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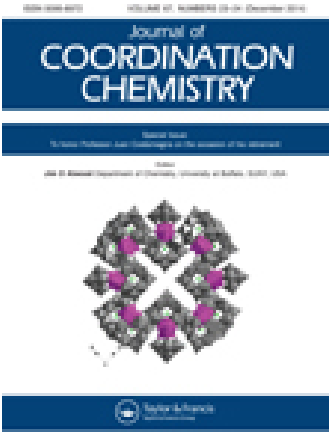

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Electrocatalytic reduction of carbon dioxide on conducting glass electrode modified with polymeric porphyrin films containing transition metals in ionic liquid medium

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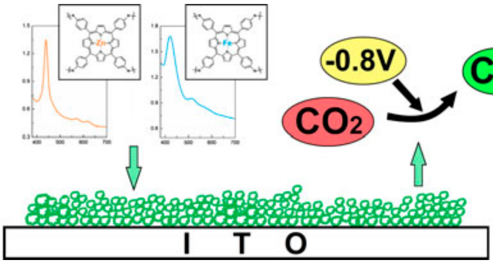

Electrocatalytic reduction of carbon dioxide has been studied using modified electrodes with conducting polymers from tetra-amino-phenyl porphyrins containing transition metals (Zn(II) and Fe(III)), on an indium tin oxide electrode in $BMImBF_4$, as solvent and supporting electrolyte. Electropolymerized Fe porphyrin is active toward the reaction under survey, while Zn derivative shows poor activity. Spectroelectrochemistry experiments on electropolymerized Fe porphyrin films have shown intermediary species like Fe–CO_2 and Fe–CO at open-circuit potential. Potential-controlled bulk electrolysis carried out in ionic liquid shows that only carbon monoxide can be detected as reaction product in the gas phase and that Fe polymeric film shows a turnover number of 9.18, while the Zn film shows a value of 2.74, corroborating the poor activity observed in cyclic voltammetry.

Keywords: Carbon dioxide; Conducting polymers; Ionic liquids; Electrochemical reduction

1. Introduction

Carbon dioxide plays a significant role in the atmospheric equilibrium giving rise to the greenhouse effect which has been beneficial for life in our geological era. However, during the last century, carbon dioxide concentration in the atmosphere have been increasing continuously as a consequence of anthropogenic activities, mainly combustion processes and

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deforestation, originating the atmospheric phenomenon called global warming [1, 2]. This fact may have considerable consequences, for human activities, if the concentration of carbon dioxide, among other greenhouse gasses, is not controlled in the next decades [3]. The conversion of this greenhouse gas into useful products such as liquid fuels or organic compounds is a topic of great interest, and thus carbon dioxide could be considered as a green source of carbon [4]. However, carbon dioxide, as the last product of carbon combustion, is a very stable molecule with a $\Delta G_f° = 394.39\ \mathrm{kJ\,M^{-1}}$ and an $E° = -1.9$ V *versus* NHE, which in an electrochemical process is interpreted as high overpotential to the reaction taking place [5]. Thus, its conversion involves important energy demands. Many science disciplines are involved in the search for sustainable ways to reconvert carbon dioxide [6]. Among them, inorganic chemistry, photochemistry, and electrochemistry are closely related by a common factor; coordination compounds may work in catalytic processes, decreasing the energetic demands [7–10]. Electrocatalysis using coordination compounds is a feasible way to overcome the overpotential required to reduce carbon dioxide [11]. Pioneering contributions in the early 80s and 90s have been the basis for the development of current research in this topic [12–17].

Macrocyclic compounds containing transition metals have been used as electrocatalysts either in homogeneous or heterogeneous approach in several reactions of environmental concerns, such as O_2 reduction [18], and NOx's [19–21] and S(IV) oxo-anions [22, 23] redox transformations.

For heterogeneous electrocatalysis, porphyrins and phthalocyanines containing transition metals have been used in several arrays on electrodic surfaces to reduce carbon dioxide, such as adsorbed monolayers [14], supramolecular attachment [24], layer by layer assemblies [25], and conducting polymers [19–23, 26–29]. Main properties of these macrocyclic complexes are kept on the electrode surface, for instance redox and coordination properties of the central metal ions. All these modified electrodes are effective for the reaction under survey, whereas the main drawbacks are still a wide distribution of reaction products and the generation of hydrogen as a byproduct when this electrochemical reaction is carried out in aqueous solution, but in some cases overpotential has been critically reduced [5].

Ionic liquids are molten salts, generally formed by highly asymmetric ions, which are often a bulky organic cation and a smaller inorganic anion. As a general rule, these salts must have a melting point below 100 °C to be considered a room temperature ionic liquid. Due to their particular structures, ionic liquids exhibit properties such as low vapor pressure, thermal, and electrochemical stability. For these reasons, ionic liquids have become a new class of solvents, which were originally studied in Diels–Alder [30] or Sn_2 organic chemistry reactions [31]. In electrochemistry, they have been studied in applications related with energy storage, photovoltaic energy production, and also electroanalysis [32, 33].

