Journal of Electroanalytical Chemistry 727 (2014) 91–98

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Iron(II) tetraaminophthalocyanine functionalized graphene: Synthesis, characterization and their application in direct methanol fuel cell

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ARTICLE INFO

Article history:
Received 16 January 2014
Received in revised form 28 April 2014
Accepted 29 May 2014
Available online 11 June 2014

Keywords:
FeTAPc-Gr
Oxygen reduction reaction
Methanol crossover
Fuel cell

ABSTRACT

A novel iron(II) tetraaminophthalocyanine graphene (FeTAPc-Gr) micro/nanocomposite as a non-noble catalyst for oxygen reduction reaction (ORR) was prepared by amidation of the carboxyl groups at the edge of graphene nanosheets with amino group of FeTAPc, meanwhile, we found that FeTAPc moieties could assemble to nanoparticles on graphene sheet trough π–π interaction in our experiment condition. FePc-Gr composite was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The electrocatalytic performance for ORR was assessed by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) methods. A well-defined characteristic ORR peak, centered at −0.148 V vs. SCE was observed on FeTAPc-Gr composite catalyst, whereas the peak potential on commercial Pt/C was −0.199 V vs. SCE at the same condition. The resulting product exhibits excellent ORR activity, super tolerance to methanol crossover and good stability, which lead to the invention of a new non-noble catalyst for ORR in fuel cell.

1. Introduction

Energy generation is expected to be one of the most significant challenges in the 21st century. This is mainly due to the decreasing natural energy resources, population growth and the goal to reduction of carbon emissions. Fuel cell technology may provide at least a partial method to the increasing societal demand of non-stationary energy. Currently, platinum (Pt)-based materials have long been regarded as the best cathodic oxygen reduction reaction (ORR) catalysts in fuel cells [1,2]. However, the main stumbling blocks hindering broad application of fuel cells are the high cost and vulnerability of the platinum catalyst as well as sluggish ORR process. Although Pt alloys have been applied as substitute catalyst for ORR, they still encounter multiple disadvantages, such as low stability, methanol crossover and CO poisoning effect. Despite recent extensive efforts have been devoted to develop high effective catalyst at low cost, it remains a great challenge. Thus, the ongoing observation of catalyst with low cost, high activity, high stability and good tolerant to methanol has been paid much attention. In this context, non-precious catalysts for ORR, such as metal chalcogenide [3], modified carbon materials [4–8], and metal-N_4 compounds [9–12], have attracted great interest.

Graphene, as a result of its unique two dimensional monolayer structure of sp^2-hybridized carbon, exhibits remarkable electronic, thermal and mechanical properties [13–15]. A variety of applications have been demonstrated for graphene materials, such as structural nanocomposites [16–18], catalyst supports [19], electronic devices [20] and energy storage in batteries and supercapacitors [21,22].

One of the most promising types of non-notable metal ORR catalysts are carbon supported transition-metal-nitrogen (C/M-N_x) materials (M = Fe, Co, Ni, etc., and $x = 2$ or 4) [23]. Various kinds of C/M-N_x compounds, such as metal porphyrins [24,25] and phthalocyanines [26,27] have been investigated and their potential applications in fuel cell have been demonstrated, since Jasinski [9] investigated cobalt phthalocyanine as an ORR catalyst for fuel cells in 1964. Iron phthalocyanine (FePc) exhibits especially better electrocatalytic activity than other metal phthalocyanine (CoPc, NiPc and CuPc) for ORR. Unfortunately, although most of attention has been paid to improve FePc catalyst for ORR, it still suffer from low stability and electrocatalytic activity. To improve the electrocatalytic activity of FePc catalyst, some researchers have found that FePc supported on carbon materials greatly enhanced the electrocatalytic performance for ORR. Baranton et al. [27] loaded FePc on

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http://dx.doi.org/10.1016/j.jelechem.2014.05.035
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Vulcan XC-72 through ultrasonic blending method and the catalyst was totally insensitive to the presence of methanol. Mamuru and Ozoemena [28] fabricated a kind of iron(II) tetrakis (diaquaplatinum) octacarboxyphthalocyanine (PtFeOCPc) catalyst supported on multi-walled carbon nanotubes (MWCNTs), which exhibited good electrocatalytic activity. Yuan et al. [29] loaded FePc on amino-functionalized multi-walled carbon nanotubes (a-MWCNTs), and found the ORR performance of FePc supported on a-MWCNTs in a microbial fuel cell was better than that for FePc supported on carbon black. Dong et al. [30] had found the ORR activity of FePc was improved greatly when it was loaded on single-walled carbon nanotubes. Mo et al. [31] loaded iron tetrasulfophthalocyanine (FeTsPc) on single-walled nanotubes (SWCNTs) by simply ultrasonic blending method and FeTSPc/SWCNTs composite shown good catalytic performance for ORR. Zhang et al. [32] synthetized an iron phthalocyanine (FePc) and nitrogen-doped graphene (NG) composite which exhibited superior ORR catalytic activity, excellent tolerance to methanol crossover and comparable stability to commercial Pt/C. Jiang et al. [33] fabricated a composite of iron phthalocyanine (FePc) supported on chemically reduced graphene through π–π interaction, which exhibited an efficient 4-electron pathway, comparable activity, long-term operation stability, better tolerance to methanol crossover and CO poisoning compared with commercial Pt/C for ORR in 0.1 M KOH media. Our group [34] fabricated an iron phthalocyanine/graphene micro/nanocomposite ORR catalyst by solvothermally assisted π–π assembling method and the catalyst exhibited positive peak potential, better stability and excellent resistance to crossover-effect to methanol than commercial Pt/C in 0.1 M NaOH solution.

