A NEW METHOD TO PREPARE NON-NOBLE METAL BASED CATALYSTS FOR THE REDUCTION OF OXYGEN IN POLYMER ELECTROLYTE FUEL CELLS

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ABSTRACT

Catalysts for O₂ reduction in PEFCs were prepared from the pyrolysis of Fe acetate adsorbed on perylenetetracarboxylic dianhydride in Ar : H₂ : NH₃ ambient. The amount of adsorbed Fe acetate ranged from 0 to 2.56 wt% Fe nominal. Catalysts are obtained when the pyrolysis temperature is at least 800°C, but 900°C gives the best results. RDE analysis demonstrates that the maximum activity is reached at about 0.2 wt% Fe.

INTRODUCTION

Recently, research on developing electrocatalysts to replace platinum at the cathode of PEFCs has centered on the pyrolysis of (Co, Fe)-N₄ macrocycles (tetraazaannulenes, porphyrins and phthalocyanines) adsorbed on high specific area carbon (1-14). Their use in PEFC single electrode membrane assemblies revealed that the highest activities are obtained for products pyrolyzed at about 600°C, but that pyrolysis temperatures exceeding 800°C are necessary to obtain products exhibiting stable currents in a PEFC (15,16). The reason for this behavior is probably related to changes in the nature of the catalytic site at about 800°C (11,15). There is general agreement that the low temperature active site is of the N₄-Metal type (3), while the nature of the high temperature active site is still controversial.

However, it has been shown that electrocatalysts can also be obtained from precursors other than metal-N₄ macrocycles (17-19). Specifically, catalysts are obtained when the following four ingredients are present in the pyrolysis chamber (20-24):

- A transition metal like Fe, Co or Cr.
- A source of nitrogen which may be: (i) a N-containing solid co-adsorbed with the metal precursor; (ii) N groups on a modified carbon support or (iii) a N-containing gas introduced in the reactor.
• A source of carbon (either carbon resulting from the pyrolysis of the molecular precursors or the conducting carbon used to support the catalytic site).
• A high temperature heat treatment (800°C and above). No catalytic properties are observed for instance for Fe(OH)₂ adsorbed on carbon black heat-treated at 600°C in acetonitrile vapour ambient (24).

Up to now, high specific area activated carbons or carbon blacks were always used to support the active site of non-noble metal catalysts for O₂ reduction. One might wonder what kind of catalyst is obtained when the carbonaceous support and the active sites are generated during the same pyrolysis step? To answer this question, various amounts of Fe⁺⁺ acetate adsorbed on perylene tetracarboxylic dianhydride (PTCDA; see Fig. 1) were heat-treated at various temperatures in NH₃ ambient. By adsorbing Fe acetate on PTCDA, the precursor of the carbon support, it is hoped to have a better control on the Fe background content of the carbonaceous support and also to have a more homogeneous distribution of active sites.

**EXPERIMENTAL**

**Preparation of pyrolysis precursors**

PTCDA was washed overnight with a 1:2 solution of d.H₂O and HCl under magnetic stirring to remove the metallic impurities present in the commercial product. The suspension was filtered, rinsed with d.H₂O, and air dried at 75°C. The above steps were repeated twice.

Fe(CH₃COO)₂ was added to suspensions of purified PTCDA in d.H₂O in sufficient quantities to yield Fe concentrations of 0, 50, 100, 200, 400, 800, 1600, 3200, 6400, 12 800, and 25 600 ppm (dry weight basis). The mixture of Fe(CH₃COO)₂, PTCDA, and d.H₂O was stirred for one hour and then placed in an oven at 75°C to evaporate the d.H₂O. The resulting cake composed of Fe(CH₃COO)₂ and PTCDA was ground into a fine powder.

