

CONTROLLED RELEASE OF CATIONS FROM CONDUCTING COMPOSITE FILMS OF POLYPYRROLE/POLYSTYRENSULFONATE (PPY/PSS).

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Abstract.

A transducer is a device that transforms the effect of a physical change like pressure, temperature, etc. in another kind of signal, normally electric. Conducting polymers could be used for the development of ionic transducers. Because they are able to interchange ions with electrolytic solutions during their redox processes to maintain the electroneutrality required in each moment. An electrical signal is then transformed in an ionic signal. In this work a quantitative study, combining Chronoamperometry (CA) and Atomic Absorption Spectroscopy (AAS), of the behavior of PPy/PSS composite films for release cations in a controllable way is done. If the release of ions from conducting polymers could be electrically controllable, potential applications like intelligent interfaces for the release of drugs or artificial nerves could be developed.

Keywords: ionic transducer, conducting polymer, release, interfaces, artificial nerves.

Introduction.

The conducting polymers have been widely studied during the last 30 years because they present potential applications like electrodes for batteries [1-3], enzymatic biosensors [4-6], electrochromic devices [7,8], etc.

During their redox processes, an ionic interchange process with the electrolytic solution accompanies the electron transfer between the polymer/metal interface to maintain the required electroneutrality. A conducting polymer like polypyrrole electrogenerated in the presence of small cations like Cl^- , ClO_4^- ... present anion doping

predominantly during its redox processes [9-12]. The same conducting polymer electrogenerated in the presence of polyelectrolytes like polystyrenesulfonate [13] (NaPSS) show predominant cation doping [14-19] during its redox processes because the polyelectrolyte became trapped within the polymer matrix due to its large size. Nevertheless, although two different systems could be differentiated, there are several studies that confirm that, generally in all the systems, the ionic interchange has a bipolar character in which both cations and anions are involved [14,20,21].

The ionic interchange process has been studied in qualitative and quantitative ways too, using analytical techniques combining with electrochemical techniques [8,22-29].

For quantitative studies the Electrochemical Quartz Crystal Microgravimetry (EQCM) has been the technique most commonly used. This technique follows the total mass variation in the polymer matrix during its redox processes and related those changes in mass to changes in the frequency of the quartz crystal. But it present a lack of selectivity to differentiate between the contribution of different ionic species when more than one are involved in the interchange process. And, usually, it used films with thickness below 1 μm to relate all the changes in mass detected to changes in frequency.

The Rotating Ring-Disk Voltammetry is another technique used for quantitative studies. But this technique employs polymeric films with very low polymerization charges (≈20mC).

Here is proposed a new quantitative analysis for the release of cations from PPy/PSS composite films with thickness close to 1.7 μm, combining electrochemical techniques like Chronoamperometry (CA) with an analytical technique like the Atomic Absorption Spectroscopy (AAS). The PPy/PSS composite films were selected for this study because its kinetic mechanism has been studied in our laboratory and because it presents a predominant cation exchange.

Results and discussion.

An aqueous solution 0.1 moldm⁻³ in NaPSS and 0.1 moldm⁻³ in Py monomer was used to electrogenerate the composite films by constant electrochemical oxidation

at 0.8V, into a three electrode cell. These electrogeneration conditions were selected from initial studies¹³.

After electrogeneration, the films were reduced by a potential step from -0.1V to -0.8V (polarization time of 10s was kept) in 0.1M electrolyte (NaNO₃, KNO₃ or Mg(NO₃)₂) aqueous solutions. Theoretically cations should be stored inside the films.

After this the films were washed with water and put into a 0.05M NaNO₃ aqueous solution, except the composite films reduced in a 0.1M NaNO₃ that were put in 0.01M K₂CO₃ aqueous solution. Films were leave in these solutions without a current flux. These aqueous solutions were analyzed by AAS.

Composite films were again reduced by a potential step from -0.1V to -0.8V (polarization time of 10s was kept) in 0.1M electrolyte (NaNO₃, KNO₃ or Mg(NO₃)₂) aqueous solutions. And after this they were washed with water and put into a 0.05M NaNO₃ aqueous solution, except the composite films reduced in a 0.1M NaNO₃ that were put in 0.01M K₂CO₃ aqueous solution. Where they were oxidized by a potential step from -0.8V to -0.1V (polarization time of 10s was kept). Theoretically cations are released from the composite films. These solutions were analyzed by AAS

The reduction and the oxidation steps are repeated different number of times to accumulate different quantities of cations during the oxidation processes in the aqueous solutions where these processes are made.

