Electrochemical reduction of CO$_2$ mediated by poly-M-aminophthalocyanines (M = Co, Ni, Fe): poly-Co-tetraaminophthalocyanine, a selective catalyst

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Abstract

The electrochemical reduction of carbon dioxide was studied on a glassy carbon electrode modified with either polymeric M-tetrakis aminophthalocyanines (M = Co, Ni, Fe) or with the polymeric free ligand, in aqueous electrolyte. The reaction products are dependent on the central ion: for Co-polymer the only reaction product found was formic acid; for Ni polymer, formic acid and formaldehyde were found, whereas formaldehyde and H$_2$ were detected for Fe polymer. For the free ligand polymer only H$_2$ was detected. Spectroelectrochemical experiments show that in the case of Co-polymer, Co(I) is the active site of the electrocatalysis but the reduced cobalt center and the reduced ligand are not enough to promote the reduction of the carbon dioxide and an extra overpotential is necessary. In the case of the Ni polymer, the reaction takes place at the same potential where the complex is double reduced and it is not necessary to apply more potential. On the other hand, there are important differences between the *morphologies* of both polymers as demonstrated by electrochemical impedance spectroscopy. The experiments show that the metallic center affects the kinetics of polymerization and the polymer morphology. On the other hand, the chemical nature of the metal center of the catalyst is the most important factor in the electrochemical reduction of CO$_2$ and the products involved.

1. Introduction

The electrochemical reduction of CO$_2$ has been extensively studied due to its increasing concentration in the atmosphere generating the so-called "green house effect" which might cause undesirable changes in the environment. It presents the possibility of recycling and transforming this raw material into a source of carbon for chemicals or fuels [1–3]. This reaction has been studied on different electrodes;

metallic cathodes such as Hg, Pb, Sn, In, Au, Ag, Pt, Ni and Cu [4–6] and semiconductors such as p-Si, p-CdTe, p-InP, p-GaP, n-GaAs [3,7,8]. Carbon electrodes have also been used but, in this case, the reaction requires high overpotential and depending on the electrolyte, evolution of H$_2$ could decrease the efficiency of the process [9–11]. However, it is possible to use carbon electrodes if transition metal complexes act as electronic mediators either in solution [12–17] or becoming modified electrodes [18–23]. Azamacrocycles like porphyrins or phthalocyanines containing different transition metals have been investigated showing good electrocatalytic behavior when forming parts of modified electrodes [24–32].

For these cases, the selectivity and efficiency will depend on the media, applied potential, and microenvironment among other factors [24–32].

In the last years the possibility of electropolymerizing aza-macrocyclic complexes on carbon electrodes surfaces has also been studied [33,34], and a wide variety of reactions has been proved like O_2 reduction [34], hydrazine [35] and thiols oxidation [36–38] among others [39–42]. Few works have been focused in the electrocatalysis of CO_2 mediated by polymeric systems derived from azamacrocyclic complexes. However, there are electrocatalytic studies that have shown a higher stability and enhanced electrocatalytic activity for polymers compared to monomers adsorbed on electrodic surfaces [39].

Therefore, this work deals with the electrocatalytic study of modified glassy carbon electrodes with poly-M (M = Fe, Co and Ni) and poly-H_2 (the free ligand) tetrakis aminophthalocyanine as electrocatalysts for carbon dioxide reduction in aqueous media. The study was carried out using cyclic voltammetry, potentiostatic electrolysis, UV–vis spectroelectrochemistry and electrochemical impedance spectroscopy (EIS) in order to analyze the polymer selectivity as well as its reactivity as a function of the metallic center.

2. Experimental

M-tetrakis aminophthalocyanines (M-TaPc, where M = Co, Ni and Fe), from Midcentury Co., were used *after vacuum sublimation*. The free ligand (H_2-TaPc), see Fig. 1, was synthesized using a modified procedure reported by Achar et al. [43,44]. The conducting transparent electrodes were prepared by SnO_2:F deposition on a glass sheet. The glassy carbon electrodes, from PINE (geometrical area of $0.19\,cm^2$) were polished with $0.25\,\mu m$ alumina before each experiment. The electrosynthesis of the polymeric films was performed by continuously cycling the electrode potential between -0.4 and $1.0\,V$ (versus Ag|AgCl) at $100\,mV\,s^{-1}$ (or $200\,mV\,s^{-1}$ for the Fe complex) during 50 potentiodynamic cycles. The electrolyte used in the electropolymerization was a 0.1 M tetrabutylammo-

nium perchlorate/dimethylformamide (DMF) solution (or dimethylsulfoxide (DMSO) solution for the Fe complex) containing the M-macrocycle or H_2-macrocycle monomer (ca. 1 mM). The electrolyte was purged with nitrogen (ultra pure grade) before and during the blank experiments and kept at room temperature. After the polymerization, the modified electrodes were rinsed with DMF or DMSO, ethanol and bi-distilled water. The electrochemical experiments were performed in a three-compartment glass cell: the working electrode, either glassy carbon ($0.19\,cm^2$) or conducting glass ($2\,cm^2$); the reference electrode, Ag|AgCl in saturated KCl; the auxiliary electrode, a Pt coil ($10\,cm^2$).

