I, N Co-doped hierarchical micro/mesoporous carbon modified separator for enhanced electrochemical performances of lithium-sulfur batteries

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Abstract
Although the high discharging capacity and coulombic efficiency can be obtained by impregnating sulfur into various conductive porous hosts in lithium-sulfur (Li-S) batteries, the low sulfur loading content and volumetric specific energy diminish their advantages. To solve this problem, a modified layer is prepared by coating I and N co-doped hierarchical micro/mesoporous kelp bio-carbon on surface of the polypropylene separator. Furthermore, the composite porous carbon is obtained by one-step thermal pyrolysis of edible dried kelp. The modified layer on separator can effectively prevent shuttle of polysulfides due to the synergistic effect from the micro/mesoporous carbon structures (physisorption effect) and I and N co-doped electrochemical active sites in carbon matrix (chemisorption effect), allowing high capacity and high coulombic efficiency. In this study, we developed Li-S batteries with 80% sulfur loading content and the area loading is higher than 2.0 mg cm−2, which are better than previous published ones. In addition, the cathode electrode could stabilize at 760 mAh g−1 after 200 cycles at 0.5 C and delivers a high retention specific capacity of 498 mAh g−1 after 500 cycles with a slight capacity attenuation of 0.07% per cycle.

1. Introduction

Sulfur, as cathode material in lithium-sulfur (Li-S) batteries, has high theoretical specific capacity (about 1670 mAh g−1), larger than that of the conventional cathode materials, such as LiCoO2, LiFePO4 and Li(NiCoMn)O2 etc [1–4]. And the energy density of Li-S batteries is about 2600 Wh Kg−1, higher than that of the current commercial lithium-ion batteries [5–8]. Moreover, with the advantages of low price, abundant raw materials, and environmentally friendliness, Li-S batteries are considered to be one of the most promising next-generation high energy storage devices. In spite of possessing the capability of obtaining high energy densities, Li-S batteries still have some inherent shortcomings such as a notorious shuttle effect, poor conductivity of sulfur and obvious volume expansion, all of which are major factors that prevent sulfur from being a promising cathode material [1]. Especially for the shuttle effect, long chain polysulfide ions (SSn−, 4 ≤ n ≤ 8) generated in the redox process of S8 are easily soluble in organic electrolytes, resulting in loss of active substances and low coulombic efficiency [5–7].

Tremendous efforts have been made to address the above issues, and one effective approach is to impregnate sulfur into porous carbon hosts [9, 10]. The carbon can enhance electrical conductivity of cathode material, and the porous structures can accommodate active sulfur and the polysulfides intermediates. However, carbon with homogeneous nonpolar surface cannot afford a sufficient suppression effect to maintain polysulfides within the cathode. The polar inorganic materials, such as MoS2, TiO2, and N-doped carbon, have been developed to
alleviate the dissolution polysulfides due to the strong chemical interaction \([8,11,12]\). In addition, the nanostructures with catalytic effect, such as MnO\(_2\), Nb\(_2\)O\(_5\), have also been introduced to accelerate the conversion of intermediate polysulfides \([13,14]\). However, their advantages have been diminished by the low sulfur loading contents and low volume energy density due to the inevitable composite porous hosts, which greatly limits the application of composite sulfur cathodes to achieve high energy density \([1,15]\). Moreover, these composite sulfur cathodes usually require elaborate design and tedious preparation processes, which are disadvantage to the large-scale application in Li-S batteries.

Recent advances have demonstrated that modified separator by an obstructive coating layer is an effective way to suppress the polysulfides migration, facilitate the conversion of polysulfides to insoluble sulfides \([16–18]\). To further block the shuttle effect, the N-doped porous carbon has also been used as the coating layer due to the dipole electrostatic interaction between the carbon hosts and the polysulfide \([9]\). Recently, Iodine-doped graphene, obtained from treating the mixture of I\(_2\) and graphene at 900 °C in argon atmosphere, has been reported to induce the triiodide \((I_3^-)\) and pentaiodide \((I_5^-)\) polyanions, resulting in the formation of negative-charge polyanides and positive-charge graphene \([19]\). And the iodine-doped graphene possesses a substantial number of electrochemical active sites, with strong electrostatic interaction to immobilize polysulfides.

