

Short Communication

The New Approach to Enhance the Activity of Fe/N/C Catalyst for Oxygen Reduction Reaction by Electrochemical Treatment

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Abstract: Non-precious Fe/N/C catalysts have attracted increased attention due to their activity in oxygen reduction reaction (ORR). To promote the activity of this type of catalysts, we applied the electrochemical treatment of the Fe/N/C sample synthesized by using the known technique. We demonstrated that two-stage anodic-cathodic treatment of the Fe/N/C sample under the certain condition leads to increase the electrocatalytic activity toward the ORR of the starting catalyst. The results may open the opportunities in finding new ways of increasing the activity of Fe/N/C catalysts by using the electrochemical treatment.

Keywords: Fe/N/C catalyst, synthesis, oxygen reduction reaction, electrochemical treatment

1. INTRODUCTION

Among the different types of fuel cell under development at the present time, the Proton Exchange Membrane Fuel Cell (PEMFC) is attracting the most attention [1-3]. The reaction of catalytic reduction of oxygen is a limiting process in PEMFC:



The use of the precious metal Pt as the preferred catalyst for the anode and cathode is one of the impediments to widespread PEMFC commercialization on account of its high cost and scarcity [4-6]. This fact stimulates researchers worldwide to look for non-precious metal electrocatalysts as alternative materials that are cheaper and yet perform better or equivalent to the Pt standard. Several kinds of unsupported or carbon supported non-precious metal electrocatalysts are discovered, including non-pyrolyzed and pyrolyzed transition metal nitrogen-containing complexes, conductive polymer-based catalysts, transition metal chalcogenides, metal oxides/carbides/nitrides/oxynitrides/carbonitrides, and enzymatic compounds [7-10]. Among these materials, pyrolyzed transition metal nitrogen-containing complexes supported on carbon materials (M-Nx/C) are considered the most promising catalysts for application in PEMFC because they have demonstrated high oxygen reduction reaction (ORR) activity and stability close to that of commercially available Pt/C catalysts [11].

In the present paper, the method of electrochemical treatment is proposed to increase the activity of Fe/N/C catalysts for the oxygen electrochemical reduction reactions. The method involves the anodic or cathodic polarization of the Fe/N/C catalyst synthesized, in an aqueous solution that contains the salt of Fe(II). Depending on the polarization processes of adsorption, oxidation or reduction may occur on the surface of the catalyst. Thereby, the surface of the catalyst and its properties (activity) is changed. Method of electrochemical treatment of catalyst is known as the method of galvanic replacement [12]. However, this method previously unused to activate the carbon-based catalysts, including Fe/N/C catalyst.

2. MATERIALS AND METHODS

2.1. Fe/N/C catalyst synthesis

Aniline (Beijing Chemical Industry, 99%) was distilled before experiments. Hydrogen peroxide (Sigma-Aldrich, 35%), nitric acid (Sigma-Aldrich, ACS reagent, 70%), as well as iron (II) nonahydrate (Sigma-Aldrich, ACS reagent, ≥98%) were used as received.

Commercial Ketjen-black EC 300J (0.5 g), used as carbon support, was treated in 0.5 M HNO₃ (50 ml) overnight, approximately 16 h, and then filtered following by washing with bi-distilled water and vacuum drying at 75±2 °C.

0.25 g of the prepared carbon support was dispersed in 45 ml bi-distilled water and sonicated for 30 minutes. 1.85 g of aniline was dissolved in 50 ml bi-distilled water then added to the slurry of

