ELECTROCHEMICAL CHARACTERIZATION OF PVC-Pt(II)PORPHYRIN-MEMBRANE

Nicoleta Plesu[1]*, Gheorghe Fagadar-Cosma[2], Anca Lascu[1], Mihaela Petric[1], Manuela Crisan[1], Eugenia Fagadar-Cosma[1]

[1]*Institute of Chemistry-Timişoara of Romanian Academy, 24 M. Viteazul Ave, 300223 Timisoara, Romania*
[2]*Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University Timisoara, Pta Victoriei 2, 300006 Timisoara, Romania*
*e-mail: plesu_nicole@yahoo.com

Abstract

The maximum water volume fraction absorbed by membrane based on Pt(II)-5,10,15,20-tetra(4-methoxy-phenyl)-porphyrin (PtTMeOPP) in poly(vinyl)chloride (PVC) matrix applied on iron substrate is 0.3 % and the permeability is $7.6 \times 10^{-12} m^2 \ s^{-1}$. After 24 h immersion in the 0.5 M 4-morpholinoethanesulfonic acid (MES) solution of pH = 5.5, the Nyquist representation of impedance data shows diffusion into the membrane of electrolytes from the buffer solution, causing a decrease of the membrane electric resistance, but no delamination was observed for immersion longer than 48 h. Furthermore, the coating resistance is still close to ~16000 ohm.cm^{-2} after 25 hours. This recommends this membrane as good material in potentiometric sensors design.

Introduction

The incorporation of compounds with special recognition properties (i.e porphyrins and metalloporphyrins) in common polymers allowed the obtaining of membranes with tailored properties [1]. Structural features and the functionalization possibility recommend porphyrin derivatives as good and sensitive compounds for sensors design (to recognize ions, neutral molecules and biologically active substances). Platinum-porphyrins were reported in oxygen detection [2-5], anions determination (perchlorate, iodide) [6-9] and alcohol sensing [10].

In membrane preparation, barrier properties against water and ionic species present in solution are important and can define if the membrane can facilitate the migration of ions through the electrode coating and if a certain membrane can act as a sensitive material for analytes detection. Electrochemical characterization of PVC-PtTMeOPP porphyrin–membrane is presented in this paper.

Experimental

Reagents. Poly(vinyl)chloride (PVC), o-nitrophenyloctylether (NPOE), tetrahydrofurane (THF) were purchased from Fluka and Merck. All reagents (salts, acids and bases) were of purum analyticum grade. Double distilled water was used. The synthesis of PtTMeOPP was already reported by our group [9].

Electrode Membrane Preparation. The studied membranes have the composition 1% metallophorphyrin, 33% PVC, 66% NPOE (plasticizer) and the appropriate amount of THF was added under stirring to obtain a transparent solution, that was deposited onto a glass plate. The solvent was slowly evaporated at room temperature and a flexible membrane was obtained. A circular membrane of 8 mm diameter was cut and sticked on the Fluka electrode body (inox electrode with an active surface equal to 0.785 cm^2) by THF.

Apparatus and Electrodes. Autolab 302N EcoChemie equipped with the FRA2 impedance module were used for Electrochemical Impedance Spectroscopy (EIS) investigations,

performed at room temperature in a conventional three-electrode cell, equipped with two stainless steel counter electrodes and Ag/AgCl as reference electrode. The sinusoidal potential amplitude was 10 mV and the tested frequency range was in the range from 0.1 Hz to 100 kHz.

The performance of membrane was investigated by measuring impedance in the frequency range at different immersion times in in 4-morpholinoethanesulfonic acid (MES) solution at pH = 5.5. The experimental data were fitted to the equivalent electrical circuit by a complex non-linear least squares method, using the ZView software - Scribner Associates Inc., Southern Pines, North Carolina, USA and Solartron Analitical , Oak Ridge, Tennessee, USA.

Results and discussion

The PtTMeOPP compound was obtained with a yield over 88% as brownish crystals after metalation of the porphyrin base, 5,10,15,20-tetra(4-methoxy-phenyl)-porphyrin, with large excess of $PtCl_2(PhCN)_2$ in the presence of $CH_3COONa \times 3H_2O$ [9]. The metalloporphyrin was further characterized by UV-vis spectroscopy in different solvents, by FT-IR and ^{1}H-NMR to confirm the structure.

