One-step vapor-pressured induced synthesis of spherical-like $\text{Co}_9\text{S}_8/\text{N,S}$ -codoped carbon nanocomposites with superior rate capability as lithium-ion-battery anode

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Abstract. As high theoretical capacity and excellent electrical conductivity, Co_9S_8 as a promising electrode material in lithium-ion batteries (LIBs) has attracted wide attention. In the present work, a simple vapor-pressured induced route is developed for fabricating spherical-like $\text{Co}_9\text{S}_8/\text{N,S}$ -codoped carbon nanocomposites ($\text{Co}_9\text{S}_8/\text{NSC}$), in which Co_9S_8 nanoparticles with an average size of 100 nm are encapsulated into N, S-codoped carbon matrix, by pyrolysis of mixture of cobalt isooctanoate dissolved into dimethylformamide and thiourea in a sealed vessel for the first time. As anode for LIBs, the $\text{Co}_9\text{S}_8/\text{NSC}$ shows an excellent reversible capacity, a superior rate performance, and a long cycling stability. For example, a high capacity of $975.3 \text{ mA h g}^{-1}$ can be achieved after 100 cycles at 0.1 A g^{-1} . When cycled at 1 A g^{-1} , it also maintains a high specific capacity of $791.5 \text{ mA h g}^{-1}$ after 1000 cycles. Besides, it also shows a superior rate performance (329.8 mAh g^{-1} at 20 A g^{-1}). Such superior performances may arise from its structural advantages that the smaller Co_9S_8 nanoparticles encapsulated into N, S-codoped carbon could enhance active sites, electrical conductivity, and structural stability.

1 Introduction

Lithium-ion batteries (LIBs) have high specific energy, long cycle life, and good safe, which have been used in electronic devices and vehicles. [1,2] So far, graphite is still used as commercial anode materials for LIBs. However, its low theoretical capacity (372 mAh g^{-1}) restricts the development of next-generation LIBs with a higher energy density. Currently, cobalt sulfides with various stoichiometric compositions, such as CoS_2 , CoS , and Co_9S_8 are considered as promising candidates for lithium ion storage due to high theoretical capacity. [3] However, cobalt sulfides face with two serious problems including large volume changes and polysulfide dissolution in the electrolyte, thus resulting in structural pulverization and continuous specific capacity fading. [4-7] Until now, several strategies including nanostructure engineering, and hybridization, etc have been developed to solve these issues. Nanostructured cobalt sulfides not only can reduce Li^+ ion diffusion distance, but also can provide extra volume for alleviating the strain during cycling, while composition of cobalt sulfides with conductive carbon materials has also been regarded as an efficient route. In fact, carbon coating layers have been confirmed to increase the electronic conductivity (EC) and trapping/adsorption of polysulfides, and thus further enhancing cycling stability. For example, a $\text{MWCNT@a-C@Co}_9\text{S}_8$ materials

exhibited a high specific capacity of 662 mAh g^{-1} at 1.0 A g^{-1} after 120 cycles. [8] A $\text{Co}_9\text{S}_8/\text{C}/\text{CNT}$ nanocomposite obtained by dispersing Co_9S_8 nanoparticles into porous C/CNT micro/nano spheres via spray-drying delivers a capacity of 546 mAh g^{-1} at 0.2 A g^{-1} after 100 cycles. [9] Besides, a $\text{Co}_9\text{S}_8/\text{C}$ nanocomposite synthesized by carbonizing metal coordination polymers and in-situ sulfurization shows a capacity of 606 mAh^{-1} at 1 C after 300 cycles. [10] From these results, the electrochemical performances of Co_9S_8 has been improved by the structural design, but more superior rate and cycling performances are required in commercial application.

In the present work, based on the above-mentioned problems, a simple vapor-pressured induced synthesis route is developed for fabricating spherical-like $\text{Co}_9\text{S}_8/\text{N,S}$ -codoped carbon nanocomposites ($\text{Co}_9\text{S}_8/\text{NSC}$) for the first time by pyrolysis of mixture of cobalt isooctanoate dissolved into dimethylformamide and thiourea. As a result, the formed Co_9S_8 nanoparticles with an average size of 100 nm are coated homogeneously by the NSC. Due to small size and the NSC, this composite not only facilitates the diffusion of Li^+ and increases EC, but also prevents aggregation and volume expansion of Co_9S_8 upon cycling. As LIB anode, this material delivers a high reversible capacity (980.4 mAh g^{-1} at 0.1 A g^{-1}), an outstanding cycling stability (up to 1000 cycles at 1 A g^{-1}

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¹), and a superior rate performance (329.8 mAh g⁻¹ at 20 A g⁻¹).

