Materials Research Express

PAPER

3DG/Se$_{4.7}$S$_{3.3}$ composites with different morphologies as new all-solid-state lithium storage electrode materials

Zhongli Shen$^1$, Fangchao Liu$^{1,*}$, Han Hu$^1$ and Zhengwen Fu$^2$

$^1$ School of Materials Engineering, Shanghai University of Engineering Science, Shanghai, People’s Republic of China
$^2$ Department of Chemistry, Fudan University, Shanghai, People’s Republic of China

* Author to whom any correspondence should be addressed.

Abstract
Selenium-sulfur(Se$_x$S$_y$) composites can be used as energy storage materials for lithium batteries benefit from their integration of the high capacity of sulfur and the high conductivity of selenium. Herein, we prepared amorphous three dimensional reduced graphene oxide/selenium sulfide(a-3DG/Se$_{4.7}$S$_{3.3}$) composites and crystalline 3DG/Se$_{4.7}$S$_{3.3}$(c-3DG/Se$_{4.7}$S$_{3.3}$) composites by in situ synthesis and hydrothermal methods, respectively, in order to research the effect of different morphologies of 3DG/Se$_{4.7}$S$_{3.3}$ composites on the electrochemical properties of all-solid-state lithium batteries. Our study found that the a-3DG/Se$_{4.7}$S$_{3.3}$ cathodes displayed greater capacity and outstanding rate performance, with an initial discharge capacity of 926 mAh g$^{-1}$ and utilization rate of 103% at 1/2C. And a first discharge capacity of up to 706 mAh g$^{-1}$ at 7 C. Although the first discharge capacity of c-3DG/Se$_{4.7}$S$_{3.3}$ was 523 mAh g$^{-1}$, its cycling stability was significantly improved compared with that of a-3DG/Se$_{4.7}$S$_{3.3}$ cathodes, and the Coulombic efficiency remained above 97% after 60 cycles at 1/2 C. In this work, we investigate the performance of solid-state batteries by preparing new Se$_x$S$_y$ composites with different morphologies and rational design of electrodes in terms of structure and morphology, which provides ideas for the preparation of electrodes in the future.

1. Introduction

To adapt to the sustainable development of power storage systems, lithium-ion battery emerges as the times require and develop rapidly in recent years [1–3]. In particular, with the advent of electric vehicles and wearable devices, carbon materials [4], metal materials [5, 6], etc have become important materials for exploring energy storage systems. Obviously, lithium-ion batteries have been unable to meet the demand, to find a higher energy density, long cycle life, high-safety, good stability of new electrode materials is the current research focus [7–13].

In the past, lithium-sulfur(Li-S) batteries have been widely studied for their high theoretical energy density (2500 Wh kg$^{-1}$) and high specific capacity (1675 mAh g$^{-1}$) suitable for high energy density storage systems. However, some shortcomings of Sulfur limit the further development of Li-S batteries [14–17]. S has poor electrical conductivity and the intermediate product polysulfide generated in carbonate-based or ether-based batteries is readily soluble in electrolytes, leading to the formation of shuttle reaction, and that the capacity rapidly decays and volume expansion during the cycle [18–26]. Se and S belong to the VI A group, the conductivity of S is not nearly as good as that of Se(Se is $1 \times 10^{-3}$ S m$^{-1}$, S is $5 \times 10^{-28}$ S m$^{-1}$). Moreover, the volume capacity of Li-Se batteries is comparable favorably with that of Li-S batteries (3253 mAh cm$^{-3}$ versus 3467 mAh cm$^{-3}$) [27–30]. The high activity of Se is due to the presence of two active terminal atoms in the selenium chain, which can bind to other atoms [31, 32]. Therefore, Se combined with S can complement each other in terms of properties. However, the low theoretical specific capacity of Se (675 mAh g$^{-1}$) is not conducive to the rapid development of lithium-selenium batteries. Therefore, adjusting the ratio of S and Se can form novel S$_x$Se$_y$ composites, making complementarity between S and Se a feasible strategy as energy storage electrode...
materials for Li-ion batteries. Li-S$_2$Se$_x$ batteries exhibit electrochemical behaviors similar to those of Li-S and Li-Se batteries [29, 33, 34].

