7. Plasma Modified CB as catalyst for oxygen reduction in PEMFC

Due to their high specific surface area, carbonaceous materials have been used as catalysts support material for a long time in various applications. However, the high electrical conductivity presented by carbon black because of its surface graphitic structures, makes it the best candidate in applications in which this property is required. An example of one of such applications are Oxygen Reduction Reaction (ORR) catalyst utilised in Fuel Cells.

Fuel Cells and more precisely Polymer Membrane Fuel Cells (PEMFC) are becoming nowadays one of the candidates in order to substitute oil injection engines in transport applications. The evidence of a need for oil substitution is clear being the two main reasons the future oil depleting and the climate change produced by the oil burning emissions.
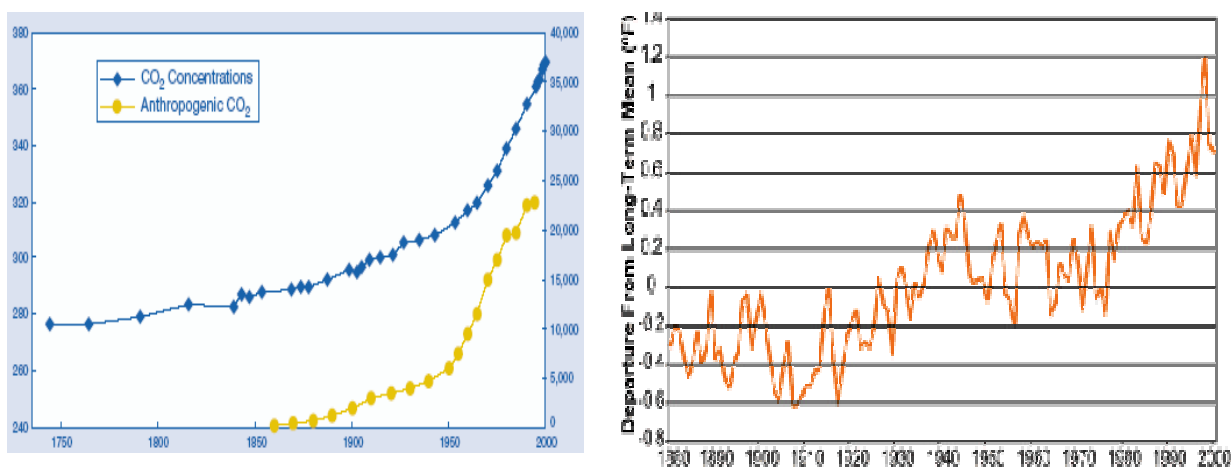

Fig.7. 1 Increase of atmospheric CO2 levels and temperature during last centuries (left and right respectively)
(http://www.epq.gov.com)

Although there is not a complete agreement about the earth heating process and velocity, it has been proved that greenhouse effect gases concentration in the atmosphere do have increased steeply during the last 50 years as it is shown in Fig.7. 1, while a temperature rise has also been detected. At this point it is remarkable to notice that CO_2 is the greenhouse gas presenting a higher atmospheric level and contributing to an 85% of the total greenhouse gases (Fig.7. 2). Therefore the decrease of CO_2 becomes a necessity in order to slow down the temperature increase of the earth.
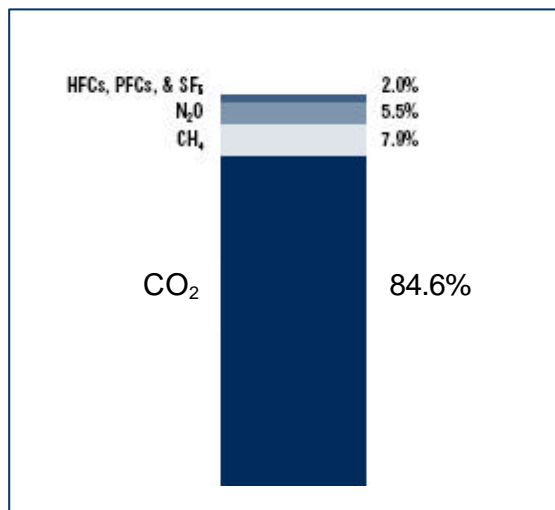
Fig.7. 2 Greehouse gas emissions by gas (2004).
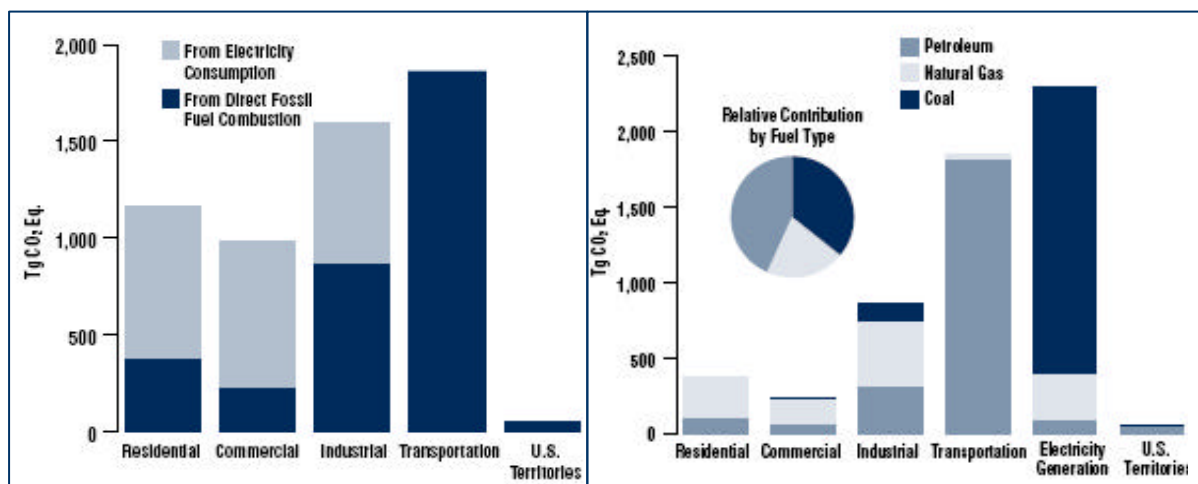(Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2004)

Fig.7. 3 a) End-Use Sector Emissions of CO_2 from Fossil Fuel Combustion (2004) b) CO_2 Emissions from Fossil Fuel Combustion by Sector and Fuel Type (Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2004)

Moreover, Fig.7. 3 remarks the high contribution of transport applications to the CO_2 emissions due to oil burning in injection engines for transportation. In conclusion whatever reason is taken into consideration, global warming or oil reserves an alternative power device in order to obtain energy for transport applications is required.

One of the most environmental friendly options for such application is found in Fuel Cells. Among the several types of fuel cells widely described in literature, Polymeric Membrane Fuel Cells (PEMFC) are presented as the best candidates due to its low temperature condition and low weight which make them very suitable for transport and portable applications.

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However, PEMFC still need some development in order to be fully used in commercial applications such as vehicles. High prices together with the need of better efficiencies are the main drawbacks that need to be solved.

7.1 Introduction to PMFC catalysts

It has just been said that the high price is one of the factors which plays a very important role in detriment of PEMFC use in transport applications. One of the parts affecting the most the final price of these devices is the catalyst which is present both at the anode and cathode of PEMFC. Contrary to the price for polymeric membranes, which could be reduce by scaling up production costs, actual catalysts price mainly obtained from noble metals would not be affected by increasing production levels.

But why it is necessary to use a catalyst in a PEMFC? This type of FC is restricted to work at low temperatures, normally at 80ºC, due to the presence of the polymeric conductive membrane which separates the cathodic and anodic reaction. These membranes should be permanently hydratated in order to be able to transport the protons resulting from hydrogen oxidation that takes place in the anode, to the cathode where they will recombine with the oxygen to form water as presented below in the reaction taking place in a PEMFC. During this process electrons are transported from the negative electrode, the anode, to the positive electrode, the cathode, giving energy through an external circuit (Fig.7. 4)

Global Reaction:

$$2 H_2 + O_2 \rightarrow 2 H_2O$$

Anode Reaction:

$$2 H_2 \rightarrow 4 H^+ + 4 e^-$$

Cathode Reaction:

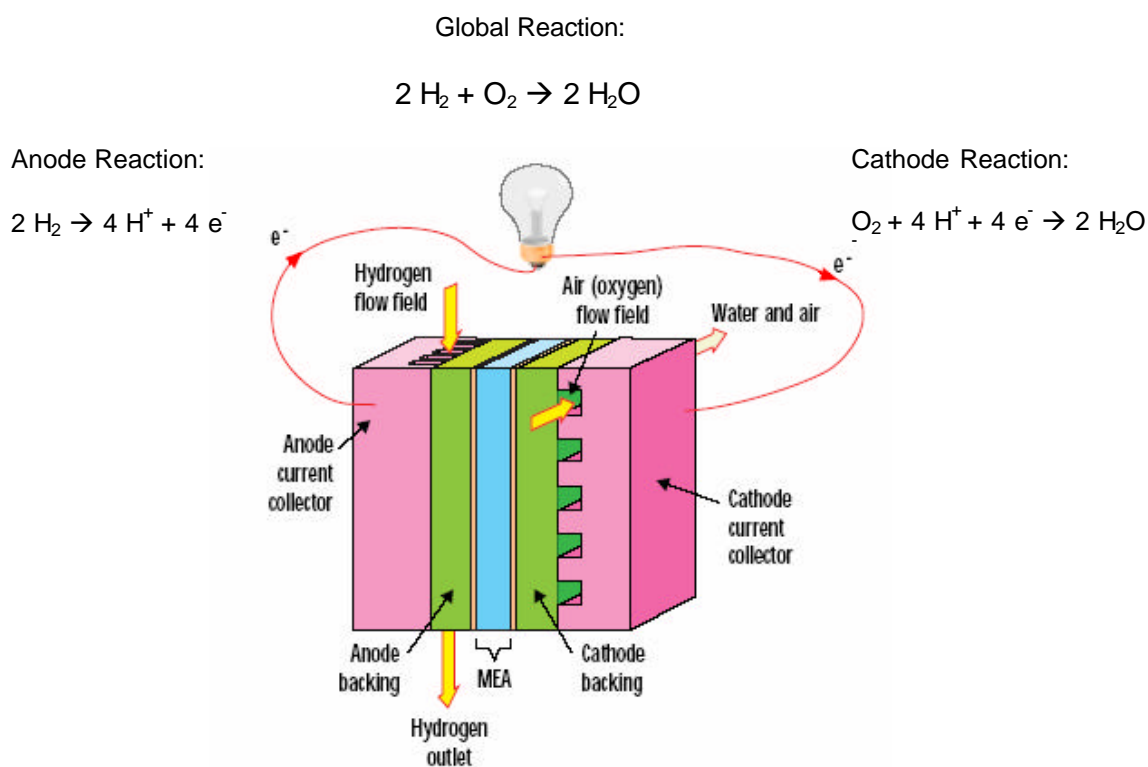$$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$$

Fig.7. 4 Scheme of PEMFC from S. Thomas et. al 1998

However, as it has been presented, due to these temperature restrictions the above mentioned process would not take place without the presence of a catalyst, being platinum the most common used catalyst nowadays. This material presents both good resistance to PEMF's acidic media as well as good catalytic properties at least as far as the anode reaction is concerned. When the oxygen reduction reaction (ORR) in the cathode is taken into consideration the catalytic capacity decreases due to a higher overpotential. This is the reason why platinum load is four times higher in the cathode than in the anode of PEMFC.

But not only platinum's high price and ORR activity are responsible for the will of a new catalyst, the scarcity and geographical location of this metal, which is practically only found in South Africa and Russia do not neither help to its usage in high volume applications such PEMFC for transportation. As a consequence, if platinum could be avoided as catalyst of oxygen reaction and replaced by a more efficient, cheaper and more available material the used of PEMFC could be much more easily extended.

Many efforts have been made in order to improve and obtain new ORR (B. Wang 2005, H.A. Gasteiger 2005). Some of them do not avoid the use of platinum but consider the approach of decreasing the loading of this catalyst (H.A. Gasteiger et al. 2004). In order to accomplish this goal the contact between the platinum surface and the reactive species should be maximized. Other studies are focused in obtaining alloys such as PtNi, PtCo or PtCr (S. Mukerjee et al. 1993).

But there is also the possibility to avoid the use of noble metals to obtain ORR catalyst. In this case the catalyst are based in metal chalcogenides (N.A. Vante et. al 1987 , I. V. Malakhov. 2000) and macrocycles containing Nitrogen-Metal coordination compounds as it was found almost 50 years ago (R. Jansinsky 1964). Some of the macrocycles presenting ORR activity are shown in Fig.7. 5).

Despite of their nature, all mentioned catalyst have a common point: in order to include the material in the PEMFC structure, the catalyst is dispersed on a carbon black support. The most popular and extended carbon black used in this application is Vulcan XC 72 that has been already presented in this work. The idea of creating ORR active sites on the surface of the carbon support seems to have a lot of advantages for the final application such as improving the electron transport due to the lack of metal-support interaction problems as well as to facilitate the electrode preparation procedure. Taking in consideration the mentioned facts the idea of using N-macrocycles or even better trying to obtain similar structures on the surface of the carbon support seems a very encouraging idea to reduce the price of ORR catalysts. These types of catalysts have also been claimed to present a higher resistance to methanol poisoning which could be very beneficial in order to use methanol as fuel in transport applications (G.Q. Sun et al. 1998). Therefore, this work is focused in improving the properties of such existing catalyst.
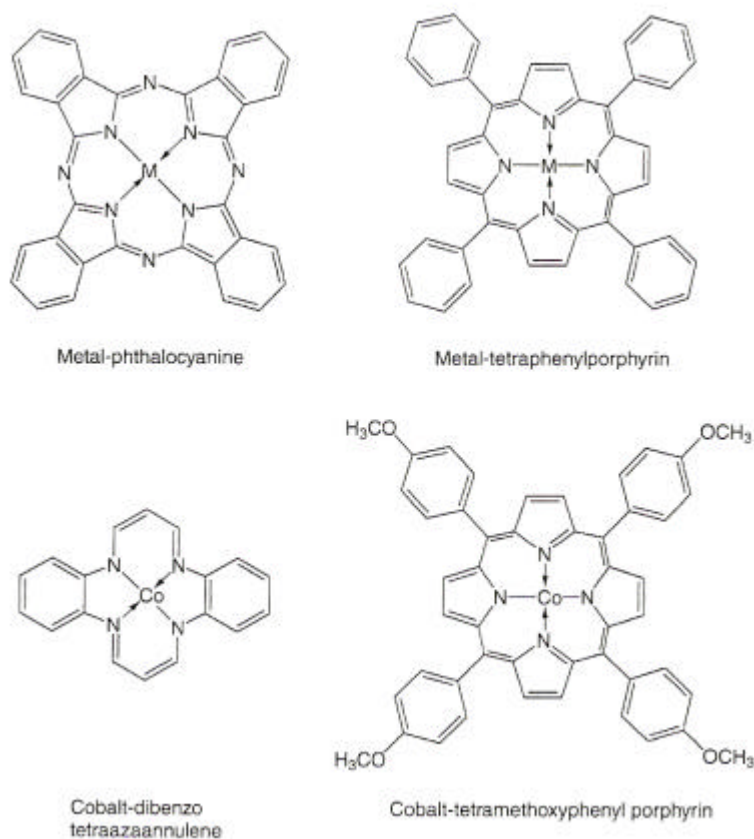
Metal-phthalocyanine   Metal-tetraphenylporphyrin

Cobalt-dibenzo   Cobalt-tetramethoxyphenyl porphyrin
tetraazaannulene

Fig.7. 5 Metal N-Macrocylces presenting ORR activity (J.H. Zagal 2003).

7.1.1 M-N-Macrocycles as ORR catalysts: State of the art

A brief introduction to the state of the art for metal coordinated and similar types of ORR catalysts is presented in order to better comprehend the finality of this study and its contributions.

As it has been already stated, the ability of N-containing macrocycles to act as catalyst for ORR is known for a long time. Many studies using several coordination metals supported on carbon have been described finding activity and mechanistic differences (Z. Zagal et. al 1980, A. Elzing et al. 1987, J.A.R Van Veen et al. 1988, C. Shi et al. 1998, B.Steiger et al 1997). However, one of the main problems of these type of structures is their low stability. Not very long after these compounds started to be studied as ORR catalyst it was found that after exposing these materials to a heat treatment step the stability was highly improved (Jahnke et al. 1974).

Many studies have been carried out to find the optimal conditions (pyrolisis temperature and macrocycle loading) in order to obtain maximum catalyst activity (J. Van Veen et. al. 1988, A. Van der Puten et al. 1986, G. Lalande et al. 1995, G. Faubert et al. 1998). Usually, the heat N-macrocycle treated catalysts are obtained in a temperature range from 600 to 1000ºC in an inert atmosphere such as Ar or in a mixture of Ar:NH$_3$. Various

studies also observed that although more active sites were obtained for a pyrolisis step below 700ºC a higher stability during working conditions was obtained for pyrolisis temperatures above 800ºC (G. Lalande et al. 1995, H. Schulengburg et al 2003).

Several research groups have also studied the evolution of the macrocycle during the heating process. For example Prof. J.P. Dodelet and coworkers described the following steps taking place during the pyrolisis treatment of adsorbed (G. Lalande and J.P Dodelet 1995):

- 220-300ºC dehydration due to adsorbed solvents and N-Macrocycle polymerization.
- 400ºC: completion of the polymerization reaction, polymer is stable up to 500-600ºC, CO and are also detected CO_2 due to decarboxylation
- 700ºC: Organic fragments are released from the carbon support
- 1000ºC: although Co is still detected no signal of the N-macrocycle is found

P. Gouérec and M. Savy also confirmed that the structure of the Co coordinated N-macrocycles was maintained up to 600ºC and that it disappeared completely when temperature raised above 800ºC (P. Gouérec et al. 1999). M. Bron et al. studied the pyrolysis of adsorbed iron phenantroline by means of Thermogravimetry/Mass Sectrometry studies. It was observed that when the iron salt (iron sulphate) was not adsorbed before the heat treatment, phenantroline decomposed during the pyrolysis but it remained on the surface if the salt was also adsorbed prior to the heat treatment (M. Bron et al. 2002a).

