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Effect of Loading Methods on the Performance of Hierarchical Porous Carbon/sulfur Composites in Lithium Sulfur Batteries

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Effect of Loading Methods on the Performance of Hierarchical Porous Carbon/sulfur Composites in Lithium Sulfur Batteries

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ABSTRACT: Lithium-sulfur batteries have shown increasing promise for high energy densities and reduced costs. Facile sulfur loading techniques demonstrate a critical way to achieving high dispersions of sulfur in the host's matrix, improving conductivity and simultaneously decreasing the active mass loss from the cathode. Here we investigate the effect of sulfur loading methods on the electrochemical performance of porous carbon/sulfur composites containing approximately 70 wt% sulfur. Three different loading techniques are tested, including one-step molten sulfur impregnation (155 °C), two-step molten sulfur impregnation (155 °C + 300 °C) and a sulfur organic solution impregnation, in which the entire microporous volume of carbon is filled by sulfur. It is found that the simple sulfur organic solution impregnation method is the most effective in enhancing the electrochemical performance of the hierarchical porous carbon/sulfur composite cathode in the lithium-sulfur battery system, due to the weaker interaction occurring between the sulfur and microporous carbon. Our work demonstrates the impact of sulfur loading method on the electrochemical performance of lithium-sulfur batteries, which offers new insights into the preparation technology of electrodes.

Keywords: lithium-sulfur battery, sulfur loading methods, hierarchically porous carbon, microporous, mesoporous

1. Introduction

With the increasing demand for efficient energy storage for electric vehicles (EVs), portable devices and smart grids applications, rechargeable lithium-sulfur (Li-S) batteries represent a promising candidate for future applications. Li-S cells can offer a theoretical capacity as high as 1675 $mAhg^{-1}$ for a sulfur electrode by accepting two electrons per sulfur atom [1-6]. Moreover, sulfur is cheap, environmentally friendly, and abundant in nature [7-9]. Despite the numerous benefits, there are still several noticeable problems that need to be solved to realize the commercialization of Li-S cells. One of the most demanding challenges is the intrinsically poor electrical conductivity of sulfur and its discharge products (Li_2S_2/Li_2S), which can lead to low utilization of the electrochemically active materials [2, 10]. The electrodes also suffer from low mechanical and cyclic stability as a result of the volume change of sulfur (approximately 80%) during the charge/discharge processes [11, 12]. Another major hurdle is the dissolution and diffusion of intermediate polysulfides (Li_2S_n, where $4 \leq n \leq 8$) into organic electrolytes [13-15]. Polysulfides can react with the lithium electrodes, causing significant active mass loss and severe self-discharging problem [16, 17]. Continuous reactions between polysulfides and Li anodes restrain their re-oxidization to elemental sulfur at the cathode side during the delithiation step [18, 19]. This is widely known as a "shuttle" phenomenon in Li-S systems and is considered as one of the main reasons for low coulombic efficiency and poor cycling performance [15, 20-22].

In order to address the above-mentioned challenges, research has taken two major routes: modifying the organic electrolyte to reduce the parasitic reactions with the

electrodes and replacing sulfur with composites and hybrids that are more conductive and more able to accommodate the volume changes [23]. Encapsulating sulfur into a conductive matrix has been demonstrated to be an effective mean to confine polysulfide species and improve the electrical conductivity of the electrode [22]. Various conductive matrixes have been explored, including porous carbon [24-26], carbon nanotubes [27], carbon nanofibers [28, 29], graphene [30, 31] and graphene derivatives [32], metal organic frameworks (MOFs) [33-36] and metal oxides [37-39]. Of particular interest, porous carbon materials, which include micropores (<2 nm) carbon, mesopores (2-50 nm) carbon and macropores (>50 nm) carbon, are attractive candidates due to their low cost and good performance in electrochemical devices. Nazar et al. [40] reported that highly ordered mesoporous carbon (CMK-3) with an average pore size of 3.33 nm could host S and improve the cycling performance of the sulfur cathode. However, mesopores in the carbon materials appeared to alleviate but not eliminate the "shuttle" phenomenon due to the relatively large pore size, which leads to the exposure of sulfur to the electrolyte [6]. Zhang et al. [41] introduced a sulfur composite with good cycle stability by confining sulfur in microporous carbon spheres with a narrow pore size of approximately 0.7 nm. Guo et al. [42] proposed S_2 and S_4 could exist in a microporous carbon matrix with a pore size of 0.5 nm, which can prevent the unfavorable cyclo-S_8 to S_4^{2-} transition reactions. Therefore, it is becoming more convincing that nanoporous carbon can effectively improve the cyclic stability of the sulfur electrode [26, 43, 44]. However, there is no systemic study of the effect of sulfur loading method on the electrochemical performance of hierarchical porous carbon-

sulfur composites.

In this study, we have selected polypyrrole as a precursor to synthesize hierarchical porous carbon (HPC) model materials. HPC produced form polypyrrole precursors has previously shown to have a high microporous volume of 1.3 cm^3g^{-1}, a total pore volume of 2.6 cm^3g^{-1} and a large (BET) surface area of 3270.4 m^2g^{-1} [45]. We studied three sulfur loading methods, each of which impacted the state of sulfur within the carbon micropores and affected the electrochemical performance of the sulfur composite significantly. Our study provides an excellent guideline to the selection of optimal sulfur loading method for sulfur cathode with excellent performance.

2. Experimental section

2.1. Preparation of microporous/low-range mesoporous carbon

The preparation process of the hierarchical porous carbon is illustrated in Fig.1. Firstly, Polypyrrole (PPy) was prepared by a simple synthesis route using $FeCl_3$ as an oxidant [46]. Typically, 5 ml pyrrole was distilled at 120 ℃ to acquire approximately 3 ml of product. The distilled pyrrole was then added to a 200 ml solution of 0.5 M $FeCl_3$, and the mixture was stirred for 2 hours using magnetic stirring until full polymerization. The resulting polypyrrole was then filtered and washed with water and ethanol before drying in the oven overnight. The dry powder was then mixed with KOH pellets in a 1:4 weight ratio and oven dried at 150 °C. Chemical activation of the polymer was conducted by heating the PPy-KOH mixture under ultra-high purity argon for 1 hour at 800 °C (heating rate: 3 $°C \cdot min^{-1}$). The activated samples were washed with hydrochloric acid (10 wt%) to remove any inorganic salt residue, followed by rinsing

with distilled water until a neutral pH was obtained. Finally, the sample was dried at 120 °C and labelled as HPC.

2.2. Preparation of HPC/sulfur composites

The synthesis procedure of the HPC/S composites is illustrated in Fig.1. The HPC prepared from the previous step was used as the matrix and sublimed sulfur (Aladdin, Shanghai) was used as the sulfur source. We have used three methods to load sulfur into the carbon matrix. In the first method, we used one single heat treatment step in which a mixture of HPC and sublimed sulfur (weight ratio of 1:2.33) was heated at 155 °C for 10 h in a sealed reactor under an argon atmosphere. At this temperature, the melted sulfur with low viscosity can quickly diffuse into the micropores of the HPC. The outcome of this process was a 70 wt% sulfur loading, which was designated as HPC/S-155-70%. The second method is a two-step process in which HPC was mixed with sublimed sulfur in a weight ratio of 1:4. The mixture was heated firstly at 155 °C for 6 h in a sealed vessel filled with argon gas, and then the temperature was increased to 300 °C and held for 2 h in order to vaporize the superfluous sulfur on the surface of the carbon. The sulfur content of the composite was calculated from the mass change before and after heat treatment to be 68 wt%. This composite was designated as HPC/S-300-68%. The third loading method used the same mixing ratio as in the first method (a weight ratio of 1:2.33), but the mixture was dissolved in 50 ml CS_2 solution and stirred vigorously until CS_2 was evaporated entirely using magnetic stirring. A composite with 70 wt% sulfur was obtained and designated as HPC/S-Sol-70%. For comparison, the graphene material (PH: 2±0.2; N, S, Cl%<0.5%; metal impurity<100ppm; ash<1.0%)

obtained from Inner Mongolia RS new Energy Co., Ltd was incorporated with sulfur using the same three methods. And the prepared composites were designated as Graphene/S-155, Graphene/S-Sol, Graphene/S-300, respectively, in which sulfur contents were all about 50 wt%.

2.3. Materials characterizations

The HPC and HPC/sulfur composites were characterized using X-ray diffraction (XRD, Bruker D8a) with Cu-Kα radiation, scanning electron microscopy (SEM, SU8010, Hitachi) equipped with energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM, JEOL JEM-3000F). Nitrogen (N_2) adsorption/desorption measurements were performed using a Quantachrome instrument (Quabrasorb SI-3MP) at -196 °C to investigate the porous structure of the samples. The sulfur content in the composites was measured using thermogravimetric analysis (TGA, Pyris Diamond6000 TG/DTA, PerkinElmer). The electrical conductivity of the cathode was determined by four probe measurements at room temperature.

