

## Preparation of non-noble metal based catalysts supported on carbon for PEMFC cathodes

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Since non-noble metal-based catalysts have more activity and selectivity in four electron oxygen reduction than platinum-based catalysts for PEMFC cathodes, the development of non-noble metal-based catalysts has been of interest. Iron-based non-noble metal catalysts were prepared by supporting various oxides and tetraphenylporphyrin complexes of iron on carbon supports by a chemical process followed by heat treatment at various temperatures. Depending on these procedures, Fe<sub>3</sub>O<sub>4</sub> and Fe-tetraphenylporphyrin catalysts supported on carbon were obtained. X-ray diffraction patterns of both Fe<sub>3</sub>O<sub>4</sub> and Fe-tetraphenylporphyrin based catalysts indicated the crystallographic structure of Fe<sub>3</sub>O<sub>4</sub>; however, selected area diffraction patterns obtained from the TEM technique showed the Fe<sub>3</sub>N phase in Fe-tetraphenylporphyrin catalysts supported on carbon. Moreover, TEM images of Fe<sub>3</sub>O<sub>4</sub> based catalysts showed a smaller particle size and more uniform distribution than Fe-tetraphenylporphyrin-based catalysts. Among the catalysts prepared, Fe-tetraphenylporphyrin catalyst supported on carbon with a heat treatment at 600 °C showed the highest electrochemical activity in an oxygen reduction reaction.

**Key words:** Non-noble metal based catalysts, PEMFC, Cathode.

### Introduction

There is now considerable interest in proton exchange membrane fuel cells (PEMFC) as energy producing devices. PEMFCs have unproved a great deal in both performance and applications [1-2]. For application in the field as energy sources for vehicles, stationary electric sources, or even portable devices, and micro fuel cells [3], PEMFCs have advantages over other energy sources due to their high efficiency, high energy density, operation at low temperature, and zero or low emission. However, in the commercialization of fuel cells, a reduction of fuel cell production cost is very important. Due to the high cost of materials, the platinum-based catalyst was one of the major contributors to the high costs of PEMFCs. In particular, in cathodes, the amount of Pt-based catalyst at the cathode for an activate oxygen reduction reaction is ten times more than at the anode. Moreover, a platinum-based catalyst has many drawbacks beside its high cost. Firstly, a platinum based catalyst in the cathode catalyst oxygen reduction is not a complete four-electron oxygen reduction. The oxygen reduction reaction is a complex process [4] as shown in Fig. 1. There are two pathways for the oxygen reduction reaction. A direct four electron oxygen reduction ( $k_1$ )

produces H<sub>2</sub>O, while a two-electron oxygen reduction ( $k_2$ ) produces H<sub>2</sub>O<sub>2</sub> as an intermediate which reduces the performance of the fuel cell and poisons the catalyst itself [5-8]. Therefore, it is necessary to find an effective catalyst that can promote the direct four-electron reduction of oxygen to give H<sub>2</sub>O, in order to improve the efficiency of a PEM fuel cell. Secondly, platinum catalysts are very sensitive to contaminants in the feeding system. The impurities in the feed stream such as CO, NO<sub>x</sub>, and SO<sub>x</sub> can easily poison platinum catalysts, resulting in performance and stability degradation [9-10]. Therefore, some solutions for catalyst cost reduction and improvements in cathode catalysis activity were developed.

The exploration of non-noble catalysts has made breakthroughs in the areas of materials and technology in order to replace the high cost platinum catalyst. There have been many researches attempting to prepare and characterize the non-noble based catalysts. Most of them used first row transition metals in N-containing macrocyclic

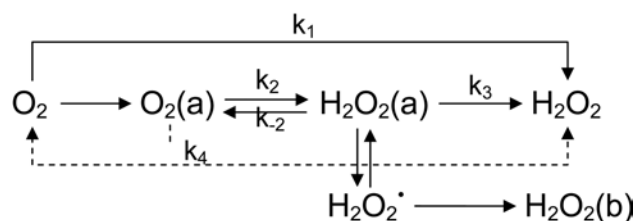


Fig. 1. Oxygen reduction reaction scheme [8].