Some years after, a very important new step forward was made when it was shown that the ORR catalytic properties of the M-N-macrocycles supported on carbon materials could also be obtained when using separate nitrogen and metal precursors. In this case the carbon structure of the support itself will be involved in the formation of the final ORR active site. It was confirmed that the presence of both Nitrogen and Iron was needed on the surface of the carbon in order to catalyze the ORR (G. Lalande et al. 1997).

Usually NH_3 or Acetonitrile are used to obtain nitrogen atoms on the carbon support, while inexpensive salts such as iron sulphate or iron acetate are employed to create the final active site. When using NH_3 in the pyrolisis as nitrogen precursor, an activity maximum is presented at a 0.2% loading of iron acetate, while up to 2% porphyrine may be used. The reason for this loading difference may be found on a better dispersion for the macrocycle on the CB surface while the iron acetate trends to form iron agglomerates above the mentioned concentration. It is thought that NH_3 may not only introduce nitrogen atoms on the surface but could also react with the carbon creating new reactive sites. This effect is manifested by a weight loss of the carbon support during the pyrolisis (G. Faubert et al 1999). On the other hand, if acetonitrile is used, the final weight increases due to the formation of new carbonaceous microstructures during the heat treatment. Catalyst

obtained by this methodology have shown thin graphitic structures which cover some type of metal oxides (G. Faubert 1998, P.H. Matter et al. 2006)

Although as presented extended efforts have been done to obtain this kind of catalyst and important progress has been done, a clear explanation for the catalytic site formation as well as for its final structure has still not been given. The group of J.P. Dodelet determined by means of ToF-SIMS analysis of the final catalyst that two types of active sites being described as an iron atom coordinated with 4 or 2 nitrogens (FeN_4/C and FeN_2/C, respectively Fig.7. 6). The first type was found to be more abundant at low pyrolisis temperatures and is often named low temperature site while the second one is preferably formed at higher pyrolization temperatures (above 700ºC) (M. Lefèvre and J.P. Dodelet et al. 2000 and 2002). It was also stated that the high coordination site (4 nitrogen) favours the reduction of oxygen to H_2O_2 while the low coordination sites favours the H_2O formation. This is in accordance with the pyrolysis temperature studies for which although high activity is obtained for low pyrolisis temperatures (below 700ºC) much more stable catalysts are obtained after high temperature pyrolysis (above 700ºC) due to the lower H_2O_2 formation (M. Lefèvre et al. 2003). It was also found that higher proportion of FeN_2/C sites are found when ammonia is used as nitrogen precursor instead of adsorbing an iron porphyrine on the carbon support (C. Médard et al. 2006).
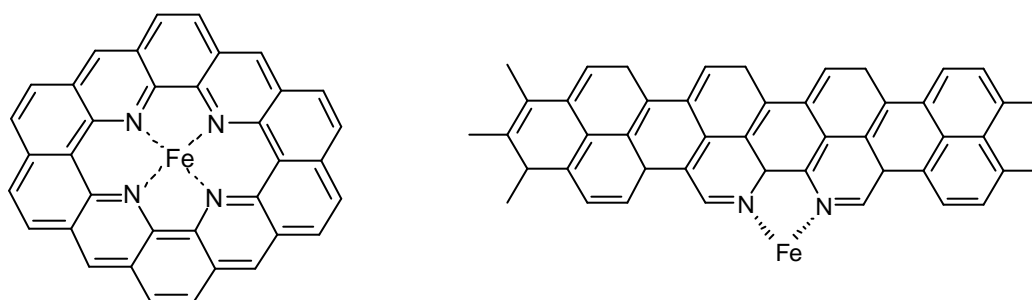

Fig.7. 6 Possible structures for the FeN_4/C and FeN_2/C left and right respectively.

However, besides these two sites other active structures have also been described. For example, some type of Iron peroxide has been also claimed to be active (F. Jaouen et al. 2003). In the previous study several CB supports were tested, the only relation found between the final activity and the CB support was the initial amount of nitrogen content.

In some cases also the doubt was presented whether iron was a real constituent of the final active site or if it was only a catalyst for the active site formation (G. Faubert et al 1998, P.H. Matter et al. 2006)

Other approaches such as the formation of ORR catalysts by means of carbonization of porous polyacrylonitrile containing salts of Fe and Co in order to obtain an aerogel and other similar alternatives have also been described, however, because they are beyond the scope of this work they will not be explained in detail (S. Ye et al. 2003 and 2005, J. Ozaki et al. 2006).

7.1.2.Use of Plasma techniques for ORR catalysts obtainment

Coming back to the objectives of this work, the aim is to use plasma as a very reactive media to modify the surface of carbon which will act as ORR catalyst: The inclusion of N atoms and activation of the carbon surface were thought to be able to improve the final activity of the CB support towards the ORR.

So far, plasma techniques have not been much exploited in order to manufacture free noble metal catalysts. As a matter of fact only one work has been found in the literature close related to the obtainment of catalyst by means of nitrogen macrocycles by using LPP. In this study the group of I. Herrmann used a plasma treatment in a RF low pressure reactor in order to substitute the pyrolisis step (I. Herrmann et al. 2005). Three different plasmas Ar, Ar:O_2 and NH_3:Ar were tested after adsorbing Cobalt Tetramethoxyphenylporphyrin on the surface of the CB (from 50 to 400W and 5 to 40 minutes). It was found that the best results were obtained for pure Ar plasma at 400W, for which comparable ORR activity results to those reached by pryrolisis were obtained.

Some two other plasma treatments have been described for the obtainment of Pt based catalysts. On one hand the group of S. Kim treated the carbon support with a RF nitrogen LPP. Power was set at 300W ant time was varied from 0 to 50 seconds. As a result of the treatment, –NH, C-N, =NH, $-NH_3^+$,C=N, and $-NH_2$ groups were detected on the surface of the carbon (not specified), and a higher activity was obtained after platinum deposition up to 30 second treatment (S.Kim et al. 2005). The last work related with plasma modification for ORR obtainment is presented by H. Shioyama and coworkers who deposited a fluorine containing groups on the surface of CB (Vulcan XC 72) by means of a C_2F_6 plasma (40W) 60 min. -CF_3 was introduced on the CB surface. The final activity after Pt deposition also increased, the increase was attributed to a higher hydrophobicity of the carbon surface which prevented the coating and deactivation of Pt by the formed water. (H. Shioyama et al., 2006)

Therefore, the work here presented is a complete new approach in order to enhance the activity of non-noble metal catalyst for ORR in PEMFC. It has to be mentioned that the catalyst preparation and Voltametric measurements were done in a collaboration with the research group of Prof. J.P. Dodelet at the INRS Energie, Matériaux et Télécommunications, Verennes, Canada.

7.2 Method description to obtain plasma modified ORR catalysts

After modifying the carbon support by plasma, the obtained material was enriched with iron to obtain 2000ppm of iron related to carbon weight. An aqueous solution of iron acetate was used to suspend the carbon black in the mentioned proportions. After stirring for two hours, water was completely removed and the material finally dried in an oven at 90ºC. A pyrolysis is the last step before obtaining the catalyst. The material is submitted to

950ºC for 20 minutes in an ammonia atmosphere. The utilized conditions were established to give optimized performance of the final catalyst by the group of Prof. J.P. Dodelet in the already presented studies. The weight loss suffered by the CB during the pyrolisis step was studied.

7.3 Catalyst activity evaluation: Cyclic Voltametry and Rotating Disk Electrode

To prepare the catalytic surface the modified carbon is mixed in a solution of Nafion (5 wt%) in ethanol. After sonicating the mixture, a small amount is deposited on the vitreous carbon of the rotating electrode. After drying it at room temperature, the electrode can be used to perform the voltammetric and RDE tests. Three different electrode preparation were prepared for each sample, presented results are a mean of the obtained results.

Experiments were carried out at room temperature in a three electrode, one compartment cell containing H_2SO_4 at pH = 1 as electrolyte to simulate PEMFC working conditions). The electrolyte was saturated in O_2 prior to running the experiment. Cyclic voltammetries were performed in a range from 0 to 0,7 V referred to SCE electrode. One cycle is completed with stationary electrode and, immediately after, one cycle is done at 1500 rpm to confirm that the cathodic wave observed at 0 rpm is associated to O_2 reduction. The activity of the catalysts tested in this work was defined by the electrode potential at which the current of the cathodic wave is maximum at 0 rpm and known as V_{pr} (static conditions). The closer this value is to the theoretical oxygen reduction potential at he mentioned conditions (0.985V) the lowest is the overtension and the highest is the selectivity of the tested material towards oxygen reduction. Moreover, the peak position has been shown to be correlated both theoretically and experimentally with the exchange current density of the oxygen reduction reaction (F. Jaouen et al. 2003).

