High-Performance Li–Se Batteries Enabled by Selenium Storage in Bottom-Up Synthesized Nitrogen-Doped Carbon Scaffolds

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ABSTRACT: Selenium (Se) has great promise to serve as cathode material for rechargeable batteries because of its good conductivity and high theoretical volumetric energy density comparable to sulfur. Herein, we report the preparation of mesoporous nitrogen-doped carbon scaffolds (NCSs) to restrain selenium for advanced lithium–selenium (Li–Se) batteries. The NCSs synthesized by a bottom-up solution-phase method have graphene-like laminar structure and well-distributed mesopores. The unique architecture of NCSs can serve as conductive framework for encapsulating selenium and polyselenides, and provide sufficient pathways to facilitate ion transport. Furthermore, the laminar and porous NCSs can effectively buffer the volume variation during charge/discharge processes. The integrated composite of Se-NCSs has a high Se content and can ensure the complete electrochemical reactions of Se and Li species. When used for Li–Se batteries, the cathodes based on Se-NCSs exhibit high capacity, remarkable cyclability, and excellent rate performance.

KEYWORDS: lithium—selenium batteries, selenium cathode, nitrogen-doped carbon scaffolds, electrochemical performances, graphene-like laminar structure

INTRODUCTION

The increasing demands of portable devices and clean-energy vehicles have largely promoted the broad interest in developing rechargeable batteries.1−11 However, the existing lithium-ion batteries (LIBs) cannot meet the growing requirements for high energy density and long cycling stability; therefore, next-generation batteries are urgently needed.5 Sulfur is a potential cathode because of its high theoretical specific capacity (1670 mA h g−1), natural abundance, cheapness, and nontoxicity.5,25 However, the application of lithium–sulfur (Li–S) batteries is hampered by several drawbacks: (1) because of the low conductivity, sulfur cathodes usually exhibit poor utilization ratio and rate capability; (2) the high solubility of polysulfides in electrolyte leads to low Coulombic efficiency and poor cycling life span.6−9 To alleviate these problems, great efforts have been made, such as confining sulfur species with conductive polymers,10−13 nanocarbons,14−18 or oxide frameworks,19−24 and looking for suitable electrolytes and additives.22−24 Although the performances of Li–S batteries have been greatly improved recently, the commercialization is still hindered by the serious capacity fading and poor rate performance.

Selenium is a promising alternative of sulfur. Because of its similar chemical properties to sulfur, selenium can react with lithium to form polyselenides (Li2Sex) as well. Compared to sulfur, the theoretical specific capacity of selenium cathode (678 mA h g−1) is lower. However, its volumetric capacity density (3278 Ah L−1) is comparable to sulfur (3467 Ah L−1) because of its high density.28,29 Furthermore, the conductivity of selenium (1 × 10−3 S m−1) is much higher than that of sulfur (5 × 10−28 S m−1), which can lead to higher utilization rate and superior rate performance.29 These advantages grant selenium the great promise as cathode for constructing secondary batteries with high power density. However, selenium may also suffer from the “shuttle effect” because of the dissolution of Li2Se intermediates in electrolyte.

Several strategies have been proposed to enhance the performance of selenium cathode, such as impregnating selenium into porous carbon matrix36,38−42 and graphene,43,44 as listed in Table S1. These reports indicated that carbon frameworks can provide many merits, such as large storage volume, smooth ion transport paths, enhanced conductivity, and buffering the volume variation. Moreover, recent studies have shown that the electrochemical properties of carbon
electrode materials can be effectively improved by the doping of heteroatoms.\textsuperscript{36,37,45} According to the research of Li—S batteries, the introduction of heteroatoms (e.g., B, S, N, P and O) can improve the interactions between the carbon matrix and intermediate species, thereby suppressing the shuttle effect and boost cycling lifespan.\textsuperscript{46—51}

Here we report a novel composite cathode with remarkable electrochemical performance by impregnating selenium into nitrogen-doped carbon scaffolds (NCSs). The obtained Se-NCSs with graphene-like laminar and porous structure can effectively encapsulate selenium, prevent the dissolution of polyselenides (Li$_2$Se$_{x}$), and accommodate the huge volume expansion. As expected, the Se-NCSs exhibits great cycling stability and rate performance far superior to pristine carbon scaffolds (PCSs).

