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Fe-Alginate Biomass-Derived FeS/3D Interconnected Carbon Nanofiber Aerogels as Anodes for High Performance Sodium-Ion Batteries

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Abstract

The development of anode materials with a high capacity, excellent rate capability, and acceptable stability for sodium-ion batteries (SIBs) is still an urgent issue. Here, we fabricated FeS nanoparticle (NP)/three-dimensional (3D) carbon nanofiber aerogels (CNA) composites utilizing Fe-alginate aerogels as the renewable precursor. In the FeS/CNA sample, well-distributed FeS NPs were embedded on a 3D-CNA network with high electron conductivity and a large specific surface area. Impressively, the FeS/CNA sample was evaluated as an anode electrode material for SIBs, and exhibited an excellent specific capacity (473 mA h g^{-1} at 0.1 A g^{-1}) and outstanding rate capacity (291 mA h g^{-1} at 5 A g^{-1}). In addition, 97.4% of the capacity, 385 mA h g^{-1} , was retained over 400 cycles at 2 A g^{-1} , indicating the prominent cycling stability of the FeS/CNA sample. The results were ascribed to the unique structure of the FeS particles embedded on interconnected CNAs, which could boost sodium ion diffusion and facilitate electrolyte access.

Keywords: Anode materials; sodium-ion batteries; Fe-alginate aerogels; three-dimensional carbon nanofiber aerogel; FeS/CNA sample

1. Introduction

Sodium-ion batteries (SIBs) have been considered a potential candidate to replace lithium-ion batteries (LIBs) because of their low cost and availability of sodium resources [1-4]. However, graphite, a classic anode material, exhibited poor performance in SIBs because of the relatively large radius of Na^+ [5,6]. To address this problem, much effort has been made to expand carbon-based anode materials for improving sodium ion storage [7,8]. However, due to the drawback of the carbon structure, the sodium ion host site could limit further increase of the capacity [9]. Thus, it is a huge challenge to fabricate anode materials to meet the demands of excellent capacity, outstanding rate capability, and acceptable stability for SIBs.

In recent years, a great number of SIB anode materials that exhibit excellent capacities have been reported such as metal sulfides [10,11], metal oxides [12], and metal selenides [13,14]. Among them, transition metal sulfides (TMSs) have aroused great interest because of their high theoretical specific capacity [15,16,17]. Specifically, iron sulfide (FeS) materials have been explored due to their excellent redox reversibility, abundance, and cost effectiveness [18,19]. For example, Xu *et al.* reported that iron sulfide-based composites can be regarded as an excellent anode material with high capacity for rechargeable batteries [20,21]. However, the employment of FeS as an anode material in SIBs often suffers from three drawbacks. (I) The obvious volume expansion of FeS particles during the Na^+ de/insertion process usually leads to electrode pulverization and electrochemical agglomeration and then causes a sharp decrease in the capacity and poor cycle stability. (II) FeS

always has poor electronic conductivity, which hinders electron transfer, resulting in poor electrochemical properties. (III) The sluggish kinetics of FeS will limit its behavior of Na^+ de/insertion process, resulting in a poor rate capability. Therefore, only when the three problems are solved, FeS can become a potential SIB anode material.

To address these problems, two kinds of strategies have been developed. On the one hand, a carbon matrix was introduced to improve the electronic conductivity. For example, Zhang *et al.* studied FeS nanoparticles (NPs) anchored in graphene/carbon nanotubes, which showed a good reversible capacity of 300 mA h g^{-1} at 0.1 A g^{-1} after 100 cycles [15]. On the other hand, special nanostructures were fabricated to inhibit the volume expansion and increase the active sites for Na^+ de/insertion. For instance, Yang's group reported CoS hollow NPs in one-dimensional (1D) carbonaceous fibers, which showed an excellent reversible capacity and outstanding cycle stability of 392 mA h g^{-1} at 1 A g^{-1} after 100 cycles [22]. It is known that 1D carbonaceous fibers can be regarded as transport channels for ions and electrons. These channels shorten the transport path and accelerate ion and electron transport, which is also good for electronic conductivity [23]. In addition, abundant 1D fibers can constitute 3D porous carbonaceous nanostructures, which play an important role in SIB anode material performance. A 3D architecture provides many micro- and mesopores, which are helpful for the constraint of volume expansion [24]. The porous nanostructures can also provide a large active surface, which enables to sufficient contact between the electrode and electrolyte to increase the electronic conductivity [25]. Therefore,

designing FeS/C composites with 3D porous nanostructures will be necessary for SIB anode materials.