As an example of the obtained results Fig.7. 7 a cycle in stationary electrode were V_{pr} can be obtained, and a rotatory at 1500 rpm in order to avoid diffusion control and confirm that oxygen is being reduced instead impurities placed on the electrode.
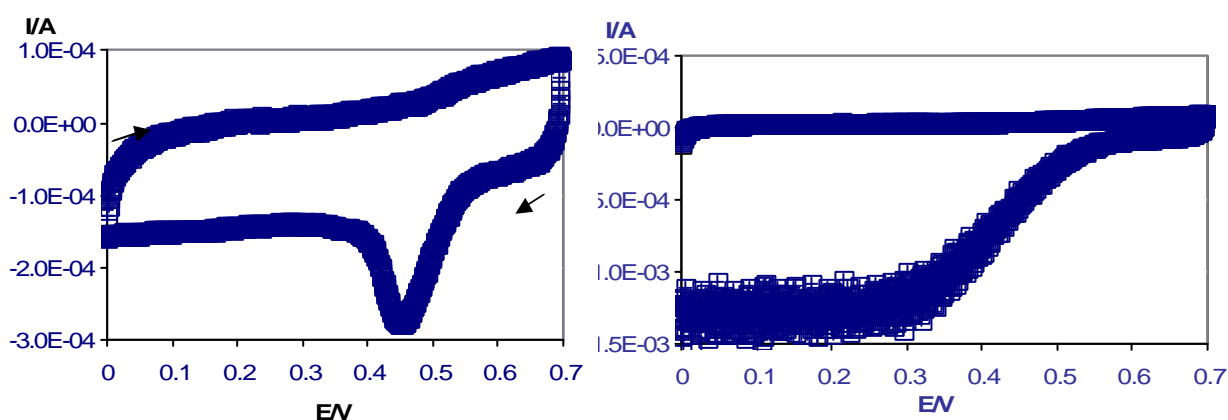

Fig.7. 7 Example of the obtained curves for a static voltametry were Vpre can be measured (left) and a rotating voltametry at 1500 ppm.

7.4 CB Oxygen Reduction activity for obtained catalysts

Results for all original, LPP and APP treated carbons (N134, Vulcan and XPB171) are next presented.

7.4.1 ORR levels for original Carbons

Since many years Vulcan XC-72 has been used as a support for Pt catalysts as the one utilised in PEMFC. The high conductivity of this material was the main reason for its use which is comprehensive when the only role of the support is to conduct the electrons to the negative pole. However, in the present case where a nitrogen precursor is used, carbon does not only act as a electron conductor but also plays an active role during the oxygen reduction. Very few studies have been done on other CB's or carbonaceous surfaces (F. Jaouen et al. 2003, F. Jaouen et al. 2006)

In the present study all presented CB's N134, Vulcan XC72 and XPB 171 were included in order to generate more information about the influence of the CB surface during the oxygen reduction by free-noble catalyst types.

Table 7. 1 ORR activity levels for umodified CB's

CB	Vpr (mV)
N-134	395
Vulcan_XC72	209
XPB171	219

Table 7. 1 presents the values obtained for Vpr for the original carbons. Some important remarks should be here stated. It could seem logical that, because the same amount of CB was used for all trials, the CB presenting a larger surface are would give a higher activity as more surface is available to create active sites. However, as it can be seen above and also more clear in Fig.7. 8. this hypothesis is not fulfilled . Not even when the STSA (outer surface without considing micropore area) there is any evidence that specific surface are is related to the oxygen reduction activity. Recent studies performed by J. Jaouen and coworkers, showed that microporous could host the active sites for the oxygen reduction. Nevertheless, no relation between microporosity and ORR was found in the presented CB's (J. Jaouen et al. 2003). It should be pointed out that microporous that were described as active sites by the mentioned study, were located in a diameter range between 4 and 10 nanometre, in the present case microporus diameter distribution was not obtained.
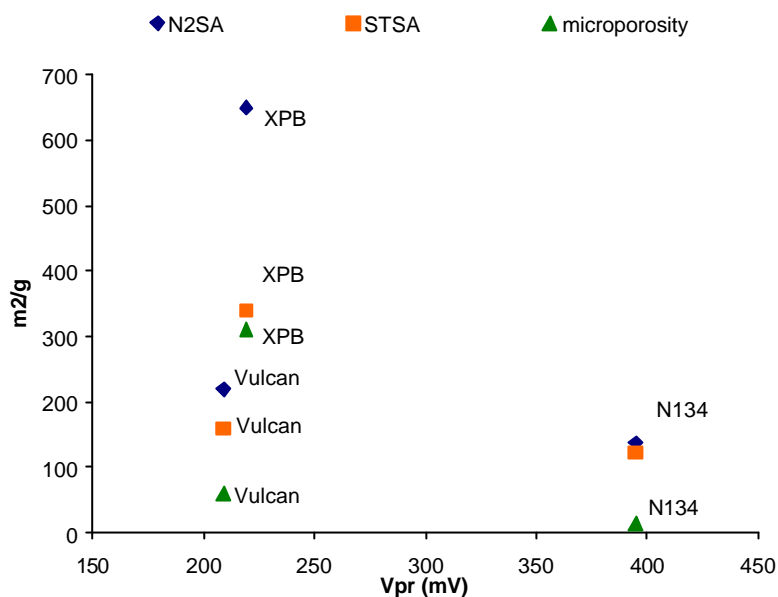
Fig.7. 8 area parameters vs. obtained activity ORR levels.

The presented phenomena indicates that the surface nature of CB (probably including structure and chemistry) are playing a key role during the pyrolisis step in order to obtain high activity catalysts. This effect does not occur when the macrocycle is adsorbed on the carbon support ad submitted to a posterior pyrolisis. Using this methodology, A. Bron et. al. studied CB's presenting different specific surface area and they found that after the pyrolisis the obtained activity was proportional to the specific surface area (M. Bron et. al 2002c)

Another recent study pointed out that activity of the final carbon was related to the initial amount of amorphous carbon on the CB surface (J. Jaouen et al. 2006), as a consequence of performed Raman studies it was observed that the carbons containing higher amorphous proportion on the surface presented a higher weight loss during the pyrolisis and a higher final activity. The highest activity near 450mV for Vpr was found for some experimental CB grades obtained from Sid Richardson Carbon Black Co. N134 was also used without further modification and results are consistent with the values here presented while Vulcan presented values around 170mV. No graphitised CB's were used during the mentioned study in order to confirm the hypothesis.

After analysing the facts presented above, it was thought to be very interesting to study the behaviour of the graphitized N134 which as shown by XRD (chapter 5) present a much graphitic structure and no impurities on the surface. It was found that submitting N134g to the same nitrogen enriching and pyrolisis treatment no activity was found in the voltammetric analysis. Therefore, it seems that surface structure is a much more relevant parameter than both surface microporosity or specific surface area values. However, it should be again pointed out that the presence of aromatic impurities on the surface of untreated N134 could favour the enhanced ORR activity presented by this particular CB. This fact will be discussed in more detail later on in this section.

Following the effect of the presented plasma modifications on the final catalyst activity for ORR is presented. Several parameters such as surface composition, final microporosity and weight loss during the pyrolisis step have been studied as possible explanation for the presented results.

7.4.2 ORR activity levels for modified carbons

As mentioned earlier, one of the aims of this work was to introduce nitrogen functionalities on the CB surface by means of plasma techniques in order to increase the nitrogen concentration which has been closely related to the ORR activity presented by non-noble metal catalysts. In this section results obtained for both LPP and APP treatments will be presented.

Although for this application much emphasis is given to the plasma treatments containing nitrogen species, it is worth to mention that oxygen may play also an important role. In this case oxygen plasma was utilized with two finalities:

- As a pre-treatment: pre-treatment with oxygen plasma was though to create oxygen acidic sites which could easily react with the ammonia plasma basic species. Results presented in chapter 5 verify an steep increase of pH when treating oxidized CB with ammonia plasma.

- As functionalization treatment: it is worth to mention that the presence of oxygen species has been observed to help the iron compounds used to enrich the CB surface. Higher iron dispersion leads to a higher number of final active sites and lower iron aggregate formation which has been reported to decrease the final ORR activity. In most cases oxygen species were introduced by wet treatment using HNO_3 (R. C. Sosa et. al. 1996, P. Gouérec et al. 1998 H. Wang et al. 1999 and N.P. Subramanian et al. 2005) .

7.4.2.1 LPP modified carbons as ORR catalysts.

Next figure presents the Vpr levels obtained for the modified N134 grades, including the extracted and graphitised samples. In these studies only treatments which included nitrogen precursors in the plasma atmosphere were evaluated, but also were included those samples which were submitted to a pre-oxidation step.

