Research Article

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N/S co-doped CoSe/C nanocubes as anode materials for Li-ion batteries

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Abstract: The transition metal selenide can be used as a potential material for the negative electrode of lithium-ion batteries (LIBs) owing to its high density and conductivity. Unfortunately, a large volume change occurs in the transition metal selenide during the charging and discharging process, which eventually results in the poor rate performance and rapid capacity decay. In response to this, the N/S co-doped CoSe nanocubes (CoSe/C–NS) can be fabricated where the S-doped cobalt 2-methylimidazole (ZIF-67) as both sacrifice template and cobalt source to directly mix with selenium powder and followed by the annealing process. In the process, the carbon frameworks derived from ZIF-67 can establish a coating layer to protect the structure of materials, and simultaneously the N/S co-doping can enhance the conductivity and broaden the interlayer of frameworks. These can further accelerate the storage capacity and the Li⁺ insertion and deintercalation process. As a negative electrode material of LIBs, the

Graphical abstract

CoSe/C–NS delivers the high capacity, high rate performance, and long-term cycle stability. This protocol opens up an approvable approach to fabricate efficient anode materials with persistent electrochemical stability in LIBs.

Keywords: lithium-ion batteries, N/S co-doped, CoSe, anode materials

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1 Introduction

In the past few decades, the ever-growing energy shortage has triggered the widespread concern due to the limitation of non-renewable fossil energy. Meantime, severe environmental pollution aroused by the use of large amounts of fossil energy considerably threatens the long-term healthy survival of humankind [1,2]. Although, renewable energy sources, such as electricity from wind or solar power, do not present the abovementioned issues, they are mainly controlled by the seasonal and regional differences, which have seriously restricted their widespread applications worldwide [3]. More impressively, the lithium-ion batteries (LIBs) with the advantage of environmental friendliness are regarded as the alternative energy equipment that contribute to the transformation of these unstable electrical energies into stable

chemical energies, which are substantially considered for the new energy vehicles, consumer electronics, and energy storage power stations. Nevertheless, it remains a big challenge to resolve the issues of both the high energy density and long lifetime of LIBs. Therefore, it is quite necessary to develop new electrode materials as a fundamental guarantee to achieve high electrochemical performance [4,5].

Artificial graphite and natural graphite are extensively applied in commercial LIBs for anode materials, while the theoretical capacity of graphite anode (372 mA h/g) cannot satisfy the requirement of various thriving applications [6]. Comparatively, transition metal chalcogenides having excellent lithium storage capacity, preferable mechanical stability, and high thermal stability are becoming one of the potential replacements for graphite anodes, and are receiving more and more attention [7–9]. Besides, the transition metal selenide has excellent electrochemical performance due to its own inherent properties of high density and high conductivity [10–12]. Unfortunately, the large volume changes in these materials during cycling often lead to structural damage, which results in poor rate performance and rapid capacity decay [13,14]. In addition, the safety problems caused by the volume expansion of graphite anodes have not been resolved so far and also attracted serious attention worldwide.

Benefiting from the different morphological structures of metal–organic frameworks (MOFs), energy storage materials derived from different MOFs are suitable for various composite systems, such as transition metal oxides [15,16] and transition metal sulfides [17,18]. Many studies have focused on MOFs as precursors for the synthesis of electrode materials with carbon frameworks, which have excellent electrochemical performance and structural stability. Recently, an N-doped and S-doped (N/S co-doped) carbon box-shaped material which uses a kind of S-doped MOFs (S-doped ZIF-67) as a template and is etched by HCl has been impressively carried out for potassium storage [19]. This is because S-doped ZIF-67 could introduce more defects and widen the interlayer spacing of carbon-based materials, thereby improving storage capacity and conductivity. For a similar reason, ZIF-67-based CoSe/C nanocomposites with N-doped have been reported as electrodes for supercapacitors, which also presented good electrochemical performance [20]. Although these aforementioned advantages exist in the N/S-doped ZIF-67 derived CoSe/C nanocomposite materials, it is believed that there have been rare investigations on them as anode materials for LIBs. To date, it is reported that only ZIF-67-derived CoSe/C is utilized for the anode of LIBs [21]. In this research, the N/S co-doped CoSe nanocubes (CoSe/C–NS) are successfully prepared, which were annealed from the S-doped ZIF-67 precursor (S-ZIF-67) as both sulfur and cobalt source. As the anode

material of LIBs, the CoSe/C–NS has a high specific capacity of 1,494 mA h/g after 300 cycles at a current density of 0.2 A/g, and the CoSe/C–NS also shows excellent performance at high current density, which demonstrates that S-doped material has better comprehensive performance such as structural stability than CoSe/C–N nanocomposite assembled in LIBs.

