

## Influence of the Cation Nature of the Sulphate Salt on the Electrochemical Synthesis of Sulfate-Doped Polypyrrole

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Received: 4 February 2011 / Accepted: 18 April 2011 / Published: 1 May 2011

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In this work, polypyrrole films were electrosynthesized from aqueous media onto a graphite-epoxy resin composite electrode (GCE) using sulphate ions as dopant. Potentiostatic electrosynthesis studies were done using different salts as  $\text{SO}_4^{2-}$  source, namely:  $\text{Na}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ . The potentiometric response of the diverse Ppy- $\text{SO}_4^{2-}$  films was evaluated by means of calibration plots; according to the slope sign the behavior of the different films can be classified in three responses: anionic, cationic and anionic-cationic. Such behaviors were observed for all synthesized films, independently of the sulphate salt used. When analyzing the current transients obtained for the different salts, similarities were found for those with the same potentiometric behavior, but significant differences were observed when comparing transients of different potentiometric responses. From the analysis of the experimental current transients it was determined that the nature of the cation of the sulphate salt influences the number density of active sites on the electrode surface where the Ppy- $\text{SO}_4^{2-}$  is deposited. Moreover, the kind of Ppy- $\text{SO}_4^{2-}$  potentiometric response also depends on the type of cation used during the polymer electrochemical synthesis. According to the results obtained, some boundaries for the potentiostatic synthesis parameters are suggested to induce a specific potentiometric response.

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**Keywords:** Polypyrrole, sulphate, electropolymerization, potentiometric

### 1. INTRODUCTION

Polypyrrole (Ppy) is one of the most studied and used conducting polymers, due to its good conductivity and stability. Ppy has found multiple applications in batteries, artificial muscles,

development of highly-selective chemical sensors, etc [1-6]. Ppy films can be obtained by electrochemical oxidation of pyrrole [4] and the oxidation of the growing polymer chains generate polarons and, when the lineal density of those radical polarons along the chains is high and the applied potential anodic enough, the extraction of new electrons from the chains originate bipolarons along the polymeric chains [7,8]; this may induce the insertion of anionic species from the support electrolyte into the polymer matrix by electrostatic attraction which compensates the positive charge of the polymer backbone, thus maintaining overall electroneutrality [1,5,9,10]. The dynamic movement of the support electrolyte anions induces the formation in the Ppy film of cavities with the anion's geometry (molecular imprint) which can restrict diffusion of other species within the Ppy [11-16]. In this way, whatever the anion used during the electropolymerization should produce a similar molecular imprint and, consequently, similar potentiometric response, however the nature of the corresponding ion involved (cation) may influence the polymerization process kinetics due to the intrinsic difference in its adsorption energy on the electrode surface. Many synthesis variables affect the properties of the final Ppy product, which include; the solvent's nature, the concentration of the support electrolyte, pH, the electrosynthesis technique, and electric potential. It has already been established in the literature that Ppy properties are directly related with the ion-diffusion characteristics of the synthesized polymer [17-21]. This suggests that potentiometric studies of Ppy, which are easy to perform with no expensive equipment or reactants, can give direct information about the Ppy properties. Among the wide variety of anions that can be used to dope Ppy films, the sulphate ion stands out due to its electrochemical and potentiometric properties that significantly differ from others most common doping anions [14,17,22-26]. Considering this, the applications for Ppy-SO<sub>4</sub><sup>-2</sup> films are considerably wide [1,2]. It has been reported that sulphate ions (SO<sub>4</sub><sup>2-</sup>) have low mobility in a Ppy polymeric matrix because of its size and due to its double charge [3,27]. Differences in anions mobility through polymeric matrixes can be associated to the different interaction strengths with the conducting polymer chain, this interaction is stronger when ions have small radii and large charge [3,5,17,27]; this means that there is a strong ionic-bond between SO<sub>4</sub><sup>-2</sup> and the positive charges of the polymeric chains, which prevents the SO<sub>4</sub><sup>-2</sup> been exchanged between the polymer matrix and the solution [17]. Cations coming from the support electrolyte can influence the properties of Ppy-SO<sub>4</sub><sup>-2</sup> films [17,28]. It has been reported that Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup> cation's mobility in Ppy-SO<sub>4</sub><sup>-2</sup> films depends on the ionic radius and the hydration-sphere; cations with larger radius are less hydrated and therefore more mobile in the polymer [17,21]. This has been used to explain why doping Ppy with low mobility anions, like sulphate, results in cationic potentiometric responses. This behavior has been demonstrated to depend on the Ppy synthesis conditions [3,27,29-31].

