청정소재제품기술

Biomass-Derived Three-Dimensionally Connected Hierarchical Porous Carbon Framework for Long-Life Lithium–Sulfur Batteries

Ying Liu[1,2], Dong Jun Lee[1], Younki Lee[2], Prasanth Raghavan[3], Rong Yang[4],
Fitria Ramawati[5], and Jou-Hyeon Ahn[1,2,*]

[1]Department of Chemical Engineering, Gyeongsang National University
501 Jinju-daero, Jinju 52828, Republic of Korea
[2]Department of Materials Engineering and Convergence Technology, Gyeongsang National University
501, Jinju 52828, Republic of Korea
[3]Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi, 682022, India
[4]International Research Center for Composite and Intelligent Manufacturing Technology, Institute of Chemical Power Sources,
Xi'an University of Technology No.5 Jinhua South Road, Xi'an city, Shaanxi province 710048, China
[5]Research Group of Solid State Chemistry & Catalysis, Chemistry Department, Sebelas Maret University,
Jl. Ir. Sutami 36 A Kentingan, Surakarta, 57126, Indonesia

Abstract

Lithium sulfur (Li-S) batteries have attracted considerable attention as a promising candidate for next-generation power sources due to their high theoretical energy density, low cost, and eco-friendliness. However, the poor electrical conductivity of sulfur and its insoluble discharging products (Li_2S_2/Li_2S), large volume changes, severe self-discharge, and dissolution of lithium polysulfide intermediates result in rapid capacity fading, low Coulombic efficiency, and safety risks, hindering Li-S battery commercial development. In this study, a three-dimensionally (3D) connected hierarchical porous carbon framework (HPCF) derived from waste sunflower seed shells was synthesized as a sulfur host for Li-S batteries via a chemical activation method. The natural 3D connected structure of the HPCF, originating from the raw material, can effectively enhance the conductivity and accessibility of the electrolyte, accelerating the Li^+/electron transfer. Additionally, the generated micropores of the HPCF, originated from the chemical activation process, can prevent polysulfide dissolution due to the limited space, thereby improving the electrochemical performance and cycling stability. The HPCF/S cell shows a superior capacity retention of 540 mA h g^{-1} after 70 cycles at 0.1 C, and an excellent cycling stability at 2 C for 700 cycles. This study provides a potential biomass-derived material for low-cost long-life Li-S batteries.

Keywords : Hierarchical porous carbon, Waste sunflower seed shells, Chemical activation method, Lithium-sulfur batteries

1. Introduction

The demand for high-performance energy storage devices has been increasing with the rapid development of electronic products. Commercialized lithium-ion batteries cannot meet the increasing demands owing to their limited theoretical capacity. Li-S batteries are considered to be the most promising candidates for next-generation power sources as they exhibit high theoretical capacity (1675 mA h g^{-1}) and energy density (2600 W h kg^{-1}); furthermore, they incur low costs and are environmentally friendly [1-3]. However, some disadvantages, such as the insulating characteristics of sulfur and its insoluble discharging products (Li_2S_2/Li_2S), large volumetric expansion, severe self-discharge, and dissolution of lithium polysulfide intermediates, largely restrict the commercial applications of Li-S batteries, which can result in rapid capacity degradation, low Coulombic efficiency, and safety risks [4-6].

Numerous methods have been developed to address these issues, such as the development of cathode materials and modification of separators. Among them, the use of a tailored carbon matrix as the sulfur host is considered one of the most effective and convenient methods as it leads to an excellent electronic/ionic conductivity and high adsorption ability to encapsulate sulfur [7-10].

However, the preparation processes for carbon matrices are complex, time-consuming, and low-volume, which hinders a large-scale production. Biomass, with the merits of low cost, abundant reserves, and unique natural structures, has been considered a promising carbon precursor. For example, Yang et al. successfully synthesized a sponge-like nitrogen-doped porous carbon derived from the fish scale as the sulfur host for Li-S batteries, which delivered a high discharge specific capacity of 473.9 mA h g^{-1} after 500 cycles at 0.1 C [11]. Lee et al. used garlic peel as a raw material to synthesize a porous carbon with large surface area (4220 $m^2 g^{-1}$) and pore volume (2.02 $cm^3 g^{-1}$) as the sulfur host for Li-S batteries [12]. Xue et al. synthesized a hierarchical porous carbon from banana peels for Li-S batteries, which delivered a high discharge capacity of 615 mA h g^{-1} after 500 cycles [13]. These results confirm that carbon derived from biomass has a high potential for application in Li-S batteries.

