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A graphene-based electrocatalyst co-doped with nitrogen and cobalt for oxygen reduction reaction

Huijuan Wu ^{a,1}, Chaozhong Guo ^{a,b,*}, Jiaqiang Li ^{a,1}, Zili Ma ^{a,c},
Qiyun Feng ^a, Changguo Chen ^{a,**}

^a College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China

^b Research Institute for New Materials Technology, Chongqing University of Arts and Sciences, Yongchuan, Chongqing 402160, China

^c Huadian Electric Power Research Institute, Hangzhou 310030, China

ARTICLE INFO

Article history:

Received 20 May 2016

Received in revised form

12 September 2016

Accepted 12 September 2016

Available online xxx

Keywords:

Milk powder

Graphene oxide

Non-precious metal catalyst

Oxygen reduction

ABSTRACT

The development of low cost, active and stable non-precious metal (Co-N/C) catalysts to replace commercial Pt-based catalysts for oxygen reduction reaction (ORR) is a hot topic to this day. In this work, we have synthesized a new graphene-based catalyst (Co-N/C-A) doped by cobalt and nitrogen atoms with high contents of pyridinic- and pyrrolic-nitrogen (planar nitrogen), which exhibits ORR electrocatalytic activity with onset and peak potentials of 0.035 and -0.082 V (versus Hg/HgO) in 0.1 mol l^{-1} KOH solution, respectively. Besides, it has much higher stability and tolerance to methanol compared to the commercial Pt/C catalyst. The overall electron transfer number is calculated to be about 3.8. The transition-metal (Co) in the precursor can promote the formation of active sites during pyrolysis process and the followed acid-treatment may effectively expose the active sites on the surface of the catalyst, helping to enhance the ORR activity. It can be also proposed that pyridinic- and pyrrolic-nitrogen groups may play a key role in the ORR process and serve as the ORR active centers.

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Introduction

Nowadays, high-performance fuel cells rapidly become the ideal power supply because of their high energy conversion efficiency, environmentally friendly and abundant fuel sources [1]. However, the extensive usage of fuel cells has been hampered thanks to the slow kinetics and diversified ways of the oxygen reduction reaction (ORR) [2,3]. Traditionally, the carbon-based Pt catalyst is considered as the most effective

electrocatalyst to catalyze the ORR owing to their high intrinsic activity [4]. However, their large-scale commercial applications are hindered because of high cost and scarcity of metal-Pt resource [5,6]. Apart from these drawbacks, Pt-based electrocatalysts are also subjected to low durability and organic molecule deactivation [7]. Therefore, the development of inexpensive non-Pt electrocatalysts with high ORR activity, long-term stability and good tolerance to organic molecules is of paramount importance so far.

* Corresponding author. College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.

** Corresponding author.

E-mail addresses: guochaozhong1987@163.com (C. Guo), cgchen@cqu.edu.cn (C. Chen).

¹ These authors equally contributed to this work, and they were considered as co-first authors.

<http://dx.doi.org/10.1016/j.ijhydene.2016.09.074>

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Since Jasinsky interestingly found that cobalt-phthalocyanine (CoPc) has exhibited a significant activity towards the ORR in 1964 [8], many researchers are actively focused on non-precious metal-nitrogen-carbon (M-N/C) catalysts for the ORR. For example, Maruyama et al. prepared a cathode catalyst by simple carbonization of hemoglobin in nitrogen atmosphere [9]. An earlier literature [10,11] also reported the preparation of an ORR catalyst from natural organic catalase. However, these kinds of ORR catalysts have poor long-term stability and low ORR electrocatalytic activity [12]. More importantly, some studies adequately demonstrate that the heat-treatment at high temperature can enhance the electrochemical stability and ORR catalytic activity of M-N/C catalysts [13,14], but it can destroy the intrinsic structure of macrocyclic complexes inside the catalyst [15]. Thereafter, it is significantly pointed out that even if there are not chemical bonds between central metal and macrocyclic ligand inside the complex, the prepared M-N/C catalysts can still exhibit high catalytic activity after heat-treatment, which is further confirmed by Gupta et al. [16]. With continuous research, some researchers have prepared highly active ORR catalysts by the simple use of nitrogen-containing compounds, such as melamine, dicyandiamide and urea, to replace macrocyclic complexes [17–19]. Our group has also formed several ORR catalysts from pyrolysis of protein-enriched biomass with outstanding long-term stability, and excellent methanol tolerance [20–22]. However, there is a large controversy about the active sites for ORR of M-N/C catalyst until now. It is largely believed that the nitrogen-modified carbon structure may be the electrocatalytically ORR-active site [23,24], whereas the transition-metal only plays a role in promoting the formation of ORR active site [25,26].