2.4. Electrochemical characterizations

To prepare the cathode, the HPC/S composite material, carbon black and polyvinylidene fluoride (PVDF) binder were mixed in a weight ratio of 70: 20: 10 with N-methyl-2-pyrrolidinone (NMP) as a dispersant. Afterwards, the resulting slurry was spread onto nickel foam with a 10 mm diameter and dried at 60 °C for 12 h in an oven, then compressed into tablets. The areal sulfur loading is approximate 1.5 mg cm^{-2}, 7 mg cm^{-2} and the electrolyte-to-sulfur mass is about 20 ml g^{-1}. The CR2032-type coin

cells were assembled in an argon-filled glovebox. The electrolyte used was LiTFSI (Sigma-Aldrich) in a solvent mixture of 1,3-dioxolane and 1,2-dimethoxyethane (1:1, v/v) (Aladdin) with 0.2 M $LiNO_3$ additive. Lithium chips were used as both the counter and reference electrode. Celgard 2400 membranes were used as separators. To evaluate the capacity and cycle stability of the electrodes, galvanostatic charge-discharge tests were conducted using Arbin Instrument BT2000 model in the voltage range of 1-3 V and 1.6-2.8 V. Cyclic voltammogram (CV) measurements were performed using Princeton Applied Research instrument in the voltage range of 1-3 V and 1.6-2.8 V with a scanning rate of 0.1 mV S^{-1}. The electrochemical impedance spectroscopy (EIS) was carried out at an amplitude of 5 mV over the frequency range from 100 kHz to 0.01 Hz. All electrochemical characterizations were conducted at ambient temperature.

3. Results and discussion

The N_2 adsorption/desorption measurements were employed to investigate the porous structure of the HPC and HPC/S composite materials. Fig. 2A ,B show the N_2 adsorption/desorption isotherm measured at -196 °C for the HPC and HPC/S composites. The isotherm shows typical type I behavior, implying the existence of a multitude of micropores in HPC[41]. The pore size distribution curve (Fig. 2C) confirmed the presence of the micropores peaked at 1.8 nm. Also, the HPC possesses a relatively high total pore volume of 2.6 $cm^3 g^{-1}$ and a large (BET) surface area of 3270.4 $m^2 g^{-1}$ based on density functional theory (DFT) calculation, which are created by classical approaches to adsorption as well as models based on modern statistical thermodynamics. More importantly, the microporous volume of the carbon material is

1.3 $cm^3 g^{-1}$, which theoretically could host up to 72% sulfur loading when calculated based on the density of sulfur (2.07 $g \cdot cm^{-3}$ for α phase at room temperature)[41]. Although different sulfur loading methods were conducted in this work, the similar sulfur content close to the theoretical value could be obtained. The calculated specific surface areas decrease sharply to 128.4, 4.7 and 16.2 $m^2 g^{-1}$ for the HPC/S-Sol-70%, HPC/S-155-70%, HPC/S-300-68% composite materials, respectively. The reason for the relatively larger specific surface and higher pore volume of HPC/S-Sol-70% can be explained through the existence of a stretching force between the nanopores and the CS_2 solution of sulfur, resulting in a deposition of some sulfur nanocrystals onto the surface of HPC[19]. Fig. 3A shows the XRD patterns of sublimed sulfur, HPC and the HPC/S composites. For elemental sulfur, characteristic sharp peaks can be observed in its XRD pattern, which is coincident with the orthorhombic crystal structure of sulfur[47]. The XRD pattern of the HPC shows two broad diffraction peaks at around 30º and 43º[47, 48], which can be assigned to the diffractions of (002) and (100) planes of graphitic carbon (JCPDS No 75-1621). The broadening and low intensity of the peaks indicate less crystallinity of the HPC. None of the HPC/S composites, regardless of the sulfur loading method, contain the characteristic peaks of crystalline sulfur, indicating that the nano-sized sulfur exists in the composite material. Despite nano-sized sulfur exists in the composite material, the three cathodes have an electrical conductivity of 7−8 S cm^{-1} at room temperature.

TGA is a technique used traditionally to determine the thermal stability of the materials. When it comes to composites, TGA could also give an idea about the energy

needed to break the interactions between the components and the composition of the composite. The three HPC/S composites in the current study have almost the same elemental composition. However, looking at their TGA curves in Fig. 3B, one can observe some differences in their response to increasing the temperature. The sulfur in HPC/S-155-70% evaporates at a slightly higher temperature than that in HPC/S-Sol-70%, indicating a stronger interaction between sulfur and carbon. This can be explained by understanding the loading mechanism and the pores structures in both composites. In the HPC/S-155-70% composites, sulfur melts and diffuses into pores that are larger than 0.69 nm in the form of S_8[49]. On the other hand, the sulfur in the HPC/S-Sol-70% composite is introduced to the pores using CS_2 as a flux, which when evaporates, leaves less solid filling inside the nanopores and some sulfur nanocrystals on the surface of HPC. The TGA curve of the HPC/S-300-68% shows an interesting feature. The mass loss above the evaporation temperature of the sulfur is somewhat gradual, suggesting the removal of sulfur is taking place over a wide range of temperature, and by a more complicated mechanism than simple evaporation. This can be explained by the difficulty of evaporating sulfur from the ultramicropores(<0.69nm) in the form of smaller sulfur molecules (S_{2-4})[42].

The SEM images of the polypyrrole (PPy), HPC and the HPC/S composites are shown in Fig. 4. Low and high magnification SEM images of polypyrrole (PPy) shown in Fig. 4A, B exhibit clusters of interconnected microparticles. After the carbonization and activation (Fig. 4C, Fig. S1A), the surface of the HPC became rougher due to the formation of a range of micropores. The SEM images of the HPC/S composites at low

magnification (Fig. 4D, E, F) and high magnification (Fig. S1B, C, D) show that there is no discernible morphological difference after loading HPC with sulfur. SEM images are also pointing out that the morphology of HPC/S composites is independent of sulfur loading method. Fig. 5 shows TEM images of the HPC (Fig. 5A) and the HPC/S composites (Fig. 5B, C). The TEM image (Fig. 5D) and EDX point analysis result (Fig. S7) of the HPC/S-Sol-70% confirms the deposition of 5 nm sulfur particles on the surface of HPC. Elemental mapping results of three HPC/S composites are shown in Fig.5E to G in which the sulfur (yellow) map is almost in full accordance with the carbon (purple) map. These results further confirm that sulfur is homogeneously dispersed in the carbon matrix.

In ordered to understand the effect of the sulfur loading method on the electrochemical performance, the cycling performances of the HPC/S composites at 200mA/g were tested. HPC/S-155-70% and HPC/S-Sol-70% show higher capacity and more stable circulation than that of HPC/S-300-68%. HPC-155-70% and HPC/S-Sol-70% are generally “open-type” composites, meaning free S_8 exist both in pores larger than 0.69 nm. In this way, sulfur can contact directly to electrolyte solvents and become electrochemically active[49]. HPC/S-300-68%, on the other hand, has a less open structure, with pores size less than 0.69 nm. The electrochemical behavior of HPC/S-300-68% appears to be significantly different from the other two composites (Fig. 6). During the initial cycle, all sulfur in the form of S_{2-4} infiltrates into micropores, leading to discharge potential hysteresis[41, 42, 53, 54] and exhibit only one shoulder peak at 1.53 V. During subsequent cycles, the cathodic peak potential shifts to about 1.42 V

(Fig. S2). There is a broad anodic peak at approximately 2.26 V with low peak current, implying severe polarization of the electrode and the poor charge capacity. This is related to the reduction of all the smaller sulfur molecules confined within the microporous (<0.69 nm) carbon, which is required to overcome the absorption energy. Also, the reactive and large surface area of carbon exposed to the electrolyte causes a large irreversible capacity[55]. Solvent molecules can also be blocked by micropores.[56] Thus, it is essential for any electrode material to have a larger pores volume and/or a significant amount of mesopores to facilitate the transport of Li^+ ions. The CV results showed the critical role of the loading methods on the electrochemical performance of sulfur-HPC electrode by changing both the morphology and the condition of the sulfur existing within the electrode.

The interfacial properties of the three materials were further studied by the electrochemical impedance spectroscopy (EIS). Fig. S3 shows the Nyquist plots of the three HPC/S composites, which are all composed of a semicircle at high frequency and an inclined line in the low-frequency region. These features represent the charge transfer resistances between electrolyte and electrode and the resistance of lithium ion diffusion into the active mass, respectively[58]. In addition, the intercept at the real Z axis corresponds to the sum resistance, which includes the ionic conductivity of the electrolyte, the inherent resistance of the cathode, anode, separator, the interphase electronic contact resistance on the cathode, and the interfacial resistance of the lithium anode[58, 59]. As expected, HPC/S-300-68% exhibits the highest charge transfer resistance (88.56 Ω), due to all the smaller sulfur molecules confined within the

microporous (<0.69 nm) carbon, resulting in blocking electrolyte contact directly to S. On the contrary, HPC/S-Sol-70% and HPC/S-300-68% exhibits almost transfer resistance. This can be explained by the fact that sulfur exists in pores larger than 0.69 nm on the surface of the porous carbon，which makes sulfur easily accessible by the electrolyte, leading to lower charge transfer resistances.