Electrochemical reduction of carbon dioxide in ionic liquids has been carried out largely on solid electrodes of different transition metals, where the overpotential required to the reaction taking place have been one of the main drawbacks [34]. Upon one electron reduction of carbon dioxide, anion radical CO_2^- is better stabilized in these media, giving rise to the study of several electrosynthesis pathways as for instance carbamates [34] or cyclic carbonates [35].

Despite these remarkable properties, ionic liquids have been poorly explored in coordination chemistry where there are few examples in literature describing coordination chemistry kinetics on porphyrins [36], electrochemistry [37, 38], and catalysis [39].

Regarding the electrocatalytic reduction of carbon dioxide in ionic liquids, recently Re(bpy)$(CO)_3$ has been used as a homogenous electrocatalyst in 1-ethyl-3-methylimidazolium tetracyanoborate ([Emim][TCB]) with a reduction potential of −1.66 V *versus* Fc^+/Fc [40].

A conducting polymer from Co(II) tetrakis(4-aminophenyl)porphyrin reduced electrochemically CO_2 to CO with a 67% faradaic efficiency at −0.8 V *versus* Ag/AgCl [41]. Both systems were selective toward CO production [40, 41].

The aim of this work is to provide electrochemical characterization of Fe(III) tetrakis(4-aminophenyl)porphyrin chloride (FeTAPP) and Zn(II) tetrakis(4-aminophenyl)porphyrin (ZnTAPP) and their electrocatalytic performance, as conducting polymers on Indium Tin Oxide (ITO) surfaces, toward the electrochemical reduction of CO_2 in 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) as solvent.

2. Experimental

2.1. *Materials*

Reagents (iron(II) chloride, zinc(II) acetate, pyrrole, propionic acid, acetic anhydride, 4-nitrobenzaldehyde, hydrazine, and palladium on carbon) and solvents of analytical grade or higher were purchased from Sigma-Aldrich and used without purification. Synthesis of 5,10,15,20-tetrakis(4-aminophenyl)porphyrin (TAPP) [42], ZnTAPP, and FeTAPP [43] followed previously reported synthetic routes and was characterized by standard spectroscopic methods. Tetrabutyl ammonium perchlorate (TBAP) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$, >98.5%) were purchased from Sigma-Aldrich and dried prior to use.

2.2. *General measurements*

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), differential pulse voltammetry (DPV), and potential controlled bulk electrolysis (PCBE) were carried out using CH Instruments 760C and BASi PWR-3 potentiostats, respectively. Working electrodes were a carbon fiber microelectrode (Fiber Glast, OH, USA. 10 μm) used for CV, LSV, and DPV experiments, and an optically transparent ITO (Delta Technologies, MN, USA, 1.5 cm^2) was used for PCBE and spectroelectrochemistry. A Pt wire was used as a counter electrode. 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 experimental timescale [44]. 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, 30 m × 0.53 mm) coupled with a microthermal conductivity detector (μTCD) using Ar as a gas carrier with an isothermal program at 40 °C.

2.3. *Complex characterization in $BMImBF_4$*

Complexes were electrochemically characterized in $BMImBF_4$. Solutions (0.5 mM) of the respective metalloporhyrins were prepared, and then DPV and CV were carried out using the three-electrode arrangement described above.

2.4. *Working electrode modification*

Polymeric films were grown after 100 potentio-dynamic cycles at 200 $mV\,s^{-1}$ between −0.9 V and 1.1 V *versus* Ag/AgCl using solutions of 1 mM M-TAPP (M: Zn, Fe) and 0.1 M TBAP in DMF. An ITO electrode (area: 1.5 cm^2) was used as a working electrode, a Pt wire (8 cm^2) as a counter electrode, and a non-aqueous Ag/AgCl system as a quasi-reference electrode [23]. After polymerization, the modified electrode was rinsed with DMF and then with doubly distilled water in order to remove starting compound on the surface. Then the remaining non-polymerized amino groups in the film were re-oxidized using cyclic voltammetry in $BMImBF_4$, thus obtaining a more ordered and homogeneous surface [20, 28].

2.5. *Electrocatalytic activity*

Carbon dioxide reduction in $BMImBF_4$ on the modified electrodes was evaluated in a CO_2 saturated solution, where the ionic liquid is a supporting electrolyte and solvent. The study of the electrocatalytic activity was carried out using LSV into an undivided glass cell and PCBE into an H-Type cell, using a three-electrode arrangement previously described [45, 46].

2.6. *Spectroelectrochemistry*

The potential dependent UV–vis spectra were recorded using a UV–vis spectroelectrochemical cell (optical path: 1 cm, total volume: 2.5 mL) using a three-electrode array, including the optically transparent ITO as a working electrode, a Ag/AgCl quasi-reference electrode, and a Pt wire as a counter electrode [46, 47].