UV–vis spectroelectrochemical experiments were performed in a one-compartment quartz cuvette containing similar, but smaller, auxiliary and reference electrodes. All the characterizations (electrochemical and spectroscopic) of the modified electrodes were carried out in an aqueous solution of 0.1 M $NaClO_4$ (pH = 7.0) purged with ultra pure N_2. The electrocatalysis of CO_2 reduction was investigated using a solution of 0.1 M $NaClO_4$ saturated with pure CO_2 (pH = 4.0).

EIS measurements were carried out at potentiostatic conditions, at several potentials in the range 0.7 to $-1.0\,V$ (versus Ag|AgCl) at a frequency range from 10 mHz up to 10 kHz. The ac potential perturbation was 10 mV in a PGSTAT 20 AUTOLAB/GPES potentiostat/galvanostat system from Eco-Chemie coupled to an EcoChemie frequency response analyzer module. An AFCBP1 Pine bipotentiostat, along with Pinechem 2.5 software was used for the electropolymerization and to obtain data on the electroreduction of CO_2. A Varian Cary 1E spectrometer, along with CARY WIN UV software, and coupled to a Wenking POS 73 Potentioscan, was used to obtain the UV–vis spectra. All the spectra recorded were baseline corrected. The potential controlled electrolysis was carried out with a Universal Programmer Model 175 coupled to a Digital Coulometer 179 both from PAR. All these experiments were performed at $-1.0\,V$ (versus Ag|AgCl) during 1.5 or 6 h. A gas tight two-compartment cell was used and the experiments were carried out at 1 atm of CO_2. Product analysis were carried out by gas chromatography in a Varian 3400 instrument equipped with a Molesiv capillary column and a Thermal Conductivity Detector for identification of gas products. The carrier gases were Ar and He for H_2 and CO, respectively. A spectroscopic, chromotropic acid, method was used in the identification of formic acid and formaldehyde [18–20]. Gas samples were monitored every 30 min and soluble substances were analyzed after finishing the experiments.
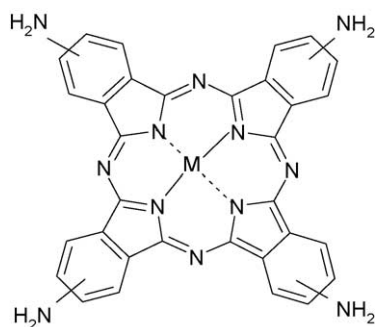

Fig. 1. Molecular structure of the ligand tetra-aminopthalocyanine H_2-TaPc. The replacement of the internal H by M gives rise to the complex M-TaPc.

3. Results and discussion

3.1. Voltammetric behavior of the polymers in presence and absence of CO_2

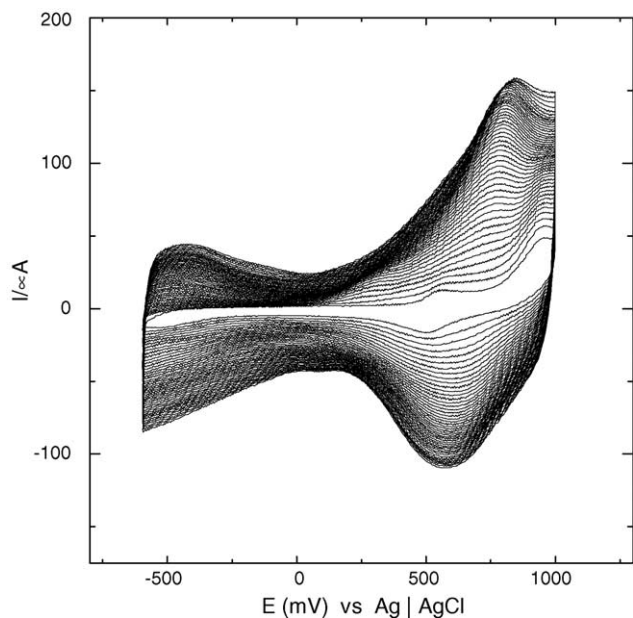Fig. 1 shows the structure of the complexes used in this work. The metal complex core has D_4h symmetry and the free

Fig. 2. Cyclic voltammetry corresponding to the electropolymerization of Ni-TaPc on a glassy carbon electrode (50 potentiodynamic cycles), in a N_2/DMF/0.1 M TBAP solution with 1 mM of the monomer. Scan rate: $100 \, mV \, s^{-1}$.