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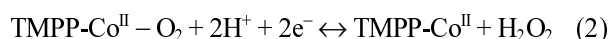
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complexes such as Co-tetramethoxyphenyl porphyrin (CoTMPP) [11], Fe-phthalocyanine (FePC) [12], and Co-tetraazaanulene (CoTAA) [13]. Some researchers have used a combination of oxides or compounds of the first row transition metals and N-containing macrocyclic compounds such as  $\text{Co}_3\text{O}_4$  + tetramethoxyphenyl porphyrin and  $\text{CoCO}_3$  + tetramethoxyphenyl porphyrin [14].

According to the electrocatalytic activity of the metalloporphyrin series, most of them can reduce oxygen to water in the oxygen reduction reaction by a two electron pathway and the byproduct of this reaction is hydrogen peroxide that can corrode the catalyst. Based on the electrochemical characterization by the cyclic voltammetry technique [11] and from the literature [15], the reaction mechanism of the oxygen reduction reaction catalyzed by CoTMPP can be as follows:

In acidic solution



However, many researches have reported that a heat treatment was an efficient way to improve the four-electron catalyst activity and catalyst stability [16-18].

There are several preparation techniques for the heat treatment of metalloporphyrin catalyst. Faubert *et al.* have reported that the preparation of CoTPP/C and FeTPP/C can be done by refluxing FeTPP with a carbon support in anhydrous pyridine and heat treating under an argon atmosphere at temperatures ranging from 100-1100 °C. The results showed that the best performing catalysts were obtained after pyrolysis of the precursor molecules between 500 and 700 °C. With this range of temperatures, the catalytic site is either the N-metal moiety or a fragment of the starting molecule containing the metal bound to nitrogen. The later one is not stable when used as a catalyst in a fuel cell. On the other hand, the most active and more stable catalysts are obtained by pyrolyzing CoTPP/C or FeTPP/C at 900 °C or above. At these temperatures, molecular fragments comprising the metal bound to nitrogen were not detected anymore. Most of the Co and Fe were found as metal clusters surrounded by a graphitic envelope [19]. Mocchi and Trasatti [20] introduced the mechanical mixing of  $\text{CoCO}_3$  with TMPP before heat treatment instead of using the refluxing technique [21]. The results showed that using  $\text{CoCO}_3$  and TMPP instead of the CoTMPP precursor in the carbon-containing mixture exhibited an increase in activity.

The aim of this study is to prepare various non-noble metal-based catalysts for the cathodes of PEMFCs using oxide or N-containing macrocyclic complexes of the first row transition metals such as iron (Fe). The catalysts prepared were expected to have a similar electrocatalytic activity to platinum-based catalyst and can replace it in the cathodes of PEMFCs to solve the commercialized problem. In order to obtain these catalysts, a chemical method

was used to obtain the catalysts supported on high surface area carbon. Then, heat treatment at various temperatures was introduced to obtain the higher active and more stable catalysts. The physical properties of the catalysts were characterized. Powder X-ray diffraction (XRD) was used for the determination of polycrystalline compounds and lattice structures. Transmission electron microscopy (TEM) was used for the determination of the particle size and the dispersion of the catalysts. Moreover, cyclic voltammetry was used for the determination of the electrocatalytic activity of the catalysts prepared compared with platinum-based catalyst.

## Experiments

### Catalysts preparation

#### Preparation of carbon support

In order to obtain clean carbon black N115, carbon black N115 (Thai carbon black public CO., LTD.) was pre-washed with 1 M  $\text{H}_2\text{SO}_4$  (Lab Scan, 98% purity) for 24 hours to dematerialize the carbon impurities and washed in distilled water to remove sulfuric acid and other impurities.

