Addition of iron (II) phthalocyanine on nitrogen functionalized graphene nanoflakes for catalyst application.

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Abstract: A thermal plasma reactor is used to grow graphene nanoflakes (GNFs), a stack of 5 to 20 graphene sheets generated from the thermal decomposition of methane. The GNFs are then functionalized with a solution of iron (II) phthalocyanine in the same thermal plasma reactor. Iron phthalocyanine molecules are attached to the surface of the GNFs in order to make an atomic dispersion of iron, and turn the GNFs into active catalysts for the Oxygen Reduction Reaction (ORR). The iron content is estimated to go up to 0.46 wt%, but the optimal samples showing the highest ORR performance have an iron content at 0.15 wt%.

Keywords: graphene nanoflakes, thermal plasma, iron (II) phthalocyanine, catalytic sites.

Introduction

Catalysts are a major part of fuel cells, these energy conversion devices consuming hydrogen and oxygen and producing water, heat and electricity. The catalyst facilitates mostly the oxygen reduction reaction (ORR) at the cathode, and replacing the platinum based catalyst by a corrosive resistant and non-noble catalyst are major issues for fuel cells market.

In 1964 Jasinski observed that iron phthalocyanine were highly active in the ORR [1], but poorly resistant to the corrosive environment of a fuel cell. Studies showed the advantage of creating catalytic sites by incorporating the iron phthalocyanine molecule in various carbon-based matrices resistant to both acidic and basic conditions [2], including graphene sheets [3]. These studies however generally use carbon-based material with poor crystalline structure, such as graphene oxide, preventing the stability of such catalysts in corrosive environment. Following the work of Pristavita on graphene nanoflakes (GNFs) [4], this work focuses on the direct addition of iron (II) phthalocyanine solution in the thermal plasma conditions as a functionalization step to add catalytic sites on the GNF surface.

Methods

A. *Catalyst synthesis*

The GNFs are grown following Pristavita et al. procedure [4], using methane decomposed by the argon thermal plasma in an inductively coupled plasma (ICP) torch at a temperature of approximately 10,000 K. Carbon atoms form nuclei under homogeneous nucleation and grow into well-crystallized graphitic nanoparticles when the plasma is cooled down to 3700 to 4900 K [5]. The high crystallinity of the GNFs comes from the axisymmetric conical shape of the thermal plasma, preventing gas recirculation as well as the formation of amorphous carbon. Then, the GNFs are deposited on the walls and the bottom plate by thermophoretic force. Nitrogen is added using a small flow rate (0.1 slpm) during the GNFs growth, leading to nitrogen content up to 2 at% at the surface of the nanoparticles.

The iron functionalization step is performed by changing the gas feeding conditions, where the methane and nitrogen gases are stopped, and an iron (II) phthalocyanine solution is introduced in the argon-based thermal plasma reactor. The solution is made with iron (II) phthalocyanine powders (Sigma Aldrich) and distilled water at a concentration of 5 mg/mL. The solution is injected through a side window of the thermal plasma reactor located 9 cm downstream of the ICP torch nozzle in a colder region of the conical reactor. The droplets are carried by nitrogen gas at a flow rate of 5 slpm and are fed using a 20 mL stainless steel syringe from Chemyx where the flow rate is controlled by an electronic push-syringe. The liquid flow rate is chosen to be 1 or 5 mL/min to vary the quench rate of the liquid feed and its influence on maintaining the phthalocyanine structure.

The total volume of iron (II) phthalocyanine solution injected during the functionalization step is also studied. The total volume injected can have an impact on the total amount of functionalities added to the surface of the nanoparticles, potentially resulting on higher ORR performances for the resulting catalysts.

The pressure in the reactor, as well as the power delivered to the ICP torch were adjusted using two sets of coupled conditions: 20 kW/55.3 kPa and 25 kW/13.8 kPa. Extensive modelling of the temperature and flow fields in the reactor [6] indicated that both conditions exhibit similar temperature profiles: the plasma (generated in the ICP torch) enters the conical reactor at approximately 10,000 K to be cooled down to 300 K in the vicinity of the water-cooled walls and the bottom collecting plate. However, the two coupled conditions differ in their velocity profile. The plasma at 25 kW/13.8 kPa reaching a maximum velocity of 160 m.s-1 presents velocities four times greater than the 20 kW/55.3 kPa [6]. The difference in these velocities implies that the time where the solution is vaporized and the phthalocyanine molecule is potentially decomposed is shorter for the 25 kW/ 13.8 kPa condition. The experimental conditions are summarized in Table 1.

Table 1: Experimental conditions of the N-Fe/GNFs synthesis.