Fig. 3. Voltammetric profile of a poly-Co-TaPc modified electrode under N_2 atmosphere (continuous line) and CO_2 atmosphere (dotted line) electrolyte: 1 mM $NaClO_4$ aqueous solution. Scan rate: $100 \, mV \, s^{-1}$.

ligand core D_2h symmetry due to the inner hydrogens of the cavity. Fig. 2 depicts the voltammetric growing signals corresponding to the electropolymerization of Ni-TaPc on glassy carbon electrode. It is known that this kind of macrocycles polymerize forming amine radical cations (by the positive potential imposed to the electrode) in a similar way that the polymerization of aniline [45]. The characteristics of the obtained films (polymerization degree, site of the radical coupling, planarity of the resultant macromolecule, specific morphology) is not known until now, however, we are making efforts along this line of work. In spite of the similar structures of all macrocyclic complexes, the kinetic of polymerization (measured as the increasing charge with time) is very different depending on the metallic center [33–35,42,46,47]. Fe and Co present a very slow kinetic with charges lower than those for the H_2 and Ni cases, either on glassy carbon or transparent SnO_2:F electrodes. Those differences (morphology and electric characteristics of the obtained polymer) are important in the electrocatalytic behavior [33,35,42,46,47]. When the complexes are electropolymerized, the modified electrodes show activity towards the electrochemical reduction of CO_2. The electrocatalytic response strongly depends on the metallic center. Fig. 3 shows the voltammetric profiles for the poly-Co-TaPc modified electrode in an aqueous media (0.1 M $NaClO_4$). Under N_2 ill-defined peaks I and II are attributed to processes centered on the ligand (peak I) and on the redox couple Co(II)/(I) (peak II), respectively [33,34,36,48,49]. At ca. -1.0 V the water reduction reaction appears with H_2 evolution. This process occurs in a reduced active site, in this case, a ligand site. However, the anodic wave corresponding to a signal at -1.0 V practically does
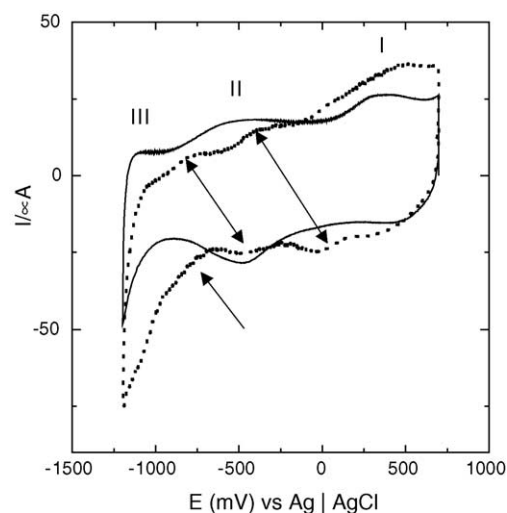
not appear. In spite of this, for comparison reasons, we have labeled this "peak" as III. When the electrolyte is saturated with CO_2, the voltammetric profiles changes: in the cathodic region, a low shift of peak I to negative potentials takes place and there is an important shift for peak II from ca. -0.5 to 0.0 V. In the case of peak III, it appears at ca. -0.5 V and becomes quasi-reversible. When CO_2 is bubbled in the solution the pH changes; then the shift in the peak potentials can be attributed to pH. However, for this modified electrode, the redox couples of the ligands and the metals shift linearly ca. 75 mV per pH unit [34,36]. The difference in pH from the solution bubbled with N_2 and CO_2 is almost 3 units; i.e. from pH 7 to 4. Then, the expected shift in terms of pH is 225 mV that is very different to the results obtained. Then, we interpreted the observed shifts in terms of the formation of an adduct or intermediate between the metal and the CO_2 molecule that changes the electronic density of all the redox couples [49–51].

On the other hand, the onset of the current discharge corresponding to the reduction of CO_2 appears at -0.7 V (see Fig. 3), at potentials more negative than the redox couples of the metal and the ligand (peaks II and III). Generally, a redox catalyst promotes a redox reaction when the applied potential generates an active site with a favorable oxidation state (usually the metal). In this case, the reduction wave does not begin at the potentials corresponding to the reduced metal or the reduced ligand, but it is necessary to apply an extra overpotential to do it. In the case of the reduction of CO_2 promoted by azamacrocycles, the behavior observed in Fig. 3 was informed for other related systems [17]. For the Co-polymer-modified electrode, only formic acid and no hydrogen was detected after potential controlled electrolysis at -1.0 V during 1.5 and 6 h. For this modified electrode the turnover number was estimated in ca. $7.9 \times 10^4 \, h^{-1}$ calculated after 1.5 h of electrolysis. In order to obtain this result,

the charge of the cathodic peak corresponding to Co(II)/Co(I) was used to measure the quantity of active sites in μM. Formic acid was also measured in μM. We did not use grams of catalysts because it was not possible to measure the weight of the polymer and we do not know the characteristics or the exposed active sites for a determined weight of the film.

The electrolysis data indicates that poly-Co-TaPc is a very selective electrocatalyst for the reaction. It is noticeable, as can be seen in Fig. 3, that at the potential of the electrolysis (−1.0 V), that poly-Co-TaPc under N_2 shows the starting wave corresponding to the evolution of hydrogen but in CO_2 atmosphere, in an aqueous solution, no hydrogen was detected. This result confirms the formation of a kind of adduct between the cobalt center and the CO_2 molecule as mentioned before. This electrode was measured during 10 days (its voltammetric response and its behavior during the electrolysis) without showing any changes. In this way, we obtained a selective and stable electrocatalyst for the reduction of CO_2. The reaction is metal centered and a simplified mechanism is presented in the following reaction:
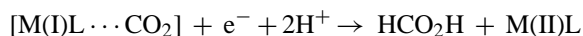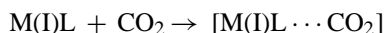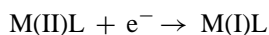
$$M(II)L + e^- \rightarrow M(I)L$$

