Controllable deposition of FeV₂S₄ in carbon fibers for sodium-ion storage with high capacity and long lifetime

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ABSTRACT Metal sulfides with high specific capacities have drawn considerable attention in the field of sodium-ion batteries (SIBs). As a typical metal sulfide, FeV₂S₄ always suffers rapid decay of capacities because of its low stability arising from large volume change. FeV₂S₄ nanoparticles with controllable sizes and distribution are encapsulated in carbon nanofibers (CNFs) with the help of graphene oxide (GO) to fabricate FeV₂S₄@GO@CNF. As a result, FeV₂S₄@GO@CNF anodes show enhanced electrochemical performances for Na⁺ storage when compared with FeV₂S₄@CNF with more particles on the surface. Typically, the capacity of FeV₂S₄@GO@CNF can be maintained at 411 mA h g⁻¹ after 200 cycles (0.1 A g⁻¹) and 227 mA h g⁻¹ over 500 cycles (1 A g⁻¹) in SIBs. Moreover, they can deliver a capacity of 170.2 mA h g⁻¹ after 150 cycles (0.1 A g⁻¹) at 0°C. In addition, full cells based on FeV₂S₄@GO@CNF anodes and Na₃V₂(PO₄)₃/C cathodes achieve a remarkable capacity of 164 mA h g⁻¹ after 100 cycles at 0.5 A g⁻¹. The high specific capacities and stability of FeV₂S₄@GO@CNF can be attributed to GO, which controls the size of FeV₂S₄ nanoparticles and their distribution in CNFs, resulting in the enhanced stability of FeV₂S₄@GO@CNF. This study may provide a new strategy for the synthesis of nanoparticle–CNF composites in catalysts and batteries.

Keywords: FeV₂S₄@GO@CNF, size and distribution, low temperature, Na-ion full cell

INTRODUCTION

Over the past few years, the rapid development of high-performance electrochemical energy storage devices (ESDs) promoted profound revolution in our lifestyle [1–

4]. Lithium-ion batteries (LIBs) [5] and Na-ion batteries (SIBs) [6,7] are crucial ESDs for efficient energy conservation and sustainable energy resources. Among them, LIBs have been widely used in practical applications. However, with the rapid development of LIBs, lithium sources have gradually declined; consequently, lithium cost gradually increased [8–10]. Sodium sources are widely distributed, abundant, and inexpensive; thus, SIBs may be substitute of LIBs. In addition, Na⁺ with similar redox potentials to Li⁺ has attracted widespread attention [11,12]. Unfortunately, on account of the large ionic radius of Na⁺ (55% large than Li⁺), the development of long-lifetime SIBs remains a great challenge [13]. Therefore, new negative electrode materials that are suitable for Na⁺ intercalation and can accelerate Na⁺ migration need to be developed.

Recently, transition metal sulfides (VS₂ [14], FeS₂ [15], SnS₂ [16], CoS₂ [17], MoS₂ [18], and Ni₃S₂ [19–21]) have been used for excellent electrodes of electrochemical ESDs [22]. Among them, ternary sulfides possess higher electronic conductivity and reversibility than single metal sulfides. Moreover, the discovery and research of ternary sulfides contribute to the development of new electrode materials for electrochemical devices of SIBs [23–26]. In recent years, ternary sulfides as energy storage materials have attracted considerable attention [27,28]. Liu *et al.* [1] reported a hydrothermal method to prepare a novel three-dimensional (3D) N-graphene/NiCo₂S₄/CC. N-graphene/NiCo₂S₄ nanoarray as air cathode grown on carbon cloth exhibits superior electrocatalytic activities and excellent mechanical flexibility. Krengel *et al.* [24]

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fabricated CuV_2S_4 by ball milling and investigated the electrochemical performance of CuV_2S_4 in SIBs. The results proved that CuV_2S_4 exhibits high cycling stability and high specific capacity. Using multiple steps of hydrothermal procedure, Guo *et al.* [29] reported $\text{FeCo}_2\text{S}_4/\text{CC@S}$ composites as binder-free cathodes for lithium-sulfur batteries. Most of the above ternary materials were synthesized by ball grinding and hydrothermal methods, which are tedious processes. Therefore, a new experimental method should be considered to synthesize ternary materials easily.

