Approach for Modulation of the Permselective Properties of Ni(II) Porphyrin Polymers.

Romina R. Carballo[a] and Irene N. Rezzano*[a]

Abstract: The electropolymerization of Ni(II) Protoporphyrin (polyNiPP) onto glassy carbon electrodes is performed in different experimental conditions, varying the supporting electrolytes, solvent, and oxidative potentials. The AFM images show different average thickness for each polymer, polyNiPP(TBAP) (0.6 μm) and polyNiPP(LiClO$_4$) (0.1μm). The polyNiPP(LiClO$_4$) describes a straight line plot of EMF versus log (C) for NO$_2^-$, with the slope of 37 mV per concentration decade while the same film is not sensitive to the thiocyanate concentration. For polyNiPP(TBAP) the slope for thiocyanate progressively increase when is oxidized in aqueous solution. A sub-Nernstian response (59 mV /decade) is obtained at 1000 mV. The Nyquist plots confirm that the method of preparation establishes the properties of films related to the movement of the ions.

Keywords: electrochemistry · polymers · permselectivity · polyNi(II) Protoporphyrin · membranes

1. Introduction

The metalloporphyrins are naturally occurring compounds that have been intensively studied due to their unique physicochemical properties; that can be modulated by varying the experimental conditions [1–4]. The oxidation state, geometry, and coordination number play a relevant role in the electrochemical behavior, for this reason, an enormous number of investigations have been reported trying to fit these variables to obtain functional materials for different applications [1, 5].

The use of electrodes modified with polymers of metalloporphyrins resulted very attractive in the field of electrocatalysis because produces adherent films on the electrode surface and increases the lifetime of the resulting modified electrodes. In these cases, the film thickness is crucial in determining the physicochemical properties of the resulting electrode [6].Then, the preferred coordination number of the central metal ion and the nature of the coordinating ligands [7] establish the matrix structure, defining selectivity [8–10]. In our experience, Co atom does not present a planar conformation in polyCo(III)PP, resulting in a less packed structure of this film [11], which explains the high and unique tendency of polyCo(III)PP to act as a selective complexing center to incorporate axial ligands [12]. The electropolymerized Ni(II) Protoporphyrin (polyNiPP) turn out to be really interesting, because its behavior was highly dependent on the method of fabrication and completely different from polyCoPP [13]. In fact, the film shows the high capacity to incorporate aromatic structures, due to π-π interaction [14] or eventually a very efficient catalytic activity to sulfite oxidation [6].

The surface architecture contributes to defining the selective-permeation profile that paves the way for practical applications such as specific sensing and separation of analytes.

In this work, the polyNiPP was prepared in the presence of different supporting electrolytes and oxidized to different potentials to modulate the selectivity. The resulting structure was evaluated by AFM microscopy and the potentiometric response to anions was measured. Considering that the movement of ions and solvent, to compensate charge, strongly influences the redox properties of the film at open circuit conditions, electrochemical impedance spectroscopy (EIS) was also performed to evaluate alternative methods of modulation.

As far as we know, this is the first report that studies the permselectivity of a film of porphyrin prepared under different experimental conditions, comparing the potentiometric and EIS responses.

2. Experimental

2.1 Reagents and Solutions

Protoporphyrin-IX dimethyl ester was obtained from hemin (Mallinckrodt). Tetrabutylammonium perchlorate (TBAP) was obtained by precipitation of a saturated solution of the tetrabutylammonium hydroxide (Sigma) with perchloric acid, twice recrystallized from ethanol, and dried under vacuum. *Caution! Perchlorate salts may be explosive. It should be handled with care and in small amounts.* Lithium perchlorate (LiClO$_4$) was purchased from Fluka. Porphyrin solutions were prepared with dichloromethane (Cl$_2$CH$_2$), or acetonitrile (CH$_3$CN) (Merck, HPLC-grade). Sodium nitrite (NaNO$_2$), sodium

[a] R. R. Carballo, I. N. Rezzano
Universidad de Buenos Aires, Facultad de Farmacia y Bioquímica, IQUIFIB CONICET, Junín 956 CP 1113 Buenos Aires, Argentina
E-mail: irezzano@ffyb.uba.ar

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thiocyanate (NaSCN), and potassium dihydrogen phosphate (KH_2PO_4) were analytical grade (Merck). Aqueous solutions were prepared with deionized water obtained from a Millipore Milli-Q purification system.

