

## **Study of the Catalytic Activity for Oxygen Reduction of Polythiophene Modified with Cobalt or Nickel**

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Carbon black supported materials based on polythiophene and cobalt or nickel were studied as oxygen reduction catalysts. Polythiophene was chemically polymerized onto carbon black, and modified with cobalt or nickel salts to obtain carbon supported polythiophene-cobalt and polythiophene-nickel. For reasons of comparison, the precursor, unmodified carbon-supported polythiophene was studied, as well as unsupported polythiophene particles. In order to study the physical, chemical and electrochemical properties, TGA, SEM, EDAX and electrochemical methods were used. SEM images show porous materials with a particle size of around 110 nm for the carbon supported materials. EDAX tests confirmed the presence of approximately 7 wt% of either cobalt or nickel in the modified materials. Cyclic voltammetry confirmed the presence of ORR peaks in the cathodic area in all materials, except for polythiophene only. Based on kinetic parameters obtained using RDE tests and on electrochemical stability as determined from potentiostatic test, it was concluded that the material with best ORR catalytic activity is carbon supported polythiophene-cobalt.

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**Keywords:** Polythiophene, cobalt, nickel, carbon-supported catalyst, oxygen reduction reaction (ORR).

### **1. INTRODUCTION**

Energy has become a basic necessity of modern society in industry, transport, communications, agriculture and many other activities. However, conventional fossil fuel sources, coal, petroleum and natural gas, are highly pollutant and the evidence of its near exhaustion are abundant [1]. Therefore, the future availability of abundant, cheap and non-contaminating energy sources has become a mayor issue.

In recent years the development of fuel cells has taken fast advances. These systems, use hydrogen and oxygen to produce electricity at high efficiency and with zero emission. One type of fuel cell is the Proton Exchange Membrane Fuel Cell (PEMFC) with advantages for transport and portable (low power) applications, due to the relatively low operation temperature (80-100°C) [2]. Research has focused on the development of low-cost efficient materials for membranes, catalysts (both anode and cathode), bipolar plates, etc. [3]. However, costs, performance and lifetime need to be further improved in order to commercialize the PEMFC.

Conventional PEMFC catalysts are based on carbon-supported platinum and some of its alloys. In the cathode, the catalyzed reaction is the Oxygen Reduction Reaction (ORR) [3-5]. This reaction is relatively slow, compared to the hydrogen oxidation reaction (HOR) in the anode and contributes up to 80% of the total loss in fuel cell performance [6]. The challenge is to substitute these precious metals for more abundant, cheaper and highly stable materials, diminishing the overpotential for the ORR [7,8].

In the literature, several non-precious materials have been reported with good electrocatalytic activity for the ORR, such as porphyrins modified with cobalt [7,9,10]. A direct relationship of the ORR activity with the number of cobalt-nitrogen bonds was reported, indicating that the Co-N bonds are the active sites [7,10-12]. Unfortunately these last materials do not have good stability under practical fuel-cell operating conditions.

Organic conductive polymers, such as polythiophene, can be applied in electronics [13,14], biosensors [13], actuators [13,15], electrocatalysis [16], corrosion protection [17], etc, because of their specific properties and low cost compared to precious metals. The applications of the conducting polymers are based on the combined properties of metals and polymers of these materials, including electronic conductivity, as well as the reversible changes of the conductivity [18,19]. New polymeric electrocatalysts for the ORR have been reported based on conductive polymers [20], conducting polymers doped with heteropolyanions and metallic complex [21-23], and polymers modified with precious metals [22,24].

In recent publications we have reported on the electrocatalytic activity of carbon supported polypyrrole (Ppy), polyaniline (Pani) and poly(3-methylthiophene) (P3MT), modified with cobalt or nickel salts [25,26]. For these conductive polymer samples, the oxygen reduction occurred at high negative overpotential, since the polymer needs to be in reduced state before catalytic activity can be observed [20]. In most of the cases the addition of cobalt or nickel in the composite, results in an improvement in electrocatalytic activity and a shift for the ORR potentials. For example, for carbon supported polypyrrole modified with cobalt the highest potential for ORR (325 mV) was found, while carbon-supported polypyrrole with nickel had the highest exchanged current density ( $4.00 \times 10^{-5}$  mA/cm<sup>2</sup>).

In this paper, we discuss the ORR catalytic activity of carbon-supported polythiophene, modified with either cobalt or nickel. The intention is to create S-Co and S-Ni sites, and determine whether activity for ORR exists. A scheme of the kind of compound obtained would be similar to a scheme presented for polypyrrole [7], with sulphur instead of nitrogen in the polymer units.

