



# Nitrogen and sulfur co-doped carbon with three-dimensional ordered macroporosity: An efficient metal-free oxygen reduction catalyst derived from ionic liquid



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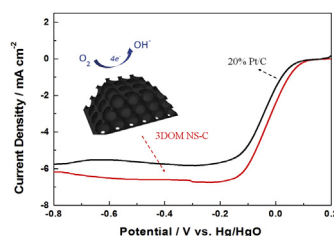
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## HIGHLIGHTS

- N and S co-doped ORR catalysts are synthesized from a novel ionic liquid.
- The obtained catalysts show superior ORR performance and excellent durability.
- The 3DOM structure of the catalyst contributes to its catalytic activity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The development of efficient and durable catalyst for oxygen reduction reaction (ORR) is critical for the practical application of proton exchange membrane fuel cell (PEMFC). A novel imidazole based ionic liquid is synthesized in this study and used subsequently for the preparation of a N and S co-doped metal-free catalyst with three dimensional ordered microstructure. The catalyst prepared at 1100 °C showed improved ORR catalytic performance and stability compared to commercial Pt/C catalyst. We demonstrate that the high graphitic N content and high degree of graphitization of the synthesized catalyst is responsible for its superb ORR activity. Our results suggest that the N and S co-doped metal-free catalyst reported here is a promising alternative to traditional ORR catalyst based on noble metal. Furthermore, the current study also demonstrate that importance of morphology engineering in the development of high performance ORR catalyst.

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## 1. Introduction

The sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode of a proton exchange membrane fuel cell (PEMFC) is the primary factor that limits the efficiency of PEMFC. To date,

platinum based catalysts are the most commonly used PEMFC ORR catalyst. However, its high cost, scarcity, as well as its susceptibility to poisoning greatly hampered its widespread use. Heteroatom doped carbon materials have emerged recently as possible alternatives to platinum based catalysts due to their high catalytic activity, relatively good stability and low cost [1]. In particular, metal and nitrogen co-doped carbon (M-N-C) material showed an excellent ORR activity that is comparable or even superior to the commercial Pt/C catalyst under alkaline conditions [2,3]. However,

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the stability of the M-N-C materials still remains a possible concern in the long-term operation due to the fact that the metal species may leach out from the catalyst in both alkaline and acid conditions [4]. Therefore, metal free doped carbon catalysts are more favorable for practical fuel cell applications. For a metal free, heteroatom doped carbon catalyst, the type and concentration of the heteroatom in the catalyst directly determines its catalytic efficiency. So far, different non-metallic heteroatom (such as N, S and B) doped carbon materials have been reported [5–10]. It is generally accepted that the presence of non-metallic heteroatom in the graphite carbon matrix could induce the charge/spin delocalization of the carbon atom, leading to the change of O<sub>2</sub> adsorption mode on the material in the way that facilitate ORR [11]. For carbon catalysts involving different non-metallic heteroatoms, the synergistic effects between heteroatoms may further improve the activity of the catalyst [4,12–15]. The micromorphology of the catalyst is another decisive factor for its performance. Since both mass transfer and electron transport is involved in ORR process, the microstructure of the non-metallic heteroatom doped catalyst has also to be tailored to balance these transport processes [16]. We have shown previously that the introduction of ordered macropores in the electrode could significantly improve the mass transport within the electrode, thus promoting the overall catalytic process [17,18].

Ionic liquid (IL) is a liquid material that has high thermal stability. IL usually contains different types of heteroatoms, which may lead to the generation of heteroatoms doped carbon materials. Owing to these favorable features, the use of IL for the synthesis of functional carbon materials has aroused great research interests in recent years [19–30]. Another significant advantage of IL is its high compatibility with hard template, which is of particular interest for the hard template directed synthesis. However, to the best of our knowledge, only few reports exploit the potential of IL for the preparation of porous carbon materials with regulated pore structures through hard template synthesis [28,31,32].

Herein, we report the synthesis of a new and low cost Ionic liquid (IL) bearing crosslinkable alkynyl group and the use of the IL for the preparation of nitrogen and sulfur co-doped ORR catalysts. We show that the obtained catalyst (abbreviated as NS-C-X, where X represents the carbonization temperature) show pronounced ORR activity and the NS-C catalyst prepared at a higher temperature generally showed a better ORR performance. To further improve the activity of the catalyst, NS-C with three dimensional ordered macropores (abbreviated as 3DOM NS-C) were prepared by using monodispersed silica as hard templates. The 3DOM NS-C exhibits a higher ORR activity than commercial Pt/C catalyst in alkaline condition, which is rarely seen for metal free ORR catalyst. Additionally, we demonstrate that the catalyst possessed improved long-term stability and better methanol tolerance than the commercial Pt/C catalyst under identical conditions.