HPC/S-155-70% and HPC/S-Sol-70% were studied in detail below to further understand the effect of the sulfur loading method on the electrochemical performance. Cyclic voltammetry (CV) methods were conducted for HPC/S-155-70% and HPC/S-Sol-70%.The CV curves of the initial three cycles of the two HPC/S composite cathodes are shown in Fig. 7A, B which was recorded between 1.6-2.8 V. It could be observed that there are two sharp peaks at 2.3 and 2.03 V, corresponding to the two-step reduction in the initial cathodic process of HPC/S-Sol-70%. The peak at 2.3 V can be attributed to the reduction of elemental sulfur into long-chain lithium polysulfides (Li_2S_n) ($4 \leq n \leq 8$) and the other cathodic peak at 2.03 V is typically associated with the conversion reaction of the polysulfides anions into short-chain lithium sulfides (Li_2S and/or Li_2S_2)[50, 51].

$$2Li+nS \leftrightarrow Li_2S_n \ (n>4) \qquad (1)$$

$$Li_2S_n + (2n-2)\ Li \leftrightarrow n Li_2S \text{ and/or } Li_2S_2 \qquad (2)$$

In the anodic scan, there are two peaks at 2.37, 2.42 V, which can be attributed to the conversion of Li_2S_2/Li_2S into high-order polysulfides and S[52]. The intensity of the reduction peaks decreases slightly with subsequent cycling. There is almost no change from the 2nd cycle onwards, indicating relatively good reversibility. With

regards to the CV profile of HPC/S-155-70%, the first two cathodic and anodic peaks are similar to those observed in HPC/S-Sol-70%, indicating the same discharge process.

We have then used the charge/discharge method to further study the electrochemical behavior of the sulfur-HPC composites as electrodes for Li-S batteries. Fig. 7C, D shows the charge/discharge voltage profiles of the HPC/S-Sol-70% , HPC/S-155-70% at first cycle of various C rates from 0.1C to 2 C. There are two voltage plateaus can be observed during the discharge process at around 2.3 and 2.1 V for the HPC/S-Sol -70%, HPC/S-155-70%, which is in good agreement with the corresponding CV profile. During the charging process, one plateau of the HPC/S composite cathode also corresponds to the oxidation reaction shown in the CV curve. Furthermore, the HPC/S-Sol-70% showed lower voltage hysteresis (ΔE=175mV) than that of HPC/S-155-70% (ΔE=200mV) due to sulfur can contact directly to electrolyte solvents and become electrochemically active implying greater electrochemical kinetics

The rate performances of the two composite cathodes were further investigated at various current densities from 0.1C to 2C. As can be seen from Fig. 8A, HPC/S-Sol-70% delivers reversible capacities of 1324.5, 778.9, 732.3, 663.5, 593.5 mAh g^{-1} at current densities of 0.1 C, 0.3 C, 0.5 C, 1 C, 2 C respectively, which are much higher than those of other HPC/composites. When the current density is returned to 0.1C, the capacity is recovered to values of 809.5, 803.5 mAh g^{-1}, for the HPC/S-Sol-70%, HPC/S-155-70% composites, respectively. This again shows how the pore structures formed by the solvent-mediated loading method facilitated the utilization of sulfur. The cycling performances of the two composites over 300 cycles at 1C between 1.6-2.8 V

are shown in Fig. 8B. After 300 cycles, the discharge capacities of the two samples reach 599, 578.8 mAh g^{-1} for HPC/S-Sol-70%, HPC/S-155-70% respectively. The HPC/S-Sol-70% composite cathode exhibited a better cycling performance, implying that the simple wet chemical synthesis route of deposition method contributes to a significant restriction of the shuttle effect for polysulfides. After 100 cycles, the morphology of the positive electrode was tested. Compared with before cycling, there is little difference, and there is no large sulfur deposit (Fig. S4). Additionally, the HPC/S-Sol-70% composite cathode with 7 mg cm^{-2} sulfur areal loading also exhibited a high areal capacity of 8.7 mAh cm^{-2} at a current density of 0.1 C and maintained a high areal capacity of 4.45 mAh cm^{-2} at a current density of 0.2 C after 98 cycles (Fig. 8b, Fig. S5).

The role of the loading method in enhancing the electrochemical performance of carbon-sulfur composites is not limited to HPC. We have conducted a series of controlled experiments as a proof of concept with other carbon nanomaterials. Figure S6 showed the performance of graphene-based electrodes loaded with sulfur using similar methods to that used with HPC, i.e, single step heating at 150 ℃, two-steps heat treatment at 150 ℃ and 300℃, and finally solution-mediated loading. The electrodes prepared by loading sulfur from organic solvents have the highest initial and subsequent capacity. Numerically, graphene/S-Sol electrode showed an initial capacity of about 1160 mAh g^{-1} and 815 mAh g^{-1} in the second cycle and dropped to 330 mAh g^{-1} after 100 cycles. The graphene sample heated in sulfur at 150 ℃ has an initial capacity of 1045 mAh g^{-1} and maintained a capacity of ~ 250 mAh g^{-1} after 100 cycles. While both

the capacity and the cyclability are less than those of HPC, it is clear that using organic solvent as a flux to load the sulfur on/in the carbon matrix significantly improve the performance of the electrodes. The hierarchical porosity of HPC enhances the performance further by restricting the parasitic reactions.

4. Conclusions

In summary, hierarchical porous carbon (HPC) with good electrical conductivity, high specific surface area and large micro- and low-range mesoporous volume has been derived from a polypyrrole precursor. When comparing three different sulfur loading methods, it was observed that each method has a significant effect on the state of sulfur existing on the carbon, and influences the electrochemical performance of the HPC/S composite cathode. For the "two-step molten sulfur impregnation" method, all the smaller sulfur molecules are confined within the microporous (< 0.69 nm) carbon (from S_{2-4} to Li_2S), causing the electrochemical reaction needs to overcome high absorption energy. The solvent molecules can also be blocked by the micropores, thus, the carbon needs far more mesopores or macropores to facilitate the transport of solvent and lithium ions. The "one-step molten sulfur impregnation" method produced a composite that slows down the electrochemical reaction due to the need to overcome a strong interaction during the discharge process. However, a sulfur organic solution impregnation method ensures that sulfur is well dispersed inside the micropores (> 0.69 nm) without strong interaction between sulfur and micropores. In addition, the sulfur within the micropores of the HPC/S-Sol-70% composite exposed to the electrolyte becomes electrochemically active, accompanied by the strong adsorbing ability for

polysulfides by HPC material. These factors contribute to the excellent electrochemical performance of the composite cathode. In order to demonstrate the universality of the conclusion, we also prepared graphene/sulfur composites with three loading methods. Their performances showed the same results. Therefore, this work can assist in designing an optimal sulfur loading method for sulfur cathode with excellent performance.

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Figure captions:

Fig. 1. Schematic of the synthesis procedure of HPC and HPC/S.

Fig.2. Nitrogen adsorption/desorption isotherms of microporous/low-range mesoporous carbon hierarchical porous carbons (HPC) (A), the HPC/S composites (B) at -196 °C. The pore distributions of HPC (C) and the HPC/S (D).

Fig. 3. (A) XRD patterns of HPC, HPC/S composites and sulfur. (B) TGA curves of the as-prepared HPC/S composites recorded under argon atmosphere with a heating rate of 10 ℃·min^{-1}.

Fig. 4. SEM images of polypyrrole(PPy) (A, B), HPC (C), HPC/S composites for HPC/S-Sol-70% (D), HPC/S-155-70% (E), HPC/S-300-68% (F).

Fig. 5. TEM images of HPC (A), HPC/S composites for HPC/S-300-68% (B), HPC/S-155-70% (C), HPC/S-Sol-70% (D) and corresponding elemental maps obtained by EDX of the sulfur-filled porous carbon matrices (E-G).

Fig. 6. The cycling performances of the HPC/S composites at 200mA/g.

Fig. 7. Cyclic voltammograms of the HPC/S composites for HPC/S-Sol-70% (A), HPC/S-155-70% (B), at a scan rate of 0.1 mV s^{-1}. Charge/discharge voltage profiles of the (C) HPC/S-Sol-70%, HPC/S-155-70% (D), at first cycle of various C rates from 0.1C to 2C .

Fig. 8. The rate performances of HPC/S composites (A), the cycling performances of the HPC/S-Sol-70% based on 7 mg cm^{-2} s at 0.2 C and (B) the cycling performances of the HPC/S composites at 1C (C).