## 2. EXPERIMENTAL PART

### 2.1. Synthesis

The synthesis of the materials was carried out based on a procedure described previously [7,25,26]. An amount of 4 g of carbon black (XC-72 Vulcan) was mixed with 30 ml of distilled water, and 1 ml of glacial acetic acid, and stirred for 20 minutes at room temperature. Next, 2 g of thiophene monomer, obtained from Sigma-Aldrich (99%), was added and stirred for 5 minutes, followed by the addition of 7 ml of H<sub>2</sub>O<sub>2</sub> (30%) as an oxidant. This mixture was stirred for 3 hours at room temperature. The carbon black-polythiophene composite was filtered, washed with distilled water (50°C) and dried at 100°C in air during 24 hrs. Finally, 0.9 g of the composite was mixed with 40 ml distilled water in a three-necked round-bottom flask, stirring for 10 minutes. This dispersion was heated under reflux to 80°C, and then 25 ml of either 0.3 M Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or 0.3 M of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution was added. This mixture was vigorously stirred for 30 minutes at 80°C, followed by the addition at 20 ml per minute of the reducing agent, comprised of NaBH<sub>4</sub> (5.23 g) and NaOH (0.37 g) dissolved in 500 ml of distilled water (solution pH 11.4).

The catalyst was filtered and washed repeatedly with distilled water (at 50°C) until the pH of the filtrate reached 7.0 and dried in air at 100°C during 24 hrs. Based on the initial reactant ratios, and assuming the successful incorporation of all reactants into the composite material, the cobalt or nickel content in the samples would be 10% of the total weight, while the carbon content in the composite would be 83% for both C-PTh-Co and C-PTh-Ni.

The synthesis of carbon black-free polythiophene was done as follows: 0.1 M of thiophene monomer was added to a solution of 0.5 M FeCl<sub>3</sub> (Aldrich 99.99%) in acetonitrile (Aldrich, 99%) under constant stirring. The reaction was considered finished when the color changed from green to black. The polymer was filtered and washed with distilled water at 50°C and dried at 100°C in air during 24 hrs.

Cathode catalyst ink was prepared by mixing the obtained catalysts with distilled water to a 1:1 weight ratio and then with recast Nafion® ionomer (5% Nafion® 1100 suspension in alcohol, Fluka Corp.) to a 1:1 volumetric ratio. The mixture was placed in an ice bath to prevent overheating and minimize evaporation of solvents, and then ultrasonically mixed for 5 minutes. By means of a graduated micropipette, 2 µl of the catalyst ink was deposited on a rotating disk electrode with an active area of 0.071 cm<sup>2</sup>. The estimated dry content of this volume of catalyst ink is about 47 µg, (0.66 mg/cm<sup>2</sup>) assuming a homogeneous mixture.

Based on the procedures above mentioned, the following materials were synthesized: polythiophene (PTh), carbon black/polythiophene (C-PTh); carbon black/polythiophene/cobalt (C-PTh-Co) and carbon black/polythiophene/nickel (C-PTh-Ni).

### 2.2. Characterization

Thermogravimetric analysis (TGA) was carried out in nitrogen atmosphere at a scan rate of 10°C/min using a Perkin Elmer TGA7.

The morphological and compositional characterization was performed by Scanning Electron Microscopy (SEM) on a JEOL JSM-6360 LV with an INCA Energy 200 microprobe.

Fourier-transform infrared (FT-IR) spectra were obtained by using a Perkin Elmer Spectrum GX. The tests were performed between 2000 and 650  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$ , a scan rate of 0.63  $\text{cm}^{-1}\text{s}^{-1}$ , and 15 sweeps per sample.

The electrochemical characterization was carried out using a three-electrode electrochemical cell. Either a stationary or a rotating disk electrode was used as working electrode, depending on the specific test (characteristics and preparation of both electrodes were commented previously). The counter electrode was a graphite electrode, while a saturated calomel electrode (SCE) was used as a reference electrode (0.241  $V_{\text{NHE}}$ ). An Autolab PGSTAT302N potentiostat was used.

Cyclic voltammetry was carried out using a stationary electrode in 0.5 M  $\text{H}_2\text{SO}_4$  at room temperature, saturated with either nitrogen or oxygen, in a potential range between -0.2  $V_{\text{NHE}}$  and 1.0  $V_{\text{NHE}}$  and with a scan rate of 20  $\text{mV s}^{-1}$ . Cathodic potentiodynamic curves were obtained at a scan rate of 1  $\text{mV s}^{-1}$ , using an RDE at 0, 200, 400, 600, 800 and 1600 rpm. Curves were started from the open circuit potential,  $E_{\text{oc}}$ , down to the potential at which the current density reached its maximum on the ORR peak, as determined from cyclic voltammetry tests for each sample. Potentiostatic tests were carried out in order to determine stability, applying the maximum potential in the ORR peak as obtained from cyclic voltammetry tests and using a stationary electrode. All potentials are reported vs NHE.