Herein, we report the synthesis of FeS NPs embedded on 3D interconnected carbon nanofiber aerogels (CNAs) where Fe-alginate aerogels are used as the precursor. Sodium alginate (SA), a sustainable seaweed extractive, can utilize the “egg box” structure to coordinate with Fe^{3+} through ion exchange. The aqueous SA solution induces gelation, which generates aerogels with a high porosity through freeze drying. In addition, this unique structure can maintain rich channels and ensure the homogeneous distribution of FeS NPs on the CNAs after carbonization and sulfuration. While employed as an anode material for SIBs, the FeS/CNA sample exhibits an excellent specific capacity of 473 mA h g^{-1} at 0.1 A g^{-1} and an outstanding rate capacity of 291 mA h g^{-1} at 5 A g^{-1} . Moreover, 97.4% of the capacity, 385 mA h g^{-1} , is retained over 400 cycles at 2 A g^{-1} , indicating the prominent cycling stability of the FeS/CNA sample. Therefore, the FeS/CNA sample with excellent performance is a promising candidate as an SIB anode material.

2. Experimental

2.1 Materials

Sodium alginate ($(\text{C}_6\text{H}_7\text{O}_6\text{Na})_n$) was obtained from Aladdin (Shanghai, China). Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and sublimed sulfur were purchased from Sinopharm Chemical Reagent of Shanghai City.

2.2 Preparation of FeS/CNA

First, a solution of 1 wt % sodium alginate was added to the 2.5 wt % ferric chloride

hexahydrate aqueous solution using a syringe needle and stirred for 30 min to encourage Fe cross-linking gelation. Second, the as-prepared gel was separated from the solution and washed with distilled water several times. Then, via a freeze-drying process, the obtained gel was dehydrated and formed a 3D alginate aerogel. Third, the aerogels were heated at 800 °C for 2 h under an Ar atmosphere at a speed of 2 °C min⁻¹ and cooled naturally. Finally, the sample was mixed with sulfur sublimed and annealed at 600 °C for 2 h, generating the FeS/CNA sample.

2.3 Characterization

A powder X-ray diffractometer (XRD) using Cu K α radiation with a λ of 1.5418 Å (DX2700, China) was used to analyze the phase structures. The morphological characterization was provided by field-emission scanning electron microscopy (FESEM) (JSM-7001F, Japan). High-resolution transmission electron microscopy (HRTEM/TEM) and energy dispersive X-ray spectroscopy (EDS) images were obtained (FEI Tecnai F20 electron microscope with an accelerating voltage of 200 kV). X-ray photoelectron spectroscopy (XPS) measurements were used to investigate the near surface region chemical compositions (ESCALab250 electron spectrometer). The thermogravimetric analysis (TGA; Seiko Instruments, Japan) was measured from 25 to 800 °C with a heating rate of 10 °C min⁻¹ in air. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method. The pore size was calculated from the adsorption data of the isotherm.

2.4 Electrochemical Measurements.

The electrochemical properties of FeS/CNA were investigated through CR2025 coin

cells assembled in an argon-filled glove box in which sodium metal was the counter electrode. To prepare the working electrode, FeS/CNA was mixed with acetylene black and poly (vinylidene fluoride) with a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone to form the slurry, which was uniformly pasted onto a copper foil substrate. The remaining solvent was removed through vacuum drying at 120 °C. The loading amount of active material was $\sim 1.4 \text{ mg cm}^{-2}$. The liquid electrolyte was 1.0 M NaCF_3SO_3 in DIGLYME (100 vol %). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) data were obtained by a CHI 760E electrochemical workstation. The electrode capacity was investigated by the battery test system (Land CT2001A) through a galvanostatic charge/discharge method. The specific capacity of the sample corresponds to the total mass of the entire electrode.

