



# Electrocatalytic activity of carbon nanoparticles from diffusion flame towards oxygen reduction



Yan Zhou<sup>a,b</sup>, Shuiliang Chen<sup>a,b,\*</sup>, Shuwu Liu<sup>a</sup>, Qin Liu<sup>b</sup>, Haoqing Hou<sup>a</sup>, Feng Zhao<sup>b</sup>

<sup>a</sup> Department of Chemistry and Chemical Engineering, Jiangxi Normal University, 330022, Nanchang, China

<sup>b</sup> Institute of Urban Environment Chinese Academy of Sciences, 1799 Jimei Road, 361021, Xiamen, China

## ARTICLE INFO

### Article history:

Received 5 May 2014

Received in revised form 16 May 2014

Accepted 16 May 2014

Available online 27 May 2014

### Keywords:

Oxygen reduction reaction

Oxygen-containing carbon nanoparticles

Electrocatalytic activity

Diffusion flame

## ABSTRACT

In this paper, we demonstrate that oxygen-containing carbon nanoparticles (O-CNPs) obtained from diffusion flame display notable ORR electrocatalytic activities in alkali media. The O-CNPs were the incomplete combustion product of hydrocarbon fuels. Electrochemical results showed that the O-CNP catalyst prepared from n-hexane could display very positive ORR peak potential of -0.24 V vs. Ag/AgCl, which was higher than the reported oxygen-containing carbon materials and common carbon black of below -0.35 V. Moreover, the ORR peak potential was varied with the unsaturation degree of the hydrocarbon fuels. It was further proposed that the remarkable ORR electrocatalytic activities of the O-CNPs was attributed to semiquinone groups bonded to the edge of the graphitic carbon layer.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

The oxygen reduction reaction (ORR) is a crucial process in fuel cells and metal-air batteries.[1] Owing to the slow kinetics of ORR, catalysts are required to increase the reaction rates and lower the over-potentials at the cathode of these electrochemical devices. Pt-based materials were the most commonly used and regarded as the most effective catalysts for ORR.[2] However, the high-cost, poor durability, together with sensitivity to fuel crossover effects from the anode largely hindered the commercialization of fuel cells.

Recently, a series of non-Pt catalysts, including non-precious metal and metal-free carbon-based catalysts, were developed as alternatives for ORR catalysts in a variety of fuel cells, as reviewed in references.[3,4] Among these, the metal-free carbon-based catalysts attracted specific attention due to their excellent ORR catalytic activities, low-cost, promising durability and selectivity, resistance to the fuel e.g. methanol crossover effect. These catalysts were commonly based on heteroatom-doped carbon materials with heteroatoms of N,[5–7] S,[8,9] P,[10,11] and B.[12] Extensive studies revealed that the incorporation of such heteroatoms changed the spin density and atomic charge distribution of carbon atoms in the graphitic layers, thus facilitated the catalytic activity towards

ORR.[13] However, besides of the heteroatoms, the effects of O atom which existed in these catalysts were rarely discussed.[6,10,14–17]

It was reported by Yeager and Applebey et al. that carbon materials only containing O atom showed low electrocatalytic activity, and usually served as the control when discussing the effect of heteroatoms on the electrocatalytic performance.[18,19] Later, Gong et al. [20] examined the catalytic activity of carbon nanotubes with oxygen-containing surface functionalities in neutral condition, whose reduction peak potentials were about -0.48 V (vs. Ag/AgCl). The relatively poor activities of carboxylic acid (-COOH) edge-selectively functionalized graphene was also reported. [21] However, it was not sufficient to conclude that the effects of O atom on the ORR electrocatalytic activity of the carbon material could be neglected since the states of oxygen, e.g. carboxylic, carbonyl, ester or quinone groups, were varied with carbon structure and preparing condition. Meanwhile, it had been reported that oxygen groups showed synergetic effect to the high electrocatalytic activity in the N-doped carbon catalysts.[17] So, understanding the real performance and catalytic mechanism of oxygen containing group in carbon would be necessary and of great significance.