### 3. RESULTS AND DISCUSSION

#### 3.1. TGA

Figure 1 shows the results obtained from TGA analysis carried out in a nitrogen atmosphere. Carbon black was included as a reference material and shows a stable region at low temperature followed by rapid decomposition at approximately 650°C.

Meanwhile, the curve corresponding to polythiophene (chemically polymerized without carbon black, PTh) shows that this material begins to decompose at approximately 300°C, while at high temperature range (after 550°C) the decomposition rate increases. C-PTh is stable until 650°C, after that, mass loss is slower than for carbon black. C-PTh-Co is stable from room temperature to 131°C, after that the sample has three distinct decomposition temperature ranges: 130-375°C, 375-580°C, and above 580°C. The first decomposition range may be related to the presence of cobalt oxides or cobalt hydroxides, the second one related to the decomposition of the polymer, and the last one to the carbon decomposition. The same could be said for C-PTh-Ni, which is stable up to 140°C. After this, of decomposition ranges can be seen: 140-300°C, 300-520°C, and above 520°C. The decomposition of cobalt or nickel-containing materials is faster than for samples not containing metal atoms, possibly related to the degradation of metal compounds, such as cobalt oxides or nickel oxides [27].

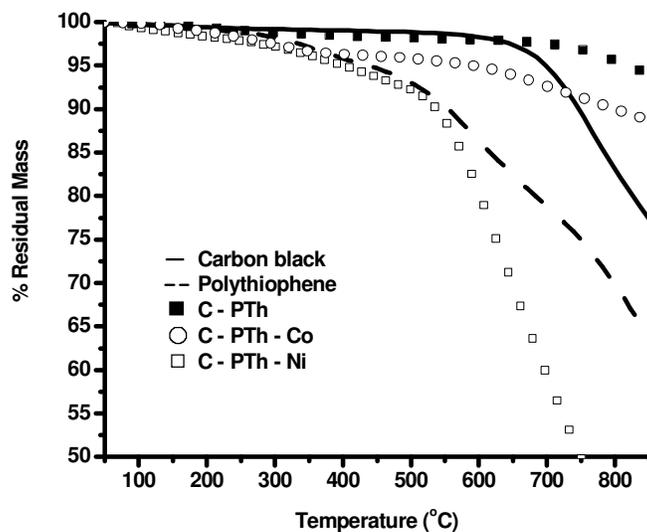


Figure 1. TGA curves obtained in nitrogen atmosphere

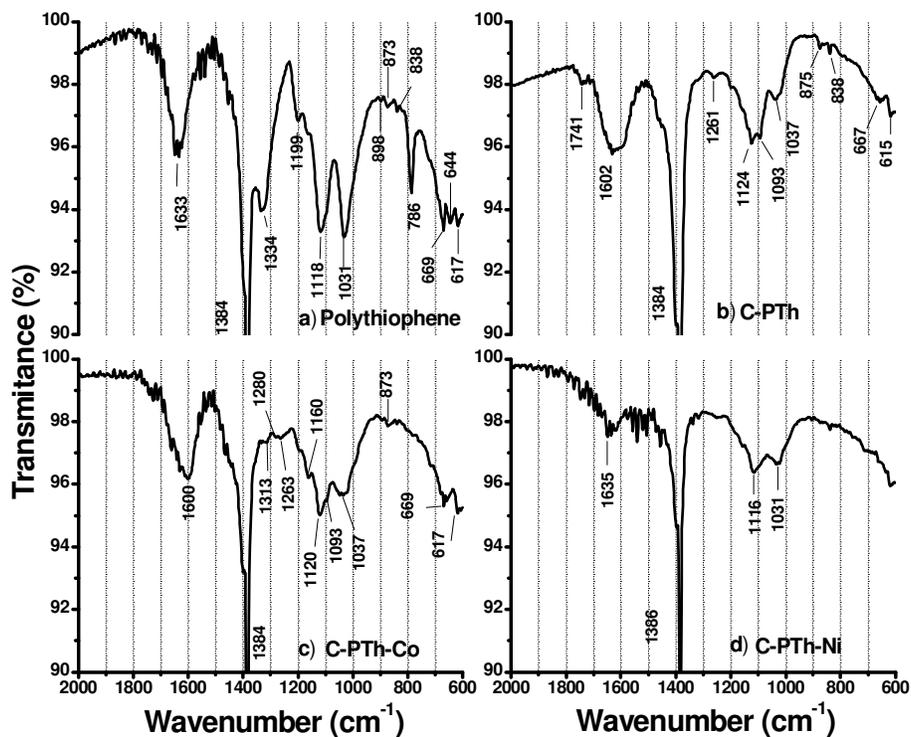


Figure 2. FTIR spectra obtained for: a) PTh; b) C-PTh; c) C-PTh-Co; d) C-PTh-Ni.

