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Abstract.

Electro-catalytic reduction of carbon dioxide has been studied with cobalt 5,10,15,20 tetrakis(4-aminophenyl)porphyrin forming a conducting polymer on indium tin oxide electrode, using an ionic liquid as a novel reaction media. Electrocatalytic reduction of CO_2 has been developed, the potential at which this occurs has been reduced from -2.4 V vs Ag/AgCl reported before, to -0.8V vs Ag/AgCl which means a significant energy gain regarding the electrochemical fixation of CO_2. Electrochemical impedance spectroscopy (EIS) experiments have been carried out in order to understand the electrical behavior of the modified electrode in ionic liquid medium. Spectroelectrochemical evidence suggests that the reactive species which promotes the reaction is an electrochemically generated Co (I) porphyrin species which can be detected in inert atmosphere but not in the carbon dioxide saturated medium.

Journal Name

ARTICLE

Electrocatalytic reduction of carbon dioxide on Cobalt tetrakis(4-aminophenyl)porphyrin modified electrode in BMImBF₄.

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Electro-catalytic reduction of carbon dioxide has been studied with cobalt 5,10,15,20 tetrakis(4-aminophenyl)porphyrin forming a conducting polymer on indium tin oxide electrode, using an ionic liquid as a novel reaction media. Electrocatalytic reduction of CO_2 has been carried out, the potential at which this occurs has been reduced from -2.4 V vs Ag/AgCl reported before, to -0.8V vs Ag/AgCl which means a significant energy gain regarding the electrochemical fixation of CO_2. Electrochemical impedance spectroscopy (EIS) experiments have been carried out in order to understand the electrical behavior of the modified electrode in ionic liquid medium. Spectroelectrochemical evidence suggests that the reactive species which promotes the reaction is an electrochemically generated Co (I) porphyrin species which can be detected in inert atmosphere but not in the carbon dioxide saturated medium.

Introduction.

Carbon dioxide from anthropogenic sources is one of the major cause responsible for global warming. The conversion of this greenhouse gas into useful products is a topic of main concern for different kinds of chemical research areas, such as chemical engineering, organic chemistry, and electrochemistry [1–4]. Hence its conversion to other useful molecules has become an important issue, in this context; electrochemical reduction of CO_2 seems to be one the most efficient way to convert and/or removal of CO_2 [5–8].

Different kinds of compounds containing transition metals have been studied toward the electrocatalytic reduction of carbon dioxide, many of them such as porphyrins have shown electrocatalytic activity toward the reduction of carbon dioxide [9–19]. The use of this compounds as electrocatalyst allows the reduction of this stable molecule to other useful carbon based products such as formic acid, methanol and carbon monoxide at low overpotentials [20], increasing the possibility of using this kind of methodologies in industrial applications due to their above mentioned properties.

 Coordination compounds have become very promising in the field of electrode modification, hence, the study of these modified surfaces toward the reduction of a variety of substrates has been extensively investigated [13,14,21,22].

Ionic liquids are salts with melting points below 100°C, many of this salts present melting points below room temperature, and in this case they are defined as room temperature ionic liquids

(RTIL). This molten salts are formed by highly asymmetric ions, often a bulky organic cation and an inorganic anion [23–26]. Due to its particular structure, ionic liquids present many interesting properties, such as low vapor pressure, low volatility, thermal and electrochemical stability among others. Probably, the most interesting characteristic of these materials is the wide range of ions that can be used to form a vast variety of ionic liquids, thus allowing the modeling of its physicochemical properties depending of the choice of the anion and the cation, giving rise to task specific solvents [25].