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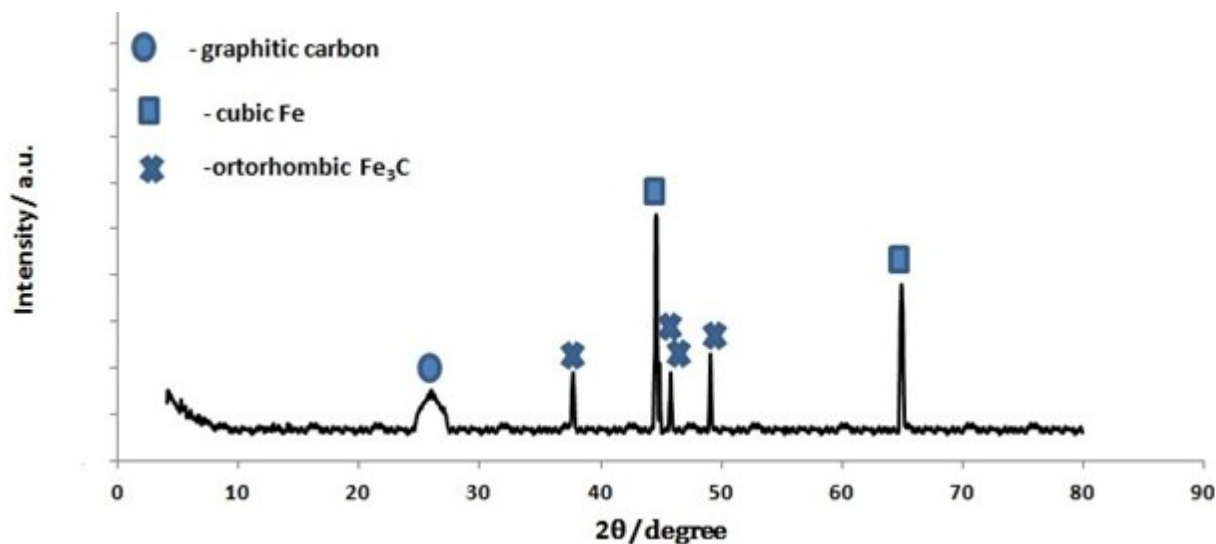


Figure 1. XRD patterns of the Fe/N/C catalyst before electrochemical treatment.

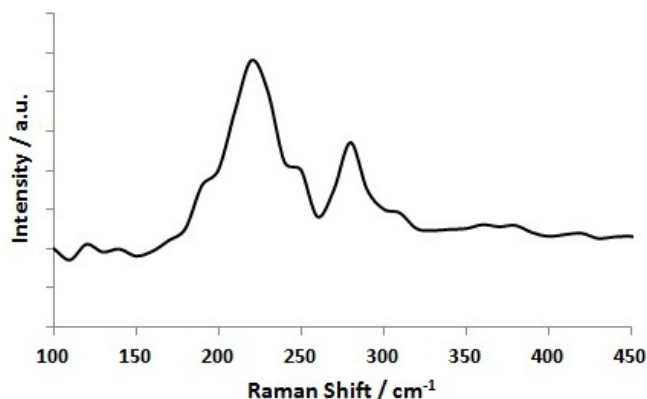


Figure 2. Raman spectra of the Fe/N/C catalyst before electrochemical treatment.

carbon support. The obtained mixture was stirred to obtain apparently homogeneous mass and then to a water bath maintained at 8 ± 1 °C. Thereafter, 4.2 g of $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ was added to the mixture; nitric acid was used to adjust the pH at the level of 1.5-2.0. 3 ml of 0.4 M H_2O_2 was added in drop wise to the mixture; the resulting mixture was kept under stirring for 24 h at 8 ± 1 °C. After that, the mixture was filtered, washed and vacuum dried at 75 ± 2 °C.

The dry powders were annealed in a tube furnace under N_2 flow at the temperature ramping rate of 30 °C/min and the annealing at 900 °C for three h. Ammonium carbonate was added to the powder before the annealing to create porosity in the final product, i.e. Fe/N/C catalyst.

X-ray diffraction (XRD) spectra were obtained using diffractometer DRON-3. Chemical analysis of the product was performed by using optical emission spectroscopy with inductively coupled plasma (OPTIMA 8000, Perkin Elmer).