To enhance the loading and conductivity of active materials, various forms of carbon-based materials have been introduced to be compounded with the Se$_x$S$_y$ composites [14, 15, 27, 30, 32, 35–37]. These carbon-based materials are readily conductive, pore-size controlled and flexible, giving a reliable propagation path for ions and electrons, and they are effective in mitigating the volume expansion caused by the charging and discharging process. The use of selenium-sulfur composites as energy storage electrode materials for rechargeable lithium batteries was first proposed by Abouimrane’s team. In 2012, Abouimrane et al. [27], prepared Se-C and SeS$_2$-C composites from Se, SeS$_2$ and carbon nanotubes by ball milling and heat treatment, respectively, and applied them to lithium and sodium rechargeable batteries. Among them, the capacity of Li/Se$_{30}$S$_{54}$ battery remained 512 mAh g$^{-1}$ after 30 cycles at 50 mA g$^{-1}$, which was higher than that of the Li/Se-C battery at 394 mAh g$^{-1}$, indicating that the theoretical capacity of the Se$_x$S$_y$ electrode was better than that of the Se electrode. Fan et al. [15], designed and synthesized three-dimensional selenium sulfide@carbon nanotube arrays (Se$_x$S$_y$/VACNTs) by encapsulating and immobilizing large amounts of selenium sulphide (Se$_x$S$_{54}$) in vertically aligned carbon nanotubes (VACNTs). At 500 mA g$^{-1}$, the capacity of the Se$_x$S$_{54}$/M32/VACNTs reached 818 mAh g$^{-1}$ after 500 cycles, with an initial coulombic efficiency of 96%. Not only carbon nanotubes, but also mesoporous carbon materials are suitable for encapsulating Se$_x$S$_y$ composites [32, 35]. Sun et al. [14], fabricated Se$_{54}$/NMC composites with melting S, Se and nitrogen-doped mesoporous carbon (NMC), where the Se$_{54}$/NMC composites had an initial coulombic efficiency of 95.6% at 250 mA g$^{-1}$ and a remaining capacity of 883 mAh g$^{-1}$ after 100 cycles, and a capacity of 780 mAh g$^{-1}$ after 200 cycles. Some reports even add a protective shell on the outside of the mesoporous carbon. For instance, Li et al. [30], prepared a mesoporous carbon (CMK-3) framework encapsulated Se$_x$S$_y$ material (CMK-3/Se$_x$S$_{54}$/PDA) with a polydopamine (PDA) protective jacket using a melt-diffusion method. CMK-3/Se$_x$S$_y$/PDA cathodes discharge capacity of more than 1200 mAh g$^{-1}$ at 0.2 A g$^{-1}$, maintains 535 mAh g$^{-1}$ at a high magnification of 5 A g$^{-1}$ and can cycle 500 times, contributed by the advantages of Se$_x$S$_y$ and the unique host framework. Hu et al. [36] proposed the synthesis of 3DG-DLHC-Se$_{0.3}$S$_{0.7}$ composites by encapsulating Se$_{0.3}$S$_{0.7}$ in double-layer hollow carbon spheres (DLHCS) wrapped in three-dimensional graphene (3DG) shell. 3DG-DLHC-Se$_{0.3}$S$_{0.7}$ cathodes maintain a reversible 627 mAh g$^{-1}$ after 200 cycles at 0.2 A g$^{-1}$, with a good rate capability and a reversible capacity of 533 mAh g$^{-1}$ at 2 A g$^{-1}$ for 500 cycles with almost 100% Coulomb efficiency. In addition to the above materials, Luo et al. [38] also synthesized Se$_{0.7}$/CPAN composites as carbonized polycrylonitrile (CPAN) materials and Se$_2$S$_4$ in 600°C. Se$_{0.7}$/CPAN electrodes showed outstanding cycling and multiplicative performance due to the encapsulation of Se$_{0.7}$S$_4$ particles by the N-containing carbon ring structure after carbonization of PAN. The Se$_{0.7}$/CPAN composites remained a reversible capacity of 780 mAh g$^{-1}$ after 1200 cycles at 600 mA g$^{-1}$. When the current density is increased from 60 mA g$^{-1}$ to 6 A g$^{-1}$, the capacity was maintained at about half, indicating its superior rate capability.

