Article
Carbon-Coated ZnS-FeS$_2$ Heterostructure as an Anode Material for Lithium-Ion Battery Applications

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Abstract: The construction of carbon-coated heterostructures of bimetallic sulfide is an effective technique to improve the electrochemical activity of anode materials in lithium-ion batteries. In this work, the carbon-coated heterostructured ZnS-FeS$_2$ is prepared by a two-step hydrothermal method. The crystallinity and nature of carbon-coating are confirmed by the investigation of XRD and Raman spectroscopy techniques. The nanoparticle morphology of ZnS and plate-like morphology of FeS$_2$ is established by TEM images. The chemical composition of heterostructure ZnS-FeS$_2$@C is discovered by an XPS study. The CV results have disclosed the charge storage mechanism, which depends on the capacitive and diffusion process. The BET surface area (37.95 m$^2$ g$^{-1}$) and lower R$_{ct}$ value (137 $\Omega$) of ZnS-FeS$_2$@C are beneficial to attain higher lithium-ion storage performance. It delivered a discharge capacity of 821 mAh g$^{-1}$ in the 500th continuous cycle @ A g$^{-1}$, with a coulombic efficiency of around 100%, which is higher than the ZnS-FeS$_2$ heterostructure (512 mAh g$^{-1}$). The proposed strategy can improve the electrochemical performance and stability of lithium-ion batteries, and can be helpful in finding highly effective anode materials for energy storage devices.

Keywords: hydrothermal; carbon coating; heterostructure; lithium-ion battery; ZnS-FeS$_2$@C

1. Introduction

Rechargeable secondary batteries are currently one of the market’s most important energy storage technologies. Particularly, lithium-ion batteries (LIBs) are the most common power sources for portable electronic devices. Most importantly, electrode materials are crucial to the battery technology’s ability to store and convert electrical charge [1]. However, because the most used graphite anode has a low theoretical capacity (372 mAh g$^{-1}$) and poor rate capability, developing a novel anode material with high energy/power density is a hot topic in LIB research [2]. Because of their high capacity, various anode materials such as transition metal oxides [3], metal sulfides [4], and metal/nonmetal have been widely investigated as promising candidate anodes for LIBs to meet the demand for increased energy and power density for LIBs. In recent years, transition metal sulfides (TMS), which have high theoretical capacities and are cheap, have turned out to be one of these alternatives [5]. Because of its high capacity, abundance, and low cost, ZnS is thought to be the most likely candidate to replace graphite as an anode for LIBs. Nanostructured ZnS could be used for energy storage, environmental remediation, photoelectrolysis, and catalysis [6]. Poor structural stability and conductivity have limited ZnS in energy storage applications [7,8]. Much research has gone into improving the structural stability and conductivity of ZnS. Carbonaceous materials are the most stable matrices for ZnS impregnation, which improves ZnS conductivity owing to its porous architecture and structural stability. However, some
factors continue to obstruct the use of ZnS. Another method for stabilizing the structure of ZnS-based electrode materials is to create a heterostructure for lithium-ion batteries [9].

Most interestingly, pyrite FeS$_2$, an abundant mineral with low toxicity in the Earth’s crust, has a theoretical specific capacity of 894 mAh g$^{-1}$ when it undergoes a four-electron electrochemical reaction between 0.01 and 3.0 V (vs. Li$^+$/Li). Sadly, a large volume expansion occurs during the conversion of FeS$_2$ to Fe$^0$ and Li$_2$S during the discharge process, resulting in a severe pulverization issue [10,11]. Consequently, a new solid electrolyte interphase (SEI) film would form on the newly generated nanoparticles’ surface, resulting in a high degree of polarization. In addition, the ground nanoparticles may escape from their original conductive networks and even detach from the anode, resulting in rapid capacity degradation. In addition, low electrical conductivity and slow ionic diffusion kinetic render the FeS$_2$ anode’s rate capability inferior. So, FeS$_2$ anodes need to be changed right away to make them last longer and increase their rate capability [12,13]. Numerous efforts have been made thus far to address the aforementioned issue with the FeS$_2$ anode.

In general, the strategy of combining two different metal sulfide nanoparticles with a carbon-based matrix often delivers features of good structural stability with poor volume expansion and boosted electrical conductivity. The uniformly coated carbon layer on the heterostructure significantly improved the Li-ion storage performances.