## 2. Experimental

### 2.1. Synthesis of 1-methyl-3-propargylimidazolium bromide (MPlm)

A solution of 1-methylimidazole (Aladdin, 2.0528 g) and propargyl bromide (Aladdin, 3.6875 g, 80 wt% in toluene) was heated to 80 °C and refluxed under N<sub>2</sub> atmosphere for 20 h. After the reaction, the solvent was removed by ethyl acetate to obtain the crude product. The crude product was then purified by washing with ethyl acetate and drying in a vacuum oven at 50 °C for 6 h.

### 2.2. Synthesis of [1-methyl-3-propargylimidazolium bromide] [bis(trifluoromethyl)sulfonyl imide] ([MPlm][Tf<sub>2</sub>N])

In a typical synthesis, 16.5 mL of bis(trifluoromethylsulfonyl)

amine lithium salt (Aladdin) solution (9.1 wt%, in DI water) was added into 15 mL 1-methyl-3-propargylimidazolium bromide solution (9.6 wt%, in DI water) dropwise under stirring. The mixture was stirred for 4 h to ensure thorough ion exchange. After ion exchange, the oil phase at the bottom of the mixture was collected and dried at 40 °C overnight.

### 2.3. Synthesis of three dimensional ordered sulfur and nitrogen co-doped carbon (3DOM NS-C)

Monodisperse silica spheres with a diameter of 300 nm was prepared using the Stober method [33] and assembled into a well-ordered array through sedimentation at room temperature. To synthesize the 3DOM NS-C catalyst, [MPlm][Tf<sub>2</sub>N] was infiltrated into the silica array and then carbonized in a tube furnace under N<sub>2</sub> atmosphere (20 mL min<sup>-1</sup>). During the carbonization process, the temperature was ramped at a rate of 1° min<sup>-1</sup> to the final temperature (700 °C, 800 °C, 900 °C, 1000 °C and 1100 °C) and then kept for 5 h. After carbonization, the obtained products were incubated in 10% HF solution for 48 h to dissolve the silica spheres. The products were further washed with 1 M HCl to dissolve the residual compounds, followed by drying.

### 2.4. Characterizations

The morphology of the samples was characterized with SEM (JSM-IT300, JEOL) with an accelerating voltage of 5.00 KeV. The Raman spectra of the samples was recorded using a Raman system (Invia, Renishaw) with an excitation energy of 2.41 eV. XRD measurements were performed with a D8 X-Ray diffraction meter (D/MAX-RB RU-200B, Rigaku) with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm). TGA analysis (NETZSCH, STA449F3) was performed under N<sub>2</sub> atmosphere from room temperature to 800 °C with a heating rate of 5 °C min<sup>-1</sup>. XPS tests were conducted on a VG Multilab 2000X-spectrometer using an Al K $\alpha$  X-ray source (1486 eV). The surface area analysis was performed through the liquid nitrogen cryosorption (ASAP 2000, Micromeritics) and the distribution of the micropore size was calculated by Dynamic Function Theory (DFT) methods with the adsorption curves.

### 2.5. Electrochemical characterizations

The electrochemical properties of the catalyst were characterized using a standard three-electrode configuration. A glassy carbon electrode, a Pt black electrode, and an Hg/HgO electrode was used as working electrode, counter electrode and reference electrode, respectively. The catalyst ink was prepared by mixing 4 mg catalyst (either NS-C catalyst or commercial Pt/C catalyst (HISPEC 3000, Alfa Aesar)), 20  $\mu$ L Nafion solution (DE 520, DuPont), 100  $\mu$ L DI water and 900  $\mu$ L isopropanol. The catalyst ink was sonicated for 20 min to improve the dispersion of the catalyst in the ink. To prepare the working electrode, 20  $\mu$ L catalyst ink was coated on the glassy carbon electrode and the electrode was dried in air. The catalyst loading is calculated to be 0.41 mg cm<sup>-2</sup>. Cyclic voltammograms (CV), rotating disk electrode voltammograms and chronoamperometry measurements were conducted in 0.1 M KOH solution saturated with N<sub>2</sub> or O<sub>2</sub>. CV measurements were carried out from -0.8 V to 0.2 V (vs. Hg/HgO) with a scan rate of 50 mV s<sup>-1</sup> and RDE measurements (400–2000 rpm) were performed from 0.2 V to -0.8 V with a scan rate of 10 mV s<sup>-1</sup>. The electron transfer number in the ORR process was determined with the Koutecky-Levich equation [34]. Chronoamperometry measurements were conducted at a potential of -0.3 V (vs. Hg/HgO) at 1200 rpm.

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