Waste sunflower seed shells (WSSSs) are an abundant waste produced by the edible oil industry as waste trash, which can largely increase the burden on the environment. If this biowaste trash can be applied in energy materials, it will reduce not only the environmental pollution but also the waste of resources [14, 15]. In this study, a three-dimensionally (3D) connected hierarchical porous carbon framework (HPCF) derived from WSSSs was synthesized via a simple chemical activation process as a sulfur host for long-life Li-S batteries. The 3D connected structure of the HPCF, originating from the raw material, can effectively enhance the electrical conductivity and access of the electrolyte, facilitating the Li^+ transfer. The micropores of the HPCF, originating from the chemical activation process, can serve as a storage and reaction space, preventing the dissolution of polysulfides and further enhancing the electrochemical performance.The proposed method can not only enhance the electrochemical performance but also realize environmental benefits and sustainable development.

2. Material and methods

2.1. Materials

WSSSs, potassium hydroxide (KOH, 95.0%, Samchun Pure Chemical Co., Ltd.), hydrochloric acid (HCl, 35.0-37.0%, Samchun Pure Chemical Co., Ltd.), sulfur (99.5%, Sigma-Aldrich), and N-methylpyrrolidone (NMP, 99.5%, Samchun Pure Chemical Co., Ltd.) were used as received.

2.2. Preparation of the HPCF

The HPCF was derived from WSSSs via a simple chemical activation process. The collected WSSSs were washed with distilled water and dried in an oven. The cleaned WSSSs were pretreated at 600 ℃ for 2 h under nitrogen atmosphere. The resulting sample was then immersed in a 1.5 M KOH solution and stirred until complete evaporation of water. Subsequently, the WSSSs char with KOH was activated at 800 ℃ for 1 h at a heating rate of 3 ℃ min^{-1} under a nitrogen flow. Finally, a 3D connected hierarchical porous carbon framework was obtained after washing and drying.

2.3. Preparation of HPCF/S composites

Sulfur was encapsulated into the HPCF using a vacuum-assisted melt-infusion method [16]. The as-prepared HPCF and sulfur were sealed in a glass tube under vacuum at a weight ratio of 1:2, followed by heating at 155 ℃ for 12 h and at 500 ℃ for 6 h, which yielded the HPCF/S composite.

2.4. Static absorption experiment

A Li_2S_6 solution was prepared to evaluate the adsorbability of the HPCF. S and Li_2S, in proportion to dissolve into a mixed solution of 1,2-dimethoxyethane/1.3-dioxolane (1/1 v/v), were stirred at 50 ℃ until the solution changed from colorless to brownish red, which was used in the HPCF absorption experiment. The solution color changes with time were recorded using digital photos, which can be used to intuitively evaluate the adsorption capacity of the HPCF.

2.5. Characterization of materials

The surface morphologies of WSSSs, WSSSs char, HPCF, and HPCF/S composites were recorded using field-emission scanning electron microscopy with an energy-dispersive X-ray spectrometer (FESEM, Philips XL30S FEG). The inner morphology of the HPCFs was observed by transmission electron microscopy (TEM, TF30ST-300 kV). Brunner-Emmet-Teller analysis (BET, ASAP 2010) and Barrett-Joyner-Halenda (BJH) method were used to determine the specific surface area, pore volume, and pore size distribution of samples. The crystal structures of the HPCF and HPCF/S were confirmed using X-ray diffraction (XRD, D2 Phaser Bruker AXS). The sulfur content of the HPCF/S composite was determined by a thermogravimetric analysis (TGA, Q50 TA Instruments).

2.6. Electrochemical characterization

To prepare the cathode electrode, the HPCF/S composite, Super-P carbon black, and poly(vinylidene fluoride) with a mass ratio of 8:1:1 were evenly mixed in the NMP solution, followed by coating on an Al current collector and vacuum drying at 60 ℃ for 12 h. Electrochemical tests were performed on stainless-steel Swagelok® cells assembled in an argon-filled glove box with a Li metal foil as an anode, Celgard 2400 as a separator, and HPCF/S electrode as a cathode. 1 M of lithium hexafluorophosphate ($LiPF_6$) salt in ethylene carbonate/diethylene carbonate (volume ratio = 1:1) was used as an electrolyte for the cell tests. Cyclic voltammetry (CV) measurements and cycling tests on cells were carried out
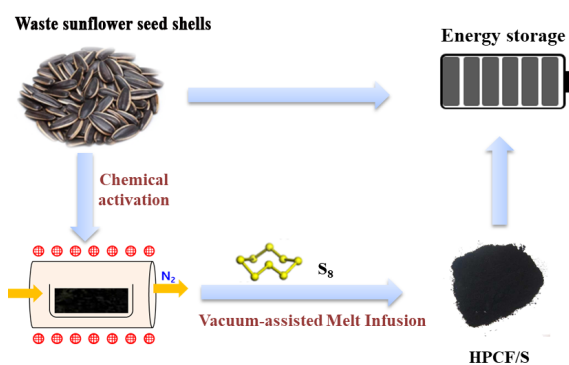
Figure 1. Schematic of the fabrication of the HPCF/S composite.

