

Titanium Sulfides as Intercalation-Type Cathode Materials for Rechargeable Aluminum Batteries

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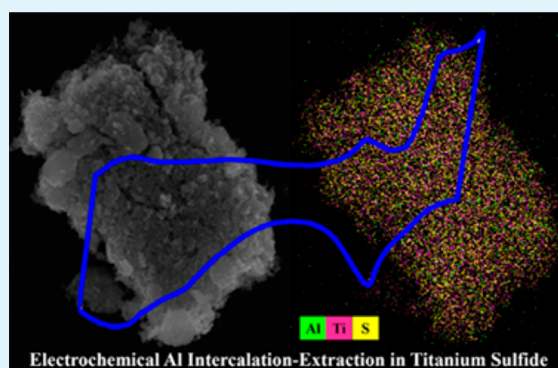
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S Supporting Information

ABSTRACT: We report the electrochemical intercalation–extraction of aluminum (Al) in the layered TiS_2 and spinel-based cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ as the potential cathode materials for rechargeable Al-ion batteries. The electrochemical characterizations demonstrate the feasibility of reversible Al intercalation in both titanium sulfides with layered TiS_2 showing better properties. The crystallographic study sheds light on the possible Al intercalation sites in the titanium sulfides, while the results from galvanostatic intermittent titration indicate that the low Al^{3+} diffusion coefficients in the sulfide crystal structures are the primary obstacle to facile Al intercalation–extraction.



KEYWORDS: aluminum-ion battery, aluminum intercalation, multivalent ion battery, titanium sulfides, ionic liquid electrolyte

INTRODUCTION

The rechargeable aluminum-ion (Al-ion) battery is an intriguing electrochemical energy storage technology based on the most abundant metal in the earth's crust. It can be a potentially interruptive technology for large scale energy storage applications.¹ However, reversible electrochemical processes involving Al are inherently difficult. One challenge is the lack of feasible electrolytes for Al deposition–dissolution at the anode. The most commonly adopted Al electrolytes to date are Lewis acidic mixtures of aluminum halides (AlX_3 , X = Cl and Br) and halide-containing ionic liquids (ILs), such as 1-butylpyridinium chloride and 1-ethyl-3-methylimidazolium chloride, with molar ratio > 1.^{2,3} Halide-free IL electrolyte⁴ and aqueous AlCl_3 electrolytes^{5,6} have also been reported. Another challenge comes from the lack of understanding of cathode materials. With increasing interest, a few potential cathode materials have been proposed based on various reaction mechanisms.^{7–17} Transition metal oxides, particularly vanadium(V) oxide (V_2O_5), were studied as intercalation-type cathode materials.^{10–14} Lin and co-workers proposed graphitic carbon as a possible cathode material based on an anion intercalation mechanism.¹⁵ Archer's and Wang's groups also presented the possibility of sulfur as a cathode material based on a redox conversion reaction.^{8,9}

We previously reported the Chevrel phase molybdenum sulfide (Mo_6S_8) as an intercalation-type metal sulfide cathode material.¹⁶ An independent investigation by Lee and co-workers further confirmed the reversible electrochemical Al intercala-

tion in Mo_6S_8 .¹⁷ Our selection of transition metal sulfides in place of oxides as Al-ion cathode materials is crucial: Due to the strong Coulombic effect, the energy barrier for multivalent ion transport in the oxide crystal structure is high.¹⁸ Therefore, a more polarizable (softer) anionic framework is needed for facile Al^{3+} ion intercalation–extraction, making transition metal sulfides promising candidates as Al-ion cathode materials. Although Mo_6S_8 showed unambiguous electrochemical Al intercalation–extraction properties, its specific capacity was not ideal due to its high molecular mass. We herein report the Al intercalation–extraction properties of two titanium sulfides, layered TiS_2 and spinel-based, cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$, as potential intercalation-type cathode materials for Al-ion batteries.

EXPERIMENTAL SECTION

Synthesis of Layered TiS_2 . Layered TiS_2 was synthesized via solid state reaction by heating stoichiometric mixture of the elements (Ti and S).¹⁹ Stoichiometric amounts of Ti powder (Alfa Aesar, 325 mesh, 99.5%) and S powder (Sigma-Aldrich 99.5–100.5%) were thoroughly mixed and then sealed in an evacuated quartz tube, which was subsequently heated in a muffle furnace. The temperature was first ramped up to 450 °C at a rate of 0.3 °C min^{-1} and then held at 450 °C for 24 h, after which the temperature was ramped up to 640 °C in 24 h and held at 640 °C for 3 days. The synthesized TiS_2 was collected in