3. Results and discussion

The 3D FeS/CNA sample was synthesized through a three-step strategy from the seaweed. First, we synthesized Fe-alginate aerogels by freeze-drying sodium alginate and FeCl_3 , as illustrated in **Fig. 1**. Fe-alginate hydrogels were formed through ion exchange with Fe^{3+} in the unique “egg-box” structure in sodium alginate [26]. In the freeze-drying process, unique crystals grew in accordance with the thermal gradient, and the Fe-alginate hydrogels were distributed on gaps of unique crystals. After the unique crystal recovery at room temperature, Fe-alginate aerogels with 3D porous structures were formed from Fe-alginate hydrogels. Second, the obtained sample was held at 800 °C to synthesize Fe NPs on the 3D porous carbon nanofiber aerogels. During the carbonization process, alginate macromolecules were decomposed, and Fe

NPs were obtained through the reduction reaction of Fe^{3+} in the “egg box” structure at the same time. In addition, Fe NPs played a key role in the transformation from alginate macromolecules to 3D carbon nanofiber aerogels [27]. Finally, Fe NPs on the carbon nanofibers changed to FeS via the sulfuration process at 600 °C for 2 h.

Fig. 2a shows the XRD pattern of the FeS/CNA sample, in which all diffraction peaks correspond to a hexagonal phase of FeS (JCPDS No. 65-1894). The four sharp and strong peaks at 29.8, 33.7, 43.6, and 53.1° are attributed to the (100), (101), (102), and (110) planes of FeS, respectively [28]. No obvious peak of carbon is found in the FeS/CNA sample, suggesting an amorphous carbon structure [29]. Based on the TGA curve (**Figure S1**), the carbon content in the FeS/CNA sample is calculated to be approximately 56.4 %. This weight loss is mainly related to the combustion of amorphous carbon to CO_2 and the oxidation of FeS to SO_2 and Fe_2O_3 [12]. The XPS survey spectrum was measured to investigate the chemical state and molecular environment of the FeS/CNA sample (**Fig. 2b-2d**). As displayed in **Fig. 2b**, the XPS survey spectrum of the FeS/CNA sample contains Fe, S, O, and C peaks. As shown in **Fig. 2c**, the peaks at binding energies of 711.1 eV corresponding to $\text{Fe } 2p_{3/2}$ and 724.4 eV assigned to $\text{Fe } 2p_{1/2}$ are related to the characteristic peaks of Fe^{2+} [30,31]. In the S 2p spectrum (**Fig. 2d**), the peaks at 162.9 eV and 161.4 eV correspond to $\text{S } 2p_{1/2}$ and $\text{S } 2p_{3/2}$, respectively, which are in accordance with the characteristics of S^{2-} [32,33]. Another clear peak observed at 163.1 eV is attributed to chemical bonds between S and C atoms (C-S-C) [34]. The result confirms that the sulfur atoms are doped into the carbon when the FeS NPs are formed.

The N₂ ad/desorption isotherm (**Fig. 2e**) and pore-size distribution (**Fig. 2f**) of FeS/CNA were measured to analyze its porous characteristics. The N₂ ad/desorption isotherm (**Fig. 2e**) is a type-IV adsorption isotherm with a specific surface area of 60.5 m² g⁻¹, which indicates presence of mesopores in the FeS/CNA sample. As shown in **Fig. 2f**, the average pore sizes of the FeS/CNA sample are centered at 2.52 and 3.18 nm based on the branch of adsorption isotherm, resulting from the thermal decomposition of alginate macromolecules. The pores offer an adequate surface for the contact between the electrode and electrolyte and provide rich transport pathways to accelerate charge transfer.