2.2. Electrochemical treatment of catalyst sample

To prepare catalyst sample for electrochemical treatment, 10 mg

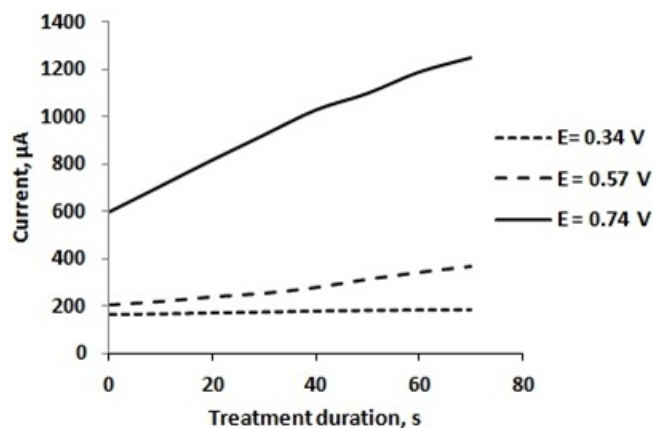


Figure 3. Anodic potentiostatic curves obtained on the Fe/N/C sample in 0.5 M iron (II) nitrate solution.

of the sample was dispersed in 0.5 ml of isopropanol with 20 μL of 5% Nafion suspension and sonicated for one h; then 30 μL of the ink was dropped on the rod-end (0.25 cm^2) of the glassy-carbon electrode. The resulting working electrode was electrochemically polarized in a 0.5 M iron (II) nitrate solution, acidified to $\text{pH} = 4$, under the certain conditions. After electrochemical polarization, the electrode was twice washed with bidistilled water and then subjected to electrochemical measurements using the rotating disk electrode method.

2.3. Rotate Disk Electrode (RDE) Measurements Technique

RDE measurements of the initial and electrochemically treated catalyst sample were performed by using the potentiostat-galvanostat Ellins in a conventional three-electrode cell filled with solution. Ag/AgCl (3.0 M NaOH, 0.235 V vs RHE) was used as a reference electrode; a graphite rod was used as counter electrode. Prior to ORR measurements, each electrode was potential cycled in

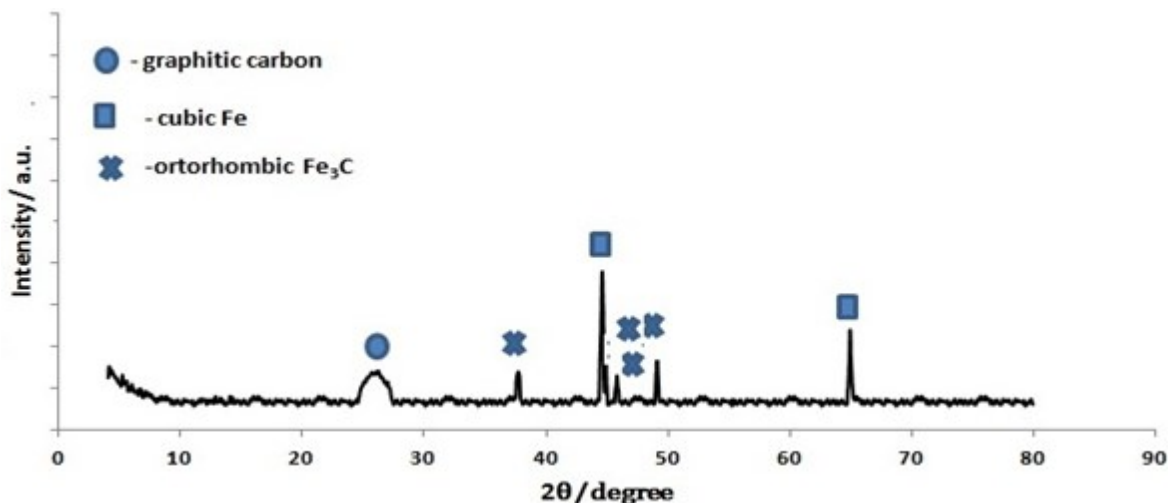


Figure 4. XRD patterns of the Fe/N/C catalyst sample #1.