3. Results and discussion

3.1. *Spectroscopic and electrochemical characterization in* $BMImBF_4$

As in molecular solvents, the electronic structure of these porphyrin complexes can be explained in terms of two groups of electronic transitions, one in the 400 nm region called the Soret band and a second group of *Q* bands which appear in the 500–640 nm region. Both groups of electronic transitions are π–π* in origin, and the difference is related to the energy of the transition as well as the probability to occur; while the Soret band is a highly allowed transition from the ground state to a high-energy state (S_2), *Q* bands are less energetic and forbidden. This last transition depends strongly on the porphyrin symmetry, working as an indicator of metallation of the molecule. Metalloporphyrins present a square-planar symmetry (D_{4h}), where, due to the metallation process, two inner protons are replaced by a metal ion increasing the symmetry. Therefore, according to the Gouterman four orbitals model [48], *Q* bands represent transitions with E_u symmetry and consist of two equivalent dipole transitions in the *x* and *y* directions. Free base porphyrins are less symmetric species due to the presence of two protons on its core, and therefore can be classified as D_{2h}; due to its asymmetric structure, *x* and *y* directions are no longer equivalent, and therefore a pair of Q_x and a pair of Q_y bands appear.

Figure 1(a) shows UV–vis spectrum of 5×10^{-5} M of ZnTAPP in $BMImBF_4$, where Soret band is centered at 438 nm and *Q* bands at 568 and 621 nm, respectively. Figure 1(b) shows the UV–vis spectrum of 5×10^{-5} M FeTAPP in $BMImBF_4$; in this case, the whole spectrum is blue shifted. Soret band is centered at 420 nm, whereas *Q* bands at 514 and 565 nm, respectively. These results are in accord with the effect of metal ions on the porphyrin rings [49].

Comparing the present results with those reported in molecular solvents such as $C_2H_4Cl_2$, $CHCl_3$, and CH_2Cl_2 [48, 50–53], the ionic liquid has no effect on the energy of the transitions represented by *Q* bands at 514 nm and 573 nm with a UV–vis spectrum

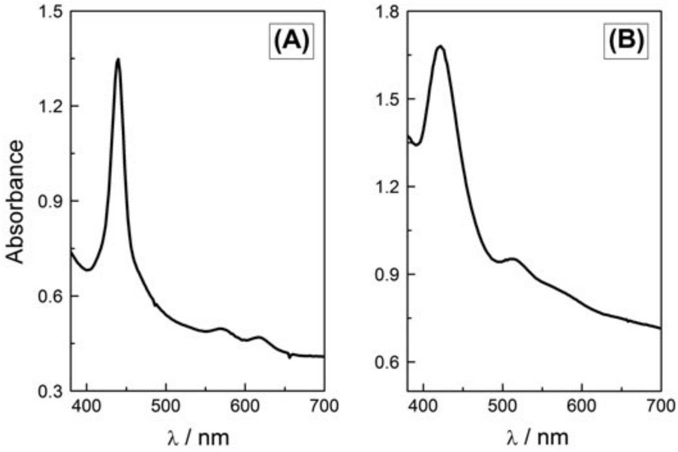

Figure 1. UV–vis spectra in $BMImBF_4$ (10 μM) of (A) ZnTAPP and (B) Fe(III)TAPP solution.

similar to those registered in CH_2Cl_2 for similar complexes in which chloride forms a stable Fe(II) five-coordinate complex, mainly represented by a *Q* band at 510 nm [50, 53].

On the other hand, Shantha *et al.* [50] reported that 1,2-dimethylimidazole used as solvent can coordinate to Fe(III) of a tetra(phenyl)porphyrin, forming a new complex that leads to three Q bands at 530, 562, and 608 nm; hence, the absence of a band at 608 nm and the high absorbance presented by the band at 514 nm confirms the presence of the five-coordinate species with the chloride anion, despite the coordinating properties of imidazole species suggested by other authors. Therefore, due to the cationic character of the imidazolium moiety of the ionic liquid, no coordination between the ionic liquid and the complex can be established.

Figure 2(a) displays a cyclic voltammogram recorded at 10 mV s^{-1} of 0.5 mM solution of the ZnTAPP complex; two clear reversible redox signals at −0.8 V and −1.8 V *versus* Ag/AgCl are observed corresponding to redox processes related to the porphyrin ring [54]. Due to lack of redox activity of the metal center, there is no signal attributed to this site in the molecule; however, at positive potentials an irreversible oxidation signal can be seen, related to the oxidation of amino groups present in the complex [22]. Differential pulse voltammograms in both positive and negative direction match very well with the redox process assigned, reinforcing the existence of the electrochemical process.