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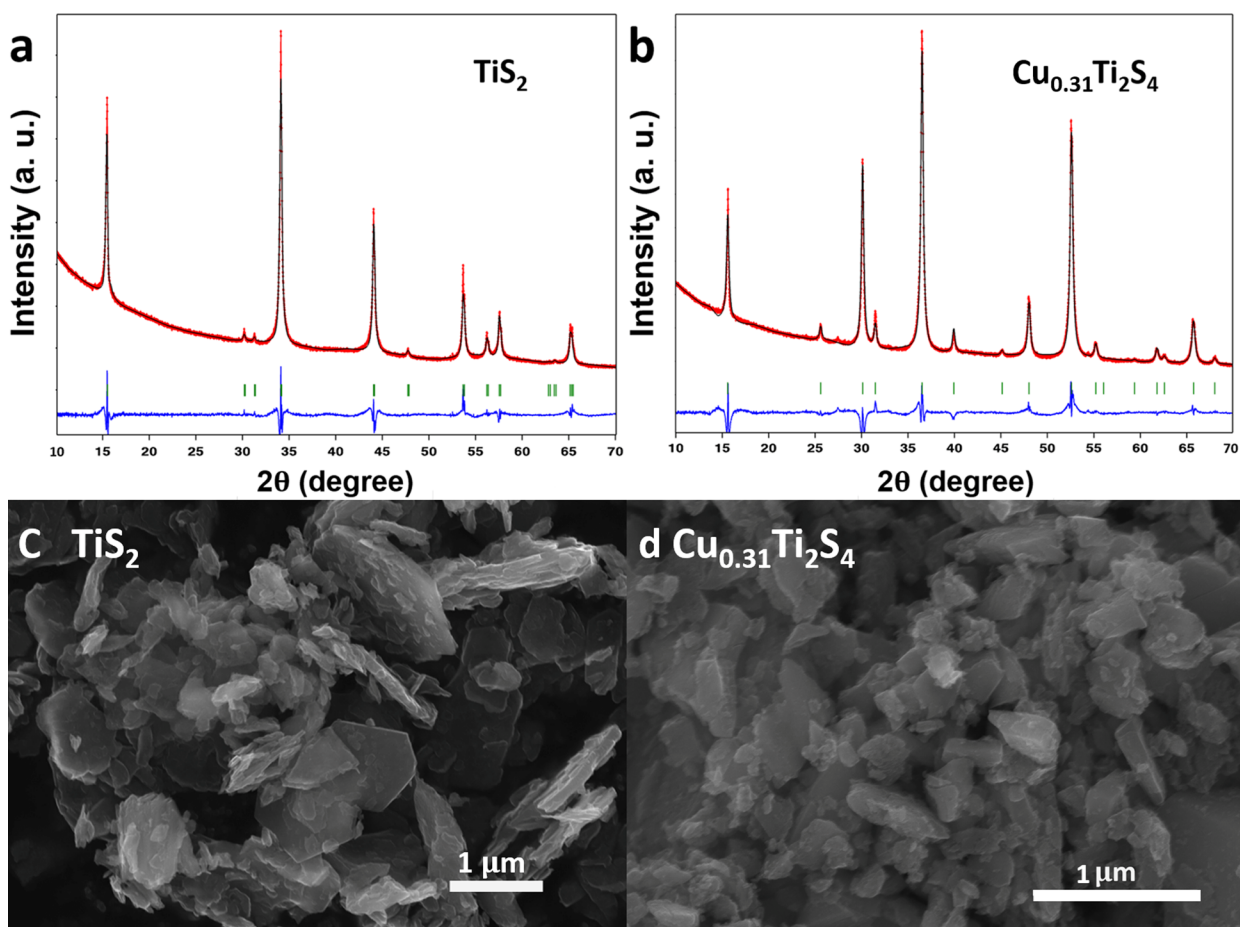


Figure 1. XRD patterns and Rietveld refinements of layered TiS_2 (a) and cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ (b); SEM images of layered TiS_2 (c) and cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ (d).

an argon-filled glovebox to prevent oxidization and hydrolysis. Mechanical ball milling was employed to reduce the particle size of TiS_2 with a Fritsch Pulverisette 23 mini-Mill. The entire ball milling process was performed in the argon-filled glovebox. In a typical ball milling process, two 10 mm diameter and 18.5 mm diameter tempered steel grinding balls along with 0.346 g of TiS_2 (weight ratio 50:1) were put into a tempered steel grinding bowl with 3 mL of anhydrous toluene. To prevent overheating, the milling was performed in 10 sessions of 5 min, each separated by 10 min of idling. After the ball milling, the TiS_2 particles were washed with anhydrous acetonitrile 3 times and then collected with a centrifuge. The scanning electron microscopy (SEM) image and the powder X-ray diffraction (XRD) pattern of the pristine TiS_2 are shown in the [Supporting Information](#) (Figure S1) with the energy dispersive X-ray spectroscopy (EDS) elemental mapping of the TiS_2 after ball milling (Figure S2 and Table S1).