The electrochemical reduction of carbon dioxide in aqueous media and other molecular solvents has been previously reported at low overpotentials [27-28], nevertheless the reduction of this substrate has been recently reported in ionic liquids at -2.4V vs Ag/AgCl, activated species from the reduction of carbon dioxide have been studied toward the reaction with amines and epoxides in order to obtain carbamates or cyclic carbonates [29,30]. However, due to the high overpotential applied and the use of metallic electrodes these systems present many practical drawbacks, mainly due to the high energy used and possible corrosion of the electrode material [31]. In order to decrease the potential necessary to reduce carbon dioxide, Rosen and coworkers designed a method to reduce carbon dioxide using a nanostructurated silver electrode in aqueous solution of 1-ethyl-3-methylimidazolium tetrafluoroborate , this compound can coordinate CO_2 molecules in order to reduce the potential applied, producing CO as reaction product at -1.5V vs Ag/Ag⁺, therefore, the use of coordination chemistry, could represent a

feasible way to activate CO_2 and then reuse this greenhouse gas as a green source of carbon [3].

This work deals with ionic liquids, specifically 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) as a reaction medium for the electrocatalytic reduction of carbon dioxide, using a conducting polymer of Cobalt 5,10,15,20 tetrakis(4-aminophenyl)porphyrin (Co-TAPP) grown in the surface of an indium tin oxide electrode (ITO).

Experimental

Materials. Reagents and solvents of analytical grade or higher, were purchased from Sigma Aldrich and used without further purification. 5,10,15,20 tetrakis(4-aminophenyl)porphyrin (TAPP) [32]; and Co-TAPP [33] were synthesized following previously reported synthetic routes and were characterized by standard spectroscopic methods. Tetrabutyl ammouium perchlorate (TBAP), sodium perchlorate and $BMImBF_4$ (>98.5%) were purchased from Sigma Aldrich and dried prior to use.

Electrochemical Measurements. Electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), linear sweep voltammetry (LSV) and potential controlled bulk electrolysis (PCBE) were carried out using a CH Instruments 760C and a BASi PWR-3 potentiostats respectively. An optically transparent indium tin oxide (ITO)(Delta Technologies, CO, USA. 1.5 cm²) and Pt wire were used as working and counter electrodes respectively. All the potential values are informed using a Ag/AgCl reference electrode which has been sealed and separated from solution, its connection has been done using a Pt bridge, working as a Luggin capillary, avoiding moisture contamination to the working solution in the experiment timescale [34], reference electrode has been previously calibrated using ferrocene/ferrocenium couple, finding that the potential of the Ag/AgCl reference electrode in $BMImBF_4$ is 0.191V vs NHE. Gas chromatography measurements of reaction products were carried out using a DANI MASTERS GC, with a fused silica capillary column (Supelco Mol Sieve 5A plot, 30m x 0.53mm) coupled with a micro thermal conductivity detector (µTCD) using Ar as a gas carrier with an isothermal program at 40°C.

Working electrode modification. Polymeric films were grown after 50 potentio-dynamic cycles at 200mV/s between -0.9V and 1.1V vs Ag/AgCl using solutions of 1mM Co-TAPP and 0.1M TBAP in DMF, an ITO electrode (Area: 1.5 cm²) was used as a working electrode, a Pt wire (8 cm²) as a counter electrode and a non-aqueous Ag/AgCl system as a quasi-reference electrode [21]. After polymerization, the modified electrode was rinsed with dimethylformamide (DMF), and then with doubly distilled water in order to remove any amount of starting compound on the surface. Then the remaining non-polymerized amino groups in the film were oxidized using cyclic voltammetry in an aqueous solution (0.1M of $NaClO_4$), thus obtaining a more ordered and homogeneous surface. This process is subsequently called stabilization through this work [35,36].

Surface coverage has been estimated by UV-VIS measurements just as previous work reported by Li et.al [37].

Electrochemical impedance spectroscopy measurements. The EIS measurements were carried out using ITO electrodes, prior and after the modification process. All the measurements were carried out in $BMImBF_4$ at a working potential of -0.8V vs Ag/AgCl, with amplitude of 5mV measured frequencies were from 10^{-2} to 10^5 Hz. Experimental data obtained from the EIS measurements were fitted using CHI760c software.

