

Full paper

Phthalocyanine tethered iron phthalocyanine on graphitized carbon black as superior electrocatalyst for oxygen reduction reaction



Zhengping Zhang, Meiling Dou, Jing Ji, Feng Wang*

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, PR China

ARTICLE INFO

Keywords:

Oxygen reduction reactions
Electrocatalysts
Phthalocyanine
Electrocatalytic durability

ABSTRACT

Despite the superior electrocatalytic activity of iron (II) phthalocyanine (FePc) for oxygen reduction reaction (ORR) in alkaline media, the large-scale applications of these FePc-based materials are still greatly hindered by their rapidly declined activity. To overcome this obstacle, it is essential to enhance the catalytic durability of FePc-based electrocatalysts. Herein, we demonstrate a superior FePc-based catalyst by employing low-cost graphitized carbon black as carbon supports, and tuning the Fe coordination environment in FePc, via the delocalized π coordination. Owing to the excellent ORR catalytic activity (the specific activity of 2.26 mA cm^{-2} , 3.6-fold enhancements compared with the commercial Pt/C catalyst), the remarkable durability (after 3000 potential cycles, 3-mV shifts for the half-wave potential, only 4.2% decreases from the initial specific activity) and the outstanding selectivity (good methanol tolerance, and free from interfering species effects, including NO_3^- , SO_4^{2-} , PO_4^{3-} , Br^- , Cl^- and SCN^-), the novel FePc-based electrocatalyst is promising substitutes for Pt-based catalysts for ORR. Furthermore, to better elucidate the origin of the ORR performance, the density functional theory (DFT) calculation indicates that the unique structure of phthalocyanine tethered iron phthalocyanine (Pc-FePc) plays a key role in improving of both the catalytic activity and durability.

1. Introduction

Nowadays, the fuel cell technology gains more and more concerns due to the current global energy issues and environmental pollution challenges [1,2]. Considering the specific performance characteristics of different fuel cells, the relatively simple alkaline fuel cells (AFCs), with high energy densities and high reliability, will continue to dominate the large-scale market space [3,4]. Although the AFCs technology has reached technical maturity, the economics of AFCs is still hindered by the high cost of catalyst and other expensive materials [4–6]. To reduce the cost of AFC technology, it remains a strong barrier that needs to be broken through for replacing the platinum (Pt)-based materials as oxygen reduction reaction (ORR) catalysts [5–7]. As the cathodic reaction in AFCs, ORR possesses the sluggish nature due to the tough bonding force of the bimolecular structure of oxygen [8]. Although great efforts have been devoted to developing various types of low-cost ORR catalysts (e.g. transition metal oxides, heteroatom-doped carbon and metal-macrocycle compounds [9–19]), the Pt-based catalysts are still applied as the commercial catalysts for large-scale commercialization, in virtue of the state-of-the-art activity and relatively good durability [6,20]. For sustainable and large-scale applica-

tion, it still remains a big challenge to develop the non-precious metal catalysts (NPMCs) and promote their ORR performance in term of both catalytic activity and durability [2,5]. Among the whole NPMCs systems, iron phthalocyanine (FePc)-based catalysts are generally considered a leading candidate for replacing Pt-based materials, by their superior electrocatalytic activity via a 4-electron transfer pathway [21,22].

Although FePc-based catalysts are generally acknowledged as typical electrocatalysts for facilitating the ORR, the applications of FePc-based catalysts are limited by their rapidly declined activity [22,23]. In the harsh oxygen reducing environments, FePc-based catalysts will lose the ORR catalytic activity due to the demetalation of the central Fe atom and “intoxication” by ORR intermediates (e.g. $^*\text{OH}$) [22–24]. Traditional strategies have conducted a high-temperature pyrolysis process for converting the FePc molecule into the relatively stable Fe-N-C complex [25,26]. However, due to the uncontrollable structure and inevitable agglomeration, it is hard to tailor the proper molecular catalytic site and the interface between electrocatalysts and electrolytes [26–28]. In addition, the precise identification of true active site for the Fe-N-C complex is still very difficult, leading to more unreliable and unpredictable results that can hardly

* Corresponding author.