The morphology and structure of the FeS/CNA were determined by SEM, TEM, and HRTEM. **Fig. 3a-3b** shows the SEM images of FeS/CNA, where many carbon nanofibers are shown. The FeS NPs (~100-200 nm) show a uniform distribution on the carbon nanofibers. The TEM and HRTEM images of FeS/CNA are shown in **Fig. 3c-3e**. We can observe that FeS with diameters of 100-200 nm are embedded on the carbon nanofiber. The HRTEM image exhibits clear lattice fringes with a spacing of 0.26 nm (**Fig. 3e**), which corresponds to the (101) plane of FeS NP [12]. **Fig. 3f** reveals the EDS mappings of FeS/CNA, which show the distribution of Fe, S and C elements. The C element has a uniform distribution in the whole sample, in which the S and Fe elements are located in the FeS NPs.

The sodium ion storage performances of FeS/CNA were studied with CR2025-type cells. **Fig. 4a** illustrates the cyclic voltammetry (CV) profiles of the FeS/CNA anode during the initial three cycles at a scan rate of 0.1 mV s⁻¹ in a

potential window of 0.01-3.0 V vs. Na⁺/Na. The first cathodic scan displays two developed peaks at ~ 0.87 and ~ 0.16 V. The peak at 0.16 V comes from the formation of Na₂S and Fe (1) [28]. The peak at ~ 0.87 V is ascribed to the appearance of Na₂FeS₂ (2) and the solid electrolyte interphase (SEI) through the decomposition of electrolytes [35]. Two oxidation peaks are observed at ~ 1.36 and 1.85 V which are ascribed to the formation of Na₂FeS₂ (2) and Na_xFeS₂ (3), respectively [36]. In addition, the peak located at 0.16 V resulted from sodium extraction from pores of the FeS/CNA sample [37]. In the second and third cycles, the cathodic scans show peak at ~ 0.91 V which is ascribed to the intercalation process of Na⁺ and the conversion to Na₂FeS₂ from Na_xFeS₂ [28]. No obvious change in the second and third cycles was observed, indicating excellent stability of the FeS/CNA sample during the Na⁺ de/insertion process. The discharge/charge profiles of FeS/CNA at 2 A g⁻¹ are exhibited in **Fig. 4b**. The original discharge curve showed a plateau at ~0.81 V due to the formation of Na₂FeS₂ and SEI [19]. This discharge profile is in good accordance with that of the CV curve. The initial discharge and charge capacities of FeS/CNA are 532 mA h g⁻¹ and 395 mA h g⁻¹, respectively. Therefore, the initial Coulombic efficiency of FeS/CNA is 74.2% (**Fig. 4b**).

The specific capacity and cycling performance of FeS/CNA at 2 A g^{-1} is displayed in **Fig. 4c**. The FeS/CNA shows a high reversible charge capacity of 385 mA h g^{-1} at 2 A g^{-1} with the capacity retention of 97.4% after 400 cycles. Additionally, the pure CNA electrode shows a reversible capacity of 60 mA h g^{-1} (**Fig. S2**). Compared with other reported iron sulfide-based anode materials (**Table S2**), the sodium storage performance of FeS/CNA displays excellent specific capacity and cycle stability at 2 A g^{-1} . The rate performance is exhibited in **Fig. 4d**. The average charge specific capacities of FeS/CNA are 473, 441, 413, 400, 385, 291, and 221 mA h g^{-1} at current densities of 0.1, 0.2, 0.5, 1, 2, 5, and 10 A g^{-1} , respectively. The current density is set to 0.1 A g^{-1} after 70 cycles, the specific charge capacity is recovered to 470 mA h g^{-1} . The TEM images of the FeS/CNA electrode after 400 cycles of electrochemical tests are shown in **Fig. S3**. The FeS particles after electrochemical studies of the FeS/CNA electrode maintained uniform dispersion characteristics. This means that the structure of the FeS/CNA material is stable. Therefore, the FeS/CNA sample with excellent capacity, long cycle stability, and fine rate capability is a promising candidate for SIB anode material.