The UV-vis spectra of 10^{-5}M Pt-TMeOPP in various solvents: chlorobenzene, dichloromethane, THF, DMF and DMSO, presented in the order of increasing polarity, show that the solvent with the lowest polarity generates the spectrum with the highest intensity of absorption and with the highest red shift of both Soret and Q bands (Figure 2, Table 1).
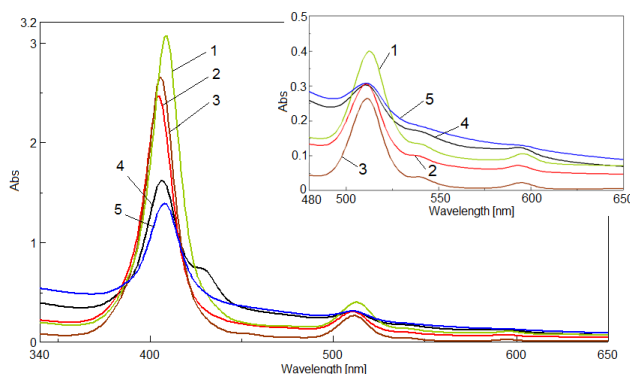

Figure 2. Overlapped UV-vis spectra of Pt-TMeOPP in various solvents (increasing polarity):
1-chlorobenzene, 2-dichloromethane; 3-THF; 4-DMF; 5-DMSO

Table 1: UV-vis parameters compared for Pt-TMeOPP in various solvents by increasing polarity:

Solvent	Soret		Q		Q	
	λ [nm]	I [u.a.]	λ [nm]	I [u.a.]	λ [nm]	I [u.a.]
chlorobenzene	409	3.062	513	0.398	596	0.1049
CH_2Cl_2	406	2.653	511	0.262	595	0.021
THF	405	2.462	511	0.304	593	0.071
DMF	407	1.613	511	0.301	593	0.122
DMSO	408	1.384	511	0.307	-	-

Electrochemical Characterization of the membranes. The Nyquist and the Bode diagrams recorded during immersion in MES solution are presented in Figure 5 and are similar with those reported in [9]. The Nyquist diagrams present one large semicircle followed by one more flat semicircle in low frequency region (Figure 5a). The modulus and the phase angle for the membrane during immersion presented in Figure 5b show a well-defined time constant at lower frequencies and a second incomplete peak at higher frequencies arising from