**Pyrolysis of PTCDA powders**

An appropriate amount of the powder was placed in a quartz boat and inserted inside a quartz reactor tube. The tube was purged of air by flowing argon through it for 30 minutes. Next, a 1:2:1 gas mixture of Ar : NH₃ : H₂ was introduced into the reactor and the reactor was placed inside a split oven. Hydrogen was added to ensure reducing conditions inside the reactor. The temperature of the oven was increased to 400°C for one hour to
ensure complete drying and reaction of the powder with the introduced gas. Next, the powder was pyrolyzed by increasing the temperature to 600, 800, 900, or 1000°C and maintained at that temperature for one hour. The usual pyrolysis temperature utilized was 900°C unless otherwise indicated. At the end of this hour, the reactor was removed from the oven and allowed to cool to room temperature under argon only. The product was then removed from the reactor and ground to a fine powder.

Three samples were also prepared using ambients other than the Ar : NH₃ : H₂ mixture. The other ambients used were the following:

1) A (1:1) Ar : H₂ mixture.
2) A (1:1) mixture of H₂ and Ar/CH₃CN vapor. To generate acetonitrile vapor the argon flow was diverted to a bubbler containing acetonitrile at room temperature before being admitted into the reaction chamber.
3) Ar : CH₃CN vapor. As above, except without hydrogen.

Electrode preparation

The catalysts were evaluated in half and full cells. Measurements in half cells were obtained by the rotating disk electrode technique (RDE). Briefly, 16 mg of finely ground catalyst, 0.400 ml of d. H₂O, and 0.400 ml of a 5 wt% Nafion in alcohol-water solution were ultrasonically blended for 10 minutes. Then 10 μl of this suspension were pipetted onto the vitreous carbon disk of the electrode. The suspension was dried in air at 75°C. RDE measurements were performed at room temperature in a three electrode, one compartment cell containing H₂SO₄ (pH = 0.5) as the electrolyte. The electrolyte was saturated with O₂ prior to the start of an experiment.

Measurements in full cells were obtained with gas diffusion electrodes (GDE) in a fuel cell test station. The catalyst suspension consisted of 17.1 mg of catalyst, 0.240 ml of d.H₂O, and 0.240 ml of 5 wt% Nafion solution blended ultrasonically for one hour. The anode consisted of a 1 cm² ELAT electrode catalyzed with 0.37 mg/cm² (20 wt%) Pt from Etek. The cathode consisted of a 1 cm² uncatalyzed ELAT electrode from Etek. On the active side of the cathode was deposited 4 layers of the catalyst suspension. Each layer was applied by pipetting 60 μl of the catalyst suspension onto the cathode. A hot plate was used to accelerate the drying of the catalyst suspension between each application. The anode received one paint brush applied coating of 5 wt% Nafion solution. Both electrodes were then placed in a vacuum oven at 75°C for one hour. A single cell assembly was prepared by pressing a Nafion 117 membrane between the anode and the cathode under 222 bars of pressure at 140°C for 40 seconds.
RESULTS AND DISCUSSION

Actual Fe content of the catalysts

Table I shows the actual Fe contents of the materials prepared in this study. The first rows of Table I concern the pyrolysis of PTCDA + 1350 ppm Fe (1600 ppm Fe nominal) in Ar : H₂ : NH₃ at different pyrolysis temperatures. Rows 5 to 7 of Table I show the effect of utilizing ambients other than NH₃ rich gas on the Fe contents of the products. Pyrolysis at high temperature in Ar : H₂ alone is sufficient to remove some organic material yielding a product with a higher Fe content than the precursor. This may be explained by the sublimation of some PTCDA during the heat treatment and also by the loss of the carboxylic moiety of the molecule during polymerization into carbon fibers occurring at temperatures above 520°C (25). Adding CH₃CN to Ar or to Ar : H₂ attenuates the loss of organic material. This is a consequence of the decomposition of CH₃CN at high temperature and the subsequent deposition of its decomposition products onto the PTCDA during pyrolysis. A similar behavior was observed in a previous study for the pyrolysis of CH₃CN over iron particles supported on carbon black (24).

