Characterization of PVC-Tetraruthenated Metalloporphyrins Modified Electrodes: Application as Electrocatalyst in the Nitrite Reduction

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Summary: This paper describes the electrochemical reduction of nitrite ion in 0.1 M $NaClO_4$, on glassy carbon or ITO electrodes modified with mixtures PVC- tetraruthenated metalloporphyrins. This electrode is able to keep the extraordinary electrocatalytic properties of the macrocycle allowing multielectronic transfers and a great stability as a consequence of the inclusion of the macrocycles into a polymeric support such as PVC. On the other hand, the electrochemical reduction of nitrite ion on these modified electrodes studied by cyclic voltammetry shows an enhancement in the current values and lower overpotential compared with the activity of the bare glassy carbon electrode. Controlled potential electrolysis experiments verify the production of ammonia, hydrazine and hydroxylamine, showing the electrocatalytic character and the stability of this modified electrode.

Keywords: electrocatalysis; modified electrodes; nitrite; PVC; tetraruthenated porphyrins

Introduction

Nitrite ions are produced by photolysis of nitrate ions and by photodegradation of aquatic humic substances present in the aquatic environment. Nitrite is a key species in global nitrogen cycle. Nitrites show environmental and biological importance. Moreover, they have an important role as additive in the alimentary industry as preservative, antimicrobial and color fixative agent.[1,2]

Nitrites are compounds that have dual threat to the human body; they can react with amines to form nitrosamines which are harmful to health and potentially carcinogenic.[3–5] Furthermore, due to the physiological condition of the body of young children, nitrite is very dangerous for them (“blue baby syndrome”), by preventing the transfer of oxygen in the blood, nitrite oxidizes Fe^{2+} in hemoglobin and this oxidized hemoglobin is unable to transport oxygen.[3–5] For these reasons, various methods have been used to determine nitrite ions, including the following: spectrophotometry,[6] chromatography,[7] and electrochemical methods.[8–13]

Direct electroreduction of nitrite ions requires high overpotential at most electrode surfaces. It is well known that modifying a traditional electrode surface properly is an effective way of enhancing its electrocatalytic activity.

The electrocatalytic reduction of NO_2^- ion has been studied with modified electrodes, with metal porphyrins[14] and protoporphyrin[15] among others, obtaining as

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reaction products NH_3, NH_2OH and N_2O. The distribution of reaction products is strongly linked to acid-base chemistry that occurs within the coordination sphere.[14–16] Cheng et al, using water soluble iron porphyrins at pH 4.5, showed that the main products at −0.9 V are NH_3 35% NH_2OH 44%, and N_2O 21%. Nitrite is converted into NH_3 and NH_2OH by almost 80% at pH 4.5, with minimum formation of N_2O. The proportion of NH_3 is reduced when the solution becomes more basic (pH> 6). The results indicate that the concentration of protons affects the formation of NO through the dismutation of nitrite, which can coordinate to the catalyst and therefore participating in the kinetics of electrocatalysis.

Catalytic and electrocatalytic properties of porphyrins can be enhanced by coordination of transition metal complexes to the periphery of the macrocycle ring. Functional groups in the periphery of the macrocycle can also be used to control the interaction with other molecular species.[17] In 1993 Toma et al. prepared a supramolecular porphyrin containing four units of $[Ru(bpy)_2Cl]^+$ (bpy = 2,2́ bypyridine) coordinated to pyridinic moiety of a meso-tetra(pyridyl)porphyrin i.e. a tetra-ruthenated porphyrin (TRP).[18] The main characteristic of this complex is that they are able to produce numerous redox process working as a pump of electrons i.e. Ru(III)/Ru(II) redox couple present a four electron simultaneous voltammetric wave. One of the most important drawbacks in the use of these compounds is related with its high positive charge (4+) make them very soluble in water, re-dissolving the complex from the electrode to the test solution.[19] Moreover, porphyrins arranged in polymeric matrices, have been used for the construction of both optical and potentiometric sensors,[20–22] incorporation of additives can improve the properties of the film. Recently, have been reported that modified electrodes with mixtures conductive polymers-PVC show electrochemical signal and significantly extends the life of the electrode.[21]