In previous reports, the use of Se$_x$S$_y$ electrode materials in liquid batteries had been the most studied, and little research had been reported in solid-state batteries. Li et al. [37] obtained Se$_x$L$_1$PS$_y$ (x = 3, 2, 1 and 0.33) cathodes by ball milling Se$_x$ powder, Li$_1$PS$_y$ and acetylene black, in which the assembled Se$_{54}$/Li$_{10}$GeP$_{12}$S$_{6}$Li/S solid-state batteries put out more than 1100 mAh g$^{-1}$ at 50 mA g$^{-1}$, which was 98.5% of the theoretical capacity, and maintained excellent stability at 100 cycles. This demonstrates that Se$_x$S$_y$ solid solutions exhibit excellent electrochemical properties as cathodes materials, providing important ideas for all-solid-state battery applications. However, the synthesis and field loading of Se$_x$S$_y$ were mostly carried out by the traditional solid-phase melt diffusion method, which was a more complex and energy-consuming operational process. In addition, there are many types of composites in Se$_x$S$_y$, and previous reports have demonstrated that different S/Se ratios exhibit different electrochemical properties and different mechanisms in different electrolytes [39]. Therefore, it is necessary to explore new Se$_x$S$_y$ electrode materials.

Here, amorphous a-3DG/Se$_{4x}$S$_{3y}$ composites were prepared by in situ synthesis, and then the a-3DG/Se$_{4x}$S$_{3y}$ composites are hydrothermally treated to obtain crystalline c-3DG/Se$_{4x}$S$_{3y}$ composites. This is a novel method, unlike previous studies using ball milling and high-temperature sintering, and the process is simple and easy to operate. The obtained a-3DG/Se$_{4x}$S$_{3y}$ composites and c-3DG/Se$_{4x}$S$_{3y}$ composites combined with a solid-state electrolyte 2LiIHPN–LiI that was easily liquefied by heat were assembled into solid-state Li-Se$_{4}$S$_{3}$ batteries. We performed a series of characterization and performance tests on the two materials and found that the electrochemical properties differed for different crystallinity. The results showed that changing the morphology of Se$_{4x}$S$_{3y}$ in 3DG/Se$_{4x}$S$_{3y}$ composites is promising to improve the performance of solid-state Li-Se$_{4}$S$_{3}$ batteries and give new synthetic ideas to other Se$_x$S$_y$ composites.
2. Experimental

2.1. Synthesis of 3DG/Se_{4.7}S_{3.3} composites

The schematic illustration for prepare production process of 3DG/Se_{4.7}S_{3.3} composites by in situ synthesis is illustrated in figure 1. Firstly, Graphene oxide (GO) dispersions were synthesized by an improved honeycomb method \[40\]. Based on a Se/S molar ratio of 4.7/3.3, appropriate amounts of Na_{2}S·9H_{2}O and selenium powder (99.99%, Sigma Aldrich) were dissolved in de-oxygenated deionised water and stirred for at least 6 h to obtain a dark brown solution. Add 1.65 ml 0.04 mmol ml\(^{-1}\) of above mixed solution and 1.65 ml 0.36 mmol ml\(^{-1}\) of Vc to 4.2 ml 3 mg ml\(^{-1}\) of GO dispersion successively and stir well. The resulting mixture was placed in an oven at 110 °C for 75 min, during which time the GO is reduced. It was cooled to room temperature and then washed with deionised water to remove impurities. After freezing, the a-3DG/Se_{4.7}S_{3.3} composites was dried in a vacuum freeze dryer for 12 h. Further, the a-3DG/Se_{4.7}S_{3.3} composites was placed in a reactor at 100 °C for 96 h. After natural cooling, it was dried to obtain c-3DG/Se_{4.7}S_{3.3} composites.

2.2. Synthesis of pure rGO

Add 1.65 ml of the deionised water and 1.65 ml 0.36 mmol ml\(^{-1}\) of Vc to 4.2 ml 3 mg ml\(^{-1}\) of GO dispersion successively and stir well. The resulting mixture was placed in an oven at 110 °C for 75 min and freeze-dried to obtain rGO.

2.3. Preparation of solid electrolyte LiIHPN-0.5LiI (SMC)

The synthesis of solid electrolyte LiIHPN-0.5LiI (SMC) was prepared by 3-hydroxypropionitrile (HPN) and high-purity lithium iodide crystals (LiI) in an anhydrous and dry glove box. The anhydrous LiI and HPN were mixed at a certain molar ratio (3:2), and the intense exothermic reaction is conducted at room temperature to form a yellowish solid-liquid mixture. The mixture is heated and stirred for 24 h at 120 °C to fully react, and a homogeneous sticky brown-yellow electrolyte is obtained, which is solid after cooling \[41\].

