Preparation of low cost catalysts for proton exchange membrane fuel cell

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Abstract. Nitrogen-doped reduced graphene oxide (NG) with high nitrogen level was synthesized by a facile pyrolysis. NG has been getting attention because of its high catalytic activity toward the oxygen reduction reaction (ORR) and reduce cost. The synthesis of NG used graphene oxide (GO) and urea as a N-precursor were dissolved in ethanol. Then the mixture was evaporated by ultrasonic bath for 30 min. The mixture was slurry then was transferred to tube furnace and pyrolyzed at 300°C and 800°C (NG300 and NG800) with heating rate of 2.5 °C/min in N₂ atmosphere for 30 min. The morphology and structure of nitrogen doped graphene oxide were investigated by Scanning Electron Microscopy (SEM) and X-ray photoemission spectroscopy (XPS). The XPS spectra of NG indicated that NG300 had the highest intensity of N1S peak among others. Mass of nitrogen of NG300 and NG800 were evaluated and had about 15.5%wt and 6.6%wt, respectively. Furthermore, N spectra at high-resolution was analysed and de-convoluted to three N chemical states of pyridinic-N, pyrrolic-N, and graphitic-N. The electrochemical properties of NG were determined by cyclic voltammetry (CV) and Linear sweep voltammetry (LSV). From the results shown that NG800 catalyst yielded highest electrochemical activity particularly for oxygen reduction reaction (ORR) over GO and NG300. Thus, N atoms doped into the graphene were responsible for the ORR catalytic activity resulting from doping N atoms and provided more density of active sites and conductivity. Moreover, NG can be applied as a supporting material for Non-precious metal group catalysts of fuel cell.

Keywords: Nitrogen doped reduced graphene oxide, Non-PGM catalysts, PEM fuel cell, ORR activity

1. Introduction
Oxygen reduction reaction (ORR) is attended in polymer electrolyte membrane fuel cells (PEMFCs). Pt is still the best of all catalysts for ORR but too expensive and rare metals. These make price of catalysts are more competitive leading to many researches being conducted to find alternate electrocatalysts that are good activities for ORR [1]. Therefore, the study of the synthesis of catalysts without platinum group metals that is called Non-platinum group metal catalyst (Non-PGM catalyst) has been attended and developed for electrochemical reaction especially in PEMFC.

The structure of the Non-PGM catalyst consists of the support without platinum, but nitrogen atoms are doped on the support, for example, N-doped carbon. The structure of the N-doped carbon is rather complex with various functionalities of N. These functionalities, N-doped carbon presents the N atoms doping in the carbon structure for example, N-doped graphene and N-doped graphene oxide etc.
Moreover, N-doped carbon was responsible for the ORR catalytic activity [2]. Various N precursors such as ammonia, urea, melamine etc.

The good catalytic properties are small particles, high surface area, good durability and high dispersions. Graphene oxide (GO) is usually chosen for catalysts due to GO can disperse in water and organic solvents such as methanol, ethanol, ethylene glycol and DMF. Furthermore, GO has high surface area and electrical properties [3]. Moreover, thermally reducing GO (rGO) can produce a higher surface area. On the other hand, a major disadvantage of this process is damaged structure by the high temperature, affect to mass loss and decrease of mechanical strength of the rGO significantly [4].

To prepare N-doped carbon, Degang Li et al. [5] prepared N-doped graphene by using graphene and urea with pyrolysis method. The urea was used as the substance of nitrogen sources. The samples were reduced in air flowing with heating at 350 °C. The percentage of nitrogen atoms was as high as 18.7% wt. Moreover, Ziyin Lin et al. [2] prepared N-doped graphene, which was a catalyst that provided a good activity of ORR reaction using a pyrolysis method. They used material similar to ref [5], but the reduced temperature was higher at 800 °C and in Nitrogen gas flow. It was found that their NG gave electrical and chemical efficiency better than the catalyst without nitrogen flow.

