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Sodium in situ modulated phase transition to construct iron/vanadium bimetallic sulfide anodes for "fast-charging" sodium-ion batteries

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Fast-charging of iron sulfides, as an advanced anode for sodium-ion batteries, is severely restricted by the poor diffusion kinetics of sodium ions and rapid capacity fading. Utilizing the mechanism of *in situ* modulated phase transition of sodium species, herein, iron/vanadium bimetallic sulfides with various phase structures are synthesized to solve this challenge. The presence and content variation of sodium species could effectively adjust the electron density of the Fe atom, thereby implementing the modulation of bimetallic sulfides' phase structure during the sulfidation process. The appropriate phase structure and promising capacitive behavior boost sodium ion transport and reduce capacity attenuation. Consequently, the iron/vanadium bimetallic sulfides exhibit superior sodium storage capacity (424.67 mAh g⁻¹ at 0.05 A g⁻¹), a high rate capability of 192.82 mAh g⁻¹ at 10 A g⁻¹, and fast sodium ion diffusion kinetics. Furthermore, the assembled full-batteries deliver a remarkable capacity retention of 43.4% after 1200 cycles at 1 A g⁻¹. This work, inspired by the use of sodium as an electron promoter for iron-based catalysts for CO_2 hydrogenation, promises a convergence of catalysis and the synthesis of bimetallic sulfides to achieve fast-charging of sulfides.

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Broader context

In recent years, transition metal sulfide anodes have attracted considerable attention, as they are expected to facilitate fast-charging of sodium-ion batteries. Iron sulfides (FeS₂, FeS, Fe_{1-x}S, Fe₇S₈, etc.) are emerging as a rising star of sodium-ion battery anodes by virtue of abundant resources, plentiful phase structures, electrocatalytic effects of iron elements, and facile synthesis approaches. However, rapid capacity fading, unsatisfactory rate performance, and dissolution of sodium polysulfides hinder their fast-charging. Building bimetallic sulfides is a highly promising strategy to address this challenge. Regrettably, most of the synthetic routes reported for fabricating bimetallic sulfides to advance Na⁺ storage are comparatively cumbersome to date. Therefore, it is imperative to exploit facile and scalable methods for synthesizing bimetallic sulfides. Inspired by the use of sodium as an electron promoter to enhance the activity and selectivity of iron-based catalysts for the CO_2 hydrogenation reaction, in this contribution, iron/vanadium bimetallic sulfides with variable phase structures are fabricated *via in situ* modulating phase transformation leveraging the electron-promoting effect of sodium species. As an anode for sodium-ion batteries, the iron/vanadium bimetallic sulfide exhibits promising sodium storage rate behavior (specific capacity is 424.67 mAh g^{-1} at 0.05 A g^{-1} and remains 192.82 mAh g^{-1} at 10 A g^{-1}), desirable capacitive contribution, and rather fast Na⁺ diffusion kinetics. Overall, this discovery promises a convergence of catalysis and the synthesis of bimetallic sulfides to achieve fast-charging of sulfides.

1. Introduction

Fast-charging of sodium-ion batteries (SIBs) has attracted considerable attention in recent years, as SIBs are regarded as a potential powertrain for electric vehicles (EVs) and other energy storage systems, echoing societal desire for green economic development. The achievement of fast-charging is conducive to developing SIB-based large-scale grid energy storage,

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and also addressing charging time constraints for EVs when SIBs are employed as power systems.^{3,4} Regrettably, fast-charging of SIBs is severely hampered by anode materials.^{5,6} Therefore, it is necessary to elaborately design anode materials to boost electrochemical reaction kinetics that could perfectly deliver the virtues of SIBs with fast-charging.⁷

Among numerous anode materials, the restriction factors of fast-charging are varied. Specifically, structural instability and sodium dendrite growth (hard carbon), and narrow interlayer spacing (soft carbon and graphite) are the dominant constraints for carbonaceous materials. The inferior theoretical capacity renders intercalated oxide incapable of achieving high-rate capacity.⁵ Severe volume expansion (even higher than

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400%) restricts fast-charging of alloy-type materials.8 In contrast, transition metal chalcogenides, especially transition metal sulfides (TMSs), are expected to realize fast-charging of SIBs given their prominent electrochemical reversibility, attractive theoretical capacity, and relatively smaller volume change. 9,10 Iron sulfides (FeS₂, FeS₂, Fe_{1-x}S, Fe₇S₈, etc.) are emerging as a rising star of SIB anodes by virtue of abundant resources, plentiful phase structures, electrocatalytic effects of iron elements, and facile synthesis approaches. 11,12 As with other TMSs, rapid capacity fading, unsatisfactory rate performance, and dissolution of sodium polysulfides hinder fast-charging of iron sulfides. 13,14 To achieve the preeminent fast-charging property, considerable effort has been devoted to modifying iron sulfides, such as carbon encapsulation, 15,16 heteroatom doping, 13 construction of heterojunctions, 11 etc., so as to reduce volume expansion, enhance electrical conductivity, accelerate Na+ diffusion kinetics, and inhibit the dissolution

of sodium polysulfides. 14,15,17,18

Out of myriad strategies, building bimetallic sulfides is a highly promising approach for enhancing the electrochemical performance of single metal sulfides. It could increase active sites for conversion reactions, provide a narrow band gap and improved electronic conductivity, and achieve satisfactory specific capacity and long cycling lifespan attributed to the buffering effect of isolated nanostructures created during the first charging/discharging cycle.7,19,20 Combined with these merits, bimetallic sulfides exhibit exceptional electrochemical capability.²¹ A representative example is employing MnCo₂S₄ as the anode of SIBs. The electrochemistry investigation indicates that MnCo₂S₄ possesses superb sodium storage performance, especially surface capacitive behavior (from 73.4% to 94.1%), prolonged cycling lifespan (>800 cycles), and high rate capability (416 mAh g⁻¹ at 10 A g⁻¹).²² Regrettably, most of the synthetic routes reported for fabricating bimetallic sulfides to advance Na⁺ storage are comparatively cumbersome to date.²³ Besides, Na⁺ storage is also hindered by side reactions arising from the nanostructures of materials.24 It should be highlighted that the capacitive behavior of anode materials is indispensable to achieving fast-charging. 10,22,25,26 Consequently, it is of considerable significance to develop iron-based bimetallic sulfide anodes using a simple synthetic route along with enriched capacitive behavior, which could rectify the inherent defects of iron sulfides, thereby realizing fast-charging of SIBs.

