Lithium sulfur battery cathode materials based on COFs ordering

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Abstract. In recent years, lithium-sulfur batteries and fuel cells, as a kind of new energy which is expected to replace traditional fossil fuels, have attracted people's attention. At present, the "shuttle effect" of lithium-sulfur batteries is one of the key factors limiting the performance and application of lithium-sulfur batteries. It is urgent to find a suitable positive electrode composite material to suppress the "shuttle effect". Covalent organic compounds (COFs) have been considered as ideal potential cathode composites for the anchors of sulfur and lithium compounds because of their regularized structure and polar functional groups. This paper mainly discusses the structure order of COF material, and gives the synthesis method of this kind of porous polymer material. The method of COFs synthesis is to design and assemble 2-D and 3-D COFs materials with different topological structures by choosing different geometrically constructed monomers and linking methods. Lithium-sulfur battery is a kind of battery with high energy density and theoretical capacity. The key to solve the shuttle effect is to find a suitable cathode composite material. Based on the order of COFs material structure, the feasibility and advantages of COFs as cathode material for lithium sulfur batteries were proposed.

Keywords: COFs, Lithium-sulfur batteries, Order of structure.

1. Introduction
The development of a new electrochemical energy storage system provides a more efficient and environmentally friendly way for sustainable production and life. In general, recharge-discharge battery devices have attracted much attention as a new type of energy. Among them, safe and environmentally friendly lithium batteries have been widely used in mobile phones, computer batteries and other fields as a new alternative energy. However, the energy density of lithium batteries is very low, and the maximum theoretical capacity (300 Wh/kg) is not enough to meet the energy requirements of electric vehicles (550 Wh/kg). Therefore, the search for a battery with higher energy density has aroused people's attention again. Compared with lithium-sulfur batteries, lithium-sulfur batteries have a great energy advantage, and the actual energy density is expected to reach 750Wh/kg [1]. Therefore, lithium-sulfur batteries are considered as a promising energy storage device. At the same time, fuel cell is recognized as a green energy conversion device with broad prospects because of its unique advantages of pollution-free products and conforms to the development concept of an environment-friendly society. In addition, fuel cells have advantages in portable, stationary, transportation and power generation due to their static characteristics of quiet and no noise and simple modular design. In short, lithium-sulfur batteries and
fuel cells have attracted great attention in the field of energy development due to their high energy density and environmental friendliness. Therefore, it is very important to choose a good cathode material for lithium sulfur battery.

Covalent organic frameworks (COFs), is by the organic structure unit Through covalent bond connection form of two-dimensional or three-dimensional porous polymer crystallization, has high thermal stability, large specific surface area, pore space is rich, the molecular structure can be harmonic active site features, can be used as a potential energy storage electrode materials and thus caused the researchers of great interest. COFs material a striking feature is its order of space structure, can be used in the design of chemical structure of skeleton and the pore mesh as the new members of the porous materials, COFs is composed of C, H, O, N, B lighter elements of first and second cycle through reversible strong covalent bond (C, C, C, O, B, O, C, N) form of 2 d and 3 d porous polymer crystals. In two-dimensional COFS materials, the layered structure is formed by the interlayer π-π phase interaction, and the whole frame structure is determined by the covalent bonds within the layers and controlled by the non-covalent forces between the layers. Therefore, it has a broad application prospect in the field of energy storage. It is believed that two-dimensional COFs with single and few layers of stripping can effectively shorten the migration distance of electrons and ions, and improve the efficiency of hyper oxygenation-reduction sites with larger amplitude.

With the development of battery science, COFS materials with good order have attracted more and more attention. Scientists have assembled two-dimensional and three-dimensional COFS materials with different topologies by selecting different geometrical building monomers. The building units are arranged periodically on the two-dimensional plane layer through covalent bond interaction, and then form different interlayer stacking forms in the three-dimensional direction through π-π interaction. Two-dimensional COFS materials have good stability under inter lamellar covalent bonds and inter lamellar non-bond interactions (π-π interactions, hydrogen bonds and van der Waals forces, etc.), while the stability of three-dimensional COFS materials is mainly provided by the extension of the building elements of non-planar geometries in three-dimensional direction. In addition, the types of linkage, such as borate ester bond, imine bond and hydrazone bond, also play an important role in the formation of stable COFs.