**RESULTS AND DISCUSSION**

The synthesis procedures of NCSs and Se-NCSs were illustrated in Scheme 1. A bottom-up synthesis approach was modified to prepare the NCSs from nitrogen- and carbon-containing precursors in the solution phase.\textsuperscript{52} During the reflux process at 350 °C, the Wurtz coupling reaction accompanied by dechlorination and carbonization was occurred. After the removal of inorganic salts and thermal annealing in N$_2$ atmosphere, the NCSs with abundant mesopores and laminar structure that composed of stacked wrinkle graphene-like carbon sheets were obtained. After impregnating selenium in NCSs, the nitrogen doping is beneficial for the trapping and charge transfer of Se species; the wrinkled laminar structure can effectively confine selenium and polyselenides and the large pore volume can accommodate the volume change during charge—discharge cycles. Both the NCSs and control sample PCSs stacked by graphene-like carbon sheets with abundant pores show wrinkled laminar structure (Figure 1a, b and Figure S1). Sufficient pathways and large electrode—electrolyte interfaces can be provided by the interconnected carbon framework for electron and ion transport and charge transfer reactions. After selenium loading, the wrinkled laminar morphology of original NCSs became compacted bulk and no selenium accumulation was observed on the surface (Figure 1c), demonstrating the uniform dispersion of Se in the pores of NCSs. The EDX spectrum of Se-NCSs (Figure 1d) indicates the high loading ratio of Se. Combined with the TGA results (Figure S2), the selenium contents are determined to be 56 and 50 wt % for Se-NCSs and Se-PCSs, respectively. The EDX mapping images of carbon and selenium elements are shown in Figure 1e, f, revealing the selenium is uniformly dispersed in Se-NCSs.

To confirm the successful nitrogen doping of NCSs, detailed XPS analysis was performed. The survey XPS spectrum (Figure 2a) shows three distinct peaks representing the energy bands of C 1s, N 1s and O 1s, respectively. The presence of O element

Figure 1. (a) SEM and (b) TEM images of NCSs. (c) SEM image and (d) EDX spectrum of Se-NCSs. (e, f) EDX elemental mapping of carbon and selenium in Se-NCSs.

Figure 2. (a) XPS survey spectrum of NCSs. (b) High-resolution XPS spectrum of N 1s region of NCSs, and the inset is the schematic structure of NCSs. (c) XRD patterns and (d) Raman spectra of Se, PCSs, NCSs, and Se-NCSs, respectively.
was ascribed to the physicochemical adsorption of trace-amount oxygen during synthesis. The atomic content of N in NCs was estimated to be 6.5 wt %. As shown in Figure 2b, the high-resolution N 1s spectrum of NCs can be divided into three individual peaks: pyridinic N (398.2 eV), pyrrolic N (401.0 eV), and graphitic N (400.1 eV), indicating the presence of nitrogen-containing pentatomic rings, hexatomic rings, and defects in NCs. According to the XPS analysis, a possible structure illustration of NCs was given by the inset of Figure 2b. The electrochemical activity can be enhanced by the nitrogen heteroatoms in carbon matrix, which is conducive to the electrochemical performance of Se-NCs.

