Synthesis of Fe Nanoparticles on Polypyrrole Covered Graphite for Oxygen Reduction Reaction

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Abstract: An amorphous Fe-based catalyst supported on polypyrrole-modified graphite is synthesized by a chemical method. The optimal Fe loading with the highest reduction current is 4 wt%. Their morphology, structure and chemical component were characterized by scanning electron microscopy (SEM), X- ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDS), respectively. The scanning electron microscopy show that the surfaces of graphite are decorated with metal nanoparticles. Under acid condition, the catalyst demonstrate high oxygen reduction reaction (ORR) activity with four-electron pathway.

Introduction

Polymer electrode membrane fuel cells (PEMFC) are considered as ideal energy converting systems for power fields in stationary and mobile devices [1]. However, the major barrier to the commercialization of PEMFC is the high costs of Pt based catalysts and their insufficient stability [2,3]. Over the last several decades, a great deal of research has focused on reducing Pt loading or completely replacing Pt using non-noble metal catalysts. Nitrogen-coordinated transition metals (Fe, Co, Ni and Mn) in a carbon matrix (M–N–C) have been extensively studied owing to their extremely effective catalytic activity for ORR, especially in acidic solution[4–6]. The performance of these catalysts is directly related to their preparation conditions including the synthesis method, metal precursor, carbon support and heat-treatment[3]. Nitrogen (N)-containing precursors play a significant role during the M-N-C synthesis in order to form an active catalyst. Conducting polymers such as PPy, polyaniline (PANI), and polythiophene[2,7,8]have been used due to their superior properties. Among these polymers, PPy is an especially interesting N precursor since it includes large of nitrogen-heterocyclic compounds in its body. The aromaticity of the pyrrole (Py) ring should imbue the polymer with some strong affinity for graphitic carbon, the typical support in ORR electrocatalysts. In addition, the uniform distribution of nitrogen atoms in PPy may significantly enhance the number of active sites for improved ORR activity [9,10].

In this article, we prepared a novel composite Fe-N/C catalysts using the activation of graphite as the carbon support. PPy/C was performed by in situ polymerization of the pyrrole monomer in the presence of graphite[2]. Fe nanoparticles were deposited onto PPy/C composites by the reduction of the metal ions (Fe^{2+}) using sodium borohydride[11]. The prepared Fe-PPy/C complexes are then treated at temperatures of 900°C under inert atmospheres to obtain Fe-N/C catalysts. Their electrocatalytic activities towards ORR were characterized by cyclic voltammetry (CV) and the rotating disk electrode (RDE) technique.

Experimental

Pyrrole monomer was distilled under reduced pressure prior to use and stored in a refrigerator. Graphite powder was treated at 80°C for 4h in 2 M HNO_3 solution. All other reagents were analytic grade and used as received without further purification. The water used throughout all experiments was deionized water.

Fe-N-C catalysts were prepared by following steps: (1) The activation of graphite and distilled pyrrole monomer was dispersed in de-ionized water. Then, an amount of $FeCl_3 \cdot 6H_2O$ was added

dropwise to the suspension and stirred for another 24h at 4°C. The resulting suspension was filtered, washed and dried under vacuum at 60°C. (2) 1g of the PPy/C and a quantity amount of $FeSO_4 \cdot 7H_2O$ were dispersed in de-ionized water and stirred for 2 h at 80 °C. $NaBH_4$ dissolved in 30mL of water was slowly added to the suspension, and stirred for 4 h at 80 °C under an inert N_2 atmosphere. The mixtures were filtered,washed and dried under vacuum at 80 ℃. (3) The catalysts were placed in quartz boats and calcined in a tube furnace at 900 °C (4 h) under Ar . And the obtained catalysts were denoted as Fe-N/C.