Electrocatalytic studies. Carbon dioxide reduction in $BMImBF_4$ on the modified electrodes was evaluated in a CO_2 saturated media (93mM) [38], where the ionic liquid acts as a supporting electrolyte and solvent. The study of the electrocatalytic activity was carried out using LSV into an undivided glass cell while PCBE was carried out into an H-type cell, using in both cases a three electrode arrangement previously described. [14,15]

Spectroelectrochemical study. The potential dependent UV-Vis spectra recorded using an UV-Vis spectroelectrochemical cell (Optical path: 1 cm, total volume: 2.5mL) using a three electrode array, including the optically transparent ITO as a working electrode, an Ag/AgCl quasi-reference electrode and a Pt wire as a counter electrode. [14,39].

Morphological characterization. Morphological properties of the polymeric films were registered using Carl Zeiss EVO MA10 microscope, images were taken to the modified electrode stabilized in $NaClO_4$, and also sequentially stabilized in $NaClO_4$ and then $BMImBF_4$. UV-Vis spectra were registered to the electrode after the immersion and proper stabilization process in order to determine the presence of the conducting polymer on the ITO surface.

Results and discussion

Electrode modification and morphology. In order to understand the as yet poorly studied interaction between conducting polymers and ionic liquids and to shed light about the influence of this interaction in the electronic properties of the modified electrodes, SEM images were recorded to two modified electrodes; the first one stabilized in aqueous media ($NaClO_4$ 0.1M) and the second in aqueous media and then in $BMImBF_4$. Figure 1a displays the SEM image taken to the modified electrode after ten potentiodynamic cycles in aqueous media containing 0.1 M $NaClO_4$ as supporting electrolyte. The conductive polymer grown on the ITO electrode has a typical heterogeneous distribution on the surface, mainly due to its well described polymerization mechanism, where the oligomers are formed from reaction between the terminal amino group and the
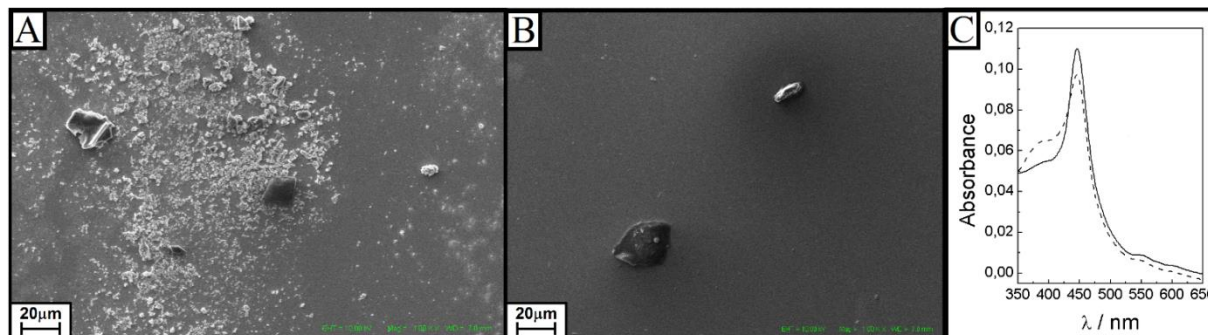
Figure 1. a) SEM image of the modified electrode stabilized in NaClO$_4$ 0.1M, and b) stabilized in BMImBF$_4$; c) UV-Vis spectra of ITO/Poly-CoTAPP modified electrode stabilized in aqueous solution of NaClO$_4$ (solid line) and stabilized in BMImBF$_4$ (dashed line).

alpha carbon of another porphyrin molecule, being similar to the electropolymerization of para substituted aniline. These oligomers lead the generation of small accumulations of conducting polymer dispersed according to defects on the surface [40].

Figure 1b displays SEM image of ITO/Poly-CoTAPP modified electrode, after treatment in the ionic liquid, the SEM image reveals a change in the morphology, leading to a more ordered and homogeneous surface, fact that is explained by chemical composition of the solvent. Hence, ions must diffuse or intercalate trough the conducting polymer frame as the potentio-dynamic cycles pass, forcing a physical rearrangement leading to a new distribution of the material on the surface.