The huge volume expansion effect of transition metal sulfides is another issue. Although metal sulfides have high theoretical capacities, their volume expansion effect is serious, which results in poor cyclic stability and low rate capability. To improve the stability of metal sulfides as electrode materials, many researchers used carbon to modify them and obtain composites. For example, FeS_2/C -45 yolk-shell nanoboxes have been designed for SIBs, which exhibit much better cycle performance and rate capability than FeS_2/C -0 [30]. Wei *et al.* [31] reported that the FeS particles in carbon shell are beneficial for reducing the volume change during cycling and hindering the aggregation of particles. Those studies suggested that controlling the distribution and morphology of metal sulfides in the carbon matrix is critical to ensure the cycling performance of electrode materials. Considering the above-mentioned issues, we adopted a universal electrospinning technology to synthesize $\text{FeV}_2\text{S}_4/\text{graphene oxide@carbon nanofibers}$ ($\text{FeV}_2\text{S}_4/\text{GO@CNF}$) in which FeV_2S_4 nanoparticles were uniformly distributed. The controllable microstructure of composites could be realized by adding GO into the precursor solution. Importantly, the size of FeV_2S_4 particles decreased, and most of the particles were distributed within the carbon fibers. As anode for SIBs, $\text{FeV}_2\text{S}_4/\text{GO@CNF}$ composites showed superior electrochemical property with long cyclic life and outstanding rate performance compared with the sample without GO. In addition, the electrochemical property of $\text{FeV}_2\text{S}_4/\text{GO@CNF}$ at low temperature (0°C) was acceptable. Furthermore, $\text{FeV}_2\text{S}_4/\text{GO@CNF}$ composites exhibited high capacity in the $\text{FeV}_2\text{S}_4/\text{GO@CNF}/\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ full cell system as an anode material.

EXPERIMENTAL SECTION

Preparation of $\text{FeV}_2\text{S}_4/\text{GO@CNF}$ and $\text{FeV}_2\text{S}_4/\text{CNF}$

Typically, 7.6 mL of *N,N*-dimethyl formamide (DMF) and 0.64 g of polyacrylonitrile (PAN) were mixed in a

bottle. Then, the mixture was stirred in a water bath at 60°C for 1 h. Subsequently, 0.4 mL of GO (~ 3 mg GO/mL)/DMF solution, 0.45 mmol of iron(III)-acetylacetonate ($\text{Fe}(\text{acac})_3$), and 0.9 mmol of vanadium(III) 2,4-pentanedionate ($\text{V}(\text{acac})_3$) were added. The mixed solution was stirred continuously for 4 h to form a homogeneous solution. The precursor solution was poured into a 10-mL syringe for electrospinning. An aluminum collector plate was placed 16 cm from the spinneret, the flow rate was set at 0.5 mL h^{-1} , and the high voltage was 10 kV. The as-collected electrospun fibers were pre-annealed in a muffle furnace at 220°C for 2 h at a heating rate of 1°C min^{-1} . Fe-V@GO@CNF was obtained by calcining the pre-oxidized nanofibers in a 600°C tube furnace under $\text{Ar}/\text{H}_2(10\%)$ atmosphere for 2 h. Then, the black Fe-V@GO@CNF cloth was mixed with sulfur powder (1:4.5, *w/w*), calcined in ferryboat at 155°C for 5 h with 1°C min^{-1} , and continually heated to 620°C for another 2 h at 2°C min^{-1} under Ar atmosphere, and then $\text{FeV}_2\text{S}_4/\text{GO@CNF}$ was obtained. The $\text{FeV}_2\text{S}_4/\text{CNF}$ was synthesized without GO in the precursor solution under the same conditions.

Preparation of $\text{FeV}_2\text{S}_4/\text{GO}$ and FeV_2S_4

First, 0.45 mmol of $\text{Fe}(\text{acac})_3$ and 0.9 mmol of $\text{V}(\text{acac})_3$ were mixed in 7.4 mL of DMF. Then, the mixture was stirred to form a homogeneous solution, which was marked as solution A. GO (0.4 mL, ~ 3 mg GO/mL)/DMF solution was dripped onto a silicon chip and dried. Then, the silicon chip was placed in a ferryboat and calcined in a tube furnace at 600°C for 2 h under $\text{Ar}/\text{H}_2(10\%)$ atmosphere. A certain amount of solution A was added to the silicon chip and dried. The dried silicon chip and a certain amount of sulfur powder were placed in the ferryboat for annealing. The annealing temperature was increased from room temperature to 155°C for 5 h at 1°C min^{-1} and then continually heated to 620°C for another 2 h at 2°C min^{-1} under Ar atmosphere. Finally, $\text{FeV}_2\text{S}_4/\text{GO}$ was obtained. For comparison, the same amount of solution A was added directly to the silicon chip and dried. Then, it was placed in a ferryboat with sulfur powder and annealed under the same conditions to obtain FeV_2S_4 .

Synthesis of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$

The $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ sample was prepared based on a typical method [32]. Then, 21 mmol of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 14 mmol of NH_4VO_3 , and 1.26 g of PAN were added into an agate jar. The precursors were ball-milled at 450 rpm for 12 h. The obtained powder sample was dried under a vacuum box at 70°C for 12 h and then calcined at 800°C

for 8 h under Ar/H₂(10%) atmosphere.

