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CTF-1 → CTF-1/S@155°C (sulfur Impregnation 155 °C)

We report the first time to construct sulfur electrode in Lithium-sulfur battery by using covalent-organic frameworks (COFs) as the host.

Journal Name

ARTICLE

Covalent-Organic Frameworks: Potential Host Materials for Sulfur Impregnation in Lithium-Sulfur Batteries

Huaping Liao, Huimin Ding, Bijian Li, Xinping Ai* and Cheng Wang*

Commercial development of lithium-sulfur (Li-S) batteries is severely hindered by their insufficient cyclability, due to the solution loss of lithium polysulfide intermediates generated during discharge processes. To overcome this problem, considerable efforts have been devoted to designing novel micro-/nanostructure host materials, aiming to trap soluble polysulfide within the network. Herein, we report a new approach to construct sulfur electrode by impregnating sulfur into the nanopores of covalent-organic frameworks (COFs). Our results clearly demonstrate that by using 2D COF as host material, e.g. CTF-1 (CTF: covalent triazine-based frameworks), the thus-prepared cathode can show a remarkable positive effect on the capacity retention of Li-S batteries. Considering the unique features of COFs, such as highly flexible molecular design and controllable pore size, this proof-of-principle research provides new opportunities for materials scientists for tailoring cathode materials in Li-S batteries.

Introduction

Electrical energy storage is one of the most critical needs in our daily life and will be more and more important in the future than ever before. As such, extensive research has been conducted on developing high-capacity electrode materials over the past few decades. Rechargeable lithium-sulfur (Li-S) batteries, due to their high theoretical gravimetric capacity (1672 mAh g^{-1}) and energy density (2600 Wh kg^{-1}) and low cost, have attracted[1] considerable attentions in recent years. However, even after decades of development, Li-S batteries still have not conquered[1] the marketplace due to a number of challenges. One is the electronic insulating nature of sulfur and Li$_2$S; the other one is the poor cycle stability due to the loss of the soluble lithium polysulfide intermediates generated during the discharge process. For the first one, it could be resolved by impregnation of sulfur into conductive matrix or addition of conducting additive. For the second one, a major strategy is to design[2] novel host materials with a large number of nano- or meso-pores to embed sulfur, aiming to trap soluble polysulfide within the nanodomains of porous framework. Various nanostructured materials, such as porous carbon,[3] conducting polymers,[4] metal-organic frameworks[5] and porous aromatic frame-works,[6] have been developed as sulfur container. For example, Nazar et al. reported[7] a carbon-sulfur cathode based on highly ordered CMK-3, which showed reversible capacity of over 1000 mAh g^{-1} after 20 cycles. However, the long-term cyclability is still a remaining issue for the most reported sulfur cathodes. As such, development of novel nanostructured materials with enhanced confined environment are highly desirable.

The optimal host material for sulfur impregnation should be lightweight and conductive and with high surface area. Covalent-organic frameworks (COFs),[8] a class of covalent crystalline porous polymers with permanent nanopores and composed of light-weight elements, could be potentially used as host materials. There are several advantages of using COFs to impregnate sulfur. Firstly, as a porous material, the existence of highly ordered nanopores and high surface area will help to trap sulfur and subsequent polysulfide intermediate during cycling process. Secondly, some reported COFs have already shown[9] semiconducting properties, which could improve the conductivity of sulfur. Finally, due to the highly flexible molecular design, COFs with different pore shape, size, and pore volume can be rationally synthesized and thus adapted to the specific needs of Li-S battery. Herein, we demonstrated for the first time that a sulfur cathode for Li-S battery could be prepared by using COFs as host. Our results clearly show that the sulfur loading within the nanopores of COFs could improve the cycle performance of Li-S batteries.

