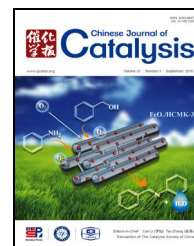


available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc

Article

Nitrogen-doped ordered mesoporous carbon: Effect of carbon precursor on oxygen reduction reactions

Xiao-hua Li^a, Kai Wan^a, Quan-bing Liu^a, Jin-hua Piao^b, Yu-ying Zheng^c, Zhen-xing Liang^{a,*}^a Key Laboratory on Fuel Cell Technology of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, Guangdong, China^b School of Food Science and Engineering, South China University of Technology, Guangzhou 510641, Guangdong, China^c School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, Guangdong, China

ARTICLE INFO

Article history:

Received 31 May 2016

Accepted 29 June 2016

Published 5 September 2016

Keywords:

Electrocatalysis

Fuel cell

Nitrogen-doped ordered mesoporous carbon

Oxygen reduction reaction

Precursor

ABSTRACT

Aniline, pyrrole and phenanthroline, which have different nitrogen compositions, are used as carbon precursors to synthesize nitrogen-doped ordered mesoporous carbons (NOMCs) by the nanocasting method. The effect of the precursor on the resultant NOMC is extensively investigated by nitrogen adsorption-desorption measurements, scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry and rotating ring-disk electrode measurements. Salient findings are as follows. First, the precursor has a significant influence on the specific surface area and textural properties. The NOMC materials derived from pyrrole (C-PY-900: 765 m²/g) and phenanthroline (C-Phen-900: 746 m²/g) exhibit higher specific surface areas than the aniline analog (C-PA-900: 569 m²/g). Second, the XPS results indicate that the total nitrogen content (*ca.* 3.1–3.3 at%) is similar for the three carbon sources, except for a slight difference in the nitrogen configuration. Furthermore, the content of the nitrogen-activated carbon atoms is found to closely depend on the precursor, which is the highest for the phenanthroline-derived carbon. Third, the electrochemical results reveal that the electrocatalytic activity follows in the order C-PA-900 < C-PY-900 < C-Phen-900, confirming that the nitrogen-activated carbon atoms are the active sites for the oxygen reduction reaction (ORR). In summary, the precursor has considerable influence on the composition and textural properties of the NOMC materials, of which the ORR electrocatalytic activity can be enhanced through optimization of the NOMCs.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) has been widely regarded as the next-generation energy technology because of advantages related to zero emission, high efficiency and energy density [1–3]. Currently, the commercialization of PEMFCs is economically unviable because of high cata-

lyst costs resulting from the requirement of large quantities of the noble metal Pt [4]. It is, therefore, highly desirable to develop non-precious metal catalysts [5], or alternatively, metal-free carbonaceous catalysts [6–9].

Among the alternatives, the nanostructured nitrogen-doped carbon is of particular interest, which shows promise in energy storage and conversion applications [10,11]. However, chal-

* Corresponding author. Tel: +86-20-87113584; E-mail: zliang@scut.edu.cn

This work was supported by the National Natural Science Foundation of China (21476087, 21576101), the Innovation Project of Guangdong Department of Education (2014KTSCX016), the Science & Technology Research Project of Guangdong Province (2013B010405005, 2014A010105041), and the Fundamental Research Funds for the Central Universities.

DOI: 10.1016/S1872-2067(16)62498-1 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 37, No. 9, September 2016

lenges remain to further increase the activity and stability of carbon catalysts. Enormous efforts have been devoted to optimizing a controllable synthesis. Among the conditions, the precursor is believed to play a key role in determining the composition, structure and resulting final properties of the final carbon catalyst. For example, diaminobenzene [12], aminoglucose [13], ethylenediamine [14], polyaniline [15], and phenanthroline [16] have been explored, which are reported to yield different activities.

It should be pointed out that the electrocatalytic activity cannot easily be directly compared as both the synthesis and evaluation were conducted by different research groups under differing conditions. As such, the precursor effect needs to be explicitly investigated as to how it influences composition, structure and electrocatalysis for oxygen reduction reactions (ORRs). In our previous work, nitrogen-doped ordered mesoporous carbons (NOMCs) were synthesized by a modified nanocasting method, which exhibited high specific surface areas, uniform pore structures and excellent electrocatalytic activity [17]. In this work, individual NOMCs are synthesized using three precursors, aniline, pyrrole, and phenanthroline, each having varying nitrogen compositional structures. The effect of the precursor on the resultant NOMC is extensively investigated by nitrogen adsorption-desorption measurements, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV), and rotating-ring-disk electrode (RRDE) methods.

