



# Tunable porous structure of metal organic framework derived carbon and the application in lithium–sulfur batteries



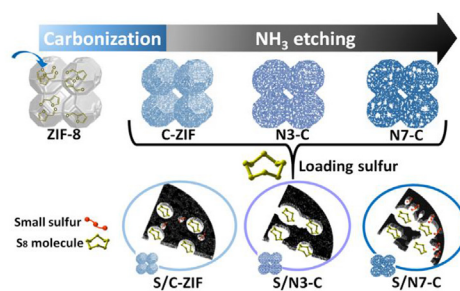
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## HIGHLIGHTS

- Tunable porous structure MOF-Cs are prepared via in-situ gas-phase treatment.
- Designed porous MOF-C improves the electrochemical performance of S/MOF-C cathode.
- Sulfur cathodes perform multi-phase electrochemical processes with tunable MOF-Cs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

For the first time, we report a facile approach to fabricate metal organic framework derived carbon (MOF-C) with tunable porous structure. Different from direct pyrolysis of MOFs and blind attempt in application, the in-situ ammonia treatment enables MOF-C with desired porous structure from enriched microporous structure to hierarchically mesoporous structure. Further, NH<sub>3</sub> treated MOF-C as carbon host for sulfur loading performing as the cathode for Li–S batteries results in twice higher capacity retention than that of pristine MOF-C. Besides, different Li–S electrochemical mechanisms regarding the different porous structures of carbon are also revealed and investigated in this paper.

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## 1. Introduction

Seeking for high energy storage systems is an inevitable challenge accompanied with the depletion of fossil energy [1–3]. Although the state-of-art Li-ion batteries have been successfully commercialized for portable electronics applications, they still cannot meet the requirements of electric vehicles (EVs) or hybrid

electric vehicles (HEVs) in terms of energy density [4–6]. Li–S batteries are one of the promising candidates due to their inherently ultrahigh theoretic capacity and energy density, which are nearly five times greater than commercial Li-ion batteries [7–9]. Sulfur itself also possesses features such as environmental benignity, economy, and sustainability [7–9]. Within this context, Li–S batteries are regarded as one of the next generation batteries for EVs and HEVs. However, sulfur cathodes are still impeded by many issues that need to be further elucidated [10–12]. Low utilization of sulfur cathodes arises in electrochemical reaction due to the

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insulating nature of sulfur. More seriously, poor reversibility of sulfur due to the dissolution of polysulfides results in limited cycle life of Li–S batteries [10–12].

Nanoporous carbon materials are prevalently used as sulfur hosts, which dominate the performance of Li–S batteries [13–15]. An ideal nanoporous carbon material should obtain following characteristics [13–15]: (1) high electric conductivity to improve the insulating nature of sulfur; (2) high pore volume to maintain high loading of sulfur; (3) fluent channels enabling sufficient electrolyte infiltration (Li-ions insertion and extraction); and (4) effective sorption to prevent polysulfides from dissolution. Further, it has been reported that the “small sulfur molecule” (short chain sulfur molecule) in micropores performed through different electrochemical processes in Li–S systems [16,17]. Therefore, designing advanced carbon materials with desirable pore distribution as a sulfur host is one of the key issues in Li–S battery systems.

Very recently, metal organic framework-derived carbon (MOF-C) has been regarded as a new and popular family of porous carbon materials inspired by the ordered structure, high surface area, and unique morphology of MOFs [18–20]. To date, several MOF structures, such as zinc based MOF-5, zeolitic imidazolate framework ZIF-8, and Al-based porous coordination polymer Al-PCP have been reported as precursors to create nanoporous carbon [21–25]. The advantages of MOF-C including microporous nanostructure, high surface area, large pore volume, specific morphology, and inherent heteroatoms doping facilitate various applications of MOF-C in gas storage, catalyst, solar cell, fuel cell, and Li-based batteries [26–30]. Actually, different energy storage systems need various porous structures of hosts [31,32]. For instance, gas storage system needs fitted microporous structure, while metal-air batteries prefer large porous structure. However, very few researches have studied the control of porous structure of MOF-C from fitted microporous structure (<2 nm) to hierarchically mesoporous structure (2–50 nm) and, especially, to large porous structure (>100 nm) because the complicated synthetic process of large-pore MOF makes it hard to obtain large porous carbon from directly carbonized MOFs [33–35].

For the first time, we report a facile in-situ ammonia treatment approach aimed at producing various porous structures of MOF derived carbon ranging from micropores to hierarchically mesopores. Different from directly attempting some MOF-Cs in application, this strategy enables to design varies of porous structure of MOF-C from one starting material. Further, the ammonia treated MOF-C as carbon host shows an impressive improvement on sulfur cathodes, which performed twice higher discharge capacity retention than that of the pristine MOF-C. Cyclic voltammetry and other physical characterizations demonstrat that ammonia treatment can tailor the MOF-C into proper nanostructure for sulfur molecule deposition and detailed electrochemical mechanisms are proposed in this study. This research sheds light to design MOF-C materials with controlled nanostructure not only for Li–S batteries, but also for expanded applications in different energy storage systems.