2.4. Material characterizations

The microstructure of 3DG/Se_{4.7}S_{3.3} composites were studied by scanning electron microscope (SEM) and HRTEM. The 3DG/Se_{4.7}S_{3.3} composites were examined by x-ray diffraction (XRD) (Panalytical X’Pert x-ray diffractometer, Netherlands) with Cu Ka radiation. The Raman spectrum was collected on a Raman spectrometer (Horiba Jobin Yvon LabRAM HR800). Under a base pressure of 10^{-7} Pa, the chemical bonds of the sample were analyzed by x-ray photoelectron spectroscopy (XPS) (ThermoFisher, Escalab 250Xi) with an Al target. Under N2 atmosphere, determination of Se_{4.7}S_{3.3} in 3DG/Se_{4.7}S_{3.3} composites by thermogravimetric analysis (TGA, TA instrument Q600) at 25 ∼ 700 °C. The Brunauer–Emmett–Teller ( BET) method was used to analyze the material’s specific surface area and porosity, and the Micromeritics ASAP 2020 instrument was used to collect physical adsorption isotherms using nitrogen at liquid nitrogen temperature.

2.5. Electrochemical measurements

Assembly of Li-SMC-3DG/Se_{4.7}S_{3.3} solid state batteries, where lithium sheet (99.999% purity) was used directly as anode, 3DG/Se_{4.7}S_{3.3} is used as the cathodes, and SMC is used as electrolyte. In an anhydrous glove box, the SMC is melted at 120 °C to maintain its fluidity, so that the battery can be assembled in good contact with positive and negative electrode materials. After the electrolyte is cooled and solidified, the all-solid-state Li-SMC-3DG/Se_{4.7}S_{3.3} batteries can be obtained. The galvanostatic charge-discharge was tested by using Land CT-2001A Battery Tester (Wuhan, China) at 50 °C. The cyclic voltammetry (CV) was evaluated on CHI 660E Electrochemical Analyzer (Chen Hua Co., China) at a scan rate of 0.06 mV s\(^{-1}\). The EIS analysis were carried out using CHI 660C (Chen Hua Co., China) in the frequency range of 0.01 ∼ 1000 kHz.
a-3DG composites. The measured O 1s composites is 78.545 m² g⁻¹. Se₄.₇S₃.₃ composites showed some crystalline peaks on the XRD pattern, which corresponded to the peaks of the XRD spectra of the a-3DG surface area of a-3DG and the results were compared in range order in the amorphous carbon matrix. In contrast, the hydrothermally treated c-3DG functional groups on the rGO. The weight loss of pure rGO starts at around 120 °C to 480 °C, mainly the loss of oxygen-containing bonds are present, indicating essentially complete reduction of GO. In addition, the peaks of S 2p₁/₂(164.46 eV), S 2p₃/₂(167.25 eV) and Se 3p₁/₂(161.5 eV) overlap significantly, with larger areas of overlap for S 2p and Se 3p, indicating the formation of Se–S bonds in the 3DG/Se₄.₇S₃.₃ composites [38].

3. Results and discussion

The XRD spectra of the a-3DG/Se₄.₇S₃.₃ composites and c-3DG/Se₄.₇S₃.₃ composites samples were recorded and the results were compared in figure 2(a). RGO showed a broad peak in the 2θ = 20° ~ 30° region, and the a-3DG/Se₄.₇S₃.₃ composites showed only (002) and (100) broad diffraction peaks, which are related to the short range order in the amorphous carbon matrix. In contrast, the hydrothermally treated c-3DG/Se₄.₇S₃.₃ composites showed some crystalline peaks on the XRD pattern, which corresponded to the peaks of Se₄.₇S₃.₃(JCPDS NO.01–071–0248), tentatively confirming the synthesis of 3DG/Se₄.₇S₃.₃ composites.

The N₂ adsorption/desorption isotherms and the corresponding pore size distributions of the rGO, a-3DG/Se₄.₇S₃.₃ and c-3DG/Se₄.₇S₃.₃ composites were shown in figure 2(b). Compared with rGO, the specific surface area of a-3DG/Se₄.₇S₃.₃ composites decreased from 486.05 m² g⁻¹ to 78.016 m² g⁻¹ and the pore volume decreased from 0.487 cm³ g⁻¹ to 0.257 cm³ g⁻¹. Analogously, the specific surface area of c-3DG/Se₄.₇S₃.₃ composites is 78.545 m² g⁻¹ and the pore volume is 0.202 cm³ g⁻¹. Both indicate that Se₄.₇S₃.₃ was encapsulated and penetrated into porous structure of 3DG. The pore size of all three is mainly concentrated around 4 nm.