in a voltage range of 1.0 to 3.0 V at a scan rate of 0.05 mV s^{-1} at room temperature by a WBCS3000 battery cycler (WonA Tech. Co.).

3. Results and Discussion

The synthesis process of HPCFs derived from WSSSs by a simple chemical activation method is shown in Figure 1. WSSSs with nonporous and tabulate structures are presented in Figure 2(a), which were used as raw materials to prepare the 3D connected HPCF. The morphology of the WSSSs char after precarbonization is shown in Figure 2(b), which has a 3D connected structure and macropores. Subsequently, the WSSSs char was reacted with KOH at a high temperature. The obtained HPCF had a highly microporous structure. The microstructure of the HPCF can be observed in the TEM image (inset of Figure 2(c)). After encapsulation of sulfur, there were no significant

differences between HPCF and HPCF/S, as shown in Figure 2(c) and (d), which indicates that sulfur permeated into the pores of the HPCF. The elemental maps of the C and S signals of HPCF/S (Figure 2(e) and (f)) were highly matched, which indicates that sulfur was uniformly distributed in the HPCF.

The porous properties of the WSSSs char, HPCF, and HPCF/S were measured by a BET analysis, as shown in Figure 3(a) and (b). The surface area of the WSSSs char was only 3 m^2 g^{-1}, in accordance with the results obtained by the FESEM image. According to the chemical activation process, the HPCF exhibits typical type-I and type-IV isotherms and H4-type hysteresis loop, which indicates that a hierarchical porous structure was generated from the chemical reaction. Notably, the desorption curve of the HPCF nearly retraces the adsorption curve, which indicates that a large number of micropores exist in the HPCF. Micropores can provide storage space for sulfur/polysulfides, while mesopores and macropores can improve the wettability and accessibility of the electrolyte and further accelerate the Li-ion transfer in the cell. After sulfur encapsulation, the specific surface area and pore volume of the HPCF/S composite largely decreased, which implies that sulfur was encapsulated in the pores of the HPCF. The specific surface areas, pore volumes, and average pore sizes of the WSSSs char, HPCF, and HPCF/S are presented in Table 1. The sulfur content of HPCF/S measured using TGA (Figure 3(c)) was 42.5 wt%. The distribution of sulfur in the carbon matrix is also reflected in the derivative weight loss rate vs. temperature plot (Figure 3(c)). Two peaks of HPCF/S are observed at temperatures of 160 and 334 ℃. The small bulge at 160 ℃ results from the evaporation of elemental sulfur in the meso-/macropores of the HPCF, whereas
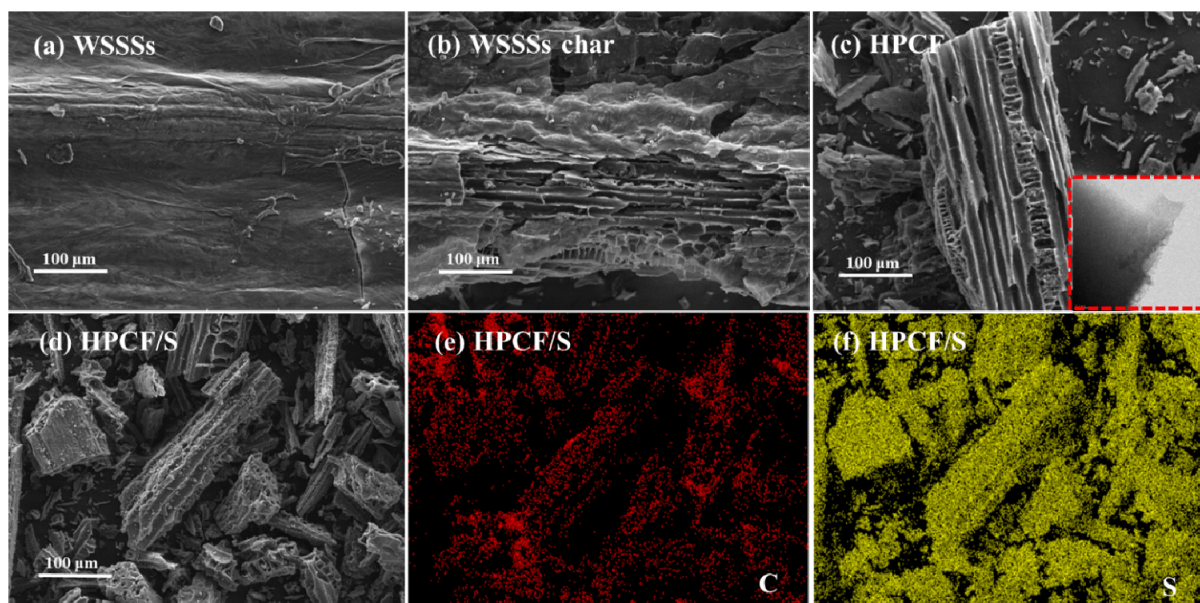