Figure 2c shows the XRD patterns of Se, PCSs, NCs, and Se-NCs. Both the NCs and Se-NCs show two broad peaks of (002) and (101), suggesting the amorphous state of carbon. No obvious selenium peaks were observed in the XRD curve of Se-NCs, demonstrating that selenium was confined as highly dispersed and tiny nanoparticles in NCs. To further investigate the interactions between Se and NCs, we characterized the samples by Raman spectroscopy (Figure 2d). For pure Se, three Raman characteristic peaks at 138, 236, and 458 cm$^{-1}$ were observed, demonstrating the presence of chain-structured and annular selenium. For NCs, the G band (associated with graphitic carbon) and D band (related to defects or disorders) are located at 1591 and 1356 cm$^{-1}$, whereas PCSs show a G band and a D band at 1574 and 1356 cm$^{-1}$, respectively. The intensity ratios of D/G bands of NCs and PCSs calculated from the Raman spectra were 0.84 and 0.73, respectively, indicating that the both samples were partially graphitized, thus favoring to the conductivity and electron transport. Previous works reported that an appropriate degree of nitrogen doping could result in a better conductivity. Moreover, the powder electronic conductivity of NCs and PCSs measured with a multifunctional powder resistivity tester (FT-301, with a mold of 4 mm diameter) are 660.7 and 525.0 S m$^{-1}$, respectively, further demonstrating the higher conductivity of NCs. After selenium loading, no apparent Raman peaks of selenium could be observed, indicating that selenium was uniformly encapsulated and dispersed in the NCs in agreement with the EDX and XRD results.

The pore structures of NCs, Se-NCs, PCSs, and Se-PCSs were investigated by the nitrogen adsorption–desorption isotherms (Figure 3). The BET surface area and pore volume of NCs are 615 m$^2$ g$^{-1}$ and 1.36 cm$^3$ g$^{-1}$, respectively. Based on the pore volume, the maximum selenium loading content can reach 86.7%. For accommodating the volume expansion during cycling both Se and polyselenides during redox reactions, as shown in Figure 3c, d, the PCSs and Se-PCSs showed similar pore structure parameters compared to NCs and Se-NCs, respectively. The wrinkled laminar structures with abundant mesopores can serve as conductive framework for encapsulating selenium and polyselenides, and also provide sufficient pathways to facilitate ionic migration. As presented in Figure S3, the binding energies of Se 3d$_{3/2}$ and 3d$_{5/2}$ in the XPS spectrum of Se-NCs are higher than those of Se-PCSs, indicating a relatively stronger affinity between the NCs and Se.

Coin cells (standard type-2032) were assembled to compare the electrochemical performances of the as-obtained electrodes. Figure 4a displays the typical CV curves of Se-NCs based electrode in the voltage range of 1.0–3.0 V with a sweep rate of 0.2 mV s$^{-1}$. In the first cycle, two obvious cathodic peaks appeared at 2.12 and 1.96 V, corresponding to the reduction from Se to polyselenides and then to Li$_2$Se, respectively. The subsequent anodic scan exhibited two anodic peaks at 1.96 and 2.26 V, corresponding to the reversible conversions from Li$_2$Se to polyselenides and then to Se, respectively. The subsequent anodic scan exhibited two anodic peaks at 1.96 and 2.26 V, corresponding to the reversible conversions from Li$_2$Se to polyselenides and then to Se, respectively. In the following scans, the CV curves are almost overlapped, indicating the high reversibility and stability. This indicated that the NCs was quite effective for confining both Se and polyselenides during redox cycles.

To investigate the cycling stability of Se-NCs and Se-PCSs based cathodes, we performed galvanostatic charge/discharge tests at 0.1 C and 100 mA g$^{-1}$ based on theoretical specific capacity of Se, as shown in Figure 4b, c. In the first cycle, the...
Se-NCSs based cathode exhibited a high capacity of 960 mA h g\(^{-1}\) and a reversible capacity of 538 mA h g\(^{-1}\). In the following 10th and 50th cycles, the specific capacity became stable. The discharge curves of Se-NCSs delivered only one sloping voltage plateau, similar to some previous works.\(^{37,60}\) This result is mainly due to the volume confinement effect of the NCSs with abundant pores and wrinkled laminar structure, in which the uniformly dispersed selenium was prevented to form higher order polyselenides.\(^{60}\) As control samples, the charge/discharge profiles of NCSs and PCSs without the loading of selenium showed very low capacities (Figure S4), indicating that the high capacity of Se-NCSs and Se-PCSs are mainly contributed from the encapsulated selenium.