In this study, we report that oxygen-containing carbon nanoparticles (denoted O-CNPs) show remarkable ORR electrocatalytic activities in alkali media. The O-CNPs are the incomplete combustion products of hydrocarbon fuels, which are synthesized by the simple combustion of hydrocarbons through a diffusion flame in air. Our study shows that the semiquinone groups bonded to the edge of the graphitic carbon layer in the O-CNPs play an important role in the process of oxygen reduction.

\* Corresponding author.

E-mail addresses: [shuiliangchen@163.com](mailto:shuiliangchen@163.com) (S. Chen), [haoqing@jxnu.edu.cn](mailto:haoqing@jxnu.edu.cn) (H. Hou), [fzhao@iue.ac.cn](mailto:fzhao@iue.ac.cn) (F. Zhao).

## 2. Experiments

### 2.1. Preparation of O-CNPs

O-CNP samples were produced by burning benzene, n-hexane, cyclohexene or cyclohexane (all purchased from Sigma-Aldrich) in air. The liquid fuel was stored in a bottled fuel reservoir with a cotton wick extending into the reservoir. O-CNPs were collected on aluminum foil suspended over the diffusion flame. When the fuel in the reservoir was changed, the cotton wick was also replaced by a new one. The benchmark commercial available Pt/C (20% mass Pt supported on Vulcan XC-72R carbon black) catalyst was purchased from Alfa Aesar. All chemicals were used as received without any further purification.

### 2.2. Electrode preparation

A glass carbon (GC) electrode with diameter  $\phi = 3$  mm was used to measure the initial electrocatalytic performances of the ORR catalysts produced in this study. The GC electrode pretreatment protocol is as follows: prior to use, the GC disk electrode was first mechanically polished with 1  $\mu\text{m}$  and then 0.05  $\mu\text{m}$  alumina powder using an abrasive paper (to obtain mirror-like surfaces), then washed with both ethanol and deionized water (sonicated for 5 min in each), and finally dried in desiccators (relative humidity RH = 0%). Catalysts (1 mg) were dispersed in a solvent mixture containing 25  $\mu\text{L}$  of Nafion dispersion (supplied as a 5% mass dispersion in aliphatic alcohol/water mixture) and 250  $\mu\text{L}$  of de-ionized water using sonication. Immediately after dispersion, 5  $\mu\text{L}$  of this catalyst slurry was then pipetted onto the GC electrode surface for the cyclic voltammetry experiments. The electrodes were dried at room temperature before being used for electrochemical testing. For the preparation of rotating disc electrode (RDE,  $\phi = 5$  mm) and rotating ring disk electrode (RRDE, disk  $\phi = 5.61$  mm, ring inner  $\phi = 6.25$  mm, and ring outer  $\phi = 7.92$  mm, collection efficiency was 40%), 15  $\mu\text{L}$  of the catalyst slurry was used.

### 2.3. Electrochemical Testing

For cyclic voltammetry, a potentiostat (CHI 660D) equipped with three-electrode system was used to conduct the tests. Ag/AgCl (25 °C, saturated KCl internal solution) reference electrodes and a Pt wire counter electrode (area ca. 200% of the working electrode disk area) were used for all experiments. The RDE and RRDE tests were conducted using a bi-potentiostat (CHI 760D) equipped with a speed controller (AFMSRCE, Pine Instrument Co., USA) and with the ring potential set at +0.5 V vs. Ag/AgCl. The current density was normalised using the geometric areas of the GC electrode being used. At least three repeated measurements were conducted for each result. All the tests were conducted in 0.1 M KOH at 25 °C.

### 2.4. Characterization

The morphologies of the catalysts were characterized by using scanning electron microscopes (a S-4800 SEM from Hitachi and a Vega3 SEM from Tescan) and transmission electron microscope (JEM-2010). The Raman spectra were recorded on a LabRAM Aramis (Horiba Jobin Yvon S.A.S) with a 633 nm wavelength laser. Infrared spectra (IR) were recorded with a Bruker Tensor 27 using the attenuated total reflectance (ATR) attachment. The flame temperatures of different hydrocarbons were detected by using a TES 1310 thermometer. The X-ray photoelectron-spectroscopy analyses were conducted on a Thermo ESCALAB 250 (with Al- $K_{\alpha}$  source).