Since the seminal work published[10] by Yaghi and coworkers in 2005, COFs have emerged as a new molecular platform for designing promising organic materials and found many applications in gas storage,[11] catalysis,[12] optoelectronic device[13]
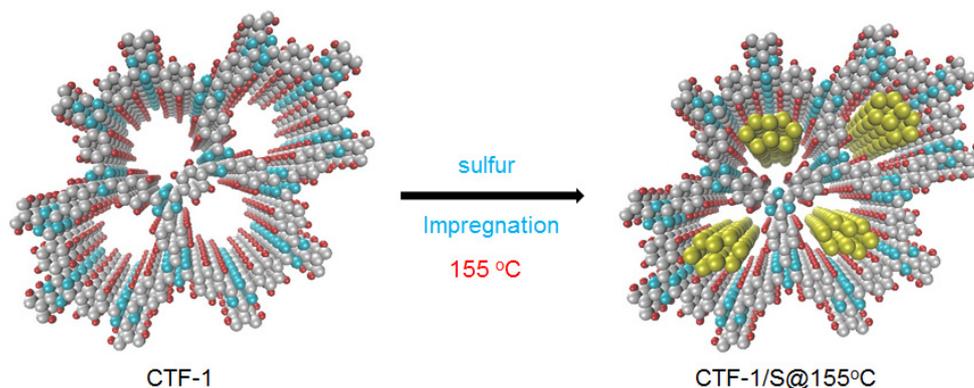
Fig. 1 Schematic diagram of composite synthesis by impregnation of molten sulfur from CTF-1. The carbon is shown in grey, the nitrogen in blue, the hydrogen in red, and the sulfur in yellow.

and energy storage.[14] Depending on the building block dimensions, COFs can be categorized into either two- (2D) or three-dimensional (3D) COFs. In 2D COFs, the 2D planar sheet can stack[15] further to form a layered eclipsed structure, which could exhibit electronic interactions between the different sheets and hence potentially become[9] a conductive materials. More significantly, the highly ordered nanoporous structure formed by the stacking of the 2D planar sheets in one direction can provide a large number of accessible voids for sulfur impregnating and thus considerably suppress the diffusive loss of soluble polysulfide intermediates in the nanodomains of the porous structure. Therefore, we focused our attention on 2D COFs. For a proof-of-concept, we chose CTF-1[16] (CTF: covalent triazine-based frameworks) as host material. CTF-1 can perform as a semiconductor[14a] and has an ordered structure with narrow pore size distribution. In addition, it shows excellent chemical and thermal stabilities. Therefore, CTF-1 seems to be a potential host for sulfur in Li-S batteries.

Results and discussion

CTF-1 is a porous crystalline polymeric frameworks consisting of benzene and triazine rings in 2D structure (Fig. 1). It was synthesized according to literature[16] by cyclotrimerization of 1,4-dicyanobenzene in molten $ZnCl_2$ at 400 °C. As measured by nitrogen-absorption isotherms (Fig. 2), CTF-1 shows a surface area of 789 m^2 g^{-1} with a total pore volume of 0.37 cm^3 g^{-1} and has a pore size of 1.23 nm, which are almost the same with literature.[16] The powder X-ray diffraction (XRD) pattern of CTF-1 displays two characteristic patterns with an intense peak at 2θ= ~7° and a broad XRD band at 2θ= ~27° (Fig. 3), which clearly demonstrates that CTF-1 has an eclipsed structure and the atoms of each layer are placed above their analogues in the next layer.

The composite of CTF-1 with sulfur was prepared by melt-diffusion strategy (Fig. 1). A 3:2 weight ratio mixture of CTF-1 and sulfur were mixed at room temperature and then heated at 155 °C for 15 h, which allows the diffusion of sulfur into the pores of CTF-1. As the pore size of CTF-1 is 1.7 times that of S_8 (~ 0.7 nm), the aggregation of S_8 is restricted in the channel, which favors the intimate contact between sulfur and CTF-1 wall. This resulting solid was labelled as CTF-1/S@155°C. For comparison, a simple physical mixture of CTF-1 and sulfur was also prepared, namely CTF-1/S@RT.
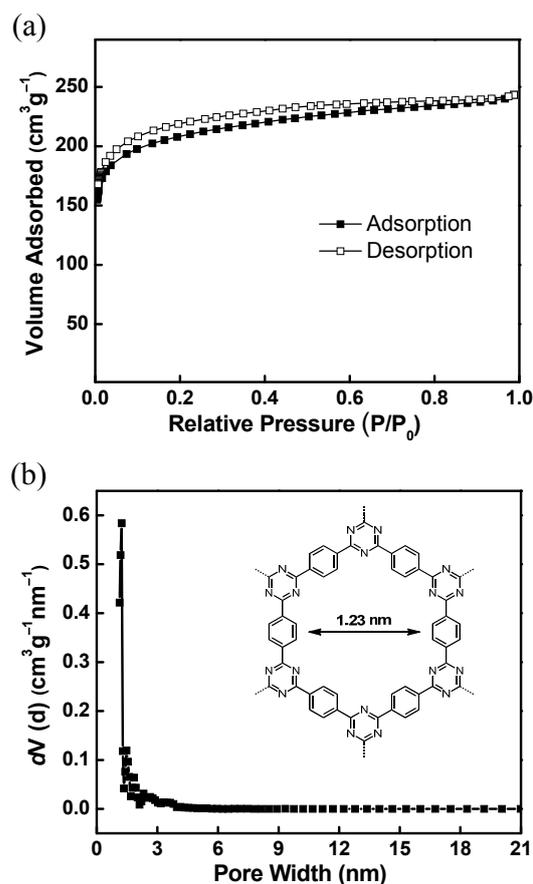