0.1 NaOH for ten cycles until a stable voltammogram was obtained. The ORR measurements were carried out with a rotating disc rate of 800 rpm at the linear scan rate of 10 mV/s. All the potentials are given vs. RHE.

3. RESULTS AND DISCUSSION

3.1. Characterization of catalyst sample before electrochemical treatment

The X-ray diffraction (XRD) pattern (Figure 1) of synthesized Fe/N/C sample shows diffraction peaks typical for graphitic carbon (about 26°), cubic Fe (distinguished peaks at 44.61 and 65.04°), as well as orthorhombic Fe₃C (small peaks at 37.81, 44.86, 45.87, and 49.15°).

The total iron content, determined by atomic-emission spectroscopy, is 29.14 wt.%, and the surface iron content determined by XPS is 0.27 at.%. The Raman spectra of the sample, presented in Figure 2, are characterized by two peaks at 221.84 and 281.72 cm⁻¹ that can be attributed to the vibrational modes involving Fe-N [13].

3.2. Electrochemical treatment of the catalyst

The starting sample of the catalyst was subjected to electrochemical (anodic or cathodic) polarization in the potentiostatic regime for a certain time. In some cases, double electrochemical treatment was used.

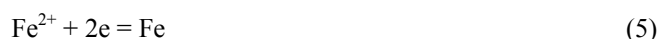
Figure 3 shows potentiostatic curves obtained by the anodic polarization of the sample. It can be seen that as the value of the po-

tential increases, the initial value of the current also increases; at E = + 0.74 V, the initial value of the current is 600 mV and sharply increases with time.

The processes of dissolution of metallic Fe, Fe₃C, as well as graphitized carbon particles that present in the starting carbon support cause this current increase:



On the cathode potentiostatic curves, current growth associated with the joint reduction of Fe (II) and hydrogen, was observed:



The presence of reaction (6) was visually confirmed by the release of gas bubbles at the working electrode.

As a result of electrochemical treatment, five samples of catalysts were obtained; processing conditions are given in Table 1.

The data of Table 1 indicate that sample # 1 was obtained by the anodic polarization of the starting sample; sample # 2 was obtained by cathodic polarization of mentioned sample. The sample # 3 was obtained successively by anodic and cathodic polarization, while samples # 4 and five were obtained by successively cathodic and anodic polarization.

3.3. Characterization of electrochemically treated catalyst samples

XRD patterns of the sample #1 are presented in the Figure 4.

The decrease in the values of the peaks of cubic Fe and orthorhombic Fe₃C confirms the assumption made about the occurrence of reactions (2) and (3). The total iron content, determined by atomic-emission spectroscopy, is 17.69 wt.%,

XRD patterns of the sample #2 are presented in Figure 5.

The increase in the values of the peaks of cubic Fe confirms the

Table 1. Conditions of the Fe/N/C catalyst sample electrochemical treatment.

Sample #	First treatment		Second treatment	
	Potential, V	Process duration, min	Potential, V	Process duration, min
1	+0.46	3	-	-
2	-0.50	3	-	-
3	+0.46	5	-0.50	5
4	-0.50	5	+0.46	5
5	-0.50	3	+0.46	3