Inspired by the I and N dopant, we can co-dope the two elements into porous carbon matrix as the modified layer, and the strong synergistic effect from the double electrochemical active sites and physisorption can prevent shuttle of lithium polysulfides, allowing high capacity and high coulombic efficiency. Here, the commercial kelp has been used to prepare the low-cost I and N co-doped hierarchical micro/mesoporous bio-carbon, and the sea salt in kelp is the cause of the mesoporous structure. And the obtained carbon materials were uniformly coated on the conventional polypropylene separator, obviously enhancing the cycle stability and rate performance due to the synergistic effect from the micro/mesoporous carbon structures (physisorption effect) and I and N co-doped electrochemical active sites in carbon matrix (chemisorption effect). More importantly, the cathode is prepared by the common sulfur powder with several microns. Thus, the electrochemical performances of proposed Li-S batteries with 80% sulfur loading content and the area loading higher than 2.0 mg cm\(^{-2}\) are better than those previously reported. And the cathode could stabilize at 760 mAh g\(^{-1}\) after 200 cycles at 0.5 C and delivers a high retention specific capacity of 498 mAh g\(^{-1}\) after 500 cycles with a slight capacity attenuation of 0.07% per cycle. Here, we report the first study of the separator modified by I, N co-doped hierarchical micro/mesoporous kelp bio-carbon enhancing the chemisorption and physisorption effects of polysulfides for improving electrochemical performances of Li-S batteries.

### 2. Experimental section

#### 2.1. Preparation of I and N co-doped hierarchical micro/mesoporous bio-carbon modified separator

Kelps were purchased from supermarket without cleaning, and carbonized in a tubular furnace under N\(_2\) atmospheres at 850 °C for 2 h. The obtained kelp bio-carbon was treated by diluted hydrochloric acid and deionized water to remove the impurities and remaining sea salts. Then, the cleaned and dried kelp bio-carbon mixed with PVDF (polyvinylidene fluoride) with weight ratio of 9:1 employing NMP (N-methyl-2-pyrrolidinone) as solvent, ground to slurry and coated on Celgard 2400 separator. Finally, the obtained kelp bio-carbon modified separator was dried in vacuum at 60 °C for 24 h, and was cut into 19 mm diameter disks. For comparison, the thermal pyrolysis of cotton-seed husks (CSHs) was conducted to achieve N-doped bio-carbon to modify separator with the same processes.

#### 2.2. Material and electrode characterization

The working electrodes were prepared by mixing the commercial sublimed sulfur (Sinopharm Chemical Reagent Co., Ltd.), PVDF and conductive additive (acetylene black) with weight ratio of 8:1:1 in a solvent of NMP solution. The slurry was coated on aluminum foil and dried in vacuum oven at 70 °C for 12 h. Lithium metal was used as anode, and the separators were coated with kelp bio-carbon and CSHs bio-carbon. 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1, v/v) were mixed to prepare the electrolyte, in which 1 mol l\(^{-1}\) LiTFSI with 0.1 M lithium nitrate (LiNO\(_3\)) were dissolved as additive. For the electrode characterization, the obtained electrodes were assembled into 2025-type coin cells. And the sulfur loading is about 2.0 mg cm\(^{-2}\) for each of cathode electrodes for the kelp bio-carbon and CSHs bio-carbon Li-S batteries. SEM (TESCAN VEGA3, ZEISS Sigma HD) was used to characterize the morphology, and Transmission electron microscope (TEM, JEM-3000F, JEOL), micro-Raman spectroscopy (WITec excited by \(\lambda = 633\) nm laser), X-ray diffraction (XRD, D/MAX 2500) with Cu–Ka Radiation and x-ray photoelectron spectroscopy (XPS, ESCA-3400) were used to visualize internal crystalline structures. Moreover, BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) were also applied to get specific surface area and porosity analysis. We conducted the contact angle measurements on the contact angle measuring instrument (Edinburgh...
Instrument). For the electrode characterization, the discharge/charge capacity of the composite electrodes is decided by galvanostatically cycling the half-cells over potential range between 1.7 V and 2.8 V (NEWARE BTS-5V 5 mA, Neware Technology Co. Ltd, China). An electrochemistry system (CHI 660D, China) helped to achieve cyclic voltammetry (CV) curves and AC impedance spectra. All the tests were carried out at room temperature.