The homogeneous dispersion of FePc on carbon materials and the high specific surface area of catalyst are very necessary to improve the catalytic activity and stability. From this perspective, in this paper, graphene (Gr) is selected as a supporting platform for electrocatalysts. The FeTAPc-Gr composite is synthesized by amidation of the carboxyl groups at the edge of graphene oxide (GO) nanosheets with amino group of FeTAPc, at the same time, the FeTAPc moieties assemble to nanoparticles trough π–π interaction between graphene and FeTAPc, FeTAPc and FeTAPc. The morphology of FeTAPc-Gr composite is characterized by SEM and TEM. The ORR activity, durability and stability of FePc-Gr catalyst are observed. The catalytic property on composite for ORR can be effectively enhanced through covalent bonding and π–π interaction.

2. Experimental

2.1. Materials

Graphite powder and 1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1-Ethyl-(3-dimethyllaminopropyl)carbodiie hydrochlide (EDC·HCl) and 4-dimethylamiopryidine (DMAP) were purchased from Sigma–Adrich. Pt/C (20 wt% Pt on Vulcan XC-72) was purchased from Alfa Aesar. All other reagents were analytical grade and used without further purification, including 1-pentanol, hydrazine hydrate solution and ethanol. Triple distilled water was used to prepare the solutions used. Glassy carbon electrode ($d = 3$ mm) was purchased from Shanghai CHENHUA company.

2.2. Characterization

Morphology of the FeTAPc-Gr was studied by scanning electron microscopy (SEM, JEOL JSM-6701F electron microscope operating at 5 kV) and transmission electron microscope (TEM, JEOL JEM-1200EX, operating at 100 kV). The analysis of X-ray photoelectron spectra (XPS) was performed on an ESCLAB 250 using Al Kα as the exciting source. The electrochemical measurements including cyclic voltammetry (CV) and linear sweep voltammetry (LSV), were operated on a CHI 660D electrochemical analyzer (Shanghai CHENHUA company) in a conventional three-electrode electrochemical system using a modified glassy carbon electrode and glass carbon rotating-disk electrode as working electrode, a platinum wire as counter electrode, and a saturated calomel electrode (SCE) as reference electrode.

2.3. Synthesis of FeTAPc-Gr composite

The graphite oxide (GO) was gained from the natural graphite by the Hummer's method published elsewhere [35]. Iron(II) tetraaminophthalocyanine was synthesized according to literature procedures [36]. FeTAPc-Gr composite was fabricated by the following procedure: 0.020 g GO (4 mL dispersion solution in DMF), 0.060 g of FeTAPc, 0.033 g EDC·HCl and 0.021 g DMAP as catalyst were added to 6 mL DMF under N_2 atmosphere. Following, the dispersion solution was heated to 90 °C and maintained this temperature for 48 h under stirring condition. Then 1 mL hydrazine hydrate was injected into the bottle and reacted for 24 h. After cooling to room temperature naturally, the powder was separated by centrifugation and washed with DMF, distilled water and ethanol for three times, respectively.

2.4. Preparation of electrode

Before modification, the surface of glassy carbon electrode (GCE) was polished with 1.0, 0.3 and 0.05 μm α-Al_2O_3 powder slurry successively and ultrasonically washed with absolute ethanol and distilled water for 5 min, respectively. In order to modify GCE, 1.0 mg FePc-Gr and 1.0 mL ethanol were mixed ultrasonically blended to obtain a homogeneous ink. Then, 10 μL of the ink was coated on a clean GCE surface, and then dried in air for 30 min. For comparison, the GC electrodes coated with FeTAPc or Pt/C (20 wt% Pt on Vulcan XC-72) was also fabricated with the same procedure.

3. Results and discussion

3.1. Characterization

The formation of FeTAPc-Gr was confirmed by FTIR spectra (shown in Fig. 1). In the GO spectrum, the characteristic band of the carboxyl group appeared at 1731 cm^{-1} (C=O stretching). The C–O vibration of epoxy groups appeared at 1244 cm^{-1}. The peak

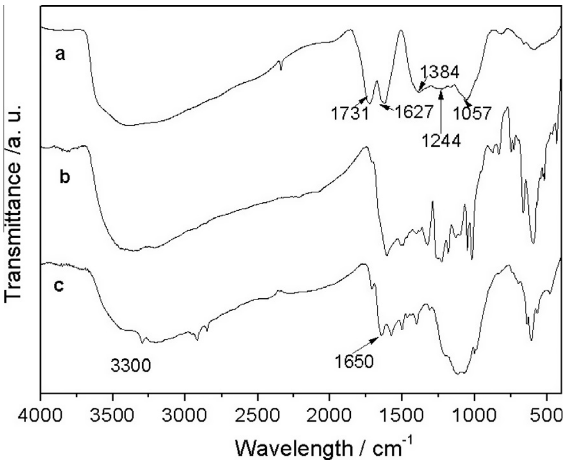

Fig. 1. FTIR transmittance spectra of GO (a), FeTAPc (b) and FeTAPc-Gr (c).