Supercritical CO₂-assisted fabrication of CeO₂ decorated porous carbon/sulfur composites for high-performance lithium sulfur batteries

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Abstract

Alleviating shuttle effect is vital to improve the electrochemical performance of lithium–sulfur (Li–S) batteries. Herein a nanosheet-like porous carbon (NSPC) with unique hierarchically porous structure and excellent electrical conductivity was synthesized as a host material of cathode, and highly-dispersed, electrochemically active CeO₂ nanoparticles as well as sulfur was deposited onto NSPC subsequently through supercritical CO₂-assisted processing to fabricate CeO₂ decorated porous carbon/sulfur (C/CeO₂/S) composites. In testing Li–S batteries, the C/CeO₂/S material shows an initial capacity of 1538 mAh g^{−1} at 0.1 C, higher than that of C/S (1194 mAh g^{−1}). The material also exhibits excellent cycling stability (~729 mAh g^{−1} at 0.5 C after 300 cycles). The gas-like viscosity, diffusivity and surface tension of supercritical CO₂, facilitate highly dispersed loading of CeO₂ and sulfur on porous carbon with less agglomeration and more intimate contact with carbon to achieve higher conductivity and utilization efficiency. Moreover the electrocatalytic material CeO₂ promotes and stabilizes the redox reaction of polysulfide species.

Keywords Supercritical CO₂ · CeO₂ · Porous carbon · Lithium sulfur battery

1 Introduction

With the soaring of electronic applications in various fields, there is tremendous need to develop new energy storage equipments with high energy density, high specific capacity and long service life [1, 2]. In recent years, Li–S batteries are deemed to be one of the most promising candidates owing to their high theoretical specific capacity (1675 mAh g^{−1}) and energy density (2500 kW kg^{−1}) [3, 4]. However, the commercialization of Li–S batteries is hindered by the insulating property of sulfur and lithium sulfides, the shuttle effect arising from the high solubility of polysulfides Li₂S_x (2 < x ≤ 8) in electrolytes, and volumetric changes during charging/discharging [5, 6]. To solve these

problems, tremendous effort has been done on the design of nanostructured materials to serve as sulfur host.

High conductivity, appropriate porosity and high mechanical strength are essential for nanostructured sulfur host materials [7]. Various carbon materials, for instance microporous carbon [8], mesoporous carbon [9], hierarchical porous materials [10], carbon nanotubes [11, 12] and carbon fibers [13], have been used as host materials of sulfur in Li–S batteries. However, the weak interaction between polar lithium polysulfides and non-polar porous carbon materials could still result in severe shuttle effect, e.g., the irreversible loss of lithium polysulfides from electrodes and therefore significant decay of Li–S battery over long-term cycling [14]. Typically, metal oxide has a very

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polar surface. Compared to porous carbon materials, metal oxide has the advantage of having more polar sites to adsorb lithium polysulfides. Cui et al. [18] combined theoretical calculations with adsorption experiments to demonstrate the existence of a single layer of chemisorption between metal oxide and lithium polysulfides. The adsorption strength of polysulfides by various metal oxides was discussed. The results showed that MgO, CeO₂ and La₂O₃ exhibited enhanced electrochemical performance. Due to the stronger adsorption of metal oxide for polysulfides, loading metal oxide (such as Al₂O₃ [15], MnO₂ [16], TiO₂ [17]) onto nanostructured carbon host could not only mitigate the shuttle effect efficiently, but also offset the disadvantages of poor electrical conductivity of metal oxides.

Metal oxide loading onto nanoporous carbon materials can be conducted through hydrothermal/solvothermal process [19, 20], precipitation [21], pyrolysis method [22], and incipient wetness impregnation [23], etc. However, it is still challenging to achieve uniform loading of metal oxides within complicated nanoporous structure as well as more intimate interaction of metal oxide with carbon substrate [24]. Recently, as a unique solvent with hybrid properties of “gas-like” and “liquid-like”, supercritical carbon dioxide (scCO₂) has received great attention [25] in materials synthesis. ScCO₂ (T_c = 31.1 °C, P_c = 7.38 MPa) exhibits high diffusivity, low viscosity, zero surface tension and powerful wettability [24, 26], therefore allowing for highly dispersed deposition of metal oxides into nanoporous structure of carbon with more intimate interaction in between, favoring improved utilization of active material in Li–S batteries. The same advantages could also be achieved if scCO₂ is used as solvent to impregnate sulfur into porous carbon host materials.