On the other hand, it was recently found that a heterostructure multi-component TMS can improve the electrochemical reactions and store more energy [14,15]. Herein, heterostructure nanoarrays have several benefits, including rich electroactive sites for redox reactions, an increased electrode–electrolyte contact area, a short electrolyte diffusion path, and attractive synergistic effects between the heterointerface [16–18]. Additionally, the junction of the heterosystem could generate the built-in electric charge, which definitely enhanced the electrical conductivity and ion transport, which will lead to better lithium-ion storage properties [17,19]. Herein, the carbon-coated ZnS-FeS$_2$ heterostructure is a novel building block for the enhanced electrical conductivity and structural flexibility of long-life lithium-ion battery applications. In this work, two-step hydrothermal methods were used to fabricate the carbon-coated ZnS-FeS$_2$ heterostructure for lithium-ion battery applications. ZnS-FeS$_2$@C has produced an initial discharge capacity of 1481 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$. After 500 cycles, it delivered the specific capacity of 821 mAh g$^{-1}$ in the 500th cycle at a current density of 1 A g$^{-1}$. This method involves merely fabricating the carbon-coated ZnS-FeS$_2$ heterostructure-based bimetallic sulphides for outstanding Li-ion storage applications.

2. Results and Discussion

2.1. Scheme Diagram and Structural Analysis

The schematic diagram in Figure 1 illustrates the various steps of fabrication of carbon-coated hetero-structured ZnS-FeS$_2$@C by a simple hydrothermal method. Firstly, the addition of sodium hydroxide solution to metal ion (Zn$^{2+}$ and Fe$^{2+}$) solution can form the respective metal hydroxides (Zn(OH)$_2$ and Fe(OH)$_2$). The thiourea react with water and ethanol and release S$^{2-}$ ions. Further, the released S$^{2-}$ ions react with Zn(OH)$_2$ and Fe(OH)$_2$ to form corresponding ZnS and FeS$_2$ during the hydrothermal process. The prepared metal sulphide was carbon coated by glucose using the hydrothermal method, which is displayed in Figure 1b. The carbon-coated heterostructure of ZnS-FeS$_2$ was annealed in an argon atmosphere, which improved the crystallinity and completely reduced the unreduced moieties of glucose in the coated-carbon network. This makes the carbon-coated electrode materials more suitable for lithium-ion battery applications. The following reactions take place during the formation of Zn(OH)$_2$, Fe(OH)$_2$, ZnS, and FeS$_2$ [20,21]:

\[
\begin{align*}
Zn^{2+} + 2 (OH)^{-} & \rightarrow Zn(OH)_2 \\
Fe^{2+} + 2 (OH)^{-} & \rightarrow Fe(OH)_2 \\
Zn(OH)_2 + Fe(OH)_2 + 3 S^{2-} & \rightarrow ZnS + FeS_2 + 2H_2O + O_2 (↑)
\end{align*}
\]
\[ \text{ZnS-FeS}_2 \]

**Figure 1.** Schematic representation for the (a) synthesis of ZnS-FeS\(_2\) and (b) carbon coating of ZnS-FeS\(_2\) by the hydrothermal method.

Figure 2a displays the obtained XRD pattern of ZnS, FeS\(_2\), ZnS-FeS\(_2\), and ZnS-FeS\(_2\)@C. The obtained XRD patterns have clearly exposed electrode material’s crystallinity and phase purity. The obtained XRD patterns have clearly exposed electrode material’s crystallinity and phase purity. The obtained XRD patterns have clearly exposed electrode material’s crystallinity and phase purity. As shown in Figure 2a, pyrite FeS\(_2\) shows diffraction peaks at 28.7, 33.2, 37.3, 40.8, 47.4, 56.2, 59.2, 61.8, 64.3, 76.6, and 78.9°, which correspond to the (111), (200), (211), (220), (311), (222), (321), (331), and (420) planes of the cubic crystal system (42-1340) [10,22]. The obtained XRD patterns have clearly exposed electrode material’s crystallinity and phase purity. The obtained XRD patterns have clearly exposed electrode material’s crystallinity and phase purity. The obtained XRD patterns have clearly exposed electrode material’s crystallinity and phase purity.