Therefore, COFS as cathode material of battery is not always foreground. Based on the previous research, the main composition method of COFS materials and its application in lithium-sulfur batteries are introduced, and its prospect is also discussed.

2. Synthesis method of COFs
The COFs synthesis method is through the bonding - breaking - bonding mode, accompanied by "self-diagnosis" and "self-repair", and finally form the crystalline materials with orderly structure. COFs were first synthesized under solvothermal reaction conditions, which is still the most commonly used method to prepare COFs. The organic synthesis of COFs materials begins with the synthesis of building units and ends with the network formation of building units. The general steps for the design and synthesis of COFS materials through network chemical principles are as follows: (1) Confirm the topological structure of the target and split it into basic geometric monomers;(2) According to their extension point and geometric shape, find the equivalent of these geometric monomers in the molecule and use them as building monomers;(3) The building monomer molecules in step 2 were placed on the vertex, and the short chain building monomer was placed on the edge (link) to obtain the building unit; First, the synthesis conditions (obtained through thermodynamics and kinetics) should be determined to ensure that strong covalent bonds can be formed between the selected building monomers to obtain stable two-dimensional and three-dimensional crystalline products [2]. (4) Expand the network of building units into the required COFS materials.

The general synthesis process of COFs includes the preparation of monomers, and the subsequent structural adjustment, side chain modification, metal binding and other processes, as shown in Figure 1.
2.1. Construction of monomer

The framework and pores of COFS materials can be designed and adjusted by topology, and the principle of topology design is the basis of COFS material formation. The specific geometry ensures the required crystal structure and pore structure. The rigid structure allows the monomer to retain its original structure in the synthesized COFS material crystal. Therefore, the monomer must have a specific geometry and rigid structure. The geometrical matching of the monomers forms a polygonal frame, and their geometrical configuration determines the pore shape and size of COFS materials. The constructed monomer must have a specific geometry and rigid structure. The geometrical matching of the monomers forms a polygonal frame, and their geometrical configuration determines the pore shape and size of COFS materials. For building units, organic monomers with different geometric configurations, such as C2, C3, C4 and C6, can be used as nodes, and symmetrical monomers with different lengths and functions, such as C2 and C4, can be used as linkers. Among them, hexagonal COFS material is the most common. It can be formed by C3 symmetric node and C2 symmetric link body (C3 + C2). Hexagonal COFs can also be formed by self-coagulation of C2 symmetric monomers [3]. The topological form of C3 + C3 is formed by two building monomers alternating as nodes. The building monomer contains organic π monomers of different sizes and functions, and can form hexagonal topology diagrams with different frames and pore sizes by exploring the combinations of different building monomers.

2.2. Key link

The geometric configuration of the monomers provides the basis for the order of COFS structure and the expansion of pores, and the selection of linkage bonds between monomers is also extremely important. Compared with other materials, COFS materials have certain molecular design properties through the selection of linkage bonds, which is very attractive as an innovative material platform for structural and functional design. Prior to the successful preparation of COFs, scientists generally believed that it was difficult to form a framework through strong bonding of the building blocks of molecules and the microscopic reversibility required for synthesis. Therefore, when synthesizing COFs, it is very important to find the precise reaction conditions that can form crystalline materials.

Scientists started from materials that have been studied extensively, such as diamond, graphite and boron nitride, etc., and first synthesized COFs based on borate ester bond links. Imine COFs were synthesized based on Schiff-base chemical reaction. They are stable in organic solvents and are not greatly affected by water, acid or alkaline conditions. The nitrogen atoms in the frame can also bind to a range of metal ions. These properties provide great potential for the future development of imide COFS materials. The most common solvent combination in imine condensation reactions is a mixture of methoxythiophene, dioxane and acetic acid, in which acetic acid acts as the core catalyst in the formation of COFS materials. In addition to hydrogen bonding, other non-bonding interactions, such as π-π
interaction, electrostatic interaction and interlayer stacking, can also play a certain role in controlling the porosity, stability and crystalinity of imidyl COFs [4]. In addition, the application of hydrazone bond formed by the condensation of hydrazine and aldehyde in the synthesis of COFS materials can make COFS materials have excellent chemical stability, higher crystalinity and surface area.

In addition to the above traditional linkage keys, scientists are actively looking for new types of COFs with new linkage and new properties to find more linkage keys. With the development of COFS materials, the types of link keys are constantly updated and expanded. Considering the stability, surface area and crystalinity, as well as the interaction force between layers, different application fields have different requirements. In the design of COFS materials, it is necessary to choose the appropriate link keys to make it give full play to the excellent performance in application.