Table 7. 2 Obtained Vpr Values for LPP modified N134

Treated CB	Vpr (mV)
N134	395
N134_NH$_3$_c (20W/50min)	416
N134_NH$_3$_c (40W/30min)	412
N134_N$_2$_c (40W/30min)	439
N134_air_NH$_3$_c	450
N134_N$_2$_O$_2$	445
N134e_NH$_3$_c	459
N134g	---
N134g_O$_2$_c	-55
N134g_NH$_3$_c	-33
N134g_N$_2$_c	---

In the results presented in the table above, it can be observed that LPP modification of N134 improved the ORR activity for all nitrogen containing treatments. Ammonia modification gives slightly higher values when using milder conditions for long treatment times. However, much higher V_{pr} values are obtained when the sample is treated in pure nitrogen plasma.

In order to study whether the impurities played a crucial role during the pyrolisis step also one N134e grade was included in the measurements. In this case it can be seen not only that high activity was obtained but also that for this series the maximum value was obtained. Therefore the high activity for N134 is not only related to its surface impurities but also to its C surface structure.

Because, as stated during the chapter introduction, oxygen presence on the carbon surface helps to disperse the iron salt and obtain a higher activity some oxygen containing carbons final activity was examined. One of the grades referred as N134_air_NH$_3$_c, was first oxidised by an APP treatment and afterwards treated with an ammonia LPP. As it can be observed activity is much higher than the one obtained after ammonia LPP, and also slightly better than the one obtained with nitrogen LPP. However, because the oxidation treatment was done using APP it has to be remembered that many impurities were also removed from the surface and as it will be presented, treating the material only with air APP already increased the ORR activity. Once again it seems that the presence of impurities on the CB surface does not contribute to the final catalyst activity.

Finally, another oxidation process was carried out to see the effect of oxygen on the surface of the catalyst. Because good results were obtained after nitrogen LPP treatment, it was thought that new structures created by ablation during process, as mentioned along this work, could be the ones responsible for the activity increase. It was thought that if oxygen plasma was applied before the nitrogen treatment could prevent the formation of such structures. However once the nitrogen LPP was carried out, an oxygen LPP could

functionalize the new structures. Sample has been named as N134_N_2_O_2. As it can be seen slight better results were obtained than for nitrogen LPP treatment by its own.

On the other hand, the impossibility to obtain a catalyst by using the graphitised CB N134g leads to very important conclusions. On one hand corroborated the low interaction between this type of carbon surface and the ammonia plasma which has been already shown during the previous characterization of this material, but it also confirms once again that not only chemistry composition but also structure plays a very important role for the obtainment of high activity catalysts. More precise information can here also be given, the introduction of oxygen groups during oxygen LPP treatment (confirmed by Bohem's titration) is also not enough to create active sites during the pyrolisis step. Therefore, amorphous carbon is needed in order to create active sites by means of the plasma-pyrolisis activation, and plasma functionalization must be located in amorphous zones. Further studies about the weight loss during the heat treatment will confirm this statement.

Table 7. 3 Obtained V_{pr} Values for LPP modified Vulcan

Treated CB	Vpr (mV)
Vulcan	209
Vulcan_NH_3_c	190
Vulcan_N_2_c	212
Vulcan_O_2_NH_3_c	196

In the case for Vulcan carbon black, which is very often used as support of catalysts in Fuel Cells, results were rather low (Table 7. 3). Not only the CB itself presents a much lower activity than N134, but also once modified by LPP presents lower or very similar V_{pr} values. This fact is probably due to the lower activity of the CB surface both towards the plasma which was shown by lower nitrogen content by means of XPS in chapter 5, but also a lower reactivity during the pyrolisis step. Similar results were observed for XPB171 for which ammonia treatment also lowered the Vpr value, however in this case an oxygen LPP treatment did highly increase the V_{pr} value (Table 7. 4).

Table 7. 4 Obtained V_{pr} Values for LPP modified XPB 171

Treated CB	Vpr (mV)
XPB 171	209
XPB 171_NH_3_c	197
XPB 171_O_2_c	347

Finally, a figure is presented with the variation in V_{pr} produced by the LPP treatments as a function of its specific surface are. Once again it is shown that modification effect is not proportional to this parameter.
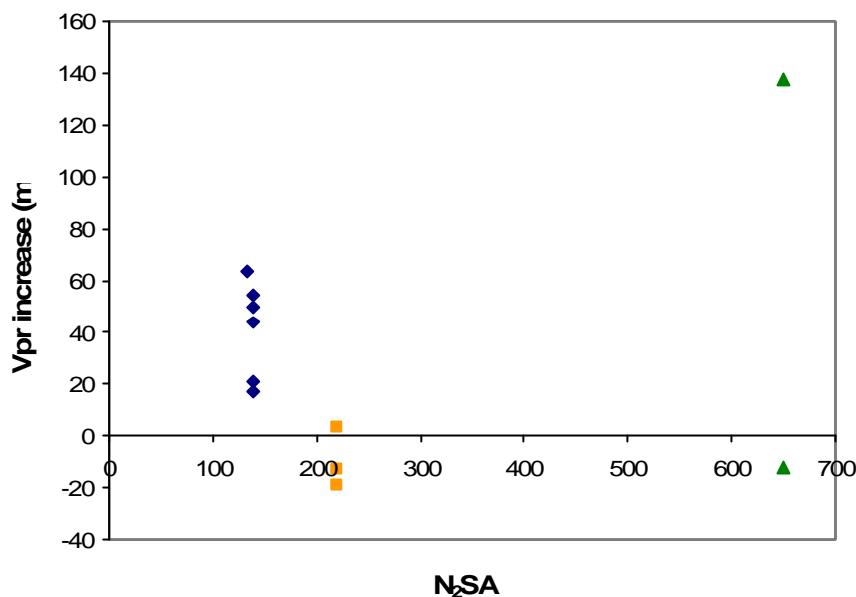
Fig.7. 9 Increase in Vpr versus specific surface area.

7.4.2.2 APP modified carbons as ORR catalysts

In this section the V_{pr} Values presented after APP treatments. For N134 results are presented in Table 7. 5. As it can be observed, Vpr highest value was obtained by a combination of a preoxidation treatment (air APP) with a second APP treatment of nitrogen containing ammonia (2L/h). However it can also be seen that air plasma alone already increased the Vpr value in 50 mV, it should not be forgotten that air plasma did already increase the nitrogen content of the CB surface by a 0.7% which could also be active.

It can also be seen that while nitrogen APP also increased V_{pr} significantly, the same treatment together with an ammonia post-reaction did not present such relevant increase but obtained values were very close to the LPP ammonia modified N134.

Table 7. 5 Obtained Vpr Values for APP modified N134

Treated CB	Vpr (mV)
N134	395
N134_(N$_2$+NH$_3$)_a	418
N134_air_(N$_2$+NH$_3$)_a	449
N134_air_a	444
N134_N$_2$_a	430

The following table presents the results for XPB 171, contrary than for LPP, in this case the produced modification during the APP did increase the final V_{pr} value (Table 7. 6). As a mater of fact an increase of almost 100 mV was obtained for the XPB 171_O$_2$_(N$_2$+NH$_3$)_a treatment. Because a clear improvement in a wide range was

obtained for these three presented XPB 171 samples they were further studied in detail as will be presented later on.

Table 7. 6 Obtained Vpr Values for APP modified XPB 171

Treated CB	Vpr (mV)
XPB 171	219
XPB 171_(N_2+NH_3)_a	269
XPB 171_O_2_(N_2+NH_3)_a	314

Fig.7. 10 presents the variation in Vpr for the presented atmospheric treatment. Although higher values are obtained for N134 relative improvement by means of APP results higher for XPB 171.
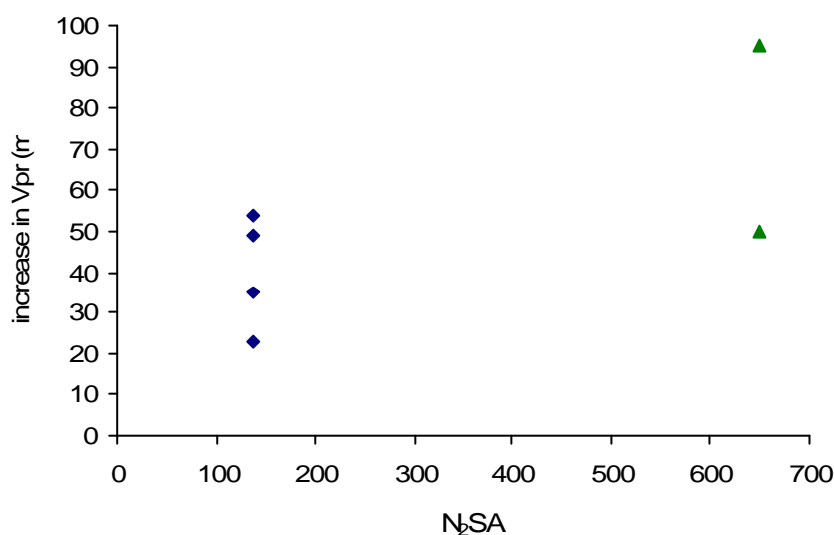

Fig.7. 10 Increase in Vpr versus specific surface area.