The carbon-coated ZnS-FeS\(_2\) has strong diffraction peaks, which exposed a crystalline nature. The average crystallite size of the electrode materials was calculated by the Scherrer formula. The sizes of ZnS, FeS\(_2\), ZnS-FeS\(_2\), and ZnS-FeS\(_2\)@C were 28.5 nm, 47.92 nm, 25.74 nm, and 28.90 nm, respectively. No more impurity peaks were observed in the electrode materials, revealing the phase purity of the products. Figure 2b shows the Raman spectra of ZnS-FeS\(_2\) and ZnS-FeS\(_2\)@C. As can be seen, ZnS-FeS\(_2\)@C shows the two peaks at 1322 cm\(^{-1}\) and 1590.6 cm\(^{-1}\) corresponding to the D band and G bands, respectively. The intensity ratio of the D and G band is 1.03 for carbon coated heterostructure of ZnS-FeS\(_2\). This suggests that carbon coating exists in the partially graphitic and disordered carbon network. Further, it may be beneficial to the improvement in conductivity of heterostructure ZnS-FeS\(_2\) nanomaterials [8]. Moreover, the surface area and pore structure are a valuable parameter to determine the electrochemical kinetics of electrode materials. The N\(_2\) absorption/desorption quantities of carbon-coated ZnS-FeS\(_2\) heterostructure is higher than ZnS, FeS\(_2\), and ZnS-FeS\(_2\), which is shown in Figure 2c. The BET surface area value of ZnS-FeS\(_2\)@C is 37.95 m\(^2\)g\(^{-1}\), which is higher than ZnS-FeS\(_2\) (29.20 m\(^2\)g\(^{-1}\)), ZnS (4.55 m\(^2\)g\(^{-1}\)), and FeS\(_2\) (3.23 m\(^2\)g\(^{-1}\)). The surface area of heterostructure is significantly enhanced by carbon coating using glucose. Additionally, in Figure 2d, the pore size of ZnS, FeS\(_2\), ZnS-FeS\(_2\), and ZnS-FeS\(_2\)@C is 1.43 nm, 1.42 nm, 0.87 nm, and 0.87 nm, respectively. The nano porous nature and high surface area of electrode materials are beneficial for the better electrochemical activities in lithium-ion batteries [8,23].

XPS measurements are carried out to understand the elements and their chemical states of electrode materials. As shown in Figure S1, the survey spectrum contained the Zn, Fe, S, and C elements in ZnS-FeS\(_2\)@C. The high-resolution spectrum of Zn 2p (Figure 3a) had two predominant peaks at 1021.04 eV and 1044.2 eV, corresponding to Zn 2p\(_{3/2}\) and Zn 2p\(_{1/2}\), respectively. This represents the zinc that exists in +2 state in ZnS-FeS\(_2\)@C [24–26]. As for the Fe 2p spectrum in Figure 3b, it has two major peaks around 710 eV and 725 eV, corresponding to Fe\(_{2}\) satellite peaks. The deconvoluted peaks of Fe 2p spectrum at 710.5 eV, 723.7 eV, and 713.8 eV, 726.5 eV are attributed to the Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\) orbitals, which correspond to Fe\(^{2+}/^{3+}\) states [10,12,27]. Figure 2c displays the carbon 1s spectrum, which holds the three deconvolution binding energies at 284.5 eV, 285.4 eV, and 288.8 eV,
designated to C-C&=C, C-O/C-S, and C=O/O-C=O, respectively [10,27,28]. However, the binding energies at 161.3 eV and 163.4 eV were attributed to the S 2p$_{3/2}$ and S 2p$_{1/2}$ orbitals with $S^{2-}$ state, respectively. The peak at 168.12 eV in S2p spectrum (Figure 2d) revealed the surface oxidation of electrode materials [28,29]. These results suggest that the existence of a carbon layer in the heterostructure of ZnS-FeS$_2$ may be helpful to enhance the structural flexibility with a good conductive carbon network system. It may long establish the electrochemical activities in lithium-ion storage applications.

Figure 2. (a) XRD pattern; (b) Raman spectra of ZnS, FeS$_2$, ZnS-FeS$_2$, and ZnS-FeS$_2$@C; (c) N$_2$ adsorption/desorption isotherm plot; and (d) pore size distributions of ZnS, FeS$_2$, ZnS-FeS$_2$, and ZnS-FeS$_2$@C.