Influence of ionic liquids in the morphology of several electrodic materials have been described, indeed Armel et.al. [41] has studied the swelling effect of phosphonium ionic liquids over PEDOT, this morphology change has been attributed to an effective intercalation of the ionic liquids molecules into the polymeric matrix. Sutto et.al. has also investigated the exfoliant effect of ionic liquids over metal dichalcogenides (TiS$_2$) [42], concluding that imidazolium ionic liquids are capable to intercalate strong assembled layers and therefore can be used as a media to obtain single layered materials.

Finally a similar behavior has been described by Lagoutte et.al. [43], in their work, authors has been studied the effect of ionic liquids in the structure of thiophene based conducting polymers (PEDOT), and concluded that ionic liquid can strongly modify both the voltammetric and structural properties of the modified electrode, authors have also concluded that polymers grown in ionic liquid media form smaller structures, leading to a more ordered polymer layer than the conducting polymers grown in molecular solvents. Having these facts in mind, the effect of BMImBF$_4$ on the ITO/Poly-CoTAPP electrode is clear, despite their large cation size, it is possible that some intercalation may occur into metalloporphyrin layers just in the case as PEDOT films [41].

Figure 1c shows spectra of ITO/Poly-CoTAPP modified electrodes, registered in air, where solid line corresponds to the electrode of Figure 1a and dashed line to electrode of Figure 1b; a signal at 446 nm which corresponds to a π- π* transition band, known as Soret band, can be observed, it is also possible to note two other characteristic transition from the same origin,

denominated as Q bands, at 550 nm and 605 nm. However, spectrum corresponding to Figure 1c shows a new band at 383nm, fact that confirms a strong interaction between the ionic liquid and the formed film, a similar behavior has been observed in solid state [44] and in solution [45].Then it is possible to note that despite of morphological change induced by BMImBF$_4$, the conducting polymer keep its electronic properties (Figure 1a) also indicating that the electroactive material remains on the surface of the electrode.

Electrocatalytic activity. Cyclic voltammetry of the ITO and ITO/Poly-CoTAPP modified electrode was studied in BMImBF$_4$ at 100 mV/s and shown in Figure 2a. A quasi-reversible couple is observed (E$_{1/2}$: -0.75V vs Ag/AgCl) corresponding to the monoelectronic reduction Co(II)/Co(I). This fact confirms the effective modification of the electrode, and the presence of cobalt confined in the electrode surface. The poor reversibility of the process is explained by the high viscosity of the ionic liquid, which affects directly the conductivity of the medium [26]. Scan rate effect on Ip does not show any linear tendency, fact explained by the intercalation phenomena above described.

Figure 2b shows LSV of ITO and ITO/Poly-CoTAPP modified electrode recorded at 5 mV/s in BMImBF$_4$ medium under N$_2$ and CO$_2$ atmospheres respectively. In the LSV recorded in inert medium (N$_2$), a reduction signal at -0.6V vs Ag/AgCl can be observed, which can be assigned to the Co(II)/Co(I) redox process according with Figure 2a. In CO$_2$ atmosphere an increase in the cathodic current at -0.6V vs Ag/AgCl is observed, which may correspond to CO$_2$ reduction, this fact suggests that the electroactive species for the CO$_2$ reduction is the Co(I) center electrochemically generated in the film [14,46].

Preparative scale electrolysis was performed in an undivided glass electrochemical cell during 4 hours. After this, no color changes in the electrode or in the ionic liquid were observed; suggesting the stability of the film. At -0.8V vs Ag/AgCl, carbon monoxide was the only reaction product detected by gas chromatography with a kinetic behavior showed in the inset of Figure 2b, showing a faradaic efficiency of 64,9%.

It can also be seen that at times longer than 200 min, there is a decrease in the carbon monoxide produced, probably related to a redisolution of the product in the ionic liquid media.