diffusion phenomena. The experimental data were fitted to the equivalent electrical circuit (EEC) presented in Figure 5c.
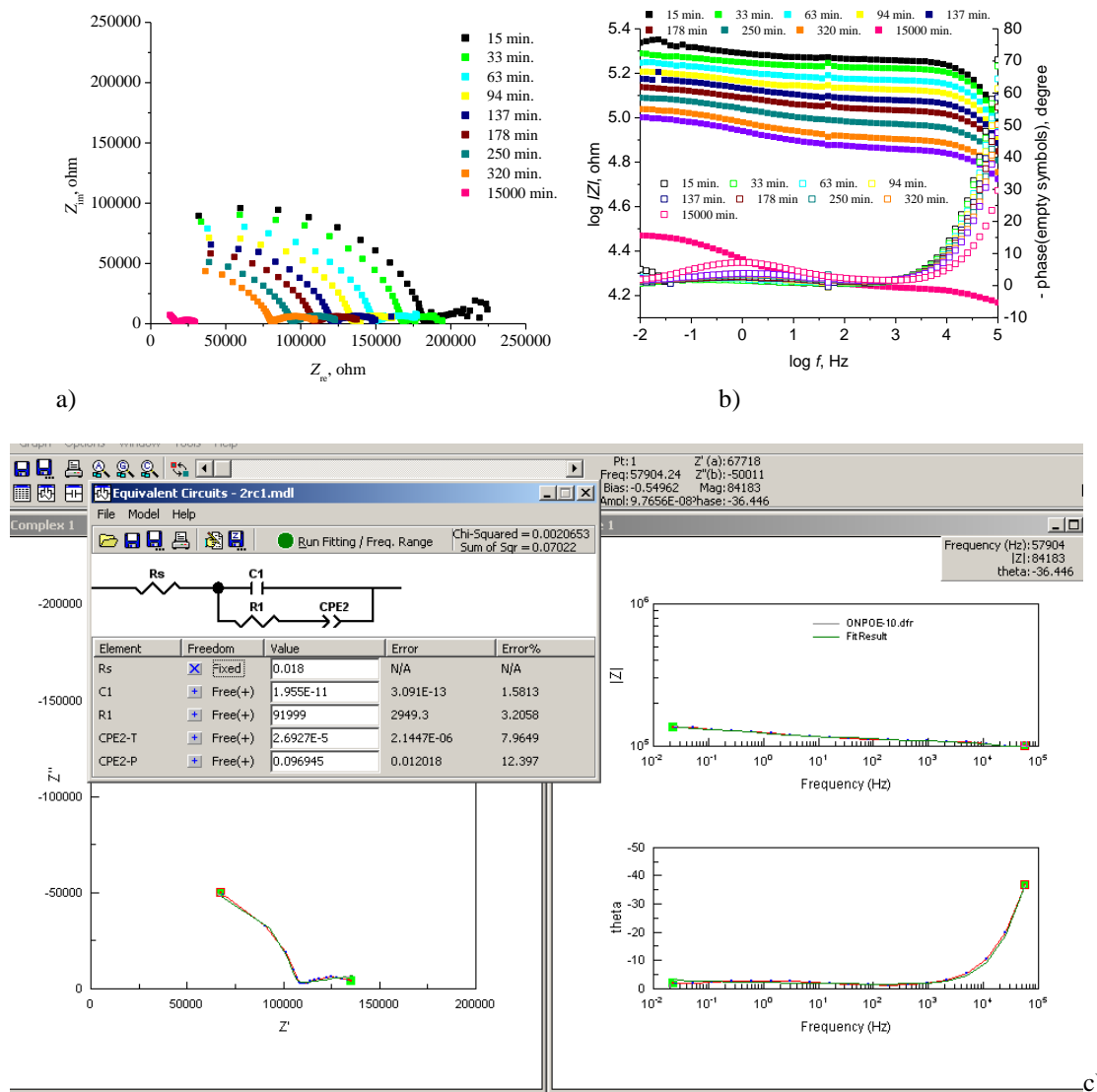

a)

b)

c)

Figure 5. Nyquist (**a**) and Bode (**b**) diagrams in case of membrane at OCP in MES buffer solution, pH= 5.5 and schematic representation of the electric equivalent circuit for EIS data and a simulation example of Nyquist and Bode diagrams with the suggested model for 15 min. immersion time of the membrane (**c**).

The EEC includes the resistance of electrolyte R_s, in series with a parallel connexion of capacitance C_1 (representing the charge/discharge process that occurs at the substrate/electrolyte interface) and the polarization resistance R_1. The concentration gradient appears as a result of ions transportation between the bulk and the interface and C_2 was used to model the diffusion phenomena. Constant phase element (CPE) was introduced to represent the double layer capacitance, for the reason of non-ideal behaviour. The impedance of a CPE can be expressed by $Z_{CPE} = [T(j\omega)^n]^{-1}$, where ω is the frequency, T is the CPE magnitude and the exponent n is between 0 and 1. The incertitude of parameters for the simulation is not higher than 16 % and the circuit was considered to model well the experimental data.