Herein, iron/vanadium bimetallic sulfides with variable phase structures are fabricated *via in situ* modulating phase transformation leveraging the electron-promoting effect of sodium species, inspired by the use of sodium as an electron promoter enhancing the activity and selectivity of iron-based catalysts for the CO₂ hydrogenation reaction.^{27,28} This is successfully accomplished relying on the dual contribution of sodium vanadate (NaVO₃). Firstly, NaVO₃ contributes a vanadium source for fabricating bimetallic sulfides, which is favorable for introducing surface capacitive behaviors.²⁹ Then, the sodium in NaVO₃ serves as an electron promoter to guarantee the *in situ* modulation of phase structure to synthesize varied sulfides during sulfidation. The *in situ* modulation of

phase transition is convincingly testified using thermogravimetry coupled with Fourier transform infrared spectroscopy, *ex situ* X-ray diffraction, and X-ray photoelectron spectroscopy. Simultaneously, electrochemistry exploration verifies that iron/vanadium bimetallic sulfide ($V_{1.87}FeS_4$, the mass ratio of ferric nitrate nonahydrate to NaVO₃ is 2:1) exhibits promising sodium storage rate behavior (specific capacity is 424.67 mAh g^{-1} at 0.05 A g^{-1} and remains 192.82 mAh g^{-1} at 10 A g^{-1}), desirable capacitive contribution (86.48% at 0.1 mV s⁻¹), and rather fast Na⁺ diffusion kinetics. Moreover, the full-batteries assembled with Na₃V₂(PO₄)₃/C also exhibit remarkable electrochemical properties (capacity retention is 43.4% at 1 A g^{-1} after 1200 cycles). Inspired by the field of catalysis, this work creates a simple and scalable idea for preparing bimetallic sulfides with fast-charging ability.

2. Experimental section

2.1. Chemicals and materials

Ferric nitrate nonahydrate (Fe(NO₃)₃·9H₂O) was purchased from Tianjin Kaixin Chemical Industry Co., Ltd. Sodium vanadate (NaVO₃), ammonium vanadate (NH₄VO₃), and polyvinyl-pyrrolidone (PVP, K30) were provided by Aladdin®. Sublimed sulfur was obtained from Guangdong Canrd New Energy Technology Co., Ltd. Na₃V₂(PO₄)₃/C was provided by Shenzhen Kejing Star Technology Company. All reagents were used directly without any pre-treatment.

2.2. Preparation of iron/vanadium bimetallic sulfides

Firstly, 2.0 g of PVP, K30 was dissolved in 60 mL of deionized water and stirred to obtain a clear solution. Following this, Fe (NO₃)₃·9H₂O and NaVO₃ were added to the PVP solution with different mass ratios and stirred continuously for 1 h. Subsequently, the above solution was transferred to a 90 °C oven for 24 h to obtain the powders named Fe: V = 1:0, Fe: V = 2:1, Fe: V = 1:1, and Fe: V = 1:2, respectively, according to the feeding ratio (mass) of Fe(NO₃)₃·9H₂O and NaVO₃. Secondly, Fe:V = 2:1, Fe:V = 1:1, and Fe:V = 1:2 were washed with distilled water four times and dried in an oven at 80 °C. Finally, the above precursor powders and sublimed sulfur were fully ground at a mass ratio of 1:3 and placed in a tube furnace with Ar ventilation for 4 h at 155 °C and then heated to 600 °C for 4 h to obtain different sulfides. The sulfurized products of Fe: V = 1:0, Fe: V = 2:1, Fe: V = 1:1, and Fe: V = 1:2 corresponded to Fe_7S_8 , $V_{1.87}FeS_4$, $V_{2.14}Fe_{0.75}S_4$, and FeS_2/V_2O_3 , respectively.

2.3. Materials characterization

The surface functional groups of the samples were tested using the IRTracer-100 instrument (Shimadzu, Japan). The crystal phase structure of the samples was analyzed by high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-F200, Japan) and X-ray diffraction (XRD, DX-2800 diffractometer, China). X-ray photoelectron spectroscopy (XPS, AXIS SUPRA, Shimadzu, Japan) and energy dispersive X-ray spec-

troscopy (EDX) were used to analyze the chemical composition and elemental distribution within the samples. XPS calibration was based on the C 1s components with binding energies of 284.8 or 284.0 eV. The morphology and microstructure of the materials were measured using a field emission scanning electron microscope (FESEM, TESCAN MIRA3, USA) and a transmission electron microscope (TEM, JEOL, JEM-F200, Japan), respectively. Using a specific surface area and aperture analyzer (JW-BK200C, JWGB, Beijing, China), the specific surface area and pore size distributions of the samples were determined. Thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR) (IRXross + DTG-60, Shimadzu, Japan) and ex situ X-ray diffraction (ex situ XRD, DX-2800 diffractometer, China) were used to analyze the synthesis mechanism of the materials. The thermal preservation procedure was consistent with the sintering procedure of the tube furnace,

and the FTIR data collection began after the 155 °C ramp-up.