As a measurement of the efficiency of the electro-catalyst turnover number (TON), defined as the number of moles of
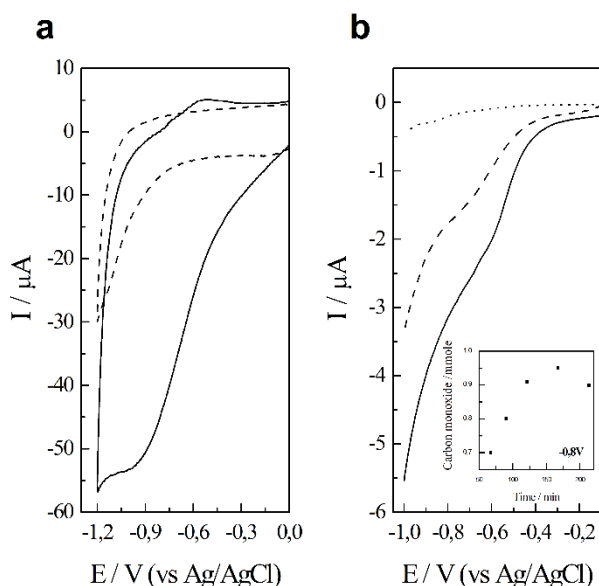
a

b

capacitance represented by a constant phase element whose impedance (Z_{CPE}) assuming no diffusional processes is described by Eq 1.

$$Z_{CPE} = T(j\omega)^{-P} \qquad (1)$$

Where ω is the angular frequency, T is an admittance parameter, and P is a dimensionless parameter which may vary from 0 to 1, being 0 for a total resistor and 1 for a pure capacitor.

This non-ideal behavior has been reported in literature [48], and has been attributed to the roughness of this electrodic surfaces.

Figure 4a and b, displays Bode plots of the ITO and ITO/Poly-CoTAPP modified electrodes, which present two clear slope changes, confirming the existence of three processes; at high frequencies, showing a constant value of |Z|, a process related to the resistance of the solution; then the slope changes to a value close to -1, which can be associated to a capacitive behavior of the electrode. At low frequencies, |Z| remains constant, process related to resistance toward faradaic current *i.e.* faradaic resistance (R_F) [48–51]. This behavior is common for all the systems studied in this work. Relevant data extracted from table 1 show that the main variables are P and R_F values.

P values for ITO electrode are similar in inert atmosphere ~0.85 and approximates to 1 (~0.91) when carbon dioxide is in solution, value close to 1 it represents a pure capacitive behavior [51]. For the system ITO/Poly-CoTAPP the behavior follows the same trend to that observed for ITO blank electrode, this capacitive behavior could be explained in terms of the presence of a new molecule in the double layer for ITO electrode. On the other hand, the increase of P value for ITO/Poly-CoTAPP modified electrode can be associated with the direct interaction of the carbon dioxide with the conducting polymer due to the electrochemical reaction which takes place between the reduced porphyrin film and the carbon dioxide.

In case of bare ITO electrode, there is no chemical layer that could resist to the current flow, hence the faradaic resistance
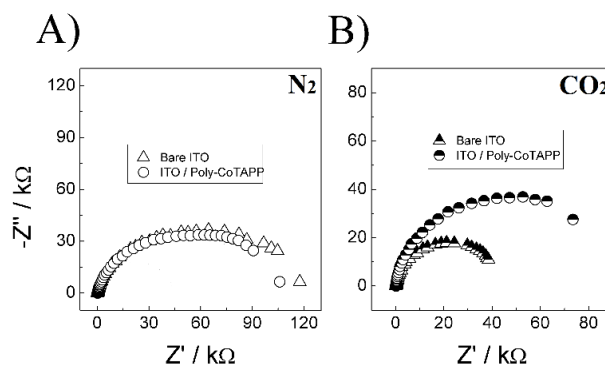
Figure 2. a) Cyclic voltammetry of bare ITO electrode (dash line) and ITO/Poly-CoTAPP modified electrode (solid line), in BMImBF$_4$; Scan Rate: 100mV/s. b) Electrochemical behavior measured by LSV at 5 mV/s of bare ITO electrode (dot line), and Poly-CoTAPP modified electrode under N$_2$ (dash line) and CO$_2$ (solid line) in BMImBF$_4$. INSET: Carbon Monoxide production as a function of the time.