Summarizing the presented results to this point, it can be said that LPP treatments did mainly increase the Vpr values for the N134 and N134e samples. No changes were obtained for N134g and Vulcan which is probably due to the low reactivity of these carbons and the low proportion of amorphous reactive areas. In the case of XBP171 activity was improved by oxygen LPP treatment however further results are needed in order to find a suitable explanation for this effect. Concerning the APP results, increase in final activity for both N134 and XPB 171 was observed.

Further characterization of the studied material is presented in order to obtain more information about the parameters involved in the process of achieving high activity ORR materials.

7.5 Influence of Carbon Support Chemistry on final ORR activity

As it has been explained, for many years the presence of nitrogen on the surface of CB was considered the limiting factor to obtain high activity towards oxygen reduction. In order to verify this hypothesis XPS measurements were also done after the pyrolisis treatment under the mentioned conditions. XPS results of nitrogen and ammonia treated samples have already been presented in chapter 5, however they are also included here in order to relate whether a high content after plasma treatment is related to the final nitrogen content after pyrolysis.
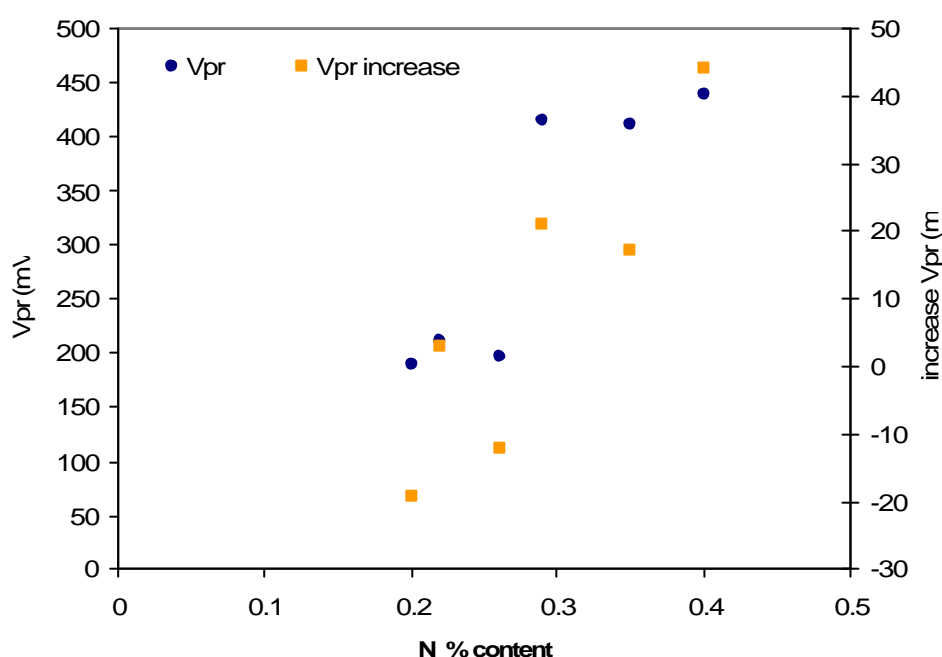
Fig.7. 11 Vpr and Vpr increase as a function of the final N content after the plasma treatment (LPP and APP)

Fig.7. 11 Presents the relation between the nitrogen content determined after several plasma treatments (LPP and APP) and the final activity of the catalyst measured as Vpr. It also includes the same information but related to the increase in V_{pr} suffered due to the plasma treatment. The presented results seem to find a relation between this two values, not only with the final V_{pr} value but also for the final increase. Therefore, although probably further studies should be carried out it seem that nitrogen inclusion during the plasma treatment does help to increase the final activity of the ORR catalyst.

This fact is in agreement with the results presented by the group of J.P. Dodelet who stated that an initial content of nitrogen although minimal could result in a higher ORR activity. They stated that the initial nitrogen could help to the dispersion of the iron salt (J. Jaouen and J.P. Dodelet et al. 2006).

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Table 7. 7 Nitrogen Content and pyridinic functionalities percentage after pyrolisis

Treated CB	N% after pyrolisis	% pyridinic N
N134	3.3	41
N134_NH_3_c (20W/50min)	2.65	39.71
N134_NH_3_c (40W/30min)	2	40
N134_N_2_c (40W/30min)	2.1	38
N134e_NH_3_c (40W/30min)	1.88	
Vulcan	0.5	
Vulcan_NH_3_c (40W/30min)	0.1	
XPB171	0.2	
XPB171_NH_3_c (40W/30min)	0.2	
N134_($N_{2+}NH_3$)_a	3.05	41
N134_air_($N_{2+}NH_3$)_a	3.51	40.62
N134_air_a	2.16	41.19
N134_N_2_a	3.03	43.03
XPB 171_(N_2+NH_3)_a	0.2	
XPB 171_O_2_(N_2+NH_3)_a	0.3	

In the table above the N content after the pyrolisis for some of the studied CB is presented. There is some relevant information to take into account which is also presented in Fig.7. 11. Although LPP N134 treated carbons presented a higher V_{pr} than for the original grade, the nitrogen final amount is not higher than the original value which means that contrary to some presented studies, nitrogen content although it can be a limiting factor, once a certain concentration is reached other variables may play a more relevant role. On the other hand, for Vulcan and XPB 171 N % is much lower than for N134 and probably they don't reach the critical N % to become active. The low reactivity of both Vulcan and XPB towards ammonia plasma was also shown in chapter 5 showing also much lower N% after the plasma treatment.
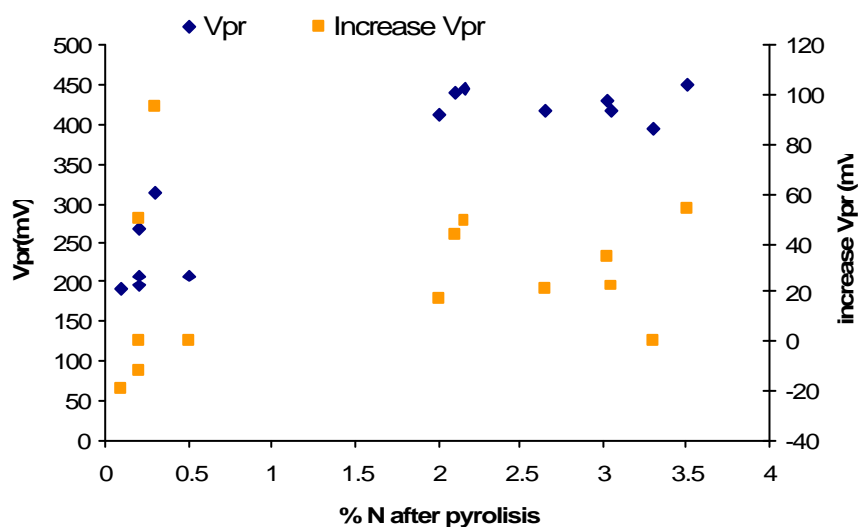

Fig.7. 12 Final Vpr and Vpr increase as a function of the final N content after pyrolisis
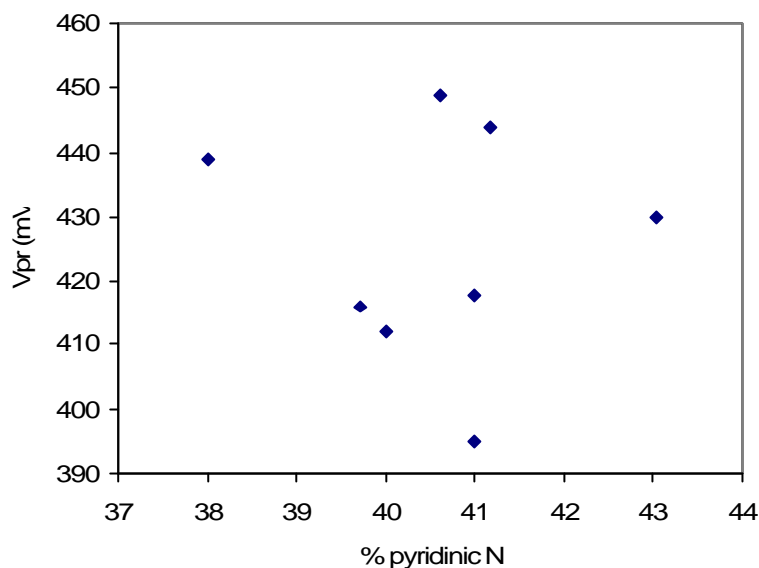
Fig.7. 13 Final Vpr as a function of the final N pyridinic content after pyrolisis

On the other hand, although N is present a pyridinic position is for all samples measured around 40% it can not be assured that a higher content of this species are related to higher final activities. As a matter of fact, Fig.7. **13** presents a completely scattered distribution when V_{pr} final values are represented as function of the final percentage of nitrogen after pyrolisis.

