High performance iron-based oxygen reduction catalyst supported on sengon wood-derived reduced graphene oxide in acidic medium

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Abstract. Non-precious metals (NPM) such as iron and nitrogen-doped carbon (Fe-N-C) have been actively studied as alternative electrocatalysts to platinum for oxygen reduction reaction (ORR) in proton exchange membrane fuel cell (PEMFC). However, its low stability is associated to the structural morphology of the electrode made of Fe-N-C and its support that has restricted the mass transfer of fuel and product. In this work, it was attempted to assess the role of RGO derived from sengon wood as catalyst support to Fe-N-C catalyst, and study the effect of the Fe-N-C to RGO ratio, on the ORR activity and durability in acidic medium. This work revealed that Fe-N-C/RGO at the weight ratio of 2:0.2 demonstrated the highest onset potential of 0.91 V, with high limiting current density of 5.7 mA/cm², owing to the uniform active site distribution on the Fe-N-C/RGO surface compared to other samples with different weight ratio. It was indicated in this work that an improve in the kinetic activity was observed with increase operating temperature from 25 to 80 °C. An electron transfer number of 3.91 indicating a complete oxygen reduction process took place on the catalyst. The durability test showed that Fe-N-C/RGO 2:0.2 retained 89 % of its current density at 0.25 V over a duration of 16000 s, higher than that of the benchmark Pt/C. These results have collectively demonstrated a high performance sustainable noble metal-free ORR catalyst for PEMFC applications with proper tailoring the mass ratio of Fe-N-C to RGO support.

Keywords : Fe-N-C/RGO 2:x, catalyst support, ORR activity and durability, porous structure

1. Introduction
Noble metal-free electrocatalyst has shown vast progress towards replacing platinum-based materials for fuel cell cathode. Seeking for an economically efficient catalyst precursor without compromising its electrochemical performance has been a challenge. Among the many attempts, pyrolyzed metal (M) with nitrogen-doped carbon catalysts (M-N-C) have been reported to possess remarkable electrochemical properties, such as promising oxygen reduction activity, good catalyst stability, and
high tolerance to poisoning by methanol, CO and CN- environment, that are desired for low-temperature proton exchange membrane fuel cell (PEMFC). Along this progression, particular attention was paid to improve the M-N-C properties in relation to particle dispersion, active sites, morphology and porous structure [1]. Carbonaceous catalyst support would increase the hydrophilicity over a long fuel cell operation, and thus caused the micropores that anchored the active sites become flooded. For the active catalysts, these sites are usually covered by the Fe/CoNx, N or O atoms, in which they have the hydrophilic character. Hence, this leads to the decrease in the site density and the catalyst performance when the fuel cell continues to operate in longer period, with the production of water that eventually flood the electrode [2]. In view of this, tailoring the porous structure in the M-N-C catalyst is seen crucial to increase reactant mass transport and electron transfer. High defective degree, mesopores structure and electrical conductivity on catalyst support material are concerned as physical properties desired to improve the ORR activity.

Among the numerous types of carbon support, reduced graphene oxide (RGO) has emerged as viable carbon support owing to its large surface area and defect-rich surface which is controllable by its synthesis process. In recent years, some attention has been given to produce RGO from sustainable biomass sources. Despite the lower purity of RGO-derived biomass as compared to that derived from graphite, the presence of higher defective sites due to impurities removal possess an advantage in the application for fuel cell electrocatalyst support. The defective sites could provide an effective anchoring sites for the catalyst. This eliminates the need to perform further oxidation of RGO derived from graphite to create the defective sites for the abovementioned purpose. Sengon wood, originated from Indonesia is reported in work, as the state-of-art precursor to produce RGO as M-N-C catalyst support using iron (M = Fe) and polyaniline as catalyst precursors. The wood vessel present in Sengon wood can be forcibly exfoliated into graphene layers through the oxidation using strong acid and oxidizing agent. The surface oxygen after the exfoliation can be converted into defective sites beneficial for anchoring of Fe-N-C catalyst after its removal through thermal heating.

