Fe-N/C Catalyst using Various Nitrogen and Carbon Ratio through Chemical Oxidative Polymerization

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Abstract. This study aims to explain the effect of variations in nitrogen and carbon composition of catalysts on electrochemical properties and physical characterization. The usage of non-precious metals supported by nitrogen-carbon is one alternative to reduce the amount of platinum as the innovation of energy materials. Iron is a transition metal that can increase catalytic activity with the addition of a nitrogen source. The polymerization process was carried out by chemical oxidative polymerization for 24 hours in an ice bath using aniline as N source. Optimization of nitrogen coating on the carbon surface is carried out by mixing carbon during polymerization. The mixing of iron precursor and N/C powder was carried out in an ultrasonic bath and continued with pyrolysis at a temperature of 700°C. Regarding Cyclic Voltammetry (CV) test, the Fe-N/C = 2/1 catalyst has the largest area and the highest current density. The presence of Fe2O3 is needed to improve the electrochemical properties compared to Fe3C compounds. The composition analysis showed that the Fe-N/C = 2/1 catalyst had the highest Fe content after pyrolysis. In addition, the Fe-N/C = 2/1 catalyst also had the highest nitrogen content which can form a nitrogen functional group from the pyrolysis process.

1. Introduction
Proton Exchange Membrane Fuel Cells (PEMFC) technology continues to evolve. PEMFC has several advantages, such as high energy and power density, ability to work at relatively low temperatures, high energy conversion efficiency, and being relatively more environmentally friendly. However, the development of PEMFCs on a larger and commercial scale has been hampered. The obstacle is the high cost of production due to the high cost of platinum-based catalysts and the lack of operating stability [1]. The strategies for improving PEMFC viability are by replacing platinum with transition metal and increasing catalytic activity [2]. Transition metals, such as cobalt, iron, and other transition metals are capable of modifying electron properties, morphology, anion adsorption characteristics, and other surface-related factors. These modifications make intrinsic activity increase up to 2 to 4 times. In general, the active site of M-N/C is related to the presence of pyrrolic and pyridinic nitrogen in the catalyst structure. The nitrogen functional group is crucial for Oxygen Reduction Reaction (ORR). Hence, it is also decisive in improving catalytic performance. Moreover, the formation of the active site is also affected by the interactions that occur between nitrogen and metal in the precursor [3].

Non-Precious Metal Catalyst (NPMC) has promising materials for ORR activity consisting of carbon materials doped with nitrogen and transition metals. These materials have good stability in alkaline and acid media. Many researchers developed various Fe-N-doped carbon structures such as Fe/N/C catalyst in graphene monolayer [4], Fe-N-doped mesoporous carbon microspheres [5], mesoporous Fe-N-doped carbon nanofibers [6], and Fe/N co-doped graphitic carbon bulb [7]. Optimization of synthetic conditions and durability of NPMC catalyst can be achieved by selecting the
material of carbon supports and N-metal precursor. Two pivotal circumstances that regulate the
catalyst performance are (i) elemental compositions and interactions of different components, and (ii)
surface structure and specific surface area to determine the transport properties of ORR. The
conventional method for preparing NPMC involves mixing carbon, nitrogen, and transition-metal
precursors followed by pyrolysis under nitrogen atmosphere to expose the ORR active site [8]. Herein,
we investigate the preparation and characterization of Iron-Nitrogen/Carbon catalysts using different
carbon and nitrogen composition. The obtained catalyst was characterized by the electrochemical
properties, XRD analysis, SEM, and EDX analysis.

2. Experimental Method

2.1. N/C powder preparation

The N/C powder consists of activated carbon and urea as a nitrogen source. On the other hand, the
promoter used in this research was Polyvinylpyrrolidone (PVP). Carbon surface was coated using
nitrogen. The coating process was prepared by various compositions between urea (N) and activated
carbon (C) using a ratio of 1:2, 1:1, and 2:1. The total amount of carbon and nitrogen was 1000 mg,
and PVP was set at 150 mg. Urea and Polyvinylpyrrolidone were dissolved in 50 mL of demineralized
water. The mixing process between PVP and urea was performed for 15 minutes. Next, 2g of carbon
was put in and agitated for 12 hours at 25°C. The slurry of carbon and nitrogen was filtered and
washed with 2L of demineralized water, followed by drying for 8 hours in a furnace at 70°C to remove
the water content. Finally, dry powder of N/C = 1:1, N/C = 1:2, and N/C = 2:1 could be obtained.