The film capacitance C_1 increases, and the resistance R_1 decreases with immersion time describing the penetration of water throw the pores and the swelling process of the membrane and possible formation of some ionically conducting paths across the membrane (Figure 6). The polarization resistance R_1 decreases with increasing immersion time. The

observed R_1 values are situated around 16000 ohm.cm^{-2} after 25 hours of immersion and show a good integrity of this membrane. A slightly decrease of the diffusion capacitance C_2 (from 4.3×10^{-5} F.cm^{-2} in the first moment of immersion to 2.6×10^{-5} F.cm^{-2}) becomes visible due to the low number of ions involved in diffusion process as the membrane became more swelled.
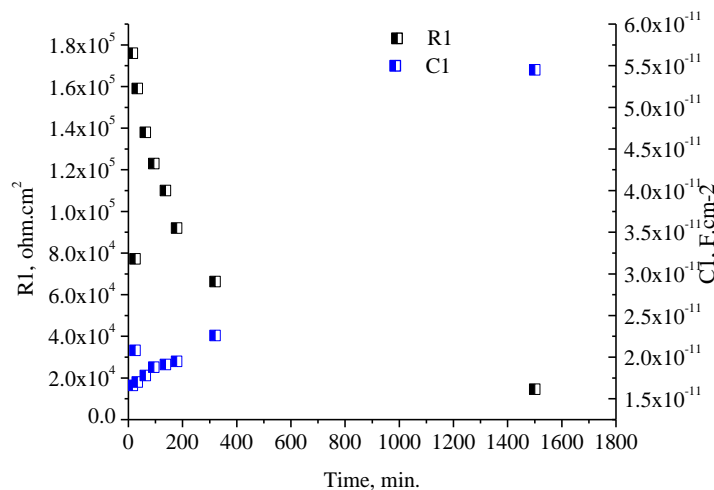

Figure 6. Variation of R_1 and C_1 with immersion time at OCP in MES buffer solution (pH= 5.5).

To estimate the volume fraction of water in membrane a uniform distribution of water was assumed. Relation (1) was used to calculate the water uptake of the membrane using the capacity obtained from EIS data (C_t at time t, C_0 at t = 0) and the dielectric constant of water (ε_{H2O} = 80). The maximum water uptake was ~0.3%. The diffusion coefficient of water (*D*) was calculated with the half-life method, relation (2), where $t_{0.5}$ is the time when the water fraction reaches a half of the saturation value and *l* is the coating thickness [12]. The permeability, P of the coating is the product of the diffusion coefficient and the solubility, relation (3). The solubility of water in coatings was derived from the water volume fraction at saturation (W_s) and water density (ρ_w).

In Figure 6 the increase of the absorption of water and the decrease of R_f in time reveal that the water saturation is reached after 25 hours and the data emphasized the necessity to introduce a membrane conditioning step, before the any use in detection.

$$W = \frac{\log[C_t / C_0]}{\log 80} \quad (1) \qquad D = \frac{0.04919x4l^2}{t_{0.5}} \quad (2) \qquad P = DxS = DxW_s x\rho_w \quad (3)$$

For a 180 micron membrane the calculated diffusion coefficient is D = $5.03 \times 10^{-11} \pm 0.22$ m^2 s^{-1} and the permeability is P= 1.45×10^{-7} kg m^{-1} s^{-1}. It was observed a considerably decreases of W by incorporation of Pt-TMeOPP salt, a lipophilic compound in plasticized or unplasticised PVC. The obtained value of the diffusion coefficient is close to the reported value for other PVC membrane (1.3×10^{-7} cm^2.s^{-1}) [13].

The values of the diffusion coefficient and the solubility are relatively comparable to some epoxy coatings where a diffusion coefficient close to 10^{-11} m^2.s^{-1} and a water solubility value of about 40 kg m^{-3} was reported [14].

Conclusion

A Pt(II)-metalloporphyrin is characterized by UV-vis, FT-IR and ^{1}H-NMR and the electrochemical characterization of PVC- PtTMeOPP porphyrin–membrane is presented. The EIS estimation of the water uptake of membrane at saturation was possible for the prepared membranes applied on an electrochemically inert material (inox) in MES. On this electrode

no corrosion reaction was observed after the saturation process. The maximum volume fraction of the adsorbed water determined was 0.29±0.015, reached after ~1600 min. The electrical resistance of the membrane decreased with the increasing of the water absorption. The diffusion coefficient is D = $5.03 \times 10^{-11} \pm 0.22$ m^2 s^{-1} and the permeability is P= 1.45×10^{-7} kg m^{-1} s^{-1}.

Acknowledgements

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