### 3.2. FTIR

The FTIR spectra obtained for PTh, C-PTh, C-PTh-Co and C-PTh-Ni are shown in figure 2 (a-d). For all samples, bands in the ranges of: 1600-1635  $\text{cm}^{-1}$ , 1386-1384  $\text{cm}^{-1}$ , 1124-1116  $\text{cm}^{-1}$ , 1093-1031  $\text{cm}^{-1}$  are related to carbon-carbon bonds [28,29].

In the case of PTh (figure 2(a)), there is a band in 1334  $\text{cm}^{-1}$  related to the stretching of the C=S bond and overlapping with a C-C band. Bands seen in 1633, 1384, and 1118  $\text{cm}^{-1}$  are related to the C=C bands within the thiophene ring [28], although the first and the third bands show overlap with the C-C band. Bands seen in 898, 873 and 838  $\text{cm}^{-1}$  are due to the C-H vibrations inside the thiophene ring. The band at 786  $\text{cm}^{-1}$  corresponds to the vibration of the thiophene ring [28-30].

For C-PTh spectra (figure 2(b)), there are bands in 1602  $\text{cm}^{-1}$  and in 1124  $\text{cm}^{-1}$ , which could be related to CO bonds in carboxylic groups [31], and overlapped by the strong C=C bands. The band corresponding to the C=S bond (as seen in PTh) is very small and could be overlapped by the high C-C band too.

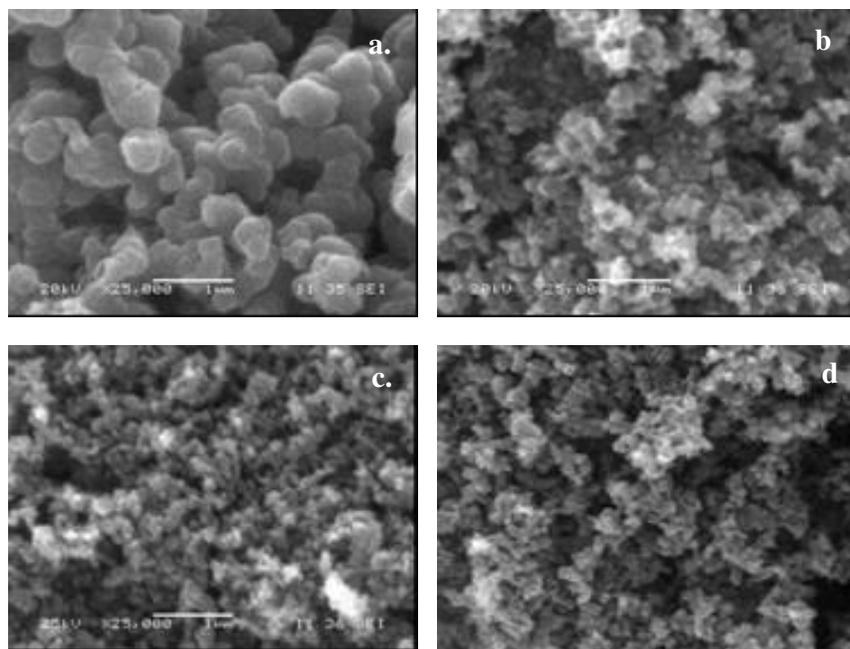
In the case of C-PTh-Co (figure 2(c)), the band located in 1600  $\text{cm}^{-1}$ , related to the C=C and C=O bond, is almost as high as the corresponding C-PTh sample; but the band seen in 1120  $\text{cm}^{-1}$ , related to the C-O bond, is higher than the mentioned precursor. The band related to the C=S bond does not appear, probably because it is overlapped by the high C-C bonds. For C-PTh-Ni, the band located at 1635  $\text{cm}^{-1}$  is smaller than its C-PTh precursor, as is the band seen in 1116  $\text{cm}^{-1}$ .