2.4. Electrochemical measurements

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The electrochemical performances of the as-synthesized materials were tested in half- and full-SIBs (CR2032, assembled in an argon-filled glove box $(O_2, H_2O < 0.01 \text{ ppm})$ by cyclic voltammetry (CV), galvanostatic charging/discharging (GCD), and electrochemical impedance spectroscopy (EIS). For half-batteries, the electrodes were manufactured via drying and cutting the current collector coated with slurries into 12 mm discs, and the mass loading of active materials on each electrode was approximately 1.2 mg. The active materials, acetylene black, and polyvinylidene difluoride (PVDF) were dispersed in NMP with a weight ratio of 8:1:1 and stirred for 12 h to prepare a slurry, which was coated on copper foil as a current collector and dried at 80 °C for 12 h in a vacuum oven. The half-batteries were assembled using the above electrode as a working electrode, sodium metal as a counter electrode, and glass fiber (GF/D 1823, Guangdong Canrd New Energy Technology Co., Ltd) as a separator. The electrolyte used was 1 M NaPF₆ in diglyme. The CV tests were conducted on a CHI660E electrochemical workstation (Chenhua, Shanghai, China) at various scan rates with a voltage range of 0.3-3 V. The GCD curves were acquired from a LAND CT2001A battery tester at various current densities in the same voltage range as that of the CV test. The sodium-ion full-batteries were assembled using commercial Na₃V₂(PO₄)₃/C as the cathode (aluminum foil as a current collector) and Fe₇S₈ or V_{1.87}FeS₄ as the anode. The separator and electrolyte were the same as those of the half-batteries. The GCD measurements were conducted in the voltage range of 1-3.8 V.

3. Results and discussion

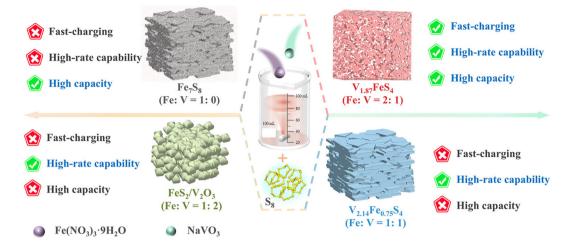
Sodium (in the form of Na_2O), as an additive for iron-based catalysts, could suppress the olefin hydrogenation reaction by increasing the electron density of active sites, thereby promoting CO_2 conversion and olefin selectivity. Given such utility of sodium species, distinct phase structure iron/

vanadium bimetallic sulfides were fabricated using a co-precipitation approach followed by an annealing technique, in which phase transition processes are favored by in situ modulation of sodium species (possibly in the form of Na₂S). The sample preparation strategy is graphically shown in Scheme 1. Due to the *in situ* modulation of the sulfidation process by sodium species, diverse iron/vanadium bimetallic sulfides were synthesized as the sodium content was varied. Fe:V = 1:0, Fe: V = 2:1, Fe: V = 1:1, and Fe: V = 1:2 were sulfurized as F₇S₈ (PDF#29-0723), V_{1.87}FeS₄ (PDF#31-0657), V_{2.14}Fe_{0.75}S₄ (PDF#31-0656), and FeS₂/V₂O₃ (PDF#42-1340/PDF#34-0187) at 600 °C, respectively. In detail, the precursors contained a series of iron/vanadium compounds, NaNO3 or NaNO2, and $Na_2V_6O_{16}$ (Fig. S1 in the SI) except Fe:V = 1:0. This is explained by the fact that a series of reactions may occur when Fe(NO₃)₃·9H₂O and NaVO₃ are added to deionized water (Fe (NO₃)₃·9H₂O is added prior to NaVO₃, even though they are added almost simultaneously, Fig. S2 in the SI. After the sulfidation process, sodium species are incorporated into the final materials as a heteroatom after fulfilling the mission of adjusting the phase transition, which is highly preferred for sodium storage (Fig. S3 and Table S1 in the SI). 13 Interestingly, distinct sodium storage behaviors are permitted since sulfides feature differing phase structures and morphologies. V1.87FeS4 offers a high specific capacity, excellent rate performance, and fastcharging capability. Noteworthily, a reasonable crystal structure is very crucial for fast-charging of materials.³¹ Therefore, the in situ modulation of phase transition employing sodium species is applied with a view to synthesizing iron/vanadium bimetallic sulfide anodes with fast-charging capability for SIBs.

The conjecture that Fe(NO₃)₃·9H₂O and NaVO₃ react in aqueous solution is validated with the aid of FTIR characteristics (Fig. 1a and b). There are significant alterations of precursor powders' FTIR spectra after the introduction of NaVO3 into the solution, especially in the fingerprint region. The V-O-V (\sim 519 cm⁻¹) and V=O (\sim 1000 cm⁻¹) peaks emerge nonnegligibly in the samples of Fe: V = 2:1, 1:1, and 1:2 compared to Fe: $V = 1:0.^{32}$ In addition, the peak at 577 cm⁻¹ observed in Fe: V = 1:0 corresponds to the Fe-O band, 33 and the peak at 1419 cm⁻¹ in Fe: V = 2:1 and 1:1 is attributed to NaNO3. These results directly demonstrate the reaction between Fe(NO₃)₃·9H₂O and NaVO₃. Additionally, the peaks located at 1288 and 1383 cm⁻¹ belong to the asymmetrical stretching vibrations of NO₃ and NO₂, respectively. Fig. 1(c) displays the XRD results after sulfidation of different precursors. It was found that the phase structure of the product could be adjusted by altering the mass ratio of Fe and V. Noteworthily, the V₂O₃ phase gradually increased with increasing of NaVO3 in the reaction system. The resultant product after sulfidation was a complex of FeS2 and V2O3 when Fe: V = 1:2 as a precursor.

The XPS technique was used to confirm the chemical state of the elements in varied samples. The full spectra indicate that there are obvious peaks of V 2p and Na 1s in $V_{1.87}FeS_4$, $V_{2.14}Fe_{0.75}S_4$, and FeS_2/V_2O_3 . Above all, the peak intensities

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Scheme 1 Schematic illustration of synthesis of different samples with varied sodium storage abilities employing the sodium species in situ modulating phase structure.

