

Highly Active and Durable Transition Metal-Coordinated Nitrogen Doped Carbon Electrocatalyst for Oxygen Reduction Reaction in Neutral Media

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Abstract. The major technical obstacles in commercialization of microbial fuel cell technology are the sluggish kinetic, high cost, and poor durability of an air cathode electrocatalyst. This research aimed to synthesize the highly active, stable and low cost non-precious metal catalyst to replace the expensive Pt electrocatalyst using a simple, low cost and scalable method. The Fe₃C and Fe-N-C catalysts were prepared by direct heating the precursors under autogenic pressure conditions. X-ray diffraction pattern revealed the phase of Fe₃C sample was cohenite Fe₃C and graphitic carbon, while the phase of Fe-N-C catalyst was only graphitic carbon. The morphology of the synthesized catalysts was a highly porous structure with nanoparticle morphology. The surface area of the Fe₃C and the Fe-N-C catalysts was 295 and 377 m² g⁻¹, respectively. The oxygen reduction reaction (ORR) activity of Fe-N-C catalyst was more active than Fe₃C catalyst. The ORR performance of Fe-N-C catalyst exhibited about 1.6 times more superior to that of the noble Pt/C catalyst. In addition, the Fe-N-C catalyst was durable to operate under neutral media. Thus, a novel autogenic pressure technique was a promising method to effectively prepare an highly active and durable non-precious metal catalyst to replace the precious Pt/C catalyst.

1 Introduction

Microbial fuel cells (MFCs) is a bio-electrochemical device directly extracting electrical energy during wastewater purification process [1-3]. The electrical energy generating from MFC has been beneficially utilized for powering small electronic devices such as sensors, pumps, clocks and mobile phones [1]. Basically, wastewater is bio-catalytically oxidized into protons and electrons at the anode. Electrons travel through an external wire to the cathode electrode, while protons diffuse through an electrolyte membrane to the cathode. Air supplied at the cathode and oxygen undergoes electrochemical oxygen reduction reaction (ORR) by combining protons and electrons producing water. MFC is suitably operated under the pH range of 6 - 8 and at room temperature due to the optimum condition of the bio-bacterial catalyst [2]. However, this operating condition leads to slow kinetic of the ORR at the air cathode, yielding low MFC performance [3]. Thus, substantial amount of catalyst is loaded at the air cathode electrode so as to accelerate the ORR under MFC operating condition. The fact that the precious platinum nanoparticles supported on carbon (Pt/C) has been widely

investigated as the most active ORR electrocatalyst for polymer electrolyte membrane fuel cells operated under acidic and alkaline environments [3]. Nevertheless, a significant disadvantage of the utilization of Pt catalyst is high cost and high ORR overpotential under the wastewater treatment conditions that is one of the main major hindering the widespread application of the MFC technology [3]. Furthermore, the surface of Pt electrocatalyst is easily deactivated by the poison of the contaminant from the wastewater, resulting in noticeable decrease of the air cathode activity, deteriorating the MFC efficiency [3]. For this reason, significant research has been focused on the development of highly active and durable non-precious ORR catalyst to replace the expensive Pt catalyst and to improve the MFC performance as well [1-3].

Carbon-based materials in the form of nanoparticle, nanosheet, nanotube and nanofiber have been potentially investigated as the non-precious ORR catalyst owing to outstanding properties: low cost, excellent electrical conductivity, biocompatibility, high surface area, easy process ability and good mechanical strength [4, 5]. However, the ORR performance of the carbonaceous catalyst was much poorer than the precious Pt/C catalyst [4, 5]. To improve the electrochemical ORR performance