#### Preparation of $\text{Fe}_3\text{O}_4$ supported on carbon support

The  $\text{Fe}_3\text{O}_4$  supported on carbon catalysts were prepared by dispersing 0.4 g cleaned carbon in 50 ml deionized water. Then 0.2531 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (RPE, 98-101% purity) and 1.5 g of glycine (Ultrapur Bioreagent, 101.2% purity) were added to the solution and stirred vigorously until a homogeneous solution was obtained. 1.0 ml of 25%  $\text{NH}_3$  solution (BDH, 25%v/v) was dropped into the solution gradually. After that, the solution was put into a microwave oven (SHARP Model: R-26 PS 800W) for 50 s and the resulting mixture was left to cool down to room temperature gradually. The product particles were collected by centrifugation which were then washed with methanol and dried in an oven at 80 °C for 24 hours. The product was pyrolyzed at 400 °C, 600 °C, and 800 °C in an argon atmosphere for 1 hour. The final catalysts were  $\text{Fe}_3\text{O}_4$  supported on carbon N115 with a heat treatment at 400 °C ( $\text{Fe}_3\text{O}_4/\text{C}$  400),  $\text{Fe}_3\text{O}_4$  supported on carbon N115 with a heat treatment at 600 °C ( $\text{Fe}_3\text{O}_4/\text{C}$  600), and  $\text{Fe}_3\text{O}_4$  supported on carbon N115 with a heat treatment at 800 °C ( $\text{Fe}_3\text{O}_4/\text{C}$  800).

### Preparation of Fe-tetraphenylporphyrin supported on carbon catalysts

#### Synthesis of tetraphenylporphyrin [22]

To obtain tetraphenylporphyrin (TPP), 1.61 g of freshly distilled pyrrole (Fluka, 97% purity) was mixed with 2.55 g of benzaldehyde (Aldrich, 98% purity) and dissolved in 100 ml propionic acid (Fluka, 99% purity). Then, the solution was stirred mechanically in a 250 ml round bottom flask and refluxed in a nitrogen atmosphere for 18 hours. After that, the solution was filtered and washed with methanol and water until a purple product was obtained. Finally, the TPP was kept dried in the dessicator.

### Preparation of Fe-tetraphenylporphyrin

Fe-tetraphenylporphyrin (FeTPP) was prepared by dissolving 0.2 mmol of tetraphenylporphyrin in 15 ml of dimethylformamide (DMF, Carlo Erba, 99.8% purity) to which was added 2 mmol of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (GPR, 99% purity). Then it was stirred until the solution was homogeneous. After that, it was refluxed in a nitrogen atmosphere for 3 hours. Then the solution was left to cool down to room temperature. The product was precipitated out by adding 15 ml of 0.1 M HCl. Then, it was centrifuged and washed with 0.1 M HCl (Merck, 37%v/v). The FeTPP product was a red color and kept dried in a dessicator.

### Preparation of 2% Fe-tetraphenylporphyrin supported on carbon

2% Fe-tetraphenylporphyrin supported on carbon (FeTPP/C) was obtained by dissolving 0.1 g FeTPP in 60 ml DMF. Then 0.4 g carbon was added to the solution and stirred mechanically. The mixture was refluxed in a nitrogen atmosphere for 18 hours and then the mixture was left to cool down to room temperature. The product was recovered by centrifuging and washed with methanol, then the product was kept dry in dessicator. Finally, the FeTPP/C products were pyrolyzed at 400, 600, and 800 °C. The final catalysts for FeTPP supported on carbon were; FeTPP supported on carbon N115 without a heat treatment (FeTPP/C), FeTPP supported on carbon N115 with heat treatment at 400 °C (FeTPP/C 400), FeTPP supported on carbon N115 with a heat treatment at 600 °C (FeTPP/C 600), FeTPP supported on carbon N115 with a heat treatment at 800 °C (FeTPP/C 800).

### Physical characterization of catalysts

The phases and elemental composition of the prepared catalysts were determined by powder X-ray diffraction (XRD, Bruker D8 Advance, Cu  $K\alpha$  line (1.54 Å) Ni filter,  $2\theta = 10\text{--}70^\circ$ ). The dispersion of particles on the carbon support and their sizes were checked using a transmission electron microscope (TEM, JEOL JEM-2010).