E-mail address: wangf@mail.buct.edu.cn (F. Wang).<http://dx.doi.org/10.1016/j.nanoen.2017.02.042>

Received 13 January 2017; Received in revised form 21 February 2017; Accepted 21 February 2017

Available online 22 February 2017

2211-2855/ © 2017 Elsevier Ltd. All rights reserved.

guide the design and synthesis of the ORR catalysts [22–28].

On the other hand, nonpyrolyzed FePc-based catalysts are appealing for the ability to effectively control the molecular structures of catalytically active sites and choose the rational supports for homogeneous dispersion of catalytically active sites. Most of the synthetic strategies based on the nonpyrolysis process stand on facilitating the electron transfer, thus improving the stability *via* choosing the rational carbon supports [29–31], and tuning the coordination environment of the central Fe atom [9,32]. In particular, since the Fe-N₄ moiety is considered as the catalytically active site, the ORR performance of FePc is strongly governed by the steric effect and the electronic state of the Fe 3d orbit [11,27]. As a rational design, tuning the coordination environment of the central Fe atom has been proven as a direct and efficient strategy to enhance both of the catalytic activity and durability of FePc-based catalysts (*e.g.* the coordination bond between pyridine and FePc can form a stable FePc-pyridine structure for the higher ORR performance than the pure FePc structure) [12,32]. Therefore, our synthesis strategy is also primarily focused on tuning the coordination environment of the central Fe atom.

In this work, we prepared a series of superior ORR electrocatalysts using the low-cost graphitized carbon black (GCB) as carbon support, by tuning the Fe coordination environment in FePc *via* the delocalized π coordination effect from the additional phthalocyanine (Pc) molecule [32,33]. Owing to the steric and electronic effects, the novel FePc-based electrocatalysts exhibit the enhanced ORR performance. Furthermore, to better elucidate the origin of the ORR performance, our theoretical calculation reveals that the unsubstituted phthalocyanine (Pc) tethered iron phthalocyanine (Pc-FePc) structure may play a critical role in improving of both the catalytic activity and durability. In addition, on the control of various modified transition metals between the carbon supports and Pc groups, the Pc-FePc complex on the Mn-modified GCB (Pc-FePc/Mn-GCB) presents the excellent ORR catalytic activity (the specific activity of 2.26 mA cm⁻², 3.6 fold enhancements compared with the commercial Pt/C catalyst), the remarkable durability (after 3000 potential cycles, 3-mV shifts for the half-wave potential, only 4.2% decreases from the initial specific activity) and the outstanding selectivity (good methanol tolerance, and free from interfering species effects, including NO₃⁻, SO₄²⁻, PO₄³⁻, Br⁻, Cl⁻ and SCN⁻).

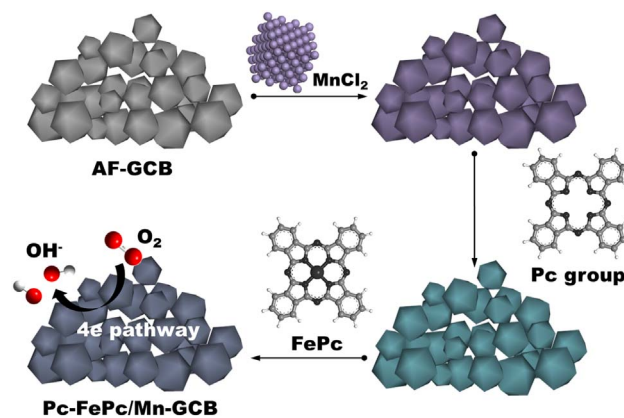
2. Experimental section

2.1. Synthesis of the Pc-FePc/Mn-GCB electrocatalyst

The acid-functional graphitized Vulcan XC-72 carbon black (AF-GCB) was derived from Vulcan XC-72 with high-temperature (2800 °C) graphitization for 1 h in an argon atmosphere followed with an acidification in concentrated nitric acid at 60 °C for 5 h. A mixture of 50 mg manganese chloride (or other transition metal chloride, including FeCl₂, CoCl₂ and NiCl₂) and 90 mg AF-GCB were placed in 40 mL ultrapure water and stirred for 30 min. Then, the mixture is separated from the mixture aqueous solution by filtration and washed by water several times. Subsequently, the Mn-modified GCB was mixed with 5 mg phthalocyanine into 40 mL ethanol solution for 1 h. After filtrated and washed with ethanol, the obtained Pc/Mn-GCB and 5 mg FePc were mixed into 20 mL tetrahydrofuran solution and sonicated for 2 h. Finally, the precipitates were filtrated and washed with pure water and ethanol several times, and generated into the final product (Pc-FePc/Mn-GCB).