According to the proposed structures [7,25,26], sulphur atoms would be the main sites for cobalt and nickel attachment, since it is assumed that nickel and cobalt does not easily attach to carbon, as reported previously for nickel [29]. The changes in the bands located in the ranges of 1635-1600 and 1116-1124  $\text{cm}^{-1}$  in C-PTh, C-Pth-Co, and C-PTh-Ni samples could be an indication, that oxygen atoms in the carboxylic or hydroxylic groups could be bonded with the cobalt or nickel atoms respectively. In either case, the functional groups of C-S and probably CO, present at the sample surface, are involved in cobalt and nickel bonding. Any bands which may have resulted from cobalt-sulphur, nickel-sulphur, carbon-cobalt, and carbon-nickel, are not shown, since they appear at lower wave numbers [30,32].

### 3.3. Morphology and elemental analysis

Figure 3 shows SEM images for PTh (fig. 3(a)), C-PTh (fig. 3(b)), C-PTh-Co (fig. 3(c)) and C-PTh-Ni (fig. 3(d)). It can be observed that the carbon-supported samples C-PTh, C-PTh-Co, C-PTh-Ni have very similar morphology, while unsupported polythiophene has a very distinct structure.

All samples show an agglomerated grain structure. For polythiophene, the grains have diameters of around 200 nm and for carbon-supported samples, the grains are smaller, with diameters between 90 and 140 nm (being principally the carbon black morphology [25]). Lighter areas in the images of carbon black samples are related to charging and have the same composition as darker areas, as confirmed by EDAX.



**Figure 3.** SEM images of: a) PTh; b) C-PTh; c) C-PTh-Co; and d) C-PTh-Ni.

**Table 1.** Chemical composition in weight percent as obtained by EDAX.

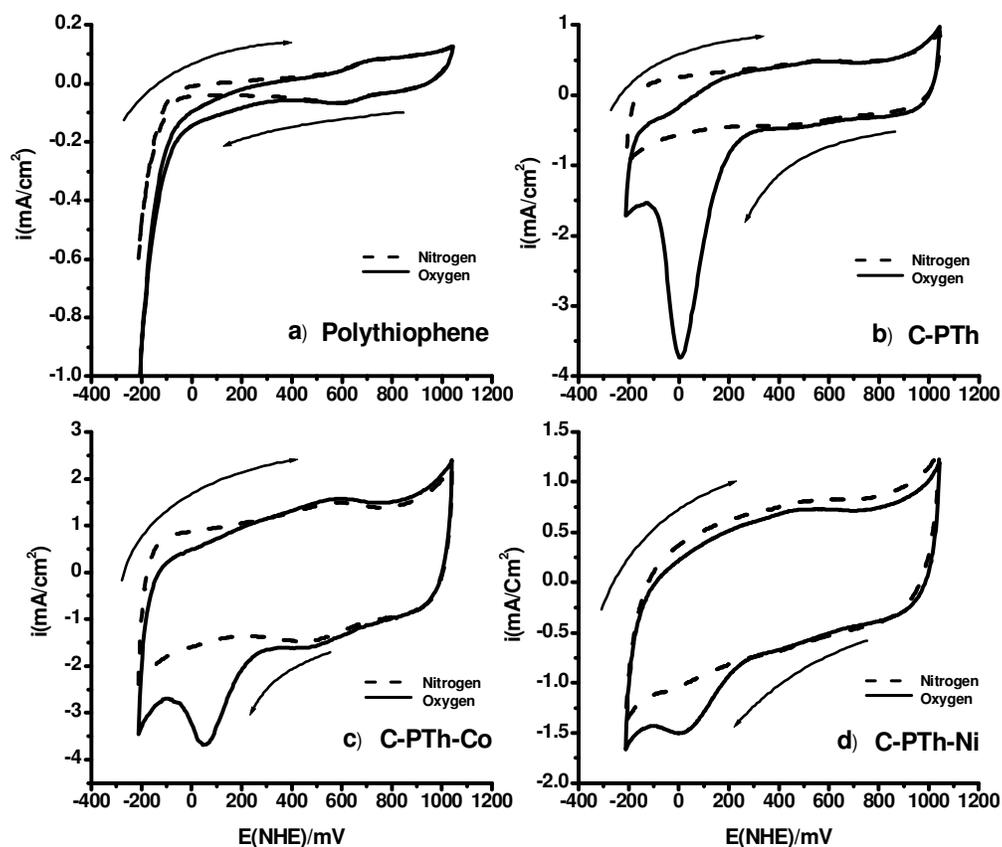
Catalyst	Composition (%wt)					Total
	C	O	S	Co	Ni	
Carbon black	94	6	--	--	--	100
PTh	69	2	29	--	--	100
C-PTh	86	13	1	--	--	100
C-PTh-Co	79	13	1	7	--	100
C-PTh-Ni	79	13	1	--	7	100