Figure 2(c) showed the Raman spectra of the rGO and a-3DG/Se₄.₇S₃.₃ composites, with only two strong peaks observed at 1343.9 cm⁻¹ (D-band) and 1584.6 cm⁻¹ (G-band). In addition, the ratio of R(R = ID/IG) represented the degree of disorder in carbon materials [42]. The higher R-value, the more defects there are [43, 44]. The R-value of a-3DG/Se₄.₇S₃.₃ composites(0.87) is greater than that of the rGO(0.78), indicating that Se₄.₇S₃.₃ was successfully loaded into graphene and thus increases the defects [36, 45].

Two masses of a-3DG/Se₄.₇S₃.₃ composites were prepared and the thermogravimetric analysis (TGA) curves determined the content of Se₄.₇S₃.₃ to be 45 wt% and 75 wt%, respectively, as shown in figure 2(d). This weight loss was mainly due to sublimation of the active material, but is also related to the loss of oxygen-containing functional groups on the rGO. The weight loss of pure rGO starts at around 120 °C, and the heat loss of a-3DG/Se₄.₇S₃.₃ ranges from 150 °C to 480 °C, mainly the loss of selenium and sulfur.

Figures 2(e)–(f) showed the x-ray photoelectron spectroscopy (XPS) results of the a-3DG/Se₄.₇S₃.₃ composites. The measured O 1s(531 eV), C 1s(283 eV), S 2p₁/₂(161 eV) and Se 3d(54 eV) are consistent with the elements measured in figure 2(d). In the C 1s spectrum (figure 2(e)), only small amounts of C–O and C=O bonds are present, indicating essentially complete reduction of GO. In addition, the peaks of S 2p₁/₂(164.46 eV), S 2p₃/₂(167.25 eV) and Se 3p₁/₂(161.5 eV) overlap significantly, with larger areas of overlap for S 2p and Se 3p, indicating the formation of Se–S bonds in the 3DG/Se₄.₇S₃.₃ composites [38].
Figure 3 showed the morphological structures of a-3DG/Se_{4.7}S_{3.3} composites and c-3DG/Se_{4.7}S_{3.3} composites, respectively. A-3DG/Se_{4.7}S_{3.3} composites showed a three-dimensional network cross-linked structure with no obvious aggregation of Se_{4.7}S_{3.3} particles (figure 3(a)). Furthermore, the TEM of figure 3(b) also observed only the folded structure of graphene and the selected area electron diffraction (SAED) pattern of a-3DG/Se_{4.7}S_{3.3} demonstrated the amorphous nature of Se_{4.7}S_{3.3}. The elemental mapping (figures 3(c)–(d)) clearly showed the homogeneous distribution of selenium-sulfur in 3DG. In the c-Se_{4.7}S_{3.3} composites, irregular crystalline particles with uniform particle size can be observed on 3DG, as shown in figures 3(e)–(f). The elemental distribution map also confirmed that the particles contain elements of S and Se (figure 3(g)), which may be the result of hydrothermal treatment driving grain growth.

To test the lithium storage performance of 3DG/Se_{4.7}S_{3.3} in different morphologies, we assembled the batteries using lithium foil as the anode and all the following electrochemical tests were carried out at a constant temperature of 50 °C. Figures 4(a)–(b) exhibited cyclic voltammetry (CV) of the a-3DG/Se_{4.7}S_{3.3} and c-3DG/Se_{4.7}S_{3.3} cathodes at a scan rate of 0.06 mV s^{-1} over the voltage range 1.6–2.7 V, respectively. A large irreversible capacity in the first cycle was observed due to an electrochemical activation process during the first lithiation [46]. In the second cycle, two reduction peaks (2.12 and 2.01 versus 2.15 and 2.04) and two oxidation
peaks (2.45 and 2.17 versus 2.40 and 2.13) were observed for both a-3DG/Se4.7S3.3 and c-3DG/Se4.7S3.3 cathodes, which may be related to the S/Se, Li2Sx/Li2Se, and Li2S/Li2Se inter reversible transformations. The retention of the cathodic and anodic peaks in further cycles indicates the reversibility of the cathodes [15].