Fig. 2 Nitrogen sorption isotherms (a) and the pore size distribution (b) of CTF-1
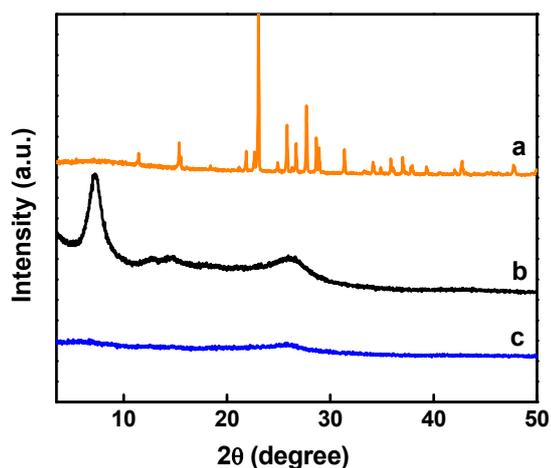
Fig. 3 Powder X-ray diffraction patterns ($\lambda = 1.54056$ Å) of sublimed ulfur (a), CTF-1 (b) and CTF-1/S@155ºC composite (c).

Fig. 3 shows the XRD patterns of elemental sulfur, CTF-1 and CTF-1/S@155ºC composite. Both sulfur and CTF-1 exhibit some intense peaks, however, the CTF-1/S@155ºC composite shows a featureless and weak band. Since CTF-1 is composed of light-weight elements, these signals disappeared in CTF-1/S@155ºC composite clearly demonstrated that the sulfur is highly dispersed inside the CTF-1 at the nanoscale and subnanoscale level.[17] Additionally, a sharp decrease in the specific surface area (from 789 $m^2 g^{-1}$ to 1.6 $m^2 g^{-1}$) and the pore volume (from 0.37 $cm^3 g^{-1}$ to 0.0036 $cm^3 g^{-1}$) was observed (See Fig. S2, ESI†), which further confirmed that the sulfur has successfully diffused into the pores of CTF-1 and the pores are almost completely occupied by sulfur.

The SEM image and the corresponding elemental sulfur mapping within CTF-1/S@155ºC are shown in Fig. 4, respectively. The sulfur mapping clearly demonstrates that sulfur is homogeneously distributed within CTF-1. The XPS spectrum of CTF-1/S@155ºC was shown in Fig. S3†. Upon impregnation of sulfur into CTF-1, the S2p binding energy of CTF-1/S@155ºC (164.1 and 165.3 eV) is almost the same as that of element sulfur (164.0 and 165.2 eV, see Fig. S4†), which means there is no chemical interaction between CTF-1 and sulfur.[18] Furthermore, thermal gravimetric analysis (TGA) shows that the sulfur loading in the composite is ~34 wt.% (see Fig. S5†).
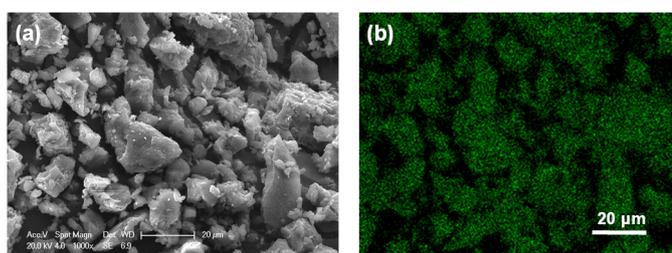

Fig. 4 SEM image (a) and the corresponding elemental mapping of sulfur (b) for CTF-1/S@155ºC composite.

To test the electrochemical performance, experimental coin cells using a metallic Li anode were assembled. All of the capacity values are calculated on the basis of sulfur mass. Each cell was duplicated to ensure the repeatable of the results. The contribution of CTF-1 to the total capacity is very little in the voltage range used in our work (see Fig. S6†).