Electrochemical measurements

Half-cell measurement

FeV₂S₄@GO@CNF anode was prepared as follows: FeV₂S₄@GO@CNF material, carbon black, and carboxyl methylated cellulose were mixed in the ratio of 8:1:1 (w/w/w). They were ground to powder, which was added to deionized water to form a slurry. Next, the slurry was coated on copper foil and dried at 70°C for 24 h in a vacuum oven. The density of active materials on each electrode was controlled at about 1.1 mg cm⁻². Na₃V₂(PO₄)₃@C cathode was prepared as follows: Na₃V₂(PO₄)₃@C, carbon black, and poly(vinyl difluoride) were mixed with the weight ratio of 8:1:1 and ground with *N*-methyl pyrrolidone (NMP) to form a slurry, which was coated onto Al foil and dried for 24 h under vacuum (the density of active materials was about ~2.3 mg cm⁻²). The half-cells were assembled in a glovebox (M. Braun) under Ar atmosphere with CR2025 coin cells. Na metal was used as a counter electrode, and glass fibers were used as separators. The room-temperature NaClO₄ (1 mol L⁻¹) in ethylene carbonate (EC):diethyl carbonate (DEC) = 1:1 (v/v) with 5% fluoroethylene carbonate (FEC) was used as electrolyte. In addition, the low-temperature (0°C) performance of SIBs was tested, and 1 mol L⁻¹ NaCF₃SO₃ in diglyme as electrolyte was used under a refrigerator. Cyclic voltammetric (CV) measurements were performed on a CHI 660E workstation. Galvanostatic charge/discharge measurements were carried out by Neware in the range of 0.01–3 V for anode materials at room temperature or low temperature (0°C). The Na₃V₂(PO₄)₃/C cathodes were tested in the range of 2.0–3.9 V at room temperature.

Full-cell measurement

The full cells were assembled by CR2032 coin-type cells.

FeV₂S₄@GO@CNF was used as anode and Na₃V₂(PO₄)₃@C as cathode. The weight ratio of anode/cathode was about 1:5. The voltage cut-off of the full cell was 0.2–3.6 V.

RESULTS AND DISCUSSION

FeV₂S₄@GO@CNF was prepared by electrospinning. PAN was used as the carbon source, and sulfur powder was used as the sulfur source. The specific synthesis process is illustrated in Fig. 1. The Fe(acac)₃-V(acac)₃-GO and PAN precursor solution was prepared. Then, pre-annealed fibers were obtained by electrospinning and pre-annealing. The pre-annealed fibers were annealed at 600°C in a tube furnace for 2 h under Ar/H₂ atmosphere to obtain Fe-V@GO@CNF. Finally, Fe-V@GO@CNF was thoroughly mixed with sulfur powder for sulfuration to obtain FeV₂S₄@GO@CNF under Ar atmosphere. This process is simple to achieve ternary mixture and avoids long time and danger.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the morphology of FeV₂S₄@GO@CNF. In Fig. 2a, the SEM image of Fe-V@GO@CNF shows uniform carbon nanofibers with homogeneous diameters of 200–250 nm. Fig. 2b, c show the morphology of FeV₂S₄@GO@CNF. Sporadic small particles can be observed on the surface of FeV₂S₄@GO@CNF. The surface of Fe-V@GO@CNF is smoother than that of FeV₂S₄@GO@CNF. For comparison, Fig. 2d shows the morphology of Fe-V@CNF, and Fig. 2e, f show the morphology of FeV₂S₄@CNF. As a result, many particles can be observed on the surface of FeV₂S₄@CNF. Furthermore, the FeV₂S₄@GO@CNF surface is smoother than the FeV₂S₄@CNF surface. As mentioned above, this phenomenon shows that the addition of GO can reduce the amount of small particles on the fiber surface. The appearance of particles on the fiber is due to the nonpolar nature of carbon materials, which contributes to its poor affinity to polar sulfides [33].

Figure 1 Schematic of the formation of FeV₂S₄@GO@CNF.

Figure 2 (a) SEM image of Fe-V@GO@CNF; (b, c) SEM images of FeV₂S₄@GO@CNF; (d) SEM image of Fe-V@CNF; (e, f) SEM images of FeV₂S₄@CNF; (g) TEM and (h) HRTEM images of FeV₂S₄@GO@CNF; (i) STEM-HAADF and their corresponding elemental mappings show the uniform distribution of C, N, O, V, Fe, and S along the nanofiber.