Adding NH₃ increases the loss of organic material during pyrolysis. It is known that ammonia acts as an etching agent in the treatment of activated carbon. Ammonia treatment not only incorporates nitrogen into carbon but also profoundly modifies the microstructure of the activated carbon treated. This effect is moderate at 600°C and increases with increasing heat treatment temperature (26). The adsorption of Fe salt on PTCDA helps to retain organic matter, as indicated by the larger increase in Fe content after pyrolysis for lower Fe content materials (compare, for instance, 50 or 100 with 25600 ppm). In the remainder of the text, samples will be identified according to their actual Fe contents.

Electrochemical results

Figure 2 presents the cyclic voltammograms for 47±12 and 1030 ppm Fe. The disk electrode is not rotated during the first scan giving only one peak for O₂ reduction in O₂ saturated H₂SO₄. The second scan is recorded at 1500 rpm. It shows an improvement of the reduction current due to an increase of the O₂ available at the electrode in rotation. It is possible to estimate the relative catalytic effect of materials by the voltage at which the maximum reduction current occurs at 0 rpm. Values closest to the theoretical reversible potential of 0.985 V vs SCE for the reduction of O₂ at room temperature indicate superior catalytic activity. The peak value is at 125 mV for 47 ppm Fe and 405 mV for 1030 ppm Fe. Voltages for maximum reduction current are reported in Table II for all samples presented in Table I. Catalytic activities < 0 mV vs SCE are characteristic of very poor catalysts.
These catalysts’ voltammograms show little difference between scans at 0 rpm and at 1500 rpm.

From Table II one may conclude that catalysts for O₂ reduction are obtained for pyrolysis at 800°C and above in Ar : H₂ : NH₃ ambient. Very poor catalytic activity is observed when NH₃ is absent from the gas mixture. This is expected since it has already been demonstrated that a source of nitrogen is necessary during the pyrolysis step to obtain catalytic activity (21). Table II indicates that catalytic activity saturates around 2000 ppm Fe, which corresponds to 0.2 wt% Fe. Below that content, the catalytic activity decreases rapidly with decreasing Fe content. Similar results (a saturation of the catalytic activity at about 0.2 wt% Fe) were obtained when Fe acetate was adsorbed on nitrogen modified carbon black (23). This saturation effect of the Fe content on activity is interpreted as being a change in the role played by Fe: below saturation, Fe is available in its oxidized state for the generation of the active site, while for Fe contents beyond 0.2 wt%, the iron is chemically reduced and aggregates.

Figure 3 presents the GDE polarization curve of the most active catalyst prepared in this study in comparison to the polarization curve of a commercially produced catalyst containing 2 wt% Pt under the same test conditions. The figure reveals that the PTCDA derived product is more active in the kinetically controlled part of the polarization curve (> 0.8 V), whereas the platinum based catalyst performs better at higher current densities. Both catalysts demonstrated stable behavior in a fuel cell cathode environment at 50°C and at 0.5 V vs RHE over a 24 hour test period. In these stability experiments, current densities of 0.24 A/cm² and 0.30 A/cm² were measured for the 0.2 wt% Fe-based catalyst and for the 2 wt% Pt catalyst, respectively. Although the Fe content is only 0.2 wt%, the current density obtained with that catalyst is among the highest measured for Fe-based catalysts prepared in our laboratory.

CONCLUSIONS

1. It is possible to obtain catalysts for the reduction of oxygen in PEFCs by pyrolyzing iron acetate adsorbed on PTCDA in Ar : H₂ : NH₃ ambient. The preferred pyrolysis temperature is, however, 900°C.
2. RDE experiments demonstrate that the catalytic activity increases rapidly with the Fe content and that a maximum in catalytic activity is obtained at about 0.2 wt% Fe. Beyond that value, the catalytic activity remains constant even if the Fe content is increased by one order of magnitude.
3. GDE testing of the catalyst containing 0.2 wt% Fe gives a polarization curve similar to the one obtained in the same experimental conditions with 2 wt% Pt. Stable currents of the order of 0.25 A/cm² have been obtained at 50°C and 0.5 V vs RHE.
Table I.
Determination of the actual Fe contents of Fe acetate adsorbed on PTCDA before and after pyrolysis. Accuracy ± 5% unless otherwise noted.