3. Application of COFS in Lithium Sulfur Battery

3.1. Problems with lithium-sulfur batteries

The traditional lithium-sulfur secondary battery uses lithium metal as the negative electrode and elemental sulfur as the active material of the positive electrode. The sulfur electrode reaction involves the breaking and forming of S-S bond to realize the conversion of electrical energy and chemical energy. The charge and discharge of lithium-sulfur battery is shown in Figure 2.

![Figure 2. Diagram of how a lithium-sulfur battery works](image)

In order to solve these problems, the early researches generally adopted porous carbon materials as the carrier of sulfur, and the physical adsorption of carbon materials reduced the "shuttle effect" of multi-lithium sulfide to a certain extent. For example, the ordered mesoporous carbon and sulfur composite prepared by Wang et al. [5] can be stably cycled for 20 times at 0.1C ratio. However, the interaction between non-polar carbon materials and polar polysulfide lithium is weak, so the use of carbon materials as sulfur carrier is not enough to significantly improve the cycle performance of lithium-sulfur batteries. The researchers further prepared materials with polar surfaces as sulfur carriers, such as nitrogen doped carbon, C3N4, TiO2, Ti3C2, etc., which enhanced the adsorption of multi-lithium sulfide to a certain extent and alleviated the shuttle effect. However, after a lot of exploration and research, Li-S battery still has many problems to be solved, which seriously hinders the industrialization of Li-S battery. The details are as follows: 1) The sulfur content per unit area of the positive electrode plate is low, usually less than 3 mg·cm-2; 2) The cathode material preparation process is complex, which increases the cost of the battery; 3) At present, most of the studies on Li-S batteries in the literature are based on button batteries, and there are few reports on soft-pack batteries. Therefore, the development of Li-S battery
anode materials with simple preparation process, high sulfur content and good cycle stability, and the verification and application of Li-S soft-pack batteries are urgent problems to be solved before industrialization.

As a kind of battery with high energy density and theoretical capacity, lithium-sulfur battery has a great development prospect and is expected to be used in electric vehicles and other equipment requiring longer endurance. The "shuttle effect" of lithium-sulfur batteries is an important problem that affects the discharge capacity of batteries and needs to be solved urgently. The key to solving the shuttle effect is to find a suitable positive electrode composite material, which has been widely paid attention to in recent years. A great deal of research has been done on the choice of cathode materials, including doped carbon materials and metal compounds.

3.2. Advantages of COFS for Lithium-sulfur batteries

COFs functional organic single frame structure can largely avoid organic active substances dissolved in the organic electrolyte, the stability of the porous COFs structure. Electrolyte injection and ion/provide open access to the electronic transmission, and with the ordinary organic phase than the electrode material, usually showed a greater electrochemical performance.

Wang et al. [6] with four amino benzene quinone (TABQ) and dimethyl benzene anhydride (PMDA) 2 kinds of active small molecules dissolved in dimethyl sulfoxide (DMSO), using graphene solvent hot method, in situ synthesized poly (imide benzoquinone) (PIBN) two-dimensional microporous structure organic skeleton PIBN COF package compounds - the total value of G (see Figure 3), and as from lithium batteries positive materials. PIBN-G provides an initial capacity of 242. 3 mAh/G and 206. 7 mAh/G at 1C and 5C rate discharge, respectively (see Fig. 1B), and a capacity retention rate is more than 86% at 182.3 mAh/G. The organic molecule has a porous structure of 1. 5 nm and a large number of carbonyl groups, which is conducive to the binding of the active groups in the molecular structure to Li+ in the electrolyte, which promotes the electrochemical reversible reaction. Due to the strong interaction force and charge transfer between graphene and PIBN molecules, PIBN-G has high electron conductivity. As a result, PIBN-G shows excellent magnification performance and high reversible capacity in the electrochemical reaction.

![Figure 3. The formation process of COFS three-dimensional structure](image)

During the synthesis process, COFS materials form an ordered frame structure with strong π-π phase interaction, and the structure is tightly stacked. A large number of active groups are trapped in the internal frame structure, which cannot effectively store lithium, and the oxidation and reduction reaction of COFS electrodes is reduced, which directly affects the reversible capacity of COFS materials.