Fig. 2g shows the TEM image of FeV₂S₄@GO@CNF. Some small aggregates in the fiber are coated with carbon. In addition, the diameter of the fiber is about 220 nm. Meanwhile, few scattered aggregates can be found on the fiber surface. These results are in accordance with the SEM images. As shown in Fig. 2h, the high-resolution TEM (HRTEM) image of FeV₂S₄@GO@CNF displays that ultra-small FeV₂S₄ nanoparticles are encapsulated by carbon, and the particles are only a few nanometers. The crystal lattice fringe is 0.20 nm, which corresponds to the (204) crystal face of FeV₂S₄. No GO can be observed in the TEM and SEM images because of its small amount. A combination of high temperature and reducing gases can turn GO into graphite [34]. The scanning transmission electron microscopy high-angle annular dark field (STEM-HAADF) is shown in Fig. 2i, and the corresponding elemental mappings of the FeV₂S₄@GO@CNF

nanofibers are also displayed. These mappings clearly show that C, Fe, V, N, O, and S are evenly distributed in the nanofibers. The homogenous dispersion of Fe, V, and S further explains the ultra-small size of FeV₂S₄ particles. This result is consistent with the HRTEM image. In sum, the addition of GO can control the size of FeV₂S₄, and the FeV₂S₄ particles are more uniformly distributed in the carbon fibers and make the surface of FeV₂S₄@GO@CNF smoother than that of FeV₂S₄@CNF. The uniform distribution of ultra-small FeV₂S₄ particles in carbon fibers improves the long-cycle performance of electrode materials.

The structures of FeV₂S₄@GO@CNF and FeV₂S₄@CNF were analyzed by X-ray diffraction (XRD) and the effect of GO on the structure and morphology of the material was investigated. Meanwhile, the morphologies of FeV₂S₄@GO and FeV₂S₄ were observed by SEM. Fig. 3a

Figure 3 (a) XRD of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$. (b) Pure GO on silicon slice; (c, d) SEM characterization of $\text{FeV}_2\text{S}_4@\text{GO}$ on silicon slice; (e, f) SEM characterization of FeV_2S_4 on silicon slice.

and Fig. S1 show the XRD patterns of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ and $\text{Fe-V}@\text{GO}@\text{CNF}$ nanocomposites, respectively. As shown in Fig. S1, the $\text{Fe-V}@\text{GO}@\text{CNF}$ composite contains Fe, V, and C (JCPDS No. 34–0529, 65–2896, and 26–1076), respectively. As shown in Fig. 3a, all the diffraction peaks of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ match the standard diffraction data of FeV_2S_4 and carbon (JCPDS No. 89–4495 and 26–1076). Furthermore, the 2θ peaks located at 45.67° , 44.83° , and 34.97° are ascribed to the (204), (–114), and (–112) lattice planes, which correspond to FeV_2S_4 . The 26.6° feature is the fingerprint of the carbon, and it coincides with the (006) lattice plane. No other impurity peaks are present in the XRD pattern, which signifies that this material contains carbon and FeV_2S_4 without other compounds. The result is consistent with the TEM image. Regarding the FeV_2S_4 particles, the control material of $\text{FeV}_2\text{S}_4@\text{CNF}$ was also tested by XRD (Fig. S2). On the basis of the XRD patterns, the average sizes of FeV_2S_4 crystallites in $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ and $\text{FeV}_2\text{S}_4@\text{CNF}$ were calculated [35], as shown in Supplementary information. Results display that the crystallite size of FeV_2S_4 in $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ is 20.2 nm, and that in $\text{FeV}_2\text{S}_4@\text{CNF}$ is 31.7 nm. Meanwhile, $\text{FeV}_2\text{S}_4@\text{GO}$ and FeV_2S_4 samples were made for comparison to explore the role of GO. The morphologies of pure GO, $\text{FeV}_2\text{S}_4@\text{GO}$ and FeV_2S_4 are shown in Fig. 3b–f. By comparison, the size of FeV_2S_4 in $\text{FeV}_2\text{S}_4@\text{GO}$ is smaller than that of pure

FeV_2S_4 . XRD measurement of pure $\text{FeV}_2\text{S}_4@\text{GO}$ was also carried out to quantify the crystal size of FeV_2S_4 (Fig. S3). The average grain size of $\text{FeV}_2\text{S}_4@\text{GO}$ is 22.5 nm, and that of pure FeV_2S_4 is 39.0 nm. This result further proves the influence of GO on the grain growth. These results are consistent with the XRD and SEM results. These phenomena prove that GO not only promotes the compatibility of carbon materials with sulfides, but also controls the size of sulfides and helps improve carbon coating.