Another possible parameter which can be related to the final ORR catalytic activity can be the weight loss during pyrolisis. As it has been mentioned, NH_3 not only may introduce final nitrogen functionalities but it may also react with the carbon support which I shown as a decrease of the pyrolised CB weight. This effect can be observed in Fig.7. 14. Once again it can be observed that for N134g very low weight loss was obtained during the pyrolisis which seem to be related to its graphitic unreactive surface. On the other hand it seems that increasing the weight loss increases the final V_{pr} value up to 40%, further weight loss does not provide any increase in the ORR activity results.

The same conclusion are obtained when the relative increase is studied as function of weight loss during pyrolisis, however it can be here seen more clearly that not always an increase in weight loss is necessary in order to obtain the bests activities (Fig.7. 15). The results stressed in the figure show tow CB's which although their weight loss is not maximum present a good improvement of the original V_{pr} values. The samples correspond to the N134e_NH_3_c and XPB171_O_2_c. Therefore other parameters beside a high reactivity during the pyrolisis seem to be involved in obtaining high activity catalyst by means of this procedure.
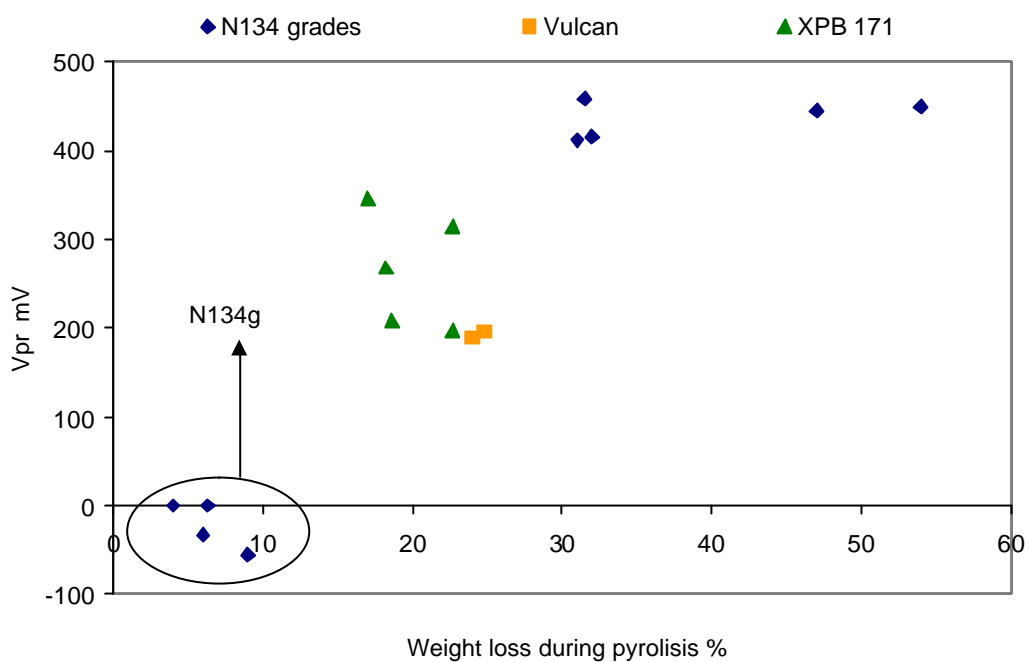
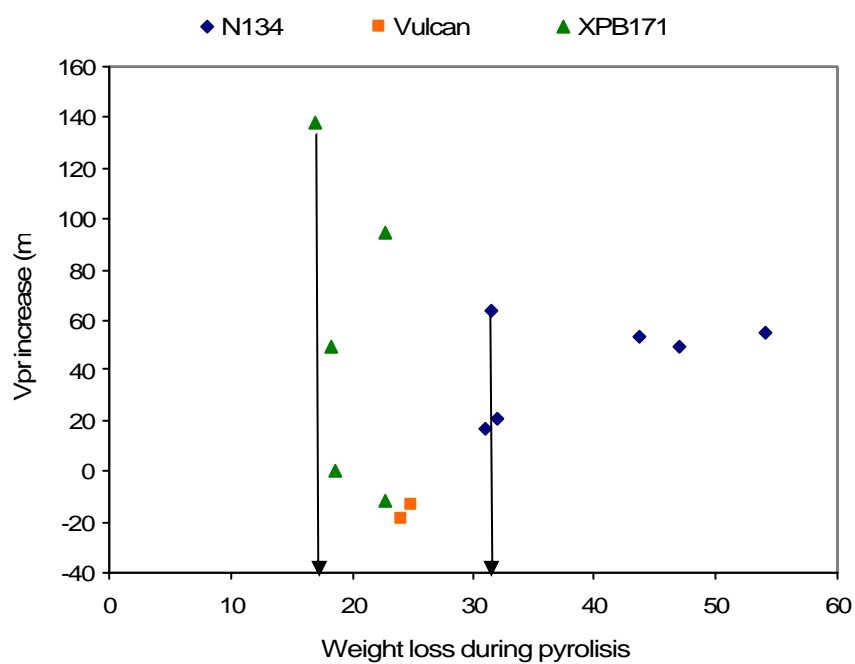Fig.7. 14 Vpr as a function of the weight loss during pyrolisis

Fig.7. 15 Vpr increase as a finction of a weight loss during pyrolisis

In order to obtain more information about the changes produced during the pyrolisis step on the CB some representatives samples were selected and characterized by means of low pressure nitrogen isotherms. The values after pyrolisation which are referred as HT (heat treated) are compared with the untreated values already presented in chapter 5.

As a first result it can be found in Fig.7. 16 the isotherms both for N134g_NH3_c, both before and after heat treatment. It can be observed not only that the N_2 adsorption capacity was not increased during the pyrolisis but as a matter of fact the N_2 adsorption was decreased. This effect is also shown by the specific surface area (BET) measurement shown in Table 7. 8 were a slight reduction of the specific surface area is observed.
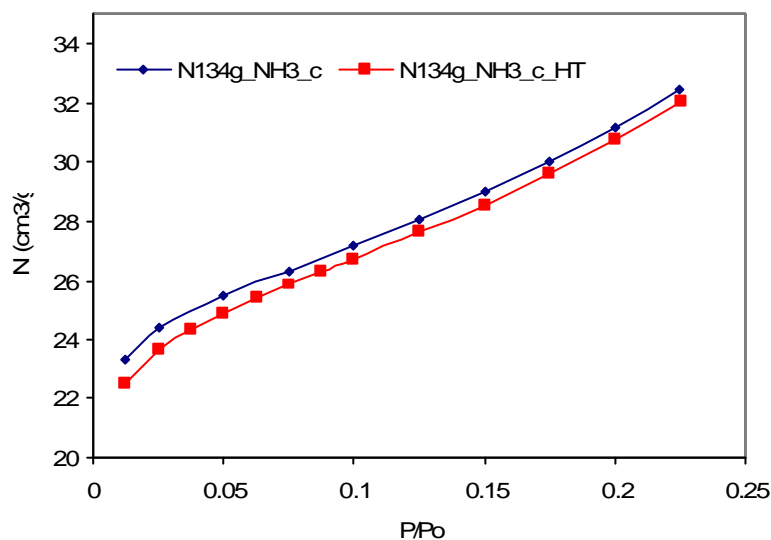

Fig.7. 16 N_2 adsorption Isoterm at 77K and low pressure before and after pyrolisis for N134g_NH$_3$_c

On the other hand, Fig.7. 17 presents the adsorption nitrogen capacity for the N134e_NH$_3$_c before and after heat treatment. In this case a large difference among the nitrogen capacity of both samples can be observed by simply looking at the isotherms. The increase in specific surface area (BET) is in this case larger than 400m^2/g with a very high contribution of microporosity formation.
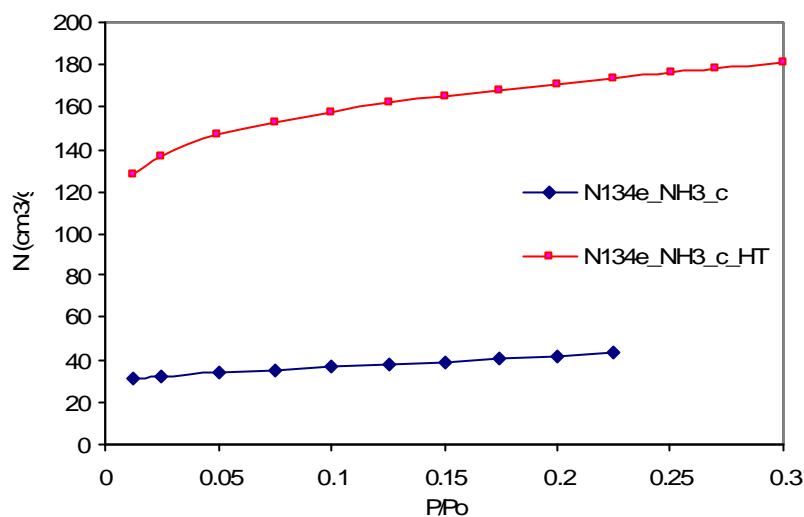
Fig.7. 17 adsorption Isoterm at 77K and low pressure before and after pyrolisis