2.2. Electrochemical measurements

All the electrochemical measurements were performed on a Rotating Ring Disk Electrode Apparatus (RRDE-3A, BAS INC, Tokyo, Japan) and controlled by CHI-760E electrochemical workstation (CH Instruments Company, Shanghai, China) with a normal three-electrode system is carried out by a glassy carbon electrode (GCE, 4.0 mm) as the



Scheme 1. Schematic illustration of the preparation process for the Pc-FePc/Mn-GCB electrocatalysts.

working electrode, a saturated calomel electrode (SCE) as the reference electrode and a Pt wire as the counter electrode. All the working electrodes were prepared as follows: 10 mg electrocatalyst and 10 μ L Nafion was dispersed in 2 mL ethanol solution and sonicated for 2 h. 5 μ L of catalyst ink was transferred onto the polished GCE and dried for 30 min at room temperature. The loading mass of all the samples on the GCE was 100 μ g cm⁻², including the commercial Pt/C catalyst (20 wt%).

3. Results and discussion

Scheme 1 illustrates the procedure used to prepare the novel electrocatalysts. Firstly, the acid-functional graphitized Vulcan XC-72 carbon blacks (AF-GCBs) were generated by high-temperature graphitization [34] (Fig. S1, S2) and followed acidification. Then AF-GCBs were mixed with Mn²⁺ ions (or other transition metal ions, including Fe²⁺, Co²⁺ and Ni²⁺) in the aqueous solution. The oxygen-containing functional groups presented on the surface of AF-GCB (Fig. S1b) allowed the Mn²⁺ ions in the solution to be adsorbed onto the AF-GCB surface by electrostatic interaction. Subsequently, the Mn-modified GCB was filtrated from the mixed aqueous solution, and then was mixed with Pc groups into ethanol solution, followed by filtrating and washing with ethanol for several times. By the coordination/electrostatic interaction, the Pc molecules are easily coated on Mn-modified GCB [33]. Then the obtained products (Pc/Mn-GCB) and FePc were mixed in tetrahydrofuran solution and sonicated for 2 h [32]. The mixture solution was generated into the final product (the Pc-FePc complex on the Mn-modified GCB, denoted as Pc-FePc/Mn-GCB) by filtration and wash with tetrahydrofuran, pure water and ethanol several times. For comparison, we also prepared FePc coated on bare Vulcan XC-72 (FePc/C) by a simple mixture of FePc and Vulcan XC-72 carbon black in tetrahydrofuran solution.

We first conducted transmission electron microscopy (TEM) images and Raman spectra of Vulcan XC-72 and GCB. In contrast to Vulcan XC-72, the TEM observation (Fig. S1) and Raman spectra (Fig. S2a) clearly reveals that GCB exhibits interconnected and uniformly dispersed structure with intensely graphitic lattice fringes and obviously high G band, under graphitization at 2800 °C. Such structure indicated that GCB is propitious for the facile diffusion of reactants and improving the electrical conductivity and stability [34]. Compared with the smooth and intact surface morphology of pure GCB, the irregular amorphous layer coated on the surface of Pc-FePc/Mn-GCB (Fig. 1a) was observed, probably originating from the adhesion of Pc-FePc compounds [26]. Due to the irregular amorphous layer, the Raman spectrum of Pc-FePc/Mn-GCB-GCB (Fig. 2b) exhibited the higher single-peak 2D band with the lower proportion of the I_G/I_D (1.48) compared with those of GCB (2.04) and AF-GCB (1.94) [32]. As seen in Fig. S3, by the acidification (Fig. S2b) and subsequent modification of

Download English Version:

<https://daneshyari.com/en/article/5451929>

Download Persian Version:

<https://daneshyari.com/article/5451929>

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