$$M(I)L + CO_2 \rightarrow [M(I)L \cdots CO_2]$$

$$[M(I)L \cdots CO_2] + e^- + 2H^+ \rightarrow HCO_2H + M(II)L$$

Fig. 4 depicts the voltammetric profile of poly-Ni-TaPc modified electrode, in an aqueous media (0.1 M $NaClO_4$). Under N_2 atmosphere the Ni polymer shows two reversible peaks I and II. Both peaks correspond to redox processes centered in the ligand [52]. However, a small cathodic peak, non-described in the literature appears at ca. −0.3 V between peaks I and II. We do not have an explanation for this peak. When the solution is saturated with CO_2, the profile changes
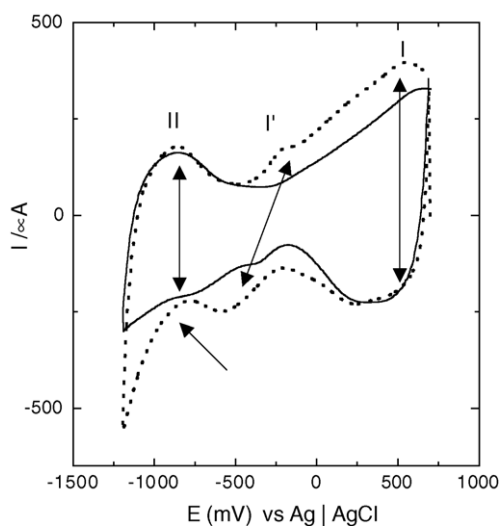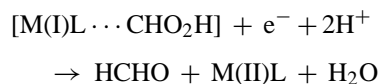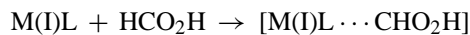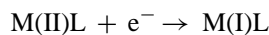

Fig. 4. Voltammetric profile of a poly-Ni-TaPc modified electrode under N_2 atmosphere (continuous line) and CO_2 atmosphere (dotted line). Electrolyte: 1 mM $NaClO_4$ aqueous solution. Scan rate: 100 mV s^{-1}.

showing an increase in the current of this small peak and the appearance of its anodic wave (peak I′). Also, the anodic charge of peak I is increased while a cathodic current discharge appears at the potentials close to the ill-defined cathodic peak II. This current discharge corresponds to the electroreduction of CO_2. In this case, there are noticeable differences between this polymer and poly-Co-TaPc. First, for poly-Ni-TaPc, the second reduction allows the onset of the CO_2 electroreduction without extra overpotential. Second, it is interesting to compare the capacitive currents observed between the voltammetric curves of cobalt (see Fig. 3) and nickel polymers (see Fig. 4); in the Ni case the capacitive current is one order of magnitude higher which can be associated with differences in the kinetic of polymerization that causes important changes in thickness and morphology of the polymers [46]. The current corresponding to the reduction of CO_2 is higher than in the case of the Co-polymer because the Ni polymer presents a higher capacitive response due to the electrolyte in the inner layers of the polymer. But simultaneously, with a higher capacitive response, the redox couples show more current indicating more active sites.

When electrolysis was carried out at −1.0 V, formic acid and formaldehyde were detected, indicating that the reduction of CO_2 proceeds on poly-Ni-TaPc via two and four electron transference. Formic acid is probably generated with a mechanism similar to that of poly-Co-TaPc. However, the formaldehyde generation in simultaneous four-electron transference is highly improbable from an electrochemical point of view. In this sense, the most reasonable explanation is that the polymer catalyzes the reduction of CO_2 to formic acid and then catalyzes the reduction of this compound to formaldehyde by a two-step mechanism. In order to confirm this assumption, the direct reduction of formic acid by the poly-Ni-TaPc is being studied. The second step of the mechanism could be described as:

$$M(II)L + e^- \rightarrow M(I)L$$

$$M(I)L + HCO_2H \rightarrow [M(I)L \cdots CHO_2H]$$

$$[M(I)L \cdots CHO_2H] + e^- + 2H^+$$
$$\rightarrow HCHO + M(II)L + H_2O$$

This modified electrode is stable (measured in the same way that the Co-polymer) but not selective. The relative yields of formic acid are higher than formaldehyde yields, practically in a 2:1 ratio.

