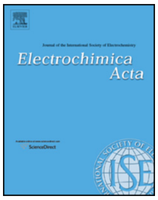
Electrochimica Acta 129 (2014) 196–202

Contents lists available at ScienceDirect

Electrochimica Acta

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



Preparation of nitrogen-doped graphitic carboncages as electrocatalyst for oxygen reduction reaction

Jing Yan[a], Hui Meng[b,*], Wendan Yu[a], Xiaoli Yuan[a], Worong Lin[a], Wenpeng Ouyang[a], Dingsheng Yuan[a,*]

[a] Department of Chemistry, Jinan University, Guangzhou 510632, PR China
[b] Department of Physics and Siyuan Laboratory, College of Science and Engineering, Jinan University, Guangzhou, 510632, PR China

ARTICLE INFO

Article history:
Received 31 December 2013
Received in revised form 17 February 2014
Accepted 18 February 2014
Available online 2 March 2014

Keywords:
Nitrogen-doped
Carboncages
Graphitization
Oxygen reduction reaction

ABSTRACT

Nitrogen-doped carbon nanomaterials have been attracted increasing research interests in lithium-O_2 and Zinc-O_2 batteries, ultracapacitors and fuel cells. Herein, nitrogen-doped graphitic carboncages (N-GCs) have been prepared by mesoporous Fe_2O_3 as a catalyst and lysine as a nitrogen doped carbon source. Due to the catalysis of Fe_2O_3, the N-GCs have a high graphitization degree at a low temperature, which is detected by X-ray diffraction and Raman spectrometer. Simultaneously, the heteroatom nitrogen is in-situ doped into carbon network. Therefore, the excellent electrocatalysis performance for oxygen reduction reaction is expected. The electrochemical measurement indicates that The N-GCs for oxygen reduction reaction in O_2-saturated 0.1 mol L^{-1} KOH show a four-electron transfer process and exhibit excellent electrocatalytic activity (E_{ORR} = -0.05 V vs. Ag/AgCl) and good stability (i/i_0 = 90% at -0.35 V after 4000 s with a rotation rate of 1600 rpm).

1. Introduction

The oxygen reduction reaction (ORR) played a very important role in direct methanol fuel cells (DMFCs), lithium (Li)-O_2 and Zinc (Zn)-O_2 batteries [1,2]. Therefore, the research on a cheap catalyst with high electro-catalytic activity for ORR has been a hot topic. Conventionally, nanostructured and/or nanoporous platinum (Pt)-containing materials has been used as the most common electrocatalysts for both the anode and cathode in these fuel cells [3–6]. However, as a precious metal, Pt is too expensive to the large-scale use as a catalyst for ORR. And Pt-based catalyst is sensitive to deactivation in the presence of CO, methanol and also susceptible to time-dependent drift. Thus Pt-based catalysts for large-scale commercial application have been hindered greatly [7,8]. Hence, the search for a low-cost catalyst with high activity and durability for ORR is absolutely crucial to the development of fuel cells.

According to the reported literatures, nitrogen-doped carbon nano-materials showed high catalytic activity and cycle stability for oxygen reduction reaction. Therefore, the non-precious metal nitrogen-doped carbon materials as catalysts to replace Pt have a potential application prospect in the field of electrochemical energy storage and conversion [9–13]. It has been commonly believed that the doped nitrogen types such as pyridinic-N (N-6), pyrrolic-N (N-5) and quaternary-N (N-Q) play a very important role in the process of oxygen reduction [14,15].

In recent years, the graphitized carbon materials have attracted a considerable interest and have been applied in different research areas for their good electric conductivity, larger specific surface area, pore structure and excellent corrosion resistance [16]. In addition, the higher graphitization degree of carbon materials is helpful for improving the cycle stability [17]. Various synthesis methods, which were the traditional method with post synthesis modification [18], laser ablation and arc discharge technology [19], chemical vapor deposition [20], plasma method [21] and so on [22] were used to prepare the nitrogen-doped graphitic carbon. However, the precursors usually have strong corrosive, high toxic and environmental sensitive characteristics, which need to be more careful operation and more demanding situations. Recently, our groups had successfully achieved the graphitic carbon materials [23] and nitrogen-doped graphitic carbon materials [24] at low temperature, using the sucrose and amino acid as precursors via easy operation and environmentally-friendly strategies, respectively.