2.2. Fe-N/C catalyst making

FeCl₃.6H₂O (Analytical grade) was used as a precursor for iron. Fe percentage of 10% was set for all
samples. FeCl₃.6H₂O was dissolved in ethanol (20 mL) and the obtained N/C = 1:1, N/C = 1:2, and
N/C = 2:1 powders were put into the solution of iron. Then, the mixture was added in the ultrasonic
bath for 30 minutes for optimum mixing. Next, the solvent was eliminated and dried into the oven at
70°C overnight. To enhance the active site, the pyrolysis process was performed for 2 hours at 700°C
using nitrogen atmosphere. Finally, the catalyst powders with varying nitrogen/carbon ratios were
obtained and named as Fe-N/C = 1:1, Fe-N/C = 1:2, and Fe-N/C = 2:1.

2.3. Characterization

Fe-N/C = 1:1, Fe-N/C = 1:2, and Fe-N/C = 2:1 samples were tested by using Cyclic Voltammetry
(CV) to study their electrochemical properties. Potential range of -0.15 V – 0.85 V in 0.1M HClO₄
solution was performed in CV test. Then, the catalyst powder was tested and observed using Energy
Dispersive X-Ray EDX, X-ray diffraction (XRD), Scanning Electron Microscope (SEM), and Fourier
transform infrared (FTIR).

3. Results and Discussion

Fig.1 illustrates the CV graph of Fe-N/C = 1:1, Fe-N/C = 1:2, and Fe-N/C = 2:1 catalysts at 10 mV s-1
in 0.1M HClO₄ solution. All samples exhibit a pair of reduction-oxidation peaks indicating
pseudocapacitive behaviour of polymer as nitrogen source [9]. The presence of reduction-oxidation
peaks confirms diffuse-controlled processes. According to this figure, the CV graph of Fe-N/C = 2:1 is
evidently larger than Fe-N/C = 1:1 and Fe-N/C = 1:2 graphs, indicating the higher specific capacitance
for Fe-N/C = 2:1. The voltammogram shape of the CV curve indicates a response of potential
capacity. Moreover, it correlates with surface area and commits to the functional groups [10]. Each
catalyst has a different position of oxidation and reduction peaks. Fe-N/C = 2:1 has the highest onset
potential indicating a more active site and has the fast movement of transferred electrons between the
metal centre and the electrode [11]. Nitrogen composition causes the differences in electrochemical
properties as shown by CV curves. Nitrogen functional groups are assumed to be formed after
pyrolysis. The high amount of nitrogen content causes a wide CV curve and high oxygen reduction reaction.

Table 1. Electrochemical properties from CV measurement

| Samples         | Capacity (F) | $E_p$ Anode (V) | $I_p$ Anode (mA/cm$^2$) | $E_p$ Cathode (V) | $I_p$ Cathode (mA/cm$^2$) |
|-----------------|--------------|-----------------|--------------------------|-------------------|---------------------------|
| Fe-N/C = 1/2    | $6.5 \times 10^{-3}$ | 0.85            | 0.69                     | 0.29              | 0.067                     |
| Fe-N/C = 1/1    | $4.6 \times 10^{-3}$ | 0.85            | 0.34                     | 0.30              | 0.012                     |
| Fe-N/C = 2/1    | $8.8 \times 10^{-3}$ | 0.845           | 0.62                     | -0.15             | 0.209                     |

The electrochemical properties of Fe-N/C catalysts using various nitrogen and carbon compositions are shown in Table 1. The highest capacity value belongs to the highest nitrogen content. Cathode peak position negatively shifted while increasing nitrogen ratio. Fe-N/C = 2/1 has the highest current density at the cathode side indicating that oxygen reduction reaction occurs faster than other compositions and showing high nitrogen content improves the oxygen reduction reaction activity.

Figure 1. CV test result of various Fe-N/C catalysts. The CV test was performed at 10 mV s$^{-1}$ of scan rate and in 0.1 M HClO$_4$

XRD pattern in Figure 2 shows the compound produced by the catalysts. Fe$_3$C, Fe$_2$O$_3$, and C peaks appear on each catalyst using different compositions but have different peak intensities. Carbon has a crystalline structure indicating a graphite peak (JCPDF#08-0415). Fe-N/C catalysts have the same slight carbon peak which confirms that it has the same graphitization level of carbon after pyrolysis [12]. Fe$_2$O$_3$ shows the highest intensity peak at 35.6°, 53.7°, and 62.9° (JCPDF#39-1346). The existence of Fe$_2$O$_3$ is more desired than other structures for iron-based catalysts. Fe$_3$C is identified at 2θ = 44.6° and 57° (JCPDS, PDF# 350772). The formations of new compounds were obtained after pyrolysis due to the disintegration between ligand and metal ions on carbon support structure [10]. The metallic state of iron (Fe peak) indicates that iron coordinated with carbon and oxide during pyrolysis. Metallic iron and iron carbide (Fe$_3$C) can reduce the ORR activity because it blocks oxygen access during oxygen reduction reactions.
Figure 2. XRD result of various Fe-N/C catalyst