For poly-Fe-TaPc and poly-H_2-TaPc, no noticeable changes were found in the voltammetric profiles when the experiments were performed either in N_2 or CO_2 atmosphere (not shown). When the potential controlled electrolysis was carried out at −1.0 V, formaldehyde and H_2 were detected for poly-Fe-TaPc. On the other side, only H_2 was detected for poly-H_2-TaPc indicating that this polymer is not a cata-

Table 1
Electrolysis products (−1.0 V vs. Ag|AgCl during 6 h)

Electrode	Product	Product	Product
Poly-Co-TaPc	HCOOH	–	–
Poly-Ni-TaPc	HCOOH	HCHO	–
Poly-Fe-TaPc	–	HCHO (1.5 h)	H_2
Poly-H_2-TaPc	–	–	H_2

lyst for CO_2 electroreduction. On the other hand, this result confirms that the ligand reduces hydrogen but the reduction of CO_2 is metal centered. The Fe-polymer is not stable because after 1.5 h of electrolysis its voltammetric profile is not recovered. The generation of H_2 by azamacrocyclic complexes has been established by other authors and the mechanism is well described [53]. However, the CO_2 reduction needs water to proceed [9] and the H_2 evolution reaction is always a competitive reaction according to the following mechanism:

$$H^+ + e^- \rightarrow H^\bullet$$

$$2H^\bullet \rightarrow H_2$$
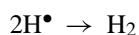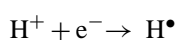
For Ni, Fe and the free ligand, it was not possible to calculate the efficiency because the quantity of active sites is unknown due to the capacitive response of the voltammetric profile. In the case of poly-Fe-TaPc and poly-H_2-TaPc hydrogen is obtained during all the time of the electrolysis and reaching a plateau at ca. 1 h of reaction. For the iron polymer at a 1.5 h is possible to detect formaldehyde but at this time the polymer is already decomposed. The bare electrode electrolysis in the same conditions does not produce detectable amounts of products.

The results of the electrolysis experiments are summarized in Table 1. It is worth noticing that the active polymers release protonated species, since it is frequently reported that phthalocyanines or porphyrins (of Co generally) [27–31] are selective catalyst for CO. Indeed the reaction products for polymeric-polypyridine metallic complexes modified electrodes were exclusively formic acid and formaldehyde [18–20]. Also, in composite systems such as Prussian blue–polyaniline–Fe complexes the reaction products obtained were mostly lactic acid and species with two carbons [21,22]. For Cu-polymers [39], the reduction products are CO and C−H. In our case, no system gives CO. In the case of the Ni-system reduction of CO_2 gives products corresponding to 2 and 4 transferred electrons. In the case of the Co, only 2 electrons were transferred. The Fe-system gives 2 and 4 electrons reduced products. The most interesting result is the selectivity for the Co-system. Although in our case we did not study the effect of the media in the reduction of CO_2, it has been informed that the electrolyte and the solvent could change the nature of the products using the same complex [39]. Indeed, it has been informed [24] that Co-phthalocyanines gives CO and formic acid as reaction products when the pH is 5 or lower, using phosphate as supporting electrolyte. If the support electrolyte is changed

to quaternary ammonium salt the distribution of products is quite different giving oxalic and glycolic acids as the main products [54]. Then, the hydrophobic nature of the ammonium salt plays a very important role and probably produces a suitable environment to obtain products with more than one carbon atom.

Another interesting system is presented by Shibata and Furuya [55,56] using gas diffusion electrodes modified with transition metals (Cr, Mo, Mn, Ru, Co, Rh, Ir, Pd, Ni, Pt, Cu, Ag, Au, Zn, Cd, Al, Ge, In, Tl, Sn and Pb) phthalocyanines. In this case, the simultaneous reduction of CO_2 and nitrate or nitrite ions was carried out toward the production of urea. With those phthalocyanines, the formation of urea, CO, formic acid and ammonia was proved, except for Al and Ge complexes. The best catalyst in this case was Ni-phthalocyanine, with a maximum current efficiency of 40% at −1.5 V versus NHE. Selectivity is dependent on the metal center and the electrochemical potential used in the experiment. Formation of urea specifically depends on the ability of the metal center to form CO and ammonia separately.

Other macrocycles with activity toward the electrochemical reduction of CO_2 include the cyclam, porphyrin and hexaazacyclophane families [9]. The Ni-cyclam derivatives have been systematically studied and the reduction of carbon dioxide is driven by the Ni(I) oxidation state and those complexes are almost 100% selective to CO generation [9,57].

3.2. Spectroelectrochemical behavior of the polymers

In order to elucidate possible interactions between the polymers and CO_2 at different potentials, the macrocycles containing Co and Ni were electropolymerized on a transparent electrode. The poly-Fe-TaPc does not polymerize on conducting glass electrodes (in the conditions described above) and for this reason, no spectroelectrochemical results are presented. H_2-system does not reduce CO_2; therefore it has no sense to study the interactions between this system and carbon dioxide.

It is known that phthalocyanines present two bands in the UV–vis spectrum corresponding to π–π transitions of the ligands [58]. The band at a lower energy is the Q band (HOMO–LUMO), and the band appearing at a higher energy is the Soret band (HOMO^{-1}–LUMO) [58]. It is possible to observe between them, in some cases, a charge-transfer band corresponding to a metal-to-ligand charge-transfer transition [58]. All these features explain the different spectra of the polymers when they are reduced and CO_2 is present in the solution.