The Se-PCSs based electrode exhibited similar electrochemical behavior compared to Se-NCSs and delivered a high initial reversible capacity (Figure 4c). However, the capacity of Se-PCSs based electrode decreased rapidly in the initial 50 cycles. The cycling performances of Se-NCSs and Se-PCSs based cathodes are shown in Figure 4d. The Se-NCSs based cathode kept a reversible capacity of 480 mA h g\(^{-1}\) after 100 cycles and a corresponding Coulombic efficiency over 96%. In contrast, the Se-PCSs based cathode exhibited a much lower capacity of 268 mA h g\(^{-1}\) after 100 cycles.

Electrochemical impedance spectroscopy (EIS) measurements were carried out for Se-NCSs and Se-PCSs based electrodes before and after 100 cycles at 0.1 C. Figure S5 shows that the fresh electrode of Se-NCSs exhibited a charge transfer resistance lower than that of Se-PCSs, indicating the electrical conductivity was improved by the introduction of N heteroatoms. After 100 cycles, the charge transfer resistance of Se-NCSs electrode further decreased. The improved conductivity of electrodes after the charge/discharge processes should be attributed to the wetting and infiltration of electrolyte into electrode.\(^{55,61–63}\) Compared to Se-PCSs, the superior conductivity of Se-NCSs can facilitate electron transport and lead to lower polarization, thus beneficial to electrochemical performance and stability.\(^{35}\)

The rate performances of Se-NCSs and Se-PCSs based cathodes were presented in Figure 5a, b and Figure S6a. For Se-NCSs based cathode, the reversible capacity reached 475 mA h g\(^{-1}\) at the rate of 0.2 C. As the current density raised to 2 C, the reversible capacity kept at 275 mA h g\(^{-1}\) (∼58% retention of the capacity at 0.2 C). After the rate was set back to 0.2 C, the reversible capacity went back to 450 mA h g\(^{-1}\), demonstrating excellent reversibility and stability. In contrast, the Se-PCSs based cathode only delivered a low capacity of 170 mA h g\(^{-1}\) at 2 C. When the current density was set back to 0.2 C, the specific capacity of Se-PCSs cathode recovered to 251 mA h g\(^{-1}\) after cycling at different rates. Notably, the cathode based on Se-NCSs exhibited incredible cycle stability and excellent reversibility. To assess the long-term cyclability, the cathodes were tested for 500 cycles at 1 C (Figure 5c and Figure S6b). For Se-NCSs cathode, the discharge capacity was 457 mA h g\(^{-1}\) at the second cycle and retained 301 mA h g\(^{-1}\) after 500 cycles, corresponding to a capacity retention of 66% and a low average capacity decay of 0.068% per cycle. The Coulombic efficiency kept at nearly 100% throughout the cycling, indicative of a prolonged cycle life. In comparison, Se-PCSs electrode only delivered a capacity of 98 mA h g\(^{-1}\) at 1 C after 500 cycles. We also compared the performance of Se-NCSs with other reported Se–C composite cathodes for Li–Se batteries, as presented in Table S1. The Se-NCSs electrode exhibits good performances superior or comparable to other Se-based electrodes in the previous works (Table S1),\(^{28,30–44}\) demonstrating the remarkable lithium storage properties of Se-NCSs.

Moreover, control samples with different nitrogen content were obtained by annealing the carbon scaffolds precursor at 800 and 1000 °C, and named as NCSs-800 and NCSs-1000, respectively. The nitrogen content of NCSs-800 and NCSs-1000 are measured to be 7.2 and 4.8 wt %, respectively, according to the XPS results (Figure S7). After loading with the same ratio of selenium, the cycling performance of Se-NCSs-800 and Se-NCSs-1000 cathodes are presented in Figure S8. The performance of Se-NCSs-800 and Se-NCSs-1000 cathodes are inferior to that of Se-NCSs annealed at 900 °C, indicating that the electrode performance can be affected by the annealing temperature and nitrogen content.

The enhanced capacity retention and rate performance of Se-NCSs should be ascribed to the introduction of N heteroatoms, which increased the conductivity and decreased the polarization. Moreover, the introduction of N atoms can accelerate lithium insertion and enhance the interaction between the NCSs and lithium polyselenides.\(^{39,64}\) These results further illustrated the superiorities of NCSs for accommodating volume change, maintaining good structural stability, and restraining the diffusion of polyselenides during long-term cycling.

