Development of free noble metal catalyst for oxygen reduction in fuel cell applications. Part I: modification of carbon based materials as catalyst substrate

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Summary

Introduction

In recent years, carbon based materials such as graphene and carbon nanotubes, as well as carbon blacks, have attracted a lot of attention acting as catalyst supports, since they have great electronic conductivity, high specific surface area, and great thermal and mechanical properties (Wei, Tong and Zhang)

In order to be able to include oxygen reduction sites on the surface of the carbon-based materials, and more specifically in this project, on the surface of SWCNT, the samples need to experience surface modifications.

The technique that was used during the project was cold plasma treatment, a very reactive media that is able to produce etching, grafting, ion implantation and polymer deposition on the carbon surfaces. By determining the best conditions to modify the surface activity of SWCNT, it is possible to obtain the best surface properties for each type of application. The most common heteroatom added is nitrogen because it presents excellent electrocatalytic performance, as well as good stability and environmental friendliness (Wei, Tong and Zhang). Therefore, if the plasma treatments with nitrogen on the SWCNT sample allow incorporating nitrogen atoms into the structure, they could become feasible candidates to be used as catalysts for the ORR.

Nitrogen-doped carbon nanotubes can be used in two different ways for the ORR: as a metal-free catalyst, and as a catalyst support. When acting as a metal-free catalyst, N-doping on the surface improves the adsorption ability of O_2 on CNTs so that the reaction can take place, and when acting as a catalyst support, N-doping creates defects on the surface of unmodified CNTs and breaks out its chemical inertness. Some nitrogenized sites become electrochemically active, and therefore CNT_N_2 are used as supports for catalyst metal nanoparticles (such as Fe, Co or Pt in lower quantities). (Wei, Tong and Zhang)

Given that it seems that modified carbon-based materials have a potential use as catalysts, the possibility to tailor the final properties of the surface of SWCNT via plasma techniques arises.

In this sense, the question to be answered would be if the modification of the surface of single walled carbon nanotubes (SWCNTs) via plasma techniques at low pressure is possible, so that SWCNTs can be used as catalysts for the oxygen reduction reaction (ORR) in fuel cells.

Thus, the goals can be summarized in the following points:

- To optimize the reactor conditions for the surface modification of CB (carbon black) and SWCNT to obtain enhanced surface properties.
- To characterize the surface of the modified SWCNT to determine the chemical composition and the type of functionalization that has occurred after the treatment
- To achieve the functionalized SWCNT surface for the potential use as catalyst support for ORR

Experimental part

Carbon black was used as a model to obtain the best plasma reactor conditions that were subsequently used for the single walled carbon nanotubes. The samples that have been studied are single walled carbon nanotubes (SWCNT) and four different types of carbon blacks (CB-990, CB-772, CB-550 and CB-330). Oxygen and nitrogen were used to modify the surface of the carbon samples. Different reactor settings were applied to be able to choose the best reactor conditions. The characterization techniques used to determine the changes that occur in the samples are: TGA, EDX, Raman spectroscopy, dispersion analysis and XPS.

Results and conclusions

After the plasma treatment, the temperature at which 15% of the sample decomposes was evaluated to determine the changes that occur in the surface activity. By studying the obtained results, the conditions that produce a greater change in the final properties of the CB sample were selected to be applied when the carbon sample was SWCNT.

Table 1 shows the decomposition temperature and final TGA residue for a CB sample (CB772) and the SWCNT before and after plasma treatment.

A decrease in the decomposition temperature of the CB sample after the surface has been modified is observed which can be related with an increase of the surface activity of CB. However, when analyzing the results obtained when the carbon sample is SWCNT, it can be observed that they present the opposite behavior compared to the CB samples: after the plasma treatment has been performed, the decomposition temperature increases, meaning that there is a decrease in the surface activity of the sample. Also, the samples present a much higher residue, meaning that there are metallic impurities in the sample due to the catalyst used to obtain the SWCNT.

Table 1: TGA results for CB772 and SWCNT before and after modification

Sample	Treatment	Temperature 15% (°C)	Residue %
CB772	-	650	1.39
	40W O_2	639	2.11
	40W N_2	642	2.27

CNT	-	420	21.1
	40W O_2 5 mins	440	32.7
	40W N_2 5 mins	430	26.3

Two hypotheses are developed to be able to explain the opposite behavior after TGA:

- The catalyst (metallic impurities) plays a role in the thermal decomposition
- The sample gets oxidized forming CO_2 during the plasma treatment.