According to this background, this article deals with the modification of glassy carbon or transparent ITO (Indium Tin Oxide) electrodes with new films based in M(II) tetra-rhutenated porphyrins (M = Co (II), Ni (II) y Zn(II) as metal center ions) supported into a PVC matrix. These modified electrodes were characterized by spectroscopic, microscopic and electrochemical techniques. Also the rotating disc electrode technique was used to elucidate the main components in the electrochemical mechanism involved in the reduction of nitrite anion in $NaClO_4$ solution. In addition, the controlled potential electrolysis was performed to determine the main soluble reaction products and the selectivity obtained in each modified electrode.

Experimental Part

Materials

All chemical reagents were of analytical grade. Cobalt (II) acetate, Ni(II) acetate, Zn (II) acetate, 5,10,15,20 tetrapyrydyl 21H, 23H porphine, tetrabutylammonium hexafluorophosphate ($TBAPF_6$), lithium trifluoromethanesulfonate (LiTFMS), polyvinyl chloride (PVC), dibutylftalate (DBP), sodium perchlorate, sodium nitrite were purchased from Sigma-Aldrich. Lithium chloride was purchased from Fisher Scientific.

Solvents Acetonitrile (ACN), N,N'-dimethylformamide (DMF), Methanol, Tetrahydrofuran (THF), Acetone and Glacial Acetic Acid and neutral alumina were purchased from Merck.

The precursor complex cis dichloro (2,2'-bipyridine) ruthenium (II) dihydrate was prepared following the procedure described in the literature.[16] The supramolecular complexes of Co (II), Ni (II) and Zn (II) μ-{*meso*-5,10,15,20-tetra(pyridyl)-porphyrin}tetrakis{bis(bipyridine)(chloride) ruthenium(II)} $(PF_6)_4$ were prepared by the method described by Toma et al. [18,19,23]. The purity of these compounds was checked by optical absorption spectroscopy, elemental analysis and ^1H-NMR.

Apparatus

Cyclic Voltammetry (CV), rotating disc electrode (RDE) and electrolysis experiments were carried out using a potenciostat CH-Instrument 620B model; furthermore RDE experiments were carried out with a speed control unit CTV101 Radiometer Analytical and a BM-EDI101 Radiometer Analytical rotation unit.

Morphologic characterization was performed by Scanning Electron Microscope (SEM) JEOL 7001F, Transmission Electron Microscopy (TEM) JEOL 2100 and Optical Profilometer (confocal technique) PLμ2300 Sensofar.

Cell and Electrodes

CV, RDE and electrolysis experiments were performed in a pyrex glass three electrode cell. Working electrodes were glassy carbon discs purchased from CH Instrument ($r = 1.5$ mm), Radiometer Analytical ($r = 3$ mm) and a Pine Instruments ($r = 0.25$ cm) respectively, an auxiliary electrode was a Pt wire and a reference electrode was Ag/AgCl both from CH Instrument.

After each experiment the GC electrode was polished with 0.3 μm alumina slurry, (Struers). The electrode was rinsed with double distilled, deionized water and cleaned in an ultrasonic water bath for 30 s, to remove any remaining alumina and then rinsed again with abundant deionized water.

All the electrocatalytic measurements were carried out in aqueous solutions 0.1 M $NaClO_4$ (pH 6). For electrolysis experiments an H-type cell was used. The products were determined by quantitative colorimetric analysis.[24–26]

Preparation of the Modified Electrodes Procedure

A mixture of 80% PVC, 16% MTRP and 4% DBP in 1:1 Acetone/THF was stirred during 90 min.[23] The salt LiTFMS was added in relation with the added amount of MTRP (M= Co(II), Ni(II) y Zn(II)). Then 5 μL of this mixture was placed on the surface of the GC electrode and it was allowed to dry at room temperature (drop coating). The electrode was left to dry at room temperature, after 10 minutes the electrode was rinsed with deionized water. The electrode modified with this procedure (**GC/PVC/MTRP**) was placed in the electrochemical cell without further modifications.

