) after beam irradiation. In fact, the uneven contrast is caused by the interstitial V, which brings in a brighter contrast, as verified in the corresponding simulated HAADF STEM image (Figure S10). Under electron beam illumination, similar to that under the heat,³² the interstitial V can migrate to the near equal octahedral sites; thus, vacancies and V become distributed randomly within this layer, leading to a uniform STEM contrast (Figure 5f).

Furthermore, our in situ TEM study has revealed a topotactic growth of Li_2S during the conversion reaction of V_5S_8 . The topotactic transition means that the crystal orientation of the product phase is correlated with the crystal orientation of the parent phase.^{42,43} The orientation of the substrate determines the crystal orientation of the product, thus influencing the nucleation and growth of a new phase considering that different orientations might have different nucleation energy and growth driving energy.⁴⁴ Different from most topotactic transformations observed in the intercalation process via shuttling lithium ions between the tunnels of the host,⁴⁵ we find a topotactic conversion transformation, which plays a vital role in understanding the structure evolutions and the related battery performance. It is reported the topotactic cation diffusion through an invariant lattice of fluoride anions

governs the reversibility of the conversion reactions.⁴² However, most studies failed to observe such behavior due to material or technique restrictions. For example, the powder and the polycrystalline materials show random orientations,^{18,46} preventing the identification of the specific orientation relationship. Also, in situ XRD techniques provide the information of a series of equivalent planes rather than one specific one. Thus, it is beneficial to clarify more information about such topotactic transformation by in situ TEM techniques of the single-crystal battery materials.

We also compare the reaction mechanism of V_5S_8 with other TMDs. Similar to MoS_2 ^{11,13} and TiS_2 ,^{16,17} the reaction process of V_5S_8 proceeds via a sequence of intercalation and conversion reactions. The difference lies in the behaviors of the superstructures. The lithiation of MoS_2 and TiS_2 enables the formation of superstructures due to the distortion of Mo¹¹ or the ordered lithium insertion.¹⁶ V_5S_8 itself shows the feature of superstructures due to the ordered interstitial V. Because of the Li–V interactions, the inserted lithium ions can destroy such V orderings with the disappearance of the superstructure. Similarly, the insertion of sodium into MoS_2 enables the formation of superstructure due to the ordered Na occupation,⁴⁷ while the insertion of sodium into V_5S_8 is expected to destroy the superstructure because of Na–V interactions.

3. CONCLUSIONS

In summary, we have investigated the lithiation mechanism of V_5S_8 by in situ TEM at an atomic scale. It is found that the lithiation process is initiated with a cationic order-to-disorder intercalation and followed by a conversion reaction. The insertion of lithium can destroy the orderings of interstitial V atoms. The intercalation reaction is found to be reversible, and the lithium ions can be extracted from $Li_xV_5S_8$ accompanying by the recovery of the superstructure. During the following conversion, heterogeneous Li_2S nanodomains are formed, maintaining the crystallographic integrity with the $Li_xV_5S_8$. The reversibility of the conversion reactions seems to be highly dependent on these Li_2S nanodomains and its topotactic growth feature, which might guide future material research to develop and identify high-energy materials with a reversible conversion reaction. This mechanistic understanding of V_5S_8 provides some insights for the intercalation-conversion type materials, which will guide the future development of high energy density materials.

4. EXPERIMENTAL SECTION

4.1. Synthesis of V_5S_8 . The bulk V_5S_8 was synthesized by the chemical vapor transport method. The precursors (vanadium and sulfur powders) and transport agent (iodine) were first put into a silica ampule under argon. The ampule was then evacuated, sealed, and heated in a two-zone tube furnace to a temperature gradient of 850–1000 °C for 2 weeks before acquiring the bulk crystals.

4.2. In Situ TEM Experiments. In situ TEM experimental setup includes a V_8S_5 working electrode, a lithium metal as the counter electrode, and a thin layer Li_xO as the solid electrolyte. The formed Li_xO can serve as a solid-state electrolyte that allows the transport of Li^+ and prevents the transport of the electron since Li_2O is a good Li^+ conductor and an electronic insulator with the diffusivity of Li^+ being 10^{-10} cm² s⁻¹ and a large band gap of ~8 eV.⁴⁸ V_5S_8 used in this work was prepared by the mechanical polishing and ion-beam milling process using argon ion milling (Leica EM RES102). The ion milling process was carried out at 5 kV until a hole appeared, and then a low voltage (0.8 kV) was used to reduce the irradiation-damaged layers.