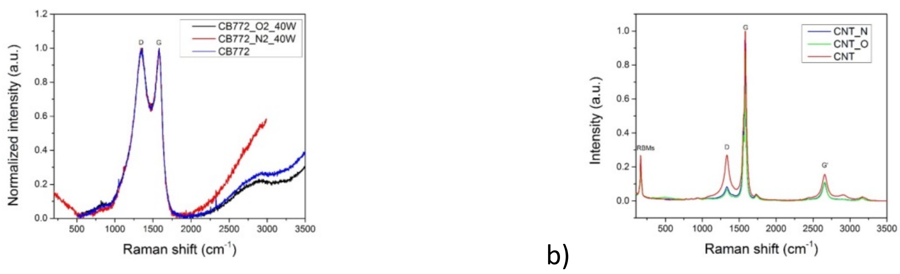
To corroborate one of the hypotheses, the elemental surface composition of the sample was determined via XPS analysis. In Table 2, the results of the elemental surface composition of the SWCNT before and after plasma treatment are presented. As it can be seen, the content of nickel and oxygen increases considerably after the modification with oxygen plasma, in good agreement with the hypothesis that the amorphous part of the sample gets oxidized forming CO_2, purifying the sample and eliminating the more active carbon of the surface.

Table 2: XPS elemental surface composition results

Element	% area (SWCNT)	% area (CNT_N2_3)	% area (CNT_O2_3)
O 1s	2.30	3.99	13.34
C 1s	97.64	91.14	83.92
Ni 2p	0.06	0.09	2.74
N 1s	-	4.78	-

The Raman results allow corroborating that the amorphous part of the sample is the one getting oxidized after oxygen plasma treatment. As seen in Figure 1 b), when modifying the sample with oxygen plasma, because the amorphous carbon present in the sample gets oxidized forming CO_2, the amorphous carbon is removed. If the sample is modified with nitrogen plasma, chemical etching occurs and nitrogen gets inserted in the grain boundaries, changing the type of defect present in the sample. Both plasma treatments reorganize the structure of the carbon surface, reducing the intensity of the defects band. Contrary to what happens when the carbon sample is SWCNT, the type of bond remains unchanged when the sample is carbon black, as seen in Figure 1 a).

a)



b)

Figure 1: a) Raman spectrum for CB330, b) Raman spectrum for SCWNT

Finally, by evaluating the high resolution XPS spectra, the new functionalities that appear in the surface of the SWCNT after modification with nitrogen can be observed. Functionalities such as pyridines, pyrroles, and N-oxide derivates are formed. According to the literature, the bands are assigned as follows (Lezanska, Pietrzyk and Sojka): the band centered at 398.5 eV corresponds to the pyridinic nitrogen, the band centered at 400.5 eV is assigned to the 5-membered ring entity corresponding to pyrrolic nitrogen and the band centered at 403.1 eV corresponds to a pyridine N-oxide, which can be produced by oxidation of the nitrogen bonds.

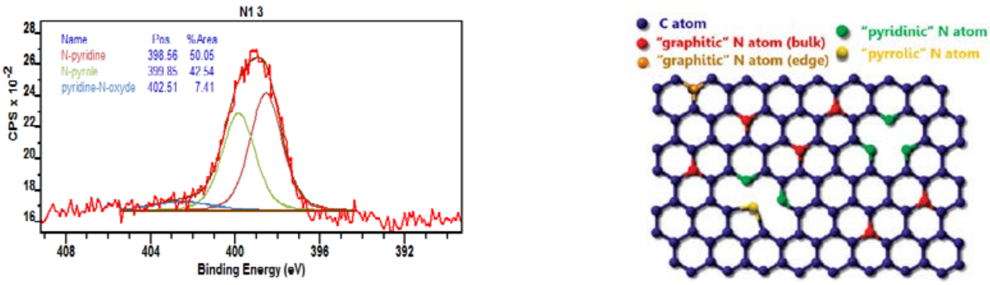


Figure 2: a) N XPS high resolution spectra for SWCNT modified with N2, b) Schematic representation of different types of N atoms in a carbon structure (Wei, Tong y Zhang)

So, it can be concluded that the sample has been modified, and as seen in this image, nitrogen is incorporated into the structure enhancing the properties of the final carbon material. The main goal of the project is therefore achieved, and this modified sample could be potentially used, if further developed, as catalyst for the oxygen reduction reaction.

References:

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