Herein, we have prepared an N-doped graphitic carboncages by using L-lysine as carbon source and nitrogen source, and mesoporous iron oxide as the catalyst at the relative low temperature. The N-GCs was used as ORR electrocatalyst and exhibited

---

* Corresponding author.
E-mail addresses: tmh@jnu.edu.cn (H. Meng), tydsh@jnu.edu.cn (D. Yuan).

http://dx.doi.org/10.1016/j.electacta.2014.02.087
0013-4686/

excellent activity and good stability compared to 15% Pt/C electrodes for oxygen reduction.

2. Experimental

2.1. Synthesis of SBA-15 silica and mesoporous Fe_2O_3

The typical method of Zhao *et al.* [25] was applied for the synthesis of the SBA-15: 2 g tri-block copolymer P123 ($EO_{20}PO_{70}EO_{20}$, EO = ethylene oxide, PO = propylene oxide, 5800) as template was dissolved in 75 mL 2 mol L^{-1} HCl solution with vigorous stirring at 35 °C, then 4 mL $Si(OCH_2CH_4)_4$ (TEOS) as silica source was added to the homogeneous solution gradually. Afterward the gel was stirred at 40 °C for 24 h, and then crystallized at 100 °C for 24 h under static conditions. The resulting solid was filtered, washed and dried at 100 °C for 24 h. The precipitated SBA-15 was collected and stored for use, after calcination in air at 550 °C for 6 h.

Mesoporous Fe_2O_3 was prepared by a modified procedure of a previous report [16]. Typically, 2.5 g $Fe(NO_3)_3{\cdot}9H_2O$ was dissolved in 30 mL ethanol to form a transparent solution. Then, 0.9 g dry SBA-15 was mixed to the solution followed by stirring until the solvent was removed by evaporation at room temperature. The obtained dry iron precursor/SiO_2 powder was calcined at 600 °C for 6 h in muffle furnace and removed the silica template via soaking in 2 mol L^{-1} hot sodium hydroxide solution overnight twice. After washing several times with de-ionized water and drying at 60 °C, the mesoporous Fe_2O_3 (named as MFe) was obtained.

2.2. Preparation of N-GCs

Nitrogen doped graphitic carboncages were prepared as follows: 1 g L-lysine was added into a 25 mL beaker containing a solution of 8 mL water and 0.5 g MFe. The beaker was sealed by saran wrap and put in the oven at 100 °C for 6 h after vigorous stirring for an hour, then the saran wrap was deserted and the temperature was raised to 160 °C for another 6 h. The as-synthesized dry material was carbonized at 900 °C for 4 h under pure N_2 atmosphere flow, and then allowed to cool to room temperature. Followed by treatment with 3 mol L^{-1} HCl solution at 80 °C for 24 h, the nitrogen doped graphitic carboncages denoted as N-GCs was obtained after the removal of the impurities.

2.3. Preparation of 15% Pt/N-GCs and 15% Pt/C catalysts

The method for the preparation of 15% Pt-doping catalysts was described particularly in Ref. [16]. Briefly, 50 mg N-GCs and the appropriate amount of glycol (EG) solution of H_2PtCl_6 (3.77 mg Pt/mL EG) were well dispersed in 50 mL EG solution by ultrasonication for 1 h. 1.0 mol L^{-1}NaOH glycol solution was then added to adjust the pH of the suspension to above 10. Then, the solution was microwave-heated in a 15 s-on/10 s-off pulse form several times; thereafter the 15% Pt/N-GCs was filtrated, washed and dried in a vacuum. For comparison, the Pt was also loaded on 50 mg Vulcan XC-72 using the same experimental procedure, named as 15% Pt/C.