Synthesis of Cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$. Thiospinel CuTi_2S_4 was first synthesized using a solid state method similar to that described above.²⁰ Stoichiometric amounts of Cu (Sigma-Aldrich, 14–25 μm , 99%), Ti, and S powders were thoroughly mixed and sealed in an evacuated quartz tube. The quartz tube was heated in a muffle furnace at 700 °C (ramp rate, 0.3 °C min^{-1}) for 3 days. The synthesized CuTi_2S_4 was collected in the argon-filled glovebox to prevent oxidization and hydrolysis. The particle size of CuTi_2S_4 was reduced via mechanical ball milling as described above. Cu was leached from the CuTi_2S_4 product by reaction with bromine. In a typical leaching process, 300 mg of CuTi_2S_4 was suspended in 100 mL of anhydrous acetonitrile. Then, 94 μL of pure bromine was added to the suspension. The mixture was stirred for 24 h. After the reaction, the product was washed twice with both acetonitrile and carbon disulfide and collected with a centrifuge. The chemical formula of the product

was determined to be $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ via XRD analysis and Rietveld refinement and was confirmed by EDS elemental mapping. The SEM images and the XRD patterns of CuTi_2S_4 before and after ball milling are shown in the [Supporting Information](#) (Figure S3) with the EDS element analysis of the synthesized $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ (Figure S4 and Table S2).

Electrochemical Analysis. CR2016 coin cells were assembled in an argon-filled glovebox using Al foil (0.2 mm thickness, Alfa Aesar, 99.9999%) as the anode. The cathode was fabricated by coating TiS_2 or $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ slurry onto a carbon paper current collector (Spectracarb 2050A-0550, Fuel Cell Store). The carbon paper current collector was demonstrated to be electrochemically inert in the applied potential window as shown in the [Supporting Information](#) (Figure S5). The slurry was made by mixing 80 wt % TiS_2 or $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$, 10 wt % carbon black, and 10 wt % polystyrene in *N*-methyl-2-pyrrolidone via a mechanical mixer for 5 min. A single Whitman glass fiber filter was used as the separator. The electrolyte was prepared by slowly adding anhydrous AlCl_3 (Sigma-Aldrich, 99.99%) into 1-butyl-3-methylimidazolium chloride (Sigma-Aldrich, 98%) with a molar ratio of 1.5:1 while stirring in the argon-filled glovebox. It is worth noting that polystyrene was selected as the binder due to its inertness in the Lewis acidic ionic liquid electrolyte compared to conventional binders such as poly(vinylidene fluoride) (Figure S6 in the [Supporting Information](#)). To prevent corrosion from the acidic electrolyte, titanium foil (Strem, 0.025 mm thickness, 99.6%) and pyrolytic graphite sheet (MTI, 0.017 mm thickness, 99.90%) were punched into discs of an appropriate size to be used as linings in the stainless-steel coin cell case. The schematic of the coin cell construction is shown in [Supporting Information](#) (Figure S7). Cyclic voltammetry (CV) with a scan rate of 0.1 mV s^{-1} was performed with a Gamry potentiostat Interface 1000. Galvanostatic discharging and constant-current–