2. Experimental

2.1. Synthesis of the NOMC catalysts

NOMCs were synthesized via a nanocasting method using SBA-15 as the template [17–19]. First, 3.2 g SBA-15 was dispersed in an ethanol solution (20.0 mL ethanol + 20.0 mL deionized water). Second, 4.0 g phenanthroline was dissolved in 10 mL ethanol and mixed with a FeCl₂ aqueous solution. The molar ratio of iron to phenanthroline was 1:3 to ensure complete coordination. Thereafter, the above two solutions were mixed and sonicated for 6 h. The resulting powder was filtered, washed and subjected to pyrolysis at high temperatures (700, 800, 900, 1000 °C) for 3 h under an Ar atmosphere. Finally, the NOMC catalysts were obtained by removing the silica template and Fe species. The template was removed by refluxing the powders in 10 mol/L NaOH at 120 °C for 24 h, and the iron species was leached by boiling the powders in 0.10 mol/L HClO₄ at 80 °C for 24 h. The samples were referred to as C-Phen-*x*. Here, *x* refers to the pyrolysis temperature, *viz.* 700, 800, 900, and 1000 °C.

The pyrrole- and aniline-derived carbon catalysts, C-PY-900 and C-PA-900, were synthesized as described in our previous work [20,21]. Pyrolysis was conducted at 900 °C for 3 h under an Ar atmosphere.

2.2. Physicochemical characterizations

X-ray diffraction (XRD) measurements were performed us-

ing a Bruker D8 ADVANCE diffractometer employing a Cu K α radiation source operating at 40 kV at a scan rate of 10°/min. XPS (Physical Electronics PHI 5600) measurements were carried out with a multi-technique system using an Al monochromatic X-ray source at a power of 350 W. Transmission electron microscopy (TEM) images were taken on a FEI Tecnai G2 F20 S-TWIN operating at 200 kV. Nitrogen adsorption-desorption isotherms were measured at -196 °C using a Micromeritics TriStar II 3020 analyzer. Total surface area was determined by the Brunauer-Emmett-Teller (BET) method, the microporous (MP) surface area was obtained via the *t*-plot method, and the pore size distribution was analyzed using the Barrett-Joyner-Halenda (BJH) method.

2.3. Electrochemical test

The electrochemical behavior of the catalysts was characterized by CV and linear sweeping voltammetry (LSV) methods using a three-electrode cell with a Zennium electrochemical work station (Zahner) at room temperature (25 °C). A gold wire and a double junction Ag/AgCl reference electrode (PINE) were used as the counter and reference electrodes, respectively. The working electrode was a 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: 10 mg of the catalyst was dispersed in 1.0 mL Nafion/ethanol (0.84 wt% Nafion) by sonication for 2 h. Thereafter, 10 μ L of the dispersion was transferred by pipette onto the glassy carbon disk, yielding a catalyst loading of 0.50 mg/cm². For comparison, we also measured the ORR electrocatalytic activity of a commercial 40 wt% Pt/C catalyst (HiSPEC4000, Johnson Matthey) having a metal loading of 20 μ g/cm².

A KOH electrolyte solution (0.10 mol/L) was first bubbled with Ar for 1 h. Thereafter, the CV test was conducted at 20 mV/s across the potential range of 0–1.23 V (vs. reversible hydrogen electrode, RHE) for 20 cycles. If unspecified, the LSV curve was collected by scanning the disk potential from 1.2–0 V at 5 mV/s in the oxygen-saturated electrolyte solution under 1600 r/min, from which the ORR polarization curve was extracted by subtracting the capacitive current. During the collection, the potential of the ring was set as 0.5 V (vs. RHE) to determine the yield of hydrogen peroxide, respectively.

The electron transfer number (*n*) and hydrogen peroxide yield in the ORR was calculated from the following equations:

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

$$H_2O_2 = \frac{2i_r/N}{|i_d| + i_r/N} \times 100\% \quad (2)$$

where *i_d* is the disk current, *i_r* is the ring current, and *N* is the collection efficiency (= 20.50%).

3. Results and discussion

Fig. 1 presents the nitrogen adsorption-desorption isotherms of the synthesized C-PA-900, C-PY-900, and

Download English Version:

<https://daneshyari.com/en/article/6506171>

Download Persian Version:

<https://daneshyari.com/article/6506171>

[Daneshyari.com](https://daneshyari.com)