2 Experimental

2.1. Preparation of Co₉S₈/NSC

Typically, cobalt isooctanoate (1 g, Macklin) dissolved into dimethylformamide (0.5 g, Macklin), and thiourea (0.2 g, Macklin) were added in a vessel with a volume of 5 ml, then sealed in a Ar-filled glove box. The vessel was heated at 500 °C for 0.5 h in a tube furnace under a Ar atmosphere (heating rate: 10 °C min⁻¹). Finally, the furnace was cooled to obtain Co₉S₈/NC powder.

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 morphologies. 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.

2.3. Electrochemical measurements

CR2032 type coin half cells were composed of working electrode, Celgard 2325 as separator, electrolyte (1 M LiPF₆ 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. Furthermore, the cells were assembled to test lithium ion storage performance of samples in Ar-filled glove box (amount of O₂ and H₂O < 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 1.5 mg cm⁻². An electrochemical workstation (Land CT 2001A, Wuhan, China) is used to test the cycling curves and rate performances in a voltage range from 0.01 V to 3.0 V (vs. Li⁺/Li) at room temperature. An electrochemical workstation (Chenhua CHI660c, Shanghai, China) is used to measure electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CV) curves.

3 Results and discussion

Figures 1a, b displays the SEM image of the Co₉S₈/NSC, and it can be found that the Co₉S₈ nanoparticles aggregate into spherical-like morphology. The TEM (Figures 1c, d) and high-resolution TEM (HRTEM) images (Figures 1e, f) show that the Co₉S₈ nanoparticles

with a size of around 100 nm were encapsulated into the carbon layers. The lattice fringe of 0.29 nm can be attributed to the interplanar spacing of the (311) plane for crystalline Co₉S₈.

Figure 2a shows that all the identified peaks can be uniquely indexed to a cubic phase of Co₉S₈ (JCPDS card no. 19-0364). The Raman spectrum (Figure 2b) shows two characteristic peaks are located at 1323.2 and 1565.6 cm⁻¹ assigned to the D and G band of carbon material, respectively. The I_D/I_G value is about 1.1, indicating vast defects exist in the carbon, which is beneficial for lithium ion storage.

Figure 2c shows the XPS survey spectrum, which shows that the main elements of the Co₉S₈/NSC composites are Co, S, N, C and O. The Co 2p (Figure 2d) shows the peaks at 778.2 and 793.2 eV attributed to the 2p_{3/2} and 2p_{1/2} of Co³⁺, respectively. Besides, the peaks at 781.2 and 797.3 eV are attributed to 2p_{3/2} and 2p_{1/2} of Co²⁺ respectively. The peaks at 785.8 and 803.1 eV are attributed to the shake-up satellite peaks. The S 2p exhibits (Figure 2e) a series of sulfur species that the two peaks at 161.6 and 162.4 eV belong to 2p_{3/2} and 2p_{1/2} of Co-S in Co₉S₈, respectively; the other two peaks at 163.7 and 164.1 eV are ascribed to C-S-C bonds to suggest the formation of S-doped C. The C 1s (Figure 2f) displays three peaks at 284.6, 285.3 and 288.7 eV are from C-C, C-S/C-N, and C=O bonds, respectively. [11,12] The N 1s spectrum (Figure 2g) shows three peaks at 398.2, 399.4, and 400.8 eV attributed to pyridinic-N, pyrrolic-N/Co-N-C, and graphitic-N, respectively. [11] The presence of Co-N-C is favorable for improving structural stability. To calculate the content of Co₉S₈ in the materials, TGA (Figure 2h) is performed in an air atmosphere, during which Co₉S₈ and C are oxidated into Co₃O₄ and CO₂, respectively. Hence, the final product is pure Co₃O₄. Hence, the weight content of Co₉S₈ in the composite is about 92.4%.

Figure 1. (a,b) SEM images, (c,d) TEM images, and (e,f) HRTEM images of the Co₉S₈/NSC nanocomposites.

Subsequently, the electrochemical performances of Co₉S₈/NSC are tested in details. Figure 3a shows, in the

first cycle, a strong cathodic peak at 1.31 V ascribed to the reduction of Co_9S_8 to Co. Besides this, a peak at 0.58 V arises from the formation of solid electrolyte interphase (SEI) layers.

Figure 2. (a) XRD pattern, (b) Raman spectrum, (c) XPS survey peak, (d) Co 2p, (e) S 2p, (f) C 1s, (g) N 1s, and (h) TGA curve of $\text{Co}_9\text{S}_8/\text{NSC}$.

During the first anodic process, three peaks appear at 0.88, 2.04 and 2.35 V are attributed to the reaction of metallic Co to form Co_9S_8 . The charge/discharge curves (Figure 3b) display similar plateaus with CV curves. Moreover, $\text{Co}_9\text{S}_8/\text{NSC}$ exhibits lithiation and delithiation capacities of 1261.3 and 980.4 mAh g^{-1} , respectively, to produce a first coulombic efficiency (CE) of 77.7%. Such a low value mainly arises from the formation of SEI layer. [11] Figure 3c represents the Nyquist plots at various cycling number, in which the value of charge transfer resistance (R_{ct} , diameter of 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 with cycling. [12] The decrease of R_{ct} is good for enhancing capacity and cycling life.