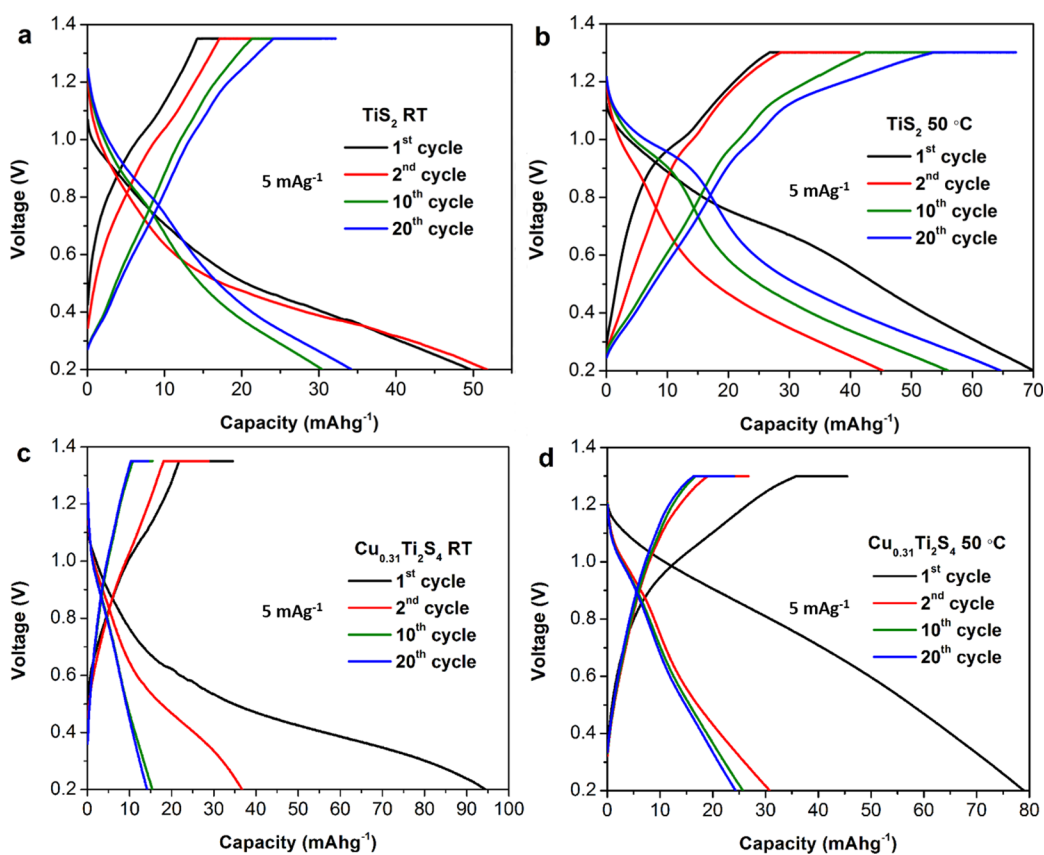


Figure 2. First, second, 10th, and 20th galvanostatic discharge and CCCV charge curves of layered TiS₂ (a and b) and cubic Cu_{0.31}Ti₂S₄ (c and d) at RT and 50 °C.

constant-voltage (CCCV) charging and galvanostatic intermittent titration technique (GITT) were performed on an Arbin battery test station. In GITT, the batteries were discharged and charged at 10 mA g⁻¹ for 15 min and rested for 2 h. The current pulse was repeated until the potential reached the cutoff limit. The diffusion coefficient of Al³⁺ was calculated according to the following equation:

$$D = \frac{4}{\tau} \left(\frac{IV_M}{Z_A F S} \right)^2 \left[\frac{\left(\frac{dE}{dx} \right)}{\left(\frac{dE}{d\sqrt{t}} \right)} \right]^2$$

where D is the Al³⁺ ion diffusion coefficient, I is the current used in titration, V_M is the molar volume of the titanium sulfides, Z_A is the number of charge of the ionic species ($Z_A = 3$ for Al³⁺), F is the Faraday constant, S is the surface area of the active materials (53.1 m² g⁻¹ for layered TiS₂ and 27.2 m² g⁻¹ for cubic Cu_{0.31}Ti₂S₄, determined by N₂ adsorption–desorption experiments), x is the content of Al in the electrode materials (Al _{x} TiS₂ and Al _{x} Cu_{0.31}Ti₂S₄), and τ is the current pulse time. The value of $dE/d\sqrt{t}$ is determined from the plot of the voltage response vs the square root of the time during each current pulse, and dE/dx is obtained by plotting the equilibrium potential vs the electrode material composition after each current pulse.²¹

Materials Characterizations. The XRD was conducted using a PANalytical EMPYREAN instrument (45 kV/40 mA) with a Cu $K\alpha$ source. SEM was performed with a FEI XL30-FEG instrument. The N₂ adsorption–desorption isotherms for surface area measurements were obtained with Micromeritics ASAP 2020 apparatus.

RESULTS AND DISCUSSION

As shown in Figure 1a, the XRD pattern of the synthesized TiS₂ matched the reference very well. As the XRD and the Rietveld refinement data show in Figure 1b, the final product of

chemically leached CuTi₂S₄ had a formula of Cu_{0.31}Ti₂S₄. The particle size of TiS₂ (diameter of the plate-like particle) and Cu_{0.31}Ti₂S₄ obtained from SEM images (Figure 1c,d) was mostly smaller than 1 μ m.

The electrochemical Al intercalation–extraction in these two titanium sulfides were characterized with discharge–charge experiments at both room temperature (RT) and 50 °C considering the slow intercalation kinetics observed in the Chevrel phase Mo₆S₈ at RT.^{16,22} Galvanostatic discharge (Al intercalation) was carried out by applying 5 mA g⁻¹ current density, and the same current density was applied first for the galvanostatic charge (Al extraction), followed by holding a constant potential of 1.35 V (RT) and 1.3 V (50 °C) vs Al, respectively, for 3 h. This constant-current–constant-voltage (CCCV) charge protocol was used to prevent the corrosion (electrochemical oxidation) of the linings and the stainless-steel cell case from the acidic IL electrolyte. CCCV charging is also a common practice to overcome the kinetic voltage polarization to achieve more complete ion extraction. Figure 2 shows the galvanostatic discharge and CCCV charge curves of TiS₂ and Cu_{0.31}Ti₂S₄ at the first, second, 10th, and 20th cycles at RT and 50 °C. It is clear that the Al interaction–extraction behaviors of either titanium sulfide are inherently the same at the different temperatures used. However, higher capacity and more distinct discharge–charge characteristics are demonstrated at 50 °C due to the improved reaction kinetics at higher temperature. As shown in Figure 2b, the first discharge curve of TiS₂ at 50 °C displays a plateau at 0.75 V followed by a slope from 0.6 to 0.2 V with a total capacity of 70 mA h g⁻¹. However, the first charge capacity is only 40 mA h g⁻¹, indicating a high