Figure 2(b) shows cyclic voltammetry of 0.5 mM solution of FeTAPP, recorded at 10 mV s^{-1}; the irreversible oxidation attributed to amine substituent is observable at 1.5 V *versus* Ag/AgCl. At negative potentials, an irreversible wave is observed at −0.75 V *versus* Ag/AgCl, another irreversible signal, detected only in DPV experiment, appears at −1.6 V *versus* Ag/AgCl. The assignment of these redox processes is not straightforward [55–57]. However, related systems, i.e. a series of non-planar σ-bonded, Cl, phenyl- and fluorophenyl Fe(III) octaethylporphyrins were electrochemically characterized and most relevant result shows that this family of compounds have at least two reduction processes. Specifically, fluorophenyl Fe(III) octaethylporphyrin, using glassy carbon electrode in a TBAP 0.1 M benzonitrile solution, has two reduction waves, one centered at −0.7 V *versus* Ag/AgCl and the other at −1.86 V *versus* Ag/AgCl. After UV–vis spectroelectrochemistry experiments, the authors assigned the first reduction process occurring at the metal center,

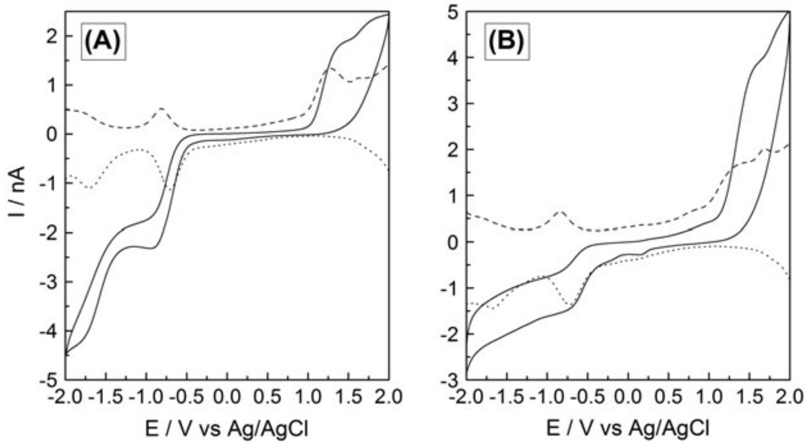

Figure 2. Electrochemical characterization of (A) ZnTAPP and (B) Fe(III)TAPP in $BMImBF_4$ (1 mM) in N_2-saturated conditions by differential pulse voltammetry in both anodic (dashed line) and cathodic (dotted line); increment 0.004 V, amplitude 0.05 V, pulse width 0.05 V, and pulse period 0.2 s by cyclic voltammetry (solid line) at 10 mV s^{-1}.

i.e. Fe(III) / Fe(II) redox process, whereas the second reduction process occurred at the porphyrin [55]. Therefore, based on literature data, it must be inferred that electrochemical processes occurring in FeTAPP are centered in the metal ion site at −0.72 V *versus* Ag/AgCl and the ligand at −1.68 V *versus* Ag/AgCl.

3.2. *Electrocatalytic activity*

Electrodes were modified following the above described method. Structure and mechanism of the resulting films have been previously studied by many authors [42, 58, 59], indicating that the mechanism of the conducting polymer formation consists of a coupling reaction between the amino group and the carbon in ortho position from other monomer molecules, and successive reactions lead to the formation of phenazine, dihydrophenazine, or diphenylamine linkages, depending on the oxidation degree of the polymer.

Figure 3 shows LSV of ITO/Poly-ZnTAPP- and the ITO/poly-FeTAPP- [figure 3(a) and (b), respectively] modified electrodes recorded at 5 mV/s in $BMImBF_4$ under N_2 and CO_2, respectively. The voltammetric profile of ITO/poly-ZnTAPP shows a reduction process which starts at −0.5 V *versus* Ag/AgCl in inert atmosphere, which can be related to a redox signal of the macrocycle [54] as can be seen in figure 2(a); under CO_2 atmosphere, a slight increase in current can be observed, and as a result, carbon dioxide reduction can be assumed as insignificant on this surface.

Cyclic voltammetry of ITO/Poly-FeTAPP under N_2 [figure 3(b)] shows a typical voltammetric profile carried out in ionic liquid medium for a conducting polymer [41], where no clear redox process can be seen due to the viscosity of the solvent. When the experiment is carried out within a saturated CO_2 $BMImBF_4$ solution, a remarkable increase in current with an onset potential at −0.3 V *versus* Ag/AgCl is observed, which corresponds to reduction of carbon dioxide by poly-FeTAPP species on the electrode surface.