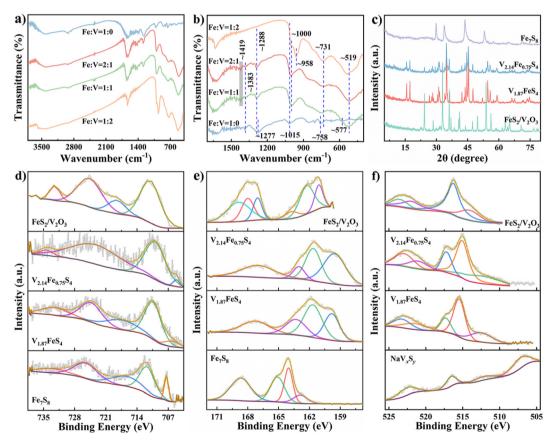


Fig. 1 (a and b) FTIR spectra of different samples before sulfidation, (c) XRD patterns, and (d) Fe 2p, (e) S 2p, and (f) V 2p of Fe₇S₈, V_{1.87}FeS₄, $V_{2.14}Fe_{0.75}S_4$, FeS_2/V_2O_3 , and NaV_xS_y .

gradually increase with the increasing mass of NaVO₃ in the system (Fig. S4 in the SI). The presence of the Na 1s peak supports the hypothesis that sodium is doped as a heteroatom in the samples. Importantly, the high-resolution Fe 2p spectra of varied samples demonstrate marked differences (Fig. 1d). For

 Fe_7S_8 , the high-resolution $Fe\ 2p$ spectrum primarily features a signal of Fe2+ at 707.3 eV (Fe-S bonding) along with a corresponding satellite at 716.2 eV and photoelectron peaks corresponding to Fe³⁺ (711.6 and 725.4 eV). 11-14,17 Obviously, the positions of these fitting peaks in the high-resolution Fe 2p

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spectra of V_{1.87}FeS₄ and V_{2.14}Fe_{0.75}S₄ are apparently shifted toward lower binding energy. This is likely attributed to the effect of sodium species on the electron density of the Fe atom. The fitted peaks for the Fe 2p orbitals of V_{1.87}FeS₄ and $V_{2.14}Fe_{0.75}S_4$ appear at 705.1, 709.8, 717.4, 724.2, and 732.3 eV and 706.1, 710.3, 723.2, and 734.3 eV, respectively. The Fe 2p orbital of FeS₂/V₂O₃ is deconvoluted into four peaks, including 710.9, 718.5, 724.6, and 732.5 eV. The Na-doped effect has been reported to weaken the Fe-S bond, as evidenced by the fitting results of S 2P high-resolution XPS spectra of Fe₇S₈ (162.9, 164.0, 165.1, and 168.7 eV), V_{1.87}FeS₄ (159.8, 161.7, 163.3, and 167.2 eV), $V_{2.14}Fe_{0.75}S_4$ (159.6, 161.6, 163.0, and 167.0 eV), and FeS₂/V₂O₃ (161.1, 162.3, 163.8, 167.1, 168.0, and 168.9 eV) (Fig. 1e). Significantly, the weakening of the Fe-S bond favors the storage of Na⁺ in TMSs. ¹³ Moreover, NaVO₃ is heat-treated with sublimed sulfur at 600 °C (NaV_xS_v), and the V 2p high-resolution XPS spectrum is compared with other samples. It can be observed that the fitted peaks for V_{1.87}FeS₄, V_{2.14}Fe_{0.75}S₄, and FeS₂/V₂O₃ exhibit a distinct degree of shift

toward the higher binding energy, which is probably related to

the formation of iron/vanadium bimetallic sulfides or V₂O₃,

and some of the sodium species (in NaVO₃) are used as promo-

ters to regulate the electron density of the Fe atom. The crystal structure of the obtained samples could be visualized via high-resolution transmission electron microscopy (HRTEM) images. The lattice spacings of 0.241 and 0.319 nm in Fig. 2(a) correspond to the (213) and (-420) crystal planes of Fe₇S₈ from the sulfidation of pure Fe(NO₃)₃·9H₂O, respectively. The HRTEM images of the as-prepared samples change dramatically after NaVO₃ was added to the precursor solution. Specifically, the HRTEM image of V_{1.87}FeS₄ indicates a representative lattice spacing of 0.287 nm for the (110) crystal plane; whereas the HRTEM image of V_{2.14}Fe_{0.75}S₄ emerges as the (006) crystal plane of V₂O₃, which is ascribed to the existence of a small amount of V₂O₃ in V_{2.14}Fe_{0.75}S₄; in addition, the (111) crystal plane of FeS2 with a lattice spacing of 0.310 nm is present in the HRTEM image of FeS₂/V₂O₃ (Fig. 2b-d). Such results are in accordance with those of XRD, and testify to the effective modulation of the sample crystalline phase during sulfidation. Furthermore, to prove that the sodium species exerts a decisive role in the modulation of the phase structure, NaVO3 was replaced using NH₄VO₃, and the same experiment was carried out with Fe: V = 2:1 as a comparison. It was noted that the sulfurized product was in line with that of pure Fe(NO₃)₃·9H₂O when NH₄VO₃ was the vanadium source (Fig. S5 in the SI). The result attests that sodium species are not only crucial for modulating phase structures but also a crucial contributor to the formation of iron/vanadium bimetallic sulfides. The high-resolution Fe 2p spectra of Fe: V = 1:0 and Fe: V = 1:02:1 further demonstrate that the sodium species modulating the phase structure may be present in the form of Na₂S (Fig. S6 in the SI). This is because the binding energy of all fitted peaks in Fe:V = 2:1 is higher than that in Fe:V = 1:0 in the high-resolution Fe 2p spectra, whereas it is just the opposite in the corresponding sulfides (Fig. 1d).