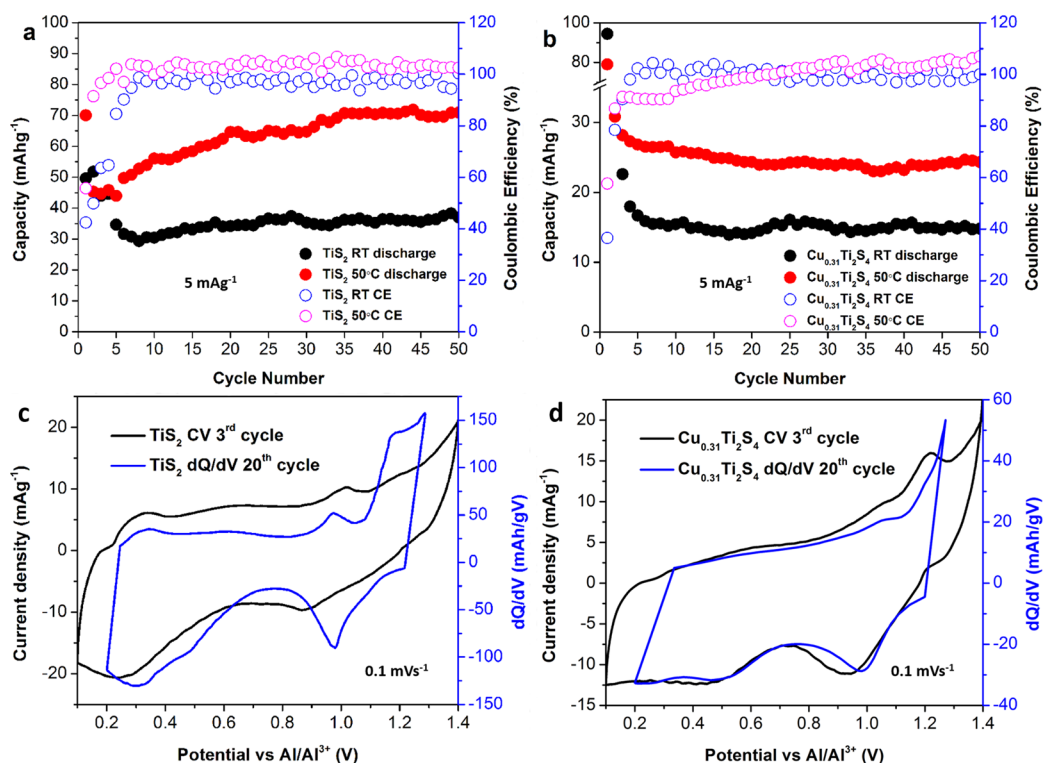


Figure 3. Cycle stabilities of layered TiS₂ (a) and cubic Cu_{0.31}Ti₂S₄ (b) at room temperature and 50 °C with 5 mA g⁻¹ current density. Cyclic voltammetry and differential capacity curves of TiS₂ (c) and Cu_{0.31}Ti₂S₄ (d) at 50 °C.

irreversibility in the first cycle. During the following cycles, the discharge–charge potential profile gradually evolves with increasing capacity. Two discharge stages can still be observed in the stabilized discharge curve with a plateau around 0.95 V and a slope from 0.6 to 0.2 V. We hypothesize that the Al intercalation–extraction process in the initial cycles slightly altered the crystal structure of TiS₂, thus facilitating the Al intercalation–extraction in the subsequent cycles. Figure 2d shows the galvanostatic discharge and CCCV charge curves of cubic Cu_{0.31}Ti₂S₄ at 50 °C. One can observe a slope-like discharge curve from the first discharge with a capacity around 80 mA h g⁻¹. The first charge also displays a slope-like potential curve with a capacity of 45 mA h g⁻¹. Unlike layered TiS₂, the discharge–charge capacity of Cu_{0.31}Ti₂S₄ does not recover during the following cycles. Instead, the discharge–charge potential profile of Cu_{0.31}Ti₂S₄ stabilizes after 10 cycles with a modest reversible capacity of 25 mA h g⁻¹.