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of carbon catalyst, heteroatoms such as nitrogen, boron, phosphorus and sulfur atoms were incorporated into the carbon framework [6-9]. Among dopants, nitrogen atom (N) that is similar size and slightly higher electronegativity value than carbon atom, has been experimentally accepted as the most efficient dopant to decrease the ORR overpotential [10-11]. Incorporation of N atom into carbon framework induces the charge of carbon atoms next to N doped atom to be slightly positive. The charge redistribution in the doped catalyst proficiently facilitates the ORR during fuel cell operation [10-11]. The overpotential of the N-C catalyst was dramatically less than the non-doped catalyst [6-7]. Compared to the noble Pt/C catalyst, the electrochemical ORR performance was still lower [6, 7]. To overcome this challenge, an inexpensive first row transition metals (M = Mn, Fe, Co, Ni) was coordinated with nitrogen doped carbon framework [12-17]. These catalysts are commonly known as M-N-C electrocatalyst. Kodali *et al.* [15] synthesized iron aminoantipyrine (Fe-AApyr) electrocatalyst by calcination of iron nitrate mixed aminoantipyrine in the presence of silica template at 950°C under ultrapure nitrogen atmosphere [15]. The ORR performance of Fe-AApyr electrocatalyst was compared with that of graphene nanosheet and activated carbon electrocatalysts under neutral media environment [15]. The Fe-AApyr sample exhibited the most efficient ORR active catalyst under neutral media due to the formation of Fe-N₄ active site [15]. Birry *et al.* [16] prepared Fe-N-C catalysts by pyrolyzing carbon black mixed various Fe precursors (Fe-acetate (FeAc), Fe-porphyrin, Fe-phthalocyanine (FePc)) at high temperature and under ammonia and/or Ar atmosphere [16]. It was found that Fe-N-C catalyst derived from macrocycles structure provided the best ORR performance under neutral solution [16]. In addition, the synthesized Fe-N-C catalyst exhibited more active and durable ORR performance than that of the expensive Pt/C electrocatalyst under MFC operation condition [16]. The highly active and durable ORR performance of Fe-N-C electrocatalyst were mainly attributed to the formation of Fe-N₄ moieties, high surface area and high electrical conductivity [16]. Based on the discovery of M-N-C catalyst, an inert and/or ammonia atmosphere are essentially required to fabricate highly active catalyst. However, fabrication of catalyst under inert atmosphere may prevent the complete decomposition of the carbonaceous materials leading to high ORR overpotential.

In this report, we aimed to seek for the highly active and durable non-precious electrocatalyst to replace the expensive Pt catalyst under neutral condition. The synthesized catalyst with high porosity was thermally prepared at high temperature under autogenic pressure method without using any inert gas or ammonia atmosphere. The ORR activity of the M-N-C catalyst under neutral media was measured using rotating disk electrode (RDE) analysis. The ORR performance of the synthesized catalyst was compared to that of the noble Pt/C catalyst. The novelty of this research was the electrochemical ORR performance under neutral media of the M-N-C catalyst fabricated using an autogenic pressure method which has not been reported to date.

2 Experiments

2.1 Preparation of electrocatalysts

The catalyst precursor was firstly prepared by refluxing melamine (3.5 g), iron acetate (1.0 g) and oxidized carbon powder (1.0 g) in ethanol at 60°C overnight. The solvent was evaporated and the powder precursor was then transferred into a Swagelok union closed cell and subjected to thermal pyrolysis at 900°C for 1 h under an ambient atmosphere. The calcination process was carried out at a heating rate of 10°C/min. The heated sample was assigned to be “Fe₃C”. The as-prepared catalyst with amount of 0.1 g was put in a vial contained 0.5 M H₂SO₄. The admixture was heated at 90°C for 8 h. The acid-treated sample was washed and dried overnight in a vacuum oven. Finally, the acid-treated sample was secondly carbonized using a Swagelok close cell at 900°C for 1 h under an ambient atmosphere. This catalyst was named “Fe-N-C”

2.2 Physical characterizations

Field-emission scanning electron microscope (FE-SEM, Hitachi S-4800II) with an accelerated voltage of 3 kV was employed to investigate the morphology of samples. Please note that the sample was coated with osmium before SEM analysis. The phase analysis of samples was estimated using powder X-ray diffraction (XRD, PANalytical-Empyrean) using K α radiation and generation voltage of 40 kV. Surface area of samples was determined by Brunauer-Emmett-Teller technique (BET).

2.3 Electrochemical characterizations

Catalyst ink was prepared by ultrasonic mixing catalyst powder, DI-water, 5% Nafion and Isopropyl alcohol followed the literature [18]. A working electrode was prepared by dropping catalyst ink on the surface of a clean glassy carbon and left it dry under ambient atmosphere. The catalyst loading on the working electrode was 0.5 mg/cm² while the amount of reference sample which is Pt/C was 60 μ g/cm². Working electrode was then connected into an electrochemical cell where Pt wire used as a counter electrode and saturated calomel electrode (SCE) used as reference electrode were also attached. The ORR catalytic activity of sample was evaluated under O₂-saturated phosphate buffer saline (PBS) solution (pH 7) rotating disk electrode (RDE) technique using Biologic, VSP.