X-ray photoelectron spectroscopy (XPS) was performed to analyze the chemical composition and valence of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$. XPS survey spectrum of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ is shown in Fig. S4. The peaks of C, S, O, N, Fe, and V are obviously observed. Given that PAN is used as a carbon source in the experiment, N element can be detected by XPS. In addition, the N 1s spectrum is shown in Fig. 4a, and it displays binding energies of 398.4, 399.9, 400.9, and 402.4 eV, which can be attributed to pyridinic N, pyrrolic N, graphitic N, and pyridine N-oxide, respectively. In Fig. 4b, C 1s is assigned to five typical functional group peaks of C–S (283.8 eV), C–C/C=C (284.7 eV), C–N (285.3 eV), C–O (286.4 eV), and C=O (288.8 eV) [36–38]. The presence of the C–S bond demonstrates that sulfur combines with carbon in $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$. The V 2p spectrum is shown in Fig. 4c. The V 2p displays three binding energies of 524.4, 517.1, and 515.5 eV, which correspond to V^{3+} , V^{3+} , and

Figure 4 High-resolution XPS pattern of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$. XPS spectra of (a) N 1s, (b) C 1s, (c) V 2p, (d) Fe 2p, (e) O 1s, and (f) S 2p.

V^{2+} [39]. The existence state of vanadium in the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ composite is proved. The presence of V^{2+} is caused by a small amount of V–O on the surface of the material. In Fig. 4d, the Fe 2p photoelectron spectra can be matched with three peaks at 711.5, 713.7, and 718.9 eV, which are attributed to the Fe^{2+} , Fe^{3+} , and the satellite in $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ [40–42]. Among them, the presence of Fe^{3+} is caused by a small amount of Fe–O on the nanomaterial surface [43]. The XPS spectrum of O 1s is displayed in Fig. 4e. The spectrum of O 1s core level has four peaks located at 530.0, 531.0, 531.8, and 532.9 eV, which can be assigned to Fe–O, V–O, defects oxygen (Ov), and adsorbed O, respectively [42,44]. The phenomenon indicates that a small amount of FeV_2S_4 on the fiber surface has been oxidized. The core-level spectrum of S 2p is displayed in Fig. 4f. The binding energies of three types correspond to S=O, C–S, and S^{2-} [45,46]. The analysis and observation of the XPS peaks prove that the as-prepared sample is FeV_2S_4 and carbon with abundant single and double bonds, which correspond to the results of XRD and TEM. The XPS analysis of $\text{FeV}_2\text{S}_4@\text{CNF}$ is shown in Fig. S5. Comparison of the XPS spectra of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ and $\text{FeV}_2\text{S}_4@\text{CNF}$ shows no obvious difference between the two materials. Moreover, inductively coupled plasma analysis shows that the Fe content in the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ is 3.21%, and the V

content is 6.35%.

The chemical property of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ was further demonstrated by Fourier-transform infrared (FT-IR) spectroscopy (Fig. S6a). The FT-IR spectrum of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ displays the characteristic peaks of Fe–O, V–O, C–S, C=O, and C–N [47,48]. The results show that a small amount of metal oxide exists on the fiber surface. This result corresponds to the XPS spectra. The FT-IR analysis results of $\text{FeV}_2\text{S}_4@\text{CNF}$ are shown in Fig. S6b. The figure shows that the type of peaks has not changed. Fig. S7 shows the result of Brunauer–Emmett–Teller (BET) measurement. BET results are shown in Supplementary information. Thermogravimetric (TG) analysis was utilized to estimate the content of FeV_2S_4 and evaluate the influence of GO on the sample quantification. The data are reported in Fig. S8. $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ has 77.3 wt% weight loss, and $\text{FeV}_2\text{S}_4@\text{CNF}$ has 75.4 wt% weight loss. The test results provide insights that GO is added with a small amount and does not affect the carbon content of the materials. The remaining products were also tested by XRD. As shown in Fig. S9, the remaining products can be divided into FeVO_4 , Fe_2O_3 , and V_2O_5 . With FeVO_4 formation, Fe_2O_3 and V_2O_5 are also generated after FeV_2S_4 decomposition at high temperatures. The content of FeV_2S_4 in $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ can be calculated by analyzing the products and TG results. The

content of FeV_2S_4 can be calculated as 24.8 wt% (Supplementary information). These results prove that the addition of GO does not affect the carbon content of the material, indicating that the GO content is very small. The results of XPS and FR-IR also indicate that a small amount of oxidation occurs on the surface of the material during sealing.