The cycle stability of layered TiS₂ and cubic Cu_{0.31}Ti₂S₄ are shown in Figure 3a,b. The reversible capacity of layered TiS₂ at 50 °C is significantly higher than that at RT: the capacity gradually increases after the first few cycles and stabilizes at approximately 70 mA h g⁻¹. On the other hand, the reversible capacity of cubic Cu_{0.31}Ti₂S₄ at 50 °C is only about 25 mA h g⁻¹. From the capacity comparison of these two titanium sulfides, it can be speculated that more Al can be reversibly intercalated in layered TiS₂ than in cubic Cu_{0.31}Ti₂S₄. This hypothesis can be attributed to the fact that the channels in the spinel structure are more rigid and less open than those of the layered structure, thus making the material less adaptive to accommodating the intercalated Al³⁺ ions. The high irreversible capacity in the first cycle of both titanium sulfides may be due to the irreversible Al intercalation (Al³⁺ ions trapped in the crystal structures). It is also worth noting that the Coulombic efficiency at 50 °C for both sulfides is higher than 100%, which

may be caused by the gradual electrochemical or chemical corrosion of the Al anode during discharge, while the protective linings and the coin cell case remain corrosion-free (Figures S8–S11 in the Supporting Information). The SEM and EDS analysis of the electrodes after 50 cycles demonstrates the consistent chemical composition with the initial materials (Figures S12 and S13 and Tables S3 and S4 in the Supporting Information). Electrolyte decomposition, i.e., possible solid electrolyte interphase formation, was not observed on either titanium sulfide using X-ray photoelectron spectroscopy (XPS) analysis (Figure S14 in the Supporting Information). It is also worth mentioning that exposure to the ambient environment can quickly form an oxide layer on the surface of both titanium sulfides, which is detrimental to Al intercalation. The surface XPS analysis of the air exposed titanium sulfides and the resulting capacity tests are described in the Supporting Information (Figure S15).

To identify the Al intercalation–extraction potential, the differential capacity curves (dQ/dV) of TiS₂ and Cu_{0.31}Ti₂S₄ at 50 °C are plotted in Figure 3c,d alongside the corresponding CV curves (complete CV cycles are shown Figure S16 in the Supporting Information). The dQ/dV and CV curves agree strongly with each other. Figure 3c clearly displays two pronounced cathodic (intercalation) peaks for layered TiS₂ at approximately 0.98 and 0.3 V and two anodic (extraction) peaks at 0.97 and 1.15 V. On the other hand, Cu_{0.31}Ti₂S₄ (Figure 3d) displays two broad and less pronounced cathodic peaks at 1.0 and 0.5 V; two broad anodic peaks with very low peak currents can barely be distinguished at 0.6 and 1.2 V, indicating the inferior intercalation–extraction kinetics of cubic Cu_{0.31}Ti₂S₄.

To confirm the intercalation of Al into the crystal structure of layered TiS₂ and cubic Cu_{0.31}Ti₂S₄, Rietveld refinements were performed on the powder XRD data of the Al-intercalated

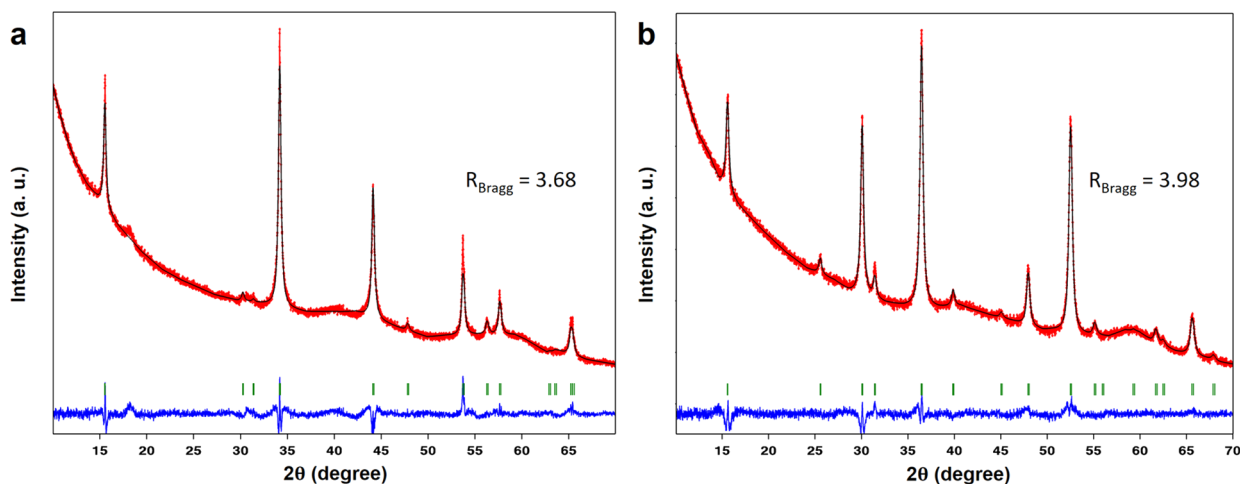


Figure 4. XRD patterns and Rietveld refinements of Al-intercalated layered TiS_2 (a) and Al-intercalated cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ (b).