2.2 Poly(Metalloprotoporphyrin IX) Electrodes Preparation

The synthesis of Me-protoporphyrins was performed as described by Adler [15]. The glassy carbon electrode (GCE) was polished with 0.3 and 0.05 μm diameter alumina particles and finally rinsed with deionized water.

The polyNiPP films were deposited on glassy carbon electrode by electrochemical cycling through the metalloporphyrin oxidation waves, from 0 to 1.8 V versus Ag/AgCl. Solutions of Ni-Protoporphyrin (0.0065 g, 10 mmol) in Cl_2CH_2 (5 mL) with TBAP (0.1440 g, 0.5 mmol) or in CH_3CN (5 mL) with $LiClO_4$ (0.0531 g, 0.5 mmol) were prepared. The film was oxidized by cycling over the required potential range in aqueous 0.050 mol/ L KH_2PO_4 solution.

2.3 Apparatus

The potentiometric measurements were carried out with a Hanna Instruments high impedance voltmeter. The Ag/AgCl reference electrode was purchased from BAS. The electrochemical system may be represented as follows: Ag/AgCl, KCl (3 M)//sample//working electrode. The working and the reference electrodes were immersed in different concentrations of test solutions. The EMF values were plotted versus the logarithmic value of the concentration of analyte.

Electrochemical techniques were performed with a purpose built potentiostat (TEQ-Argentina), with a digital signal generator for implementation of different electrochemical techniques. Electrochemical impedance spectra (EIS) were acquired with a TEQ4-Z potentiostat (TEQ-Argentina) equipped with a frequency response analyzer module.The frequency range was 10 kHz to 0.1 Hz and the amplitude of oscillation was set to 10 mV_{RMS}. Data analysis and fitting was performed with the program ZView® (Scribner Associates, USA). A glassy carbon working electrode (GCE, 0.25 cm^2 area), an Ag/AgCl KCl 3 M reference electrode (BAS) and a platinum wire auxiliary electrode were used for electrochemical experiments. All measurements were carried out at room temperature (20 ± 2 °C).

AFM images were obtained onto the gold electrodes, Nanoscope IIIa-Quadrex, Digital Veeco (AFM) was used for AFM experiments, performed in tapping mode with a resonance frequency of 300 kHz previous nitrogen bubbling. The tips were commercially available Si tips (40 N/m) supplied by Digital Instruments.

3. Results and Discussion

3.1 Morphological Characterization and Potentiometric Response of PolyNiPP Modified Electrodes

In previous experiments, we observed that the movement of ions and solvent is highly dependent of the fixed charges in the polymer [13]. To study the effect of the cation size of the supporting electrolytes in the morphological characteristics of the resulting films, the electropolymerization of Ni(II) Protoporphyrin (polyNiPP) onto glassy carbon electrode (GCE) has been performed by cyclic voltammetry, cycling over the oxidation wave of the porphyrin ring. The voltammetric experiments were done in two different supporting electrolyte solutions, lithium perchlorate ($LiClO_4$) in acetonitrile and tetrabutylammonium perchlorate (TBAP) in dichloromethane. The AFM images of the resulting films are reported in Figure 1, where a quite different morphology is observed. Although both films have a rough surface, polyNiPP($LiClO_4$) shows a more flat and compact structure than polyNiPP(TBAP). The root-mean-square roughnesses provided by these images are 0.1 μm, and 0.6 μm, respectively. These results indicate that the structure of the polymer is highly dependent on the fixed cation size and encourage us to evaluate the effect on the movement of different sized ions. The mechanical resistance to the flux of ions inside the film gives rise to a charge separation and, eventually, to the formation of a steady-state electric potential difference.