The metal lithium was scratched using an electrochemically etched sharp tungsten tip. The electrical TEM specimen holder (PicoFemto) was sealed in an argon-filled glovebox and then transferred into the TEM column. During the transfer process, the lithium probe was exposed to the air to form Li_xO on the surface. Basically, the exposure time was controlled within 5 s to obtain a 700–1000 nm Li_xO layer.⁴⁸ The tungsten tip is driven by a piezo-ceramic manipulator to contact with V_5S_8 . The lithiation of V_5S_8 was achieved by applying a small negative bias (–2 V) between the grounded tungsten probe and V_5S_8 , while a positive bias (4 V) was employed to extract the lithium ions.

4.3. Characterizations and Analysis. Powder XRD pattern was obtained on D8 Advance diffractometer using Cu $K\alpha$ radiation (40 kV and 100 mA), and the SEM image was acquired by FEI Quanta 200F. In situ ED and HRTEM techniques were carried out at a dose rate of 2 and 800 e \AA^{-2} s⁻¹, respectively, using Tecnai F20 at 200 kV equipped with a OneView IS (Gatan) camera. The atomically resolved STEM images were acquired using an aberration-corrected FEI Titan Themis G2 microscope operated at an accelerating voltage of 300 kV with a beam current of 50 pA, a convergence semiangle of 21 mrad, and a collection semiangle snap in the range of 80–380 mrad. The electron beam irradiation experiment was carried out using the STEM area scanning mode at 100 pA with an 18 nm × 18 nm scanning area. The corresponding dose rate is estimated to be 1.92×10^7 e \AA^{-2} s⁻¹.⁴⁹ The movies were prepared from time-series images. FFT patterns and the line profiles were obtained using DigitalMicrograph (Gatan) software. The simulation of the ED patterns was performed using CrystallMaker software, and the atomistic models were obtained by Vesta software. The radial intensity profiles are prepared by ImageJ software. The STEM simulation was carried out by Kirkland with COMPUTEM software.⁵⁰ The plots were drawn using Origin 2016.

4.4. First-principles Calculations. The structures of the bulk V_5S_8 , VS_2 , and their Li-adsorbed compounds were fully optimized by Vienna Ab initio Simulation Package (VASP).⁵¹ The climbing image nudged elastic band method was implemented in the VASP transition state tools to calculate the diffusion barriers of lithium ions.^{52,53} In our calculation, density functional theory with a cutoff energy of 500 eV was used; the generalized gradient approximation combined with the Perdew–Burke–Ernzerh form and the plane-wave basis set with the projector-augmented wave pseudopotential were adopted; the k -point mesh was sampled by the Monkhorst–Pack method with a separation of 0.02 \AA^{-1} ; and the convergence thresholds were 10^{-6} eV for energy and 10^{-3} eV/ \AA for a force to get the precise results.^{54,55}

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.0c08428>.

Structure and morphology of V_5S_8 ; comparison of V_5S_8 and VS_2 ; structure of V_5S_8 ; comparison of V_5S_8 and $Li_3V_5S_8$; structural evolutions under pure electrical field; plane distance changes during the lithiation of V_5S_8 ; formation of metal V; simulated ED patterns of V_5S_8 ; diffusion pathways and energy profiles; structure of V_5S_8 along the [001] direction; unfiltered HAADFSTEM images (PDF)

Migration of phase boundary between $Li_xV_5S_8$ and V_5S_8 (MP4)

Time-series in situ SAED patterns upon lithium ion insertion into V_5S_8 (MP4)

Superstructure maintained for 2 h at a dose rate of 2 e \AA^{-2} s⁻¹ under the pure electrical field (MP4)

Time-series SAED patterns showing lithium ion interaction and extraction process (MP4)

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S.C. and C.Y. contributed equally to this work. P.G., J.L., L.W., and J.L. conceived and supervised the project. S.C. performed in situ TEM experiments with the guidance of P.G. and help from R.S. and X.M.; C.Y. conducted the DFT calculations under the guidance of J.L.; J.N. grew the V_5S_8 crystals and performed SEM and XRD characterizations with the guidance from X.W.; M.W. prepared the TEM specimens. J.C., J.F., L.W., and J.Q. provided crystals. S.C., L.W., and P.G. wrote the manuscript, and all authors participated in the discussions.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was supported by the Key-Area Research and Development Program of Guangdong Province (Grant No. 2018B010109009), National Natural Science Foundation of China (Grant Nos. 51672007, 11974023, 51575135, and U1537206), National Basic Research Program of China (Grant Nos. 2016YFA0300804 and 2016YFA0300903), Fundamental Research Funds for the Central Universities, China (Grant No. ZYGX2019Z008), Natural Science Foundation of Heilongjiang Province of China (Grant No. YQ2019E023), and “2011 Program” Peking-Tsinghua-IOP Collaborative Innovation Center of Quantum Matter. We acknowledge the Electron Microscopy Laboratory at Peking University for the use of electron microscopes and the high-performance computing platform of Peking University.

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