2 Experimental methods

2.1 Synthesis of S-ZIF-67

The S-ZIF-67 was synthesized by a precipitation reaction. In a typical process, 5 mmol cobalt nitrate hexahydrate(II) was first dissolved into 100 mL of methanol. Next 20 mmol 2-methylimidazole and 15 mmol thioureas were sequentially dissolved into 100 mL of methanol. Then, the two solutions were mixed very slowly with a dropper and vigorously stirred for 24 h at ambient temperature. Finally, the precipitate was collected by centrifugation and washed with methanol 3 times and then dried in the oven at 80°C overnight. The as-prepared sample was denoted as S-ZIF-67. For comparison, a similar procedure was used to prepare ZIF-67, but thiourea was not added.

2.2 Synthesis of CoSe/C–NS

The as-prepared S-ZIF-67 and selenium powder were ground together with a mass ratio of 1:1 for about 10 min. Then, the mixture was heated at 600°C for 4 h under a nitrogen atmosphere at the heating rate of 5°C/min. In addition, CoSe/C–N was fabricated using ZIF-67 as the sacrificial template by a similar procedure.

2.3 Materials characterization

The morphological details of CoSe/C–NS and CoSe/C–N were characterized by field emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEOL, JEM-2100F). Crystal structures of all samples were investigated by Bruker D8-Advance diffractometer at the θ – 2θ mode using the $K\alpha$ radiation of Cu at 1.5418 Å with a scan rate of 2°/min. X-ray photoelectron spectra (XPS) were recorded on a Thermo Fisher K-Alpha spectrometer.

2.4 Electrochemical measurements

The electrochemical performance of CoSe/C–NS and CoSe/C–N as anode materials was researched by CR2016 coin

cells, which were packaged in a glove box (MIKROUNA, Super 1220/750/900) with O_2 and H_2O content less than 0.1 Pa. The working electrode was coated on a copper foil collector by an active material mixture consisting of active material, acetylene black, and polyvinylidene difluoride with a mass ratio of 8:1:1. The counter electrode used a metal Li foil and the electrolyte was 1 mol $LiPF_6$ solution, and the solvent was composed of ethylene carbonate, ethyl methyl carbonate, and dimethyl carbonate with a volume ratio of 1:1:1. The separator was a Celgard 2400 type of membrane. The charge/discharge tests were performed by the Neware BTS-5V5mA system at a potential range of 0.01–3 V. The CHI660C type of electrochemical workstation was employed to obtain an electrochemical impedance spectrum (EIS) of 0.01 Hz to 100 kHz and a cyclic voltammetry (CV) of 0.01–3 V at a scan rate of 0.1 mV/s.

3 Results and discussion

As shown in Figure 1a, ZIF-67 presents a regular polyhedron-like structure, which was also mentioned in many previous reports [19]. Similarly, the S-doped ZIF-67 also delivers polyhedron-like structure, which eventually remains intact although its surface is widely attached by many attached nanoparticles (Figure 1b). In addition, some particles with a semi-fragmentized surface are also found, indicating details about the internal particle aggregation. The morphological details of CoSe/C-NS is shown in Figure 1c and d. Both CoSe/C-NS and CoSe/C-N retain the regular polyhedron-like structure. The surface of CoSe/

C-NS particles was flat after the selenide process, and the CoSe/C-NS particles are larger than CoSe/C-N particles.

In addition, high-resolution TEM (HRTEM) images illustrate the interplanar spacing of CoSe/C-NS and CoSe/C-N (Figure 2a and b). The plane spacing of these two samples is 0.269 nm, which is equivalent to the (101) plane of CoSe nanoparticles. Noticeably, the 0.563 nm interplanar spacing of CoSe/C-NS is assigned to the (200) plane of CoSe nanoparticles, which is larger than that of CoSe/C-N (0.514 nm) due to the successful doping of S into the CoSe/C-NS, thereby facilitating the insertion and deintercalation of Li^+ during charging and discharging process. The study of the external framework is also shown in Figure 2a and b, demonstrating that the carbon frameworks originated from MOFs' precursor can establish an encapsulated layer to protect the migration of CoSe nanoparticles over CoSe/C-NS and CoSe/C-N. Furthermore, the TEM mapping images further confirm that there were C, N, S, Co, and Se elements existing in the CoSe/C-NS composite (Figure 2c–g).