Sample Name	Liquid flow rate (mL/min)	Pressure/Power Conditions	Total volume injected (mL)
N/Fe-GNF1	1	20 kW / 55.3 kPa	05
N/Fe-GNF2	5		
N/Fe-GNF3	1	25 kW / 13.8 kPa	
N/Fe-GNF4	5		
N/Fe-GNF5	1	20 kW / 55.3 kPa	10
N/Fe-GNF6	5		
N/Fe-GNF7	1	25 kW / 13.8 kPa	
N/Fe-GNF8	5		

B. Physical characterization

After synthesis, the powders are collected and analysed. The N-Fe/GNFs are observed by Transmission Electron Spectroscopy (TEM) on a FEI Tecnai G2 F20 200 kV Cryo-STEM. The elemental composition of the N-Fe/GNFs is determined by X-ray Photoelectron Spectroscopy (XPS) on a Scientific K-Alpha XPS from Thermo Scientific using an aluminium x-ray source on 400 µm spot size area. The total amount of iron contained in the N-Fe/GNFs has been determined by Neutron Activation Analysis (NAA) on the SLOWPOKE nuclear reactor, an Ortec GEM30185-P germanium semiconductor gamma-ray detector, an ortec DSPEC ProTM multichannel analyser, a Sartorius precision balance and the EPAA analysis software [139]. The NAA has been conducted at the SLOWPOKE Laboratory of the Institute of Nuclear Engineering located at École Polytechnique de Montréal.

C. Electrochemical characterization

The electrocatalytic activity of the N-Fe/GNFs is studied through Rotation Disk Electrode RDE) technique. The catalysts are suspended in an ink that consists of the powder, a solvent made of 70 wt% of isopropyl alcohol and 30 wt% water, and a 5 wt% Nafion© solution purchased at Sigma Aldrich. After sonication for 1h in an ice bath, the ink is then deposited on a 5 mm diameter glassy carbon electrode to obtain a thin and homogenous deposit of 0.1 mg·cm-2 of catalyst. The alkaline solution consists in a 0.1 M KOH solution having a pH of 13. The electrode is immersed in the alkaline solution and rotated at 1600 rpm when Linear Sweep Voltammetry (LSV) is performed against a silver/silver chloride (Ag/AgCl) reference electrode and a platinum wire counter electrode. The catalysts pass first through a conditioning protocol based on loops between -1 and +1 V at a scan rate of 500 mV·s^{-1} under N2 bubbling until the LSVs do not shown any variation. The aim of this process is to remove any impurities from the electrode surface and allow the maximum utilization of the electrocatalytic area [7]. The LSVs are then recorded under O2 bubbling between +1 and -1 V, cathodic sweep, at a scan rate of 20 mV·s^{-1} to evaluate the ORR performance. The contribution of the capacitive current is subtracted from the measurements by recording LSVs under N2 bubbling with the same conditions. The potential is converted from Ag/AgCl to Reversible Hydrogen Electrode (RHE) using Equation 1.

$$E_{RHE} = E_{Ag/AgCl} + E^{0}_{Ag/AgCl} + 0.059\,pH \qquad \text{Equation 1}$$

where $E^{0}_{Ag/AgCl}$ is the standard potential for Ag/AgCl electrode and equal to 0.1976 V.

Results and discussion

A. Chemical composition of the N/Fe-GNFs

The surface of the samples was analysed by XPS. From the spectra shown on Figure 1, the samples appear to be composed of carbon, nitrogen and oxygen with respective amounts summarized in Table 2. The presence of iron is not confirmed by XPS.

A closer inspection of the high resolution peaks of carbon, nitrogen and oxygen gives some insight on the chemical bonding in the samples. Carbon is mostly in its sp2 form, characteristic of the asymmetric XPS peak at 284.4 eV. Functionalities of nitrogen and oxygen are attached to the carbon, at respectively 286.0 and 287.5 eV [8]. The oxygen functionalities are involving C-O and C=O bonds, at 531.6 and 532.9 eV [9]. Also, some nitric oxide functionalities are found at 534.2 eV. The oxygen functionalities originate mainly from the water based solution, where water molecules are decomposed by the thermal plasma and form species which react with the surface of the deposited GNFs. Four different types of nitrogen functionalities are found in the N/Fe-GNFs [10]. Oxidized nitrogen is found at 402.2 eV and confirms the observation based on the oxygen peak. Quaternary nitrogen at 400.9 eV corresponds to atoms of nitrogen substituting an atom of carbon in the graphitic structure. Pyrrolic nitrogen at 399.9 eV is the type of nitrogen found in the phthalocyanine molecule and represents between 35 and 50% of the total nitrogen for the samples. Pyridinic nitrogen is found at 398.9 eV. Both pyridinic and pyrrolic nitrogen have the potential to form catalytic sites. The nitrogen functionalities originate from the phthalocyanine molecules themselves, but also from the nitrogen gas used to carry the injected solution during the functionalization step.