The utilisation of biomass as support in noble free catalyst has reported on role of mesopores in carbon layers into high performance catalyst and. The Feculum bombycis and seaweed were incorporate with iron and some nitrogen sources to generate a porous nanosheet with large surface area that were shown to contribute to high ORR activity in both acidic and alkaline medium [3,4]. As mentioned, the design of catalyst with carbon support with the presence of mesopores is believed to play a crucial role in improving the mass transport of the reactants and products, and thus improve the overall fuel cell performance. Hence, the objective of this work is to study the effect of mass ratio of RGO derived from Sengon wood carbon support to the Fe-N-C catalysts on the oxygen reduction activity in acidic medium. It is hypothesised that the variation in the Fe-N-C: RGO ratio could alter the number of active sites and the ease of fuel flow through the catalyst layer. In addition, the ORR kinetic and the stability of the Fe-N-C/RGO with highest activity will be revealed.

2. Experimental section

Initially, graphene oxide (GO) powder was prepared from Sengon wood biomass through microwave assisted carbonisation method and followed by Hummer’s method. The as-prepared GO was added into 0.5 M HCl solution with different mass ratio (g/g) of aniline (as nitrogen source for Fe-N-C catalyst) to carbon (2:0.1 ; 2:0.2 and 2:0.8). The mixture was stirred continuously in an ice bath. Meanwhile, a constant amount of 0.3 grams iron chloride with 2 mL aniline, 99%, purchased from Acros organic were added into 0.5 M HCl, and ammonium persulphate, 99%, purchase from Systerm at molar ratio 1:1. The obtained suspension was oven dried to obtain a black powder after being left over for 24 hours for the polymerisation process. Subsequently, the collected powders were subjected to pyrolysis at 900 °C under 100mL/min flow of nitrogen gas for 1 hour. The pyrolyzed powder, herein labelled as Fe-N-C/RGO 2:x (x refer to mass of GO addition), underwent acid wash using 0.5 M sulphuric acid to remove excess metal residues. A second pyrolysis was performed at the same temperature for two hours and the sample were cooled to room temperature prior to storing and further analysis. The morphology of Fe-N-C/RGO was studied on Transmission Electron Microscopy (Thermo Fisher Model: Talos 120C). The pore
structure and pore size distribution were examined using Brunauer–Emmett–Teller (Micromeritic 2020) and was predicted by BJH adsorption method. For the electrochemical tests, the Fe-N-C/RGO samples were prepared into catalyst ink by mixing an amount of sample powder with 5 wt.% of Nafton, ethanol and deionized water and underwent sonication for 1 hour. Cyclic voltammetry (CV) and rotating-ring disk voltammetry (RRDE) were employed to measure the ORR activity. Prior to CV and RRDE testing, 496 µg/cm² of catalyst was deposited onto a glassy carbon (GC) electrode (Pine Instrument) and was dried overnight. A three-electrode system with GC electrode, Pt wire and Ag/AgCl as working, counter and reference electrode, respectively was used and was connected to a potentiostat (Autolab PGSTAT128N). The ORR studies on the catalyst samples were conducted in both the nitrogen saturated and oxygen saturated environment, in 0.1 M HClO₄ electrolyte. For CV measurement, the scan was performed from 1.2 V to -0.2 V vs Ag/AgCl in the negative sweep, with a scan rate of 25 mV/s. While for RRDE measurement using linear swept voltammetry technique, the GC electrode was connected to a rotary shaft with rotating rate set at 1600 rpm, and was scanned from 0.9 V to -0.1 V vs Ag/AgCl to obtain the polarisation curve. It is noted herein that the measured potential was converted to RHE with the correction of +0.2885 V vs Ag/AgCl. For RRDE calculation, ring current (I_R) and disk current (I_D) were collected to calculate number of electron transfer, n and peroxide production with a ring efficiency, N of 0.26 based on equation (1) and equation (2).

\[
\begin{align*}
    n &= 4 \frac{I_D}{I_D + \frac{2I_R}{N}} \quad \text{(1)} \\
    \text{HO}_2 &= 100 \times \frac{2I_R}{I_D + \frac{I_R}{N}} \quad \text{(2)}
\end{align*}
\]

