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Highly dispersed iron nitride nanoparticles embedded in N doped carbon as a high performance electrocatalyst for oxygen reduction reaction

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ARTICLE INFO

Article history:

Received 6 August 2016

Received in revised form

30 December 2016

Accepted 31 December 2016

Available online xxx

Keywords:

Oxygen reduction reaction (ORR)

Pyrolysis temperature

Electrocatalytic activity

ABSTRACT

The iron nitride nanoparticles embedded in N doped carbon catalyst material has been successfully synthesized and employed as a promising alternative for oxygen reduction reaction (ORR). The resultant catalyst exhibits superior electrocatalytic activity, good stability and low cost. Here, we pay more attention to “high dispersion” of iron, nitrogen and carbon. We developed a uniform dispersed Fe–N–C catalyst synthesized by one-pot method, which exhibits superior electrocatalytic activity for ORR in alkaline media. Moreover, we also studied the influence of various pyrolysis temperatures and different mass ratio of nitrogen precursors and iron source on ORR electrocatalytic activity.

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Introduction

With the increasing demand of high power density and safe energy storage device, the metal/air batteries and fuel cells were regarded as the next-generation energy storage devices owing to its environmental friendliness, low-cost and high energy density. The rate of ORR occurring at the cathode serves as the bottleneck in the commercial utilization of metal/air batteries and fuel cells [1–4]. The noble metal-based materials exhibit excellent ORR electrocatalytic performance, but it cannot be in large scale application because of its high cost. Therefore, catalyst with high ORR electrocatalytic activity and low cost is in urgent demand [5–12]. After Jasinski firstly used Co–N–C as a kind of ORR catalytic, the transition

metal-nitrogen-carbon (Me–N–C) catalysts have attracted increasing attentions [13].

The iron nitrogen-doped carbon (Fe–N–C) catalyst materials can be regarded as a desirable electrocatalyst owing to their high performance for ORR and low cost [13,14]. The catalyst with excellent performance even over commercial Pt/C can serve as highly promising but still challenging. Recent researches on Fe–N–C catalysts have mainly focused on several aspects, such as the selection of iron species, nitrogen precursors, carbon support morphology, and pyrolysis process temperature, which have directly influence the electrocatalytic activity of materials [15–18]. Yang et al. [19] prepared a kind of bamboo-like CNT/Fe₃C nanoparticle hybrid by using soft-template method. The Fe(NO₃)₃, melamine and PEG-PPG-PEG Pluronic P123 were chosen as precursors and were

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<http://dx.doi.org/10.1016/j.ijhydene.2016.12.148>

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annealed at high temperature. The resulting catalysis exhibited excellent ORR performance in both acidic and alkaline solutions. Liu et al. [20] studied nitrogen doped porous carbon nanosheets with highly dispersed iron carbide nanoparticles. The iron carbide nanoparticles with graphitized carbon outlayer were formed and embedded in the N-doped porous nanosheets through annealing a mixture of FeSO_4 , melamine and 1, 10-phenanthroline. Wang et al. [21] developed a synthesis of N-doped carbon on Fe_3O_4 nanorods by annealing FeOOH nanorods with urea at a relatively low temperature. The as-synthesized hybrid exhibits excellent ORR catalytic performance, which are superior to that reported so far for the Fe_3O_4 -based materials and N-doped carbons. Nevertheless, the application of some materials are still constrained owing to the complicity of the synthesis process or the scarcity of the raw carbon materials [22,23]. In order to search for the low-cost synthesis method, previous researchers almost concentrated on the simple synthesized process. Especially, grinding is used frequently for mixing carbon, nitrogen and transition-metals precursors [24]. However this method can't ensure the homogeneously mixing of precursors.