2.2. Morphological Analysis

The surface morphology of ZnS, FeS$_2$, ZnS-FeS$_2$, and ZnS-FeS$_2$@C was investigated by SEM, with images displayed in Figures 4, S2 and S3. Figure S2a–c shows the nanoparticle morphology of ZnS powder sample. The EDS mapping exposed the uniform distribution of zinc and sulphur elements in Figure S2d,e. The elemental map sum spectrum reveals the
The SAED pattern of FeS2@C revealed an average particle size of 22 nm and 25 nm, confirming the crystalline nature of ZnS and FeS2 phases. The high-resolution imaging confirmed FeS2 in the plate-like structure, but ZnS in the uniform nanoparticle structure. The high-resolution images contain two different lattice fringes, which are associated with ZnS and FeS2 phases. The SAED pattern of ZnS-FeS2 has clear diffraction spots, which confirm the crystalline nature of ZnS-FeS2. Figure S4g–i images were exposed the consistent distribution of Fe, Zn, and S elements.

Moreover, carbon-coated heterostructure ZnS-FeS2 exhibits the same agglomerated nanoparticle morphology for the prepared powder sample in Figure 4a.b, which exposed that the heterostructured ZnS-FeS2 nanoparticles are coated with a thin layer carbon by the hydrothermal method. The hydrothermally carbon-coated layer is annealed to improve the crystallinity of the final composition. The high magnification image at 5 nm (Figure 4e) comprise different kinds of lattice fringes, which associated with 0.305 nm and 0.263 nm d spacing, corresponding to (0120) and (1037) planes of ZnS, and 0.314 nm d spacing, corresponding to the (111) plane of FeS2 nanoparticles. The selected area electron diffraction image in Figure 4f demonstrates a clear diffraction pattern, which further agrees with the crystalline nature of ZnS-FeS2@C. The uniform distribution C, Zn, Fe, and S elements in ZnS-FeS2@C is confirmed by elemental mapping images in Figure 4g–j. More specifically, the TEM results of ZnS-FeS2 and ZnS-FeS2@C revealed an average particle size of 22 nm and 25 nm, respectively. These results are in good agreement with the calculated average grain size.
of electrode materials obtained from the XRD results. However, this study reveals the presence of carbon-coated heterostructured nanoparticles, which is beneficial for a higher amount of lithium-ion intercalation/de-intercalation rate with improved structural stability.

Figure 4. (a,b) FE-SEM images and HRTEM images with (c) low magnification, (d,e) high magnification, (f) SAED pattern, and (g–j) EDS mapping images of ZnS-FeS$_2$@C.

2.3. Electrochemical Analysis

In order to strengthen the structural features of the carbon-coated ZnS-FeS$_2$ heterostructure by galvanostatic charge/discharge studies, cyclic voltammetry study and electrochemical impedance spectroscopy were studied. The above-mentioned studies were carried out by assembled 2032 half cells. Figure 5a displays the initial galvanostatic charge/discharge cycles of ZnS nanoparticles. It delivered the first cycle discharge/charge capacity of 773/424 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$, with a coulombic efficiency of 55%. The subsequent cycle curve shape was more intact with each other, which increased to a coulombic efficiency of 94% in the fifth cycle, with a specific capacity of 344 mAh g$^{-1}$. Figure 5b displays the discharge/charge curve of FeS$_2$, which delivered the specific capacity
of 687/469 mAh g\(^{-1}\) at a current density of 0.1 A g\(^{-1}\). The initial coulombic efficiency of FeS\(_2\) was 68\% in the continuous cycle, it was increased to reach the maximum (96.3\% in the fifth cycle). Figure 5c,d shows the charge/discharge plot of heterostructure ZnS-FeS\(_2\) and ZnS-FeS\(_2\)@C at a current density of 0.1 A g\(^{-1}\). The charge/discharge capacities of the first cycle were 579/839 mAh g\(^{-1}\) and 1039/1481 mAh g\(^{-1}\) for heterostructure ZnS-FeS\(_2\) and ZnS-FeS\(_2\)@C, respectively, with the corresponding coulombic efficiency of 69 and 70\%, respectively. The capacity loss in the very first cycle corresponds to solid electrolyte interphase film formation [22,30]. The subsequent cycle plot was overlapped, which represents the good lithium-ion insertion/extraction behaviour of ZnS-FeS\(_2\)@C.