In detail, the process of in situ modulation of phase structure by virtue of sodium species was investigated using the TG-FTIR technique and ex situ XRD. Fig. 2(e-h) show FTIR spectra of Fe_7S_8 , $V_{1.87}FeS_4$, $V_{2.14}Fe_{0.75}S_4$, and FeS_2/V_2O_3 during the TGA testing. Similar profiles indicate that the gases volatilized by diverse precursors during the sulfidation under hightemperature are nearly identical. This is also affirmed by the top-view of FTIR spectra during TGA testing (Fig. S7 in the SI). The ex situ XRD patterns of each precursor under different sulfidation temperatures reveal their diversity (Fig. 2i-1). The characteristic peaks of sulfur appear in all precursors at 155 °C, with no significant deviation even when held for 4 h, signifying that the formation of sulfides exceeds 155 °C. Continuing to increase the temperature, a pronounced disparity is detectable at 300 °C. The ex situ XRD pattern of Fe:V = 1:0 at 300 °C is consistent with features at 155 °C (Fig. 2i), while no characteristic sulfur peaks are observed in Fe:V = 2:1 and Fe:V = 1:1, and even the peaks of $V_{1.87}FeS_4$ and V_{2.14}Fe_{0.75}S₄ appear at about 16°, respectively (Fig. 2j and k). In contrast, the characteristic peaks of sulfur in the ex situ XRD pattern of Fe: V = 1:2 are merely weakened as the temperature rises to 300 °C, probably as a result of fewer substances reacting with sulfur in the system (Fig. 21). What is more, the compounds in the Fe: V = 1:2 system are not fully converted into FeS₂/V₂O₃ even when the temperature rises up to 600 °C, whereas Fe:V = 1:0, Fe:V = 2:1, and Fe:V = 1:1 already possess an identical crystalline structure as the final product at the same temperature. This observation could be interpreted by TGA characterization results. After sulfur diffusion into the interior, Fe:V = 1:0 exhibits only a slight mass change at 241 °C, and a greater decline in mass would require an increase in the annealing temperature to about 360 °C, unlike Fe: V = 2:1 and Fe: V = 1:1, which exhibit a sustained mass decrease after 284 °C and 275 °C, respectively, which is consistent with the considerable change at 300 °C in the ex situ XRD patterns. However, Fe: V = 1:2 consistently exhibits an inconspicuous mass decline beginning at 275 °C (Fig. 2m). The sulfidation temperature is visibly lower for Fe: V = 2:1and Fe: V = 1:1, signifying that the effect of sodium species on the electron density of the Fe atom, in turn, reduces the activation energy of the reaction to generate sulfides. In contrast, the sulfidation of pure Fe(NO₃)₃·9H₂O requires relatively high temperatures. Incidentally, it can be found that NaVO₃ in Fe: V = 1:2 is far in excess based on the reaction conditions, resulting in relatively few substances (same as in Fe: V = 2:1 and Fe: V = 1:1), which could react with sublimated sulfur at 300 °C. This also accounts for the lack of no apparent variation in ex situ XRD and TGA curves of Fe: V = 1:2 at 300 °C.

The micro-morphologies of four samples were observed by SEM and TEM, as illustrated in Fig. 3. All samples are micronsized, and in addition, ${\rm Fe_7S_8}$ consists mainly of relatively small particles attached to larger particles. With the gradual introduction of NaVO₃ and the modulation of crystalline phase structure with sodium species, the sizes of ${\rm V_{1.87}FeS_4}$, ${\rm V_{2.14}Fe_{0.75}S_4}$, and ${\rm FeS_2/V_2O_3}$ gradually became smaller, and the structure went from fluffy to smooth. In comparison, ${\rm V_{1.87}FeS_4}$

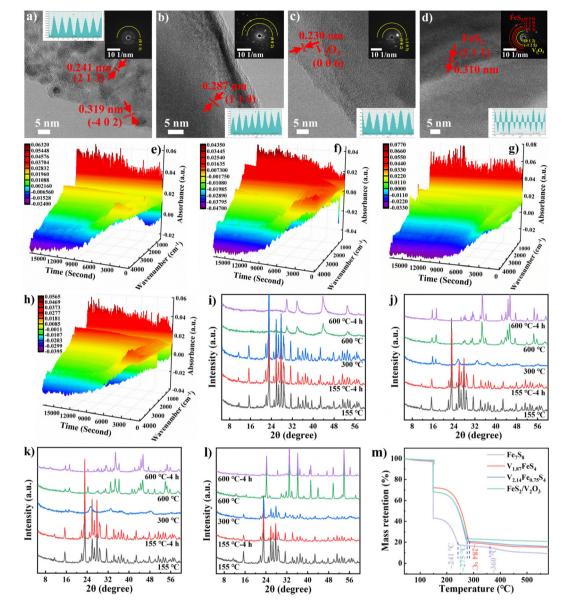


Fig. 2 (a-d) HRTEM and SAED patterns (insets), (e-h) FTIR spectra during the TGA test, (i-l) ex situ XRD patterns of different precursors at different sulfidation temperatures, and (m) TGA curves of Fe₇S₈, V_{1.87}FeS₄, V_{2.14}Fe_{0.75}S₄, and FeS₂/V₂O₅.

possesses a relatively fluffier structure, which is favorable for Na⁺ transport (Fig. 3a-d). The regularity of TEM images is similar to that of SEM, that is, FeS₂/V₂O₃ is composed of relatively smaller particles, while the other three samples are composed of a larger bulk (Fig. 3e-h). Meanwhile, EDX mapping results show that Fe and S elements are uniformly distributed in Fe_7S_8 , while $V_{1.87}FeS_4$, $V_{2.14}Fe_{0.75}S_4$, and FeS_2/V_2O_3 are mainly composed of uniformly distributed Fe, V, and S elements (Fig. 3i-l). Furthermore, EDX spectroscopy tests revealed the types of elements present in different samples and the percentage of each element's content (Fig. S8 and Table S2 in SI). The analysis of the specific surface area and pore size of different samples further verified the effect of the pore structure and microscopic morphology on the electro-

chemical performance of the materials (Fig. S9-S10 and Table S3 in the SI). The specific surface area and pore size analyses revealed that the specific surface areas of Fe₇S₈, V_{1.87}FeS₄, $V_{2.14}Fe_{0.75}S_4$, and FeS_2/V_2O_3 are 4.444, 9.448, 5.017, and 7.329 m² g⁻¹, respectively (Fig. S9 in the SI). Comparatively, V_{1.87}FeS₄ owns a higher specific surface area, allowing for the presence of a greater number of Na⁺ storage sites, improving the specific capacity of the electrode. 34,35 The pore size distribution of all samples was evaluated by the Barrett-Joyner-Halenda (BJH) method (Fig. S10 in the SI). The mesoporous structure could extend the contact area between the electrolyte and the electrode materials, and mitigate the volume change during charging/discharging, which is conducive to the storage of Na⁺.10

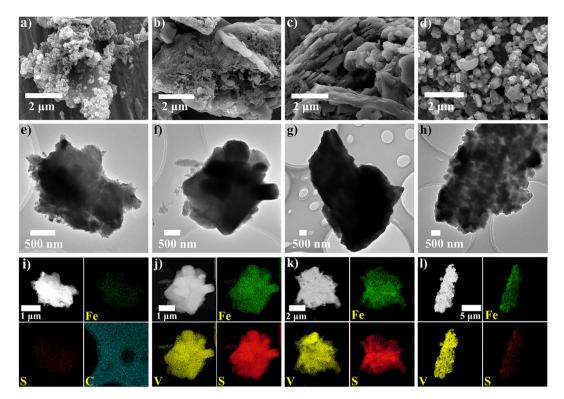


Fig. 3 SEM, TEM, and EDX mapping of (a, e, and i) Fe₇S₈, (b, f, and j) V_{1.87}FeS₄, (c, g, and k) V_{2.14}Fe_{0.75}S₄, and (d, h, and l) FeS₂/V₂O₃.