3.3. Influence of different COFS structures on battery performance

As a newly developed multi-porous material, the structure and composition of COFS can be precisely controlled through clever design to achieve the desired function. Therefore, COFs have been used as the main material for sulfur storage in lithium/sulfur batteries. The ordered accumulation of COFs in the
two-dimensional plane presents abundant nanopores, which can be used for sulfur impregnation, providing more active elements for absorbing multi-lithium sulfide. In addition, lithiophilicity and thiophilicity are considered to be the two main chemical pathways for stabilizing multisulfide lithium. With the lithiophilic phase interaction between nitrogenon and lithium-ion, triazinyl framework and porphyrinyl COFs are used as the fitting capture matrix to improve the stability of lithium batteries. Liao et al. [7] synthesized the borate COF-1 and prepared the complex COF-1/S with sulfur by melting method. At a high current density of 0.5C, the specific capacity of COF-1/S electrode material can reach 1,032mAh/g for the first discharge, and still reach 770mAh/g after 200 cycles, with a capacity decay of only 0.13% after each cycle. Therefore, the positive polarized boron and negative polarized oxion can absorb the polysulfide anion and lithium ion at the same time, thus inhibiting the polysulfide shuttle effect.

Cheng et al. [8] studied a kind of compact arrangement active vinyl (COF-V) mesoporous imine COFs and sulfur reverse vulcanization composites are used as cathode materials for lithium/sulfur batteries. The results show that the electrochemical properties of the cell can be enhanced due to the binding beam of COFS mesoporous channels and the co-interaction between sulfur and COF. Therefore, the initial specific capacity of S-COF-V type reverse vulcanization cathode material is as high as 1400mAh/g, and the discharge specific capacity of 959mAh/g can be maintained after 100 cycles, which is the best performance of COFs-based cathode materials reported before the date of application.

4. Conclusion

COFs material is organic structural unit by strong covalent bond of interconnected porous polymer crystalline materials, with high thermal stability, large specific surface area, pore is rich, the molecular structure can be harmonic active site features, such as in lithium ion batteries, sodium ion batteries, lithium/sulfur batteries, and other areas of the electrochemical energy storage has achieved rapid development. At present, the research and development of COFs organic electrode materials is still in the initial stage. In the future, we should continue to explore COFs materials with low molecular weight, high electrical conductivity, and many active sites, and should have a simple operation, high yield, pollution-free synthesis method, so that they can be large-scale industrial production.

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References

[1] Liao H, Ding H, Li B, et al. Covalent-organic frameworks: potential host materials for sulfur impregnation in lithium–sulfur batteries [J]. Journal of Materials Chemistry A, 2014, 2(23): 8854-8858.
[2] Yang X, Hu Y, Dunlap N, et al. A Truxenone - based Covalent Organic Framework as an All - Solid - State Lithium - Ion Battery Cathode with High Capacity [J]. Angewandte Chemie International Edition, 2020, 59(46): 20385-20389.
[3] Xiao Z, Li L, Tang Y, et al. Covalent organic frameworks with lithiophilic and sulfiphilic dual linkages for cooperative affinity to polysulfides in lithium-sulfur batteries [J]. Energy Storage Materials, 2018, 12: 252-259.
[4] Yang D H, Yao Z Q, Wu D, et al. Structure-modulated crystalline covalent organic frameworks as high-rate cathodes for Li-ion batteries [J]. Journal of Materials Chemistry A, 2016, 4(47): 18621-18627.
[5] Wang Z, Li Y, Liu P, et al. Few layer covalent organic frameworks with graphene sheets as cathode materials for lithium-ion batteries [J]. Nanoscale, 2019, 11(12): 5330-5335.
[6] Wang D G, Li N, Hu Y, et al. Highly fluoro-substituted covalent organic framework and its application in lithium–sulfur batteries [J]. ACS applied materials & interfaces, 2018, 10(49):
42233-42240.

[7] Liao H, Wang H, Ding H, et al. A 2D porous porphyrin-based covalent organic framework for sulfur storage in lithium–sulfur batteries [J]. Journal of Materials Chemistry A, 2016, 4(19): 7416-7421.

[8] Cheng Z, Pan H, Zhong H, et al. Porous organic polymers for polysulfide trapping in lithium–sulfur batteries [J]. Advanced Functional Materials, 2018, 28(38): 1707597.