Figure 3 presents the FTIR spectra for Fe-N/C catalyst using various nitrogen and carbon ratios. FTIR analysis investigates the bonding interactions and functional groups. The broad peaks appear at 3420 cm\(^{-1}\) which is attributed to O-H bonding and indicates that water was absorbed [13]. Different ratios of nitrogen and carbon similarly affect the FTIR through the bonding of C-O, C=N, C=N, and C=O. The bonding interaction of C-N and C=N indicates the impregnation of carbon during polymerization. Additionally, the presence of C=O formation plays an important role to adsorb the oxygen due to being a strong electrode positive carbon in the carbonyl groups [14].

Figure 3. FTIR spectra of catalyst using various N and C ratio

The chemical composition of the catalyst products was analysed using EDX. The elements detected from EDX are C, N, Fe, O, and Mo elements as summarized in Table 2. The existence of these elements was confirmed in the XRD pattern, with the exception of N and Mo which cannot be detected in XRD analysis due to their low amount. The C content is observed to be the highest proportion. The higher ratio of carbon usage in the catalyst correlates to a high atomic percentage of carbon from the EDX. It can be correlated that the C content increases linearly to the amount of
carbon added to the catalyst. Nitrogen content in Fe-N/ catalyst increases linearly with an increase in nitrogen ratio in the catalyst composition. The electrochemical properties can be enhanced due to the high amount of nitrogen existing in Fe-N/C [10]. Fe plays an important role in nitrogen decomposition to become a nitrogen functional group after pyrolysis. The Fe content in each catalyst has a different value even though the percentage of Fe remains at 10wt% Fe. The existence of iron weight loss is caused by iron-catalyzed re-adsorption of the disintegrated product [15]. The linear increase of Fe and N allows the interaction between iron and nitrogen to form the Fe-N structure and plays a role in the formation of active sites [16].

| Samples           | Wt% C  | Wt% N  | Wt% Fe | Wt% O  | Wt% Mo |
|-------------------|--------|--------|--------|--------|--------|
| Fe-N/C = 1/2      | 79.41  | 1.12   | 4.41   | 11.17  | 3.88   |
| Fe-N/C = 1/1      | 76.66  | 3.67   | 4.97   | 10.07  | 4.64   |
| Fe-N/C = 2/1      | 65.08  | 6.13   | 8.29   | 16.35  | 4.16   |

**Table 2.** Elemental Composition of Fe-N/C using EDX analysis

![Figure 4](image-url)  
**Figure 4.** SEM images of Fe-N/C catalyst using variation ratio of carbon and nitrogen (a) N/C = 1/2 (b) N/C = 1/1 (c) N/C = 2/1 in 2500x of magnification and (d), (e), (f) in 10.000x magnification

All various Fe-N/C catalysts have a composite morphology in which nitrogen is coated on the carbon surface as shown by Figure 4. Nitrogen cannot be homogeneously distributed due to the high nitrogen content. Nitrogen from urea decomposes to form nitrogen functional groups during pyrolysis. The smaller particles and lighter colours present the nitrogen component [17]. The presence of nitrogen is derived from the polymerization from aniline ionomer and form the nitrogen functional groups due to decomposition after pyrolysis. Therefore, nitrogen doped carbon can improve the properties of Fe-N/C catalyst [18]. The highest carbon content of Fe-N/C =1/2 resulted in nitrogen unable to reach homogeneous particle distribution and locally gathered in one spot. It is caused by the increased resistance which can reduce the active site. Additionally, iron as a metal interrelates with C and encourages surface rearrangement post-pyrolysis [19].
4. Conclusions
Based on the analysis and discussion, it can be determined that the difference in carbon and nitrogen compositions affects the electrochemical properties. It was supported with CV and XRD characterization, EDX analysis, and morphological analysis. The more nitrogen content produced by nitrogen-doped carbon causes high current density for the reduction reaction. Fe-N/C catalysts with different compositions have the same XRD pattern for C, Fe₂O₃, and Fe₃C peaks. The slight differences in the XRD pattern for catalysts using various nitrogen carbon ratios are the crystalline peaks and the intensity. The presence of C, Fe, and O from the EDX analysis will form a new iron compound as confirmed by XRD analysis. A high amount of nitrogen content correlates with the high iron loading after catalyst fabrication. Moreover, the morphological analysis shows that the nitrogen particles are more distributed on the carbon surface after pyrolysis.

5. References
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