3 Results and discussion

Fig. 1 represented the X-ray diffraction pattern of the Fe₃C and Fe-N-C electrocatalysts. According to standard data base (JCPDS), peaks observed in Fe₃C (Fig. 1a) were perfectly matched to cohenite (Fe₃C) and carbon. While, peaks generated in the XRD pattern of Fe-N-C (Fig. 1b) corresponding to carbon. In addition, two broad

peaks were observed at 2θ of 24.5 and 43.3 degree for Fe-N-C sample (Fig. 1b), indicating the typical graphitic C(002) and C(100) turbo static carbon structure [7]. The graphitic C(002) plane of the carbon was usually found at 26.9 degree. The negative shift of graphitic C(002) plane of the Fe₃C and Fe-N-C catalysts suggested an increase in the interlayer-distance due to the incorporation of N and Fe in the carbon framework, leading to excellent electron mobility throughout the catalyst.

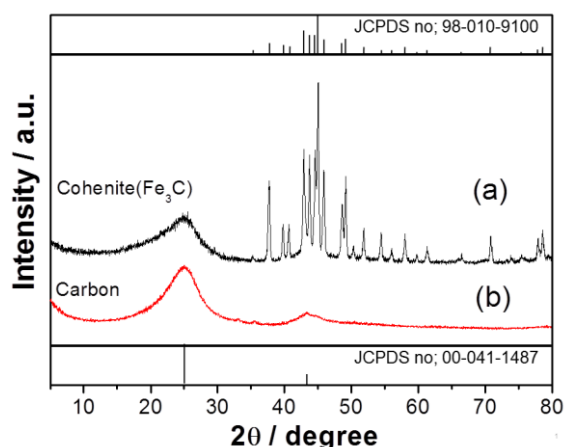


Fig. 1. XRD pattern of the Fe₃C (a) and Fe-N-C (b) electrocatalysts.

Fig. 2 illustrated the morphology of the Fe₃C and Fe-N-C electrocatalysts observed by FE-SEM. SEM image of Fe₃C catalyst showed nanoparticle morphology and high porosities. However, the particle size of the Fe₃C catalyst was not uniform distribution and its particle size was found to be in the range of 40 – 600 nm (Fig. 2a). SEM image of Fe-N-C sample presented high porosities and uniform size distribution without agglomeration (Fig. 2b). An average particle sizes of the Fe-N-C samples was found to be 50 nm. The larger particle size (> 100 nm) observed in Fe₃C catalyst (Fig. 2a) may be the Fe₃C and the small particle size (30 nm) corresponded to the VXC-72R carbon. The surface area of the Fe₃C and Fe-N-C catalysts was evaluated by Brunauer-Emmett-Teller (BET) technique and BET surface area of Fe₃C and Fe-N-C catalysts was calculated to be 295.7 and 377.5 m² g⁻¹, respectively (Table 1). It should be emphasized that pyrolysis of the Fe, N and C precursors at 900 °C under autogenic pressure resulted in the formation of Fe₃C, Fe-N_x and doped N into the carbon structure [19-20] (Fig. 1a). On the other hand, iron carbide was chemically dissolved in 0.5 M H₂SO₄, remaining only carbon (Fig. 1b). X-ray photo electron spectroscopy (XPS) was employed to verify the elemental composition of the Fe-N-C catalyst [18]. Elemental Fe, C, O and N were observed in XPS survey spectra [18]. The observed valence of Fe was Fe²⁺ which was able to bond with N forming Fe-N_x active site [18]. In addition, High resolution N1s spectra suggested the pyridinic, pyrrolic and graphitic N functional group, confirming the incorporation of N into the carbon framework of Fe-N-C catalyst [18].

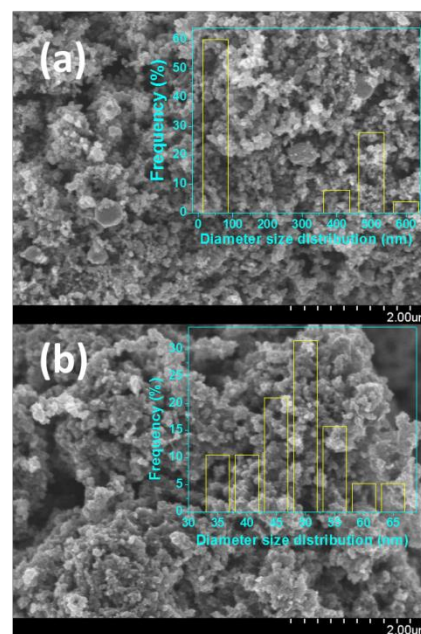


Fig. 2. FE-SEM image of Fe₃C (a) and Fe-N-C (b) electrocatalysts.