The electrochemical storage property of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ is presented in Fig. 5. The CV curves show the Na^+ insertion/extraction behaviors of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$. The CV curves of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode are displayed in Fig. 5a. In the first cycle scan, two pronounced irreversible cathodic peaks are located at 1.02 and 0.78 V *versus* Na^+/Na at 0.1 mV s^{-1} because of the decomposition of the electrolyte on the surface of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode and the formation of solid electrolyte interphase (SEI) [49,50]. The sharp cathodic peak at the low-voltage region near 0 V is due to the sodium insertion in carbon [51]. Then, the peak located at 1.9 V is due to the conversion of FeV_2S_4 and the formation of Na_2S with the embedding reaction of Na^+ [23]. The anodic peak at 2.1 V could be indexed to the extraction reaction of Na^+ . In addition, the redox peaks are almost superposition in the subsequent cycles, which displays the superior storage stabilization of Na^+ .

Fig. S10a displays the galvanostatic voltage–capacity

curves of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode with a current density of 0.1 A g^{-1} under a potential window of 0.01–3 V. During discharge, a potential plateau at around 2.1–1.5 V can be found along with a charge curve potential plateau at around 1.8–2.3 V. The charge and discharge plateaus agree with the result of CV curve scan, which indicates that the redox reaction occurs between Na^+ and $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode. Furthermore, the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode delivers initial discharge and charge capacities of 593 and $422.8 \text{ mA h g}^{-1}$, respectively, which correspond to a coulombic efficiency of 71.3% at a current density of 0.1 A g^{-1} . The initial large irreversible capacity is most likely due to the formation of the SEI layer and the electrolyte decomposition on the electrode/electrolyte surface [52]. The cycle performances of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ and $\text{FeV}_2\text{S}_4@\text{CNF}$ are shown in Fig. 5b. The $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ anode exhibits better and more stable cycle performance as compared with the $\text{FeV}_2\text{S}_4@\text{CNF}$ electrode. In specific, the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode displays durable cycling stability at a current density of 0.1 A g^{-1} for 200 cycles, with a high reversible capacity of 411 mA h g^{-1} retained after 200 cycles. However, the reversible capacity of the $\text{FeV}_2\text{S}_4@\text{CNF}$ sample only remains at 289 mA h g^{-1} after 200 cycles at 0.1 A g^{-1} . In addition, the capacity of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode is much higher than that of

Figure 5 Electrochemical Na^+ storage property of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$. (a) CV curves of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ at a scan rate of 0.1 mV s^{-1} ; (b) cycling capacities at 0.1 A g^{-1} ; (c) rate performance; (d) cycling capacity of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ at 1 A g^{-1} and its coulombic efficiency; (e) electrochemical properties of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ composites as anodes of SIBs at a low temperature (0°C).

the $\text{FeV}_2\text{S}_4@\text{CNF}$ electrode. The data comparison results show that the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode has better stability than the $\text{FeV}_2\text{S}_4@\text{CNF}$ electrode. This result is because the addition of a small amount of GO can reduce the size of FeV_2S_4 crystal particles, which makes them more covered by carbon. This phenomenon is conducive to improving the stability of the material. Thus, the addition of GO not only improves the microscopic morphology of the sample but also ameliorates the electrochemical properties and stability of the material. Pure CNF was prepared and its cycling performance was tested to distinguish the contribution of CNF in the whole capacity (Fig. S11). The figure shows that the capacity contributed by pure CNF is 209 mA h g^{-1} . Notably, the SEM images of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ and $\text{FeV}_2\text{S}_4@\text{CNF}$ after 200 cycles are shown in Fig. S12. The structure of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ remains more intact without any damage than that of $\text{FeV}_2\text{S}_4@\text{CNF}$, and this phenomenon confirms that the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrodes are highly robust and suitable as anode materials for SIBs.

Fig. 5c displays the rate capability of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode. The $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode affords reversible capacities of 399.8, 388.5, 370.6, 343.1, and $314.8 \text{ mA h g}^{-1}$, respectively, at rates of 0.05, 0.1, 0.2, 0.5, and 1 A g^{-1} , respectively. When the current reverts to 0.05 A g^{-1} , the capacity of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode can be recovered to $399.1 \text{ mA h g}^{-1}$ and remain stable. The outstanding rate capability exhibits excellent tolerance for good sodiation/desodiation, which suggests the superior stability of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode. The long-term cycling performance of electrode materials is a challenging issue for the application of SIBs. In Fig. 5d, the long-term cycling stability of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode was evaluated by a test of charge/discharge for 500 cycles at 1 A g^{-1} . After five cycles of activation at a low current density, the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode maintains an excellent reversible capacity of about 227 mA h g^{-1} after 500 cycles at 1 A g^{-1} (the capacity retention is calculated to be 70%). In addition, the coulombic efficiency of the electrode is near 100%. On the basis of the data, the long-term cycling of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode was also tested at 5 A g^{-1} . In Fig. S13, after 300 cycles, the capacity remains at 150 mA h g^{-1} at a current density of 5 A g^{-1} , showing excellent stability. Moreover, the low-temperature cyclic performance of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode is shown in Fig. 5e. Impressively, the reversible capacity of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode is 490 mA h g^{-1} at the first cycle. In addition, Fig. 5e shows that the performance of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode drops sharply in the first 50