### Electrochemical characterization of catalysts

All of the prepared catalysts were electrochemically characterized by the cyclic voltammetry (CV) technique which was performed in a single cell with three different electrodes. A 5 mm dimension glassy carbon disk electrode was used as the working electrode (CH Instruments, Inc.), Pt wire was used as the counter electrode, and a standard Ag/AgCl 3M KCl electrode was used as the reference electrode. The prepared catalyst was applied to the surface of the glassy carbon disk electrode in the form of a constant drop of ink. The ink was prepared by mixing 10 mg of catalyst with 100 mg of Nafion solution and 0.5 ml of deionized water. Then, the mixture was ultrasonically blended for 15 minutes to obtain the ink catalyst. Fifty microlitres of ink catalysts was dropped on the surface of the glassy carbon disk electrode by a micropipette and dried in an oven at 60 °C for 30 minutes. 1 M  $\text{H}_2\text{SO}_4$

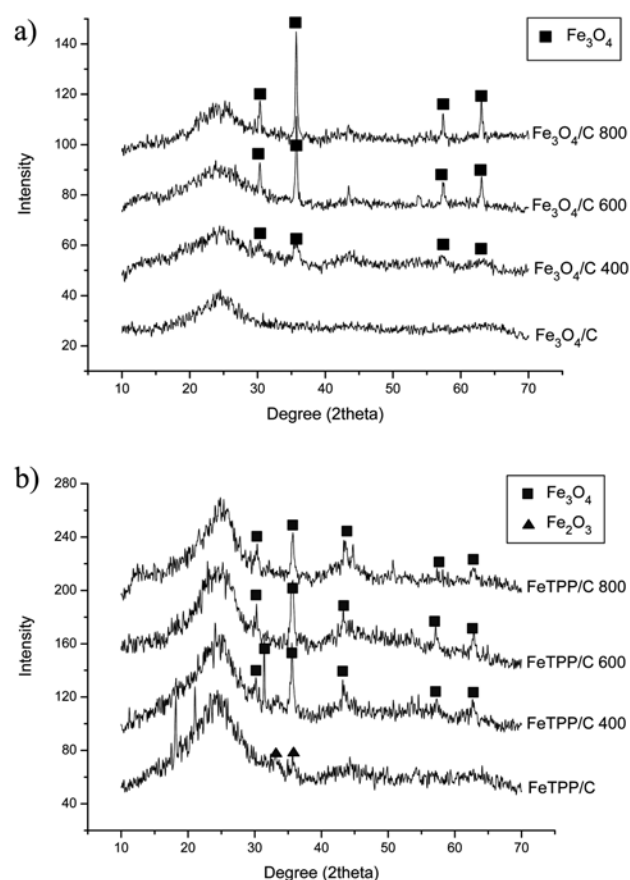
purged with  $\text{O}_2$  was used as the electrolyte and the cyclic voltammogram was recorded by scanning the potential from 1.20 V to  $-0.20$  V versus Ag/AgCl at a scan rate of  $50 \text{ mVs}^{-1}$ . The tenth cycle of each catalyst was recorded.

## Results and Discussions

### Physical characterization of catalysts

#### Powder X-ray Diffraction (XRD) Results

Powder X-ray Diffraction was first introduced to analyze the prepared catalysts in order to identify the elemental composition and their structural type. X-ray diffraction patterns of iron oxide based catalysts are shown in Fig. 2(a) which indicates a typical crystallographic structure of  $\text{Fe}_3\text{O}_4$  (220) at  $2\theta = 30.064^\circ$ , (311) at  $2\theta = 35.452^\circ$ , (400) at  $2\theta = 43.038^\circ$ , (511) at  $2\theta = 57.168^\circ$ , and (440) at  $2\theta = 62.728^\circ$  according to JCPDS number 01-1111. It was observed that the prepared catalysts without heat treatment,  $\text{Fe}_3\text{O}_4/\text{C}$  gave no evidence of the  $\text{Fe}_3\text{O}_4$  structure. The sharper peak at the higher heat treatment temperature as shown in the XRD pattern of  $\text{Fe}_3\text{O}_4/\text{C}$  800 shows a crystalline  $\text{Fe}_3\text{O}_4$  structure, because heat treatment at the high temperature provided sufficient energy that the iron and oxygen ions can slowly arrange themselves to form the crystalline structure on the topmost layer.