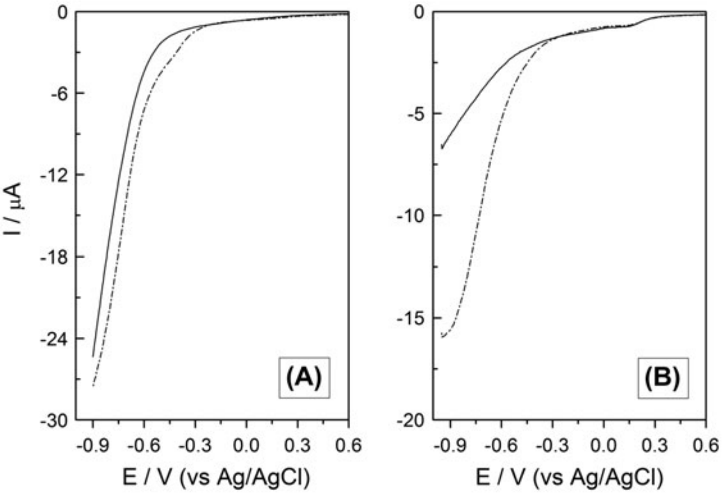

Figure 3. Linear sweep voltammetry of (A) Poly-ZnTAPP-modified electrode and (B) Poly-FeTAPP-modified electrode in N_2-saturated atmosphere (solid line) and CO_2-saturated atmosphere (dashed line).

In order to compare both modified electrodes in terms of its catalytic activity, turnover numbers (TON) have been calculated for the different systems. Then, TON values have been calculated as the quotient of moles of product formed and moles of catalyst deposited on the surface of the electrode.

Potential-controlled bulk electrolysis during 3 h were carried out in order to determine reaction products from the catalytic reduction of carbon dioxide with FeTAPP, and ZnTAPP in both solution and as a conducting polymer, as well as the poly H_2TAPP; parameters and results are summarized in table 1.

It is clear that using the catalyst in solution, a greater production of carbon monoxide occurs. However, if we analyze the magnitude of the TON values, the efficiency of the catalytic process is poor, probably due to diffusion problems in the ionic liquid.

H_2TAPP and ZnTAPP have similar catalytic behaviors, which is not as high as other metal derivatives. Hence, it is possible to infer that the catalytic activity of the Zn conducting polymer may be carried out by reduced species of the porphyrin, whose redox potentials are very close to the potential at which the electrolysis have been carried out.

At −0.8 V *versus* Ag/AgCl, where a constant electrolysis regime was fixed, both electrodes produce only carbon monoxide in the headspace of the cell. It can be seen that poly-FeTAPP-modified electrode presents a TON almost three times larger than the poly-ZnTAPP, as well as a larger faradaic efficiency toward the formation of CO. This

Table 1. Potential-controlled electrolysis results.

Catalyst	CO produced (μM)	TON	Faradaic efficiency (%)
Poly-FeTAPP	1.15	9.18	79.6
FeTAPP (s)	6.64	0.52	12.8
Poly-ZnTAPP	0.376	2.74	14.5
ZnTAPP (s)	4.51	0.33	9.21
Poly-H_2TAPP	4.31	1.99	18.55
No catalyst	0.376	–	14.5

suggests that the reduction of carbon dioxide at the poly-FeTAPP film is more effective and also the catalyst performs more catalytic cycles toward formation of CO. Recent studies with similar Co-TAPP film shows analogous electrochemical behavior; however, its TON toward the formation of carbon monoxide is 69 [41], almost 6 times larger than the poly-Fe-TAPP-modified electrode.

Since CO is one of the reaction products, and according to previously reported mechanism [60], other products from the reduction of carbon dioxide should be formed in aprotic solvents; however, molecules such as carbonate or oxalate were not determined.

3.3. *Spectroelectrochemical measurements*

UV–vis spectroelectrochemical experiments were carried out in order to evaluate probable reaction intermediates for the reaction under survey. The experiments were recorded in $BMImBF_4$ under inert atmosphere, CO_2, and CO, respectively. Poly-ZnTAPP does not show significant spectroscopic changes upon electrochemical reduction (not shown). Figure 4(a) shows dependent potential spectra recorded from open-circuit potential to −0.8 V. Poly-FeTAPP displays at open-circuit potential a Soret band at 423 nm and a broad absorption in *Q* bands region. After application of −0.8 V *versus* Ag/AgCl, the spectra are well defined and a red shift is observed in the whole UV–vis region with the Soret band centered at 448 nm and two *Q* bands present at 576 and 620 nm, respectively. This unequivocally demonstrates that the reduction process leads to the formation of a new species that resembles the spectrum of a Fe(II) porphyrin [56].

Figure 4(b) shows the potential dependent spectra of poly-FeTAPP under CO_2 atmosphere. The spectrum recorded at open-circuit potential immediately shows a shape similar to the one observed at −0.8 V in figure 4(a), indicating Fe(II) species in the polymeric film [56]. Also, it might be inferred an open-circuit potential adduct between poly-FeTAPP and CO_2 [27].

