Journal of Power Sources 259 (2014) 138–144

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# A simple and green pathway toward nitrogen and sulfur dual doped hierarchically porous carbons from ionic liquids for oxygen reduction

Zhentao Cui [a], Shuguang Wang [a], Yihe Zhang [b,*], Minhua Cao [a,*]

[a] Key Laboratory of Cluster Science, Ministry of Education of China, Beijing Key Laboratory of Photoelectronic/Electrophotonic Conversion Materials, Department of Chemistry, Beijing Institute of Technology, Beijing 100081, PR China

[b] National Laboratory of Mineral Materials, School of Materials Sciences and Technology, China University of Geosciences, Beijing 100083, PR China

## HIGHLIGHTS

- N–S co-doped hierarchical porous carbons were prepared by using ionic liquid.
- They exhibit high specific surface area.
- They exhibit significantly enhanced electrocatalytic activity for ORR.

## ARTICLE INFO

*Article history:*
Received 27 December 2013
Received in revised form
20 February 2014
Accepted 22 February 2014
Available online 4 March 2014

*Keywords:*
Co-doping
Hierarchically porous
Ionic liquid
Carbon
Oxygen reduction

## ABSTRACT

We for the first time demonstrate a simple and green approach to heteroatom (N and S) co-doped hierarchically porous carbons (N–S-HC) with high surface area by using one organic ionic liquid as nitrogen, sulfur and carbon sources and the eutectic salt as templating. The resultant dual-doped N–S-HC catalysts exhibit significantly enhanced electrocatalytic activity, long-term operation stability, and tolerance to crossover effect compared to commercial Pt/C for oxygen reduction reactions (ORR) in alkaline environment. The excellent electrocatalytic performance may be attributed to the synergistic effects, which includes more catalytic sites for ORR provided by N–S heteroatom doping and high electron transfer rate provided by hierarchically porous structure. The DFT calculations reveal that the dual doping of S and N atoms lead to the redistribution of spin and charge densities, which may be responsible for the formation of a large number of carbon atom active sites. This newly developed approach may supply an efficient platform for the synthesis of a series of heteroatom doped carbon materials for fuel cells and other applications.

## 1. Introduction

One of the current technological bottleneck for the industrial development of fuel cells (FCs) is the high cost and poor durability of the Pt-based electrocatalyst as well as the sluggish oxygen reduction reaction (ORR) on the cathode [1,2]. Pt-based materials have been the most universal electrocatalysts for the ORR so far, they still suffer from serious intermediate tolerance, anode crossover, sluggish kinetics, and poor stability in an electrochemical environment [3]. As a result, numerous efforts have been made to reduce or replace the Pt-based catalysts in FCs [4–6]. In particular, the ongoing search for new non-precious-metal catalysts with excellent electrocatalytic performances for ORRs has attracted increasing interest [7]. However, common metal or metal oxide catalysts frequently suffer from dissolution, sintering, and agglomeration during fuel cell operation, which can greatly reduce activity and durability. This problem can be solved by using metal-free doped carbon materials [8]. In this regard, metal-free heteroatom-doped carbon materials have been the most popular choice because they can overcome CO poisoning or crossover effects. In addition, they also have long-term operational stability and that are relatively cost-effective [9–12]. Among the available heteroatoms that can be suitable for doping in carbon materials, nitrogen is the most widely studied candidate [8]. For example, N-doped carbon nanotubes, graphene, and graphite have been shown to exhibit high electrocatalytic activities for ORR [3,9,10,13–15]. Dai et al. [16] demonstrated that the larger electronegativity of N atoms (electronegativity: 3.04 for N and 2.55 for C) and the resulting positive

---

* Corresponding authors. Tel.: +86 10 68918468.
*E-mail addresses:* zyh@cugb.edu.cn (Y. Zhang), caomh@bit.edu.cn (M. Cao).

http://dx.doi.org/10.1016/j.jpowsour.2014.02.084
0378-7753/

charge density on the adjacent C atoms may be responsible for the high activity [4,17]. Recently, besides N, other elements (e.g. B, S, P, or I) have also been introduced into carbon materials and they also show enhanced catalytic activity for ORRs [2–4,9–11], but the low content of the doped elements has very limited improvement in the ORR catalytic activity.

To address this, some researchers have proposed to dope carbon materials with dual or multi heteroatoms to further improve the ORR catalytic activity, since this can be controlled not only by the increased number of dopant heteroatoms but also by the synergistic effect arising from co-doping of heteroatoms [2,3,18].

It is has been well documented that the density of the catalytically active sites on the surface is closely related to the catalytic activity [19]. Although heteroatom doping for carbon materials could create catalytically active sites for ORR, it is still on a less competitive level if we ignore other factors that affect the density of the active sites. The catalytic activity of common catalysts has been reported to be proportional to the surface area since high surface area could provide more active sites, facilitate more efficient contact with reactants and enhance material transfer [20]. Thus it can be seen that combining dual heteroatom doping and high surface area may be a potential solution to achieve high catalytic activity for ORRs.

