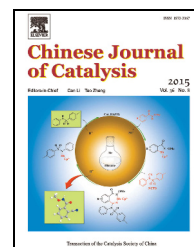


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## Article

# Effect of pyrolysis conditions on nitrogen-doped ordered mesoporous carbon electrocatalysts

Guifa Long<sup>a</sup>, Kai Wan<sup>a</sup>, Mingyao Liu<sup>a</sup>, Xiaohua Li<sup>a</sup>, Zhenxing Liang<sup>a,\*</sup>, Jinhua Piao<sup>b</sup><sup>a</sup> Key Laboratory on Fuel Cell Technology of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, Guangdong, China<sup>b</sup> School of Light Industry and Food Science, South China University of Technology, Guangzhou 510641, Guangdong, China

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## ABSTRACT

Pt is the most effective and widely used electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells; however, its scarcity and high cost pose a great challenge to the commercialization of the fuel cell technology. N-doped carbon materials have been regarded as one of the most promising Pt-alternative catalysts. In this work, the N-doped ordered mesoporous carbon was synthesized by the nanocasting method using SBA-15 as the template. The effect of the pyrolysis conditions (pyrolysis temperature, pyrolysis duration, and ramp rate) on this material was investigated. N<sub>2</sub> adsorption-desorption isotherms, X-ray photoelectron spectroscopy, and Raman spectroscopy were used to investigate the intrinsic properties of the resultant materials. Cyclic voltammetry and rotating ring-disk electrode were used to investigate the electrochemical behavior for ORR in an alkaline medium. It was found that the resultant mesoporous carbon materials exhibit high electrical conductivity, high specific surface area, and unique pore structure. The pyrolysis temperature was the most important parameter in determining the thermodecomposition of the carbon precursor, and the microstructure, elemental composition, and chemical configuration of the resultant mesoporous carbon materials. To achieve reasonable electrocatalytic activity and selectivity, a high pyrolysis temperature above 800 °C is required for effective N doping to form active sites and for graphitization to facilitate charge transfer, whereas the pyrolysis duration and ramp rate have a much less significant effect. This indicates that both the surface composition/structure and consequent electrochemical properties are more dependent on the thermodynamics than the kinetics during the pyrolysis process. Finally, the optimal N-doped ordered mesoporous carbon catalyst showed superior electrochemical activity for ORR than the commercial Pt catalyst and is promising for fuel cell and metal–air battery applications.

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## 1. Introduction

Oxygen reduction reaction (ORR) is one of the most important reactions in both fuel cells and metal–air batteries [1].

Pt is the most effective electrocatalyst for the ORR [1–3]. However, its scarcity and high cost has long been the main issue hampering the commercialization of fuel cells [4–6]. In the past decades, enormous efforts have been made to investigate al-

\* Corresponding author. Tel: +86-20-87113584; E-mail: [zliang@scut.edu.cn](mailto:zliang@scut.edu.cn)

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ternative non-precious-metal catalysts [7,8].

Among the potential candidates, carbon-based catalysts have attracted intensive attention [9]. N-doping can effectively alter the electronic and geometrical properties and thus improve the electrochemical performance of carbon catalysts [10]. Both the content and chemical configuration of the nitrogen dopant on the surface are of great importance in the electrocatalytic activity of the carbon catalyst. Effective N-doping can be achieved by either etching the carbon material in a N-containing gas [11,12] or direct pyrolysis of N-containing carbon sources such as melamine [13], polypyrrole [14–16], and polyaniline [17,18]. In both methods, the pyrolysis conditions are known to have a significant effect on the composition and structure of the resultant carbon. Jaouen et al. [19,20] investigated the effect of heat treatment on the activity and structure of carbon black etched by  $\text{NH}_3$ .

In previous work, we synthesized N-doped ordered mesoporous carbon (NOMC) by a modified nanocasting method, and the NOMC had high specific surface area, uniform pore structure, and excellent electrocatalytic activity [21]. The pyrolysis conditions are known to have a significant effect on the catalyst. However, this effect has not been explicitly investigated. In this work, the effects of the pyrolysis conditions, including the pyrolysis temperature, pyrolysis ramp rate, and duration, on the intrinsic properties and electrocatalytic activity of the NOMC catalyst were extensively investigated.