Figure 2. FESEM images of (a) WSSSs, (b) WSSSs char, (c) HPCF (inset: TEM image of the HPCF), and (d) HPCF/S and (e,f) energy-dispersive spectroscopy mapping of HPCF/S.
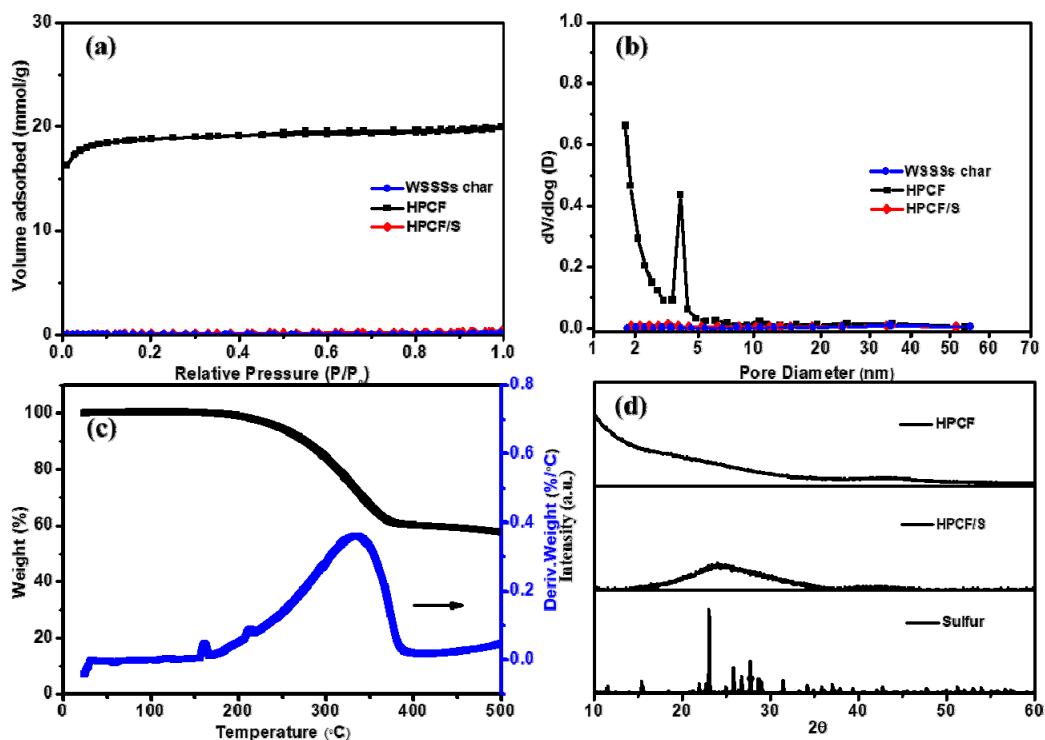
Figure 3. (a) Nitrogen adsorption isotherms and (b) BJH pore size distributions of the WSSSs char, HPCF, and HPCF/S. (c) TGA of HPCF/S. (d) XRD patterns of HPCF, HPCF/S, and sulfur.

the main peak at 334 ℃ results from the loss of small sulfur molecules encapsulated in the micropores of HPCF [16, 17]. The XRD characteristics of HPCF and HPCF/S were measured (Figure 3(d)). The HPCF exhibits the typical peaks of amorphous carbon structures. HPCF/S also exhibits the typical amorphous carbon structure, rather than sulfur orthorhombic crystalline diffraction peaks, which indicates that sulfur was confined to the HPCF, which is consistent with the BET results.