Herein, we have developed a simple and green approach to heteroatom (N and S) co-doped hierarchical porous carbons (N–S-HC) by using one organic ionic liquid (IL) as nitrogen, sulfur and carbon source for the first time and the KCl–$ZnCl_2$ eutectic salt as “salt templating” [21–24]. The resultant N–S-HC can be used as metal-free ORR electrocatalyst and exhibits excellent activity with electron transfer number of 3.8 and stability superior to the commercial Pt/C (20 wt% platinum on carbon, Johnson Matthey) electrocatalyst in alkaline solution. To the best of our knowledge, such excellent electrochemical performance in the ORR has rarely been observed for metal-free catalysts [16]. The N–S-HC shows high specific surface area (1056 $m^2\ g^{-1}$) and a relatively high heteroatom loading (N: 2.80%; S: 5.16%). The heteroatom loading and specific surface area can be easily controlled by simply changing the reaction temperature. The high heteroatom loading for N–S-HC can provide larger numbers of active sites, whereas the high specific surface area ensures an excellent electron transfer and reactant transport rate towards ORRs. This newly developed method for the dual heteroatom doping can thus provide simple “green” route to low-cost mass production of N–S-HC as efficient metal-free ORR electrocatalysts for fuel cells and other applications.

## 2. Experimental

### 2.1. Materials and methods

1-butyl-1-methyl-pyrrolidinium bis ((trifluoromethyl)sulfonyl) imide (Bmp-tfs) was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, and potassium chloride and zinc chloride (99%) were acquired from Sinopharm Chemical Reagent Co., Ltd. All chemicals used were analytical grade without further purification. The eutectic salt mixture (KCl–$ZnCl_2$) used in our experiment was freshly prepared prior to the following synthesis by grinding and mixing KCl and $ZnCl_2$ in the ratio of 50 mol% KCl, and then the KCl–$ZnCl_2$ eutectic salt mixture was fully dissolved in deionized water. In a typical synthesis for the N-S-HC, the carbon precursor, Bmp-tfs (2 g) was fully mixed with the KCl–$ZnCl_2$ eutectic salt mixture (6 g) prior to the calcination process. The resulting mixture was placed in a ceramic crucible and heated to 850 °C with a heating rate of 2.0 °C $min^{-1}$ in a chamber oven. After holding this temperature for 2 h the samples were allowed to cool to room temperature. All steps were carried out under nitrogen flow. In order to remove the residual salt porogen, the materials were grinded and washed in hydrochloric acid and deionized water for several hours and finally filtrated and dried in vacuum.

### 2.2. Materials characterization

The sizes and morphologies of the resulting products were studied by a H-8100 transmission electron microscopy (TEM) operating at 200 kV accelerating voltage. The field emission scanning electron microscopy (FE-SEM) of the sample was taken on Hitachi S-4800 SEM unit. X-ray photoelectron spectroscopy (XPS) data were recorded with an ESCALAB 250 electron spectrometer using Al K irradiation. The Brunauer-Emmett-Teller (BET) surface area of the as-synthesized samples was measured using a Belsorp-max surface area detecting instrument by $N_2$ physisorption at 77 K. The pore size distribution (PSD) was calculated via a non-local density functional theory (NLDFT) method using nitrogen adsorption data with a slit pore model. The calculations presented in this work were performed in the framework of density functional theory (DFT), as implemented in Gaussian 03 program [25]. All atoms were fully relaxed, with uB3LYP functional and 6-31G (d,p) basis set. Charge and spin density on each atoms were calculated by Mulliken population analysis.

### 2.3. Electrochemical measurements

The electrochemical measurements of cyclic voltammetry (CV) and rotating disk electrode (RDE) were carried out in a three-electrode system in 0.1 M KOH at 25 °C using a CHI 760E electrochemical analyzer. A glass carbon RDE after loading the electrocatalyst was used as the working electrode, an Ag/AgCl (KCl, 3 M) electrode as the reference electrode, and a Pt foil (1 $cm^2$) as the counter electrode. The glassy carbon disk was rinsed with double distilled water and dried at room temperature before the catalyst layer was applied to the disk. The thin film electrode was prepared as follows: 5 mg of catalyst was added into 1.0 mL of ethanol and 40 μL of 5 wt% Nafion (Dupont) and dispersed by ultrasonication for approximately 30 min to obtain a homogeneous suspension. Next, 30 μL of the dispersion was uniformly dropped onto a freshly polished glassy carbon electrode (3 mm in diameter) surface and was dried under ambient conditions. By using the same electrode configuration, GCs and commercial Pt/C catalyst (20wt% platinum on carbon black) with the similar amount were also studied for comparison.

The electrochemical experiments were carried out in $O_2$ saturated 0.1 M KOH electrolyte for the oxygen reduction reaction. The potential range is cyclically scanned between −0.8 and +0.2 V at a scan rate of 10 mV $s^{-1}$. Cyclic voltammetry curves were recorded by applying a linear potential scan at a sweep rate of 10 mV $s^{-1}$ between −0.8 and 0.2 V after purging $O_2$ or $N_2$ gas for 30 min. The cycling was repeated until a reproducible cyclic voltammetry curve was obtained before the measurement curves were recorded. RDE measurements were conducted at different rotating speeds from 400 to 2500 rpm. Durability test of the N–S-HC and Pt/C (Vulcan, 20 wt%) was also conducted with $O_2$ continuous flow in 0.1 M KOH. All the experiments were conducted at room temperature (25 ± 1 °C).

## 3. Results and discussion

A schematic illustration of the fabrication process of N–S-HC is shown in Scheme 1. Briefly, the nitrogen-sulfur containing Bmp-tfs and KCl–$ZnCl_2$ eutectic salt was fully mixed in deionized water and ethanol. The resultant mixture was then pyrolyzed under nitrogen atmosphere at different temperatures (650, 750, 850, and 950 °C),