From the oxidation charges the theoretical quantities of cations released (eq. 1) could be obtained if we assume that all the oxidation charge is involved in the release process. The analysis by AAS of the aqueous solutions where the oxidation steps are made should give the experimental quantities of cations released.

$$\sum Q_{ox.} (mC) \times \frac{10^{-3}}{nF} \times \text{Atomic mass of cations} \times 10^6 \times \frac{1}{V(ml)} = \frac{\mu g \text{ cation}}{ml}$$

Equation 1.- *Theoretical relation between the oxidation charge and the quantity of cations released from the PPy/PSS composite films employed.*

The figure 1 shows the evolution of the theoretical and the experimental quantities of sodium cations released when different oxidation steps are accumulated in different 0.01M K₂CO₃ aqueous solutions. As can be when different numbers of oxidation processes are accumulated, the quantity of cations released is increased. For

the case of sodium cations both theoretical and experimental quantities are similar. This involves that the transport of sodium cations through the composite films should be very fast so the participation of anions in the interchange process should be despicable.

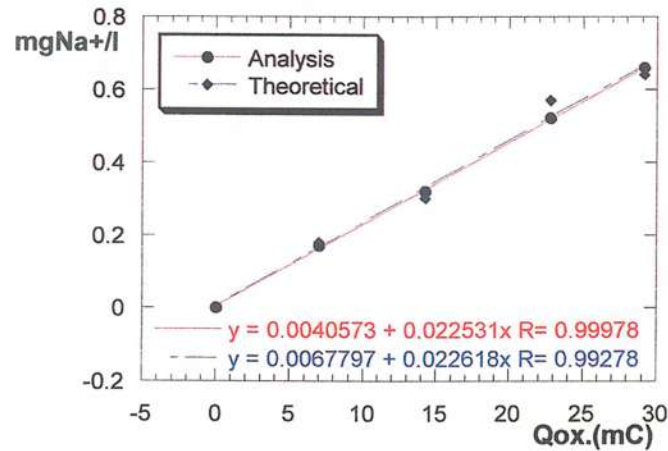


Figure 1.- Evolution of the theoretical and experimental quantities of sodium cations released during different number of oxidation processes done (different quantity of oxidation charges accumulated) in different 0.01M K₂CO₃ aqueous solutions.

Figures 2 and 3 present results similar as figure 1 for potassium and magnesium cations. Again is shown that exists a quantitative relation between the oxidation charges accumulated during different numbers of oxidation processes and the quantities of cations released. But in these cases the experimental quantities are lower than the theoretical ones. So the transport of potassium and magnesium cations through the PPy/PSS composite films should not be as rapid as the transport of sodium cation. Not all the theoretical quantities are released. An anion flux from the aqueous solutions inside the films must be produced to maintain the electroneutrality required.

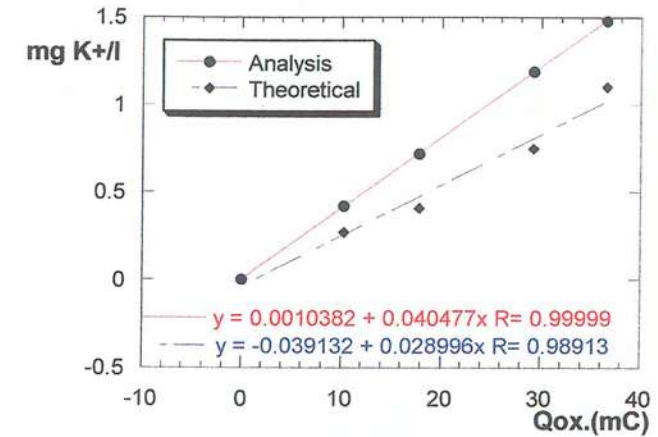


Figure 2.- Evolution of the theoretical and experimental quantities of potassium cations released during different number of oxidation processes done (different quantity of oxidation charges accumulated) in different 0.05M NaNO₃ aqueous solutions.