To alleviate the shuttle effect of Li–S batteries, herein a nanosheet-like porous carbon (NSPC) was synthesized with corn flour as carbon source, and CeO₂ and sulfur were loaded on NSPC stepwisely using scCO₂-assisted deposition

to obtain Li–S batteries cathode material, CeO₂ decorated porous carbon/sulfur (C/CeO₂/S) composites. The preparation of C/CeO₂/S was shown in Scheme 1. CeO₂ could provide a strong absorption to polysulfides as well as excellent electrocatalytic activity, facilitating the redox reactions of polysulfides during charging/discharging. NSPC would not only provide porous structure for sufficient accommodation and effective confinement of sulfur, ample channels for lithium ion transportation, but also improve the electrical conductivity of CeO₂. Moreover, the scCO₂-assisted deposition is beneficial for more highly dispersed loading of CeO₂ and sulfur, which might improve the utilization efficiency of active materials. Compared with the traditional methods, the preparation of Li–S batteries cathode material by scCO₂ deposition is beneficial for the sulfur nanoparticles to enter the porous channels with high aspect ratio and achieve high dispersion. ScCO₂ deposition is also advantageous for improving the dispersibility of CeO₂ on NSPC with complicate surface features and controlling the size of CeO₂ nanoparticles, which is difficult to achieve by conventional methods. To the best of our knowledge, this is the first time that metal oxides deposited by scCO₂-assisted process have been utilized in Li–S batteries, with the potential to enable improved cycling performance and rate performance.

2 Experiment

2.1 Preparation of NSPC

NSPC was synthesized using corn flour and KOH. Typically, corn flour was pre-carbonized by heating in N₂ atmosphere at 450 °C for 3 h. Afterwards 2 g of pre-carbonized solid was mixed with 40 ml of 5 mol/L KOH aqueous solution, and the mixture was dried at 110 °C for 8 h to evaporate water. The resultant solid was chemically

Scheme 1 Schematic illustration of the synthesis process for C/CeO₂/S

activated in a tubular furnace under nitrogen atmosphere at 800 °C for 2 h. The obtained powder was washed with dilute HCl solution and then deionized water until the eluate reached a pH value of 7. The powder was finally dried at 100 °C for 12 h in a vacuum oven.

2.2 Preparation of C/CeO₂

CeO₂ was loaded onto NSPC through scCO₂-assisted deposition. In a 50 ml high-pressure reactor, 0.1 g of Ce(NO₃)₃·6H₂O, 4 ml of ethanol and 0.2 g of NSPC was mixed to form a slurry and sealed. The reactor was then charged with 6.0 MPa of CO₂ and heated at 150 °C for 2 h. Subsequently the reactor was cooled down to ambient temperature and depressurized slowly. The powder retained in the reactor was collected and calcinated in flowing N₂ at 600 °C for 2 h. The solid after calcination was labeled as C/CeO₂. For comparison, CeO₂ was loaded onto NSPC using pyrolysis method, named C/CeO₂-p.

2.3 Preparation of C/CeO₂/S

C/CeO₂/S was prepared according to a similar process of preparing C/CeO₂. 0.2 g of C/CeO₂ and 0.4 g of sulfur were milled for 1.5 h and then transferred to a 50 ml high-pressure reactor. The reactor was then filled with 6.0 MPa of CO₂, heated at 100 °C for 3 h with agitation applied, and discharged at room temperature to harvest black powder, which was further treated at 250 °C for 1 h under N₂ atmosphere to remove sulfur on the external surface. The product was denoted as C/CeO₂/S. For comparison, sulfur was also loaded onto NSPC directly using the identical process, giving rise to composite material C/S.