The rate capability of ZnS, FeS\(_2\), ZnS-FeS\(_2\), and ZnS-FeS\(_2\)@C was measured at various current densities, as shown in Figure 5e. The ten continuous cycles were performed at every current density to estimate the average specific capacity of ZnS-FeS\(_2\)@C, which was 921, 700, 540, 447, and 382 mAh g\(^{-1}\) at current densities of 0.1, 0.2, 0.5, 1, and 2 A g\(^{-1}\), respectively. Again, the current density was switched to 0.1 A g\(^{-1}\), and it delivered the specific capacity of 811 mAh g\(^{-1}\). Additionally, the ZnS, FeS\(_2\), and heterostructure ZnS-FeS\(_2\) achieved a discharge capacity of 329/129.4 mAh g\(^{-1}\), 443/254 mAh g\(^{-1}\), and 650/328 mAh g\(^{-1}\), respectively, at a current density of 0.1/2 A g\(^{-1}\). Moreover, the rate capability plot expressed an improved specific capacity when the current density reaches 0.1 A g\(^{-1}\). The reactivation of electrode materials leads to an attained maximum specific capacity.

Further, Figure 5f displays the long-term cycle stability of the electrode materials at a current density of 1 A g\(^{-1}\). The ZnS nanoparticle has shown the 1st and 500th cycle discharge capacity of 241 and 68 mAh g\(^{-1}\), respectively. This plot conveyed that ZnS has a decreasing trend of discharge capacity, caused by the poor electrical conductivity of ZnS. The pristine plate like FeS\(_2\) shows a discharge capacity of 429 mAh g\(^{-1}\) in the 500th cycle. This plot has revealed the increasing specific capacity of FeS\(_2\) from the 100th cycle, achieved by a high amount of reactivation of electrode materials. The heterostructured ZnS-FeS\(_2\) delivered a specific capacity of 512 mAh g\(^{-1}\) in the 500th cycle. Additionally, this cyclic stability plot of ZnS-FeS\(_2\) has revealed the flatly increasing trend compared with

Figure 5. Charge–discharge voltage profiles of (a) ZnS, (b) FeS\(_2\), (c) ZnS-FeS\(_2\), and (d) ZnS-FeS\(_2\)@C, as well as (e) rate capability study of all the electrode materials and (f) cyclic performance of ZnS, FeS\(_2\), ZnS-FeS\(_2\), and ZnS-FeS\(_2\)@C at a current density of 1 A g\(^{-1}\) over 500 cycles.
pristine FeS$_2$. Finally, the carbon-coated heterostructured ZnS-FeS$_2$ nanoparticles delivered a specific capacity of 567 mAh g$^{-1}$ in first cycle, which was increased to 821 mAh g$^{-1}$ in 500th continuous cycle, with a coulombic efficiency of around 100%. The cyclic graph of ZnS-FeS$_2$@C was depicted the initial cycles it was decreasing capacity which corresponds to the formation of a stable SEI film and activation electrode materials. From the 50 to 250th cycle, the specific capacity was well improved to reach a maximum; after the 250th cycle, it underwent stabilization up to the 435th cycle. After the 435th cycle, it underwent the capacity fading; finally, it reached a specific capacity of 821 mAh g$^{-1}$ in the 500th cycle. The hydrothermal carbon coating of the heterostructure definitely improved the electrical conductivity and prevented the pulverization of electrode materials, leading to good structural flexibility. The reactivation of electrode materials was a commonly noted behaviour in metal-based nanomaterials and carbon-based materials [31,32]. The obtained specific capacity value was compared with reported ZnS- and FeS$_2$-based anode materials in LIB applications, which are given in Table 1.

| Materials                  | Reversible Capacity—(mAh g$^{-1}$) | Current Density—(A g$^{-1}$) | Cycles | Reference |
|----------------------------|-----------------------------------|-------------------------------|--------|-----------|
| ZnS-FeS$_2$@C              | 821                               | 1                             | 500    | This work |
| FeS$_2$/SG                 | 400.1                             | 1                             | 400    | [11]      |
| rGO@FeS$_2$@C              | 820.7                             | 1                             | 300    | [12]      |
| FeS$_2$@NSC/SG             | 392                               | 2.5                           | 400    | [22]      |
| Ni doped Co$_x$S$_y$@ZnS   | 758                               | 1                             | 500    | [26]      |
| FeS$_2$@N/S-C              | 528                               | 1                             | 1000   | [27]      |
| ZnS@NSC-800                | 571.4                             | 1                             | 1000   | [28]      |
| CoxZn$_{1-x}$S$_x$/Co$_y$S$_y$@rGO | 786                         | 1                             | 1000   | [29]      |
| ZnO/ZnS@N-C/CNT            | 386.6                             | 1                             | 400    | [33]      |
| Co$_x$S$_y$/ZnS@NC         | 411.2                             | 1                             | 300    | [34]      |
| FeS$_2$@CNT                | 750                               | 1                             | 200    | [35]      |