3. Results & discussions

TEM image has identified the catalyst morphology as thin layer RGO structure embedded by dense agglomerated pani and metal atoms as can be observed in Figure 1(a). Vivid graphitic lattice was observed on Fe-N-C/RGO 2:0.2 inferring high crystallinity on carbon matrix. On pore analysis via BET, it was shown that the single point surface area of RGO produced from Sengon wood was 402.3 m²/g and was decreased to 222.58 m²/g with the anchorage of Fe-N-C on the RGO. Type-IV adsorption and desorption isotherm on both RGO and catalyst Fe-N-C/RGO 2:0.2 samples have indicated multilayer micro/mesopores size between 0.2-10 nm. The iron and nitrogen atom from the precursors anchored onto the RGO surface has reduced the number of carbon pores which lead to the decrease in BET surface area [5].
Interestingly, the current density of the catalysts was shown to increase by 2-70\%.

Testing potential and half wave potential has changes on the ORR activity with increase in operation temperature. The suitable amount of RGO support and O₂ has drastically reduced the current density. This is reasoned by that the ratio (C/RGO) for the catalyst to support ratio. In the low overpotential region which indicates kinetic controlled activity, LSV in Figure 1(c) demonstrated that RGO exhibited an inferior activity in acidic medium with low limiting current density owing to absence of active sites on carbon surface. With the presence of Fe-N-C on the RGO, apparent current limiting plateau was achieved in the mass transport controlled region (< 0.5 V vs RHE). Interestingly, the current density of the catalysts was shown to increase by approximately 1.5-fold with the increase in the mass of RGO from 0.1g to 0.2 g to 5.7 mA/cm². This positive increase in the current density was accompanied by the increase in onset potential, showing that the ORR kinetic was improved with the alteration of the catalyst to RGO support ratio. The result was similar to the work performed by Li and co-worker, reported on the incorporation of carbon nanotubes into one dimensional core shell Fe-N-C has gained the current density value of 6 mA/cm² [6]. High performance of ORR activity was attributed to the rational catalyst design, where the existence of Fe-N\(_x\) could have a synergetic effect with its carbon support [7]. The suitable amount of RGO support enable the more uniform distribution of the active sites as well as to provide a balance between the active sites (attributed to higher onset potential) and the transport sites (attributed to higher limiting current density) for the ORR activity. Nonetheless, this work has showed that further increase in RGO mass to 4-fold (0.8 g) has drastically reduced the current density. This is reasoned by that the excessive RGO at ratio of 2:0.8 has caused particles agglomerated and formed a bulky morphology. This aggregation has blocked the interspace pores on RGO matrix, lowered the active sites, Fe-N\(_x\) and also decreased the mass transfer channel [8]. It is also worth noting that the achievement of a flat current limiting plateau on the Fe-N-C/RGO 2:0.2 sample as compared to other catalysts has proved that the catalytic active sites was uniformly distributed over the RGO support at this catalyst to support ratio.

LSV measured at varying temperatures from 25 °C to 80 °C was conducted on the Fe-N-C/RGO 2:0.2 catalyst in order to elaborate the kinetic behavior. Figure 2(a) demonstrated that there are significant changes on the ORR activity with increase in operation temperature. On the kinetic region, onset potential and half wave potential has shown a gradually increased from 0.83 V and 0.73 V at room testing temperature to 0.88 V and 0.77 V at 80 °C. Meanwhile, the limiting plateau current density

Figure 1. (a) TEM micrograph of Fe-N-C/RGO 2:0.2 sample, (b) Cyclic voltammogram of Fe-N-C/RGO 2:0.2 sample measured in N\(_2\) and O\(_2\) at 0.1 M HClO\(_4\) and (c) linear sweep voltammogram of Fe-N-C/RGO (2:x) samples measured at 1600 rpm under O\(_2\) condition in 0.1 M HClO\(_4\).

vitamin A and D. The role of vitamin A and D is to regulate the cell cycle, which is crucial for DNA synthesis and repair, as well as for immune response and inflammation. Vitamin A and D are also involved in the regulation of the growth of cells, particularly in the development of the nervous system and the immune system. Vitamin A and D are also important for bone growth and the development of the lungs, heart, and liver. Vitamin A and D are also important for the development of the brain, particularly in the development of the optic nerve, which is important for vision. Vitamin A and D are also important for the development of the skin, particularly in the development of the hair, nails, and the barrier function of the skin. Vitamin A and D are also important for the development of the reproductive system, particularly in the development of the ovaries and the testes. Vitamin A and D are also important for the development of the immune system, particularly in the development of the immune cells, such as the T cells and the B cells.
present at all temperatures, indicating that the catalyst is solely controlled by oxygen mass transport in this high overpotential region. In Figure 2(b), it was demonstrated that the electron transfer number, \( n \) obtained on Fe-N-C/RGO 2:0.2 sample achieved close to 3.91. This electron transfer number remains significantly unchanged over the temperature range studied, indicating no deterioration in the active sites [9].