After application of −0.8 V, a slight red shift is observed in the Soret band with *Q* bands located at 570 (blue shift) and 620 (no change), respectively. Also, an increase in Soret band is observed.

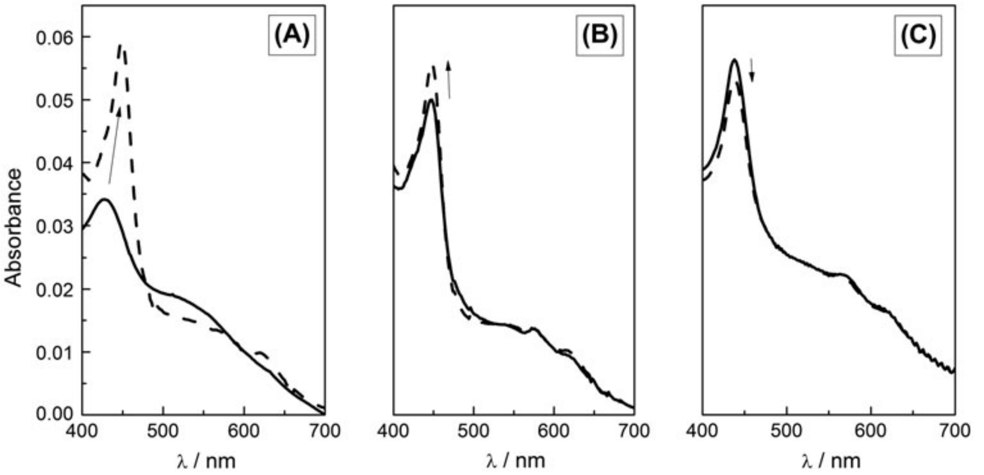

Figure 4. Spectroelectrochemical behavior of poly-FeTAPP-modified electrode under (A) N_2, (B) CO_2, and (C) CO-saturated atmosphere at open-circuit potential (solid line) and at −0.8 V *vs.* Ag/AgCl (dashed line).

Table 2. Spectroelectrochemical measurement's summary.

Atmosphere	Soret band (nm)	Q bands (nm)
N_2	448	576, 620
CO_2	446	573, 620
CO	437	571, 621

However, when the same experiment is recorded under CO atmosphere [see figure 4(c)] at open-circuit potential, the same behavior already observed in 4A at −0.8 V and 4B OCP is present, i.e. the spectrum resembles a Fe(II) species in poly-FeTAPP but after application of −0.8 V *versus* Ag/AgCl, important spectral changes are observed. Indeed, the Soret band undergoes a blue shift centered at 437 nm, whereas *Q* bands kept the values observed in the previous experiments, as can be seen in table 2.

The behavior observed in figure 4(a) and (c) at −0.8 V *versus* Ag/AgCl can be explained as two extreme cases, where 4a is the polymeric film in its pure reduced state and 4c represents a Fe(II)–CO stable intermediate in the time scale of the experiment and under bias application. Thus, spectra recorded in figure 4(b) at −0.8 V *versus* Ag/AgCl may be interpreted as a mixed electronic state between a Fe(II) and a Fe(II)–CO polymeric species. Based on the fact that at open-circuit potential, poly-FeTAPP spectra (Fe(III) complex) can only be detected under N_2 atmosphere in both CO_2 and CO saturated media only; UV–vis spectra of the reduced species can be seen. These results imply that stable intermediates are formed at open-circuit potential.

4. Conclusion

Based on cyclic voltammetry, bulk electrolysis, and spectroelectrochemistry experiments, it is possible to establish a tendency between coordination properties of metal centers used in this work and the electrocatalytic activity toward carbon dioxide reduction. Poly-ZnTAPP, due to the inexistence of free coordination positions, shows poor catalytic formation of CO.

Spectroelectrochemistry at open-circuit potential shows that ITO/poly-FeTAPP-modified electrode is able to form new spectroscopic species resembling Fe(II) porphyrins. ITO/poly-FeTAPP-modified electrode at −0.8 V *versus* Ag/AgCl presents a reduced metal center, which could "coordinate" a molecule of carbon dioxide and release CO upon electron transfer. Thus, poly-FeTAPP is able to reduce CO_2 at low overpotential with a turnover number of 9.18 and a faradaic efficiency of 79.6%. It has been established that analogous films containing CO can reduce CO_2 in a better performance than Fe porphyrin film. Indeed, results of figure 4(c) shows the possibility for existence of a strong coordination bond (Fe–CO), and thus the reduction product is partially stopped.

However, poly-FeTAAP as an insoluble film on the electrode presents several advantages over homogeneous setups that are mainly related with the high-effective concentration of the catalyst in the area of the double layer, where the electrochemical reaction takes place. Furthermore, since the electrode is coated with a thin layer of poly-FeTAPP, the approach uses minimal quantities of catalyst materials and removal of the electrocatalyst following the reaction is facile, avoiding product–catalyst separation steps and contributing with the green chemistry postulates.