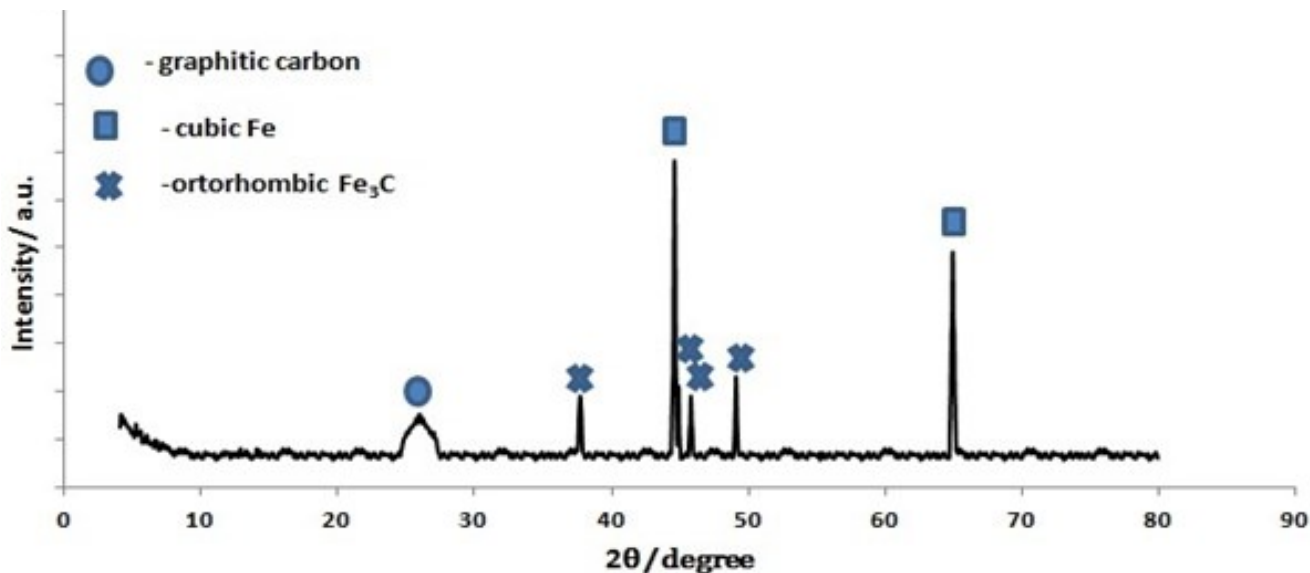


Figure 5. XRD patterns of the Fe/N/C catalyst sample #2.

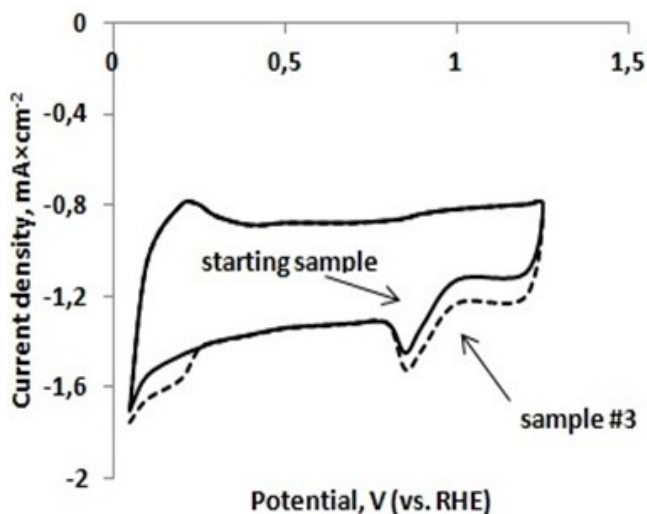


Figure 6. CV curves of the initial sample and sample #3.

assumption that reaction (5) proceeds during cathodic processing of the sample. Increasing the total iron content to 37.19 wt.% also confirmed this suggestion.

Cyclic voltammetry on RDE was used to evaluate and to compare the electrocatalytic activities of the Fe/N/C samples. Voltammogram of the initial Fe/N/C sample, presented in Figure 6, indicates that the catalyst has an on-set potential of 0.860 V (versus RHE) and relatively high current density at this value of potential ($1.51 \text{ mA} \times \text{cm}^{-2}$).

The sample #3 demonstrates more high electrocatalytic activity than initial sample as can be seen by comparison current densities of both catalysts at the on-set potential. The mentioned sample, as can be seen from Table 1, was obtained by a two-stage electrochemical treatment of the original catalyst. The sample was anodi-

cally polarized at $E = 0.46 \text{ V}$ for 5 min followed by cathodic treatment at $E = -0.50 \text{ V}$ for 3 min. The total iron content of the sample #3 is 27.85 wt.%, and the surface iron content is 0.24 at.%.