Fig. 5A shows the spectra of poly-Co-TaPc at open circuit potential and at −0.4 V in 0.1 M $NaClO_4$ aqueous solution under N_2 atmosphere. Fig. 5B shows the spectra of poly-Co-TaPc at an open circuit potential and −0.4 V in 0.1 M $NaClO_4$ aqueous solution under CO_2 atmosphere. In both cases, the Q band shows a maximum close to 725 nm and a part of the Soret band appears between 300 and 400 nm. At −0.4 V (close to the Co(II)/(I) couple), a new band appears with a maxi-
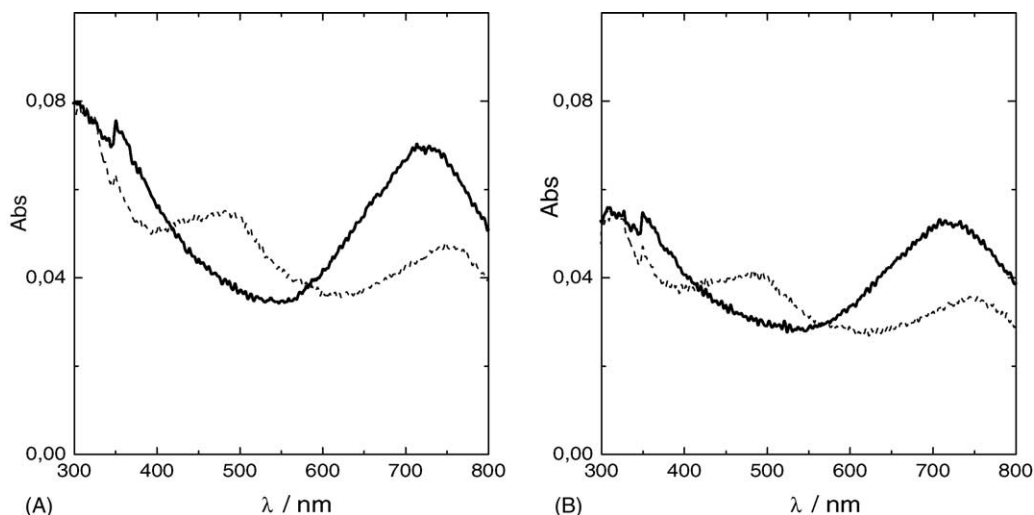
Fig. 5. (A) UV–vis spectra for the SnO_2:F/poly-Co-TaPc modified electrode in 1 mM $NaClO_4$ aqueous solution at two potentials under N_2 atmosphere. Continuous line: open circuit potential; dashed line: −0.4 V vs. Ag|AgCl. (B) UV–vis spectra for the SnO_2:F/poly-Co-TaPc modified electrode in 1 mM $NaClO_4$ aqueous solution at two potentials under CO_2 atmosphere. Continuous line: open circuit potential; dashed line: −0.4 V vs. Ag|AgCl.

mum at 480 nm. This band corresponds to a metal-to-ligand charge-transfer band [36,37,48,59–64], due to the presence of Co(I). When CO_2 is bubbled in the solution, Soret, charge-transfer and Q band decreased. A similar behavior has been described by Lehn and co-workers when photoreduced solutions containing Co(I)–polypyridine complexes are used as catalyst for the photo-electrochemical reduction of CO_2 [65,66].

In the case of the Ni-system, a very different behavior is observed. Fig. 6A shows the corresponding spectra for poly-Ni-TaPc under N_2, at open circuit potentials and at −0.8 V. In this case, the Q band practically shows the same intensity at OCP and −0.8 V. But when CO_2 is bubbled in the solu-

tion (see Fig. 6B) a great difference in the intensity of this band appears when the potential is changed from OCP to −0.8 V. The difference in the behavior of both systems indicates different interactions between the CO_2 and the reduced polymers. These results confirm the voltammetric profiles obtained in the presence of CO_2, for both systems. In the case of Co, the reduction wave appears at potentials more negative than the wave corresponding to the second reduction of the polymer and in the case of the Ni system, the current discharge coincides with a redox process of the ligand. Then, the different interaction between the polymer and the CO_2 is the responsible of the obtained products in the electrolysis [16].
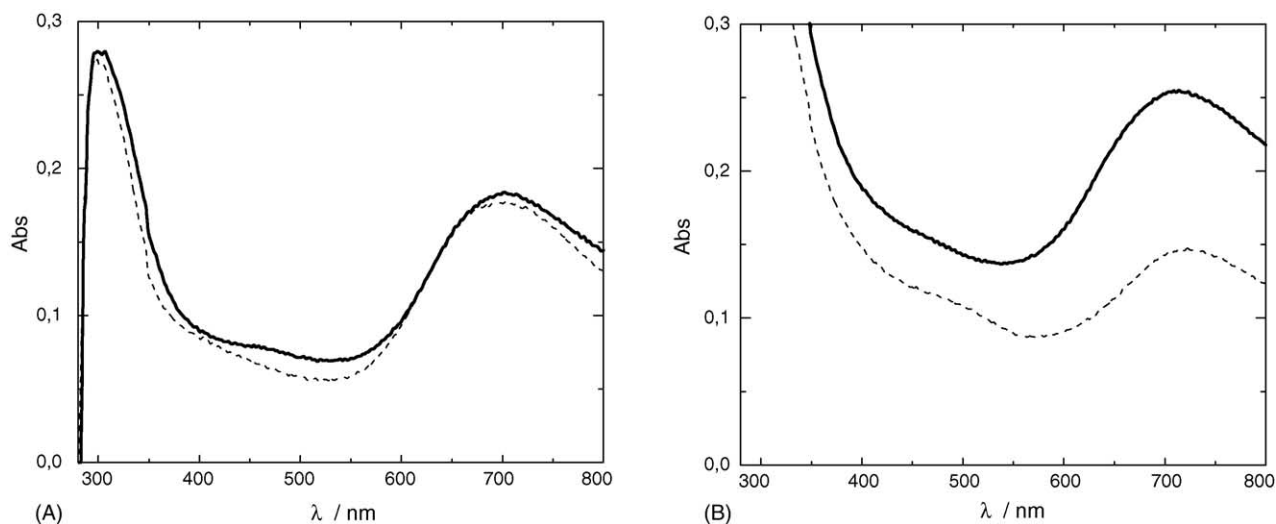