3. Results and discussions

Figure 1 is the schematic of synthesis process of the I and N co-doped porous kelp bio-carbon coating layer on the separator, and the specific experimental processes have been described in the experimental section. As we know, kelp is a common edible food in our daily life, which is rich in nitrogen elements, such as amino acid, vitamins and pectin. Moreover, kelp contains a key element of iodine, which exists in the form of organic iodine (3,5-diiodotyrosine, C₉H₉I₂NO₃), and I is directly bonded to the carbon in benzene ring in the organic iodine molecule, as shown in figure 1(a). Briefly, the kelp bio-carbon powder was synthesized by one-step carbonization of commercial dried kelp at 850°C in N₂ atmosphere, while the brown dried kelp changed to black bio-carbon. Meanwhile, the chemical components, such as crude cellulose, organic iodine and amino acids, were thermally decomposed, forming the required I and N co-doped porous kelp bio-carbon materials, as shown in figure 1. After grinding and coating, the kelp bio-carbon powder can tightly attach on one side of separator, and the black coating surface is smooth and flat. Although after many times of bending test, the kelp bio-carbon powder did not fall off, indicating that the modified separator can bear strong mechanical stress.

To understand the structure of the prepared kelp bio-carbon, multiple characterization techniques have been employed, and we can see the corresponding results in figure 2. For the XRD pattern in figure 2(a), there are two manifest diffraction peaks at 25° and 43°, both of which attribute to (002) and (110) peaks of graphite. However, the two diffraction peaks are relatively wide indicating low graphitization. On the other hand, the Raman spectrum is exhibited in figure 2(b), and two distinct peaks at 1342 and 1597 cm⁻¹ belong to the D and G band respectively. Moreover, the intensity of G-band is a little higher than D-band, which is resulted from that the component of SP² carbon is more than that of the disorder carbon [20]. The partial graphitized carbon is due to the catalysis function of the iron in kelp at high temperature [21]. Furthermore, it can also suggest that the kelp bio-carbon has better electrical conductivity than the common amorphous carbon.

Because of the rich organic ingredients in kelp, it is easy to form natural N-doped carbon after carbonization. Thus, FTIR absorption spectrum and XPS spectrum have been used to analyze the chemical composition. We can see from figure 2(c) that three covalent bonds formed by N with C, O and H (C–N–O, N–H, C–N, and –N=C=O), corresponding to the absorption peaks at 484.06 cm⁻¹, 619.17 cm⁻¹, 1085.78 cm⁻¹ and 1402.06 cm⁻¹ [22]. The surface chemical compositions of kelp bio-carbon were analyzed by the XPS spectrum. In figure 3(d), we can clearly see the C 1s, O 1s and N 1s in the prepared kelp bio-carbon, and a weak peak about
619 eV illustrates the presence of I 3d. In figure 3(e), the two binding energy peaks at 618.1 and 619.7 eV correspond to triiodide (I₃⁻) and pentaiodide (I₅⁻) polyanions, respectively, inducing to form the negative-charge polyiodides and positive-charge carbon matrix, helping to block the shuttle of polysulfides [19]. Three different nitrogen environments in the N1s spectrum are showed in figure 2(d), which include graphitic, pyrrolic, and pyridinic N, corresponding to 401.2, 400.1, and 398.5 eV, respectively [23, 24]. And the doped N atoms as electron-withdrawing atoms can make a difference to the nearby electronic structure and have high activity in interacting with the intermediate polysulfides. Additionally, the element composition and distribution can also be observed by the element mapping of SEM. It’s clearly to see that carbon (C 1s), nitrogen (N 1s) and Iodine (I 3d) are distributed evenly in the kelp bio-carbon matrix, as shown in figures 2(g)–(j). On the basis of the above results, it can be concluded that the elements of I and N have been uniformly doped into the kelp bio-carbon, formed corresponding bonds with carbon. And the I and N co-dopant in carbon matrix can further enhance the electrochemical active sites in the modified layer on separator to block the shuttle of polysulfides.