Table 1 shows the chemical composition obtained by EDAX. The main element is carbon, with quantities varying from 86 to 79% in carbon-supported samples, coinciding with the estimated values (see experimental section). Significant quantities of oxygen are found for all samples. For carbon black, superficial oxygen is present in the form of oxygen functional groups, such as the carbonyl, carboxylic, phenolic, anhydride, lactonic, and etheric groups [27]. The amount of oxygen increases for polymer-containing samples (compared to carbon black only), which is in agreement with FTIR results, which confirmed the existence of CO bonds, and suggested the presence of cobalt or nickel oxides or hydroxides. PTh, which is not carbon supported, contains smaller quantities of oxygen (2%), with a considerable high quantity of sulphur (29%wt). This correspond to a atom ratio of around 1:6 for S:C. For ideal polythiophene this ratio should be 1:4. The carbon black containing samples have small quantities of sulphur (1%wt), which is less than expected, based on the initial reactant ratios (8% for C-PTh, 7% for C-Pth-Co and for C-P3MT-Ni). For C-PTh-Co significant quantities of cobalt are found (7%wt) and the same quantity of nickel is found for C-PTh-Ni. In both cases this is less than the initial reactant ratios. In both samples, the Co:S and Ni:S ratio (7:1 in weight in both cases) does not

correspond to the proposed structures, which have an atomic ratio of 1:1, equivalent to a ratio of around 2:1 in weight. Therefore, the amount of cobalt or nickel in the C-PTh-Co and C-PTh-Ni respectively, is roughly three times higher than the proposed structure allows, indicating that other cobalt and nickel compounds are present, possibly as oxides and/or hydroxides.

### 3.4. Electrochemical characterization

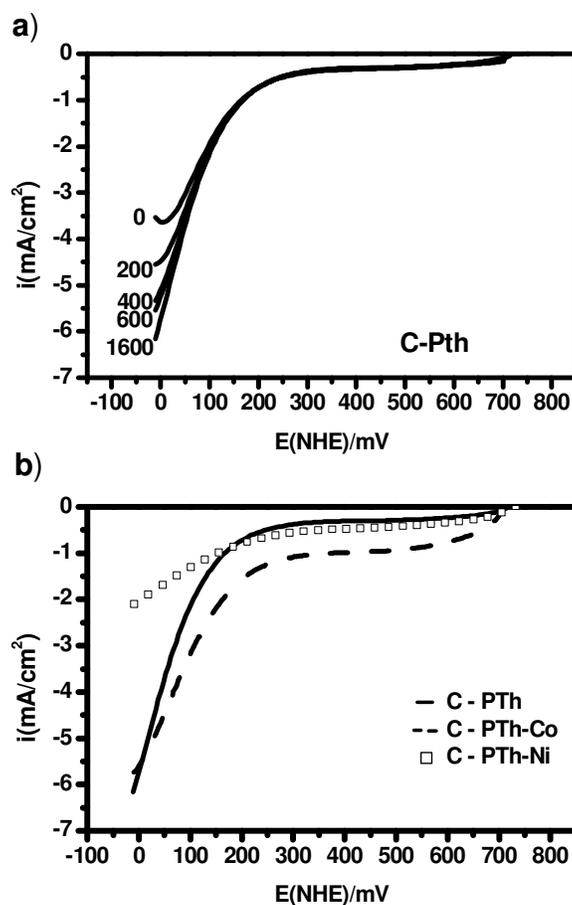
In order to study the activity of these materials for the oxygen reduction reaction (ORR), cyclic voltammetry was carried out. In figure 4(a-d) the obtained cyclic voltammograms are shown. The continuous curves were obtained in an electrolyte saturated with oxygen, while dashed lines correspond to oxygen-free atmosphere (under nitrogen). In oxygen-free electrolyte, curves show characteristic polymer oxidation at around 700 mV for PTh and 530 mV for carbon-supported samples and reduction at 600 and 450 mV, respectively, [16,20], as well as some hydrogen evolution at low potentials. Under oxygen, additional reduction peaks can be seen in the cathodic zone for all carbon-supported materials, indicative of the oxygen reduction reaction (ORR).



**Figure 4.** Cyclic voltammetry for: a) PTh; b) C-PTh; c) C-PTh-Co and d) C-PTh-Ni. Tests carried out at room temperature in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 20 mV/s.