Fig. 5a shows the discharge-charge curves for a typical CTF-1/S@155ºC cathode at a current rate of 0.1 C (1 C = 1680 mA g^{-1}) in the voltage range of 1.1–3.0 V. As observed, the CTF-1/S@155ºC cathode gave two staged potential profile with

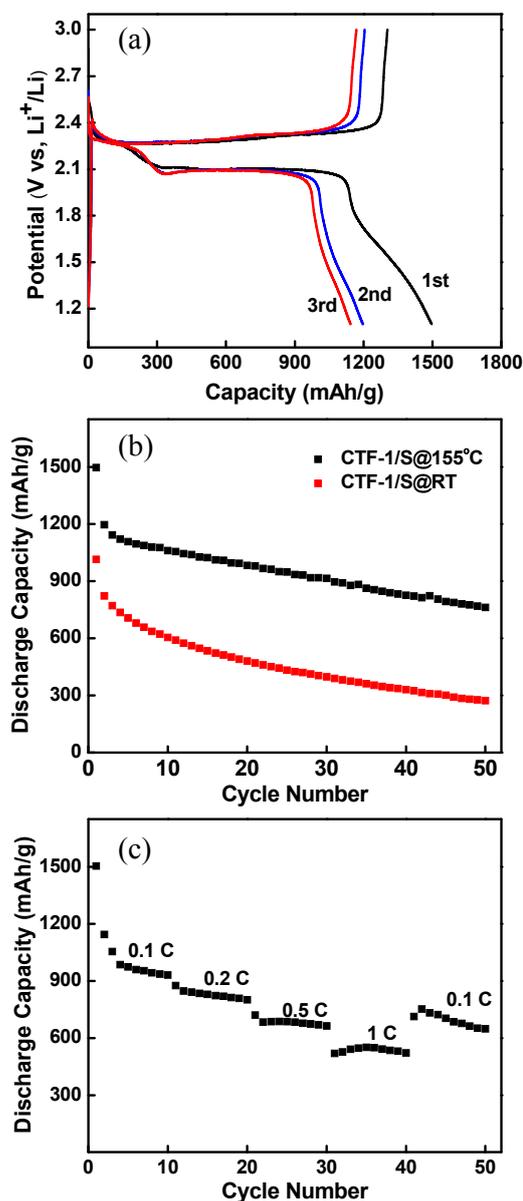**Fig. 5** (a) galvanostatic discharge and charge profiles of CTF-1/S@155ºC composite at 0.1 C rate; (b) cycling performance of CTF-1/S@155ºC and CTF-1/S@RT at 0.1 C rate; (c) discharge capacity for the CTF-1/S@155ºC composite at different rates. The voltage range used was between 1.1 and 3.0 V vs Li and the electrolyte was 1 M lithium bis(trifluoromethane sulfonyl)imide in dimethoxyethane and 1,3-dioxolane (1:1, v:v).

a short plateau at a higher potential of 2.3 V and a long plateau at a lower potential of ~ 2.1 V, corresponding to the first reduction of sulfur to lithium polysulfides (Li_2S_n, 2<n<8) and the further reduction of polysulfides to solid lithium sulfides Li_2S_2 and Li_2S, respectively. In the following charge process, the CTF-1/S@155°C cathode showed a single charge plateau at a potential of ~ 2.3 V, characterizing oxidation potential of Li_2S_2 and Li_2S to Li_2S_n (2<n<8) and eventually to S_8. These electrochemical behaviors are well in consistent with the cyclic voltammetry (CV) features of the CTF-1/S@155°C composite (see Fig. S7†). During the first cycle, the composite cathode delivers a discharge capacity of 1497 mAh g^{-1} and a charge capacity of 1304 mAh g^{-1}. From Fig. 5a, it can also be found that the potential hysteresis between discharge and charge is 0.2 V, indicating a fast kinetics for the transition between lithium polysulfides and lithium sulfides in the pores of the CTF-1 substrate. Obviously, this fast kinetics is benefited from the electric contact between the embedded sulfur and CTF-1 wall.