In addition, this near to four electron transfer number obtained also inferred a direct conversion of oxygen reactant into water in acidic media. An insignificant amount of peroxide as intermediate product (approximately 3%) was obtained. This result obtained is comparable to Pt/C and is found very promising with the use of noble-free catalyst on biomass derived RGO support. To further support the results above, Tafel plot was used to extract the kinetic data of the Fe-N-C/RGO 2:0.2 catalyst. Tafel slope was calculated based on two regions, namely the low overpotential region represented with the low current density (lcd) at 1.06-1.01 V and the high overpotential region represented by the high current density (hcd) at 0.8-0.7 V. As depicted in Table 1, the slope values on lcd decreased with elevated temperature and reach the value of 73 mV/dec at 80 °C close to 60 mV/dec, indicating that the activation energy of the catalyst has reduced with increase in temperature, thus increase the kinetic of the catalyst. On high current density, the slope are shifted about 22 mV/dec compared to Pt/C (120mV/dec). Higher slope has indicated a coarse surface on Fe-N-C/RGO 2:0.2, possibly affected by poorer nanoparticle dispersion compared to Pt/C [10].

Furthermore, stability test was performed using chronoamperometry technique in oxygen-saturated 0.1 M HClO₄ electrolyte at 1600 rpm for 16 000 second. After 16000 s stability test on acidic electrolyte, Fe-N-C/RGO 2:0.2 showed 3 % higher in efficiency than Pt/C, which inferred that mesoporous structure in RGO showed the capability to retain and distribute the Fe-N-C catalyst, allowing a balance in the oxygen reduction and fuel transport process. In addition, it can also be inferred that the presence of RGO showed a good tolerance to carbon oxidation in 0.1 M HClO₄ medium.

![Figure 2](image_url)

**Figure 2.** (a) LSV polarisation curve of Fe-N-C/RGO (2:0.2) b) electron transfer number, \( n \) and peroxide yield at temperature range 25°C - 80°C, 1600 rpm oxygen saturated on 0.1 M HClO₄.

**Table 1.** ORR parameter on Fe-N-C/RGO 2:0.2 at elevated temperature.

| Temperature | Onset Potential (V vs RHE) | Half wave (V vs RHE) | Current Density (mA/cm²) | Tafel plot at lcd (mV/dec) | Tafel plot at hcd (mV/dec) |
|-------------|---------------------------|----------------------|--------------------------|---------------------------|----------------------------|
| 25          | 0.83                      | 0.73                 | 2.75                     | 103                       | 148                        |
| 40          | 0.85                      | 0.74                 | 3.04                     | 91                        | 176                        |
| 60          | 0.88                      | 0.77                 | 3.48                     | 88                        | 144                        |
| 80          | 0.88                      | 0.78                 | 3.88                     | 73                        | 156                        |
4. Conclusion
In summary, this work has successfully showed that the rational design of RGO addition to the Fe-N-C catalyst was crucial to improve the ORR activity due to the needs of a balance between the active sites and fuel transport sites. Also, it is highlighted that RGO in this work was produced from a sustainable natural source of sengon wood with the advantage of possessing high defective sites. It is studied that the ratio of Fe-N-C to RGO 2:0.2 displayed the highest ORR kinetic and activity as observed from the highest onset potential and stable current limiting plateau in the LSV analysis owing to the more uniform active sites distribution and fuel transport sites with this ratio. Higher RGO ratio has resulted in the deterioration in the ORR activity due to particle agglomeration. The stable ORR activity of the Fe-N-C/RGO 2:0.2 catalyst performed under different temperatures up to 80 °C also suggested that this sustainable noble-free catalyst can be utilised as a promising and high-performance catalyst for low temperature PEMFC application.

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