In order to compare the ORR electrocatalytic activity for the different samples, the difference between the maximum current density for each ORR peak and the current density in its base were determined (as a measure for the activity). This current difference was highest for C-PTh ( $-3.174 \text{ mA cm}^{-2}$ ), followed closely by C-PTh-Co ( $-2.172 \text{ mA cm}^{-2}$ ) and at last C-PTh-Ni ( $-0.474 \text{ mA cm}^{-2}$ ).

In figure 5 the curves for electrochemical reduction of molecular oxygen in  $0.5 \text{ H}_2\text{SO}_4$  obtained using a rotating disk electrode (RDE) and a scan rate of  $1 \text{ mV/s}$  are shown. The experiments were carried out starting from the open circuit potential ( $E_{oc}$ ) of each electrode until reaching the potential where highest current density on the ORR peak was obtained. In figure 5(a) results for C-PTh are shown for different rotation speeds of 0, 200, 400, 600, and 1600 rpm. As expected, at lower potentials, increasing rotation speed leads to increasing current density. This behavior was observed for all samples. In figure 5(b) a comparison of results obtained at 1600 rpm for different samples under oxygen atmosphere are shown.



**Figure 5.** Results from rotating disk voltammetry, carried out at  $1 \text{ mV/s}$  in  $0.5 \text{ M H}_2\text{SO}_4$  saturated with oxygen: a) for C-PTh at 0, 200, 400, 600 and 1600 rpm; (b) for different samples at 1600 rpm.

In the polarization curves in semi-stationary state as shown in figure 5(a) for C-PTh, three areas can be identified. At overpotentials above  $0.130 \text{ V}$ , the reaction rates are determined by electron

transfer. At low overpotentials, below 0.023 V the process is controlled by oxygen diffusion. Mixed control is observed from 0.023 to 0.130 V. Kinetic parameters were obtained from these curves [4,5,25,33] and are presented in table 2 . Also the open circuit potential,  $E_{oc}$  is given.

It can be seen that all the materials have similar open circuit potentials ( $E_{oc}$ ) of around 0.7 V<sub>NHE</sub>. The Tafel slopes ( $-b$ ) are also similar, between 111 and 120 V/dec, as well as the charge transfer coefficients ( $\alpha$ ). The values obtained for the Tafel slopes indicate that the first electron transfer is the limiting step in the global ORR [2,33]. C-PTh has the highest exchange current density ( $i_o$ ) with  $3.65 \times 10^{-6}$  mA/cm<sup>2</sup>, followed by C-PTh-Co with  $1.35 \times 10^{-6}$  and C-PTh-Ni with  $1.48 \times 10^{-7}$  mA/cm<sup>2</sup>.

In order to further compare the performance of these materials as oxygen reduction catalyst, the potentials at which oxygen reduction takes place (at maximum current density for ORR from figure 4) were determined and are also listed in table 2. It can be seen that highest potential is obtained in the order of C-PTh-Co > C-PTh > C-PTh-Ni. For C-Pth, the addition of cobalt shifts the ORR reaction to more positive potentials, while the addition of nickel shifts it to lower potentials.

**Table 2.** Electrokinetic parameters obtained from RDE experiments.

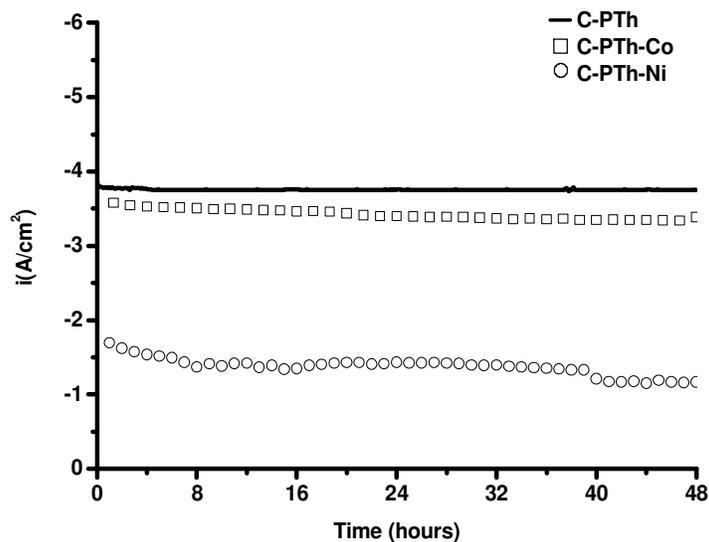
Electrode	$E_{oc}$ (V <sub>NHE</sub> )	$-b$ (V/dec)	$\alpha$	$i_o$ (mA/cm <sup>2</sup> )	$E$ (mV) at $i_{max}$ ORR
C-PTh	0.717	0.111	0.60	$3.65 \times 10^{-6}$	4
C-PTh-Co	0.701	0.116	0.55	$1.35 \times 10^{-6}$	46
C-PTh-Ni	0.720	0.120	0.46	$1.48 \times 10^{-7}$	1

Based on these data, of the materials studied, C-PTh-Co shows the best performance for ORR, with highest ORR potential, and intermediate exchange current density value ( $i_o$ ), tafel slope ( $-b$ ) and transfer coefficient value ( $\alpha$ ).