In this work, we pay more attention to “high dispersion” of iron, nitrogen and carbon, which means these elements are homogeneously, particularly regularly distributed in the material. We have developed a highly dispersed iron-coordinated nitrogen-doped carbon (HD Fe–N–C) catalyst by one-pot synthesis method, using melamine as the nitrogen-rich precursor and carbon source, using ferric chloride hexahydrate as iron source. A novel route was proposed to fabricate highly dispersed Fe–N–C nanocatalysts materials by controlling PH, pyrolysis temperature and proportion of melamine and ferric chloride hexahydrate. The HD Fe–N–C catalyst revealed superior catalytic activity with a half-wave potential of -0.15 V (vs. Ag/AgCl), which is comparable with commercial Pt/C (20 wt.%). The excellent electrochemical performance should be attributed to the high dispersion of nanosized iron-coordinated nitrogen-doped carbon catalyst.

Experimental section

Preparation of HD Fe–N–C

As shown in Scheme 1, the resultant product HD Fe–N–C composite was prepared by one-pot synthesis. The melamine (5 g; AR, 98% purity) were dissolved in deionized water (200 mL) at 80°C with constantly stirring. And HCl (AR, 38% purity) was trickled into the solution until the PH reached 1. Just then, white emulsion turns clarify. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (1 g; AR, 98% purity) was dissolved in deionized water (100 mL). Then the FeCl_3 solution and the melamine solution were mixed in one pot, the mixture was dried in glass culture dish maintained at 100°C for 10 h and then naturally cooled to room temperature. The remaining powder was pyrolyzed at 800°C for 2 h at a heating rate of 3°C per minute in argon flow. For comparison, 5 g melamine and 1 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were ground together in an agate mortar for about half an hour followed by the same heat treatment. In addition, the experiments of various pyrolysis temperature

(700°C , 800°C , 900°C) and different melamine/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ mass ratio (3/1, 4/1, 5/1, 6/1) have been conducted.

Material characterizations

The morphologies and elemental compositions of the materials were examined by SEM (JSM-6360LV) and TEM (Titan G2 60-300). The elements on the surface of the samples were assessed by EDX. The crystalline phase of samples be investigated with XRD (Rigaku TTRIII). XPS data was determined by using an Escalab 250Xi X-ray photoelectron spectrometer with an Al $K\alpha$ X-ray source (1486.6 eV). Raman spectra were measured with a Labram-HR 800. The pore size distribution and the surface area were obtained using N_2 adsorption/desorption measurements with a Quantachrome instrument (Quabrasorb SI-3MP). The pore size distribution was indicated by the desorption branch.

Electrochemical characterization

All electrochemical measured data of the as-prepared sample were acquired by using a standard three-electrode cell with an electrochemical workstation (Solartron 1470E) on a rotating disk electrode (RDE). The electrochemical catalytic activity characterization of composite was conducted in the O_2 -saturated alkaline solution (0.1 M KOH). The linear sweep voltammetry (LSV) measurement was conducted using a catalyst loaded glassy carbon as the working electrode, spiral platinum wire as the counter electrode, and Ag/AgCl electrode as the reference electrode, respectively [25]. The working electrode was prepared as follows: 8 mg catalyst was ultrasonically dispersed in a mixture containing 2 mL ethanol and 80 μL Nafion solution (5 wt.%). And then, 5 μL of the sample ink was pipetted onto a glassy carbon electrode ($\Phi = 5$ mm). The catalyst loading of all samples was 0.1 mg cm^{-2} .

The transferred electron number (n) is analyzed using Koutecky–Levich equation [11].

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_K} \quad (1)$$

$$B = 0.2nFC_{\text{O}_2}D_{\text{O}_2}^{2/3}v^{-1/6} \quad (2)$$

where j is the overall current density, j_L is referred to the diffusion-limiting current density, j_K is the kinetic current density, ω is the rotation speed, F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), C_{O_2} is the bulk concentration of O_2 ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_{O_2} serves as the diffusion coefficient of O_2 ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), v is the kinematics viscosity of the electrolyte ($0.01 \text{ cm}^2 \text{ s}^{-1}$) and n is the transferred electron numbers. The constant 0.2 is adopted when the rotation speed is expressed in rpm.

Result and discussion

As shown in process A and B in Scheme 1, when the HCl (AR, 38% purity) was trickled into the solution drop by drop, white emulsion gradually turns clarify, which can be explained by Eq. (1). As shown in Eq. (2), during the pyrolysis process,

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