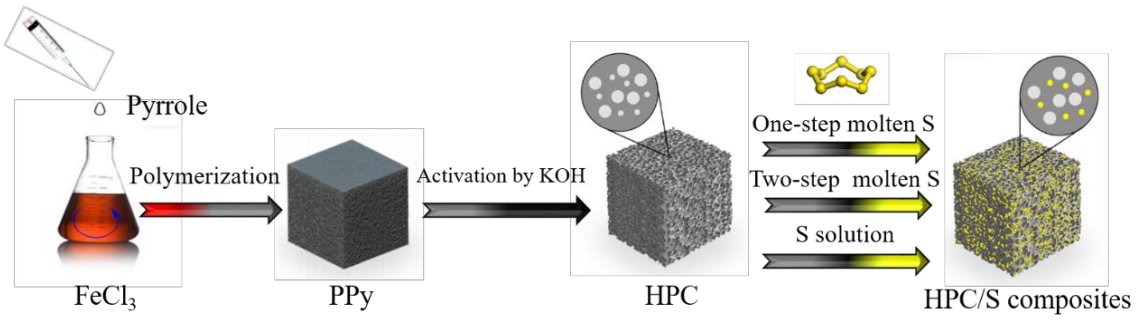

Fig. 1

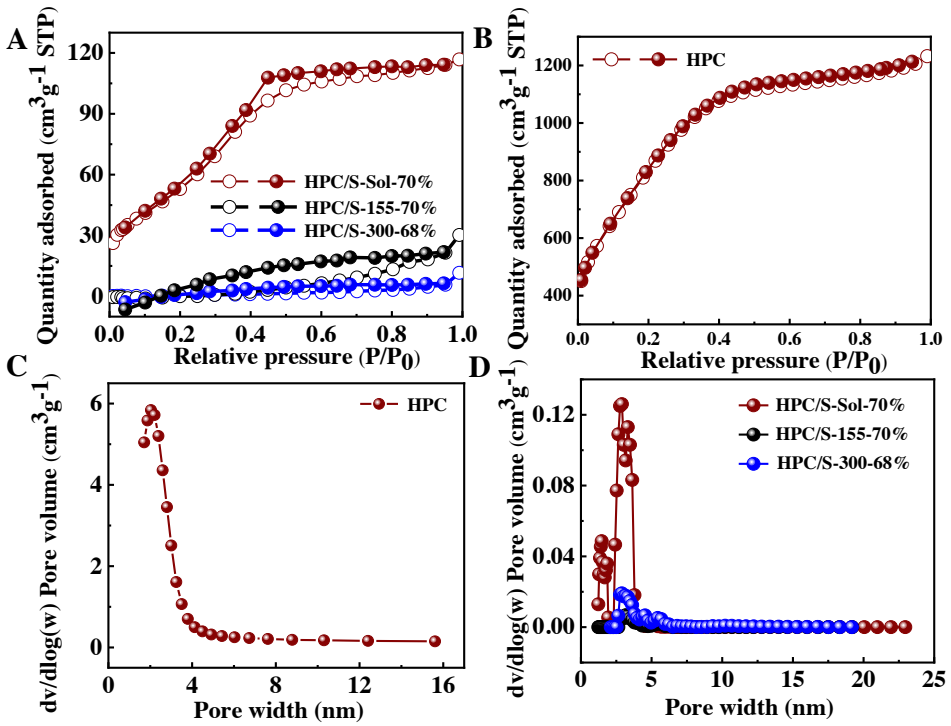

Fig. 2

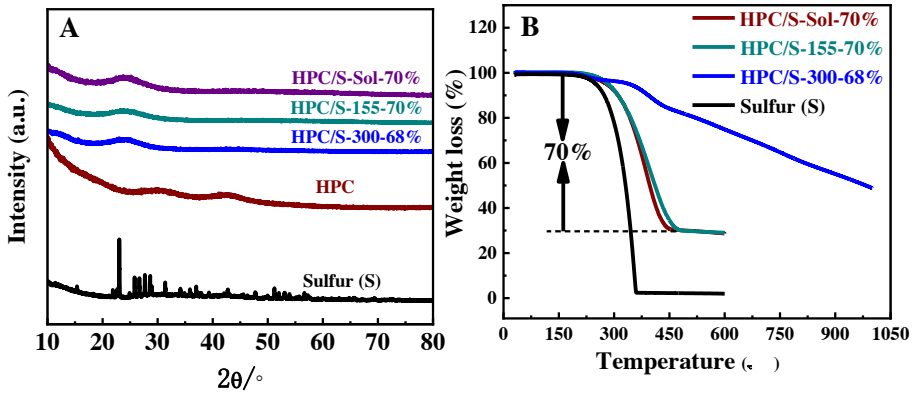

Fig. 3

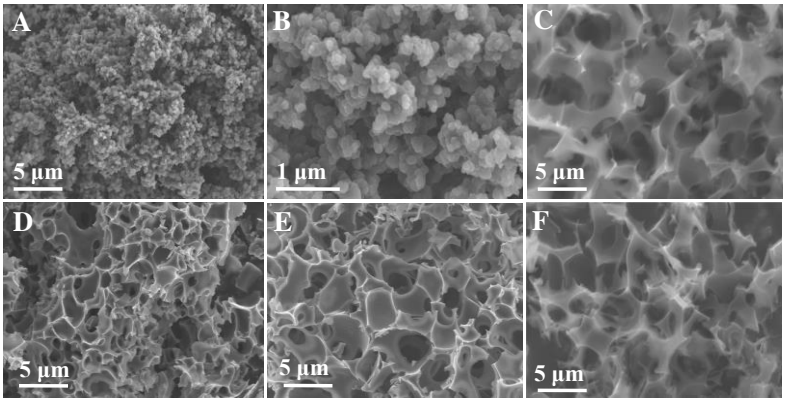

Fig. 4

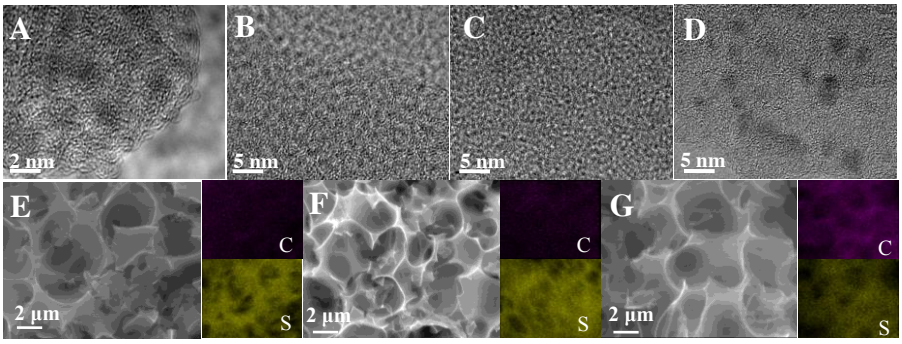

Fig. 5

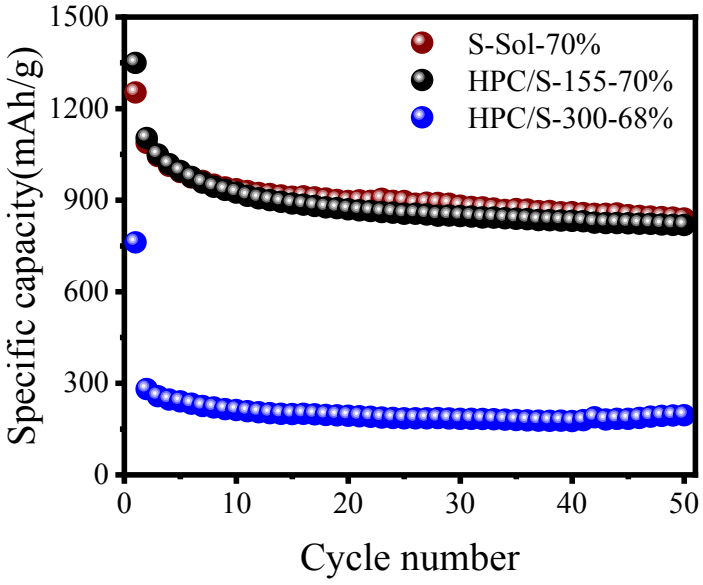

Fig. 6

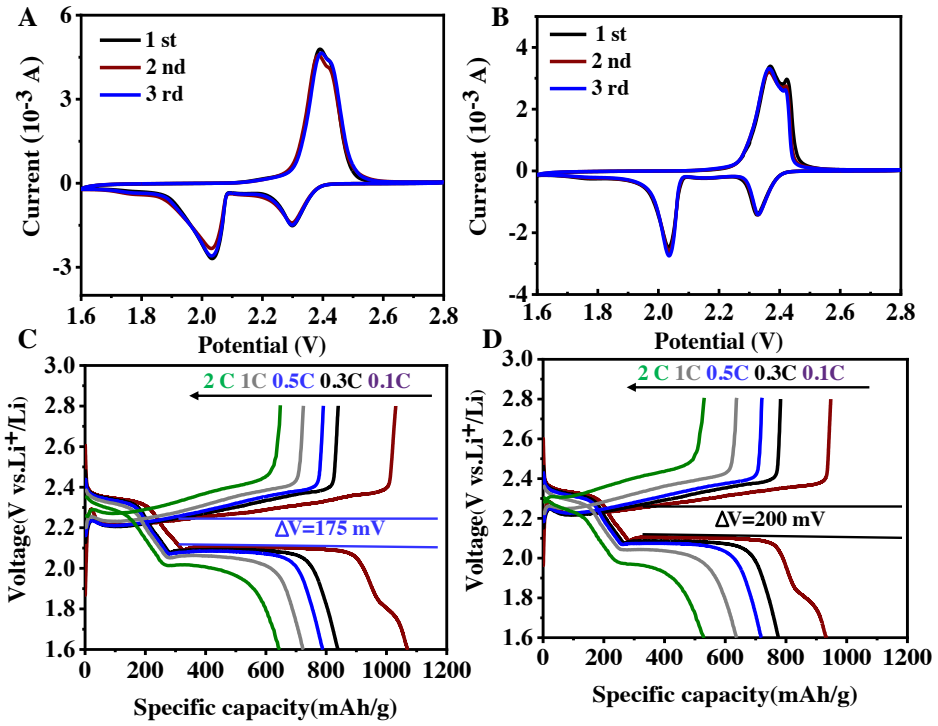
A
1 st
2 nd
3 rd
Current (10-3 A)
Potential (V)
B
1 st
2 nd
3 rd
Current (10-3 A)
Potential (V)
C
2 C 1C 0.5C 0.3C 0.1C
ΔV=175 mV
Voltage(V vs.Li+/Li)
Specific capacity(mAh/g)
D
2 C 1C 0.5C 0.3C 0.1C
ΔV=200 mV
Voltage(V vs.Li+/Li)
Specific capacity(mAh/g)

Fig. 7

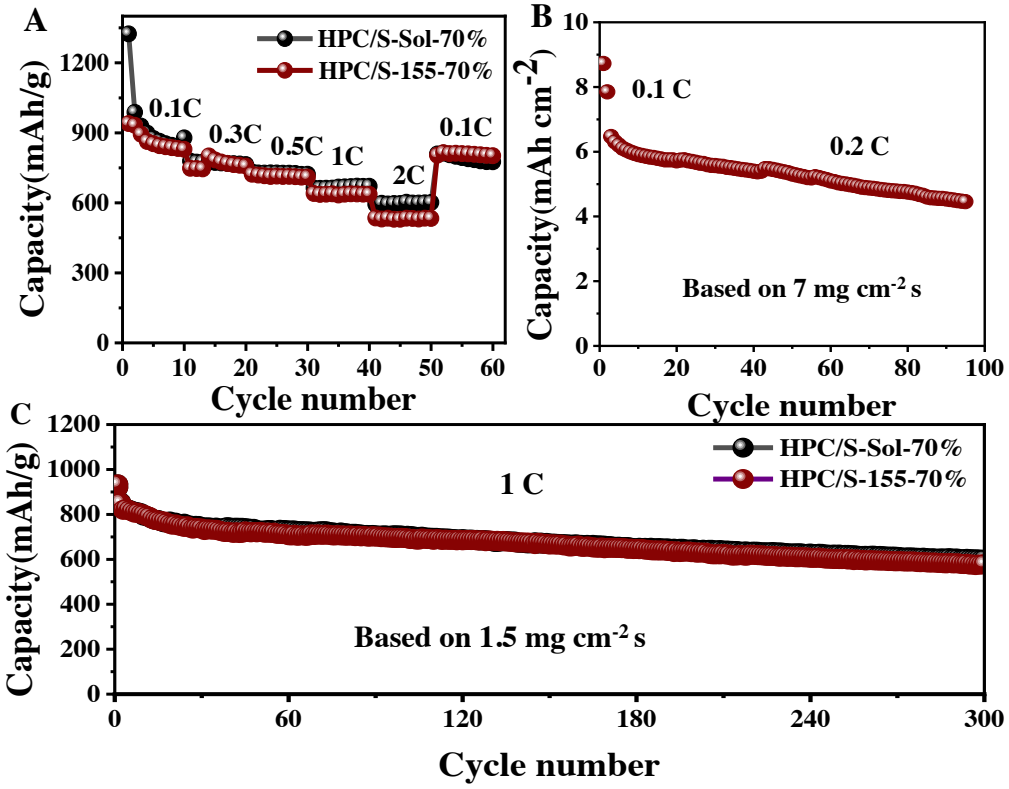
A
HPC/S-Sol-70%
HPC/S-155-70%
0.1C
0.3C
0.5C
1C
2C
0.1C
Capacity(mAh/g)
Cycle number
B
0.1 C
0.2 C
Based on 7 mg cm-2 s
Capacity(mAh cm-2)
Cycle number
C
1 C
HPC/S-Sol-70%
HPC/S-155-70%
Based on 1.5 mg cm-2 s
Capacity(mAh/g)
Cycle number

Fig. 8

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Bo Zhang, Zhijie Guo, Yingming Zhao, Birong Luo , Dejun Li, Teng Zhao, Jagadeesh Sure, Sri Maha Vishnu, Amr Abdelkader, Chris Harris, Kai Xi

Authors' Replies to Reviewers' Comments

Dear Editor :

Thanks for your kind handling about our paper "*Effect of Loading Methods on the Performance of Hierarchical Porous Carbon/sulfur Composites in Lithium Sulfur Batteries*". We greatly appreciate your tremendous efforts for the edition of our manuscript, and it is our great pleasure to receive the comments from you and the referees. The constructive comments and insightful suggestions from them are highly important for further improving the quality of our research. According to those comment and suggestion, we have revised the manuscript. The concerns have been carefully addressed and the mistakes have also been corrected in the revision. We sincerely hope this manuscript can be finally acceptable to be published in Electrochimica Acta.

The response to referees' comments

Reviewer # 1