2.4. Characterization

The X-ray diffraction (XRD) patterns were collected with a MSALXD2 X-ray diffractometer (Cu $K\alpha$, 36 kV, 20 mA, and $\lambda = 1.54056$ Å). The degree of crystalline structure of N-GCs was investigated by Raman spectroscopy, which was recorded in a backscattering configuration using the 514.5 nm line of an Ar^+ ion laser and a Renishaw in Via Plus Raman spectrometer. Field-emission scanning electron microscopy (FE-SEM, ZEISS ULTRA 55) and high-resolution transmission electron microscopy (HR-TEM) (JEOL JEM-2100F, 200 kV) were used to study the morphology of the samples. The X-ray photoelectronic spectroscopy (XPS) characterization was carried out by the ESCALab250 spectrometer with Alumina *K*a (1486.6 eV) source. The specific surface area and pore volume of the N-GCs were measured by nitrogen sorption isotherms using a Micromertics ASAP 2020 analyzer at 77 K. The loadings of Pt for Pt/N-GCs and Pt/C were 15.0 wt. % and 15.1 wt. %, respectively, which were detected by inductively coupled plasma-atomic emission spectrometry (ICP) (Optima 2000DV). In addition, 0.39 at. % Fe in N-GCs was also obtained by ICP analysis.

2.5. Electrochemical measurement

All electrochemical measurements were conducted on a CHI660D electrochemical workstation (CH Instruments, China) at 25 °C with a conventional three-electrode system was used for the electrochemical experiments. Platinum wire and Ag/AgCl (saturated KCl) were applied as the counter electrode and a reference electrode, respectively. A rotating disk electrode system (OrigaTrod RDE, France) was used as working electrode, the glassy carbon electrode (5 mm diameter) was polished before each experiment with 1, 0.3 and 0.05 μm alumina power, respectively, and then washed in a mixture of ethanol with water before each experiment. The ORR activities of N-GCs, 15% Pt/N-GCs, XC-72 and 15% Pt/C were evaluated in 0.1 mol L^{-1} KOH solution and recorded with the electrochemical workstation at a scan rate of 10 mV s^{-1}. Pure O_2 or pure N_2 gas was directly bubbled into the solution for at least 30 min before measurements and was flushed over the cell solution during the tests, to make KOH solution oxygen or nitrogen saturated.

All the working electrodes for cyclic voltammetries (CVs) and chronoamperometric(*i-t*) responses were prepared with the same procedure as follows: 2 mg catalyst was put into 1 mL ethanol solution mixed with 100 μL Nafion (5 wt. %). The mixture was sonicated for 30 min, and 10 μL of the dispersion was deposited on the glassy carbon electrode and dried under ambient conditions to obtain a catalyst thin film.

3. Results and discussion

The wide-angle powder XRD pattern of the N-GCs is shown in Fig. 1a. The graphitized carbon material shows several well-resolved diffraction peaks with very close at 26.5°, 42.4°, 44.6°, 54.7° and 77.8°, which can be assigned to the (002), (100), (101), (004) and (110) planes reflections of graphitized carbons, respectively, indicating N-GCs with a high-degree graphitization [26]. Simultaneously, the (002) diffraction peak is sharp and narrow, also suggesting that the carboncages prepared with the MFe are high crystallinity. Therefore, it can be concluded that the highly graphitic porous carbon can be successfully synthesized via using mesoporous iron oxide as both the catalyst and template. According to the previous report [16,27] and our XRD results, the probable mechanisms are proposed as follows:

$$Fe_2O_3 + \text{L-lysine} \rightarrow Fe_3C + Fe + H_2O/H_2 + CO/CO_2 + CxNmOn \quad (1)$$

$$Fe_3C + 6HCl = 3FeCl_2 + C + 3H_2 \quad (2)$$

$$Fe + 2HCl = FeCl_2 + H_2 \quad (3)$$

Raman spectrum in Fig. 1b is used to further study the graphitic structure of the N-GCs. It can be seen that three distinct peaks at around 1350 cm^{-1}, 1580 cm^{-1} and 2710 cm^{-1},corresponding to the D-band, G-band and 2D-band. The G-band is assigned to the stretching vibration of sp^2 bonded carbon atoms in the basal plane of a two-dimensional hexagonal single-crystal lattice of ordered graphite or graphene layers. In addition, the 2D-band is another symbol of a higher graphitic crystalline and can be observed only