2.4 Electrochemical measurements

To compare electrochemical performance of C/S and C/CeO₂/S as cathode materials of Li-S battery, CR2025 type cells were fabricated and tested. The cathode slurry was constituted by dispersing 10 wt% of acetylene black, 80 wt% of active materials and 10 wt% of PVDF in NMP solvent. The mixed slurry was pasted on aluminum foil and then dried in vacuum at 90 °C for overnight. Sulfur loading is approximately 2.8 mg cm⁻². Lithium metal and Celgard 2400 polyethylene were served as counter electrode and separator, respectively. The electrolyte consisted of 1.0 M lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) dissolved in 1,3-dioxolane and 1,2-dimethoxyethane (1:1 by volume) solution with 1 wt% LiNO₃ as additive. The amount of electrolyte used to assemble a cell is 20 μL. Fresh coin cells were assembled in glove box under argon atmosphere. The galvanostatic discharge/charge tests were carried out with Battery Test System 7.5.x (NEWARE,

China) between 1.7 and 2.8 V versus Li⁺/Li⁰. Cyclic Voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements was performed on CHI660E (Shanghai Chenhua, China). EIS were measured in the frequency range of 100 m Hz–100 k Hz.

3 Results and discussion

The morphology and structural feature of NSPC were imaged by SEM and TEM. As shown in Fig. 1a and S1a, NSPC displays an irregular nanosheet-like structure which facilitates rapid ion diffusion and electron transfer [27, 28]. High-resolution TEM image (HRTEM) in Fig. 1b reveals exhibits the existence of numerous micropores in NSPC.

The TEM images of C/CeO₂ are shown in Fig. 1c, d. CeO₂ has been impregnated into NSPC as highly dispersed nanoparticles with approximate size of 3 nm. But for C/CeO₂-p, on the external surface of NSPC, there exist some obviously agglomerated CeO₂ nanoparticles with approximate size of 5 nm as shown in Fig. S1c and S1d. This indicates that supercritical CO₂ facilitate highly dispersed loading of CeO₂ on NSPC with less agglomeration than pyrolysis method. HRTEM images (inset in Fig. 1c and S1d) of the nanoparticles reveals a main interplanar lattice distance of 0.31 nm, which is match well with the (111) plane of CeO₂, implying the highly crystalline nature of the loaded CeO₂. As Fig. S1b indicates, the TEM image of C/S make clear that sulfur exists in a highly dispersed amorphous state after supercritical CO₂ treatment. Furthermore, as shown in Fig. 2e–g, the EDS mapping images of C/CeO₂/S demonstrate the uniform dispersion of C, S and Ce in the material.

The specific surface area and porous characteristics of NSPC and C/CeO₂/S were illustrated by nitrogen adsorption/desorption isotherms (Fig. 2a) and pore size distribution curves (Fig. 2b). NSPC displays a hybrid isotherm of type-I and type-IV according to the IUPAC, and causes steep uptakes at low relative pressure range ($P/P_0 < 0.1$), indicating a huge amount of micropores [29] which are beneficial to confine polysulfide dissolution and relocation [30]. In addition, the appearance of very narrow hysteresis loop within the P/P_0 range of 0.5 and 0.9 (type H4) reveals the existence of mesopores [31] which are facilitate the access of electrolyte [32]. BET specific surface area, which is as high as 2329.4 m² g⁻¹ for NSPC, dramatically decreases to 18.5 m² g⁻¹ after CeO₂ and sulfur loading, implying that CeO₂ and sulfur have been successfully incorporated into NSPC, which has been further demonstrated by the significant difference of pore size distribution profiles between NSPC and C/CeO₂/S. In addition, the sulfur content in C/CeO₂/S and C/S was measured through TGA method. As shown in Fig. S2, the TG curves indicate

Fig. 1 Morphological and structural characterizations of NSPC and C/CeO₂/S. **a** SEM images of NSPC. **b–d** TEM images of NSPC and C/CeO₂/S. **e–g** EDS mappings (C, S and Ce) of C/CeO₂/S

Fig. 2 **a** N₂ adsorption–desorption isotherms, and **b** pore size distributions of NSPC and C/CeO₂/S, respectively. **c** XRD patterns of S, NSPC, C/CeO₂, C/S and C/CeO₂/S. **d** Raman spectra of NSPC and C/CeO₂/S

that the sulfur content in C/CeO₂/S and C/S is 54 wt% and 59 wt%, respectively.

XRD patterns of S, NSPC, C/CeO₂, C/S and C/CeO₂/S materials are shown in Fig. 2c. For NSPC and C/S, a broad diffraction peak can be observed in the 20°–25° range, which is caused by the (002) plane of graphite [33]. However, this peak is covered by strong diffraction of CeO₂ in C/CeO₂ and C/CeO₂/S. Furthermore, different from the crystalline state of sulfur at normal temperature, no diffraction peak of S could be found in both C/S and C/CeO₂/S samples, indicating that sulfur exists in a highly dispersed amorphous state, which could improve the utilization of sulfur in the process of charging/discharging [34]. In addition, the XRD pattern also reveals that the sharp diffraction peaks of C/CeO₂ and C/CeO₂/S are in coincide with CeO₂ compound (JCPDS no. 34-0394).