Overall comment: This work reported hierarchical porous carbon/s cathode and compared the electrochemical performance of three different loading techniques. As the carbon based sulfur cathodes have been widely reported. The performance is not impressive and the novelty is poor. Therefore, I think this manuscript is not proper for the publication on Electrochimica Acta. Following are some concerns need to be addressed.

Response: Thank you very much for your comments and suggestions. We have made detailed modifications to the manuscript according to your suggestions. Although the three methods of loading sulfur are used in many literatures, they have not been systematically compared in hierarchical porous carbon. Therefore, we think our work is very meaningful.

Comment 1: There are a few typo errors in the manuscript and Figure.

Many thanks for your valuable suggestions. We've realized that the TEM & SEM images are incorrectly labelled. We have corrected the mistake.

Comment 2: The sulfur loading and sulfur content are very low.

Thanks very much for your suggestive comment. We've tested the high-load sulfur cells with a sulfur loading of 7 mg cm^{-2}. The HPC/S-Sol-70% electrode showed 4.4 mAh cm^{-2} after 98 cycles as shown in the following figure . Hence, with the reviewer's comments and suggestions, we have revised the corresponding part in the manuscript "Additionally, the HPC/S-Sol-70% composite cathode with 7 mg cm^{-2} sulfur areal loading also exhibited a high areal capacity of 8.7 mAh cm^{-2} at a current density of 0.1C and maintained a high areal capacity of 4.45 mAh cm^{-2} at a current density of 0.2C after 98 cycles (Figure 8b)". According to your comments and suggestions, we have clarified this point in Page 15, Line 7-10.

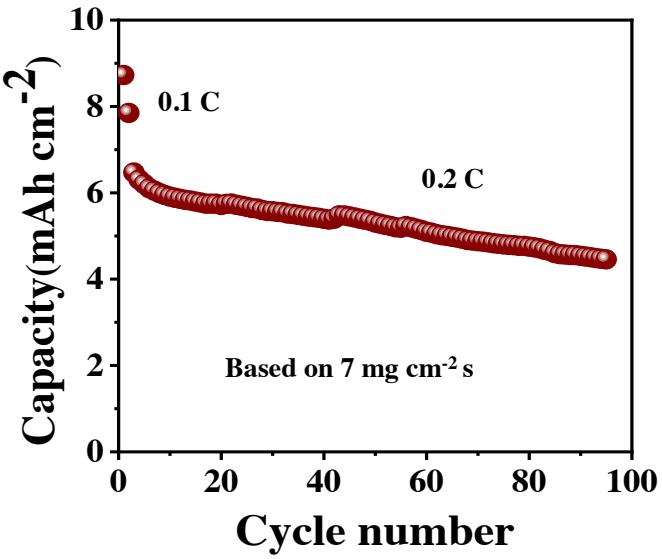

Fig. 8b. Cycling performance of the HPC/S-Sol-70% at 0.2C based on 7 mg cm^{-2} **s**.

Comment 3: The cycling performance is not impressive.