In this work the potentiometric behavior of Ppy-SO<sub>4</sub><sup>-2</sup> films synthesized over a graphite-epoxy resin composite electrode is studied. Composites are homogeneous mixtures of different insoluble materials that when used as electrodes, they usually consist on a conductive phase in conjunction with an insulating phase used as support [32]. Graphite-epoxy resin composites are a very good alternative to traditional metallic electrodes, due to their versatility (they can easily afford different geometries), low cost and easy miniaturization [32,33]. When the Ppy is synthesized potentiostatically, the parameters considered for potentiostatic electrosynthesis are: the imposed potential (E),

electrosynthesis time (t), pyrrole concentration and sulphate salt concentration due to their influence on the Ppy properties [34-38].

In order to evaluate the effect of the cation on the kinetics of Ppy-SO<sub>4</sub><sup>-2</sup> films formation, different sulphate salts were used during the potentiostatic electrosynthesis and the corresponding current transients were analyzed in the framework of the electrochemical phase formation theory [39-44].

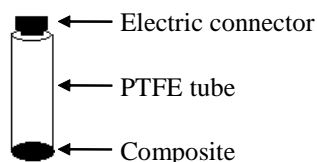
## 2. EXPERIMENTAL

### 2.1. Reagents

All reagents used as support electrolytes, namely, Na<sub>2</sub>SO<sub>4</sub>, Li<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> (Aldrich), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Fluka) were analytical grade. Pyrrole (Py) (Aldrich) was distilled in pure N<sub>2</sub> atmosphere. Ultrapure monocrystalline graphite powder 99,999% and Araldit epoxy resin with H.Y hardener were used to manufacture the working electrodes. All solutions were prepared with deionised water obtained from a Milli Q (Millipore) system with 18.2 MΩ resistivity. All solutions were bubbled with pure N<sub>2</sub> prior to beginning all experiments [37].

### 2.2. Instrumentation.

A typical electrochemical cell with three electrodes is used for Ppy electrosynthesis, where a platinum wire acts as counter electrode, an Ag/AgCl 900200 Orion electrode serves as reference, and the graphite-epoxy resin as working electrode. Composite electrodes are prepared with graphite powder and Araldit epoxy resin – H.Y hardener in a 60:40 proportion. The prepared composite is then supported using a 0.5 cm diameter PTFE tube with an electrical connector in contact with the composite, as shown in Figure 1. Hardening of the composite is achieved heating 12 h at a constant temperature of 60 °C. Thereafter, the exposed surface is polished before the electrochemical growth of the polypyrrole film. The Ppy films are obtained potentiostatically using a PGSTAT 30 AUTOLAB electrochemical system (Ecochemie).



**Figure 1.** Schematic representation of the composite electrodes (GCE) used.

Potentiometric measurements are registered using a Mettler Toledo AG Potentiometer. All potentiometric measurements are referred to an Ag/AgCl saturated electrode. The images of the Ppy films were obtained by scanning electron microscopy (SEM), with a JEOL JSM 6300 microscope.

### 2.3 Synthesis of Ppy films using different sulphate salts

Ppy-SO<sub>4</sub><sup>2-</sup> films are electropolymerized by chronamperometry onto the exposed surface of the composite electrode, the synthesis variables controlled are: the imposed potential (E), time (t), pyrrole concentration [Py] and sulphate salt concentration [SO<sub>4</sub><sup>2-</sup>]. Using the Box-Behnken method [38] a series of experiments are proposed in order to find any sensitivity of the Ppy-SO<sub>4</sub><sup>2-</sup>-GCE modified electrode towards the SO<sub>4</sub><sup>2-</sup> ion, using the corresponding sulphate salt as supporting electrolyte. The potentiometric response is evaluated by constructing the corresponding calibration plots using different sulphate standards. The potentiometric data is then analyzed by statistical fitting of the linear zone.

## 3. RESULTS AND DISCUSSION

### 3.1. Potentiostatic Synthesis

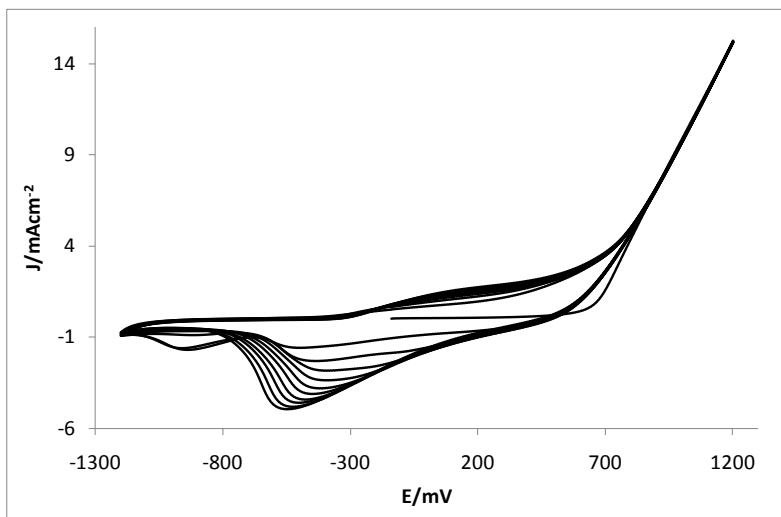
Boundaries for the potentiostatic synthesis variables were established to ensure an adequate polymerization of the Ppy films, values are presented in Table 1. Boundary values are based on the results of the following observations:

- To establish the working potential (E) during the potentiostatic synthesis, a set of cyclic voltammograms was obtained using Na<sub>2</sub>SO<sub>4</sub> 0.1 M and Py 0.1 M in deionized water. The potential scan is set from -1200 to 1200 mV (starting from the zero-current potential) at a rate of 100 mVs<sup>-1</sup>. This potential program was repeated 10 times and the resulting voltammograms are shown in Figure 2.

**Table 1.** Boundaries for potentiostatic parameters used for the Ppy-SO<sub>4</sub><sup>2-</sup> electrosynthesis.

Parameter	Low	High
E / V	0.52	1.2
t / min	4.0	15
[Py] / mol L <sup>-1</sup>	0.05	0.4
[SO <sub>4</sub> <sup>2-</sup> ] / mol L <sup>-1</sup>	0.005	0.7

An oxidation wave is observed at potentials above -300 mV, that are associated with the Py oxidation and its subsequent polymerization; this suggests that in chronamperometric experiments potentials above -300 mV will be enough to electrosynthesize the Ppy. However, in practice, with potentials between -300 and 200 mV no modification occurs on the electrode's surface, between 200 and 520 mV only some small cumuli of the Ppy were observed. Only with potentials above 520 mV an adequate synthesis is achieved, as complete coverage of the electrode's surface is observed. A possible explanation is that at these potentials the applied energy is high enough to make the insoluble Ppy oligomer predominate instead of the soluble oligomers formed also during the oxidation process.



**Figure 2.** Cyclic voltammograms, 10 cycles, recorded in the system GCE / 0.1 M Py, 0.1 M Na<sub>2</sub>SO<sub>4</sub>, at 100 mVs<sup>-1</sup> scan rate.

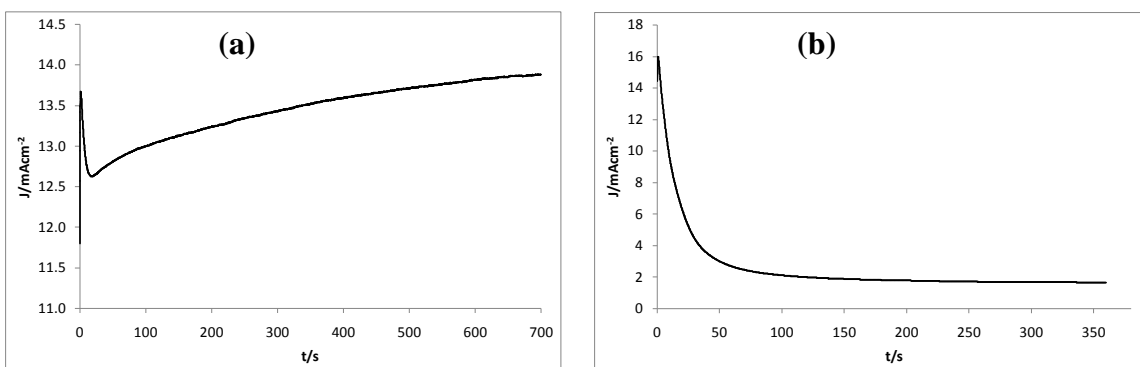
- When evaluating the synthesis time (t), it was observed that less than four minutes are not enough for an adequate polymer growth; times larger than 15 minutes have the disadvantage of long stabilization times when potentiometric measurements are carried out. This is attributed to the polymer thickness hindering ions diffusion, so that equilibrium is established at longer times. Considering this, the time interval used was established between 4 and 15 minutes.