As a blank the same procedure was carried out but without MTRP (**GC/PVC**).

Finally the modification of ITO electrodes it was carried out by dip-coating for 30 s in the mixture above explained (**ITO/PVC/MTRP or ITO/PVC**).

Results and Discussion

Characterization of Modified Electrodes

The modified electrode has been characterized by SEM, TEM, confocal microscopy, Raman spectroscopy and cyclic voltammetry.

Figure 1 displays the scanning electron microscopy characterization (SEM) of GC/PVC/MTRP modified electrode. Figure 1A displays the ITO/PVC modified electrode, where the surface presents several nodes, where estimated diameter varies from 100 to 500 nm. In Figure 1B it is possible to observe the image corresponding to the ITO/PVC/MTRP modified electrode. It is seen a more homogeneous surface and the number of nodes is greater than the analogous observed in 1A. In order to obtain more quantitative information transmission electron microcopy (TEM) was carried out, as can be observed in Figure 2.

The main features observed in Figure 1 are confirmed by this technique (see Figure 2A, 2B), but it is also possible to discriminate several zones with a large electronic density inside of these nodes. From the maximum resolution it can be estimated that the diameter of these new nodes is around 3–5 nm as confirmed in Figure 2C (ZnTRP). The sizes of these new nodes are according with the diameter of a tetraruthenated porphyrin.[19] This fact allows us to infer that probably PVC nodes

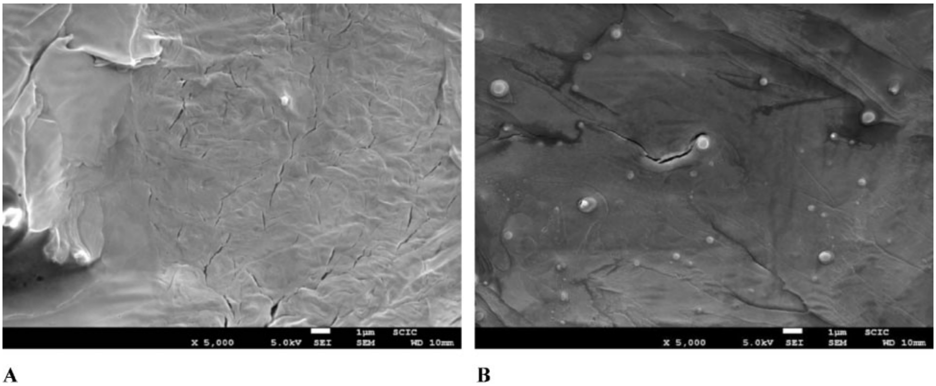

Figure 1.
SEM images of A) ITO/PVC 5000X, B) ITO/PVC/MTRP 5000X.

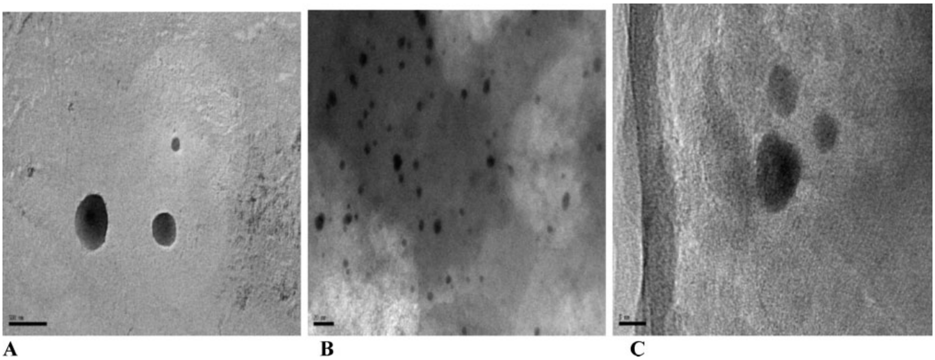

Figure 2.
TEM images of mixtures A) PVC 500 nm, B) PVC/MTRP 20 nm and C) PVC/MTRP 5 nm.

are formed in the filming process on the electrodic surface and inside of these nodes the porphyrins arrangement are allocated. By means of confocal microscopy the thickness of the films was calculated, where the average is 60 μm.