Many thanks for your valuable suggestions. We've tested HPC/S-Sol-70%, HPC/S-155-70% again between 1.6-2.8 V at 1C as shown in the following figure. We have revised the corresponding part in the manuscript "The rate performances of the three composite cathodes were further investigated at various current densities from 0.1C to 2C. As can be seen from Fig. 8A, HPC/S-Sol-70% delivers reversible capacities of 1324.5, 778.9, 732.3, 663.5, 593.5 mAh g^{-1} at current densities of 0.1 C, 0.3 C, 0.5 C, 1 C, 2 C respectively, which are much higher than those of other HPC/composites.

When the current density is returned to 0.1C, the capacity is recovered to values of 809.5, 803.5, for the HPC/S-Sol-70%, HPC/S-155-70%, composites respectively. This again shows how the pore structures formed by the solvent-mediated loading method facilitated the utilization of sulfur.

The cycle performances of the three composites over 300 cycles at 1C between 1.6-2.8 V are shown in Fig. 8C. After 300 cycles, the discharge capacities of the two samples reach 599, 578.8 mAh g^{-1} for HPC/S-Sol-70%, HPC/S-155-70% respectively. The HPC/S-Sol-70% composite cathode exhibited the best cycling performance, implying that the simple wet chemical synthesis route of deposition method contributes to a significant restriction of the shuttle effect for polysulfides." According to your comments and suggestions, we have added this point in Page 14.

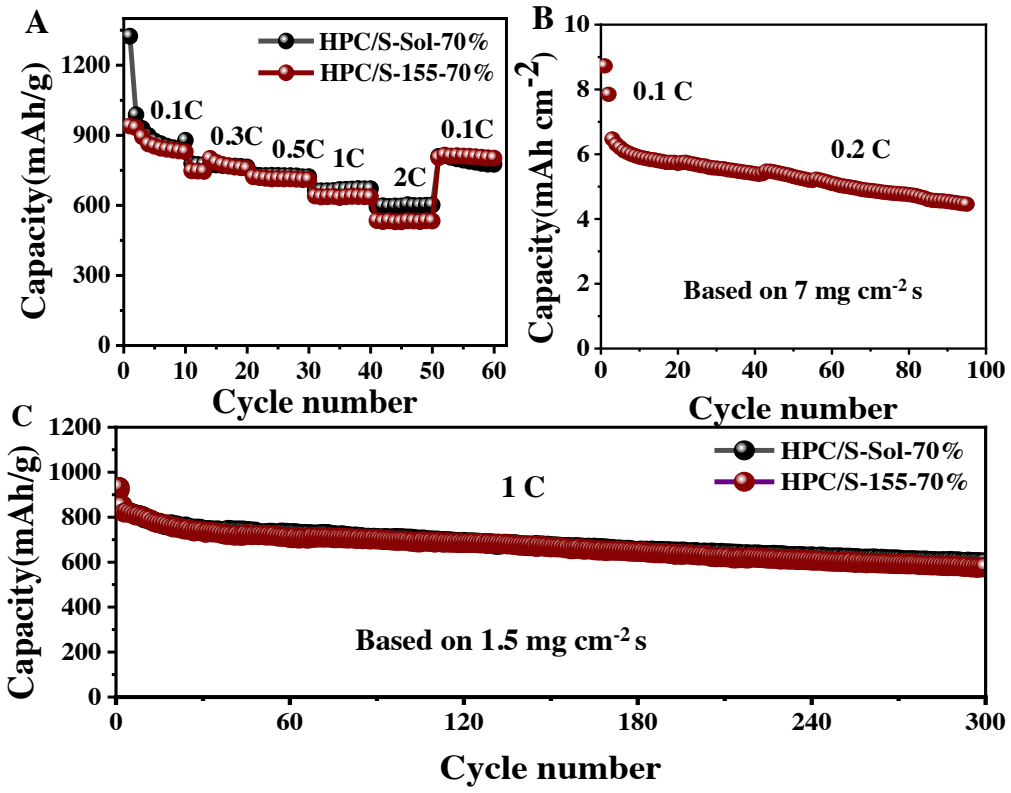

Fig.8. The rate performances of HPC/S composites (A), the cycling performances of the HPC/S-Sol-70% based on 7 mg cm-2 s and (B) the cycling performances of the HPC/S composites at 1C (C).

Comment 4: The cycled electrode should be studied.

Many thanks for your valuable suggestions. We've researched the cycled electrode

and added in in the manuscript “After 100 cycles, the morphology of the positive electrode was tested. Compared with before cycling, there is little difference, and there is no large sulfur deposit (Figure S4).” According to your comments and suggestions, we have added this point in Page 15, Line 5-7.

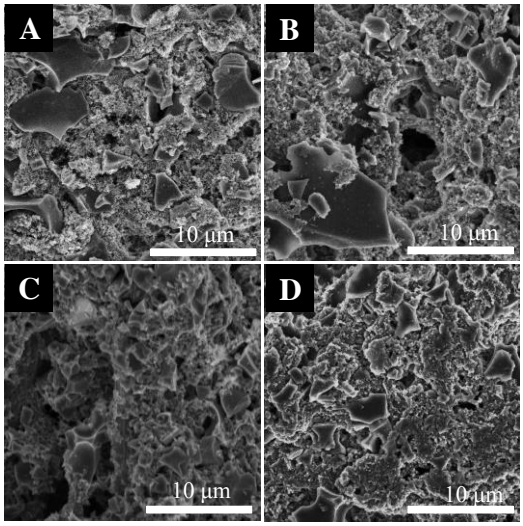

Fig. S4. SEM images of cathodes before cycling for HPC/S-Sol-70% (A), HPC/S-155-70% (C), and after one hundred cycles for HPC/S-Sol-70% (B), HPC/S-155-70% (D).

Comment 5: It is weird that the HPC/S-300 electrode shows poor electrochemical performance but has the lowest Rct.

Many thanks for your valuable suggestions. To confirm the result, we've re-tested electrochemical impedance spectroscopy and the HPC/S-300 electrode shows the highest Rct exactly. We have updated the EIS data in supporting information.

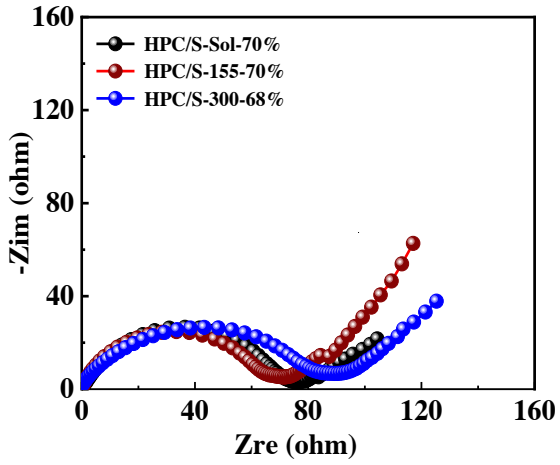

Fig. S3. Nyquist plots for the HPC/S composite cathodes before cycling.

Reviewer #2:

With the requirement of clean energy in modern everyday life, lithium-sulfur batteries become one of promising energy storage technologies. However, a couple of their drawbacks hinder their applications. In the manuscript "Effect of loading methods on the performance of hierarchical porous carbon/sulfur composites in lithium sulfur batteries", the authors adopted three loading approaches to prepare hierarchical porous carbon/ sulfur composite cathode, and found the "simple sulfur organic solution impregnation method" is the most effective approach to improve the electrochemical performance of the cathode. The morphologies and electrochemical performance of cathodes from different methods were examined. It is an interesting manuscript. However, I have some concerns.

Response: Thank you very much for the positive comments and recommendation on our research work. As the reviewer mentioned, our finding is an interesting study, and we try to provide an effect of loading method on the performance of hierarchical porous carbon/sulfur composites in lithium sulfur batteries, which can also inspire the broad interest in lithium sulfur batteries.

Comment 1: Please provide SEM images of cathodes from the three approaches after one hundred cycles.

Many thanks for your valuable suggestions. We've researched the cycled electrode and added in in the manuscript “After 100 cycles, the morphology of the positive electrode was tested. Compared with before cycling, there is little difference, and there is no large sulfur deposit (Figure S4).” According to your comments and suggestions, we have added this point in Page 15, Line 5-7.

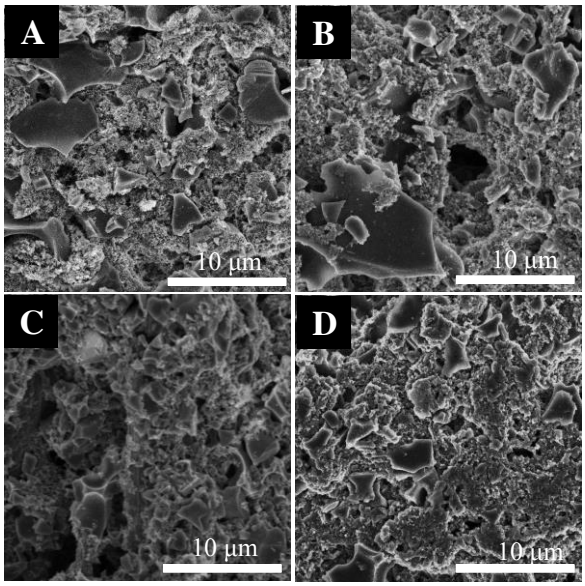

Fig. S4. SEM images of cathodes before cycling for HPC/S-Sol-70% (A), HPC/S-155-70% (C), and after one hundred cycles for HPC/S-Sol-70% (B), HPC/S-155-70% (D).