Figures 3(a) and (b) are the SEM images of kelp bio-carbon under different magnification. Obviously, there are large number of micron pores about 10 ~ 50 um in the kelp bio-carbon. These irregular micropores attribute to the dehydration of water from plant cells and the fragmentation at high-temperature carbonization process, effectively increase the specific surface area and facilitate the physisorption of polysulfide. In addition, the typical BET surface area and pore size spread curves are also presented in figures 3(c) and (d). The BET surface area is 488.27 m² g⁻¹ in figure 3(c), and the pore volume is 0.394 cm³ g⁻¹. Except microporous structures observed by SEM, we can also find mesoporous structure with the pore size distribution in about 2 ~ 3 nm existing in our prepared kelp bio-carbon, as shown in figure 3(d). To explore the cause of mesoporous structures, the cleaned kelp was carbonized under the same treatments. However, the mesoporous cannot be found, and the specific surface area also reduces to 152.1 m² g⁻¹ (the supporting information of both results can be seen in figure S1 (available online at stacks.iop.org/MRX/8/115002/mmedia)). Based on the above results, we conclude that the sea salt (main ingredients NaCl) is the key factor to form the mesopores in the kelp bio-carbon. For the kelp without cleaning, a large amount of solid sea salt with nanoscale distributes in the dried kelp, and the high-temperature carbonization does not destroy the nanoscale sea salt. However, after cleaning, the sea salt...
existing in the carbon hosts can be removed away, leaving a large number of mesopores in the kelp bio-carbon. On the contrary, if the sea salt in kelp is washed away before carbonization, the mesoporous structure cannot be formed. It should be noted that the formation of these mesoporous structures avoids the extensive use of chemically activated reagents, such as KOH. These mesoporous can not only significantly facilitate the permeation of the electrolyte and the rapid transport of Li ions, but also sufficiently alleviate the shuttle effect.

Additionally, the microstructure of the prepared kelp bio-carbon powder is also further characterized by TEM, as shown in figures 3(e)–(g). Under the low magnification of TEM image, the kelp bio-carbon has no regular morphology in figures 3(e) and (f). However, we can still observe some flocculent morphology, in which has a large number of mesoporous structures, consistent with the BET results in figure 3(d). For the HRTEM image, we can clearly observe the partial graphitization, with discernible interplanar spacing in a very small area in figure 4(c). Therefore, the bio-carbon prepared by the commercial dried kelp not only has the micro/meso hierarchical porous structures with physisorption effects, but also has the double electrochemical active sites contributing to the I and N dopant in carbon matrix with chemisorption effects.

By the common slurry blade coating method, the ground kelp bio-carbon powder can be uniformly coated on the surface of the pristine separator, with the thickness of about 25 μm, and the thickness of pristine separator is about 30 μm, as shown in figure 4(a). Due to the intrinsic hard features of kelp bio-carbon, it is difficult to achieve a completely smooth coating surface. Therefore, we can observe some undulating topography from the section and top view of this coating layer in figures 4(a) and (b), but this will not affect its electrochemical performance at all. In addition, the electrolyte contacts angle of the kelp bio-carbon modified separator is also an important factor to affect the electrochemical performances. Here, we have evaluated the wettability of the pristine separator and the kelp bio-carbon modified separator, as shown in figures 4(c) and (d). And the pristine