cycles. This result is due to the fact that ion movement is blocked at low temperatures and that the material structure changes significantly during the initial cycles under the influence of temperature [53,54]. Thus, a dramatic capacity decay occurs during the first 50 cycles. Then, the capacity gradually stabilizes, and the capacity remains at $170.2 \text{ mA h g}^{-1}$ after 150 cycles. This proves that $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode can maintain good stability under low-temperature conditions (0°C). The galvanostatic charge/discharge curve at the current density of 0.1 A g^{-1} is shown in Fig. S10b. The potential platform during charging and discharging at low temperature is similar to the potential platform at normal temperature.

Previous studies reported that the binding of S and carbon matrix can promote the adsorption of Na^+ and exhibits a pseudo-capacitance effect [36,55]. Therefore, CV test was performed at various sweep rates from 0.2 to 5 mV s^{-1} to assess the contribution from pseudo-capacitance. The result is shown in Fig. 6a. The relationship between the measured current (i) and the scan rate (ν) can be described by Equation (1) [56]:

$$i = a\nu^b \quad (1)$$

The b -value is determined from the slope of the $\log(\nu)$ - $\log(i)$ plots. The b -value has two clear definitions. When b is 0.5, the current response is diffusion-controlled. When $b = 1$, the current response is capacity-controlled [57]. The b -values are shown. As shown in Fig. 6b, the b -values for both anodic and cathodic materials are 0.89 and 0.85, respectively, when the scan rates range from 0.2 to 5 mV s^{-1} . These results indicate that the current has a predominantly capacitive characteristic. Moreover, CV tests at various scan rates indicate that the diffusion-based intercalation and capacitive contributions are calculated via Equation (2) [58]:

$$i(V) = k_1\nu + k_2\nu^{1/2}, \quad (2)$$

where i is the current response at a fixed voltage (V), ν is the scan rate, $k_1\nu$ represents the capacitive effect, and $k_2\nu^{1/2}$ is a diffusion-controlled reaction [59]. In Fig. 6c, capacitive effects and diffusion-controlled reaction can be distinguished by determining k_1 and k_2 . When the scan rate is 1 mV s^{-1} , the current can be divided into capacitive (pink) and diffusion-controlled (purple) types. The capacitive contribution ratio is shown in Fig. 6d, which increases with the sweeping speed. The minimum capacitive contribution is 60.3% at 0.2 mV s^{-1} , and the maximum capacitive contribution is 86.4% at 5 mV s^{-1} . This result proves that the excellence storage capability of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ electrode is partly due to the contribution of the pseudo-capacitance effect. For the

Figure 6 Capacitance effect of FeV₂S₄@GO@CNF in SIBs. (a) CV curves at scan rates from 0.2 to 5 mV s⁻¹; (b) b -value is determined from the relationship between the peak current and CV scan rates; (c) current separation based on the capacitance effect (capacitive) and diffusion-controlled (battery) at 1 mV s⁻¹; (d) total capacity contribution ratio of the capacitive effect and diffusion-controlled at different scan rates.

FeV₂S₄@CNF sample, a capacitance analysis was also executed. Fig. S14 displays similar CV curves, b -value, and the capacitive effect of the FeV₂S₄@CNF sample. The percentage of capacity contribution of FeV₂S₄@CNF shows that the capacitive effect of FeV₂S₄@GO@CNF is larger than that of FeV₂S₄@CNF under the same scan rates. The addition of GO can improve the adsorption of the material to Na⁺, and more capacitive effect of the material can be shown. Na⁺ diffusion coefficient obtained based on CV data and electrochemical impedance spectroscopy result of FeV₂S₄@GO@CNF is shown in Fig. S15.

Taking into account the practical application capabilities of the electrode materials, the full cells were assembled using FeV₂S₄@GO@CNF as the anode and Na₃V₂(PO₄)₃@C as the cathode. The electrochemical performances of the Na₃V₂(PO₄)₃@C cathode are shown in Fig. S16. Fig. S16a shows that the reversible capacity of Na₃V₂(PO₄)₃@C is about 83.5 mA h g⁻¹ after 100 cycles in the voltage range of 2–3.9 V at 100 mA g⁻¹. The charge–

discharge curves are shown in Fig. S16b.