Comment 2: Figure 7: The cycle number is too small. Is it possible to provide a large cycle number for the discharge capacity.

Many thanks for your valuable suggestions. We've tested HPC/S-Sol-70%, HPC/S-155-70% again between 1.6-2.8 V at 1C as shown in the following figure. We have revised the corresponding part in the manuscript "The rate performances of the three composite cathodes were further investigated at various current densities from 0.1C to 2C. As can be seen from Fig. 8A, HPC/S-Sol-70% delivers reversible capacities of 1324.5, 778.9, 732.3, 663.5,593.5 mAh g^{-1} at current densities of 0.1C, 0.3C, 0.5C, 1C, 2C respectively, which are much higher than those of other HPC/composites. When the current density is returned to 0.1C, the capacity is recovered to values of 809.5, 803.5, for the HPC/S-Sol-70%, HPC/S-155-70%, composites respectively. This again shows how the pore structures formed by the solvent-mediated loading method facilitated the utilization of sulfur.

The cycle performances of the three composites over 300 cycles at 1C between 1.6-2.8 V are shown in Fig. 8C. After 300 cycles, the discharge capacities of the two samples reach 599, 578.8 mAh g^{-1} for HPC/S-Sol-70%, HPC/S-155-70% respectively. The HPC/S-Sol-70% composite cathode exhibited the best cycling performance,

implying that the simple wet chemical synthesis route of deposition method contributes to a significant restriction of the shuttle effect for polysulfides." According to your comments and suggestions, we have added this point in Page 14-15.

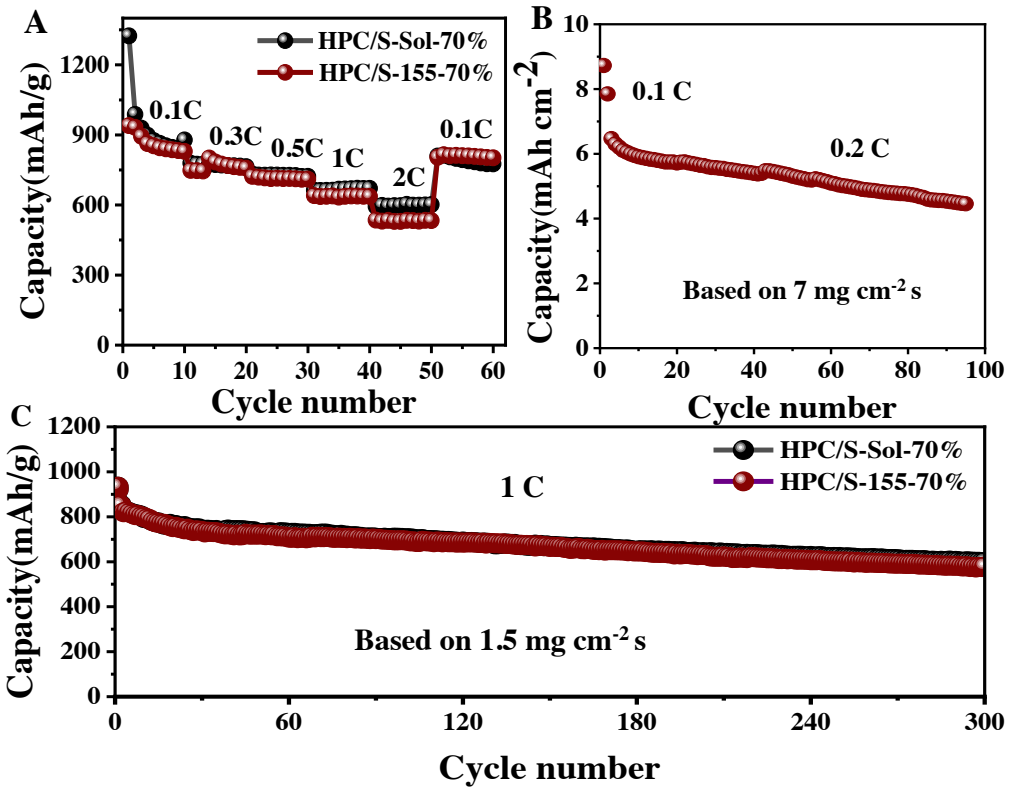

Fig.8. The rate performances of HPC/S composites (A), the cycling performances of the HPC/S-Sol-70% based on 7 mg cm^{-2} s and (B) the cycling performances of the HPC/S composites at 1C (C).

Comment 3: The authors claim that the cathodes have good electrical conductivity. Can they prove it?

Thanks for your valuable suggestions. We have tested the electrical conductivity of the positive electrode with the four-probe method. The three cathodes have an electrical conductivity of 7−8 S cm^{-1} at room temperature. "Despite nano-sized sulfur exists in the composite material, the three cathodes have an electrical conductivity of 7−8 S cm^{-1} at room temperature." We have added this point in Page 9 line16.

Comment 4: Introduction "Encapsulating sulfur into a conductive matrix has been

demonstrated to be an effective mean to confine polysulfide species and improve the electrical conductivity of the electrode. Various conductive matrixes have been explored, including porous carbon, carbon nanotubes, carbon nanofibers, graphene, and graphene deriatives, metal organic frameworks (MOFs) and metal oxides." More references (e.g. Journal of Materials Chemistry A, 2018, 6, 16574 -16582; Energy Storage Materials, 2019, 17, 118-125) are needed to support this statement.

Many thanks for your valuable suggestions. We have added the two references in the manuscript in Page 4, Line 6

[35] C. Zha, D. Wu, T. Zhang, J. Wu, H. Chen, Energy Storage Materials, 17 (2019) 118-125.

[36] C. Zha, F. Yang, J. Zhang, T. Zhang, S. Dong, H. Chen, Journal of Materials Chemistry A, 6 (2018) 16574-16582.

Comment 5: Section 2.2 "The HPC prepared form the previous step was used as the matrix…" Is it "from" or "form"?

Thanks very much for your suggestive comment. This is our mistake, we have correct it in the manuscript "The HPC prepared from the previous step was used as the matrix and sublimed sulfur (Aladdin, Shanghai) was used as the sulfur source"

Comment 6: Section 2.2 "For comparison, the graphene material obtained from Inner Mongolia RS new Energy Co., Ltd was incorporated with sulfur using the same three methods." Please provide the properties of the graphene materials adopted in this manuscript.

Many thanks for your valuable suggestions. We have added properties of the graphene materials in Page 6 line 22 (PH: 2±0.2; N, S, Cl%<0.5%; metal impurity<100ppm; ash<1.0%).

Comment 7: Section 3 "Also, the HPC possesses a relatively high total pore volume of 2.6 cm3 g-1 and a large (BET) surface area of 3270.4 m2 g^{-1} based on density function

theory calculation." Please provide the details of computational method and modeling of DFT.

Response:

The DFT models are created by classical approaches to adsorption as well as models based on modern statistical thermodynamics. Two simulation techniques are commonly used to determine the distribution of gas molecules in a system in equilibrium: the molecular dynamics method and the Monte Carlo method. Both of these are used as reference methods because their results are considered exact. We have added the details in page 8, line 18-20.

Reviewer #3:

This study looks at the impact of producing hierarchical material to produce a LSB. This is a good solid study, but more work is required to bring all of the pieces together. At present, one hypothesis is generated for each experimental observation, but the reader lacks one cohesive story at the end which draws all these components together. At some points there even seems to be conflicting findings.

Response: Thank you very much for the positive comments and recommendation on our research work. As the reviewer mentioned, our finding a good solid study, and we try to provide an effect of loading method on the performance of hierarchical porous carbon/sulfur composites in lithium sulfur batteries, which can also inspire the broad interest in lithium sulfur batteries.

For example, the CT resistance from the EIS for the HPC/S-300-68% cell is the lowest, but this cell performs very poorly. The current hypothesis provided is that the 300 cell has an excellent dispersion, but if this is the case, why does the cell perform so poorly in the battery testing? Also, this cell shows the highest over potential loss, which would suggest a low impedance.