X-ray diffraction (XRD) is also employed to analyze the formation of CoSe/C-NS. As shown in Figure 3a, the XRD patterns of ZIF-67 and S-ZIF-67 are in line with the previous studies, indicating their successful preparation in our condition [19]. Figure 3b shows the XRD patterns of the CoSe/C-NS and CoSe/C-N composites after selenization at 600°C for 4 h. It can be observed that all the samples exhibit prominent diffraction peaks at 28.4°, 33.2°, 44.8°, 50.4°, 60.2°, 61.7°, and 69.7° corresponding to (100), (101), (102), (110), (103), (201), and (202) of CoSe (JCPDS no. 70-2870). The XRD patterns of the two samples are similar, and no significant peak shift is observed, disclosing the identical crystal structures of CoSe/C-NS

Figure 1: SEM images of (a) ZIF-67, (b) S-ZIF-67, (c) CoSe/C-NS, and (d) CoSe/C-N.

Figure 2: HRTEM images of (a) CoSe/C-NS and (b) CoSe/C-N; (c–g) TEM mapping of C, N, S, Co, and Se element.

and CoSe/C-N. The same crystal structure also shows that S-doping does not damage the carbon framework. No other diffraction peaks of impurities are observed, suggesting the high purity of these samples.

The XPS is utilized to provide details about the elemental composition and chemical valence of the prepared samples. The XPS survey results prove the presence of Se, S, C, O, and Co in these samples (Figure 4a). The high-resolution XPS spectrum of Co 2p displays peaks at 802.9 and 785.2 eV corresponding to the shake-up satellites (sat.), and the peaks at 797.0 and 793.4 eV are assigned to Co 2p_{1/2}, and the peaks at 781.2 and 778.7 eV are attributed to Co 2p_{3/2}, as exhibited in Figure 4b [22]. Figure 4c displays the XPS spectrum of Se 3d, which can be reasonably deconvoluted into 4 main characteristic peaks at 53.9 and 54.7 eV for Se 3d, 58.8 eV for Se–O, and 60.2 eV for shake-up satellite peak [23]. The XPS spectrum of C 1s can be completely fitted by three distinguished

peaks at 284.7, 286.1, and 287.6 eV, corresponding to the binding energies of C–C, C–N, and C=O, respectively, which can be also counted as evidence for its successful doping of N due to the presence of C–N bond in the CoSe/C-NS, as displayed in Figure 4d [19]. Figure 4e shows the high-resolution spectrum of N 1s. There are three peaks at 398.1, 399.8, and 402.6 eV, which are indexed to pyridinic-N, pyrrolic-N, and graphitic-N, respectively [24]. Correspondingly, the percentages of pyridinic-N, pyrrolic-N, and graphitic-N are calculated to be 53, 30, and 17%, respectively. Accordingly, the highest content of pyridinic-N in the CoSe/C-NS can be more beneficial to enhance the electrochemical performance [25]. The S 2p spectrum is revealed in Figure 4f, which has disintegrated main characteristic peaks. More specifically, the noticeable peak at 160.5 eV is related to sulfide [26]. Another considerable peak at 165.1 eV can demonstrate the existence of C–S as a consequence of the successful doping of S into C in this

Figure 3: XRD patterns of (a) ZIF-67 and S-ZIF-67 and (b) CoSe/C-NS and CoSe/C-N.

Figure 4: (a) XPS survey scan spectra of CoSe/C-NS; (b–f) High-resolution Co 2p, Se 3d, C 1s, N 1s, and S 2p spectra of CoSe/C-NS.

sample [27]. And the other two peaks at 173.3 and 178.1 eV can be interpreted as the peaks for satellite peak and Se auger [28,29].