Figures 4(c)–(d) displayed the capacity of Li-SMC-3DG/Se4.7S3.3 batteries at different C-rates. The a-3DG/Se4.7S3.3 cathodes (figure 4(c)) showed the initial capacity values of 972, 932, 890, 831, 755 and 706 mAh g\(^{-1}\) at rates of 1/8 C, 1/4 C, 1 C, 2 C, 4 C and 7 C respectively. Similarly, the first discharge capacity of c-3DG/Se4.7S3.3 cathodes (figure 4(d)) is 584, 557, 491, 377, 333 mAh g\(^{-1}\) at rates of 1/8 C, 1/4 C, 1 C, 2 C, 4 C, respectively. When at the 1/2 C rate, the a-3DG/Se4.7S3.3 and c-3DG/Se4.7S3.3 cathodes exhibit initial capacities of 926 mAh g\(^{-1}\) and 523 mAh g\(^{-1}\) (1 C = 899 mAh g\(^{-1}\)) respectively. At the end of 60 cycles, the Coulometric efficiencies remained above 95% and 97%, respectively (figure 4(e)), while the capacity attenuation of c-3DG/Se4.7S3.3 cathodes was slower than that of a-3DG/Se4.7S3.3 cathodes in subsequent cycles. This may be related to the particle size of the active material, the amorphous form of Se4.7S3.3 had a larger specific surface area and was more active but at the same time easier for the reaction process to dissolve in the electrolyte [47, 48].

To further investigate the electrochemical performance of the a-3DG/Se4.7S3.3 cathodes and the c-3DG/Se4.7S3.3 cathodes, electrochemical impedance spectroscopy (EIS) analysis was performed before the cycle, the 5th cycle and the 20th cycle, respectively. The experimental data were fitted using ZView software, and the fitted Nyquist plots are shown in figures 5(a)–(b), and the corresponding equivalent circuits were shown in figure 5(c). Where R0 corresponds to the electrolyte resistance, Rr represents the electrode/ electrolyte interface resistance, corresponding to the semicircle that appears at high frequencies, Rct is the charge transfer resistance, corresponding to the semicircle that appears at medium frequencies, and W1 belongs to the lithium ion diffusion resistance, corresponding to the straight line at low frequencies [38, 49]. As can be seen from the fitting data in table 1, the a-3DG/Se4.7S3.3 cathodes and the c-3DG/Se4.7S3.3 cathodes used the same electrolyte, so the variation of the R0 value remains basically the same. Before cycling, the Rr and Rct of a-3DG/Se4.7S3.3 cathodes are much lower than those of c-3DG/Se4.7S3.3 cathodes as a whole, so the initial discharge capacity of a-3DG/Se4.7S3.3 cathodes was higher, probably due to the homogeneous contact of the amorphous Se4.7S3.3 on the 3D graphene, which increased the electron transfer rate to the electron interface. However, the Rr values of c-3DG/Se4.7S3.3 cathodes decreased in the 5th and 20th cycle, while the Rct did not change much, indicating that the interface formation of c-3DG/Se4.7S3.3 cathodes had stabilized, thus explaining the better cycling stability of c-3DG/Se4.7S3.3 cathodes than a-3DG/Se4.7S3.3 cathodes in figure 4(e) [50, 51]. In contrast, amorphous Se4.7S3.3 tended to agglomerate compared to large particles, leading to a sharp decrease in specific surface area, which hinders ion transport and leads to slow transport reaction kinetics and sharp capacity decay [52, 53].

**Table 1.** The fitting results of the electrochemical impedance spectroscopy of a-3DG/Se4.7S3.3 and c-3DG/Se4.7S3.3 cathodes.

|                   | a-3DG/Se4.7S3.3 | c-3DG/Se4.7S3.3 |
|-------------------|-----------------|-----------------|
| Rs (Ω)            | 51.09           | 51.78           |
| Rr (Ω)            | 2.15            | 48.11           |
| Rct (Ω)           | 4.90            | 10.68           |
| Before            |                 |                 |
| 5th               | 61.12           | 57.91           |
| 20th              | 77.14           | 78.81           |

![Figure 5](image-url). The Nyquist plots of before the cycle, the 5th cycle and the 20th cycle (a) a-3DG/Se4.7S3.3 and (b) c-3DG/Se4.7S3.3 cathodes (c) the equivalent circuit.
4. Conclusions