XRD pattern of the sample #3 shows the absence of a peak of graphitized carbon (Figure 7).

This fact can be explained by the occurring the reaction (4) during the anodic polarization of the electrode. The values of the peaks of Fe_3C correspond to those for sample # 1; at the same time, the values of the peaks of cubic Fe are approximately equal to those for the initial sample. Obviously, the decrease in the iron content in sample # 3 due to the reaction (2) is compensated by the reaction (5) that takes place during cathodic polarization.

4. CONCLUSIONS

In summary, for the first time, the new approach has been proposed for increasing the electrocatalytic activity of the Fe/N/C catalyst. The approach assumes the consistent anodic and cathodic treatment of the starting material in the aqueous solution of iron (II) nitrate. Occurring electrochemical reactions lead to a change in the content of the main components of the catalyst. This, in turn, changes the catalytic activity of the catalyst toward oxygen reduction reaction. The proposed approach may inspire new investigations in the field of electrochemical treatment of Fe/N/C catalysts.

5. ACKNOWLEDGEMENTS

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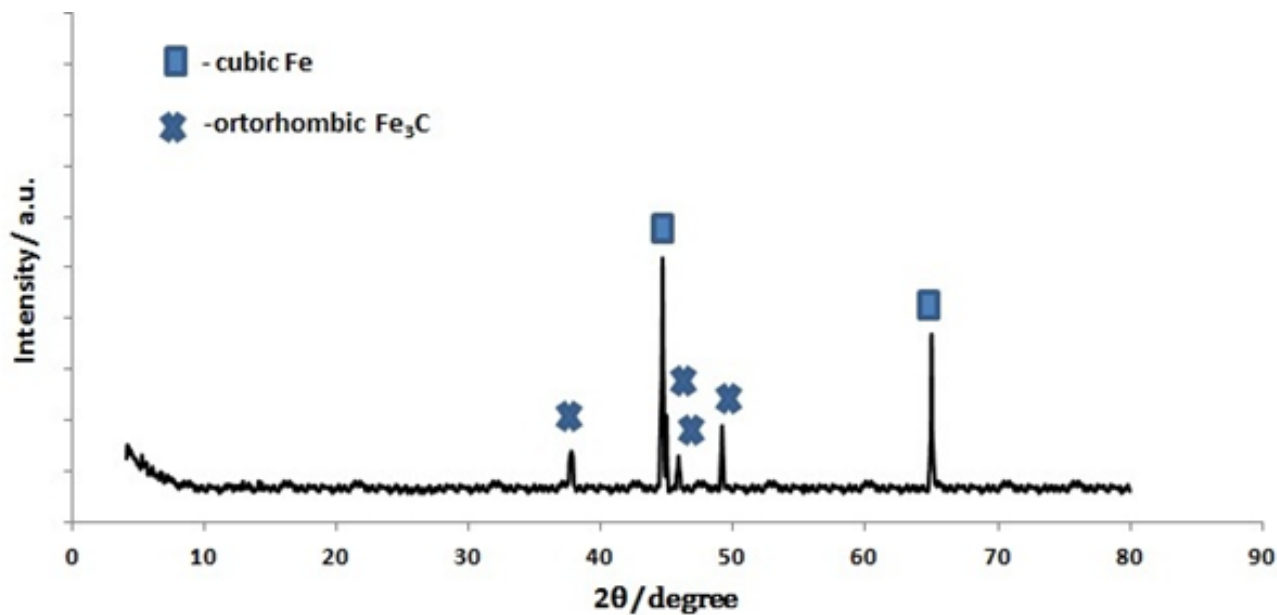


Figure 7. XRD patterns of the Fe/N/C catalyst sample #3.

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