Finally, N_2 adsorption isotherms are presented for the XPB 171 APP treated grades. As mentioned before in this chapter, XPB171_(N_2+NH_3) and XPB171_air_(N_2+NH_3) presented an increase in Vpr and therefore were selected to be studied. Fig.7. 18 shows the N_2 adsorption isotherms for XPB 171 and the APP modified samples, an increase in the N_2 adsorption capacity can be observed for all three heat treated samples.
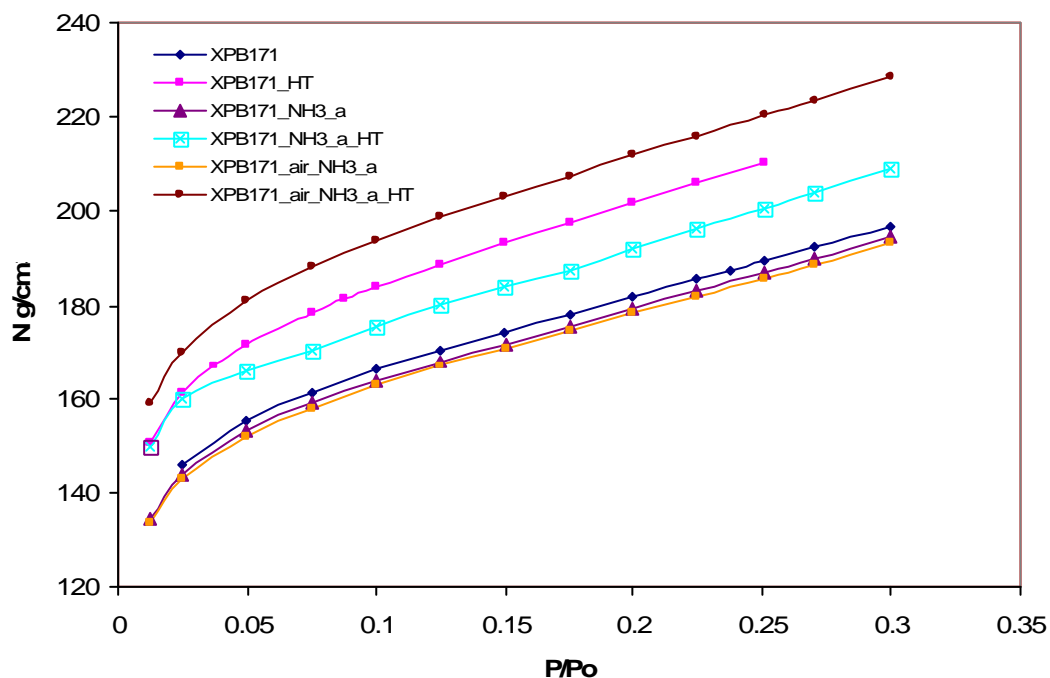

Fig.7. 18 Low pressure N_2 isoterms at 77K for XPB171 APP treated grades

Therefore it seems that an increase in specific surface area during the pyrolisis is needed in order to obtain ORR active surfaces.

Table 7. 8 Spcific surface area parameters for several heat treated (HT) CBs.

CB type	BET (m²/g)	STSA (m²/g)	Microporosity (m²/g)	C	Na
N134g_NH$_3$_c	109.31	109.31	-----	472.17	25.11
N134g_NH$_3$_c_HT	108.10	96.61	-----	369.55	24.83
N134e_NH$_3$_c	134.07	124.17	9.90	108.40	30.79
N134e_NH$_3$_c_HT	619.12	260.28	358.84	1092.20	142.22
XPB171	656.49	347.39	309.10	797.27	150.80
XPB171_HT	717.23	416.13	26.90	1258.70	164.70
XPB171_(N$_2$+NH$_3$)_a	638.01	352.37	285.64	1726.97	146.56
XPB171_(N$_2$+NH$_3$)_a_HT	718.16	418.14	300.02	1026.10	164.97
XPB171_air_(N$_2$+NH$_3$)_a	643.97	391.43	252.54	713.92	147.93
XPB171_air_(N$_2$+NH$_3$)_a_HT	751.22	413.89	337.33	1460.87	172.56

From the presented results it can be thought that an increase of specific surface area during the heat treatment process is needed in order to create the new reactive sites. In order to study this hypothesis the increase in V_{pr} and final V_{pr} are respresented as function of the N_2SA change during the pyrolisis step in Fig.7. 19 . It is observed that both for V_{pr} as well as for V_{pr} increase it seems to be a relation between N_2SA increase and final activity results. However, once again the relation does not seem to be linear but to present a maximum value for such increase.
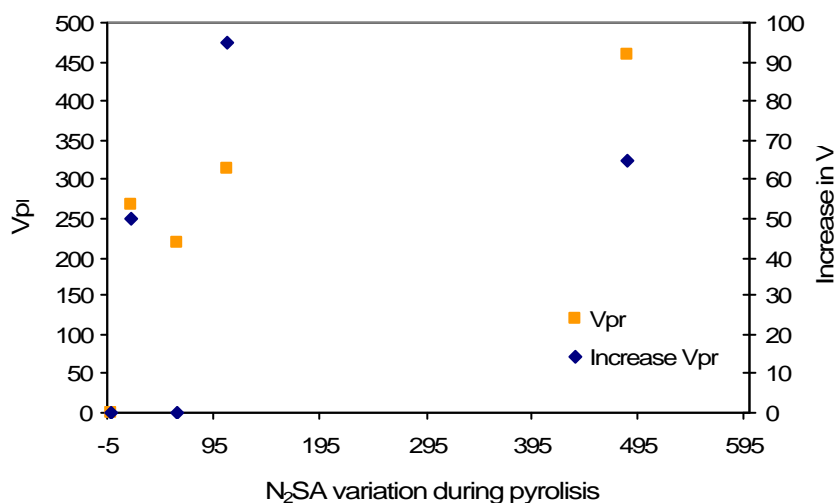

Fig.7. 19 Vpr and Vpr increase as function of the N_2SA variation during pyrolisis

Finally if the same results are studied from the micropososity point of view the trend is similar. However in this case, a pretty linear relation is observed when comparing the final V_{pr} and the increase in microporosity during the pyrolisis step.
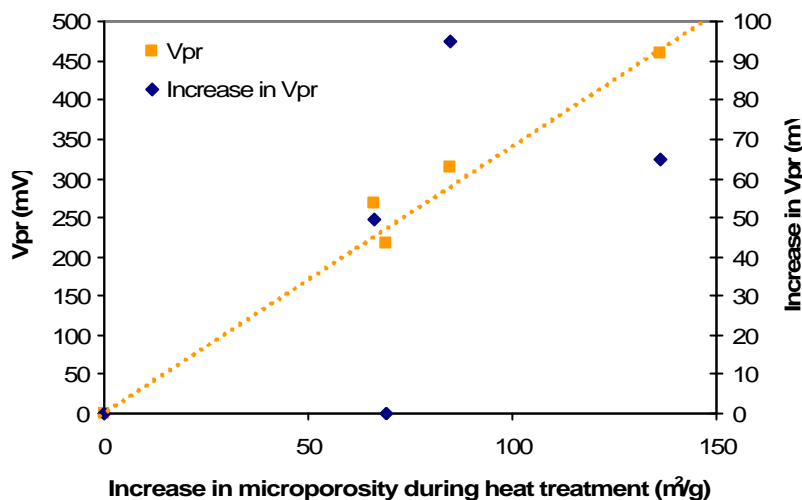

Fig.7. 20 V_{pr} and increase in V_{pr} as a function of the microporosity change during the pyrolisis

From the presented results in this chapter, it seems possible to confirm that final activity of ORR non-noble metal catalyst is not dependent on one unique parameter. It has been shown that plasma treatments both LPP and APP help to increase the final activity, and it is possible that initial increase of nitrogen content after plasma may be one of the responsible parameters but not the only one.

As a conclusion of this study it can be established that many parameters play a key role in order to obtain high activity ORR catalysts from nitrogen and iron precursors on carbon materials. Following the carbon characteristics which have been found to have a higher influence are presented:

- Initial Carbon Structure: N134 graphitization prevented the carbon to become active. Possible surface structure changes caused by plasma activation may also benefit the final activity of the catalyst (e.i. air APP plasma)

- Initial N content: Increase of nitrogen percentage by means of plasma techniques both LPP and APP has been shown to increase the final ORR activity of the treated surface. On the other hand CB surfaces that presented low reactivity towards plasma modification presented also low ORR catalysation abilities.

- Carbon reactivity during pyrolisis: It has been shown that those CB's presenting higher weight losses during pyrolisis do also present higher ORR catalysis. However, it is not a linear relation and a maximum catalytic activity is obtained at 40%.

-   <u>Final microporosity:</u> Increase in microporosity during the pyrolisis have also been related to the obtainment of higher activity level of ORR catalysts. Although a small number of samples were tested a linear relation was obtained when relating this increase with he final V_{pr} value.

On the other hand, no evidence of the influence of other parameters such as final nitrogen concentration or final pyridinic nitrogen on the carbon surface were found as determinant parameters as was stated by other previous works.

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