The potentiometric response of polyNiPP modified electrodes, prepared with different supporting electrolytes, is significantly different for nitrite and thiocyanate activity in solution (Figure 2). The polyNiPP($LiClO_4$) shows a straight line plot of EMF versus log(C) for NO_2^-, with the slope of 37 mV per concentration decade differing from the bare electrode that does not suffer any change in presence of the ion (Figure 2 A). The same does not apply to SCN^- since in this case; the film is not sensitive to the concentration (Figure 2B). These findings led to conclude that the porous generated in the presence of $LiClO_4$ are small enough to carry out a mechanical resistance to the movement of SCN^- [16], acting more likely as a molecular sieve. On the contrary, the potentiometric response of the electrode modified with polyNiPP(TBAP) shows a better response to SCN^- (slope 44 mV/decade) than to NO_2^- (39 mV/decade) (Figure 3). This result reinforces the idea of the formation of different porous size in the polymer, ruled by the presence of a voluminous cation such as tetrabutylammonium. Another aspect to be considered is that the redox process Ni(II) to Ni(III) produces a stable Ni-O–Ni bridge and changes from a square planar to octahedral conformation in porphyrin polymers [17]. These facts could alter the permselectivity and increase the hydrophobicity of films [18]. Consequently, we also decided to oxidize the thicker polyNiPP(TBAP) at 600, 1000 and 1800 mV vs Ag/AgCl, in aqueous solutions. Figure 3 A shows the nitrite response in each film, which in terms of slope remains the same except for the highest
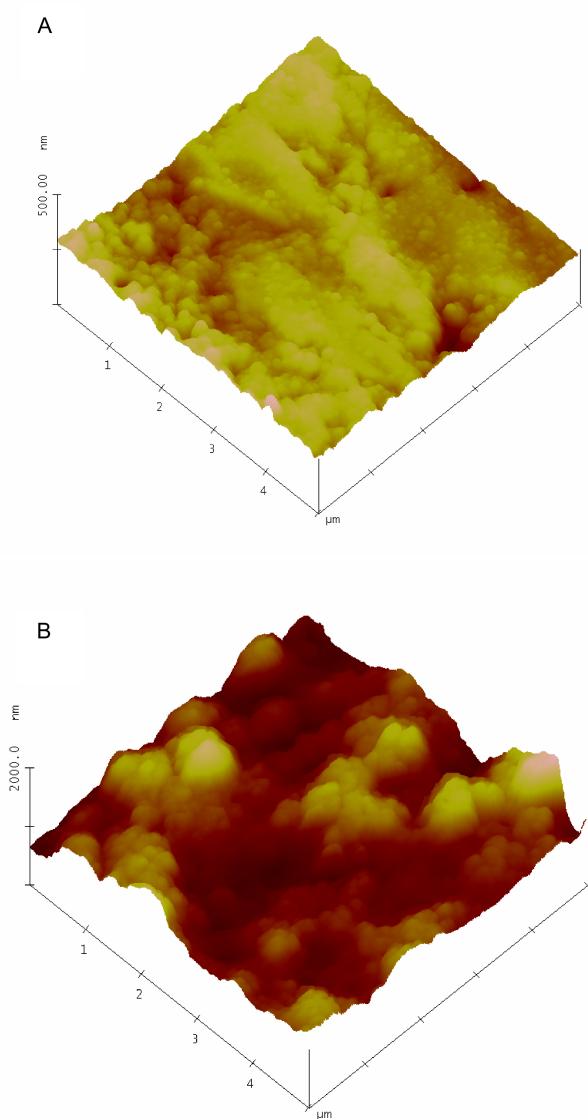
A

B

Fig. 1. AFM images of gold surfaces covered with (A) polyNiPP (LiClO$_4$) and (B) polyNiPP(TBAP).

potential tested (1800 mV). On the contrary, the slope for thiocyanate progressively increases to rich a sub-Nernstian response in the film oxidized to 1000 mV (Figure 3B). Undoubtedly, in this last case, the ratio between the ionic radius and the pore radius along with the membrane fixed charge concentration establish the optimum experimental conditions. It is worthy to note that the porphyrin ring is completely oxidized at 1800 mV, due to the nucleophilic attack of H$_2$O on the porphyrin radical, leading to the dioxoporphomethene [19] with the lack of the film properties.
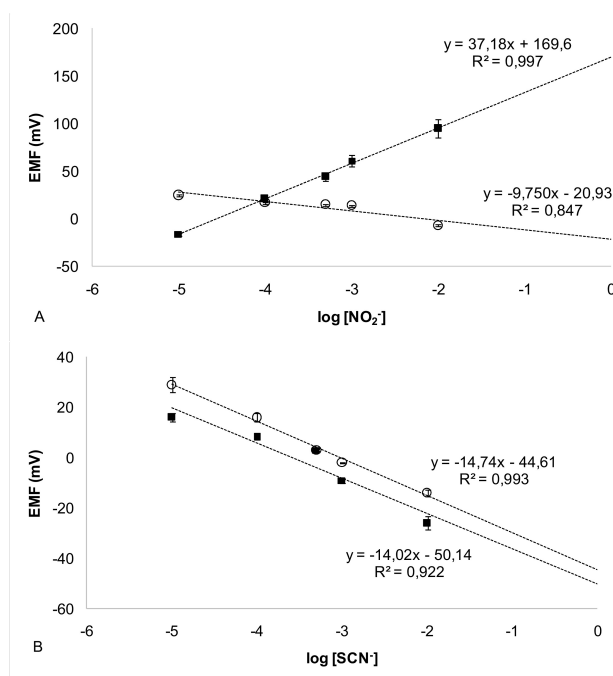