## 2. Experimental

### 2.1. Preparation of SBA-15

The details of the SBA-15 synthesis have been described elsewhere [22]. Typically, 4.0 g Pluronic P123 (Aldrich Chemistry, German) was dissolved in a mixture of 126 mL deionized water and 20 mL hydrochloric acid (37 wt%, Sinopharm Chemical Reagent Company Limited, Shanghai), and then 9.2 mL tetraethyl orthosilicate (Guangzhou Chemical Reagent Factory, Guangzhou) was added and the solution was stirred for 20 h at 35 °C. The slurry was hydrothermally treated at 110 °C for 12 h. Finally, the product was filtered, dried, and then calcined at 550 °C for 6 h in air to remove the organic template.

### 2.2. Preparation of N-doped ordered mesoporous carbon

Newly distilled pyrrole (PY, 1.20 mL, 99%, Xiya Reagent, Shandong) together with 1.0 g SBA-15 was added into a vacuum container, which was then kept in an oven at 133 °C for 2 h. The obtained light-yellow powder was added to 40 mL 2.0 mol/L  $\text{FeCl}_3$  (Sinopharm) aqueous solution, which was then vigorously stirred for 24 h at room temperature for polymerization. The product was filtrated and thoroughly washed with deionized water to remove the metal salt. After drying, the obtained black power was pyrolyzed at high temperature (600, 800, 900, or 1000 °C) for a given duration (1, 2, or 3 h) in argon (99.999%, Zhuozheng Gases Company Limited, Guangdong) with a certain pyrolysis ramp rate (10 or 30 °C/min). Finally, the silica template was removed in 10 mol/L NaOH at 120 °C

for 24 h, followed by rinsing with deionized water. The NOMC catalyst samples were denoted as C-PY-Temp-Duration-Rate.

### 2.3. Characterization

X-ray photoelectron spectroscopy (XPS) was carried out with a Physical Electronics PHI 5600 multi-technique system using an Al monochromatic X-ray at a power of 350 W. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 S-TWIN microscope operated at 200 kV. Raman spectra of the samples were performed on a LabRAM Aramis spectrometer with a 632.81 nm helium-neon laser. Nitrogen adsorption-desorption isotherms were measured at -196 °C using a Micromeritics TriStar II 3020 analyzer. Before adsorption measurements, each sample was outgassed under vacuum for 3 h at 200 °C. The total surface area ( $A_{\text{BET}}$ ) was analyzed by the well-established Brunauer-Emmett-Teller (BET) method, the microporous surface area ( $A_{\text{MP}}$ ) was obtained by the micropore (MP) method ( $t$ -plot method), and the pore size distribution ( $D_{\text{BJH}}$ ) was analyzed by the Barrett-Joyner-Halenda method.

### 2.4. Electrochemical characterization

The electrochemical behavior of the catalyst was characterized by cyclic voltammetry (CV) and linear sweeping voltammetry (LSV) using a three-electrode cell with a Zennium electrochemical workstation (Zahner) at room temperature (25 °C). A platinum wire and double junction Ag/AgCl reference electrode (PINE) were used as the counter and reference electrode, respectively. The working electrode was a rotating ring-disk electrode (RRDE; glassy carbon disk: 5.0 mm in diameter; platinum ring: 6.5 mm inner diameter and 7.5 mm outer diameter). The thin-film electrode on the disk was prepared as follows. First, 10 mg of the catalyst was dispersed in 1.0 mL Nafion/ethanol (0.84 wt% Nafion) by sonication for 120 min. Then, 10  $\mu\text{L}$  of the dispersion was transferred onto the glassy carbon disk using a pipette, giving the catalyst loading of 0.50 mg/cm<sup>2</sup>. For comparison, we also measured the electrocatalytic activity of the commercial 40 wt% Pt/C catalyst (HiSPEC4000, Johnson Matthey) for the ORR with metal loading of 20  $\mu\text{g}/\text{cm}^2$ .

The electrolyte solution was first bubbled with Ar for 60 min. Then, a CV test was conducted at 20 mV/s in the potential range 0–1.23 V (vs. reversible hydrogen electrode, RHE) for 20 cycles. Unless otherwise specified, the LSV curve was collected by scanning the disk potential from 1.2 V down to 0 V at 5 mV/s in  $\text{O}_2$  saturated electrolyte solution under 1600 r/min, from which the ORR polarization curve was determined by subtracting the capacitive current. During the collection, the potential of the ring was set to 0.5 V (vs. RHE) in alkaline solution to determine the yield of  $\text{H}_2\text{O}_2$ .

The electron-transfer number ( $n$ ) and  $\text{H}_2\text{O}_2$  yield ( $\text{H}_2\text{O}_2\%$ ) in the ORR were calculated from [23,24]

$$n = \frac{4|i_d|}{|i_d| + i_r / N} \quad (1)$$

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