**Fig. 2.** XRD patterns of a)  $\text{Fe}_3\text{O}_4$  supported on carbon N115 with different heat treatment temperatures and b) FeTPP supported on carbon N115 with different heat treatment temperatures.

Diffraction patterns of FeTPP based catalysts are shown in Fig. 2(b). The FeTPP based catalysts without heat treatment (FeTPP/C) presented the crystallographic structure of the  $\text{Fe}_2\text{O}_3$  (104) and (110) at  $2\theta = 33.28^\circ$  and  $35.74^\circ$ , respectively, according to JCPDS number 02-0915. The heat treated FeTPP based catalysts (FeTPP/C 600, and FeTPP/C 800) displayed the peaks of  $\text{Fe}_3\text{O}_4$  phase according to JCPDS number 01-1111. However, the pattern from FeTPP supported on carbon N115 with a heat treatment at  $400^\circ\text{C}$  (FeTPP/C 400) corresponded to the  $\text{Fe}_3\text{O}_4$  structure with JCPDS number 02-1053. The typical structure of  $\text{Fe}_2\text{O}_3$  presented in the FeTPP-based catalysts without heat treatment could have occurred between the preparation processes when the reaction was refluxed, and the presence of the  $\text{Fe}_3\text{O}_4$  structure in the heat treated FeTPP might be due to the reduction of the oxidation state of Fe when heat treated in an Ar atmosphere.

### Transmission Electron Microscopy (TEM) Results

The prepared catalysts were characterized by TEM in order to determine the morphology, particle size, distribution, and crystallographic and composition obtained from diffraction patterns of catalysts.

TEM images of  $\text{Fe}_3\text{O}_4$  supported on carbon N115 with a heat treatment at  $600^\circ\text{C}$  ( $\text{Fe}_3\text{O}_4/\text{C}$  600) as shown in Fig. 3(a) gave the particle size and distribution of catalyst particles on carbon supporters.  $\text{Fe}_3\text{O}_4$  supports on carbon N115 with a heat treatment at  $600^\circ\text{C}$  ( $\text{Fe}_3\text{O}_4/\text{C}$  600) showed a small particle size and a uniform distribution; while FeTPP supported on carbon N115 with a heat treatment at  $600^\circ\text{C}$  (FeTPP/C 600) did not give an

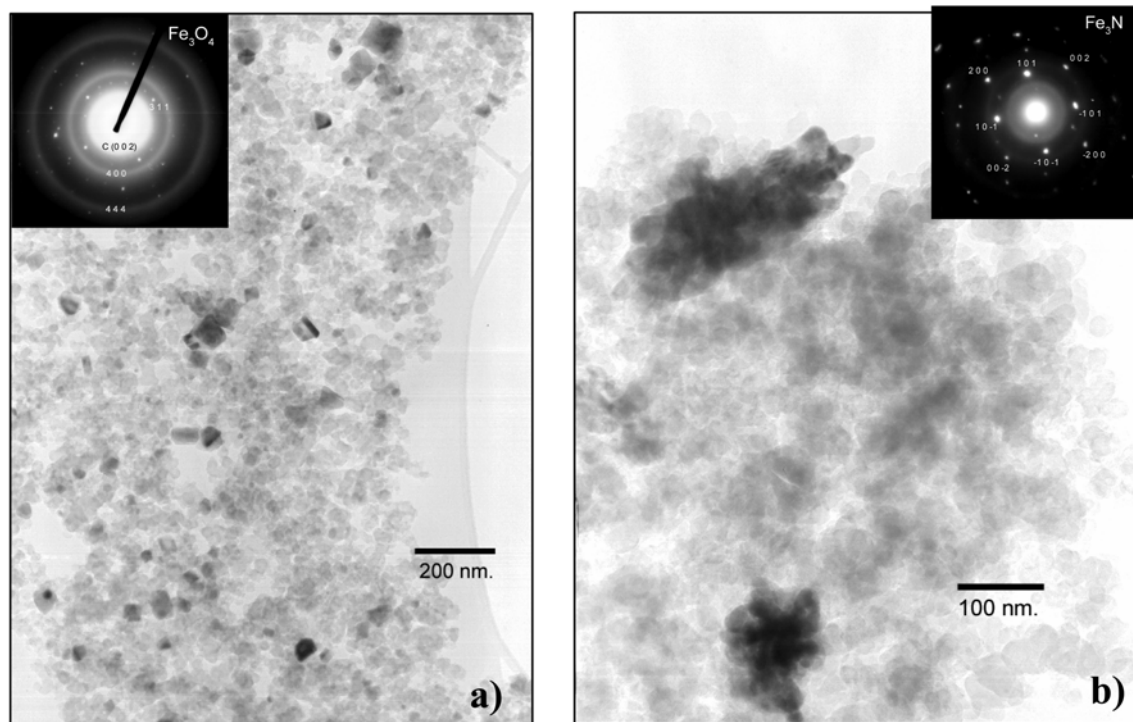
observable the distribution of catalysts particle. The agglomerated particles of FeTPP are shown in Fig. 3(b). The selected area diffraction (SAD) patterns of  $\text{Fe}_3\text{O}_4$  based catalysts displayed the crystallographic structure of  $\text{Fe}_3\text{O}_4$  (Fig. 3(a)) which corresponded to their XRD patterns (Fig. 2(a)). However, the SAD pattern of FeTPP/C 600 indicated the crystallographic structure of  $\text{Fe}_3\text{N}$  (Fig. 3(b)) which did not correspond to the XRD pattern showing the crystallographic structure of  $\text{Fe}_3\text{O}_4$  (Fig. 2(b)). Since XRD is a technique that analyses the composition of matter by detection at a large scale, while TEM with the selected area diffraction technique uses electron beam to analyze the matter at a specific point; therefore, it is possible that the diffraction pattern of some crystallographic structures by the SAD technique may not be present in the pattern obtained from the XRD technique.