We have previously reported on the performance for ORR of carbon-supported polypyrrole (Ppy), polyaniline (Pani) and poly(3-methylthiophene) (P3MT), modified with cobalt or nickel [25,26]. In most cases, the addition of cobalt or nickel in the composites improved the electrocatalytic activity for the ORR, for example, nickel modified polypyrrole had the highest exchange current density with  $4 \times 10^{-5}$  mA/cm<sup>2</sup>, followed by nickel modified poly(3-methylthiophene) with  $3.5 \times 10^{-5}$  mA/cm<sup>2</sup> and cobalt modified poly(3-methylthiophene) with  $3.0 \times 10^{-5}$  mA/cm<sup>2</sup>. For the case of the ORR potentials, cobalt modified polypyrrole had the most positive potential (325 mV), followed by unmodified C-Ppy (93 mV) and nickel-poly(3-methylthiophene) (74 mV). For the case of the polyaniline containing samples, cobalt or nickel addition leads to similar values for the exchange current density and potential for maximum ORR, and in both cases, the composites had the lowest exchange current densities of all samples. Therefore, it can be concluded that the modification with nickel only improves performance in the case of poly(3-methylthiophene) and the addition of cobalt shifts the ORR reaction to more

positive potentials in all prepared composites [25,26]. For application purposes, the active potential range needs to be further increased.

In order to determine the stability of the materials in the acid environment during oxygen reduction, chronoamperometry was carried out during 2 days (see figure 6), applying for each sample the potential at which the maximum current density for ORR was observed from cyclic voltammetry (see figure 4 and table 2).



**Figure 6.** Chronoamperometric curves for C-PTh, C-PTh-Co, and C-PTh-Ni in 0.5 M H<sub>2</sub>SO<sub>4</sub> under oxygen

For C-PTh-Ni, a continuous decrease is observed, indicating a possible slow degradation of the sample. For C-PTh-Co, after a slight initial decrease in current response during the initial hours, a stable region is observed. In the case of C-PTh a constant current density, indicating good stability is observed in all tests.

#### 4. CONCLUSIONS

The electrocatalytic activity in acid medium of carbon-supported materials based on polythiophene with/without cobalt or nickel were studied. Also the synthesis and characterization of polythiophene were shown as a reference

FTIR, EDAX, and TGA results show that the addition of cobalt and nickel modifies the chemical structure of C-PTh, causing a change in physical and electrochemical properties. SEM images show similar morphology for all samples, except for polythiophene polymerized without carbon black. Changes in the FTIR bands suggest the existence of Co-S and Ni-S bonds for C-PTh-Co and C-PTh-Ni materials respectively. TGA results reveal that C-Pth is stable in a wide range of

temperature, nevertheless, the addition of cobalt and nickel reduces the thermal stability in an intermediate temperature range, possibly due to the presence of metal oxides or hydroxides, or carboxylic groups which decompose the polymeric chain at medium temperatures, but improves stability at high temperature in the case of C-PTh-Co, suggesting modification of the carbon support. Nevertheless, the composite catalysts are thermally stable in the range of the PEMFC operation temperature, between 80 to 100°C.

Based on cyclic voltammetry it was determined that in the potential range studied all materials, except polythiophene, have electrocatalytic activity for the ORR. The addition of cobalt results in more positive potentials for ORR for C-PTh, although it does not improve the electrocatalytic activity. The potential at which ORR occurs was determined to be highest for C-PTh-Co, followed by C-PTh and at last C-PTh-Ni.

Kinetic parameters, calculated from linear voltammetry using RDE, show that C-PTh has highest exchange current densities. All samples have Tafel slopes between -111 and -120 mV/dec, which indicate that the first electron transfer is the determining step in the global ORR. Based on exchange current densities, it is concluded that C-PTh presents the best electrocatalytic sites for ORR, while C-PTh-Co shows the most positive potential range for ORR. However, the potential range for ORR still needs to be shifted further upwards, before being able to apply these materials in commercial systems. Chronoamperometry shows a good stability for C-PTh and adequate stability of C-PTh-Co as cathode catalyst for ORR in acid medium.

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