In this study use graphene oxide (GO) and urea (N-precursor) to synthesize N-doped carbon by pyrolysis at 300 °C and 800 °C in nitrogen atmosphere. graphene oxide (GO) was reduced by thermal in pyrolysis and N atoms were doped in the rGO, to produce N-doped rGO, it is denoted as NG.

2. Experimental

2.1 Preparation of N-doped rGO
Materials: Single-Layered Graphene oxide (GO) was purchased from Cheap tubes (USA). Urea, Ethanol and H2SO4 (96%) was purchased from RCI Labscan (Thailand).

NG was prepared by pyrolysis of GO and N precursors. Firstly, 0.5 g of GO and 0.6 g of urea were dissolved in ethanol of 30 ml and treated in ultrasonic bath for 30 min [5]. The solvent was evaporated from the mixture on a hotplate at 60-100°C, while the mixture was being stirred until the brown mixture was obtained and become a slurry. Then transferred the mixture to the tube furnace and heated to 300°C and 800°C for 30 min in ultra-high pure N2 gas at heating rate of 2.5°C/min. The products were black sheet. Then were crushed by mortar and denoted as NG300 and NG800.

2.2 Physical characterization
Surface morphologies of N-doped reduced graphene oxide (NG) were investigated by scanning electron microscopy (SEM). The surface elemental compositions were obtained from X-ray photoelectron spectroscopy (XPS) analysis equipped with a monochromatic Al anode.

2.3 Electrochemical measurements
The catalytic activities of the GO and NG catalysts were measured by a bi-potentiostat (Pine Instrument, USA) and rotating-disk electrode (RDE) apparatus at room temperature. The solution of isopropanol (20%) and Naion ionomer (0.02%) is prepared from 20 ml of isopropanol, 79.6 mL of deionized water and 0.4 ml of Naion solution (5 wt%). Next, the preparation of catalyst ink, 10 mg of the catalyst is measured into a 5 ml of the stock isopropanol/Naion solution is added [6]. The 10 μL of catalyst ink (i.e., GO, NG300 and NG800) was dropped to cover the glassy carbon electrode with a geometric area of 0.196 cm² for working electrode. The 3M of Ag/AgCl electrode used as a reference electrode, where the Pt wire was the counter electrode.

Cyclic voltammograms (CVs) were recorded in the potential between 0.05-1.2 V vs SHE and studies at scan rate of 50 mV s⁻¹ in the solution of 0.5 M H2SO4 in flowing of N2 gas. Linear sweep voltammetry (LSV) for ORR analysis measurement was performed between the potential of 0.4 and 1.0 V (SHE) on the RDE in 0.5 M H2SO4 with saturated O2 at a scan rate of 2.5 mV s⁻¹ at 1600 rpm. The CVs were carried on again after the 2,000 potential cycles of LSV. The LSV data was recorded the potential cycles to estimate the stability of the catalysts.
3. Results and discussion

3.1 Physical characterization

The figure 1(a) shows the high-resolution Scanning Electron Microscope (JSM -IT300) analysis (5000× magnification) of single layer graphene oxide (GO). The structure of GO is observed, it is hardly crystalline and many interlayer spacings. In contrast, figure 1(b) and 1(c), graphene sheets are observed, indicate that GO is conversed to rGO at 300°C and 800°C completely and confirming the accomplished synthesis of NG [7].

The electronic state and chemical character of catalysts were explained with XPS spectra as shown in figure 2. The XPS survey spectra of GO, NG300 and NG800 show the elemental of C, N and O. The spectrum shows the peak of C 1s, N 1s and O 1s found that N 1s peak of GO is invisible because there is no urea in the synthesis.