### Electrochemical characterization of catalysts

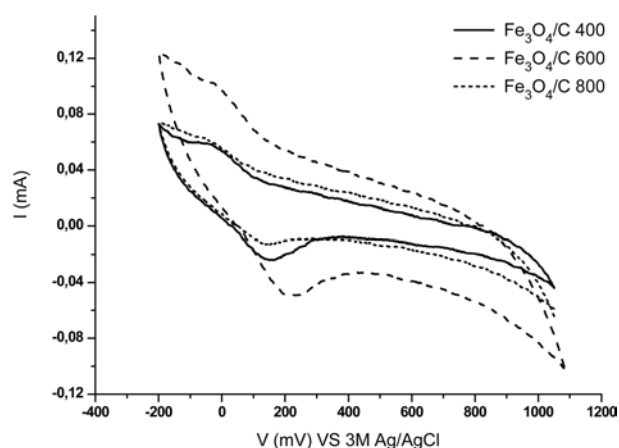
All of the catalysts were tested by CV under the same conditions. The results were compared and discussed in terms of the effects of heat treatment, and types of non-noble catalysts by using the results from the physical characterization to support the results from electrochemical characterization. The reaction that was emphasized was the oxygen reduction reaction which took place around 200-400mV against Ag/AgCl 3 M KCl. The results and discussions of the effects of the parameters are presented below.

### Effects of heat treatment

All of the catalysts were pyrolyzed in an argon atmosphere



**Fig. 3.** TEM images and SAD patterns of a)  $\text{Fe}_3\text{O}_4$  supported on carbon N115 with heat treatment at  $600^\circ\text{C}$  and b) FeTPP supported on carbon N115 with heat treatment at  $600^\circ\text{C}$ .

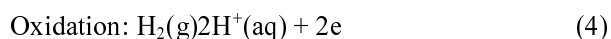
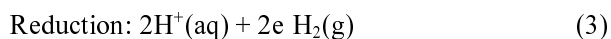


**Fig. 4.** Cyclic voltammograms of  $\text{Fe}_3\text{O}_4$  supported on carbon N115 with different heat treatment temperatures.

at different temperatures in order to study the effects of heat treatment on the physical properties that affected the electrochemical activity of catalyst. The optimum heat treatment temperature of each catalyst is reported and discussed in the following sections.