product that a mole of catalyst can generate before becoming inactivated, was determined; showing a dimensionless value of close to 69, similar of those previously reported for similar systems [46].

Cyclic voltammograms carried out with the modified electrode prior and after 4 hours of electrolysis show that the Co(II)/Co(I) redox process keeps a 75.7% of its charge, meaning that even when the electrode is active to the reduction of CO$_2$, its activity decreases in terms of active material deposited over its surface as the electrolytic process occurs.

Electrochemical impedance spectroscopy. Figure 3 shows the Nyquist plots of the ITO and ITO/Poly-CoTAPP in BMImBF$_4$ at -0.8V under N$_2$ and CO$_2$ atmospheres (Figure 3a and 3b respectively). In both cases an imperfect semicircle shape is observed and since all the maxima on phase angles for the systems studied are far from 90° (~75°), (see Figure 4) a non-ideal capacitive behavior has been assumed which can be associated to the electrical behavior of a pseudo-capacitor in parallel to a resistance, using this model (Scheme 1), data were fitted within an error of 2%. Relevant data of the electrodes in different media has been summarized in Table 1.

This equivalent circuit (see Scheme 1) describes the interaction of three elements, the solution resistance (R_S), the electrode resistance to faradaic process (R_F) and the double layer

A)   **B)**

Figure 3. Nyquist plots carried out under: a) N$_2$ atmosphere of bare ITO electrode (circle) and ITO/Poly-Co(TAPP) (triangle); and b) CO$_2$ atmosphere of bare ITO electrode (half-filled circle) and ITO/Poly-Co(TAPP) (half-filled triangle). Measurements were carried out in BMImBF$_4$ without any other species in solution.

Figure 4. Bode plots carried out carried out under: a) N_2 atmosphere of bare ITO electrode (circle) and ITO/Poly-Co(TAPP) (triangle); and b) CO_2 atmosphere of bare ITO electrode (half-filled circle) and ITO/Poly-Co(TAPP) (half-filled triangle). Measurements were carried out in $BMImBF_4$ without any other species in solution.
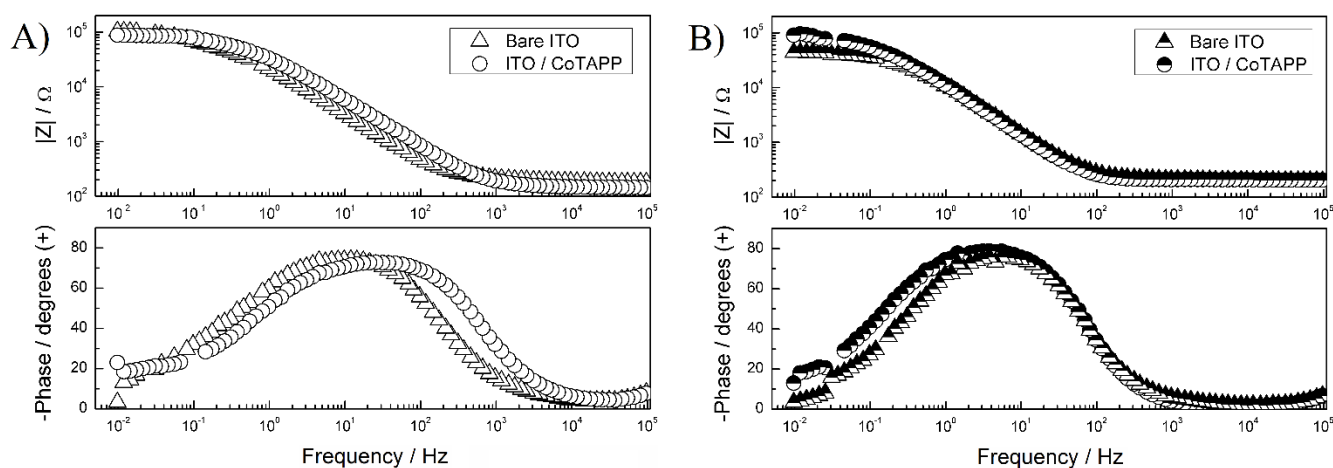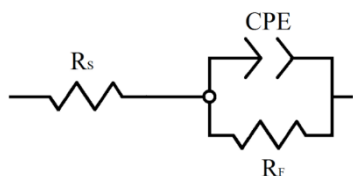