### 2.5. Calculation of electron transfer number

The electron transfer number ( $n$ ) of the ORR was calculated by two methods as follows:

(a) Based on the RDE tests according to the Koutecký-Levich equations (1)–(2):

$$j^{-1} = j_k^{-1} + (B\omega^{1/2})^{-1} \quad (1)$$

$$B = 0.62nFCD^{2/3}\nu^{-1/6} \quad (2)$$

where  $j$  is the measured current density ( $\text{A cm}^{-2}$  normalized to geometric electrode areas),  $j_k$  is the kinetic current density,  $\omega$  is the angular velocity of the disk ( $\text{rad s}^{-1}$ ),  $n$  is the overall electron transfer numbers for oxygen reduction,  $F$  is the Faraday constant ( $F = 96,485 \text{ C mol}^{-1}$ ),  $C$  is the bulk concentration of  $\text{O}_2$ ,  $D$  is the coefficient of  $\text{O}_2$ , and  $\nu$  is the kinematic viscosity of the electrolyte. We used the values  $C = 1.2 \times 10^{-6} \text{ mol cm}^{-3}$ ,  $D = 1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,  $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$  (0.1  $\text{mol dm}^{-3}$  aqueous KOH) for the calculation.

(b) Based on the RRDE tests according to the equation according to previous reports [22]:

$$n = 4 \times \frac{I_d}{I_d + I_r/N}$$

Where  $I_d$  is the disk current,  $I_r$  is the ring current.  $N$  refers to the collection efficiency of Pt ring, and here the value 0.4 is adopted.

## 3. Results and Discussion

### 3.1. Preparation and characterization of O-CNPs

n-Hexane was firstly chosen as the hydrocarbon precursor for the synthesis of the O-CNPs (denoted O-CNPs-*n*-hexane). As shown in Fig. 1A, the O-CNPs were collected over a *n*-hexane flame. Morphological characterization by scanning electron microscope (SEM) (Fig. 1B) showed that the O-CNPs were chain-like agglomerates of primary particles. High resolution transmission electron microscopy (TEM) (Fig. 1C) and Raman spectroscopy (Figure S1D) revealed that the O-CNPs consisted of perturbed graphitic layers, disordered carbon, and amorphous carbon, which was consistent to the observations reported in a previous study.[23] Raman spectra in Figure S1D showed that the ratio of intensity of the G band and D band ( $I_G/I_D$ ) for the O-CNPs-*n*-hexane was about 0.758.

The element analyses were conducted by using X-ray photoelectron-spectroscopy. As shown in Fig. 2A, the O-CNPs-*n*-hexane contained the elements of C and O and with O content of 8.31%. Although the O-CNPs were synthesized by diffusion flame in air, the XPS spectra did not show any N1s peaks, which indicated the absence of surface bound N (Fig. 2B gives the absence of N1s fine spectrum). The C1s fine spectrum could be deconvoluted into three peaks at 284.6, 286.4, and 288.6 eV, which were assigned to C=C, C-O, and C=O groups respectively (Fig. 2C). The high resolution O1s spectrum could likewise be divided into two peaks at 531.8 and 533.1 eV, which were assigned to C=O and C-O groups, respectively (Fig. 2D).[24] The ATR-IR spectrum of the O-CNPs-*n*-hexane is presented in Fig. 3D (along with the spectrum of O-CNPs synthesized using different precursors—see later) and the assigned primary peaks are summarized in Table S1. The wide peak at  $3300 \text{ cm}^{-1}$  relates to -OH. The peak at  $1731 \text{ cm}^{-1}$  was assigned to the C=O stretching vibration and the  $1550 \text{ cm}^{-1}$  band to the stretching vibration of C=C in the polyaromatic ring (graphitic layer). The strong peak at  $1025 \text{ cm}^{-1}$  is the C-O stretching vibration.

Download English Version:

<https://daneshyari.com/en/article/185400>

Download Persian Version:

<https://daneshyari.com/article/185400>

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