Further, the electrochemical activity of the electrode materials was evaluated in 2032 coin-type half cells. The CV of all of the electrode materials was conducted between 0.01 and 3.0 V versus Li$^+$/Li at various scan rates from 0.2 to 1.2 mV s$^{-1}$. As shown in Figure S5a, at the very first cathodic scan of ZnS, 0.25, 0.55, 0.67, and 1.36 V correspond to the decomposition of ZnS and formation of Li$_2$S, LiZn alloy, and SEI film, respectively. The anodic scan of ZnS shows the peak current at 0.76 and 0.35 V, which were associated with the decomposition of Li$_2$S, LiZn alloy, and ZnS formation [36–38].

\[
\text{ZnS} + 2\text{Li}^+ + 2e^- \rightarrow \text{Zn} + \text{Li}_2\text{S} \quad (4)
\]

\[
\text{Zn} + \text{Li}^+ + e^- \rightarrow \text{LiZn} \quad (5)
\]

The above redox reactions occurred in the continuous scans, corresponding to the multistep alloying/dealloying process of lithium-zinc alloys [39]. In Figure S6a, the CV curve of plate-like FeS$_2$ is displayed, and the cathodic scan of the FeS$_2$ contained peak current at 1.95 V corresponds to the decomposition of FeS$_2$ and formation of Li$_2$S and Fe. The oxidation peak current at 0.91 and 1.34 V corresponds to conversion of Fe to FeS$_2$. The electrochemical reactions are described below in Equations (4) and (5) [12,22,27].

\[
\text{FeS}_2 + 2\text{Li}^+ + 2e^- \rightarrow \text{Zn} + \text{Li}_2\text{FeS}_2 \quad (6)
\]

\[
\text{Li}_2\text{FeS}_2 + 2\text{Li}^+ + 2e^- \rightarrow \text{Fe} + \text{Li}_2\text{S} \quad (7)
\]

Furthermore, the heterostructured ZnS-FeS$_2$ in Figure S7a has a strong reduction/oxidation peak at 1.58/0.82 V, corresponding to the decomposition of ZnS and FeS$_2$ as well as formation of Li$_2$S and their reverse reactions. The carbon-coated ZnS-FeS$_2$ has smothered

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Table 1. Comparison of Li-ion battery performance of ZnS-FeS$_2$@C with other reports.
redox peaks in Figure 6a, and the subsequent cycles at different scan rates also have an identical shape. This represents the good reversibility of ZnS-FeS$_2$@C electrode material. Additionally, the dependence of charge storage mechanism was evaluated by power law [40]:

$$i = a v^b$$

where $i$ is the peak current, $v$ is the scan rate (mV s$^{-1}$), and $a$ and $b$ are constant parameters. A $b$ value close 1 indicates that the capacitive behaviour is dominant, while a $b$ value close to 0.5 represents that the charge storage depends on the diffusion process. Figure S5b displays that the $b$ values of anodic peak 1 to 3 and cathodic peak 1 to 2 are 0.63, 0.66, 0.83, 0.68, and 0.79, respectively, representing that the charge storage mechanism majorly depends on the combined process. The $b$ value of FeS$_2$ in Figure S6b indicates that the charge storage mechanism corresponds to a diffusion-controlled process. The heterostructured ZnS-FeS$_2$ has a $b$ value of 0.72/0.87, attributed to the combined charge/discharge mechanism in Figure S7b. Here, Figure 6b displays that the $b$ value of the anodic and cathodic peak is 0.5/0.69, which characteristics the combined charge storage mechanism. In addition, the exact contribution of the current response was predicted by the following equation:

$$i = k_1 v + k_2 v^{0.5}$$

where $k_1$ and $k_2$ are parameters and $k_1 v$ and $k_2 v^{0.5}$ are assigned to capacitive and diffusion-controlled contribution, respectively. Figures S5c,d, S6c,d and S7c,d display the charge contributions of ZnS, FeS$_2$, and ZnS-FeS$_2$ at various scan rates, respectively. When increasing the scan rate from 0.2 to 1.6 V, the capacitive contributions also increase. Figure 6c reveals that the carbon-coated heterostructured ZnS-FeS$_2$ have 57% of the diffusion process in the total capacity at a scan rate of 1.2 mV s$^{-1}$. Figure 6d reveals that the capacitive behaviour increased from 17 to 51%, with a corresponding scan rate of 0.2 to 1.6 mV s$^{-1}$. The combined charge storage mechanism of ZnS-FeS$_2$@C composition has revealed excellent cycle stability, which agrees with the good cycle stability nature of the carbon-coated ZnS-FeS$_2$ heterostructure.

