Vapor-pressured induced synthesis of chemically bonded Fe$_{1-x}$S/N-doped carbon composite nanoflakes as high-capacity, ultralong-cycle-life, and high-rate lithium-ion-battery anode

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Abstract

Ascribed to its high reversible capacity, Fe$_{1-x}$S is taken as a promising lithium-ion-battery (LIB) anode material. Regrettably, unsatisfactory electrical conductivity, large volume change, and structural deterioration upon cycling of Fe$_{1-x}$S severely delay its commercial application. Herein, a one-step vapor-pressured induced route is first proposed for synthesizing Fe$_{1-x}$S/N-doped carbon composite nanoflakes (Fe$_{1-x}$S/NC), in which Fe$_{1-x}$S nanoflakes with an average thickness of 30 nm are tightly coated by N-doped carbon layers via chemical bonds of Fe-N-C, by pyrolysis of mixture of iron isooctanoate dissolved into dimethylformamide and thiourea in a sealed vessel. As LIB anode, the Fe$_{1-x}$S/NC exhibits a high reversible capacity of 1106.8 mAh g$^{-1}$ at 0.1 A g$^{-1}$, an ultralong cycling life (722.7 mAh g$^{-1}$ after 1400 cycles with 0.0098% capacity loss per cycle at 1 A g$^{-1}$), and an excellent rate performance (219.8 mAh g$^{-1}$ at 20 A g$^{-1}$). This excellent performances may arise from its structural advantages that the smaller Fe$_{1-x}$S nanoflakes are tightly wrapped into N-doped carbon layers via Fe-N-C bonds, which can increase lithium ion storage sites, electrical conductivity, and structural stability.

1. Introduction

Lithium ion batteries (LIBs) have been widely used in various electronic devices and automobiles due to their unique advantages such as high specific energy, long cycle life, high safety, and environmental protection [1,2]. So far, graphite is still used as main anode material for commercial LIBs. However, its low theoretical capacity (372 mAh g$^{-1}$) limits the development of high-energy-density lithium-ion battery. Therefore, it is crucial to seek an alternative anode material with high capacity for the next generation of lithium-ion batteries to meet the practical application, which need higher energy demand. In recent years, Fe$_{1-x}$S has become a focus of electrode research due to its large theoretical capacity, low cost, and non-toxic property [3-5]. Regrettably, the polysulfide dissolution into the electrolyte and large volume change during cycling lead to poor cycling stability and electrode pulverization, which seriously impedes the commercial application of Fe$_{1-x}$S [6-8]. These impedance has prompted...
researchers to the development of novel and effective measures to enhance the cyclability and suppress volume expansion of Fe$_{1-x}$S, including fabricating Fe$_{1-x}$S nanostructures [9-11] and creating Fe$_{1-x}$S/C composites [12,13]. Especially, the latter has attracted extensive attention because of simple synthesis step and good improvement effect on cycling life. For example, Fe$_{1-x}$S/N,S co-doped carbon composite was synthesized by the high-temperature reaction of a S-containing precursor and a Fe-containing metal-organic framework, which showed a high capacity of 1135 mAh g$^{-1}$ at 0.1 A g$^{-1}$, an excellent cycle stability (707 mAh g$^{-1}$ after 200 cycles at 1 A g$^{-1}$), and a good rate performance (586 mAh g$^{-1}$ at 5 A g$^{-1}$) as LIB anode [14]. A hierarchical Fe$_{1-x}$S-microporous carbon nanocomposite was prepared by growing Fe-containing precursor into microporous carbon following by reacting with S powders at high temperature and exhibited an ultra-high specific capacity (1185 mAh g$^{-1}$ after 200 cycles) and a good rate capability (375 mAh g$^{-1}$ at 8 A g$^{-1}$) [15]. Although the electrochemical performances of Fe$_{1-x}$S-based anode materials are enhanced via the above-mentioned routes to a certain extent, in practical applications, especially at high current density, a longer cycling life with thousands of cycles and a better rate capability are needed [16]. In addition, the preparation process in the above-mentioned routes of Fe$_{1-x}$S/C composites is complex and tedious, which shows that a simple method to prepare Fe$_{1-x}$S/C composites is very important.