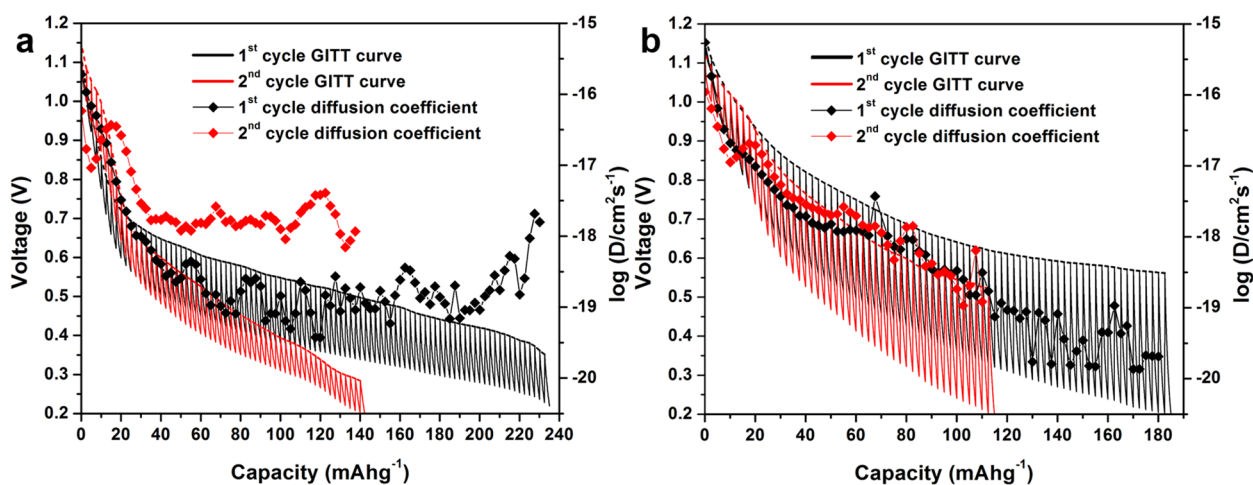


Figure 5. Galvanostatic intermittent titration technique (GITT) curve of layered TiS_2 (a) and cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ (b) at 50 °C.

titanium sulfides, which were obtained from chronopotentiometry with a small current density of 2 mA g^{-1} at 50 °C (Figure S17 in the Supporting Information). Figure 4a shows the refinement result of Al-intercalated TiS_2 . TiS_2 and Al-intercalated TiS_2 crystallized in space group $P\bar{3}m1$. The unit cell parameters of Al-intercalated TiS_2 , $a = b = 3.4106(8) \text{ \AA}$ and $c = 5.703(2) \text{ \AA}$, are, surprisingly, smaller than those for pristine TiS_2 . Consequently, the volume of the unit cell decreases upon intercalation, and there is an additional reflection at 18.2° . We hypothesize that this additional reflection could indicate Al ordering and consequently an ordered superstructure. The decreased lattice parameter could be caused by the very small, highly charged Al^{3+} ions in the van der Waals gap reducing the repulsion between the S-layers in TiS_2 . The position of Al^{3+} in the unit cell used for the refinement is (0, 0, 0.5), which is the position 1b with octahedral coordination between the S-layers. We also attempted to refine Al^{3+} on the tetrahedral site 2d. This increased the Al^{3+} concentration, but the quality of the refinement did not improve significantly. Due to short S–Al distances and the limited available space, whether Al occupies the tetrahedral site remains questionable. Thus, the final result of the refinement is that Al occupies 11% of the octahedral intercalation positions 1b which corresponds to a composition of $\text{Al}_{0.11(1)}\text{TiS}_2$. Upon calculating the electrochemical capacity from the composition information, we derive a capacity of

about 79 mA h g^{-1} , which is in good agreement with the electrochemical experimental results. The Rietveld refinement of Al-intercalated cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ is shown in Figure 4b. The spinel-type structure has the space group structure $Fd\bar{3}m$. The unit cell parameters of Al-intercalated cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ are $a = b = c = 9.855(1) \text{ \AA}$, which is approximately 1% smaller than CuTi_2S_4 but larger than $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ ($a = b = c = 9.834(2) \text{ \AA}$). In order to perform the refinement on Al-intercalated $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$, the following assumptions are made: (1) Al^{3+} occupies the same position as Cu^+ ; (2) the amount of Cu^+ does not change during the intercalation process. The refinement yields that Al occupies 9% of the intercalation positions, resulting in a composition of $\text{Al}_{0.09(1)}\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$. This yields a capacity of about 32 mA h g^{-1} based on composition, which is also in good agreement with the electrochemical experimental results.