In summary, amorphous a-3DG/Se$_{4.7}$S$_{3.3}$ composites is synthesized by in situ synthesis and crystalline c-3DG/Se$_{4.7}$S$_{3.3}$ composites is synthesized by hydrothermal reaction method. The presence of 3DG/Se$_{4.7}$S$_{3.3}$ composites is further confirmed by Raman, XRD, XPS, SEM and TG characterisation. The 45 wt% a-3DG/Se$_{4.7}$S$_{3.3}$ composites and the c-3DG/Se$_{4.7}$S$_{3.3}$ composites are assembled into batteries for electrochemical performance testing. The experimental results show that the a-3DG/Se$_{4.7}$S$_{3.3}$ cathodes have the advantage of high capacity and high current capacity. It can put out initial capacity of 890 mAh g$^{-1}$ at 1C and 706 mAh g$^{-1}$ at a high current density of 7C. C-3DG/Se$_{4.7}$S$_{3.3}$ cathodes can only reach a capacity of 523 mAh g$^{-1}$ at 1/2C, but the capacity retention in subsequent cycles is better than that of a-3DG/Se$_{4.7}$S$_{3.3}$ cathodes. Clearly, our work provides a simple synthetic idea for the study of new Se$_X$S$_Y$ electrode materials, which also lays the foundation for the subsequent study of the mechanism of different morphological Se$_X$S$_Y$ composites in solid electrolytes.

Acknowledgments

The authors acknowledge support from the National Natural Science Foundation of China (NO.2170031075).

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Zhongli Shen © https://orcid.org/0000-0001-6968-5296