In this paper, based on these mentioned problems, a one-step vapor-pressure induced synthesis method for Fe$_{1-x}$S/N-doped carbon composite nanoflakes (Fe$_{1-x}$S/NC), in which Fe$_{1-x}$S nanoflakes with an average thickness of 30 nm are tightly wrapped by N-doped carbon layers via Fe-N-C bonds, are proposed for the first time by pyrolysis of mixture of iron isoctanoate dissolved into dimethylformamide and thiourea in a sealed vessel. The small size of Fe$_{1-x}$S, N doping in the carbon matrix, and the formation of Fe-N-C bonds not only benefit for fast diffusion of Li$^+$, improve the conductivity of the hybrid composites, but also prevent the aggregation and volume expansion of nanoflakes during cycling. As LIB anodes, Fe$_{1-x}$S/NC composite nanoflakes show a great reversible capacity (1106.8 mAh g$^{-1}$ at 0.1 A g$^{-1}$), an outstanding cycle stability (86.3% capacity retention after 1400 cycles at 1 A g$^{-1}$), and an excellent rate capability (219.8 mAh g$^{-1}$ at 20 A g$^{-1}$).

2. Experimental

2.1. Preparation of Fe$_{1-x}$S/NC

In detail, a vessel with a volume of 5 ml, in which iron isoctanoate (1 g, Macklin) dissolved into dimethylformamide (0.5 g, Macklin) and thiourea (0.2 g) were added, was sealed in a Ar-filled glove box and heated at 500 °C for 0.5 h in a tube furnace with a flowing Ar gas (heating ramp: 10 °C min$^{-1}$). At last, the furnace was naturally cooled, and the Fe$_{1-x}$S/NC sample was collected.

2.2. Characterizations

X-ray diffraction (XRD) pattern was used to determine crystalline structures. Thermogravimetric analysis (TGA) was tested in air with a heating rate of 10 °C min$^{-1}$. Scanning electron microscopy (SEM, Hitachi 4800) was used to observe morphology. Transmission electron microscopy (TEM, TECNAI G2 F20) with energy dispersive spectroscopy (EDS) was used to test the microstructures. Raman spectroscopy was performed to test carbon material. X-ray photoelectron spectroscopy (XPS, ESCALAB 250) was operated to investigate the valence structure of elements and surface composite. The electrical conductivity (EC) of sample was tested by a Powder Electrical Resistivity Tester (ST-2722, Suzhou Jingge Electronic Co., Ltd., China).

2.3. Electrochemical measurements

CR2032 type coin half cells composing of working electrode, Celgard 2400 as separator, electrolyte (1 M LiPF$_6$ in a mixture of 1:1:1 volume ratio of ethylene carbonate, ethylene methyl carbonate, and dimethyl carbonate), and lithium foil as a counter electrode were assembled to test lithium ion storage performance of sample in an Ar-filled glove box (amount of O$_2$ and H$_2$O < 0.01 ppm). Coating a slurry containing 80 wt% samples, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride on copper
foil is performed to make working electrodes, which were dried at 120 °C under vacuum overnight. The active mass loading of the electrodes was ~1.2 mg cm⁻². An electrochemical workstation (Land CT 2001A, Wuhan, China) was used to test the cycling and rate performances in a voltage range from 0.01 to 3.0 V (vs. Li⁺/Li) at room temperature. An electrochemical workstation (Chenhua CHI660c, Shanghai, China) was used to measure electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) curves.

3. Results and discussion

Figures 1a-c represent the SEM images of the Fe₁₋ₓS/NC, which show nanoflake structure with an average thickness of 30 nm. The TEM (Figures 1d,e) and high-resolution TEM (HRTEM) images (Figure 1f) show that the carbon layers coat on the surface of Fe₁₋ₓS nanocrystals and a lattice fringe of 0.30 nm contributes from interplanar spacing of (200) crystal plane of Fe₁₋ₓS. Fe, S, C, and N elements are dispersed uniformly in Fe₁₋ₓS/NC composite nanoflakes, confirmed by high angle annular dark field image (HAADF, Figure 1g) and corresponding EDS mapping images (Figures 1h-k), indicating that N-doped carbon layers uniformly coat on the surface of Fe₁₋ₓS nanoflakes.

![Figure 1](image_url)

Figure 1 (a-c) SEM images and (d-f) TEM images, (g-k) HAADF and its corresponding EDS mapping images of Fe₁₋ₓS/NC.