Fig. 2. Potentiometric response curves of (■) polyNiPP(LiClO$_4$) and (○) bare electrode towards (A) NO$_2^-$, and (B) SCN$^-$.($n = 3$).
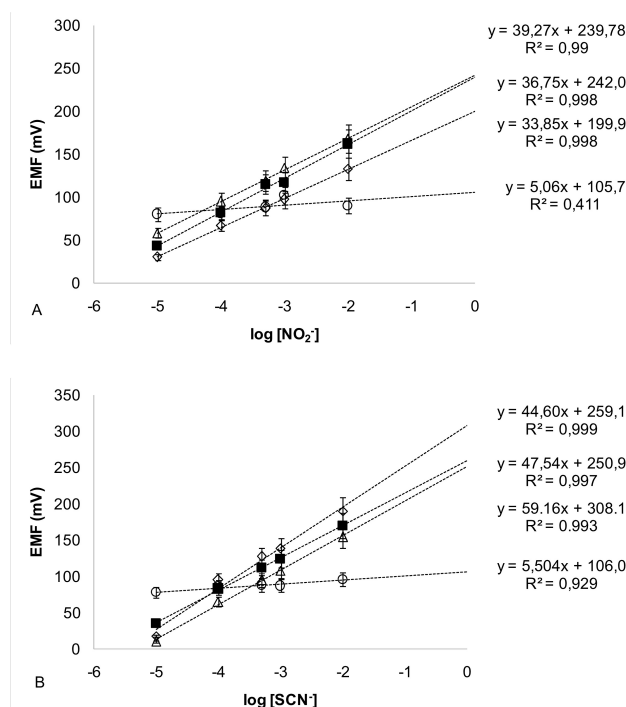

Fig. 3. Potentiometric response curves of (■) polyNiPP(TBAP) without oxidation, and polyNiPP(TBAP) oxidized at (Δ) 600 mV, (◇) 1000 mV and (○) 1800 mV vs Ag/AgCl, towards (A) NO$_2^-$, and (B) SCN$^-$.($n = 3$).