The structure and phase analyses of the catalyst samples were performed using X-ray diffraction (XRD) with Cu $K\alpha$ radiation (λ=0.15406 nm) and operating at 40 kV and 40 mA. The SEM images were obtained by a JSM-6500LV electron microscope. The EDS data were also collected to analyze the element component of the Fe-N/C catalysts

The electrocatalytic activity toward the ORR was evaluated by CV technique in 0.1M $HClO_4$ solution saturated with O_2. A catalyst ink was prepared by ultrasonically mixing 10mg of the Fe-N/C catalyst with 100μL of Nafion solution (5 wt.%) and 500μL of anhydrous ethanol for 30 min. The obtained ink (10μL) was then dropped onto a glassy carbon electrode ($0.196cm^2$). A porous catalyst layer was formed on a glassy carbon electrode after drying at room temperature in air. CV measurements were performed in a three-electrode system. A Pt sheet and a saturated calomel (SCE) electrode were used as counter electrode and reference electrode, respectively.

Results and discussion

The SEM image and the energy dispersive X-ray (EDS) analysis of the Fe-N-C catalysts were presented in Fig. 1. As can be seen, After being heat-treated at 900 °C, there are many Fe nanoparticles on the surfaces of the sample(Fig.1(a)). Fig.1(b) show the nitrogen loading of 3.69 wt.% and the metallic Fe loading of 2.34 wt.% in the sample. The content of iron is lower the original reactant stochiometric proportion of 4 wt.%, which indicates formation of Fe nanoparticles or clusters even without calcination as Fe^{2+} was reduced to Fe by $NaBH_4$ in solution.
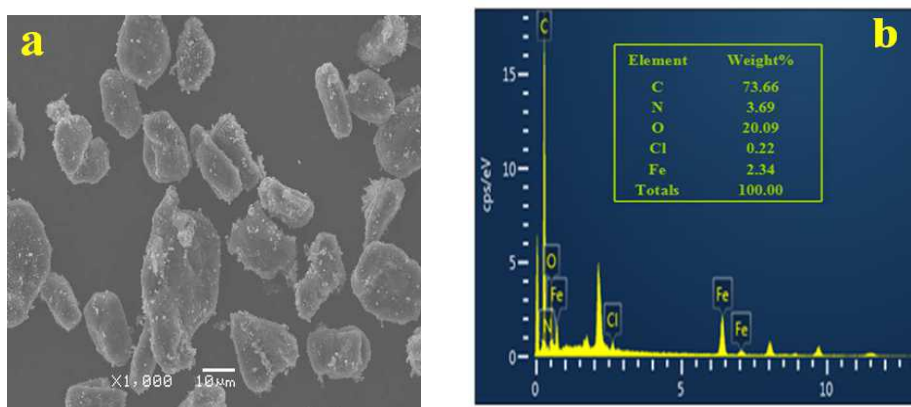

Fig. 1   SEM images of Fe-N-C (a) pyrolyzed at 900°C, and EDS spectra of Fe-N-C(b)

XRD was employed to gain insights into the crystalline structure of the Fe-N-C catalysts heat-treated at 900°C. Fig. 2 shows the XRD patterns of Fe-N-C catalysts. The broad diffraction peaks at 26.36° of Fig. 2 is attributable to the (002) planes of graphitic form[12]. The diffraction peak centred at 35.6° attributed to (101) plane in Fe-N-C could be due to "Fe_3C" [13] . The (110) diffraction peaks centred at 45° overlapped by the signals from bulk carbon in the catalyst could be attributed to Fe-N functionalities and/or Fe nanoparticles, in good agreement with some work reported in the literature [14,15]. The Fe cluster can be observed from Fig.1a.
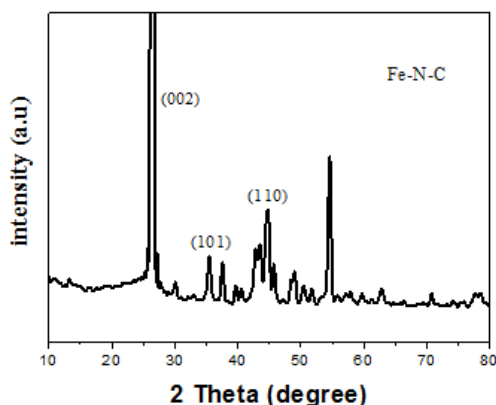
Fig. 2. XRD patterns of Fe-N-C catalysts obtained after heat treatment in Ar at 900∘C.