![Figure 1. FE-SEM image of (a) GO, (b) NG300 and (c) NG800.](image)

Table 1 describes the elemental compositions of GO, NG300 and NG800 from XPS analysis. The NG800 had very high carbon that was found to be 88.3% which was more than NG300 (66.5%) and GO (60.5%). On the other hand, the O content of NG800 was the lowest with 7.5%, where NG300 and GO were 17.9% and 39.5% respectively. Result from the high temperature of pyrolysis process can reduce oxygen [8]. The N content of NG300 reaches 15.5%, which is much larger than NG800 (6.6%) and GO without N-doping.

|       | C   | O   | N   |
|-------|-----|-----|-----|
| GO    | 60.5| 39.5| -   |
| NG300 | 66.5| 17.9| 15.5|
| NG800 | 88.3| 7.5 | 6.6 |

The electronic state and chemical character of catalysts were explained by XPS spectra as shown in figure 2. The XPS survey of GO, NG300 and NG800 show the C, N and O composition. The spectrum shows the peak of C 1s, N 1s and O 1s found that the peak of N 1s of GO is invisible because there is no urea in the synthesis.
The C 1s spectra of the GO in figure 3(a) are deconvoluted into three Gaussian peaks, with the 283.0, 285.3 and 286.5 eV of binding energy, which can be interpreted as C-C, C-O-C and C=O group, respectively [9]. The C 1s spectra of NG300 in figure 3(b) with 285.0, 285.8 and 289.0 eV of binding energy can be related to C-C, C-O-C and O-C=O group, respectively. Figure 3(c) shows the C 1s spectra of NG800 that can interpret as C-C, C-O-C group and a shake-up satellite peak (π-π*) with the binding energy of 285.0, 286.0 and 291.5 eV, respectively [10].

Moreover, spectra of three Gaussian N 1s peaks of GO were showed in figure 3(d), with binding energy of 398.0, 399.7 and 400.4 eV, that related to pyridinic N, pyrrolic N and graphitic N respectively. Figure 3(e) shows two peaks of pyridinic N and pyrrolic N for NG300 with binding energy of 398.7 and 400.5 eV, respectively. The N 1s spectra of NG800 shows in figure 3(f) with binding energy of 398.0, 399.0 and 401.2 eV, that were interpreted as pyridinic N, pyrrolic N and graphitic N, respectively. It indicates that graphitic N peak appeared on NG800 probably due to the high temperature reduction step, whereas pyrrolic N was disappeared. The most of all was convert to pyridinic N and graphitic N [11]. The graphitic N will enhance the active regions [12] by improve the conductivity of the materials, which is more transport electrons in the electrode [8].

**Figure 2.** The XPS survey spectra of GO, NG300 and NG800.
3.2 Electrochemical characterization and ORR analysis

The CV of the first cycle from all samples are shown in figure 4(a). The NG300 shows a blunt peak during hydrogen desorption from 0.05 V to 0.30 V at the positive current. After 2,000 cycle of electrochemical cyclic in figure 4(b), the hydrogen desorption peak was significant decreased indicating the loss of catalytic activity. On the other hands, there was no notable peak of hydrogen desorption peak for GO and NG800. It infers that GO and NG800 were not active for the hydrogen oxidation reaction (HOR).

For the oxygen reduction reaction (ORR), the results are illustrated in figure 5. All samples were active for the ORR. As it can be seen, the onset potential of NG800 is higher than the others with $E_{\text{onset}}$ of -0.325 V vs SHE. It indicates that chemical state of Graphitic-N in NG800 are most active for ORR [13]-[15]. Furthermore, NG300 shows the active ORR less than NG300, but higher than GO due to the state of Pyrrolic-N and Pyridinic-N. Although NG300 had more nitrogen than NG800 (more than 2 times), but the ORR activity was lesser. This is mainly due to the influence of Graphitic-N in NG800.
4. Conclusions

In summary, the catalysts of the NG300 and NG800 were prepared by pyrolysis and applied for PEMFCs. In comparison, NG800 and NG300 performed higher ORR onset potential than GO without N-doping. The N-doped reduced graphene oxide from urea indicated enhancement to catalytic activity of ORR. The influences of urea and doping conditions made N atoms occur which plays the role of enhancing active sites by improving the activity of the catalysts. This work opens up a new way to synthesize N-doped rGO, which is promising for PEMFCs may be used alone or combined with other metals for the non-platinum group metal.

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