To further investigate the electrochemical performance of the electrode materials at room temperature, an EIS study was conducted. As depicted in Figure 6f, the Nyquist plot was comprised of a semicircle in the high frequency region attributed to the charge transfer resistance ($R_{ct}$), where the y-axis intercept in the x-axis represents the solution resistance ($R_s$) and tilted line at a low frequency corresponds to the Warburg impedance ($\sigma$). The fitted equivalent circuit of the Nyquist plot is shown in Figure S8 and the fitted parameters are described below. The solution resistance of the carbon-coated heterostructure is 1.12 $\Omega$, which lower than heterostructured ZnS-FeS$_2$ (1.2 $\Omega$). The charge transfer resistance of ZnS-FeS$_2$@C is 137 $\Omega$, which is lower than that of other electrode materials. The lower charge transfer resistance of ZnS-FeS$_2$@C is beneficial to the high amount of lithium-ion or electron transport between the anode and cathode. It leads to an excellent performance in lithium-ion battery applications. As shown in Figure 6f, the Warburg factor ($\sigma$) value of ZnS, FeS$_2$, ZnS-FeS$_2$, and ZnS-FeS$_2$@C is 154.7, 251, 145.6, and 132.3, respectively. A lower Warburg factor value indicates better ionic conductivity of ZnS-FeS$_2$@C. The lower $R_s$, $R_{ct}$, and $\sigma$ values of ZnS-FeS$_2$@C have endorsed the obtained good rate capability and cyclic stability behaviour [41].

On the basis of the preceding analysis, the significantly enhanced electrochemical performance is primarily attributable to the amplified conductivity, enhanced $e^-$/Li$^+$ transfer efficiency, and retarded volume expansion during the electrochemical process, which is closely related to the structural advantages of the carbon-coated heterostructured ZnS-FeS$_2$ and can be assumed to be due to the following aspects: (1) the presence of nano-structured materials can shorten the ion diffusion path length, (2) the synergistic effect between the heterostructure interface, (3) the carbon coating can improve the electrical conductivity and structural stability of ZnS-FeS$_2$, (4) the combined charge storage mechanism is helpful for long cyclic performance, and (5) the lower charge transfer and ionic diffusion resistance
may lead to an excellent rate capability and improve the capacity of the electrode materials. The as-prepared carbon-coated ZnS-FeS₂ heterostructure anode materials exhibit excellent electrochemical performance in higher lithium-ion storage applications owing to the above-mentioned factors.

Figure 6. (a) CV curves of the ZnS-FeS₂@C electrode at different scan rates from 0.2 to 1.6 mV s⁻¹. (b) Linear fitting of log (peak current) versus log (scan rate) plot of ZnS-FeS₂@C. (c) Capacitive and diffusion contribution of ZnS-FeS₂@C electrode @ 1.2 mV s⁻¹. (d) Percentage of capacitive and diffusion contribution ratio of ZnS-FeS₂@C electrode at different rates. (e) Nyquist plot of ZnS, FeS₂, ZnS-FeS₂, and ZnS-FeS₂@C. (f) Straight line fitting of Z' versus ω⁻¹/₂.

3. Methods and Materials

3.1. Chemicals

Zinc nitrate hexahydrate (Zn(NO₃)₂ 6H₂O), iron nitrate nonahydrate (Fe(NO₃)₃ 9H₂O), sodium hydroxide (NaOH), thiourea ((NH₂)₂CS), ethanol (C₂H₅OH), sulphur powder (S) was purchase from Sigma Aldrich (Seoul, Korea) and Millipore water was used in this work. The chemical used these experiments without further purification.

3.2. Synthesis of ZnS, FeS₂, and ZnS-FeS₂ Heterostructure

In a typical synthesis of ZnS-FeS₂, 0.744 g Zn(NO₃)₂ 6H₂O and 1.01 g of Fe(NO₃)₃ 9H₂O were dissolved in 40 mL of ethanol. Then, 2.0 g of NaOH in 40 mL water was added to the above metal ion solution dropwise. After the complete addition of NaOH, it was continuously stirred for an hour. To the above mixture, 0.762 g of thiourea was added and continuously stirred for an hour. After that, it was transferred into a 120 mL Teflon-lined stainless-steel autoclave. It was kept in an oven at 180 °C for 12 h. The final products were centrifuged and washed with water and ethanol to remove impurities. The hydrothermally prepared ZnS-FeS₂ was annealed at 600 °C for 2 h in the Ar atmosphere. The bare ZnS and FeS₂ were synthesized using the same procedure using corresponding precursors of 1.487 g Zn(NO₃)₂ 6H₂O and 2.02 g of Fe(NO₃)₃ 9H₂O, respectively.