![Figure 3.](image) (a) and (b) SEM images of the kelp bio-carbon under different magnification, (c) N₂ adsorption-desorption isotherm and (d) pore size spread of the kelp bio-carbon, (e) and (f) TEM images of the obtained kelp bio-carbon at different magnification, (g) HRTEM image of the kelp bio-carbon.
separator demonstrates a contact angle of about 38.4° ~ 38.8°. As comparison, the contact angle of kelp bio-carbon modified separator is only 30.8° ~ 33.4°, indicating the better wettability, which attributes to the oxygen-containing functional groups of the kelp bio-carbon [25]. And the better wettability can increase the hydrophilicity of the modified separator, and facilitate the contact between electrolyte and the modified separator, advantageous to the transportation of Li ions. Furthermore, the interface resistance can also be decreased due to the intimate contact between electrolyte and the modified separator.

To evaluate the kelp bio-carbon modified separator, CV and galvanostatic charge-discharge have been done for the Li-S batteries between 1.7 and 2.8 V, as shown in figure 5. Firstly, the CV curves of the Li-S batteries with kelp bio-carbon modified separator at a scan rate of 0.1 mV s⁻¹ are showed in figure 5(a). It must be noted that the two pairs of redox peaks correspond to reversible reactions between sulfur and soluble polysulfides. The two cathodic peaks at 2.3 V and 2.0 V can be assigned to the reduction of long-chain polysulfides and further formation to short-chain insoluble lithium sulfides [26, 27]. And the two anodic peaks correspond to the successive oxidation of Li2S2/Li2S to Li2S8/S8 [28]. Obviously, the peak position and the corresponding currents keep almost stable after the first three cycles, which is a good indicator of the stable cycling performance and electrochemical reversibility. For comparison, the Li-S batteries with CSHs bio-carbon (refer to figure S2 for the morphology) modified separator have also been tested. However, the Li-S batteries with CSHs bio-carbon modified separator have one pairs of half redox peaks in figure 5(c). And the kelp bio-carbon modified separators show higher cathodic reaction potentials and lower anodic reaction potentials, suggesting its better reaction reversibility. Moreover, the kelp bio-carbon modified separators perform higher peak current density, manifesting higher capacity and better redox reactivity.

In addition, the galvanostatic charge-discharge profiles of the two Li-S batteries are showed in figures 5(b) and (d). The discharge capacity of kelp bio-carbon modified separators reaches to 1100 mA h g⁻¹ at 0.1 C, while that of the CSHs bio-carbon modified separator is only about 800 mA h g⁻¹. Furthermore, the Li-S batteries with kelp bio-carbon modified separators have about 125 mV lower potential polarization than that of the Li-S batteries with the CSHs bio-carbon modified separators (about 208 mV). Consequently, the kelp bio-carbon coated separator in Li-S batteries can facilitate the conversion of polysulfides to insoluble sulfides, decrease the polysulfides concentration and suppress the shuttle of polysulfides. And the enhancement of redox kinetics contributes to the smaller voltage hysteresis [29, 30].

The rate performances and cycling stability at high current density are important evaluation factors for the Li-S batteries. So, the rate capabilities of the Li-S batteries with kelp bio-carbon modified separator are tested, as shown in figure 6(a). When the current density is at 0.1, 0.2, 0.5, 1.0 and 2.0 C (1.0 C is 1670 mA), the Li-S batteries deliver initial capacities of 1151, 933, 892, 714, and 685 mA h g⁻¹, respectively. When the current rate returns to 0.1 C, the specific capacity continues to demonstrate 1000 mA h g⁻¹, revealing a superior rate capability and reversible performance at high-rate condition. In comparison, the obtained specific capacity of
the Li-S batteries with kelp bio-carbon modified separator is obviously higher than that of CSHs bio-carbon modified separator. These advantages can also be reflected in the following long-life cycle test at high current density, as shown in figures 6(b) and (c). After 200 cycles at 0.5 C, the specific capacity could stabilize at 760 mAh g⁻¹. However, the specific capacity with CSHs bio-carbon modified separator shows relatively poor electrochemical stability, maintaining approximately 360 mAh g⁻¹ after 200 cycles, as shown in figure 6(b). Even increasing the current density to 2.0 C, the obtained specific capacity continues to demonstrate excellent cycle stability. A high reversible capacity about 498 mAh g⁻¹ after 500 cycles with a low-capacity decay of 0.07% per cycle is transferred, as shown in figure 6(c). The excellent electrochemical performances are attributed to the I, N co-doped and the large number of mesoporous structures in kelp bio-carbon, which can effectively repel the negatively charged polysulfide ions and increase the utilization of active materials.