The Na^+ storage performance of the FeS/CNA electrode was further characterized by electrochemical impedance spectra (EIS) (**Fig. S4**). The fitting curves well agree with the Nyquist plots, and reveal typical semicircles at high frequencies, which are related to the charge transfer resistance (R_{ct}) of the electrode [38]. The smaller the diameter of the semicircle is, the smaller the R_{ct} . It can be found that the R_{ct} for the first cycle of FeS/CNA is larger than the R_{ct} for the third cycle due

to the transformation of FeS NPs into ultrafine nanocrystals during the Na^+ de/insertion process [39,40]. To further research the rate capabilities and kinetic effects of the FeS/CNA, cyclic voltammetry (CV) tests at different sweep rates (**Fig. S5**) were carried out. With the increase in the scan rates, the peak currents increase, and the anodic peaks move to a high potential, suggesting the excellent rate performance of FeS/CNA [41,42]. The fitted lines are calculated through $\ln(\text{peak current})$ vs. $\ln(\text{sweep rate})$ at different oxidation/reduction states to obtain the b-value (**Fig. S6**). The b-value of FeS/CNA is 0.60, implying that the redox process of FeS/CNA is primarily dominated by pseudocapacitive behaviors [43,44].

As illustrated in **Fig. 5**, the FeS NPs embedded on 3D carbon nanofibers play a key role in their remarkable electrochemical performance for several reasons [45]. (1) The 1D carbon fibers provide abundant paths for ion and electron transmission to increase electronic conductivity [46]. (2) The interconnected 3D CNA networks composed of 1D carbon fibers can offer sufficient void space to alleviate volume expansion and increase cycle stability [47]. (3) The mesopores in the 3D porous nanostructures promote sufficient electrode/electrolyte connection, thereby improving the diffusion kinetics of Na^+ . (4) Compared to pure FeS, the 3D porous nanostructures of FeS/CNA can easily interact with Na^+ in the electrolyte and because of the shortening of the ion diffusion distance, show improved electrochemical performance.

4. Conclusions

In summary, we report a facile approach to fabricate FeS NPs embedded on a 3D CNA network from the Fe-alginate precursor. As a promising SIB anode material, the

FeS/CNA shows outstanding capacity, excellent cycle stability (385 mA h g⁻¹ at 2 A g⁻¹ over 400 cycles), and good rate capability. The outstanding performance is primarily ascribed to the interconnected 3D CNA networks composed of 1D carbon fibers which can provide paths for ion and electron transport, enhance electronic conductivity, offer sufficient void space to alleviate volume expansion, and improve the transport kinetics of Na⁺. This work opens up a new approach to construct TMS@C composites from sustainable biomass, which can promote the development of anode materials for SIBs.

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Scheme and Figure captions

Figure 1. Schematic illustration on the synthesis process of FeS/CNA.

Figure 2. (a) XRD patterns of FeS/CNA. The high resolution XPS spectra of FeS/CNA (b) survey spectrum, (c) Fe 2p and (d) S 2p. (e) Nitrogen ad/de-sorption isotherm of FeS/CNA. (f) Pore size distribution of FeS/CNA.

Figure 3. SEM images of (a, b), TEM images of FeS/CNA (c, d, e), and EDS mapping of FeS/CNA (f).

Figure 4. (a) CV curves of FeS/CNA electrode at a scan rate of 0.1 mV s^{-1} . (b) Galvanostatic charge-discharge curves for FeS/CNA electrode of first three cycles between 0.01 and 3.0 V (vs Na^+/Na) at a current density of 2 A g^{-1} . (c) Cycling performance of FeS/CNA electrode at 2 A g^{-1} . (d) Rate performances of FeS/CNA electrode.

Figure 5. Schematic illustration of FeS NPs embedded on 3D carbon nanofiber and Na^+ de/insertion in FeS with carbon nanofibers.

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Highlights

- Fe-alginate aerogels assure uniform dispersion of FeS NPs on porous carbon matrix.
- 1D carbon fibers as transport channels can constitute porous 3D porous network.
- FeS NPs and 3D network CNAs have a synergistic effect on sodium storage.
- The FeS/CNA electrode reveals an excellent and stable electrochemical performance.