The electrochemical ORR activity was performed using a rotating disk electrode (RDE) under O₂-saturated PBS solution (pH 7) with a scan rate of 10 mV/s and the ORR result was compared to the ORR result of the commercial Pt/C (10 wt% Johnson Matthey) (Fig. 3). Linear sweep voltammogram (LSV) plots of Fe₃C and Fe-N-C catalysts recorded at a rotating speed of 1200 – 2500 rpm (Fig. 3a-b) showed that current density increased as the rotation speed was increased due to the shortening flux-diffusion. Fig. 3c compared the ORR performance of Fe₃C and Fe-N-C electrocatalysts in comparison with the commercial Pt/C at rotation speed of 1600 rpm in neutral media solution. The ORR activity of Fe₃C catalyst was poorer than the Fe-N-C catalyst. On the other hand, the Fe-N-C electrocatalyst exhibited comparable ORR performance to the noble Pt/C catalyst. Table 1 represented the onset potential and steady state current density of the Fe₃C and Fe-N-C catalysts in comparison with the Pt/C catalyst. The onset potential of the Fe₃C and Fe-N-C catalysts was 0.175 and 0.190 V vs. SCE, respectively. The onset potential of the commercial Pt/C was 0.200 V vs SCE. The onset potential of the Fe-N-C catalyst was nearly the same as the precious Pt/C catalyst. On the other hand, the steady state current density of the Fe₃C, Fe-N-C and Pt/C catalysts was -2.62, -4.00 and -2.55 mAcm⁻², respectively. The steady state current density of the Fe-N-C catalyst was about 1.6 times higher than the precious Pt/C catalyst. Furthermore, the ORR catalytic activity per catalyst cost of Fe-N-C was much higher than that of the Pt/C catalyst. The Koutecky-Levich (K-L) plots shown in the insets in Fig. 3a and b were derived from the LSV plots and these plots exhibited good linearity and parallelism over all the potential range, indicating the first order reaction kinetics for the ORR [18]. The electron transfer number of the Fe₃C and Fe-N-C catalyst at 0.5 V vs. SCE was calculated to be 2.9 and 3.7, respectively, suggesting the Fe-N-C catalyst

possessed a direct four electron transfer but not for Fe₃C catalyst. The superior ORR performance of the Fe-N-C relative to the Fe₃C catalyst was mainly due to the presence of the more stable OOH species on the surface of Fe-N-C rather than Fe₃C [19].

Table 1 Surface area, onset potential and steady state current density of electrocatalysts at 1600 rpm under neutral pH

Catalyst	Surface area (m ² /g)	Onset potential (V vs SCE)	Steady state current density (mA cm ⁻²)
Pt/C	N/A	0.200	-2.55
Fe ₃ C	295.7	0.175	-2.62
Fe-N-C	377.5	0.190	-4.00