Based on the findings described above, we speculate that the difficulty of Al interaction in both titanium sulfides is imposed by the kinetic limitation: The energy barrier for Al intercalation in both titanium sulfides comes from the strong Coulombic attraction between the Al^{3+} cations and the sulfide anion framework. Thus, the near-equilibrium Al intercalation properties of these two titanium sulfides were studied with GITT at 50 °C. The GITT curve of the first Al intercalation in layered TiS_2 (Figure 5a) shows a much higher capacity than the one obtained by galvanostatic discharge (Figure 2b) due to the

relaxation of potential to equilibrium after pulse titration. The GITT capacity of 235 mA h g^{-1} in the first intercalation indicates one electron transfer per TiS_2 ($\text{Al}_{1/3}\text{TiS}_2$). However, the capacity GITT demonstrates in the second Al intercalation is significantly reduced to 140 mA h g^{-1} , which suggests large irreversibility of Al^{3+} trapped in the TiS_2 crystal structure. The equilibrium Al intercalation potential curve displays solid solution type of behavior. Therefore, the Al^{3+} diffusion coefficient in layered TiS_2 at 50°C can be calculated from the GITT data as a function of intercalation capacity (i.e., Al content in the intercalated TiS_2). The Al^{3+} diffusion coefficient is in the range of 10^{-18} to $10^{-19} \text{ cm}^2 \text{ s}^{-1}$ in the first intercalation cycle. Interestingly, the Al^{3+} diffusion coefficient increases by 1 order of magnitude in the second intercalation cycle, which may be due to the structural change of TiS_2 induced by the initial Al intercalation. Figure 5b shows the GITT data of Al intercalation in cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ at 50°C . The achievable capacity is approximately 180 mA h g^{-1} in the first intercalation, and the Al^{3+} diffusion coefficient in cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ at 50°C varies from $\sim 10^{-18}$ to $10^{-20} \text{ cm}^2 \text{ s}^{-1}$ as Al content increases in the first Al intercalation cycle. In general, the Al^{3+} diffusion coefficient in cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ is lower than that in the layered TiS_2 . The Al intercalation capacity in the second cycle is also significantly lower than that in the first cycle. However, the Al^{3+} diffusivity in the second cycle is very consistent with that in the first, which is different from what was observed in layered TiS_2 . Another difference between the behaviors of layered TiS_2 and cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ is that the overpotential (difference between equilibrium potential and working potential) is greatly reduced in the second cycle for TiS_2 while the overpotential of $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ does not change in the second Al intercalation. We hypothesize that this may also be due to the more rigid and less open crystal structure of the cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$. Nevertheless, Al^{3+} ions have very low diffusivity in both titanium sulfides, which is the obstacle to facile Al intercalation–extraction. For comparison, the Li^+ diffusivities in layered TiS_2 and cubic Ti_2S_4 are approximately 10^{-9} and $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at RT^{23,24} respectively, which are several orders of magnitude higher than the Al^{3+} diffusivities in those materials at 50°C . This comparison illustrates the high-energy barrier for Al transport in these two titanium sulfide materials.

CONCLUSIONS

In summary, we examined the electrochemical Al intercalation–extraction of layered TiS_2 and cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ as potential cathode materials for rechargeable Al-ion batteries. Both titanium sulfides were evidenced to be electrochemically active toward Al intercalation–extraction, although layered TiS_2 appeared to possess better electrochemical properties than cubic $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$ as demonstrated by its higher specific capacity. Through crystallographic studies, we identified that Al^{3+} ions occupy the octahedral sites in layered TiS_2 . It is also clear through GITT analysis that the main obstacle to achieving high Al intercalation capacity is the slow diffusion of Al^{3+} through the titanium sulfide crystal structures. Our future investigations will focus on shortening the Al^{3+} diffusion pathway using the nanostructure of titanium sulfides and facilitating Al^{3+} transport via ion doping at selected sites in the crystal structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b04161.

XRD and SEM of various TiS_2 and CuTi_2S_4 ; SEM and EDS of TiS_2 , $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$, and Al anode, linings, and battery case; electrochemical control experiments; cell structure schematic; SEM, EDS, and XPS spectral and electrochemical analyses of TiS_2 and $\text{Cu}_{0.31}\text{Ti}_2\text{S}_4$; CV scans; chronopotentiometry curves; and room temperature GITT data (PDF)

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Notes

The authors declare no competing financial interest.

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