The carbonization degree and structural features of NSPC and C/CeO₂/S were investigated by Raman spectroscopy. As shown in Fig. 2d, the D peak at 1347 cm⁻¹ and G peak at 1595 cm⁻¹ could be related to the disordered structures and graphite in-plane vibrations of carbon materials [27]. The I_D/I_G ratio of NSPC is 0.95, indicating the partially graphitic nature with a relatively good electronic conductivity [35]. In addition, the Raman spectrum of C/CeO₂/S also shows a peak at ~461 cm⁻¹, which is caused by the F_{2g} vibration of cerium oxide [36].

The surface chemical state of C/CeO₂/S was further confirmed by XPS analysis. In the full scan spectrum of Fig. 3a, the peaks in 228.4, 163.9, 284.6 and 531.9 eV can

be assigned to S_{2s}, S_{2p}, C_{1s} and O_{1s}, respectively. From the high-resolution XPS spectrum of Ce_{3d} (Fig. 3b), six peaks collected from CeO₂ are visible [37]. Furthermore, as displayed in Fig. 3c, four different peaks centering at 284.6, 285.1, 286 and 286.7 eV are consistent with C–C/C=C, C=O, C–O/C–S and O–C=O, respectively. In addition, the state of sulfur could be identified through peak fitting of S_{2p} spectrum in Fig. 3d. The S_{2p3/2} (163.9 and 164.3 eV) and S_{2p1/2} (165.1 and 165.5 eV) peaks could be attributed to S–S and S–O bonds [38].

The charge/discharge mechanism of prepared C/CeO₂/S and C/S materials in Li–S battery could be identified through cyclic voltammetry (CV). The CV curves of C/CeO₂/S and C/S cathodes with a potential window of 1.5–3.0 V at a scan rate of 0.1 mV/s are shown in Fig. S3a and S3b, respectively. The two cathodic peaks at 2.31 V and 2.08 V are respectively correspond to the conversion from S₈ to soluble long-chain polysulfides (Li₂S_x, 4 ≤ x < 8) and further reduction to low order Li₂S and Li₂S₂ [9]. One anodic peak near 2.46 V which is associated with the oxidation from Li₂S and Li₂S₂ to Li₂S₈ [7]. Besides, during the initial three CV cycles, the anodic peak potential of C/CeO₂/S shifts more slightly than C/S, ascribed to the catalytic effect of CeO₂ in the redox reaction [39]. Fig. S3c and S3d present the charge/discharge curves of C/CeO₂/S cathode after different cycles at 0.1 C and 0.5 C, respectively. As shown in Fig. S3c, two discharge plateaus and one charge plateaus match well with the two cathodic peaks and one anodic peak in CV curves. Even after 300 cycles at a high current

Fig. 3 **a** XPS spectra of C/CeO₂/S composites. **b** Ce_{3d}, **c** C_{1s} and **d** S_{2p} XPS spectra

density of 0.5 C, the charge/discharge plateaus still remain stable, illustrating that CeO_2 is favorable to improve the utilization of active materials [40].

The cycling performance of C/S and C/ CeO_2 /S at 0.1 C is described in Fig. 4a. The initial discharge capacity of C/ CeO_2 /S is 1538 mAh g^{-1} , and decreases to 929 mAh g^{-1} after 100 cycles. Compared with C/ CeO_2 /S cathode, the C/S cathode delivers a lower initial discharge capacity of 1194 mAh g^{-1} and decreases to 482 mAh g^{-1} after 100 cycles. The higher discharge capacity and better cycling stability of C/ CeO_2 /S can be ascribed to the adsorption effect of CeO_2 to lithium polysulfides [36]. The O^{2-} makes CeO_2 to have a strong polar surface, which is beneficial to enhance the interaction with Li_2S_x . Therefore, the addition of CeO_2 is advantageous for facilitating the Li_2S_x trapping and promoting the attachment of Li_2S_2 and Li_2S and improving the cycling stability of Li-S batteries.