The main bands of Raman spectrum of solid CoTRP complex (not shown), correspond to 1369, 1249 and 404 cm^{-1} peaks associated to porphyrin skeletal modes, 1500 and 1318 cm^{-1} peaks associated with vibrational modes of bipyridine ligand, 1217 and 1020 cm^{-1} peaks corresponding to pyridine or porphyrin vibration strongly coupled with the π ring. Finally bands at 1608 and 1564 cm^{-1} are observed as a consequence of the connection between pyridine and bipyridine moieties.[27,28]

On the other hand, the Raman spectrum of the modified electrode (not shown), no remarkable differences are observed, indicating that CoTRP complex does not change its structure, and no strong interactions between the PVC matrix and CoTRP complex are present.

Figure 3 shows the voltammetric profile of GC/PVC/ZnTRP modified electrode (the results for Co and Ni are analogous) in a 0.1 M $NaClO_4$ solution at pH 6. The inset shows the structure of the macrocycle used in this study. The main feature observed in Figure 3 is the quasi-reversible process involving the Ru(III)/Ru(II) redox couple at 720 mV. No other processes involving the metal center ion or the porphyring ring were observed there.

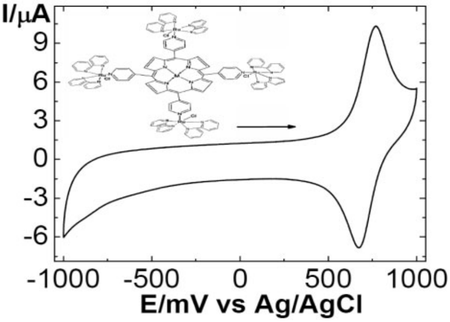

Figure 3.
Voltammetric Profile of GC/PVC/ZnTRP modified electrode in 0.1 M $NaClO_4$ solution. Initial and final potential was 0 V and scan rate 0.1 V/S, the arrow indicates the direction of potential sweep. Inset: Structure of μ-{meso-5,10,15,20 tetra(pyridyl)porphyrin} tetrakis{bis(bipyridine) (chloride) ruthenium (II)}$(PF_6)_4$.

Voltammetric Studies of NO_2^- Reduction in Aqueous Solution using GC/PVC/MTRP Modified Electrodes

The voltammetric behavior of GC/PVC/MTRP modified electrodes toward the electrochemical reduction of NO_2^- is depicted in Figure 4. In absence of NO_2^- GC/PVC/MTRP, modified electrodes do not show any significant voltammetric peaks. However, when 0.01 M of NO_2^- is added into the test solution a current starting at −350 mV for CoTRP and −530 mV for NiTRP and ZnTRP are seen and a peak centered at −720 mV is also observed. In all cases this voltammetric process is related with the electrocatalytic reduction of NO_2^-. The reduction current of NO_2^- obtained with ME is several times bigger than the obtained with GC, which confirms its electrocatalytic character.

RDE Measurements of NO_2^- Reduction in Aqueous Solutions using Modified Electrodes

In order to understand the mechanism and kinetic factors that controlled the electrochemical reduction of NO_2^-, rotating disc electrode experiments were performed. Figure 5 depicts the I-E polarization curves of the electrocatalytic reduction of NO_2^- at GC/PVC/CoTRP, modified electrode registered at different rotation rates (ω) at $5\,mV\,s^{-1}$.

The expression that governs the convective regime given by the rotating disk electrode is known as the Levich equation (Eq. 1), this provides excellent test currents which are entirely controlled by mass transport.[29,30]

$$I_L = 0,62\ n\ F\ A\ D^{2/3}\ \omega^{1/2}\ \upsilon^{-1/6}\ C^* \qquad (1)$$

F is Faraday's constant, D is the diffusion coefficient, ν is the kinematic viscosity of the solution, and C is the bulk concentration.[29,30]