Subsequently, the cycling life are assessed. The $\text{Co}_9\text{S}_8/\text{NSC}$ delivers a first reversible capacity of 980.4 mAh g^{-1} with the CE of 77.7%, and 975.3 mAh g^{-1} after 100 cycles with an average CE of 99.9% (Figure 3d). A high capacity retention of 99.5% is achieved to fully prove a good reversibility of $\text{Co}_9\text{S}_8/\text{NSC}$. An ultralong cycling lifetime was obtained at 1 A g^{-1} (Figure 3e). The capacity is 791.5 mAh g^{-1} after 1000 cycles with a CE of

99.7% and 98.1% capacity retention. Such low capacity loss per cycle of 0.0019% further demonstrates the superior stability of electrode materials on cycling. The rate capability of $\text{Co}_9\text{S}_8/\text{NSC}$ was tested at 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 A g^{-1} (Figure 3f), which delivers the capacities of 992.2, 950.6, 889.2, 792.9, 664.1, 577.8, 491.4 and 329.8 mAh g^{-1} , respectively, and the capacity can be back to 976.2 mAh g^{-1} when the current density returns to 0.1 A g^{-1} to testify superior rate performance. The outstanding lithium ion storage performances mainly are attributed to its unique structural advantages, such as smaller particle size of Co_9S_8 , NSC coating layers, and formation of interfacial chemical bonds of Co-N-C and Co-S-C. [11-13]

To confirm ion storage mechanism and determine specific capacity contribution of the $\text{Co}_9\text{S}_8/\text{NSC}$, the electrochemical kinetics and pseudocapacitive contribution are surveyed by CV curves at different scanning rates (v). The CV (Figure 4a) curves display similar Li^+ storage behavior at v of 0.2 to 1 mV s^{-1} to confirm a stable pseudocapacitive behavior. Generally, peak current (i) and v is directly related, expressed by the Eq. $\log i = b \log v + \log a$. [13-15] It can be obtained 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.

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 2 A g^{-1} , and (f) rate curves of $\text{Co}_9\text{S}_8/\text{NSC}$.

It can be seen that b value is 0.84-0.88 for the two peaks (Figure 4b) to exhibit that both the diffusion-controlled and pseudocapacitive-controlled process contribute the total capacity. To survey their specific contribution, Eq. $i = k_1 v + k_2 v^{0.5}$ was presented, where i composes of pseudocapacitive process ($k_1 v$) and diffusion-controlled behaviors ($k_2 v^{0.5}$). [13-15] Clearly, the percentage of pseudocapacitive contribution rises gradually with v increasing from 0.2 to 1 mV s^{-1} (Figure 4c) to demonstrate high effect of pseudocapacitive

contribution on the enhancement of the capacity and rate performances. The high pseudocapacitive contribution mainly arises from extra Li^+ storage sites, such as interfaces and defects. [13-19]

Figure 4. (a) CV curves at different v , (b) The line relationship of $\text{Log}(i)$ vs $\text{Log}(v)$ at peaks 1 and 2 marked in (a), and (c) The percentages of pseudocapacitive contribution at different v of $\text{Co}_9\text{S}_8/\text{NSC}$.

4 Conclusions

Here, a one-step vapor-pressured induced synthesis route is developed for preparing $\text{Co}_9\text{S}_8/\text{NSC}$ composite nanoflakes for the first time by pyrolysis of mixture of cobalt iso-octanoate dissolved into dimethylformamide and thiourea in a sealed vessel. The unique structures, including small size of ~100 nm of Co_9S_8 , N, S-codoped carbon, and Co-N-C/Co-S-C bonds between Co_9S_8 and NSC, endow the nanocomposites with a high pseudocapacitive contribution, a fast Li^+ transport rate, and an extremely good structural stability, thus leading to an excellent lithium ion storage performances. As LIB anode, the $\text{Co}_9\text{S}_8/\text{NSC}$ nanocomposite shows a high first reversible capacity of 980.4 mAh g^{-1} at 0.1 A g^{-1} , an excellent cycling stability, which can cycle up to 1000 cycles at 1 A g^{-1} , and an outstanding rate capability, which can show a high reversible capacity of 329.8 mAh g^{-1} at 20 A g^{-1} .

Acknowledgements

Meisheng Han acknowledges support from Guangdong Basic and Applied Basic Research Foundation (2020A1515110762).

Thank for technical support from “Ceshigo Research Service agency for TEM, “www.ceshigo.com”.

Thank Eric Zhang from ZhongKe BlueOcean (TianJin) Technology Co., Ltd (www.zkbotj.com) for BET analysis.

Thank Jiaojiao Fang from Shiyanjia Lab (www.shiyanjia.com) for the SEM analysis.

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