References

[1] Zhou L, Zhang K, Hu Z, Tao Z, Mai L, Kang Y-M, Chou S-L and Chen J 2018 Advanced Energy Materials 8 1701415–1701415
[2] Meng J, Guo H C, Niu C J, Zhao Y L, Xu L, Li Q and Mai L Q 2017 Joule 1 522–47
[3] Anwar A W, Majeed A, Iqbul N, Ullah W, Shuaib A, Byas U, Bibi F and Rafique H M 2015 Journal of Materials Science & Technology 31 699–707
[4] Jiang L L, Cheng X B, Peng H J, Huang J Q and Zhang Q 2019 eTransportation 2 100033–100033
[5] Zhang H, Tian Y H, Wang S F, Peng J Y, Hang C J, Wang C X, Ma J X, Hu X Y, Zheng Z and Dong H J 2021 Chemical Engineering Journal 426 131438
[6] Zhang H, Tian Y H, Wang S, Huang Y L, Wen J Y, Hang C J, Zheng Z and Wang C X 2020 Chemical Engineering Journal 399 125075
[7] Nirmale T C, Kale B B and Varma A J 2017 International Journal of Biological Macromolecules 103 1032–43
[8] Choubey P K, Chung K S, Kim M S, Lee J C and Srivastava R R 2017 Minerals Engineering 110 104–21
[9] Zeng X L, Li H J and Liu L L 2015 Renewable & Sustainable Energy Reviews 52 1759–67
[10] Choi N S, Chen Z, Freunberger S A, Ji X, Sun Y K, Amine K, Yushin G, Nazar L F, Cho J and Bruce P G 2012 Angewandte Chemie International Edition 51 9994–10024
[11] Kim W, Lee J, Lee S, Eom K, Pak C and Kim H J 2020 Applied Surface Science 512 145632–145632
[12] Ellis B L, Lee K T and Nazar L I F 2010 Chemistry of Materials 22 691–714
[13] Goodenough J B and Kim Y 2009 Chemistry of Materials 22 587–603
[14] Sun F, Cheng H, Chen J, Zheng N, Li Y and Shi J 2016 ACS Nano 10 8289–98
[15] Fan H N, Chen S L, Chen X H, Tang Q L, Hu A P, Luo W B, Liu H K and Dou S X 2018 Advanced Functional Materials 28 1805018–1805018
[16] Bresser D, Passerini S and Scrosati B 2013 Chemical Communications 49 10345–62
[17] Fang R, Zhao S, Sun Z, Wang D W, Cheng H M and Li F 2017 Advanced Materials 29 1608623–1608623
[18] Manthiram A, Fu Y, Chng S H, Zu C and Su Y S 2014 Chemical Reviews 114 11751–87
[19] Cheng L, Curtis L A, Zavadil K R, Gewirth A A, Shao Y and Gallagher K G 2016 ACS Energy Letters 1 503–9
[20] Cheng X B, Zhang R, Zhao C Z and Zhang Q 2017 Chemical Reviews 117 10403–73
[21] Jung S C and Han Y K 2016 Journal of Power Sources 325 495–500
[22] Li L, Hou L, Cheng J, Simmons T, Zhang F, Zhang L T, Linhardt R J and Korotkar N 2018 Energy Storage Materials 15 388–95
[23] Li M, Carter R, Douglas A, Oakes L and Pint C L 2017 ACS Nano 11 4877–84
[24] Nanda S, Gupta A and Manthiram A 2018 Advanced Energy Materials 8 1801556–1801556
[25] Nazar L F, Cuisinier M and Pang Q 2014 MRS Bulletin 39 436–42
[26] Zhang S S 2013 Electrochemical Communications 31 10–2
[27] Abouimrane A, Dambournet D, Chapman K W, Chupas P J, Weng W and Amine K 2012 Journal of the American Chemical Society 134 4505–8
[28] Cui Y, Abouimrane A, Lu J, Bolin T, Ren Y, Weng W, Sun C, Maroni V A, Heald S M and Amine K 2013 Journal of the American Chemical Society 135 8047–56
[29] Yang C P, Yin Y X and Guo Y G 2015 The Journal of Physical Chemistry Letters 6 256–66
[30] Li Z, Zhang J T, Wu H B and Lou X W 2017 Advanced Energy Materials 7 1700281–1700281
[31] Zeng L, Yao Y, Shi J, Jiang Y, Li W, Gu L and Yu Y 2016 Energy Storage Materials 5 50–7
[32] Wei Y, Tao Y, Kong Z, Liu L, Wang J, Qiao W, Ling L and Long D 2016 Energy Storage Materials 5 171–9
[33] Xu G-L, Liu J, Amine R, Chen Z and Amine K 2017 ACS Energy Letters 2 605–14
[34] Li S, Zhang W, Zeng Z, Cheng S and Xie J 2020 Electrochemical Energy Reviews 3 613–42
[35] Zhang Z A, Jiang S F, Lai Y Q, Li J M, Song J X and Li J 2015 Journal of Power Sources 284 95–102
[36] Hu J, Zhang C and Zhang L 2019 Journal of Alloys and Compounds 806 146–52
[37] Li X et al 2019 Advanced Materials 31 e1808100
[38] Luo C, Zhu Y, Wen Y, Wang J and Wang C 2014 Advanced Functional Materials 24 4082–9
[39] Du H, Feng S, Luo W, Zhou L and Mai L 2020 Journal of Materials Science & Technology 55 1–15
[40] By William S, Hummers J and Richard E O 1958 Journal of the American Chemical Society 80 1339–1339
[41] Liu F C, Shadike Z, Wang X F, Shi S Q, Zhou Y N, Chen G Y, Yang X Q, Weng L H, Zhao J T and Fu Z W 2016 Inorganic Chemistry 55 6504–10
[42] Ferrari A C et al 2006 Physical Review Letters 97 187401
[43] Maitra T, Sharma S, Srivastava A, Cho Y K, Madou M and Sharma A 2012 Carbon 50 1753–61
[44] Ra E J, An K H, Kim K K, Jeong S Y and Lee Y H 2003 Chemical Physics Letters 413 188–93
[45] Wang L, Deng J, Deng J T, Fei Y H, Fang Y and Hu Y H 2020 Journal of Materials Chemistry A 8 13385–92
[46] Zhang Y G, Zhao Y, Bakenov Z, Konarov A and Chen P 2014 Journal of Power Sources 270 326–31
[47] Jin J, Tian X, Srikanth N, Kong L B and Zhou K 2017 Journal of Materials Chemistry A 5 10110–26
[48] Zhou X M, Gao P, Sun S C, Bao D, Wang Y, Li X B, Wu T T, Chen Y J and Yang P P 2013 Chemistry of Materials 27 6730–6
[49] Takami N, Ohsaki T and Inada K 2019 Journal of The Electrochemical Society 139 1849–54
[50] Balakumar K and Kalaiselvi N 2017 Carbon 112 79–90
[51] Deng Z F, Zhang Z A, Lai Y Q, Liu J, Li J and Liu Y X 2013 Journal of The Electrochemical Society 160 A553–8
[52] Fan J and Fedkiw P S 1998 Journal of Power Sources 72 165–73
[53] Ramireddy T, Xing T, Rahman M M, Chen Y, Dutercq Q, Gunzelmann D and Glushenkov A M 2015 Journal of Materials Chemistry A 3 5572–84