Fig. 5b compares the cycling performance of the CTF-1/S@155°C with CTF-1/S@RT cathodes at a current rate of 0.1 C. The CTF-1/S@155°C cathode delivers a specific discharge capacity of 1197 mAh g^{-1} at 2nd cycle and maintains a capacity of 982 mAh g^{-1} at 20th cycle. After 50 cycles, the capacity is still maintained at 762 mAh g^{-1}. From the second cycle, the charge-discharge columbic efficiency of the composite approaches ~97%, indicating an effectively depressed shuttle effect of soluble polysulfide intermediates, which could be possibly explained by the strong adsorption of S_8 molecules in the nanopores of the CTF-1. However, as displayed in Fig. 5b, the CTF-1/S@RT cathode with the same composition can only deliver a low initial capacity of 1015 mAh g^{-1} and exhibit a poor cycling stability with the discharge capacity down to 480 mAh g^{-1} after only 20 cycles, because the sulfur particles are not embedded in the pores of CTF-1 and the intermediate products can easily diffuse into the electrolyte. These results further confirmed that the stable cycling performance of the CTF-1/S@155°C cathode was brought by the strong adsorption of S_8 molecules in the nanopores of the CTF-1 substrate and the sulfur loading within the pores of CTF-1 could significantly improve the cycle performance of the sulfur electrode.

Fig. 5c shows the rate capability of the CTF-1/S@155°C composite electrode at various rates. When the current density was increased successively from 0.1 C to 0.2 C and further to 0.5 C, the capacity declined slightly from 920 mAh g^{-1} to 848 mAh g^{-1} and 686 mAh g^{-1}. Even at a very high current of 1 C, the composite cathode can still deliver a reversible capacity of 541 mAh g^{-1}, showing a good rate capability. Once the current density was changed back to 0.1 C, a capacity of ~750 mA g^{-1} can be recovered.[19] Apparently, the good rate capability of the CTF-1/S@155°C composite benefits from the highly ordered nanoporous structure of the CTF-1 substrate, which provides not only the great improvement of electrical conductivity for sulfur, but also sufficient transport tunnels for the electrolyte penetration.

Conclusions

In summary, we successfully prepared a sulfur cathode for Li-S battery by using COFs as host for the first time. Our results clearly show that CTF-1 can perform as a sulfur container and the redox process can take place in the pores. Since CTF-1 is a kind of COFs, we can imagine it is possible to use other COFs as host materials for sulfur in Li-S batteries. Considering the unique[8] properties of COFs, such as low density, large surface area, diversity of available building blocks, we believe this proof-of-principle research provides new opportunities for materials scientists for tailor design of cathode materials in Li-S batteries. However, although our results are promising, we still need to improve the performance of COF-S cathode. We should find a suitable COF with big pore volume and suitable pore size to load more sulphur. For example, ILCOF-1[20] has a pore volume with 1.21 $cm^3 g^{-1}$ and could load 71% sulfur in theory. We also need to modify the surface of COFs to further restrict the diffusion of polysulfides. Further investigations with other COF-S cathodes are undergoing in the lab.

Experimental Section

Preparation of CTF-1: It was synthesized according to literature.[16] 1,4-Dicyanobenzene (1.0 g, 7.8 mmol) and $ZnCl_2$ (1.06 g, 7.8 mmol) were transferred into a pyrex ampoule (2.5 × 11 cm) under an inert atmosphere. The ampoules were evacuated, sealed and then placed in a muffle furnace and calcined at 400 °C for 40 h, yielding a black solid along the tube. After that, the ampoule was cooled down to room temperature and opened. The resulting black solids were grounded, washed thoroughly with water, and subsequently stirred in diluted HCl for one day. After this purification step, the solids was filtered, washed with a large amount of water and THF and dried in vacuum at 120 °C. Finally, black solid (0.9 g) was obtained with 90% yield.

Preparation of CTF-1/S@155°C composite: CTF-1 powder (0.3 g) and sublimed sulfur (0.2 g) was mixed and then grounded in a mortar, followed by heating at 155 °C for 15 h. At this temperature, the melt sulfur can easily diffuse into the pores of CTF-1. The composite was then heated at 300 °C under nitrogen for 1 h to evaporate the surface sulphur. After cooling down, the CTF-1/S@155°C composite was obtained.

Acknowledgements

Notes and references

Key Laboratory of Biomedical Polymers (Ministry of Education), College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

Email: chengwang@whu.edu.cn, xpai@whu.edu.cn

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17 The XRD signal of CTF-1 could be restored after removing sulfur, see Fig. S1†.

18 Another peak at a different binding energy (167.5-171.5 eV) was also detected, which can be assigned to sulfur atoms in a sulfate-like environment, see reference 5.

19 Since the charge-discharge columbic efficiency of the composite is ~97%, the diffusion process cannot be totally restricted. Therefore, the capacity cannot be fully recovered after the current density was changed back to 0.1 C.

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