3.3. Carbon Coating of ZnS-FeS₂

Here, 200 mg of ZnS-FeS₂ was dispersed in 40 mL water. Then, 400 mg of glucose in 40 mL water was added dropwise and continuously stirred for an hour. It was transferred
to 120 mL of Teflon-lined stainless-steel autoclave and kept in an oven at 180 °C for 24 h. The final product of carbon-coated ZnS-FeS$_2$ was collected by centrifuge process, and it was washed with ethanol and water several times. It was annealed at 600 °C for 2 h in an Ar atmosphere. Further, it was used for the analysis.

3.4. Material Characterizations

The crystal structure and phase purity of ZnS, FeS$_2$, ZnS-FeS$_2$, and ZnS-FeS$_2$@C were investigated by X-ray diffraction analysis using PANalytical instrument with Cu Kα radiation. Raman spectra of ZnS-FeS$_2$ and ZnS-FeS$_2$@C were recorded using Renishaw Inc. (Wotton-under-Edge, UK), Raman instrument. N$_2$ adsorption/desorption isotherm spectrum was recorded using nano POROSITY-HQ Mirae Instruments (Seoul, Korea). The chemical state of elements in the final composition was examined by X-ray photoelectron spectroscopy equipped with Al Kα radiation (Thermo Scientific Inc., Waltham, MA, USA). The surface morphology of the materials is noted by FE-SEM (SU08010) Tokyo, Japan and HR-TEM system equipped with an energy-dispersive X-ray spectroscopy system operated at an accelerating voltage of 200 kV (JEM-ARM200F). Electrodes are made up using a 70:10:20 ratio of active material, sodium carboxy methyl cellulose, and super P with 1 mL of water as solvent. The slurry was coated on the surface of copper foil, which is dried in a vacuum oven overnight. The Li-ion storage capability was investigated by an assembled 2032-type coin cell. It was fabricated in an Ar-filled glove box using Li metal and polypropylene as counter/reference electrodes and a separator with 1.2 M LiPF$_6$ in ethylene carbonate and dimethyl carbonate with 3 wt% of vinyl carbonate as an electrolyte additive. Cyclic voltammetry was carried out with a potential window of 0.01 to 3.0 V using different scan rates 0.2 to 1.2 mVs$^{-1}$. Electrochemical impedance spectroscopy was analysed using the frequency range from 0.1 kHz to 100 mHz with an applied amplitude of 5 mVs$^{-1}$ in biologic instrument. Cycle stability and rate capability of (lithium-ion storage and conversion) were measured using a WonAtech battery tester (WBCS3000S WonAtech Co., Seoul, Korea).

4. Conclusions

In conclusion, a facile composition of the ZnS-FeS$_2$@C heterostructure is prepared by the hydrothermal method for high-performance LIB anode materials. The crystalline carbon-coated ZnS-FeS$_2$ heterostructure has a high surface area of 37.95 m$^2$g$^{-1}$, which is higher than that of the heterostructured ZnS-FeS$_2$. The nanoparticle morphology of ZnS and the plate-like morphology of FeS$_2$ have their own advantages of higher hetero interface as well as shorter ion diffusion paths. During the charge–discharge process, ZnS-FeS$_2$@C has followed both capacitive and diffusion mechanisms, which leads to good rate capability behaviour. These features have definitely improved the Li-ion storage-ability, in terms of the ZnS-FeS$_2$@C, which delivered an initial discharge capacity of 1481 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$. Additionally, ZnS-FeS$_2$@C nanoparticles delivered a specific capacity of 567 mAh g$^{-1}$ in the first cycle, which is increased to 821 mAh g$^{-1}$ in the 500th cycle at a current density of 1 A g$^{-1}$. Overall, this work offers more insights that novel heterostructures will have broad application prospects in lithium-ion storage applications.

Supplementary Materials: The supporting information can be downloaded at: https://www.mdpi.com/1422-0067/23/22/13945/s1.

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