The half-batteries were assembled to evaluate the sodium storage behavior of the synthesized samples as SIB anodes in a voltage range of 0.3-3.0 V. The redox peaks in the CV curves of the different samples appear as visible voltage deviations, which arise perhaps from inconsistencies in the crystalline phase structure of samples (Fig. 4a).³⁶ In the CV curves, it can be observed that after the introduction of vanadium, significant changes occurred in the CV curves of the materials. V_{1.87}FeS₄ exhibits weak oxidation peaks at 2.09, 1.51, and 1.26 V and reduction peaks at 0.87 and 1.52 V compared to that of Fe₇S₈. A series of oxidation-reduction peaks mentioned above corresponds to the reactions that occur when the V element stores sodium ions.37 Furthermore, as the amount of vanadium in the system increases (V2.14Fe0.75S4 and FeS2/ V₂O₃), the intensity of the redox peaks gradually increases. This clearly indicates that vanadium actively participates in the redox process during the electrochemical process and realizes the storage of sodium ions. Meanwhile, GCD curves also show major differences; compared to the other samples, V_{1.87}FeS₄ demonstrates the highest stabilized specific capacity at 0.05 A g⁻¹ and maintains this superiority until the current density is increased 200-fold (Fig. 4b and c). This preeminent performance may be attributed to the crystal structure of V_{1.87}FeS₄, which is far more favorable for Na⁺ diffusion and storage. Although the specific capacities of $V_{2.14} Fe_{0.75} S_4$ and FeS₂/V₂O₃ are lower than that of Fe₇S₈ at low current densities, a reversal will occur when the current density is increased to 2 A g^{-1} or even 10 A g^{-1} (Fig. 4c and d). This phenomenon,

together with the fact that $V_{1.87} FeS_4$ exhibits admirable sodium storage performance at any current density, firmly certifies that synthesis of bimetallic sulfides or composites could actualize high-rate ability of TMSs. ^{7,19,38}

Fig. 4(e) reveals the superior rate performance of V_{1.87}FeS₄ (45.4%) than Fe_7S_8 (13.4%) when the current density is increased from 0.05 to 10 A g⁻¹, confirming that the creation of iron/vanadium bimetallic sulfides is in favor of addressing the inability to perform fast-charging of iron sulfides. Furthermore, comparison with previously reported bimetallic sulfides reveals that V_{1.87}FeS₄ offers exciting Na⁺ storage capacity and rate performance (Fig. 4f). ³⁹⁻⁴² Fig. 4(g) presents the cycling performances of Fe_7S_8 and $V_{1.87}FeS_4$ at 0.2 A g^{-1} . The batteries were first activated for 5 cycles at a low current density of 0.05 A g⁻¹, and then continuously tested for 100 cycles at 0.2 A g⁻¹. Finally, V_{1.87}FeS₄ delivers a specific capacity of 486.62 mAh g⁻¹, while Fe₇S₈ merely achieves a specific capacity of 215.50 mAh g⁻¹. The specific capacities and discharging time of the different samples at varying current densities are listed in Table S4 in the SI. Comparatively, V_{1.87}FeS₄ exhibits a much higher specific capacity at the same discharging duration, or a considerably shorter duration for attaining the equivalent specific capacity, justifying a remarkably fast sodium storage trait. The brilliant performance of V_{1.87}FeS₄ indicates that fabricating bimetallic sulfides by in situ modulation of phase transition of sodium species could effectively overcome the intrinsic defects of Fe7S8, thereby realizing the ultrafast Na⁺ storage. In order to investigate the stability of the

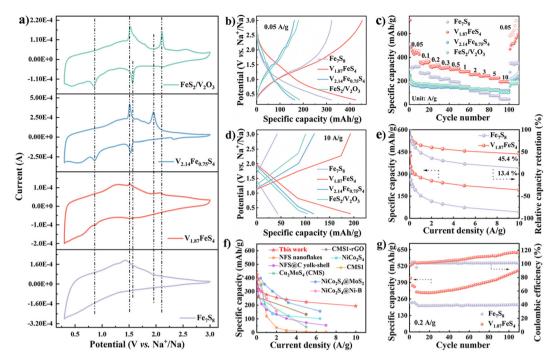


Fig. 4 Comparison of electrochemical performance: (a) CV curves at 0.2 mV s⁻¹, (b) GCD profiles at 0.05 A g^{-1} , (c) rate performance, (d) GCD profiles at 10 A g^{-1} of Fe₇S₈, V_{1.87}FeS₄, V_{2.14}Fe_{0.75}S₄, and FeS₂/V₂O₃, (e) relative capacity retention at various current densities from 0.05 to 10 A g^{-1} of Fe₇S₈ and V_{1.87}FeS₄, (f) comparison with other bimetallic sulfide anode materials for SIBs, and (g) cycling performance of Fe₇S₈ and V_{1.87}FeS₄ at 0.2 A g^{-1} .

material during the electrochemical process, scanning electron microscopy characterization is conducted on $V_{1.87} FeS_4$ after a long-term cycling (Fig. S11 in the SI). It can be seen that the microstructure of the material is still maintained during the cycling process, except for forming a dense solid electrolyte layer on the material surface.