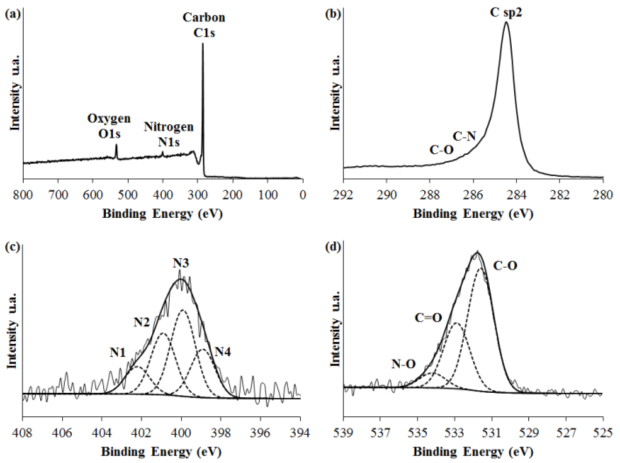

Figure 1: (a) Typical XPS survey obtained for N-Fe/GNF7. High resolution peaks of (b) carbon C1s, (c) nitrogen N1s, (d) oxygen O1s for the sample N-Fe/GNF7. N1, N2, N3 and N4 respectively correspond to oxidized, quaternary, pyrrolic, and pyridinic nitrogen.

By inspecting the elemental composition of the samples, it appears that the samples functionalized under the 25 kW/13.8 kPa conditions (N-Fe/GNF3,4,7,8) generally contain more nitrogen and oxygen functionalities than the samples functionalized with the 20 kW/55.3 kPa conditions (N-Fe/GNF1,2,5,6). This trend has been already confirmed by previous studies and come from the much shorter transit time of the flow stream between the higher temperature plasma region and the deposited GNFs of the 25kW/13.8 kPa conditions. This allows more reactive species to reach the deposited GNFs and then a higher functionalization rate [6]. However, the elemental composition also shows that the samples functionalized with 10 mL of iron (II) phthalocyanine have smaller amounts of nitrogen and oxygen compared to the samples functionalized with 5 mL of solution. This observation contradicts the intuitive hypothesis that adding a higher volume of solution would increase the level of functionalization. It however goes along the influence of the temperature and flow profiles modifications generated by the phthalocyanine solution injected.

Table 2: Elemental composition of the N-Fe/GNFs surface.

Samples	Carbon (at%)	Nitrogen (at%)	Oxygen (at%)
N-Fe/GNF1	90.87	2.96	6.17
N-Fe/GNF2	89.96	4.71	5.33
N-Fe/GNF3	87.40	4.76	7.83
N-Fe/GNF4	90.55	4.29	5.16
N-Fe/GNF5	93.28	1.92	4.80
N-Fe/GNF6	96.12	1.13	2.75
N-Fe/GNF7	91.63	2.72	5.65
N-Fe/GNF8	90.17	4.30	5.53

The iron amount being too low to be detected by XPS, NAA has been used to determine the total weight of iron contained in the N-Fe/GNFs. Based on the previously established elemental composition, the iron concentration has been converted from wt% to at%. This conversion requires to assume the surface composition and the bulk composition are identical; this may not be completely true because functionalization occurs mostly on the surface of the nanoparticles. However, the depth of penetration of the x-rays used in the XPS technique (~5-10 nm) being higher than the thickness of the GNFs and the small difference in molecular weight between carbon, nitrogen, and oxygen, the conversion is estimated to give acceptable values of iron concentration in at%. These values are lower than or equal to 0.1 at%, confirming the impossibility to detect iron by XPS.

Table 3: Iron level in the N-Fe/GNFs and conversion to an elemental composition.

Samples	Fe concentration (wt%)	Converted concentration (at%)
N-Fe/GNF1	0.17	0.04
N-Fe/GNF2	0.14	0.03
N-Fe/GNF3	0.15	0.03
N-Fe/GNF4	0.39	0.09
N-Fe/GNF5	0.06	0.01
N-Fe/GNF6	0.16	0.04
N-Fe/GNF7	0.17	0.04
N-Fe/GNF8	0.46	0.10

B. Observation of the N/Fe-GNFs

The N-Fe/GNFs are observed using electron microscopy, and the sample containing the highest amount of iron, N-Fe/GNF8, is represented on Figure 2. The samples contain no amorphous carbon, which typically exhibits a cauliflower-like structure [11], this being confirmed by the shape of the carbon peak in XPS. Also, the absence of iron oxide nanoparticles has been confirmed in all of the observed samples, mostly by TEM. This observation confirms the hypothesis that the iron phthalocyanine molecule can be incorporated to the GNFs without being decomposed and forming sub-products such as amorphous carbon and iron oxide nanoparticles.