■ CONCLUSION

In this work, a novel strategy is demonstrated to prepare the composite of Se-NCSs for rechargeable Li–Se batteries. The unique framework of NCSs with favorable pore structure and improved conductivity can effectively confine selenium and polyselenides, thus lead to high capacity and long-term cyclability. On the basis of the outstanding electrochemical performances, the NCSs should be considered as a promising selenium host material to develop high-performance lithium–selenium batteries.

■ EXPERIMENTAL SECTION

Material Synthesis. Synthesis of NCSs: A bottom-up solution-phase method modified from previous work\(^2\) was developed to prepare the NCSs. Typically, 100 mL of paraffin oil was poured into a dry three-neck round-bottom flask (200 mL) stocked with an air reflux condenser. Then, 2.5 mL of tetrachloroethylene, 3.7 g of cyanuric

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Figure 5. (a) Charge/discharge profiles and (b) rate capability of Se-NCSs based cathode at 0.2–2 C. (c) Long-term cycling performance and corresponding Coulombic efficiency of Se-NCSs based cathode at 1 C.
chloride, and 5.0 g of chopped sodium metal were put into the flask under N₂ protection. The flask was heated to 350 °C under continuous stirring and refluxed for 6 h with N₂ protection. After cooling down to ambient temperature, the mixture was filtered through PTFE membrane and sequentially washed with petroleum ether, acetone, deionized water and ethanol to get rid of residual salts and organic compounds. After dried under vacuum at 120 °C, the brown solid product was annealed in an electric furnace under Ar atmosphere for 1 h at 900 °C with a ramp rate of 2 °C min⁻¹. The resulting NCSs solid was ground to powder. Control samples with different nitrogen content were also obtained by annealing the product at 800 and 1000 °C, and named as NCSs-800 and NCSs-1000, respectively.

Synthesis of PCSs: For comparison, PCSs without nitrogen heteroatoms were prepared as a control sample through the same synthesis process as above, except for less sodium (2.5 g) and no cyanuric chloride (nitrogen source) were used.

**Instruments and Characterizations.** The morphologies of products were characterized with a scanning electron microscope (SEM, Hitachi S-4800) equipped with an energy-dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) observation was performed on a JEM-2100 instrument. Powder X-ray diffraction spectra (XRD) were measured by an X-ray diffractometer (Bruker D-8 Advance, Cu Kα radiation at 40 kV and 40 mA). Thermogravimetric analysis (TGA, Netzsch STA 449 C) was carried out in a N₂ atmosphere with a heating rate of 10 °C min⁻¹. The LiTFSI used for Lithium−sulfur Batteries. Angew. Chem., Int. Ed. 2008, 47, 2930–2946.

- **Electrochemical Measurements.** The cathodes based on Se-NCSs or Se-PCSs were prepared as follows. Se-NCSs or Se-PCSs (80 wt %), super P (10 wt %), and sodium alginate (10 wt %) were mixed and stirred in distilled water to form a slurry, then casted on Al foil and dried in vacuum at 100 °C for 12 h. The loading weight of active material is 0.8–1.0 mg cm⁻². The Li−Se batteries were assembled with Celgard-2400 separators and Li foil anodes in an Ar-filled glovebox. The electrolyte is 1.0 M of bis(trifluoromethane) sulfonimide lithium (LiTFSI) in a mixed solvent of dimethoxyethane and dioxolane (1:1 by volume). Galvanostatic charge/discharge tests were performed between 1.0 and 2.5 V vs Li⁺/Li on a Wuhan Land-CT2001 system. Cyclic voltammetry (CV) was performed using an electrochemistry workstation (Chenhua CHI-760E) at a scan rate of 0.2 mV s⁻¹. Nyquist plots of the Li−Se cells with different Se composite cathodes after 100 cycles at 0.1 C rate capability of Se-PCSs based cathode at 0.1 C (PDF).

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**Notes**
The authors declare no competing financial interest.

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