#### $\text{Fe}_3\text{O}_4$ based catalysts

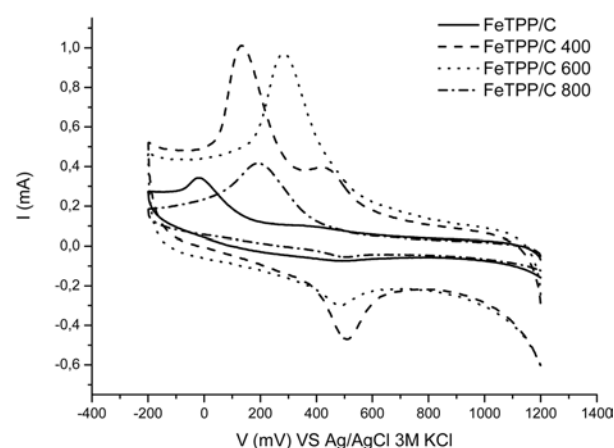
Cyclic voltammograms of  $\text{Fe}_3\text{O}_4$  supported on carbon N115 catalysts ( $\text{Fe}_3\text{O}_4/\text{C}$ ) with different heat treatment temperatures are shown in Fig. 4. This figure presents a reduction reaction peak around 0 mV against Ag/AgCl 3 M KCl and 200 mV against SHE. An oxidation reaction peak was around 97-169 mV against Ag/AgCl 3 M KCl and 297-369 mV against SHE. The various cathodic and anodic currents of the redox peak depended on the heat treatment temperature. The reaction which took place in the oxidation-reduction reaction could be considered to be the following equation [23]:



The results from cyclic voltammograms of  $\text{Fe}_3\text{O}_4$  based catalysts showed that the heat treatment temperature played an important role on the electrochemical activity of catalysts.  $\text{Fe}_3\text{O}_4$  based catalysts with a heat treatment at 600 °C displayed the highest electrochemical activity in the hydrogen oxidation reaction. However, there was no presence of the oxygen reduction reaction in the cyclic voltammograms, which means  $\text{Fe}_3\text{O}_4$  based catalysts did not catalyze the desired reaction.

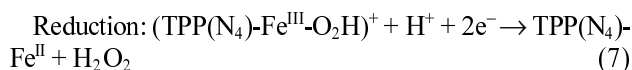
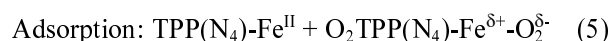
#### FeTPP based catalysts

Cyclic voltammograms of FeTPP supported on carbon N115 at different heat treatment temperatures are shown in Fig. 5. This shows the difference in cathodic potential. It is suggested that heat provided to the FeTPP complexes destroyed the structure of the TPP ring and left partial  $\text{N}_4\text{-Fe}$  moieties which can catalyze the oxygen reduction reaction. The reduction reaction of FeTPP and  $\text{N}_4\text{-Fe}$  moieties was taken via an adsorption and reduction scheme

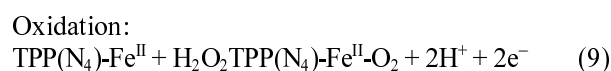
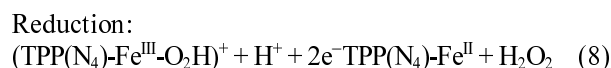


**Fig. 5.** Cyclic voltammograms of FeTPP supported on carbon N115 with different heat treatment temperatures.

as shown in the following equations [24]:



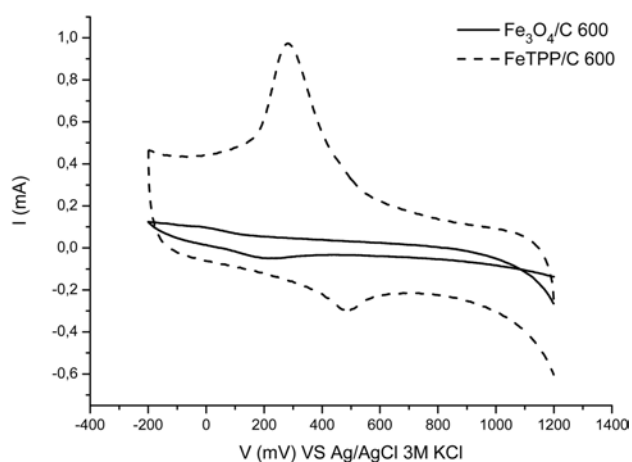
The oxidation reaction peak of FeTPP/C at different heat treatment temperatures presented a similar anodic potential (Epa) which was the reverse reaction of  $\text{H}_2\text{O}_2$  production, the oxidation-reduction reaction are shown in the following equations [24]:



The highest electrochemical activity among the FeTPP/C series was FeTPP/C with a heat treatment at 600 °C, because of the presence of  $\text{Fe}_3\text{N}$  according to the TEM image and SAD pattern (Fig. 3(b)) which gave the evidence that nitrogen bonded with a metal provided an active site for the oxygen reduction reaction. Thus, the presence of  $\text{Fe}_3\text{N}$  provided information that there are nitrogen and iron atoms which can form some active sites for the oxygen reduction reaction. Some researchers [16-18] have reported that heat treatment at an appropriate temperature can improve the electrochemical activity of a metal-macrocylic with nitrogen-containing complexes based catalysts. However, a heat treatment temperature higher than 800 °C lowered the electrochemical activity but raised the stability of catalysts.

#### Effects of types of catalysts

Two types of catalysts have been investigated in term of their electrochemical activity. Metal oxide based catalyst including  $\text{Fe}_3\text{O}_4$  based catalysts and metal-TPP based catalysts including FeTPP based catalysts were examined. Cyclic voltammograms of  $\text{Fe}_3\text{O}_4/\text{C}$  600 °C catalysts and FeTPP/C 600 °C catalysts which gave the highest activity of



**Fig. 6.** Cyclic voltammograms of  $\text{Fe}_3\text{O}_4$  supported on carbon N115 and FeTPP supported on carbon N115 with heat treatment at  $600^\circ\text{C}$ .

each type of catalyst are shown in Fig. 6. This figure contrasts the reaction that took place in each cyclic voltammogram. The  $\text{Fe}_3\text{O}_4/\text{C } 600^\circ\text{C}$  displayed a major oxidation reaction peak and a reduction reaction peak which corresponded to equations 3 and 4. The  $\text{FeTPP}/\text{C } 600^\circ\text{C}$  catalysts presented an oxygen reduction peak via adsorption and the reduction reaction and a minor peak of oxidation that was the reverse reaction of reduction reaction which are presented in equations 5-9. The electrochemical characterization results of  $\text{Fe}_3\text{O}_4$  based catalysts and FeTPP based catalysts can be summarized in that FeTPP based catalysts can catalyze the oxygen reduction reaction via an adsorption and reduction mechanism.

FeTPP supported on carbon N115 with a heat treatment at  $600^\circ\text{C}$  provided the highest activity with  $E_{\text{pc}} = 484 \text{ mV}$ ,  $I_{\text{pc}} = 6.67 \times 10^{-4} \text{ A}$ ,  $E_{\text{pa}} = 684 \text{ mV}$ , and  $I_{\text{pa}} = 1.06 \times 10^{-4} \text{ A}$  against SHE.

## Conclusions

The results can be summarized that  $\text{Fe}_3\text{O}_4$  and FeTPP based catalysts can be prepared by a chemical method and a heat treatment process. The electrochemical activity of the prepared catalysts depends on the heat treatment temperature and type of catalyst. A suitable heat treatment temperature for  $\text{Fe}_3\text{O}_4$  and FeTPP based catalysts was  $600^\circ\text{C}$ . Metal-TPP based catalysts had more activity in oxygen reduction than metal oxide based catalysts. Moreover, FeTPP supported on carbon N115 with a heat treatment temperature at  $600^\circ\text{C}$  (FeTPP/C 600) showed the highest electrochemical activity among all of the catalysts prepared.

## Acknowledgements

This work was supported in part by Thailand Research Fund (contract number MRG5080254), National Metal

and Materials Technology Center, Thailand (MTEC), and Synchrotron Light Research Institute (SLRI). Finally, the Electron Microscopy Research and Service Center is thanked for the electron microscopy facilities.

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