The electrochemical performance of V_{1.87}FeS₄ is comprehensively analyzed after identifying that it exhibits optimal sodium storage properties. The GCD profile indicates that V_{1.87}FeS₄ exhibits a high and stable specific capacity of 424.67 mAh g^{-1} at 0.05 A g^{-1} for the fifth discharging (Fig. 5a). In comparison, the specific capacities of Fe₇S₈, V_{2,14}Fe_{0,75}S₄, and FeS_2/V_2O_3 are only 320.95, 163.35, and 183.98 mAh g^{-1} , respectively (Fig. S12 in the SI). The CV profiles of the first three cycles demonstrate excellent electrochemical reversibility of V_{1.87}FeS₄ (Fig. 5b), and a broad oxidation peak of around 1.5 V associated with electrochemical reactions occurring in the iron compound, which also appears in the CV curve of Fe7S8 (Fig. S13 in the SI). 13,36,43 Also, multiple pairs of redox peaks are evident in CV curves of V2.14Fe0.75S4 and FeS2/V2O3 with increasing V element content (Fig. S13 in the SI), which corresponds to a series of reactions occurring with Fe and V species during sodium storage, respectively. 12,37,44,45 The GCD profiles at varied current densities suggest that V_{1.87}FeS₄ possesses splendid sodium storage capacity as well as favorable reversibility compared to the other three samples (Fig. 5c and S14 in the SI). Strikingly, the highly superior specific capacity at 10 A g^{-1} proves the fast-charging nature of $V_{1.87}FeS_4$, thus stimulating an exhaustive investigation of the electrochemical reaction kinetics of samples.

$$i = a \times v^b \tag{1}$$

$$i(V)/v^{1/2} = k_1 v^{1/2} + k_2$$
 (2)

The capacitive-controlled electrochemical reaction process exhibits faster reaction kinetics compared to that of the diffusive-controlled reaction, favoring Na⁺ diffusion. Therefore, the capacitive- and diffusive-controlled contributions of different samples were quantified with the help of CV curves at different scanning rates (Fig. 5d and S15 in the SI) according to eqn (1) and (2), where i (V) represents the peak current, ν represents the scanning rate, and a and b denote constants. The capacitive contribution of $V_{1.87}FeS_4$ is 86.48% at 0.1 mV s^{-1} (Fig. 5e), whereas Fe_7S_8 , $V_{2.14}Fe_{0.75}S_4$, and FeS_2/V_2O_3 only contribute 23.49%, 72.97%, and 57.12%, respectively, at the identical scanning rate (Fig. S16-18 in the SI). Meanwhile, the capacitive contributions gradually increase with the increasing scanning rate and increase to 96.84%, 63.54%, 93.67%, and 88.49%, respectively, for $V_{1.87}FeS_4$, Fe_7S_8 , $V_{2.14}Fe_{0.75}S_4$, and FeS_2/V_2O_3 when the scanning rate is up to 3.0 mV s⁻¹ (Fig. 5f and S16-18 in the SI). The higher capacitive contributions denote fast diffusion kinetics of Na⁺ and excellent reversible sodium storage qualities when V_{1.87}FeS₄ is employed as the SIB anode.

Furthermore, the diffusion characteristics of Na⁺ in varied samples were examined employing the galvanostatic intermit-

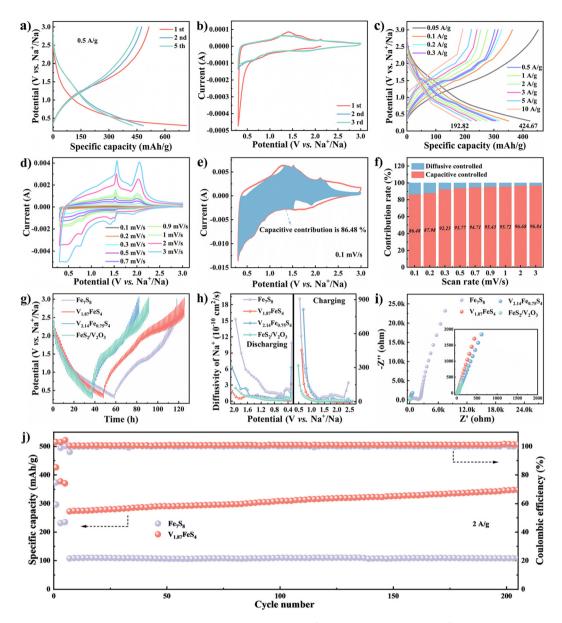


Fig. 5 Electrochemical performance of $V_{1.87}FeS_4$: (a) GCD profiles at 0.05 A g^{-1} , (b) CV curves at 0.1 mV s^{-1} , (c) GCD profiles at different current densities, (d) CV curves at different scan rates, (e) separation of capacitive (shadow region) and diffusive controlled contributions at 0.1 mV s^{-1} , and (f) the percentages of capacitive and diffusive controlled contributions at different scan rates; compared electrochemical performance: (g) GITT curves, (h) diffusivity of Na⁺, and (i) Nyquist plots of Fe₇S₈, V_{1.87}FeS₄, V_{2.14}Fe_{0.75}S₄, and FeS₂/V₂O₃, (j) cycling performance at 2 A g^{-1} of Fe₇S₈ and $V_{1.87}FeS_4$.

tent titration technique (GITT) at a pulse current of 0.025 A g^{-1} (Fig. 5g), and the specific Na⁺ diffusion coefficients (D_{Na^+}) were calculated in conjunction with eqn (3):

$$D_{\mathrm{Na^{+}}} = \frac{4}{\pi \cdot \tau} \left(\frac{m_{\mathrm{B}} \cdot V_{\mathrm{m}}}{M_{\mathrm{B}} \cdot S} \right)^{2} \left(\frac{\Delta E_{\mathrm{s}}}{\Delta E_{\mathrm{t}}} \right)^{2} \tag{3}$$

where τ is for the pulse duration, m_B (g) and M_B denote the mass and molar mass of samples, V_m represents the molar volume, and S (cm²) represents the area of the electrode. ΔE_s (V) presents the steady-state potential change due to the

current pulse, and $\Delta E_{\rm t}$ (V) presents the potential difference during the constant current pulse after eliminating the IR drop. As reflected in Fig. 5(h), $D_{\rm Na^+}$ of different samples are in the range of 10^{-9} – 10^{-10} cm 2 s $^{-1}$. It is worth noting that $D_{\rm Na^+}$ is not consistent with the kinetic feature observed from CV curves, and even anomalies appear. In contrast, the result from EIS testing demonstrates the same Na $^+$ diffusion kinetics characteristics as CV testing. The EIS results reveal that Fe $_7$ S $_8$ exhibits a larger semicircle in the high-frequency region compared to the other three materials. Moreover, a magnified view of the low-frequency region demonstrates that V $_{1.87}$ FeS $_4$