Scheme 1. Equivalent circuit proposed for the systems studied in this work.

(R_F) is only given by the inherent reactivity of the ITO surface in the ionic liquid medium, which has been described as a densely packed arrangement of ions [52] mainly due to the inexistence of solvent molecules than could solvate the ionic species that form the double layer; then, depending of the polarization of the electrode, a highly ordered ionic layer is generated [53,54]. In summary, charge transfer processes for ITO electrode are defined and limited by the double layer properties.

Table 1. Electrochemical impedance spectroscopy data for the systems studied in this work where R_F represent the resistance to faradaic processes, T and P represent parameters of Z_{CPE} [44].

Electrode	Atmosphere	R_F (Hz)	T	P
Bare ITO	N_2	99843	9.8×10^{-6}	0.85
	CO_2	41774	16.7×10^{-6}	0.91
ITO / CoTAPP	N_2	95844	5.7×10^{-6}	0.84
	CO_2	79750	16.3×10^{-6}	0.93

Therefore for the bare ITO electrode in N_2 saturated media the magnitude of R_F is related to electronic transfers that takes place on the electrodic surface and will strongly depend of the double layer properties. On the other hand, for the CO_2 saturated media, there is a decrease in the magnitude of R_F related to the deformation of the double layer due to the inclusion of CO_2 molecules, which will interact strongly with imidazolium [55,56], therefore, the double layer loses its characteristic density

and could allow an easier electron transfer and as a result, decreasing the value of R_F.

On the other hand, the poly-CoTAPP modified electrode in N_2 atmosphere has a R_F value similar to the bare ITO electrode, even when the polymeric film attached to its surface should increase R_F, this fact can be explained by the stronger effect of the ionic liquid double layer over the migration of species through the polymer. Finally, the charge transfer due to the reduction of the cobalt centers will depend strongly on the deformation of the double layer that must exist in order to allow the electron transfer i.e. the polymeric surface presents the same oxide – electrolyte behavior than the ITO surface and then, both magnitudes must be similar.

Moreover, the poly-CoTAPP electrode in CO_2 present a decrease in R_F compared to the value obtained in inert atmosphere; but its analysis is slightly more complex than the other system due to the reduction of the carbon dioxide that takes place at those potentials, and the migration of reduced and oxidized species that must occur in order to complete the electrochemical reaction; thus, this resistance can be explained in terms of two components, the resistance associated to the deformation of the electric double layer, and the mobility of the chemical species through the polymeric film. As a consequence of both phenomena R_F for the modified electrode in CO_2 is lower than the electrode in N_2 but higher than the bare ITO electrode, in which the effect of the migration through the film does not exist.

Spectroelectrochemical characterization. The potential dependent UV-Vis spectra of the ITO/Poly-CoTAPP modified electrode (Figure 5a) showed the classic profile of a cobalt porphyrin, with a band at 446 nm which corresponds to the Soret band, transitions at 553 nm and 606 nm which correspond to Q bands. [32,57].