To understand the improved electrochemical performance of the two kinds of Li-S batteries, electrochemical impedance spectroscopy (EIS) measurements were performed in figures 6(e) and (f). Because of the more electrochemical active reaction area of kelp bio-carbon modified separator, the Rct of the Li-S batteries is smaller than that of the Li-S batteries with CSHs bio-carbon modified separator. At the same time, the slope of the low-frequency line with kelp bio-carbon modified separator is larger than that of the CSHs bio-carbon modified separator, which means that the diffusion coefficient of the lithium ions in the active material is obviously increased by using the kelp bio-carbon modified separator. In addition, we also compared our work with the results of relevant reports, and the details are shown in table 1.

To further understand the difference electrochemical performances, we disassembled the two kinds of Li-S batteries after 200 cycles at 2.0 C, and observed the change of the surface morphology of the modified separators, cathode, and lithium metal electrodes by SEM, as shown in figure 7. For the cycled kelp bio-carbon modified separator, some pieces of Li,S solid adhere on the surface in figure 7(a), which is significantly different from the separator without cycling (in figure 4(b)). For the cycled CSHs bio-carbon modified separator, we can observe the relative less Li,S in figure 7(d). Secondly, for the cathode sulfur electrode, there is some smaller regrowth of reduced sulfur (in figure 7(b)) on the surface of kelp bio-carbon modified separator’s cathode than that of the CSHs bio-carbon modified separator’s cathode. It can also be used to explain that the shuttle of polysulfides has been effectively suppressed in the kelp bio-carbon modified separator. On the contrary, polysulfides can partially pass through the CSHs bio-carbon modified separator, which make the reduced sulfur have a long regrowth path along the modified separator, resulting in the reduced sulfur slowly growing into a large block shape in figure 7(e) [36–38]. Of course, this can also be proved by the morphology change of lithium metal anode. Due to the shuttle of polysulfides, the surface of lithium metal (CSHs bio-carbon modified separator’s anode) is damaged greatly, leading to obvious fractures in figure 7(f). In contrast, the kelp bio-carbon modified separator
can effectively block the migration and deposition of polysulfides to the lithium anode, resulting in less surface damage in figure 7(c). By being compared with sole N-doped porous CSHs bio-carbon, the separator modified by I, N co-doped hierarchical micro/mesoporous kelp bio-carbon enhancing the chemisorption and physisorption effects of polysulfides, thus increasing the utilization of active sulfur and achieving enhanced electrochemical performances Li-S batteries.
4. Conclusions

We successfully prepared I and N co-doped hierarchical micro/mesoporous bio-carbon by a high efficiency and low-cost one-step carbonization method. And we concluded that the sea salt (main ingredients NaCl) is the key factor to form the large number of mesopores in the kelp bio-carbon. With the synergistic effect from the micro/mesoporous carbon structures (physisorption effect) and I, N co-doped sites in carbon matrix (chemisorption effect), the Li-S batteries with kelp bio-carbon modified separator can obviously enhance the cycle stability and rate performances. As a result, the initial specific capacity can reach to 1151 mAh g$^{-1}$ at 0.1 C, and the specific capacity could stabilize at 760 mAh g$^{-1}$ after 200 cycles at 0.5 C. Even up to 2.0 C, a high reversible capacity of 498 mAh g$^{-1}$ after 500 cycles with a low-capacity decay of 0.07% per cycle can be achieved. Coupled with the I, N co-doped hierarchical micro/mesoporous bio-carbon, the modified separators developed in this work will be an effective method for exploring large-scale preparation of enhanced electrochemical performances Li-S batteries.

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Data availability statement

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

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