A cyclic voltammogram of the HPCF/S cell at a scan rate of 0.05 mV s^{-1} is presented in Figure 4(a), with two cathodic peaks at 2.42 and 1.31 V in the initial reduction process. The peak at 2.42 V resulted from the reduction of elemental sulfur, whereas the large reaction peak at 1.31 V in the initial reduction process resulted from the reaction of small sulfur molecules in the micropores [18, 19]. In subsequent cycles, the peak at 2.42 V disappeared completely, while the peak at 1.31 V shifted to 1.77 V, which suggests that a stable cyclic pathway was established

after activation. One plateau of the HPCF/S cell was observed in the charge-discharge curves (Figure 4(b)) which were different from conventional carbon/sulfur composites of Li-S batteries. In general, sulfur is reduced to long-chain polysulfides (Li$_2$S$_x$, $4 \leq x \leq 8$) at 2.3 V and short-chain polysulfides at 2.0 V [20], undergoing a "solid-liquid-solid" reaction mechanism. However, in the case of the HPCF/S cell in which small chain sulfur molecules were present in micropores, a "solid-solid" reaction mechanism was shown, which means that long-chain polysulfides were not formed in the HPCF/S cell. A stable cycling performance with a capacity retention of 540 mA h g^{-1} after 70 cycles at 0.1 C and high Coulombic efficiency of HPCF/S are shown in Figure 4(c). The excellent rate capability of the HPCF/S cell is presented in Figure 4(d), which delivered a capacity retention of 400 mA h g^{-1} even at a higher rate of 1 C. Figure 4(e) shows that the HPCF/S cell exhibited an exceptional cycling stability and long life span, with a capacity retention of 270 mA h g^{-1} after 700 cycles at a rate of 2 C. These results confirm that the HPCF/S composite possesses excellent electrochemical performance and cycling stability even under extreme test conditions with high C rates owing to the unique 3D connected hierarchical porous structure. The macro- and mesopores of the HPCF can provide a good electrolyte accessibility. The micropores of the HPCF can prevent the generation of polysulfides, thereby enhancing the electrochemical performance.

To intuitively evaluate the adsorbability of the HPCF for polysulfides, the HPCF was soaked in the Li$_2$S$_6$ solution (Figure

Table 1. Specific surface areas, pore volumes, and average pore sizes of the WSSSs char, HPCF, and HPCF/S composite.

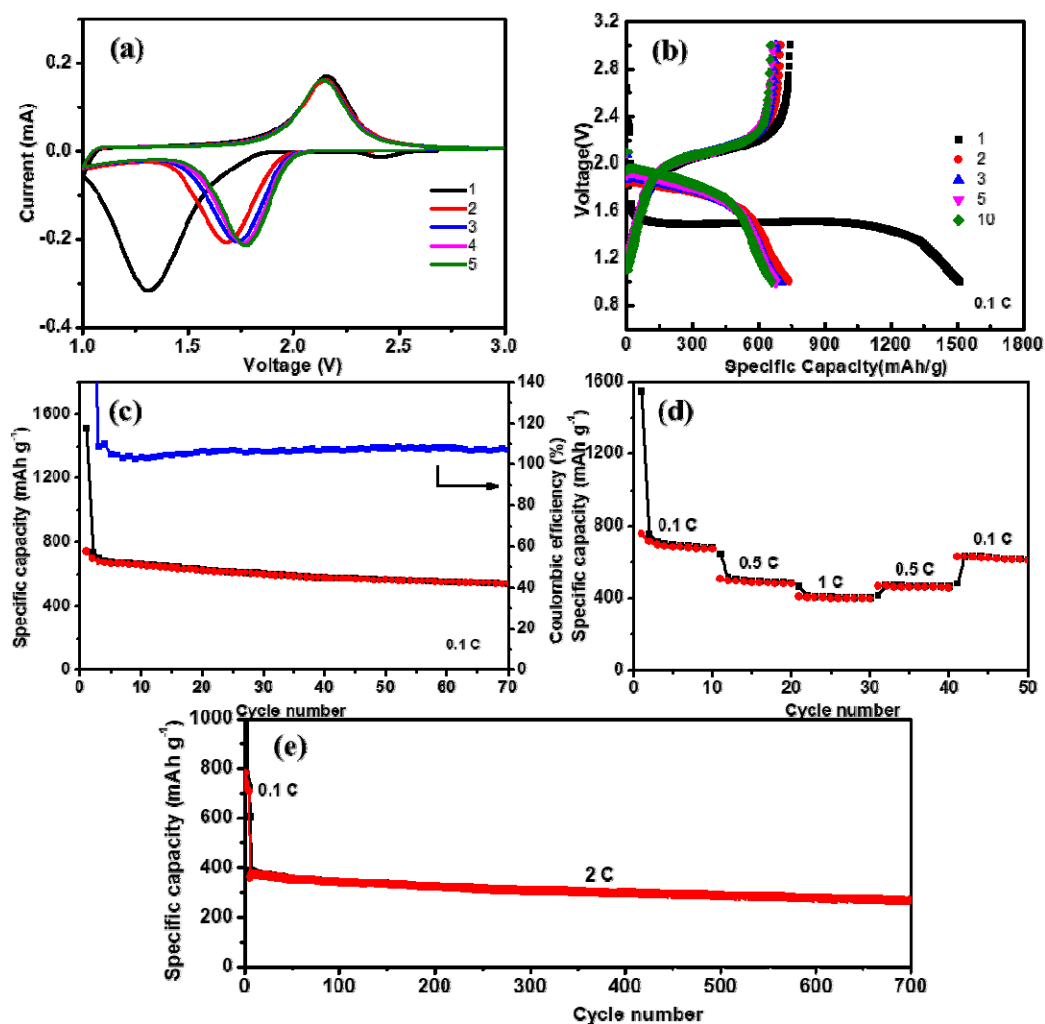| Sample	Specific surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore size (nm)
WSSSs char	3.0	0.007	22.1
HPCF	1867	0.69	2.7
HPCF/S	24	0.018	7.2