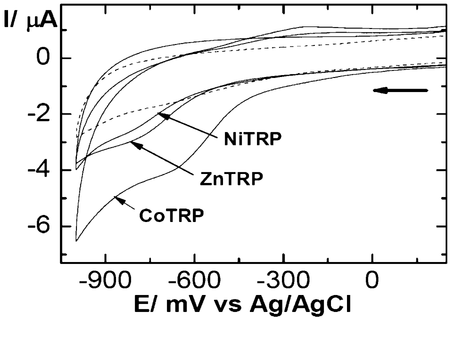

Figure 4.
Cyclic voltammograms of GC/PVC/MTRP modified electrodes at pH 6 in 0.1 M $NaClO_4$ in presence of 0.01 M NO_2^-, dash line corresponds to the glassy carbon electrode with 0.01 M NO_2^-. Initial and final potential was 0 V and scan rate 0.1 V/s. The arrow indicates the direction of potential sweep.

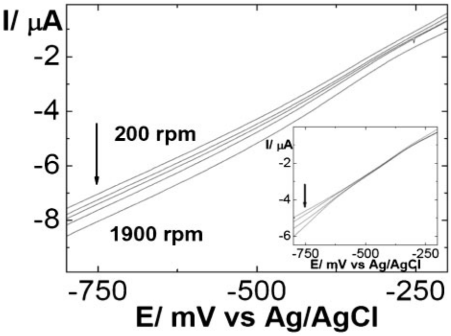

Figure 5.
Rotating Disc Electrode Voltammetry of GC/PVC/CoTRP electrode at pH 6 in 0.1 M $NaClO_4$ in presence of 0.01 M NO_2^-. Sweep rate: $5\,mV\,s^{-1}$. Inset: RDEV of GC in the same conditions.

For irreversible reactions the I-E curve from RDE experiments will present a series of plots, with 3 characteristic regions:

1) Plateau region of the limiting current (I_L), where the current density depends only on the rate of mass transport and I_L is proportional to $\omega^{1/2}$,
2) At low current densities, the current density is entirely determined by the electron transfer kinetics and the mass transport rate will not affect the current density. Here I is independent of ω,
3) Intermediate zone of mixed control-zone, the current density is partially controlled by mass transport and I will vary with ω, but the shape of the plot I vs $\omega^{1/2}$ is not linear.

None of the I-E graphs outlined in Figure 5 shows a limiting current. As described above, nitrite reduction occurs on average at −0.8 V and considering that the discharge of hydrogen is presented at potential nearby would not be surprising that both reductions are assembled. Despite the absence of limiting current, graphs were made of I vs $\omega^{1/2}$ at −0.5, −0.6, −0.7 and −0.8 V, poor linearity was obtained from these plots since r^2 parameter was not observed higher than 0.75. This suggests that the reaction is in a mixed control zone, where electron transfer is slower than the mass transport rate.

Controlled Potential Electrolysis

In order to test the catalytic activity of GC/PVC, GC/PVC/CoTRP, GC/PVC/NiTRP and GC/PVC/ZnTRP electrodes, as well as to evaluate the reaction products, controlled potential electrolysis was performed.

From voltammetric profiles it can be determined that the reduction of nitrite is highest at −0.8 V as average for the three modified electrodes. To test the electrodes at more extreme conditions of electrolysis these experiments were carried out at −1.0 V, demonstrating that even though at a potential where the production of hydrogen is possible, the modified electrodes are very stable and selective in the conversion of substrate. For the electrolysis experiment, 20 mL of a 0.01 M $NaNO_2$ solution in 0.1 M $NaClO_4$ supporting electrolyte (pH 6) was used, under argon atmosphere at −1 V with stirring during the entire experiment (6 hours). Once the experiment is finished the catholyte solution is acidified with 3 M H_2SO_4 and stored in sealed bottles for further analyses.

Table 1.
Apparent surface coating. Before and after of controlled potential electrolysis.