N/A was not available

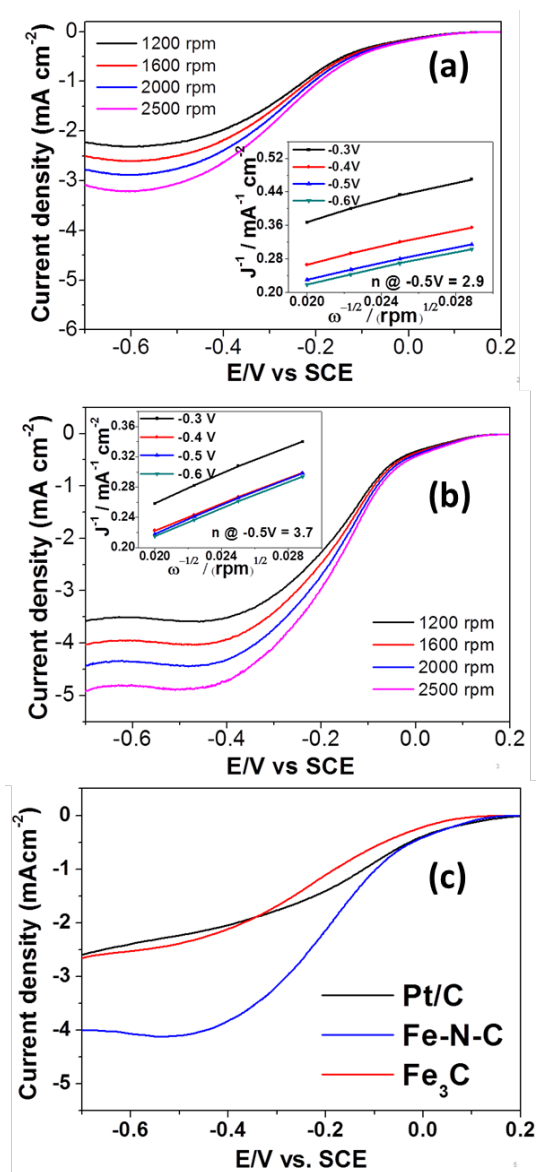


Fig. 3. ORR polarization curves of Fe₃C catalyst (a), Fe-N-C catalyst (b) in an O₂-saturated PBS media at different rotation speed (insets in (a) and (b) are Koutecky-Levich plots of Fe₃C and Fe-N-C catalysts, respectively). (c) comparison of LSV plots of Fe₃C, Fe-N-C and Pt/C catalysts under O₂-saturated PBS media.

It has been reported that ORR mechanism are involved in the OOH species on the surface of the catalyst. The OOH species further generates O* species and electrochemically reduced to -OH species and finally production of water [19]. Furthermore, the outstanding ORR catalytic activity of Fe-N-C electrocatalyst was mainly thanks to the incorporation of N into C framework as well as the formation of Fe-N_x which was efficiently increased binding capabilities of oxygen and higher ionization potentials [18]. In order to determine the outstanding catalyst synthesis technique, we compared ORR performance of the Fe-N-C catalyst prepared using autogenic pressure method with conventional method. The ORR performance of the prepared Fe-N-C catalyst was much superior to that of activation carbon [15], graphene nanosheet [15], N-doped carbon nanoparticle [7], N and B codoped carbon nanoparticle [7] catalysts. Compare to M-N-C catalyst, the fabricated Fe-N-C catalyst generated higher ORR performance than that of NiAApyr [13], MnAApyr [13], CoAApyr [13], Fe-Quinine [14], Fe-sulfadiazene [14], FeAc/Vulcan XC-72R [16] catalysts. This information suggested that an autogenic pressure method was a promising technique to fabricate a highly active ORR catalyst operated under neutral media.

Fig. 4 presented the chronoamperometric response of the Fe-N-C catalyst compared to the commercial Pt/C catalyst at 0.05 V vs. SCE under O₂ saturated neutral media. It was found that the current of the Fe-N-C catalyst at initial was -0.0431 mA and the current was decay to -0.0435 mA after 10,000 s at 0.05 V vs. SCE. On the other hand, the current of the Pt/C catalyst at the beginning was -0.0422 mA and the current remained -0.046 mA after 10,000 s operation at 0.05 V vs. SCE. After 10,000 s operation, the current of the Fe-N-C catalyst decay 0.9 %, while the decay current of Pt/C catalyst was 10 %. The decay current of Pt/C catalyst was faster than the Fe-N-C catalyst. These results suggest that the Fe-N-C catalyst was durable to operate under neural media and showed promising an ORR electrocatalyst to replace the expensive Pt/C catalyst for microbial fuel cells.

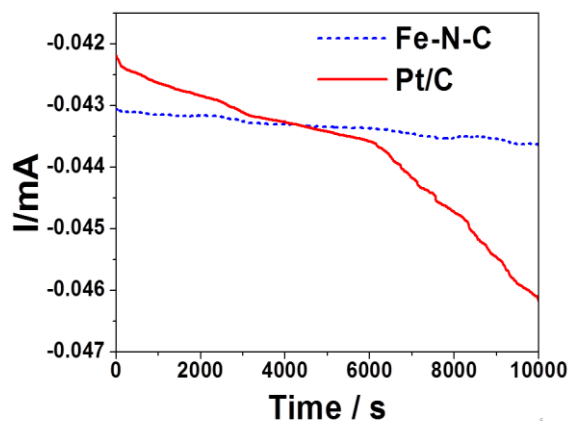


Fig. 4. Durability test of the Fe-N-C and Pt/C catalysts under O₂-saturated PBS media at 0.05 V vs. SCE.

4 Conclusion

We demonstrated that non-precious metal coordinated nitrogen doped carbon catalyst fabricated using an autogenic pressure method exhibited highly active and durable ORR in PBS media (pH 7). Especially, Fe-N-C catalyst showed superior ORR performance relative to the state of the art Pt/C catalyst. In addition, the ORR activity of the Fe-N-C catalyst was stable during operation under neutral pH.

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