To further explore the cycling stability of the C/ CeO_2 /S, the long-term cycling was conducted at 0.5 C (Fig. 4b). After 300 cycles, the specific capacity gradually decreased to 729 mAh g^{-1} , corresponding to high capacity retention of approximately 70%. Upon further increasing of cycling rate to 2.0 C and 5.0 C, the C/ CeO_2 /S still exhibits stable capacity and long cycle life (Fig. S4). The cycling performance of C/ CeO_2 /S at 2.0 C is presented in Fig. S4a. The initial discharge capacity reaches 730 mAh g^{-1} , and decreases to 561 mAh g^{-1} after 400 cycles, accompanied

with 0.058% capacity decay per cycle. The C/ CeO_2 /S cathode delivers stable cycling performance with the lower discharge capacities of 407 mAh g^{-1} at 5.0 C after 300 cycles with 74% capacity retention (Fig. S4b). This suggests that C/ CeO_2 /S as the cathode of Li-S battery could effectively mitigate shuttle effect. In addition, unlike most studies that conduct electrochemical tests in calorstats, this study was conducted in a real-world environment. The effects of day and night temperature differences lead to instability of Coulomb efficiency were inevitable.

Rate performances of the C/ CeO_2 /S and the C/S cathodes were compared under various current densities (Fig. 5a). The C/ CeO_2 /S cathode delivers a specific discharge capacity of 1404.6, 1076.1, 932.2 and 782.4 mAh g^{-1} at 0.1, 0.2, 0.5 and 1 C, respectively, higher than that of C/S cathode. When the current density returns to 0.1 C, the discharge capacities of the C/ CeO_2 /S can be recovered well to $1092.4 \text{ mAh g}^{-1}$. However, the C/S only retains 706.9 mAh g^{-1} of discharge capacity after multi-rate tests. Such remarkable improvement in the rate capability of the C/ CeO_2 /S indicates the importance of CeO_2 in adsorbing polysulfide and catalyzing redox reaction.

EIS measurement was employed to further reveal the improved electrochemical performance of C/ CeO_2 /S. Figure 5b exhibits the Nyquist plots of C/ CeO_2 /S and C/S cathodes before cycling and after 100 cycles. The Nyquist plots consist of one depressed semicircle in the

Fig. 4 **a** The cycling performance of C/S and C/ CeO_2 /S at 0.1 C rate for 100 cycles. **b** The cycling performance of C/ CeO_2 /S at 0.5 C rate for 300 cycles

Fig. 5 **a** The rate performances of two electrodes at different current densities. **b** Nyquist plots of C/S and C/CeO₂/S cathodes before cycling

high-frequency region and almost vertical-line in the low-frequency region. The depressed semicircle represents the charge transfer resistance (R_{ct}) [9]. The line in the low-frequency range correlates to the Warburg impedance, associated with Li ion diffusion into the active mass. For the C/CeO₂/S and C/S composites, the charge transfer resistances before cycling are 40.5 and 60.5 Ω , respectively, indicating a higher electrochemical activity of C/CeO₂/S composite material, which could be ascribed to that the CeO₂ can promote the charge transportation during the redox reactions [39]. As Fig. S5 indicates, after 100 cycles, the R_{ct} of C/CeO₂/S and C/S are 213.3 and 578.6 Ω , respectively, suggesting that the C/CeO₂/S delivers a better electrochemical contact and much lower polarization.

4 Conclusions

A new porous carbon material NSPC was prepared using corn flour as precursor and KOH as activator. A green strategy, supercritical CO₂-assisted deposition was developed to deposit CeO₂ nanoparticles and then impregnate sulfur on NSPC for the synthesis of cathode material C/CeO₂/S for Li-S batteries. Owing to the unique properties of scCO₂, the impregnated S is amorphous and highly dispersed, and the deposited CeO₂ nanoparticles, which are catalytically active as well as chemically adsorptive to polysulfide, contact intimately with carbon. Consequently, the shuttle effect of the assembled Li-S batteries is greatly depressed with the electrochemical performance being significantly improved. Compared with C/S, the C/CeO₂/S material exhibits a higher discharge capacity of 1538 mAh g⁻¹ in the first cycle of Li-S battery, and delivers a capacity of 729 mAh g⁻¹ with a capacity retention of approximately 70% after 300 cycles at 0.5 C.

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Compliance with ethical standards

Conflict of interest The author(s) declare that they have no competing interests.

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