During the application of -0.8V vs Ag/AgCl in N_2 saturated $BMImBF_4$, a decrease in the intensity of the Soret band can be seen, this fact suggests a decrease of the concentration of Co(II) porphyrin in the surface due to the electrogeneration of new
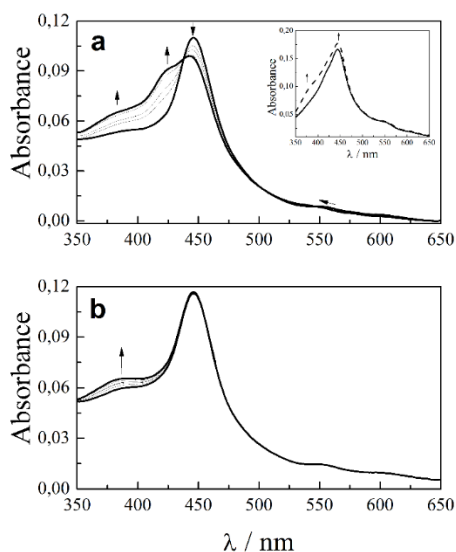
Figure 5. Spectroelectrochemical behavior of the modified electrode at constant potential (-0.8V vs Ag/AgCl) under a) N_2 and b) CO_2. INSET: Spectroscopic behavior of the film as a function of the time.

species at the electrode; also a new transition can be seen at 423 nm that corresponds to the Soret band of the electrogenerated Co(I) porphyrin [58–60].

The dynamic behavior of the film without the application of potential can be seen in the inset of Figure 5a, in which a progressive increase of the Soret band, and the apparition of a new band at 383nm can be seen; which correspond to physical rearrangements, previously discussed. However both results are not contradictory, since spectra in Figure 5a are consequence of one minute of applied potential (-0.8V vs Ag/AgCl), while spectra in the inset of Figure 5a is about 5 min of continuous record. Thus, both process present different kinetic behaviour.

Figure 5b shows the spectroelectrochemical behavior of the modified electrode in CO_2 saturated medium, during the application of -0.8V vs Ag/AgCl no shifts can be observed, just the increase of the intensity at 383 nm which correspond to the same physical rearrangement seen in the inset of Figure 5a.

The spectroelectrochemical changes in each spectrum give an interpretation of the electronic behavior of the film, while the electrogeneration of the Co(I) porphyrin in inert atmosphere is clear [46], in carbon dioxide these changes cannot be seen; this fact can be explained by the reactivity of the Co(I) species toward the reduction of CO_2 [46,61-63], once the reduced porphyrin is electrogenerated, it is rapidly reoxidized by the carbon dioxide, forming activated species of CO_2 which can act as reaction intermediates in the formation of various products, including carbon monoxide [20].

Conclusions

Morphological characterization of the electrode has been performed in two different media, notable changes has been detected in both cases. In ionic liquid media the conducting polymer is rearranged by effect of strong interaction with the ionic liquid molecules. It is also possible to note that ionic liquid can penetrate under the poly-metalloporphyrin layer, leading to a more homogeneous surface.

EIS characterization of the modified electrode describe the effect of the ionic liquid into the polymeric matrix, showing that the mobility of the bulky ions of the ionic liquid directly affect the faradaic resistance of the electrode. Also, the electrochemical behaviour of the electrodes has been studied, showing that the reduction of carbon dioxide can be detected as a resistance due to the mobility of the substrate trough the film.

Carbon dioxide has been reduced at -0.8V vs Ag/AgCl instead of -2.4 V vs Ag/AgCl reported previously using the same reaction media, or the -1.5V vs Ag/Ag$^+$ reported using a ionic liquid as catalyst, in both cases involving a major energy gain in order to the electrochemical fixation of CO_2 in molecules of interest.

The electrogenerated Co(I) porphyrin is the responsible of the electrocatalytic response of the electrode. In addition, the detection of CO as the only reaction product, is a clear evidence of the electrode selectivity, avoiding the production of common sub-products like H_2, which can be detected when trace amounts of water is present in the system.

Acknowledgements

Notes and References

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