The fundamental operating principle of such FeV₂S₄@GO@CNF//Na₃V₂(PO₄)₃@C full-cell unit is shown in Fig. 7a. The sodiation/desodiation process of Na⁺ can be observed in this figure. Fig. 7b shows that the capacity of a full cell is about 164 mA h g⁻¹ at 0.5 A g⁻¹ after 100 cycles. The rate performance (the capacity is evaluated by the weight of anode materials) of the full cell is shown in Fig. 7c. The potential window range of full battery performance test is 0.2–3.6 V. As the current densities increase, the capacity decreases. When the current density returns to 0.2 or 0.1 A g⁻¹, the capacity returns to the original value, which displays the excellent stability of the full cell. The charge/discharge profiles from 0.1 A g⁻¹ to 1 A g⁻¹ are shown in Fig. 7d. The primary discharge plateaus are 1.5–2.2 V, which originate from the unstable anode plateau. With the increase in current density, the sluggish dynamic activity can be shown. The FeV₂S₄@GO@CNF//Na₃V₂(PO₄)₃@C full cell can facily light an

Figure 7 Electrochemical tests and practical applications of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}//\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ full-cell system. (a) Operating schematic of the full cell; (b) cycle stability at 500 mA g^{-1} ; (c) charge/discharge capacity at different current densities; (d) charge/discharge profiles at various currents; (e) one coin-type full-cell lights up an “HNU” logo.

“HNU” logo (Fig. 7e), which consists of more than 70 LED bulbs. The good electrochemical performance indicates that the material has potential application value in the SIBs.

CONCLUSION

In this paper, $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ composites were synthesized for SIB anodes *via* a facile electrospinning strategy. After adding GO, the diameters and distribution (in or outside the fibers) of FeV_2S_4 nanoparticles become controllable, and FeV_2S_4 nanoparticles are homogeneously embedded in CNF. Those morphological features confer $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ with good Na^+ storage performance. For example, $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ displays a high capacity of 411 mA h g^{-1} at 0.1 A g^{-1} . Their specific capacities and long life time are 227 mA h g^{-1} after 500 cycles at 1 A g^{-1} . The SEM images of the $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ anode after charge–discharge tests indicate that the stability of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ is better than that of $\text{FeV}_2\text{S}_4@\text{CNF}$. The low-temperature property and full-cell performance of $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ were also investigated in detail to estimate their potential application. The present strategy of using GO to control the sizes and

distribution of nanoparticles may promote the development of CNF composites in catalysts and other batteries.

Received 31 March 2020; accepted 16 October 2020;
published online 13 January 2021

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Acknowledgements This work was supported by the National Natural Science Foundation of China (51772082, 51804106 and 51574117), China Postdoctoral Science Foundation (2018T110822 and 2017M610495), and the Natural Science Foundation of Hunan Province (2019JJ30002 and 2019JJ50061).

Author contributions Li P designed and performed the experiments, analyzed the data, and wrote the paper; Chen C, Cai M and Cai Y gave pivotal advice; Huang Z, Ding S and He H analyzed the data; Zhang M conceived the framework of this paper and wrote the paper. All authors contributed to the general discussion.

Conflict of interest The authors declare no conflict of interest.

Supplementary information

Supporting data are available in the online version of the paper.

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碳纤维中可控修饰 FeV_2S_4 及其高容量长寿命储钠研究

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摘要 拥有高比容量的金属硫化物作为负极材料在钠离子电池(SIBs)领域备受关注。 FeV_2S_4 作为一种典型的金属硫化物,由于体积变化大,存在容量衰减快、稳定性差的问题。本文利用氧化石墨烯(GO)实现了对 FeV_2S_4 纳米粒子尺寸和分布的调控,使其更好地包裹在碳纳米纤维(CNFs)中,从而制备了 $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ 。 $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ 负极与表面拥有更多粒子的 $\text{FeV}_2\text{S}_4@\text{CNF}$ 负极相比具有更优异的 Na^+ 存储性能。 $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ 用于钠离子电池负极时,200次循环(0.1 A g^{-1})后容量仍然可保持在 411 mA h g^{-1} ,500次循环(1 A g^{-1})后可保持在 227 mA h g^{-1} 。此外,在 0°C 下,经过150次循环(0.1 A g^{-1})后,仍可以输出 $170.2 \text{ mA h g}^{-1}$ 的容量。以 $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ 作为负极, $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ 作为正极的全电池在 0.5 A g^{-1} 下循环100次后,其容量达到 164 mA h g^{-1} 。 $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ 表现出高比容量和稳定性,这是由于GO控制了 FeV_2S_4 的颗粒大小及其在CNFs中的分布,从而提高了 $\text{FeV}_2\text{S}_4@\text{GO}@\text{CNF}$ 的稳定性。本研究为纳米CNF复合材料的制备提供了新思路。