The XRD pattern (Figure 2a) shows all the diffraction peaks can be completely indexed to crystalline Fe₁₋ₓS (JCPDS card no. 29-0726), confirming the formation of Fe₁₋ₓS crystals. The Raman spectrum (Figure 2b) shows typical characteristic peaks of Fe₁₋ₓS at 218.4 and 285.5 cm⁻¹, ascribed to symmetric and asymmetric stretching modes, respectively, and D and G band of carbon material at 1309.6 and 1578.1 cm⁻¹, respectively [17,18]. The I_D/I_G value of 1.06 demonstrates that vast defects exit in the carbon, which is favorable for the enhancement of Li⁺ storage capacity [17]. The XPS survey peak (Figure 2c) exhibits that the contained elements of the Fe₁₋ₓS/NC composites are Fe, N, C and O. The Fe 2p (Figure 2d) shows a peak at 710.9 eV arising from 2p₁/₂ of Fe²⁺, a broad peak centered at 724.4 eV arising from 2p₃/₂ of Fe²⁺ and Fe³⁺, respectively, [18]. A peak appears at 709.4 eV contributed from Fe-N bonds, confirming the presence of Fe-N-C bond [18]. The S 2p spectrum (Figure 2e) involves four peaks: two peaks at 161.5 and 162.5 eV ascribed to S 2p₁/₂, and S 2p₃/₂ of S²⁻,
respectively; two peaks at 163.3 and 164.6 eV attributed to S\textsuperscript{n2-}. The C 1s spectrum (Figure 2f) exhibits three peaks at 284.3 (C-C), 285.8 (C-N), and 288.6 (C=O). The formation of C-N bond demonstrates that N is doped into the carbon. The N 1s (Figure. 2g) displays four peaks at 398.4 (pyridic N), 399.3 (Fe-N), 400.4 (pyrrolic N), and 401.9 eV (graphitic N)\cite{18,19}, further confirming the presence of N-doped C and Fe-N-C bonds. The pyridic and Fe-N-C bonds are highly chemically active sites and can induce vast defects and store more Li\textsuperscript{+} to the improvement of the capacity\cite{17,19}. N-doped C can highly improve the EC of composites. As measured, the value of EC is 7.2x10\textsuperscript{2} S/m. So high value can accelerate Li\textsuperscript{+} transport to obtain excellent rate performances. The presence of chemical bond of Fe-N-C between Fe\textsubscript{1-x}S nanoflakes and C layers suggests that the Fe\textsubscript{1-x}S nanoflakes are tightly coated by the carbon layers, which is conducive to preventing the aggregation and to relieving large volume expansion Fe\textsubscript{1-x}S upon cycling. To calculate the content of Fe\textsubscript{1-x}S in the products, TGA (Figure 2h) was performed in an air atmosphere, during which Fe\textsubscript{1-x}S and C were oxidated into Fe\textsubscript{2}O\textsubscript{3} and CO\textsubscript{2}, respectively. Hence, the weight percentages of Fe\textsubscript{1-x}S and N-doped C are about 82.2\% and 17.8\%, respectively.

Figure 2 (a) XRD pattern, (b) Raman spectrum, (c) XPS survey peak, (d) Fe 2p, (e) S 2p, (f) C 1s, (g) N 1s, and (h) TGA curve of Fe\textsubscript{1-x}S/NC.

Afterwards, the Li\textsuperscript{+} storage performances of Fe\textsubscript{1-x}S/NC are measured in detail. Figure 3a displays the typical CV curves of Fe\textsubscript{1-x}S/NC, during which a broad peak at 0.58 V appears but subsequently disappears in the first cathodic scan, which arises from the formation of solid electrolyte interface (SEI) film\cite{20}. Besides, the CV curves of the 2nd and 3rd cycles overlap well to suggest a good reversibility of the Fe\textsubscript{1-x}S/NC materials. In the following cathodic scan, two peaks at 0.78 and 1.36 V are contributed from the conversion of Fe\textsubscript{1-x}S into Li\textsubscript{2}Fe\textsubscript{1-x}S and Fe. In anodic scans, three peaks at 1.18, 1.98, and 2.34 V are contributed from the formation of Li\textsubscript{2}Fe\textsubscript{1-x}S\textsubscript{2}, the conversion of Li\textsubscript{3}Fe\textsubscript{1-x}S\textsubscript{2} to Li\textsubscript{2}Fe\textsubscript{1-x}S\textsubscript{2}, and the formation of Fe\textsubscript{1-x}S, respectively\cite{18}. The charge/discharge curves (Figure 3b) display similar plateaus with CV curves. Moreover, Fe\textsubscript{1-x}S/NC exhibits lithiation and delithiation capacities of 1457.9 and 1046.8 mAh g\textsuperscript{-1}, respectively, to produce a first coulombic efficiency (CE) of 71.8\%. Such a low value mainly arises from the formation of SEI layer\cite{21}. Figure 3c represents the Nyquist plots at various cycling number, in which the value of charge transfer resistance (R\textsubscript{ct}, the diameter of the depressed semicircle) first increases after the 1st cycle because of the formation of SEI layer, and then gradually decreases, presumably due to activation of electrode material. The decrease of R\textsubscript{ct} is good for enhancing capacity and cycling life. The cycling life are assessed. The Fe\textsubscript{1-x}S/NC delivers a first reversible capacity of 1046.8 mAh g\textsuperscript{-1} with the CE of 71.8\%, and 1106.8 mAh g\textsuperscript{-1} after 500 cycles with a CE of 99.98\% (Figure 3d) at 0.1 A g\textsuperscript{-1}. A high capacity retention of 105.7\% is achieved to fully prove a good cyclability of Fe\textsubscript{1-x}S/NC materials. The increase of capacity may be ascribed to the activation of electrode material. A longer cycling lifetime was obtained at 1 A g\textsuperscript{-1} (Figure 3e). The capacity is 722.7 mAh g\textsuperscript{-1} after 1400 cycles with a CE of 99.1\% and 86.3\% capacity retention. Such low capacity loss per cycle of 0.0098\% further demonstrates the superior stability of
electrode materials on cycling. The rate capability of Fe$_{1-x}$S/NC was tested at 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 A g$^{-1}$ (Figure 3f), which delivered the capacities of 1078.2, 1030.6, 942.1, 828.9, 654.1, 462.8, 341.4, and 219.8 mAh g$^{-1}$, respectively, and the capacity can be back to 1026.2 mAh g$^{-1}$ when the current density returns to 0.1 A g$^{-1}$, testifying superior rate performance. The outstanding Li$^+$ storage performances mainly are attributed to its unique structure, such as smaller particle size of Fe$_{1-x}$S, N-doped carbon coating layers, and formation of interfacial chemical bonds of Fe-N-C.