C. Electrocatalytic activity of the N/Fe-GNFs

The N-Fe/GNFs are tested through the RDE technique to evaluate their respective electrocatalytic activity, in terms of onset potential, half-wave potential and limiting current density, measured at 0.4 V vs RHE. The onset potential is the potential where the current density starts to decrease and is no longer equal to 0. The onset potential for platinum based catalysts is generally between 0.8 and 0.9 V vs RHE, while the onset potential of non-functionalized graphene nanoflakes is closer to 0.7 V vs RHE. The half-wave potential is the potential at which the current density is equal to half of the limiting current density and denotes the sharpness of the LSV, related to the kinetics of the ORR. The limiting current density is directly proportional to the rate of reduction of oxygen. The LSVs of some typical samples compared to non-functionalized GNFs are shown in Figure 2, while the numerical values of onset potential, half-wave potential and limiting current density are summarized in Table 4.

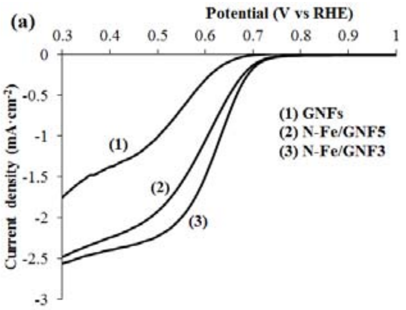

Figure 2: LSV of two typical catalysts compared to the non-functionalized GNFs.

Table 4: Quantitative evaluation of the electrocatalytic activity of N-Fe/GNFs through the onset potential, the half-wave potential and the limiting current density.

Sample	Onset Potential (V vs RHE)	Half-Wave Potential (V vs RHE)	Limiting current density @0.4V (mA.cm^{-2})
GNFs	0.66	0.55	-1.38
N-Fe/GNF1	0.73	0.62	-2.35
N-Fe/GNF2	0.73	0.59	-2.31
N-Fe/GNF3	0.74	0.62	-2.40
N-Fe/GNF4	0.73	0.62	-2.27
N-Fe/GNF5	0.73	0.60	-2.25
N-Fe/GNF6	0.74	0.61	-2.34
N-Fe/GNF7	0.73	0.60	-2.38
N-Fe/GNF8	0.74	0.63	-2.23

The overall ORR performances of the N-Fe/GNFs remain in a close range of values. The onset potential values of the N-Fe/GNFs are comprised between 0.73 and 0.74 V vs RHE, which shows an improvement compared to the non-functionalized GNFs. However, these values are still around 0.1 V lower than the onset potential of platinum based-catalyst. Due to close range of onset and half-wave potential, the best parameter to compare the ORR performances of the N-Fe/GNFs is the limiting current density. The sample showing the best performance is N-Fe/GNF3, with a limiting current density of -2.40 mA·cm-2. From the composition of the N-Fe/GNFs, this sample is containing one the highest amount of nitrogen with a particular strong proportion of pyrrolic nitrogen. Aside from the nitrogen level, N-Fe/GNF3 show a low level of iron (0.15 wt%), indicating that optimal iron content is not always the highest, as several studies suggest [12]. N-Fe/GNF3, and the other samples functionalized with the 25 kW/13.8 kPa have globally better performances than the one functionalized with the 20 kW/55.3 kPa and correspond to samples which have a higher amount of functionalities, as observed in the chemical composition section. The flow rate had no real impact on the composition of the samples, and the same observation can be done on the ORR performance of the catalysts. A lower volume of solution was related to higher functionalization rates, resulting in slightly better ORR performance for the samples N-Fe/GNF1,2,3,4.

Conclusion

Graphene nanoflakes have been grown and functionalized with iron (II) phthalocyanine to create catalytic sites based on the atomic dispersion of iron on the surface of the GNFs. Previous attempts to atomically incorporate iron by thermal plasma lead to the formation of iron oxide nanoparticles, but the method used in the present study showed no presence of iron oxide nanoparticles. The effective presence of iron has been confirmed by NAA, at amounts lower than the detection limit of the XPS technique. The resulting catalysts see their overall ORR performances increase after the addition of iron (II) phthalocyanine, the best results being observed for 0.15 wt% of iron in the sample.

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