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References

[1] K. Trenberth, A. Dai, G. van der Schrier, P. Jones, J. Barichivich, K. Briffa, J. Sheffield. *Nat. Clim. Change*, **4**, 17 (2014).
[2] E. Maginn. *J. Phys. Chem. Lett.*, **1**, 3478 (2010).
[3] J. Canadell, C. Le Quere, M. Raupach, C. Field, E. Buitenhuis, P. Ciais, T. Conway, N. Gillett, R. Houghton, G. Marland. *Proc. Natl. Acad. Sci. USA*, **104**, 18866 (2007).
[4] J. Qiao, Y. Liu, F. Hong, J. Zhang. *Chem. Soc. Rev.*, **43**, 631 (2014).
[5] B.A. Rosen, A. Salehi-Khojin, M.R. Thorson, W. Zhu, D.T. Whipple, P.J.A. Kenis, R.I. Masel. *Science*, **334**, 643 (2011).
[6] A. Dibenedetto, A. Angelini, P. Stufano. *J. Chem. Technol. Biotechnol.*, **89**, 334 (2014).
[7] M. Panda, K. Ladomenou, A. Coutsolelos. *Coord. Chem. Rev.*, **256**, 2601 (2012).
[8] C. Windle, R. Perutz. *Coord. Chem. Rev.*, **256**, 2562 (2012).
[9] J. McAlpin, T. Stich, W. Casey, R. Britt. *Coord. Chem. Rev.*, **256**, 2445 (2012).
[10] A. Zarkadoulas, E. Koutsouri, C. Mitsopoulou. *Coord. Chem. Rev.*, **256**, 2424 (2012).
[11] J. Inglis, B.J. MacLean, M.T. Pryce, J.G. Vos. *Coord. Chem. Rev.*, **256**, 2571 (2012).
[12] J. Costamagna, G. Ferraudi, J. Canales, J. Vargas. *Coord. Chem. Rev.*, **148**, 221 (1996).
[13] J. Collin, J. Sauvage. *Coord. Chem. Rev.*, **93**, 245 (1989).
[14] S. Kapusta, N. Hackerman. *J. Electrochem. Soc.*, **131**, 1511 (1984).
[15] M. Schneider, H. Bippi. *J. Am. Chem. Soc.*, **102**, 7363 (1980).
[16] B. Fisher, R. Eisenberg. *J. Am. Chem. Soc.*, **102**, 7361 (1980).
[17] E. Lamy, L. Nadjo, J. Saveant. *J. Electroanal. Chem. Interfacial Electrochem.*, **78**, 403 (1977).
[18] M. Isaacs, M.J. Aguirre, A. Toro-Labbé, J. Costamagna, M. Páez, J.H. Zagal. *Electrochim. Acta*, **43**, 1821 (1998).
[19] C. San Martín, P. Dreyse, C. García, K. Calfumán, D. Villagra, M. Isaacs. *J. Chil. Chem. Soc.*, **52**, 1305 (2007).
[20] A. Camargo, M.J. Aguirre, W. Cheuquepán, Y. Chen, G. Ramírez. *Electroanalysis*, **20**, 2635 (2008).
[21] P. Dreyse, M. Isaacs, K. Calfumán, C. Cáceres, A. Aliaga, M. Aguirre, D. Villagra. *Electrochim. Acta*, **56**, 5230 (2011).
[22] F. Fuenzalida, P. Dreyse, D. Villagra, B. Matsuhiro, L. Mendoza, M.J. Aguirre, M. Isaacs. *J. Coord. Chem.*, **62**, 130 (2009).
[23] P. Dreyse, D. Quezada, J. Honores, M.J. Aguirre, L. Mendoza, B. Matsuhiro, D. Villagra, M. Isaacs. *Electroanalysis*, **24**, 1709 (2012).
[24] G. Ramírez, M. Lucero, A. Riquelme, M. Villagrán, J. Costamagna, E. Trollund, M. Aguirre. *J. Coord. Chem.*, **57**, 249 (2004).
[25] M. García, M. Aguirre, G. Canzi, C. Kubiak, M. Ohlbaum, M. Isaacs. *Electrochim. Acta*, **115**, 146 (2014).
[26] M. Riquelme, M. Isaacs, M. Lucero, E. Trollund, M.J. Aguirre. *J. Chil. Chem. Soc.*, **48**, 89 (2003).
[27] P. Ardiles, E. Trollund, M. Isaacs, F. Armijo, M.J. Aguirre. *J. Coord. Chem.*, **54**, 183 (2001).
[28] M. Lucero, G. Ramírez, A. Riquelme, I. Azocar, M. Isaacs, F. Armijo, J.E. Förster, E. Trollund, M.J. Aguirre, D. Lexa. *J. Mol. Catal. A: Chem.*, **221**, 71 (2004).
[29] C. Friebe, M.D. Hager, A. Winter, U.S. Schubert. *Adv. Mater.*, **24**, 332 (2011).
[30] J. Soto-Delgado, A. Aizman, R. Contreras, L. Domingo. *Molecules*, **17**, 13687 (2012).
[31] D. Millán, M. Rojas, P. Pavez, M. Isaacs, C. Diaz, J. Santos. *New J. Chem.*, **37**, 3281 (2013).
[32] C. Díaz, C. García, P. Iturriaga-Vásquez, M. Aguirre, J. Muena, R. Contreras, R. Ormazábal-Toledo, M. Isaacs. *Electrochim. Acta*, **111**, 846 (2013).
[33] D. MacFarlane, N. Tachikawa, M. Forsyth, J. Pringle, P. Howlett, G. Elliott, J. Davis, M. Watanabe, P. Simon, C. Angell. *Energy Environ. Sci.*, **7**, 232 (2013).
[34] M. Feroci, M. Orsini, L. Rossi, G. Sotgiu, A. Inesi. *J. Org. Chem.*, **72**, 200 (2007).
[35] H. Yang, Y. Gu, Y. Deng, F. Shi. *Chem. Commun.*, **2002**, 274 (2002).
[36] M. Schmeisser, R. van Eldik. *Inorg. Chem.*, **48**, 7466 (2009).
[37] X. He, B. Hou, C. Li, Q. Zhu, Y. Jiang, L. Wu. *Electrochim. Acta.*, **130**, 245 (2014).
[38] E. Barrado, R. Couto, M. Quinaz, J. Lima, Y. Castrillejo. *J. Electroanal. Chem.*, **720–721**, 139 (2014).
[39] A. Carmichael, M. Earle, J. Holbrey, P. McCormac, K. Seddon. *Org. Lett.*, **1**, 997 (1999).
[40] D. Grills, Y. Matsubara, Y. Kuwahara, S. Golisz, D. Kurtz, B. Mello. *J. Phys. Chem. Lett.*, **5**, 2033 (2014).
[41] D. Quezada, J. Honores, M. García, F. Armijo, M. Isaacs. *New J. Chem.*, **38**, 3606 (2014).
[42] A. Bettelheim, B.A. White, S.A. Raybuck, R.W. Murray. *Inorg. Chem.*, **26**, 1009 (1987).