Figure 4. (a) CV profiles in the voltage window of 1.0-3.0 V at a scanning speed of 0.05 mV s^{-1} for the HPCF/S cell, (b) charge-discharge profiles of HPCF/S at 0.1 C, (c) cycling performance and Coulomb efficiency of the HPCF/S cell at 0.1 C-rate, (d) rate performance of the HPCF/S cell, and (e) long cycling performance of the HPCF/S cell at a high rate of 2 C.
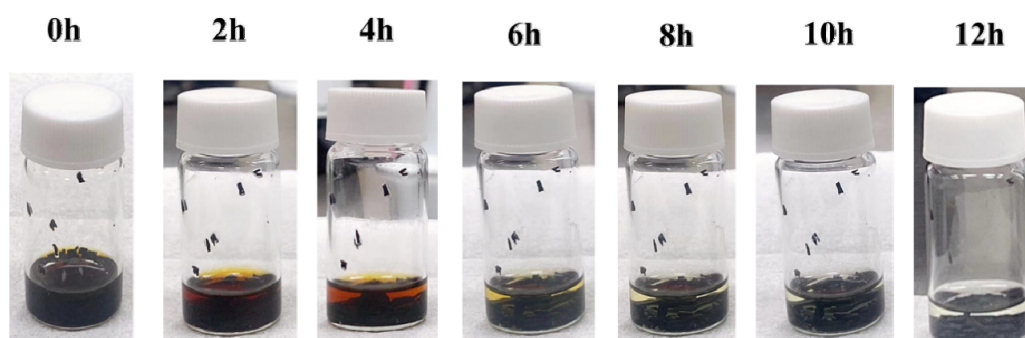

Figure 5. Photographs of the Li_2S_6 solutions exposed to the HCPF adsorbent in the period of 0 to 12 h.

5). The typical brownish-red color of the Li_2S_6 solution gradually faded. The solution became colorless after 12 h, which indicates that the HPCF has a strong adsorption ability on polysulfides, which can effectively trap polysulfides and relieve the shuttle effect in the cell.

4. Conclusions

A 3D connected HPCF derived from WSSSs as the sulfur host was applied to a Li-S battery, exhibiting an excellent cycling stability and long life span. The 3D connected structure of the HPCF could effectively enhance the accessibility of the electrolyte

and electrical conductivity, facilitating the Li^+ transfer. The micropores of the HPCF as the reaction space prevented the dissolution of polysulfides and enhanced the electrochemical performance. Therefore, the proper construction of porous carbon structures can largely improve the electrochemical performances of Li-S batteries, providing new insights for the design of porous electrode materials.

Acknowledgement

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