## 2. Experimental

### 2.1. Preparation of ZIF-8 derived carbon and ammonia treated carbon

The synthesis of ZIF-8 derived carbon follows the approach reported by Xu's group [22]. Typically, commercial zeolite-type metal-organic framework ZIF-8 (Basolite Z1200, Sigma–Aldrich) and furfuryl alcohol (FA, Sigma–Aldrich) were used as the starting materials. FA was firstly introduced into ZIF-8 to obtain FA/ZIF-8 composites under an evacuated environment. The FA/ZIF-8

composites were then transferred into a furnace under Ar atmosphere and heated in a program at 80 °C for 24 h, then at 150 °C for 6 h, and finally at 1000 °C for 8 h to obtain ZIF-8 derived carbon (C-ZIF). The obtained C-ZIF was then in-situ treated under ammonia atmosphere at 1050 °C for 3, 5, and 7 min. The obtained samples are referred as N3–C, N5–C, and N7–C.

### 2.2. Preparation of sulfur-carbon composites and electrodes

Sulfur-carbon composites (S/C) were synthesized via a two-step thermal-treatment procedure. The as-prepared carbon materials (C-ZIF, N3–C, N5–C, and N7–C) were mixed with sulfur powders (>99.5%, Sigma–Aldrich) and dried at 80 °C for 12 h to remove moisture. The mixture was then transferred to a sealed steel reactor and was heated at 150 °C for 9 h and 300 °C for 3 h to obtain the S/C composites. A reference S/C composites sample using commercial porous carbon (KJ-600, US) as carbon host is also synthesized followed same procedure. As-prepared sulfur-carbon black composites maintained 60–65 wt% sulfur load from TGA results (Fig. S8). The electrodes were prepared by slurry casting onto aluminum foil. The slurry mass ratio of active material, acetylene black, and polyvinylidene fluoride (PVDF) is 70:20:10. The as-prepared electrodes were finally dried at 80 °C over 12 h under vacuum. The areal mass load of sulfur in our electrode is around 0.80 mgcm<sup>-2</sup>.

### 2.3. Physical and electrochemical characterization

The morphologies and structure of the samples were characterized by Hitachi S-4800 field emission scanning electron microscope (FE-SEM) operated at 5 KeV, high-resolution transmission electron microscopy (HRTEM) (JEOL 2010 FEG) equipped with energy dispersive spectroscopy (EDS), and X-ray diffraction system (XRD) (Bruker D8 Advance, Cu K  $\alpha$  X-ray source). Thermo gravimetric analysis (TGA) was carried out on a TA SDT Q600 in an N<sub>2</sub> atmosphere from room temperature to 700 °C at a rate of 10 °Cmin<sup>-1</sup>. Raman scattering (RS) spectra was obtained using a HORIBA Scientific LabRAM HR Raman spectrometer system equipped with a 532.4 nm laser. CR-2032 type coin cells were assembled in argon filled glove box. The coin-type cells consisted of Li metal as anode, a polypropylene separator (Celgard 2400), and as-prepared electrode as cathode. The electrolyte was composed of 1 M LiTFSI salt dissolved in dioxolane (DOL): dimethoxyethane (DME) of 1:1 volume ratio. Each coin-cell we added 3–5 drops of electrolyte which is around 0.20 ml/cell. Cyclic voltammograms were collected on a versatile multichannel potentiostation 3/Z (VMP3) under scanning rate of 0.1 mV s<sup>-1</sup> between 1.0 V and 3.0 V (vs. Li/Li<sup>+</sup>). Charge–discharge characteristics were galvanostatically tested in the range of 1.0 V–3.0 V (vs. Li/Li<sup>+</sup>) at room temperature using an Arbin BT-2000 Battery Tester.

## 3. Result and discussion

As shown in Fig. 1, commercial ZIF-8 was immersed in furfuryl alcohol (FA) which allows FA penetrating into ZIF-8 framework and producing extra surface area for ZIF-8 derived porous carbon (C-ZIF) [22]. The FA/ZIF-8 composites were then annealed under a delicate pyrolyzing program to vaporize the zinc metal and form porous carbon material C-ZIF. During the annealing process, C-ZIF was simultaneously treated by ammonia for different lengths of time to build various porous structure, which is denoted as Nx–C (x = 3 min, 5 min, 7 min). By using as-prepared porous carbon as hosts, sulfur was filled into the Nx–C materials to build S/C composites and are proposed to form different polyatomic molecules in porous Nx–C, which is aimed to improve the Li–S batteries performance via optimizing MOF-C hosts.

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