Response: Many thanks for your valuable suggestions. To confirm the result, we've re-tested electrochemical impedance spectroscopy and the HPC/S-300 electrode shows the highest Rct exactly. We have updated the EIS data in supporting information

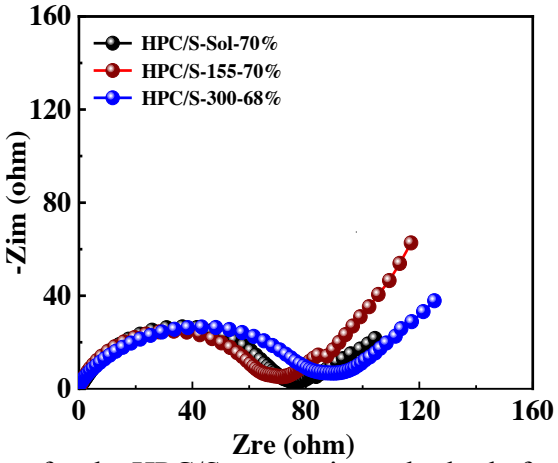

Fig. S3. Nyquist plots for the HPC/S composite cathodes before cycling.

From XRD is looks like you have diffuse sulfur peak, this may simply suggest you have nano-sized sulfur and not amorphous sulfur.

Response: Thanks very much for your suggestive comment，after careful analysis and study, we have the same opinion with you. Some nano-sized sulfur exist in the composite material. We have added the corresponding part in the manuscript. "None of the HPC/S composites, regardless of the sulfur loading method, contain the characteristic peaks of crystalline sulfur, indicating that the nano-sized sulfur exists in the composite material." According to your comments and suggestions, we have added this point in Page 9, line16-18.

Details missing from the SEM & TEM. Are these FEG instruments? If so, you would expect very low pressures. This could easily sublime the sulfur - especially in cases where the authors suggest that the sulfur is on the surface.

Response: Yes, these are FEG instruments for SEM and TEM with very low pressures, which can lead to some sublimation of the sulfur. However, this has almost no impact

on the SEM and TEM according to the obvious sulfur elemental maps obtained by EDX.

The TEM & SEM images are incorrectly labelled. Some images are labelled as TEM, but they are clearly SEM images. Can the authors please provide EDS point analysis data to check that the sulfur is being mapped. As stated above, sulfur easily sublimes, so it would be good to confirm that sulfur is being mapped and it isn't an artefact from another peak. It is not possible from these TEM images to confirm that sulfur is on the surface.

Response: We are sorry to make a mistake. We have corrected it carefully. And we also provided EDS point analysis data in supporting information according to the reviewer's suggestion, which can confirm that sulfur is on the surface of HPC accompanied with TEM images.

I cannot see any noticeable difference in the porous structures in the TEM images.

Response: It is almost indistinguishable from the observation on TEM, because the pore size is too small. We have modified the content in manuscript. The micropores and mesopores can be found out distinguishable from BET results.

I do not understand the argument presented on page 9 line 15 "The reason for the relatively …" I am not sure what CS2 solution is being referred to and why this leads to stretching and why this may lead to sulfur on the surface. If you have an opened structures, would you not expect more sulfur inside?

Response: Thanks very much for your suggestion. There is surface tension between the solution and the micropores, so that part of the sulfur cannot enter the pores. If all the elemental sulfur is in the micropores, the active material will not fully contact the electrolyte, resulting in increased polarization and incomplete utilization of the active material.

The key point of the paper the "hierarchical" structure seems to be brushed over in most of the discussions. Once again, this could be strengthened by drawing the findings

together more cohesively at the end of the paper. A schematic would help illustrate what your hypothesis is.

Response: Thanks for your suggestions. We have shown the "hierarchical" structure in the schematic of synthesis procedure of HPC and HPC/S. And the schematic was further modified based on your suggestions.

Why is a cut off voltage of 1 V used? This is very low for a LSB.

Response: Many thanks for your valuable suggestions. We've tested again between 1.6-2.8 V as shown in the following figure.

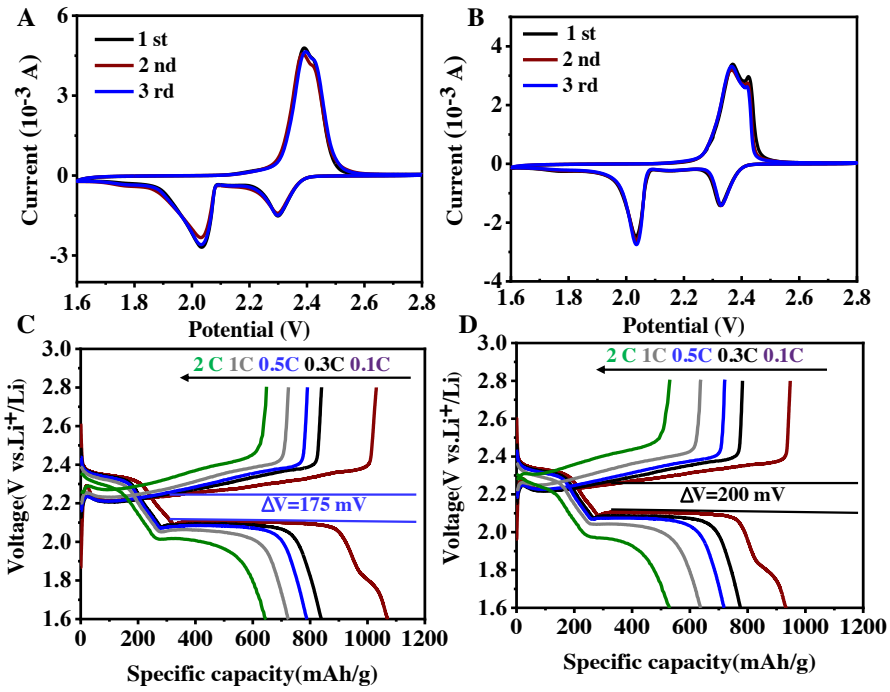

Fig. 7. Cyclic voltammograms of the HPC/S composites for HPC/S-Sol-70% (A), HPC/S-155-70% (B), at a scan rate of 0.1 mV s^{-1}. Charge/discharge voltage profiles of the (A) HPC/S-Sol-70% , HPC/S-155-70% (B), at first cycle of various C rates from 0.1C to 2C .

It is easier for the reader to have the sample labels directly on the images or graphs. For example in Figure 6 and the SEM and TEM images. Also as these figure labels are incorrect, I was really unsure what was being discussed.

Response: Many thanks for your valuable suggestions. We've realized that the TEM & SEM images are incorrectly labelled and corrected the mistake.

Although it is good to know the current density, please also include C-rates - this will be necessary to compare with other studies.

Response: Many thanks for your valuable suggestions. We've tested the properties of C-rates as shown in the following figure. The rate performances of the three composite cathodes were further investigated at various current densities from 0.1C to 2C. As can be seen from Fig. 8 A, HPC/S-Sol-70% delivers reversible capacities of 1324.5, 778.9, 732.3, 663.5,593.5 mAh g^{-1} at current densities of 0.1C, 0.3C, 0.5C, 1C, 2C respectively, which are much higher than those of other HPC/composites. When the current density is returned to 0.1C, the capacity is recovered to values of 809.5, 803.5, for the HPC/S-Sol-70%, HPC/S-155-70%, composites respectively. This again shows how the pore structures formed by the solvent-mediated loading method facilitated the utilization of sulfur.

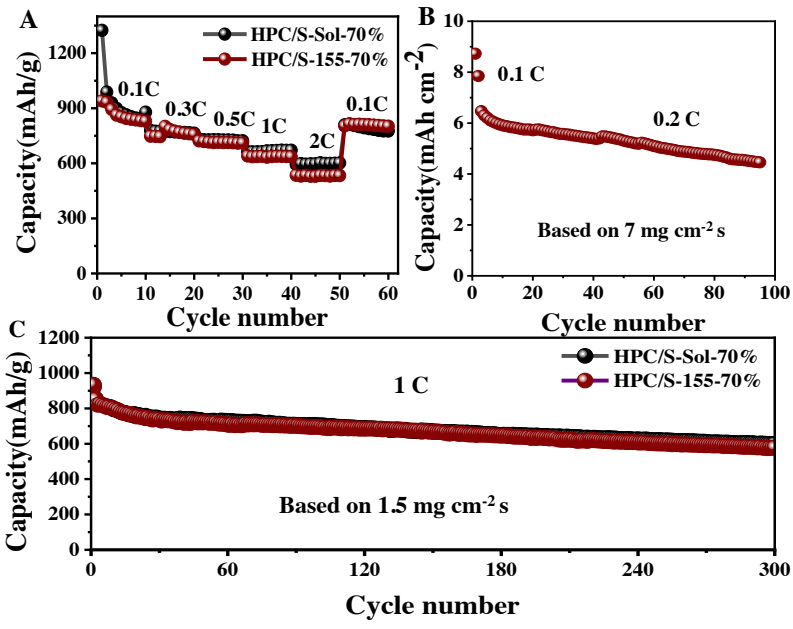

Fig.8. The rate performances of HPC/S composites (A), the cycling performances of the HPC/S-Sol-70% based on 7 mg cm^{-2} s and (B) the cycling performances of the HPC/S composites at 1C (C).