[43] A.D. Adler, F.R. Longo, F. Kampas, J. Kim. *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

[44] G.A. East, M.A. del Valle. *J. Chem. Educ.*, **77**, 97 (2000).

[45] M. Isaacs, F. Armijo, G. Ramírez, E. Trollund, S.R. Biaggio, J. Costamagna, M.J. Aguirre. *J. Mol. Catal. A: Chem.*, **229**, 249 (2005).

[46] M. Isaacs, J.C. Canales, M.J. Aguirre, G. Estiú, F. Caruso, G. Ferraudi, J. Costamagna. *Inorg. Chim. Acta*, **339**, 224 (2002).

[47] C. García, G. Ferraudi, A.G. Lappin, M. Isaacs. *Inorg. Chim. Acta*, **386**, 73 (2012).

[48] M. Gouterman. *J. Mol. Spectrosc.*, **6**, 138 (1961).

[49] B. Berezin. *Coordination Compounds of Porphyrins and Phthalocyanines*, Wiley, New York, NY (1981).

[50] P. Shantha. *J. Raman Spectrosc.*, **29**, 997 (1998).

[51] N. Carnieri, A. Harriman. *Inorg. Chim. Acta*, **62**, 103 (1982).

[52] K. Kadish, R. Rhodes. *Inorg. Chem.*, **22**, 1090 (1983).

[53] F. Walker, M. Lo, M. Ree. *J. Am. Chem. Soc.*, **98**, 5552 (1976).

[54] G. Closs, L. Closs. *J. Am. Chem. Soc.*, **85**, 818 (1963).

[55] K. Kadish, E. Van Caemelbecke, F. D’Souza, C.J. Medforth, K.M. Smith, A. Tabard, R. Guilard, R. Guilard. *Inorg. Chem.*, **34**, 2984 (1995).

[56] D. Lexa, M. Momenteau, J. Mispelter. *Biochim. Biophys. Acta*, **338**, 151 (1974).

[57] I. Bhugun, D. Lexa, J. Savéant. *J. Am. Chem. Soc.*, **118**, 3982 (1996).

[58] M.G. Walter, C.C. Wamser. *J. Phys. Chem. C*, **114**, 7563 (2010).

[59] E. Bruti, M. Giannetto, G. Mori, R. Seeber. *Electroanalysis*, **11**, 565 (1999).

[60] C. Amatore, J.M. Saveant. *J. Am. Chem. Soc.*, **103**, 5021 (1981).