The electrochemical performance of CoSe/C-NS and CoSe/C-N is displayed in Figure 5. As shown in Figure 5a, the CV curves at a scan rate of 0.1 mV are utilized to demonstrate the redox process of the CoSe/C-NS as an anode material. In the first cycle, there are three distinct

reduction peaks appearing at 1.15, 0.90 and 0.45 V. Thereinto, the corresponding peak at 1.15 V is attributed to the process of Li^+ insertion, which leads to a transition from CoSe to Li_xCoSe . And the characteristic peak at 0.9 V indicates the formation of the solid electrolyte interface (SEI) film. In addition, the formation of Co and Li_2Se can be verified by another reduction peak at 0.45 V. The oxidation peaks are found at 1.38 and 2.18 V, which

Figure 5: (a) CV curves and (b) charge-discharge curves of CoSe/C-NS; (c) Cycling performances at 0.2 A/g, (d) cycling performances at 2 A/g, (e) rate capabilities, and (f) Nyquist plots of CoSe/C-NS and CoSe/C-N.

demonstrate the process of Li^+ deintercalation with the re-formation of CoSe [22,30]. In the CV curves of the second and third cycles, the first cycle reduction peak at 0.9 V disappears and the other two reduction peaks shift to 1.35 and 0.52 V, respectively, for the insertion process of Li^+ , and the oxidation peaks are exactly similar to the first cycle at 0.9 V mainly due to the process of Li^+

deintercalation, confirming that CoSe/C-NS anode has good reversibility [22,30]. Figure 5b shows the discharge-charge diagram of CoSe/C-NS anode of 1st, 2nd, 3rd, 5th, and 50th under 200 mA/g, and the plateaus are consistent with the CV results. In the first cycle, the CoSe/C-NS shows the discharge capacity of 1,292 mA h/g and the charge capacity of 1,043 mA h/g, and the Coulombic efficiency

Table 1: Cycling performance of anode materials

Anode materials	Current density (mA/g)	Reversible capacity (mA h/g)	Capacity retention (%)
CoSe/C–NS	200	1,494/300th cycle	115
CoSe/NC composites [21]	100	1,244/190th cycle	118
CoSe–MS [31]	200	481.6/100th cycle	80
CoSe@carbon nanoboxes [32]	200	860/100th cycle	108

(CE) is 80.7%. This part of irreversible capacity loss is attributed to the formation of SEI film. Figure 5c exhibits the cycling performance of CoSe/C–NS and CoSe/C–N anode; after 300 cycles, their specific capacities are 1,494 and 797 mA h/g, respectively, at the rate of 0.2 A/g. Furthermore, a high current density of 2 A/g has also been studied, which indicates that the specific capacity of CoSe/C–NS remains 513 mA h/g after 500 cycles, while the specific capacity of CoSe/C–N has decreased sharply since the 384th cycle (Figure 5d). Obviously, CoSe/C–NS anode has better cycle performance than CoSe/C–N in terms of cycle capacity and structural stability, because S-doping introduces more defects and larger interplanar spacing [20]. Impressively, the cycling performance of CoSe/C–NS is comparable or even superior to some recently reported state-of-the-art similar anode based on CoSe-type materials in LIBs, as shown in Table 1. In addition, CoSe/C–NS also affords the excellent rate performance, showing average capacity of 725, 682, 992, 811, 687, 644, and 872 mA h/g at the rate of 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, and 0.05 A/g (Figure 5e). By comparison, CoSe/C–N delivers the average capacity of 592, 614, 802, 671, 591, 528, and 676 mA h/g at the rate of 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, and 0.05 A/g, respectively. The CoSe/C–NS also has better rate performance than CoSe/C–N. As shown in Figure 5f, the EIS results of CoSe/C–NS and CoSe/C–N are employed to present the detailed information on electrical conductivity. Obviously, the semicircle of CoSe/C–NS is significantly smaller than the semicircle of CoSe/C–N, which demonstrates that both the charge transfer resistance and the internal resistance of CoSe/C–NS are smaller, which is more conducive to enhancing its integrated electrochemical performance.

4 Conclusion

In summary, this work develops a facile and feasible strategy to realize the synthesise of CoSe/C–NS nanocubes by using S-ZIF-67 as sacrificial templates through annealing treatment. In contrast to CoSe/C–N, the CoSe/C–NS sample has

the favorable merits of the N and S co-doped carbon framework, higher specific capacity, and long-term cycling stability, which is favor of accelerating the electrochemical performance at high current density. This is because the N/S co-doping not only broadens interlayer spacing of carbon framework to encourage the insertion and deintercalation of Li^+ during charging and discharging processes, but also improves storage capacity and conductivity, which is more advantageous in improving the integrated electrochemical performance. As an anode material, the CoSe/C–NS delivers a high specific capacity of 1,494 mA h/g after 300 cycles at a current density of 0.2 A/g. Besides, it also shows excellent performance at high current density. Therefore, this composite material can provide more reliable electron transmission for LIBs and has good structural stability.

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