To clarify ion storage mechanism and specific capacity contribution of the Fe$_{1-x}$S/NC, the electrochemical kinetics and pseudocapacitive contribution were investigated by CV curves at different scanning rates ($v$). The CV (Figure 4a) curves display similar Li$^+$ storage behavior at $v$ of 0.2 to 2 mV s$^{-1}$ to confirm a stable pseudocapacitive behavior. Generally, peak current ($i$) and $v$ is directly related and expressed by the Eq. log$i$ = log$b$ + log$v$. It can be seen that the $b$ is the slope of log$i$-log$v$ plots, which is 1.0 to suggest a capacitive-controlled process and is 0.5 to indicate a diffusion-dominated process. It can be seen that $b$ value is 0.75 and 0.76 for peaks 1 and 2, respectively (Figure 4b), exhibiting that both the diffusion-controlled and pseudocapacitive-controlled process contribute the total capacity. To survey their specific contribution, Eq. $i$ = $k_1$v + $k_2$v$^{0.5}$ is presented, where $i$ composes of pseudocapacitive process ($k_1$v) and diffusion-controlled behaviors ($k_2$v$^{0.5}$). Clearly, the percentage of pseudocapacitive contribution rises gradually from 33.1 to 57.5% with $v$ increasing from 0.2 to 2 mV s$^{-1}$ (Figure 4c), demonstrating high effect of pseudocapacitive contribution on the enhancement of the capacity and rate performances. The high pseudocapacitive contribution mainly arises from additional lithium ion storage sites, such as interfaces and defects [22,23].

Figure 3 (a) CV curves at a scanning rate of 0.1 mV s$^{-1}$, (b) Charge/discharge curves at 0.1 A g$^{-1}$, (c) EIS spectra, (d) cycling curve at 0.1 A g$^{-1}$, (e) cycling curve at 1 A g$^{-1}$, and (f) rate curves of Fe$_{1-x}$S/NC.

Figure 4 (a) CV curves at different $v$, (b) The line relationship of Log($i$) vs Log($v$) at peaks 1 and 2 marked in (a), and (c) The percentages of pseudocapacitive contribution at different $v$ of Fe$_{1-x}$S/NC.
4. Conclusions
In this work, a one-step vapor-pressure induced synthesis route was developed for preparing Fe$_{1-x}$S/NC composite nanoflakes for the first time by pyrolysis of mixture of iron isoctanoate dissolved into dimethylformamide and thiourea in a sealed vessel. The unique structures including small size of 30 nm, N-doping, and Fe-N-C bonds of Fe$_{1-x}$S/NC composite nanoflakes endow the composite with a high pseudocapacitive contribution, a fast Li$^+$ transport rate, and a good structural stability, thus leading to excellent electrochemical performances. As LIB anode, Fe$_{1-x}$S/NC shows a high reversible capacity (1106.8 mAh g$^{-1}$ at 0.1 A g$^{-1}$), an excellent cycling stability (up to 1400 cycles at 1 A g$^{-1}$), and rate capability (219.8 mAh g$^{-1}$ at 20 A g$^{-1}$).

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