Modified electrode	Γ_{before} *10^{-11} (mol/cm^2)	Γ_{after} *10^{-11} (mol/cm^2)	% mass loss
GC/PVC/CoTRP	3.07	2.27	25.99
GC/PVC/NiTRP	7.38	5.73	22.35
GC/PVC/ZnTRP	5.25	3.60	31.39

Additionally, a voltammetric profile of the modified electrodes is registered before and after the electrolysis experiments calculating the apparent surface coating. The differences observed (see Table 1) are an indirect way to test the stability of the modified electrodes. After six continuous hours of electrolysis none of the modified electrodes lost more than 30% of their original mass, and probably this loss of material is due to the stirring conditions and the applied potential value and it occurs at the most external layers.

For each electrolyses performed, the number of moles of product formed from 1 mol of catalyst in unit time and area (TOF) were calculated. This parameter provides the relative selectivity of the modified electrode toward a particular product.

$$\mathrm{TOF} = \frac{\text{mol of product}}{\text{mol of catalyst} * t * A} \qquad (2)$$

where "t" is the electrolysis time in seconds

$$\text{Mol of catalyst} = \frac{Q}{n * F * A} \qquad (3)$$

where :
"Q" = Area under cupla oxidation of Ru (II)
"n" = Number of electrons involved
"F" = Faraday constant (96500 C/mol)
"A" = Electrode area (0.196 cm^2)

Table 2.
Turnover frequency (TOF).

	TOF (s^{-1})		
	GC/PVC/CoTRP	GC/PVC/NiTRP	GC/PVC/ZnTRP
Hydroxylamine	12230	6005	7168
Hydrazine	6934	3561	5128
Ammonia	12434	6673	8867

TOF were determined after each electrolysis and are presented in Table 2. Under the experimental conditions used in this work, the reduction products for the three modified electrodes are hydrazine, hydroxylamine and ammonia, being the most prominent the last two ones.

Also from Table 2, it can be observed that the electrocatalytic activity of the modified electrodes present the following order: GC/PVC/CoTRP $>$ GC/PVC/ZnTRP $\geq$ GC/PVC/NiTRP.

Worth mentioning is that Zn complex is more active than Ni complex. This fact can shed some light regarding the active site in the catalyst. It has been informed[31–36] that open shell transition metals are active toward the reduction of several molecules such as O_2, CO_2 etc. because they are able to form an intermediary complex before the electron transfer or bind the analyte in a lower oxidation state. It is well known that Zn(II) does not present this property, since it is a closed shell transition metal, then according to this fact it is very possible that the reduction of nitrite would be activated for an electron transfer resulting from the macrocycle ring without the intervention of the metallic ion center.[36–41] Therefore Co (II) center could provide a more stable reduced macrocycle where the nitrite molecule can reacts.

Conclusion

A simple and stable modification method of a glassy carbon electrode has been developed by drop-coating of PVC- tetraruthenated metalloporphyrins mixtures. The modification protocol presented in this work is less complex compared with other methodologies involved in the modification of glassy carbon electrodes such as layer by layer adsorption or electrochemical polymerization.

The morphology characterization of GC/PVC/MTRP modified electrodes was carried out by SEM, TEM, confocal microscopy and Raman spectroscopy. The provided information make us suppose that in the modification process, PVC form nodes on the electrode surface (with a diameter between 100–500 nm) and that within such agglomerations would include the tetraruthenated metalloporphyrin. Moreover it was established that there is no bonding between macrocycle - polymer matrix and that the thickness of the modification is in the order of 60 micrometers.

On the other hand, these modified electrodes exhibit good electrocatalytic activity towards the electrochemical reduction of nitrite ions in neutral media (pH 6), voltammetry studies shows an enhancement in the current values and lower overpotential compared with the activity of the bare glassy carbon electrode. Controlled potential electrolysis experiments verify the production of ammonia, hydrazine and hydroxylamine even at very negative potentials, showing the electrocatalytic character and the stability of this modified electrode.

Finally, RDE experiments suggest that the reaction is in a mixed control zone, where electron transfer is slower than the mass transport rate; therefore, more kinetic information is currently under survey.

Acknowledgements: K.C., P.D. and C.G. are grateful CONICYT scholarships for PhD studies in Chile. K.C acknowledges PhD scholarship support AT 24091042 and PhD exchange student program (BECAS CHILE). This work was supported by FONDECYT program grant N° 1100203.

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