Here we report a new strategy to design the Co-N/C-A catalyst by using cheap milk biomass as the nitrogen source, graphene oxide (GO) as the carbon source and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ as the metal source, followed by an acid-treatment process. The structure characterization and electrocatalytic activity towards the ORR in alkaline electrolytes were evaluated in detail. We interestingly found that this catalyst can exhibit excellent ORR activity, high durability and good tolerance to methanol molecule, which may be a promising alternative to the commercial Pt catalysts.

Experimental

Catalyst preparations

All catalysts were prepared by pyrolysis process in a tube furnace. 0.05 g of GO nanosheets (provided by Jiangshu Nano Co.), 0.05 g of pure milk powder (purchased from local supermarket), and 0.15 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were absolutely mixed and milled in a mortar. The obtained sample was then pyrolyzed in flowing N_2 at 900 °C for 1 h to obtain the “Co-N/C”. In order to further examine the real role of metal in the ORR process, the prepared Co-N/C catalyst was chemically treated with 0.5 mol l^{-1} H_2SO_4 solution at room temperature to remove metal Co or its compounds. After acid-treatment, the produced sample was hereafter called “Co-N/C-A”. Besides, as a control, a mixture of GO nanosheet and milk powder was also annealed in N_2 atmosphere at 900 °C for 1 h. Analogously,

we have named it as “N/C”. We further prepared the “GO-900” and “N-900” catalysts through the pyrolysis of GO and milk in same condition, respectively.

Physical characterizations

The X-ray diffraction (XRD) analysis was conducted on Shimadzu XRD-6000 (Japan) with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54178 \text{ \AA}$) at 4° min^{-1} . The scanning electron microscopic (SEM) images were performed on FEI Quanta 200 Scanning Electron Microscope. High-resolution transmission electron microscopy (HR-TEM) was carried out on FEI Tecnai F30 instrument and acceleration voltage is 300 kV. The X-ray photoelectron spectroscopy (XPS) analysis was carried out by using a VG Scientific ESCALAB 220 I XL spectroscopy with an Al K_{α} ($h\nu = 1486.69 \text{ eV}$) X-ray source.

Electrochemical measurements

All electrochemical tests were performed on CHI 660 electrochemical workstation (CH Instruments, USA) at room temperature. The electrolyte was 0.1 mol l^{-1} KOH solution, which was purged by nitrogen or oxygen for 30 min prior to the electrochemical test. A conventional three-electrode cell was adopted, which included an Hg/HgO/1 mol l^{-1} KOH electrode as the reference electrode, and a ring-shaped Pt wire electrode as the counter electrode, respectively. A rotation disk electrode (RDE) with a glass carbon (GC, 4 mm diameter, 0.1256 cm^2 geometric area) electrode (5-mm diameter, LKXZ-1, Tianjing Lanlike Electrochemical Instruments, China) was employed as the working electrode. To prepare the modified-GC-RDE working electrode, the doped-carbon catalyst was well-dispersed in the 0.5 wt.% Nafion/ethanol solution. 5.0 μl of 10 mg ml^{-1} dispersion was transferred onto the GC-RDE surface and then dried at room temperature. The mass loading was calculated to be $\sim 400 \mu\text{g cm}^{-2}$. A commercial Pt/C catalyst (20 wt.% Pt) on the GC electrode was prepared in the same way. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) experiments were performed over the potential range of 0.3 to -0.7 V at a scan rate of 5 mV s^{-1} in 0.1 mol l^{-1} KOH solution. The number of electron transfer (n) per oxygen molecule was calculated by Koutecky–Levich (K–L) equation [25]:

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

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

where j_d was the measured current density; j_k was the kinetic current density of the ORR; F was the Faraday constant ($96,485 \text{ C mol}^{-1}$); C_O was the concentration of dissolved oxygen ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$); D_O was the diffusion coefficient of oxygen ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$); ν was the kinetic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$); and ω was the electrode rotation rate (rpm).

Results and discussion

The structural analysis of the catalysts

Fig. 1a shows the XRD patterns of the obtained products. A pronounced peak at $\sim 26^\circ$ and a weak peak at $\sim 43^\circ$ are assigned

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