Fig. 3 compares the cyclic voltammograms (CVs) for the prepared catalyst in the nitrogen- and oxygen-saturated 0.1 M $HClO_4$ solution. It can be seen that there were no clear redox features in nitrogen-saturated electrolyte. After the electrolyte was saturated with oxygen, there are conspicuous redox peaks at potential of 0.2V to 0.4V, the catalytic current reached a peak maximum at about 0.3V and decreased as the overpotential was further increased.

Fig. 4 shows the ORR polarization curves of the Fe-N-C catalyst obtained at rotating rate range from 200 to 1800rpm. Typically, the reaction seems to be under a combined kinetic-diffusion control of charge transfer and mass transport. It is Shown that the electrode rotation has an effect on the reaction rate at lower potentials for ORR.According to the Koutecky-Levich equation and plots (the inset of Fig.4) [14], the electron number involved in the Fe-N-C catalyst for ORR is 3.8. This suggests that most of the molecular oxygen is reduced to H_2O_2 via a four-electron process.
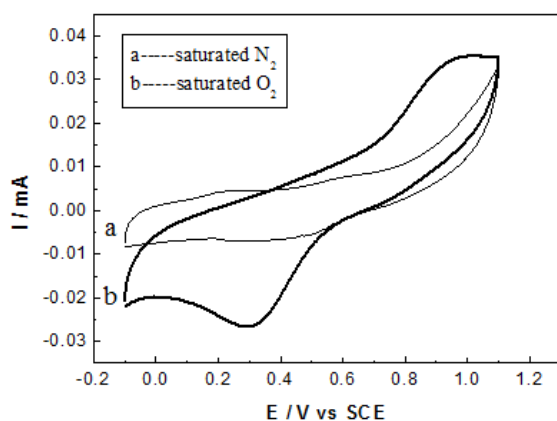

Fig. 3. CVs of the catalyst recorded in nitrogen and oxygen saturated $HClO_4$ (0.1 M).
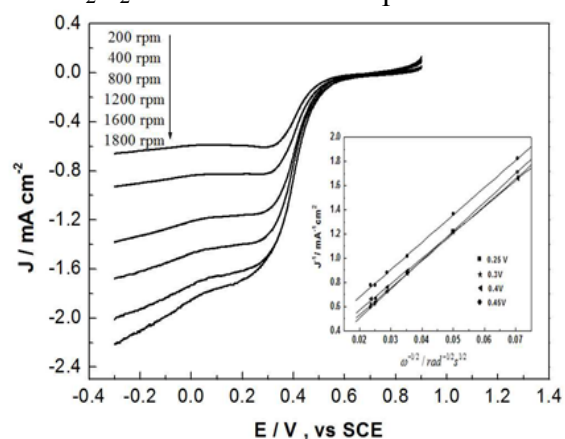

Fig.4 The ORR polarization curves of the catalyst . Inset is the corresponding Koutecky-Levich plots.

Conclusions

Polypyrrole was selected as one N-containing precursor to prepare carbon-supported Fe-polypyrrole /C complexes for the purpose of developing a new ORR catalyst. The complexes were then heat-treated at 900 °C to synthesize the Fe-N/C catalysts. The catalyst with a Fe loading of 4 wt% shows the highest ORR activity. The overall electron transfer number is calculated to be 3.8, suggesting that the catalyzed ORR is mainly a 4-electron transfer pathway from O_2 to water. The result of the SEM and EDS indicates that there are many Fe nanoparticles on the surfaces of the catalyst and and the metallic Fe loading of 2.34 wt.% . This work offers a novel route to design and development of nitrogen-doped carbon catalysts for ORR.

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