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b) a) Dischargin Na⁺/Na) **E** 400 0.05 A/g capacity V.S. 300 2.5 Na₃V₂(PO₄)₃/C||Fe₇S Cu foil Potential (V ia, V, (PO,),/C||V, o,FeS 100 Separator 150 $V_{1.87}$ FeS₄ Specific capacity (mAh/g) NVP/C Cycle number d)₆₀ Specific capacity (mAh/g) Coulombic efficiency (%) Charging Na₃V₂(PO₄)₃/C||Fe₇S₈ Discharging Na₃V₂(PO₄)₃/C||V_{1.87}FeS Charging Discharging 600

Fig. 6 Electrochemical performances of sodium-ion full-batteries: (a) the model of $Na_3V_2(PO_4)_3/C||Fe_7S_8$ or $V_{1.87}FeS_4$, (b) GCD curves at 0.05 A g^{-1} , (c) rate performances at various current densities, and (d) cycling performance at 1 A g^{-1} .

Cycle number

possesses the smallest diffusion impedance, which clearly indicates that it is conducive to the diffusion and transmission of sodium ions (Fig. 5i). This may be caused mainly by the shorter pulse duration setting during GITT testing, which must ensure that $\tau \ll L^2/D$ (L and D represent the diffusion length and coefficient, respectively).46 In this work, the synthesized materials hold a micrometer scale and gradually change from a fluffy structure to a dense one with the introduction of the V source, so setting τ to 1 h may not be sufficient. This also illustrates the significance of choosing rational parameters based on the material during GITT testing. Given that V_{1.87}FeS₄ is equipped with a relatively faster Na⁺ diffusion kinetics, superb specific capacity, and electrochemical reversibility. The long cycling performance of V_{1.87}FeS₄ (batteries are subjected to activate for 5 cycles at 0.05 A g⁻¹) is compared to that of pristine Fe₇S₈ at a current density of 2 A g⁻¹ (the discharging time of each cycle is around 7.50 min). As demonstrated in Fig. 5j, withstanding 200 cycles of repeated charging/discharging, V_{1.87}FeS₄ still maintains a specific capacity of 348.17 mAh g⁻¹ along with a coulombic efficiency of 101.38%, whereas the specific capacity of Fe₇S₈ faded to 108.25 mAh g⁻¹ accompanied by a coulombic efficiency of 100.35%.

Considering the practicality of materials, the sodium ion full-batteries were assembled with commercial Na $_3$ V $_2$ (PO $_4$) $_3$ /C as the cathode and V $_{1.87}$ FeS $_4$ or Fe $_7$ S $_8$ as the anode (Fig. 6a). The typical charging/discharging curves of Na $_3$ V $_2$ (PO $_4$) $_3$ || V $_{1.87}$ FeS $_4$ or Fe $_7$ S $_8$ are depicted in Fig. 6(b). Impressively, Na $_3$ V $_2$ (PO $_4$) $_3$ ||V $_{1.87}$ FeS $_4$ exhibits a rosy charging/discharging capacity of 244.51/215.11 mAh g $^{-1}$ with an 87.97% coulombic

efficiency in the voltage range of 1.0–3.8 V at 0.05 A g⁻¹. While Na₃V₂(PO₄)₃||Fe₇S₈ only achieves a specific capacity of 186.60/173.89 mAh g⁻¹ at the same current density (both current density and capacity are calculated based on the mass of the anode material). Furthermore, Na₃V₂(PO₄)₃||V_{1.87}FeS₄ could maintain a significantly higher reversible capacity than Na₃V₂(PO₄)₃||Fe₇S₈ when the current density was increased to 1 A g⁻¹ (Fig. 6c). The cycling lifespan of Na₃V₂(PO₄)₃||V_{1.87}FeS₄ full-batteries features outstanding cycling behavior after 1200 cycles of charging/discharging at a current density of 1 A g⁻¹ (Fig. 6d). Accordingly, the excellent rate performance and long-term cycling stability of Na₃V₂(PO₄)₃||V_{1.87}FeS₄ suggests promising potential practical applications. Table S5 in the SI presents the cycling performance of the full-batteries in comparison with that reported previously.

4. Conclusions

In conclusion, iron/vanadium bimetallic sulfides were synthesized through *in situ* modulation of phase structure via sodium species based on their role in regulating the electron density of the Fe atom. It was noted that iron/vanadium bimetallic sulfides with varied phase structures could be obtained by adjusting the mass ratio of $Fe(NO_3)_3 \cdot 9H_2O$ and $NaVO_3$. Meanwhile, the existence of sodium species could reduce the energy required for the formation of bimetallic sulfides. As a result, distinct materials exhibited various electrochemical behaviors as they were employed as SIB anodes. The study suggests that $V_{1.87}FeS_4$ possesses brilliant Na^+ storage

capacity (the specific capacity is 424.67 mAh g $^{-1}$ at 0.05 A g $^{-1}$ and remains 192.82 mAh g $^{-1}$ when the current density is increased 200-fold) when the mass ratio of Fe(NO₃)₃·9H₂O and NaVO₃ is 2:1. In addition, the full-batteries assembled with commercial Na₃V₂(PO₄)₃/C also demonstrate remarkable electrochemical performance (43.4% capacity retention at 1 A g $^{-1}$ after 1200 cycles). This work provides a novel, straightforward, and feasible preparation strategy for the development of micron-sized bimetallic sulfides applied to SIBs with fast-charging capability combined with the research in the field of catalysis.

Conflicts of interest

There are no conflicts to declare.

Data availability

EES Batteries

Data will be available while required.

Supplementary information incorporates the XRD patterns, XPS spectra, element analysis, BET test, and electrochemical performance of different samples. See DOI: https://doi.org/10.1039/d5eb00127g.

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