3.2 Electrochemical Impedance Spectroscopy (EIS) Studies

To get additional information about the membrane properties we performed the electrochemical impedance spectroscopy for both polymers, polyNiPP(LiClO$_4$) and polyNiPP(TBAP) in the presence of the anions tested at open circuit conditions. Figure 4 A shows the Nyquist plot of the former, where only one semicircle is found (Scheme 1 A). This result is coincident with the thinner structure observed in the AFM experiment. It is interesting to notice that the R_{CT} values are higher than the obtained with the polyNiPP(TBAP) for both anions, that could be attributed to the tighter polymeric structure.
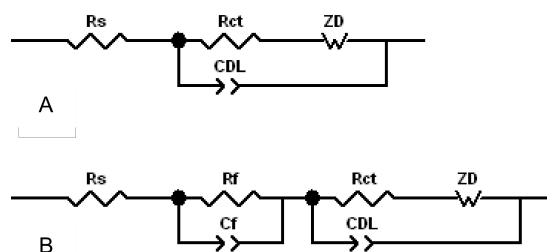
Scheme 1. Scheme of the electrical equivalent circuits proposed for (A) polyNiPP(LiClO$_4$) and (B) polyNiPP(TBAP).
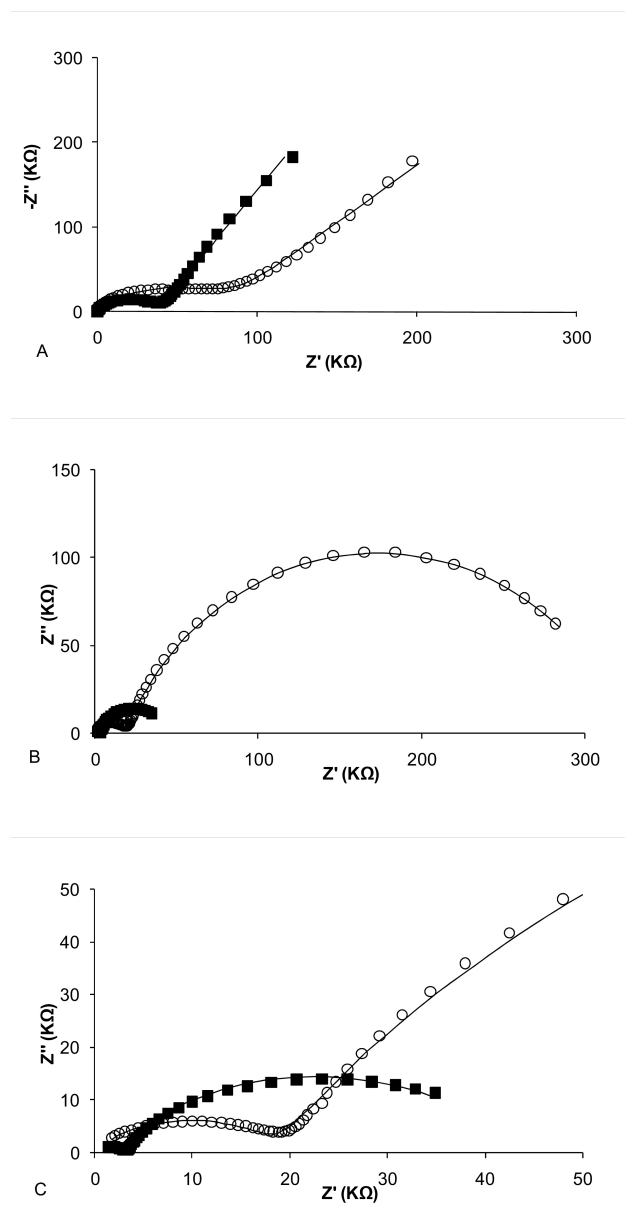
In turn, the impedance spectra of polyNiPP(TBAP) shows two semi-circles, corresponding to process with two different time constants, which is in agreement with the thicker polymeric structure (Figure 4B and C). Then, if we consider that each time constant corresponds to one equivalent circuit, it can be thought as a combination of two RC circuits (Scheme 1 B) [20]. The first of them can be ascribed to the film resistance (R_F) and film capacitance (C_F), while the other RC circuit can be assigned to the polymer/solution interface. R_{CT} is the charge transfer resistance between polymer and electrolyte solution, C_{DL} is the double layer capacitance which is replaced by a constant phase element when roughness effects and surface inhomogeneity exist, and Z_D is the diffusional impedance (Warburg) [21]. The presence of differentially sized ions, that cannot equally permeate inside the film, produces the variations in film resistance. This in our case, means 10 times smaller values of R_F and R_{CT} for the smaller hydrated anion (NO$_2^-$). Table 1 summarizes the fitting values for both polymers.

4. Conclusions

The permselective properties of the electropolymerized polyNiPP onto glassy carbon electrodes are highly dependent on the size of the cation of supporting electrolyte. It can behave either as a thin film with a tight structure and low permeability to anions or as thicker membrane modulated by an oxidative process in aqueous solutions.

These results point to understand the mechanisms of selective response of polymers of porphyrins that does not incorporate ligands to a large extent, in order to predict and adjust their permselectivity to separative and sensing aplications

5. Acknowledgements

Fig. 4. Nyquist plots for (A) polyNiPP(LiClO$_4$) and (B) polyNiPP (TBAP) in presence of : (■) 0.01 M NaNO$_2$ solution; (○) 0.01 M NaSCN solution. (C) Amplification of (B) in the high frequencies range. The frequency range was 100 kHz to 0.1 Hz. The amplitude of oscillation was set to 10 mV $_{RMS}$, at open circuit potential condition. Fitted data (—).

Table 1. Summary of estimated EIS parameters obtained for polyNiPP(LiClO$_4$) and polyNiPP(TBAP), at open circuit potential ($n = 3$, error bars ± 1 SD).

| | polyNiPP(LiClO$_4$) | | | polyNiPP(TBAP) | | | | |
	R_S (Ω)	R_{CT} (Ω)	C_{DL} (F.s^{n-1}) (x 10^{-6})	R_S (Ω)	R_F (Ω)	C_F (F.s^{n-1}) (x 10^{-6})	R_{CT} (Ω) (x 10^6)	C_{DL} (F.s^{n-1}) (x 10^{-6})
NO$_2^-$	96.5	38000 $\pm$ 400	0.10 $\pm$ 0.01	46.01	3220 $\pm$ 20	0.025 $\pm$ 0.002	0.0388 $\pm$ 0.0003	1.85 $\pm$ 0.03
SCN$^-$	102.2	80900 $\pm$ 1000	0.225 $\pm$ 0.001	56.90	19000 $\pm$ 100	0.019 $\pm$ 0.001	0.305 $\pm$ 0.003	1.22 $\pm$ 0.01

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R. R. Carballo, I. N. Rezzano*

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