| Powder & Conditions | Parameters | Actual Fe content before pyrolysis (ppm) | Actual Fe content after pyrolysis (ppm) |
|---------------------|------------|------------------------------------------|----------------------------------------|
| PTCDA + 1600 ppm Fe<sup>III</sup> acetate + Ar : H<sub>2</sub>; NH<sub>3</sub> | 600°C | 1350 | 3480 |
|                     | 800°C | 1350 | 4320 |
|                     | 900°C | 1350 | 4660 |
|                     | 1000°C | 1350 | 4600 |
| PTCDA + 1600 ppm Fe<sup>III</sup> acetate + 1000°C | Ar : H<sub>2</sub> | 1350 | 3840 |
|                     | Ar : CH<sub>3</sub>CN | 1350 | 2610 |
|                     | Ar : H<sub>2</sub>; CH<sub>3</sub>CN | 1350 | 3510 |
| PTCDA + Fe<sup>III</sup> acetate + Ar : H<sub>2</sub>; NH<sub>3</sub> + 900°C | 0 ppm Fe | <35 | 47 ± 12 |
|                     | 50 ppm Fe | 38 ± 12 | 300 |
|                     | 100 ppm Fe | 107 ± 12 | 790 |
|                     | 200 ppm Fe | 210 | 1030 |
|                     | 400 ppm Fe | 370 | 2030 |
|                     | 800 ppm Fe | 740 | 2530 |
|                     | 1600 ppm Fe | 1350 | 4660 |
|                     | 3200 ppm Fe | 2950 | 8100 |
|                     | 6400 ppm Fe | 5500 | 14 660 |
|                     | 12 800 ppm Fe | 11 060 | 25 160 |
|                     | 25 600 ppm Fe | 20 390 | 55 640 |

a: determined by neutron activation analysis at the University of Montreal.
Table II.
RDE analysis of catalysts obtained by the pyrolysis of Fe acetate adsorbed on PTCDA.

| Powder & Conditions | Parameters | O₂ reduction maximum (mV vs SCE) |
|--------------------|------------|----------------------------------|
| PTCDA + 1600 ppm Fe³⁺ acetate + Ar : H₂ : NH₃ | 600°C | <0 |
|                    | 800°C | 400 |
|                    | 900°C | 400 |
|                    | 1000°C | 350 |
| PTCDA + 1600 ppm Fe³⁺ acetate + 1000°C | Ar : H₂ | <0 |
|                    | Ar : CH₃CN | <0 |
|                    | Ar : H₂ : CH₃CN | <0 |
|                    | 47 ± 12 ppm Fe | 125 |
|                    | 300 ppm Fe | 275 |
|                    | 790 ppm Fe | 360 |
|                    | 1030 ppm Fe | 405 |
|                    | 2030 ppm Fe | 450 |
|                    | 2530 ppm Fe | 375 |
|                    | 4660 ppm Fe | 400 |
|                    | 8100 ppm Fe | 375 |
|                    | 14 660 ppm Fe | 375 |
|                    | 25 160 ppm Fe | 375 |
|                    | 55 640 ppm Fe | 400 |
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Figure 1. Structure of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA).

Figure 2. RDE voltammograms (10 mV/s) recorded between 0 and 0.7 V vs SCE for two catalysts at 0 and 1500 rpm. Catalyst A: pyrolyzed PTCDA + 47±12 ppm Fe; catalyst B: pyrolyzed PTCDA + 1030 ppm Fe.

Figure 3. Polarization curves obtained at 50°C in a H₂/O₂ fuel cell using a single cell assembly. PO₂ = 4.14 bars @ 402 cm²/min, PH₂ = 2.07 bars @ 127 cm²/min. Humidifier temperature for both gases = 75°C. Resistances were measured by AC impedance.