Fig. 6. (A) UV–vis spectra for the SnO_2:F/poly-Ni-TaPc modified electrode in 1 mM $NaClO_4$ aqueous solution at two potentials under N_2 atmosphere. Continuous line: open circuit potential; dashed line: −0.8 V vs. Ag|AgCl. (B) UV–vis spectra for the SnO_2:F/poly-Ni-TaPc modified electrode in 1 mM $NaClO_4$ aqueous solution at two potentials under CO_2 atmosphere. Continuous line: open circuit potential; dashed line: −0.8 V vs. Ag|AgCl.
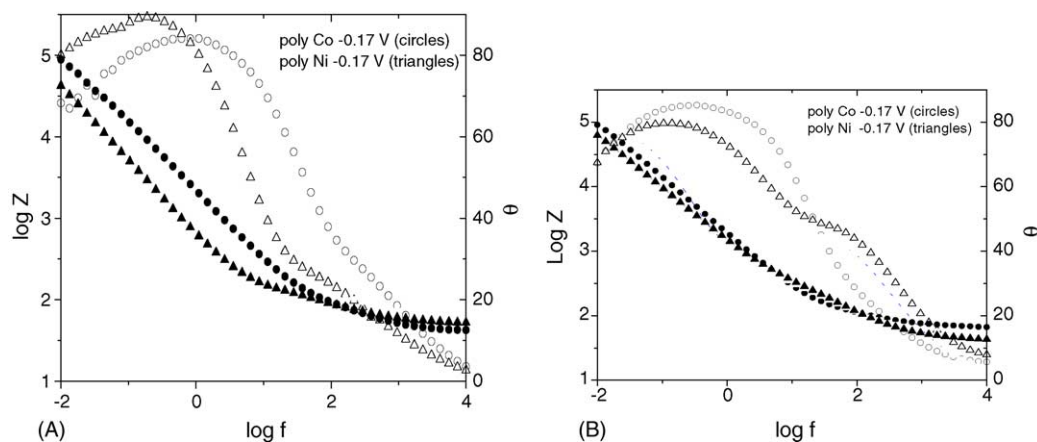
Fig. 7. (A) Bode plots at (−0.17 V vs. Ag|AgCl) for the GC/poly-Co-TaPc and poly-Ni-TaPc modified electrodes, under N_2 atmosphere, in 1 mM $NaClO_4$ aqueous solution. Open symbols: phase angle θ vs. log f. Filled symbols: log Z vs. log f. Circles: GC/poly-Co-TaPc, triangles: GC/poly-Ni-TaPc. (B) Bode plots at (−0.17 V vs. Ag|AgCl) for the GC/poly-Co-TaPc and GC/poly-Ni-TaPc modified electrodes, under CO_2 atmosphere, in 1 mM $NaClO_4$ aqueous solution. Open symbols: phase angle θ vs. log f and filled symbols: log Z vs. log f. Circles: GC/poly-Co-TaPc, triangles: GC/poly-Ni-TaPc.

3.3. Electrochemical impedance spectroscopic analyses

Impedance measurements were carried out for Co and Ni polymers immersed in 0.1 M $NaClO_4$ electrolyte saturated with N_2 or CO_2, at steady state potentiostatic conditions. Due to the complexity of the studied systems and the unknown nature of the polymeric films, it is not possible at this point to elaborate circuit equivalent models. For that reason we only compare in a qualitative way the EIS response of our systems. Our conclusions are focused to enhance the comprehension of the different behavior of the modified electrodes and for this goal a simple model can be useful. The characteristic impedance profiles, using the Bode representation, can be seen in Fig. 7A and B. At low frequencies the impedance is generally capacitive, i.e. the phase angle approaches 90 degrees indicating charge saturation caused by finite thickness of the polymer. In this case, a redox capacitance or low-frequency capacitance (C_{lf}) is defined [36,67–69]. For very thin films, the kinetic control region appearing at high frequencies may overlap with the charge saturation and no diffusion region is defined. For a porous electrode, C_{lf} is proportional to the thickness (or to the film/solution interface area) and therefore to the total concentration of redox centers. It can be obtained through the relationship [36,67–69]:

$$C_{lf} = \frac{1}{2\pi f Z_{img}}$$

where C_{lf} is the low frequency capacitance, f the frequency, Z_{img} the capacitive impedance.