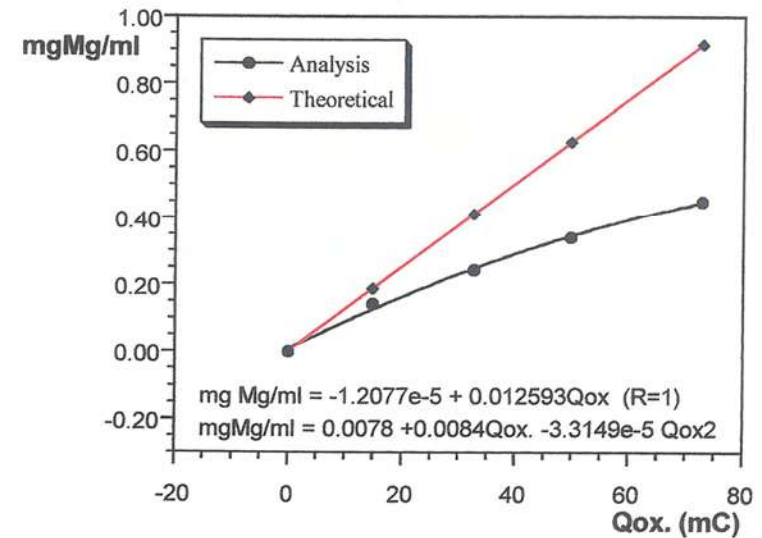


Figure 3.- Evolution of the theoretical and experimental quantities of magnesium cations released during different number of oxidation processes done (different quantity of oxidation charges accumulated) in different 0.05M NaNO₃ aqueous solutions.

Experimental.

The PPy/PSS composite films were prepared from aqueous solutions containing pyrrole monomer and the sodium salt of polystyrenesulfonate. The monomer (Jansen) was distilled at 59°C and reduced pressure (50mmHg). After distillation it was stored at low temperature (4°C) in dark before used. The polyelectrolyte (Aldrich, 12% Na content) and all other chemicals (reagent grade) were used as received. The solvent (water) used in all experiences was obtained from a Milli Q Reagent Water System feed by a Milli R04 Water Purification System.

A platinum sheet with a surface area of 1cm² was used as working electrode, and a stainless steel having 3 cm² of surface area was used as counter electrode. Ag/AgCl (KCl 3M) electrode (Crison Instruments) was used as reference electrode.

All the experiments were performed under nitrogen atmosphere and at room temperature. The pH was turned to neutral values.

A 4504 MP8 Sartorius Ultramicrobalance (10⁻⁷g precision) was used to evaluate the weight of the composite polymeric films electrogenerated.

A M273 potentiostat-galvanostat connected to a PC computer and driven by means of M273 software from EG&G was used for the electrochemical processes involved (polymerization, electrochemical control (CV) and potential steps (CA) to oxidize and reduce the composite films).

A GBC Avanta Σ Absorption Spectrometer (GBC Scientific Equipment Pty Ltd.) connected to a PC computer and driven by means of GBC software was used to detect the amount of cations released from the composite films during the oxidation steps.

The atomic absorption spectroscopy (AAS) is an analytical technique that permits a direct analysis of elements in solutions independently of how they are combining. The base of this technique is that the majority of free atoms in the commonly used flames are in the ground state. A light source can be used to excite these free atoms. The decrease in energy (absorption) is then measured. Using the Lambert-Beer law (eq. 1) the concentration of free atoms in the flame can be determined.

$$\text{Abs.} = \log_{10} \frac{I_0}{I} = K \times C \times L. \quad \text{where:}$$

I_0 = Incident intensity in the flame from the light source.

I = Transmitted intensity (amount not absorbed).

C = Concentration of sample (mole/l).

K = molar absorptivity (l/mole cm).

L = Path length.

Equation 1.- *Lambert-Beer law.*

Final Comments.

The properties of polymeric composite films of PPy/PSS to act as storehouses of different cations was evaluated. Different quantities of cations were accumulated inside the films during the successive reduction processes done in presence of each of the cations studied. The application of a different number of oxidation steps involved the electrochemically controlled released of different quantities of cations. Quantitative relations between the summation of oxidation charges accumulated and the concentration of cations detected in solution by AAS were obtained. The results obtained for the three cations studied show that although cations should be released during oxidation processes the participation of anions in the interchange process should be necessary to maintain the electroneutrality required.

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