Fig. 7A and B show the Bode plots for the polymers under N_2 and CO_2 atmosphere, respectively. The log Z versus log f plots show at high frequencies practically the same impedance values for both metallic complexes, indicating that their charge-transfer resistance does not depend on the metallic center. From the phase angle versus log f plot of

Fig. 7B, it is possible to observe a second time constant (τ) where $\tau = RC$ (R: charge-transfer resistance, C: double layer capacitance) appearing at intermediate frequencies with a phase angle value near to 45°. It is interpreted as a diffusional process taking place only when CO_2 is present for poly-Ni-TaPc. This diffusional process is assigned to the early stages of incoming CO_2 (see Fig. 4) as a result of the polymeric frame modification by the applied potential. In the case of poly-Co-TaPc no diffusional process is set, due to the smaller thickness of the film as already pointed out in the voltammetric results.

Fig. 8 shows a plot of C_{lf} as a function of the applied potential. Capacity data were obtained from Bode plots at low frequency regions (ca. ≈0.1 Hz) and when the phase angle approached to 90°. Considering the substrate geometrical area of 0.19 cm^2, the capacitance values of ≈100 μF (poly-Co-TaPc) and ≈300 μF (poly-Ni-TaPc) obtained at −0.2 V indicate rather rough or porous electrodes [45,67–70].
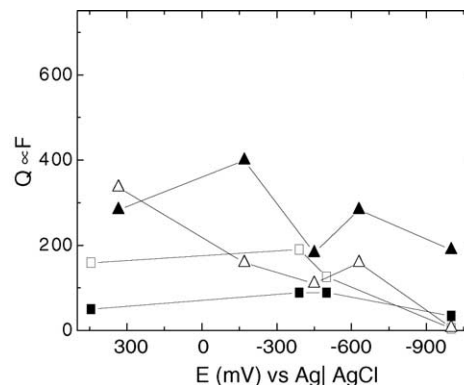

Fig. 8. Plot of C_{lf} as a function of applied potentials for the GC/poly-Co-TaPc and GC/poly-Ni-TaPc modified electrodes. Filled symbols: N_2 atmosphere and open symbols: CO_2 atmosphere. Squares: poly-Co-TaPc, triangles: poly-Ni-TaPc.

From the capacitance values presented in Fig. 8, it can bee inferred that the electroformed polymers poly-Ni-TaPc is thicker than poly-Co-TaPc as has been pointed out. On the other hand, it is worth noticing that that polymeric porphyrins and phthalocyanines usually show a rough and porous morphology [45,46,71]. Indeed, Li et al. have demonstrated that phthalocyanines electropolymerized in tetraalkyl ammonium perchlorate solution containing monomer concentration between 0.5 and 4 mM a porous structure is obtained [45,46,71].

For poly-Co-TaPc the C_{lf} values in CO_2 atmosphere are larger than in N_2 atmosphere at a potential near to Co(II)/(I) redox couple. This fact is explained in terms of the interaction of CO_2 with the cobalt polymer at different potentials. When the polymer is at potentials more positive than -0.5 V, the CO_2 molecule is a component of the interface polymer-solution (larger values of C_{lf}). It is possible to confirm this explanation observing the changes in the voltammogram (see Fig. 3) and observing the decrease in the Q band at open circuit potential in Fig. 5. However, at potentials more negative than -0.5 V, the behavior is inverted indicating a polymer with a smaller number of redox centers unoccupied as a consequence of the faradaic process that takes place in that region of potential.

On the other hand, for poly-Ni-TaPc the C_{lf} values in CO_2 atmosphere are lower than in N_2 atmosphere. This fact is due to the faradaic process that appears at potentials close to 0.0 V in the presence of CO_2 as shown in the voltammogram corresponding to Fig. 4.

All the results shown here indicate that products of the reduction of CO_2 are strongly dependent on the nature of the redox site. In all the cases, the metal acts as the redox site [16,17] but in each polymer they have different electronic density.

4. Conclusions

Poly-Co-TaPc, poly-Fe-TaPc and poly-Ni-TaPc catalyses the electroreduction of carbon dioxide in aqueous media. In the case of poly-Co-TaPc, only formic acid is obtained, indicating a very selective electrocatalyst. For poly-Ni-TaPc, formic acid and formaldehyde were obtained as products. Formaldehyde and H_2 were detected for poly-Fe-TaPc. On the other hand, only H_2 was detected for poly-H_2-TaPc indicating that this polymer is not a catalyst for CO_2 electroreduction. The spectroelectrochemical experiments indicate a strong interaction between CO_2 and poly-Co-TaPc and poly-Ni-TaPc. In the case of poly-Co-TaPc, both the reduced metallic center and the reduced ligand are necessary for the electrochemical reduction of CO_2. In contrast, it seems that only the reduced ligand is enough to reduce CO_2 on poly-Ni-TaPc. The electrochemical impedance spectroscopy results allow inferring different polymer morphologies for poly-Co-TaPc and poly-Ni-TaPc.

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