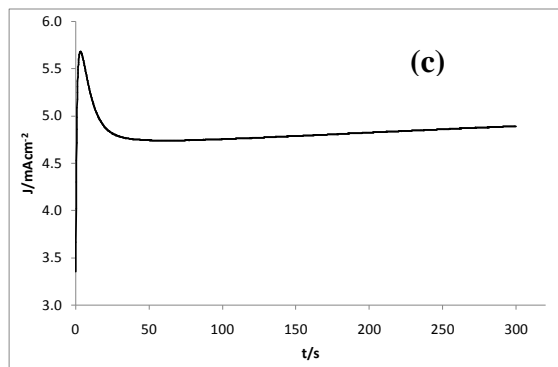
- In the case of sulphate concentration, it was observed that under  $5 \times 10^{-3}$  M the polymer synthesis is not favored, whereas using concentrations higher than 0.7 M the sodium salt does not dissolves completely, so a concentration interval between  $5 \times 10^{-3}$  and 0.7 M, thus is established.

- The same considerations used to establish the sulphate concentration interval are used to establish the Py concentration boundaries; this interval is then set between 0.05 and 0.4 M.

### 3.1.1. Potentiostatic current density transients

Figure 3 shows three typical current-density transients recorded under different experimental conditions. Significant differences are observed when comparing each other, indicating that the polymerization kinetics is different for each case, and so the morphology of the different Ppy films, resulting in different potentiometric responses observed.

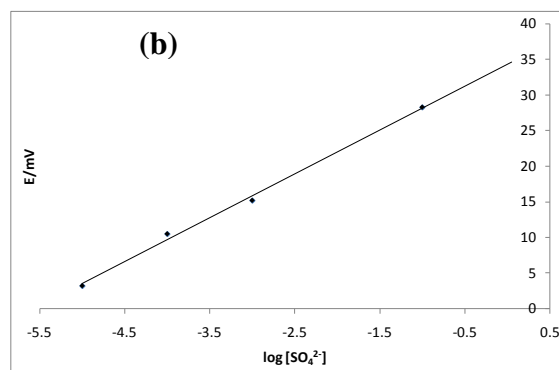
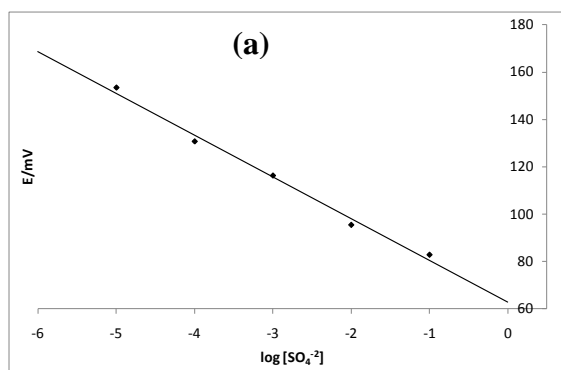


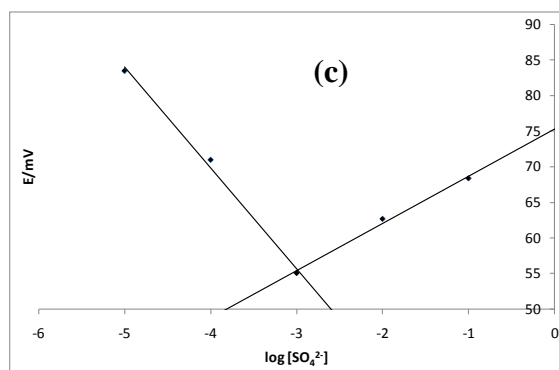


**Figure 3.** Experimental current-density transients recorded in the system GCE / x M Py, y M Na<sub>2</sub>SO<sub>4</sub> applying a potential step of z V during w minutes. (a) x = 0.29, y = 0.55, z = 0.96, w = 10.8 (b) x = 0.05, y = 0.50, z = 1.0, w = 6.0 (c), x = 0.10, y = 0.10, z = 0.80, w = 5.0.

3.1.2. Potentiometric evaluation of the Ppy-SO<sub>4</sub><sup>-2</sup> films

Calibration curves are obtained from a set of experiments suggested by the Box-Behnken method [40], considering the boundaries already established, and with the least squares method to fit the experimental data. The Box-Behnken method is a statistical factorial design used for optimization; it was used in this investigation to explore possible sensitivity to sulphate ions by maximizing a negative slope value. However, analyzing the results for all the experiments suggested by the Box-Behnken method, and according to the Nernst equation, three different potentiometric responses were found: one corresponding to an anionic sensitivity (negative slope), where the response is attributed to the diffusion of SO<sub>4</sub><sup>2-</sup>; a second response-type with cationic sensitivity (positive slope, the response is attributed to counter-ion diffusion) and a third response where both sensitivities anionic-cationic were observed; some representative calibration plots are shown in Figure 4. Such different behaviors can be attributed to the change in the morphology that results from the different electrosynthesis conditions. These results are interesting, considering that only cationic responses are reported for Ppy-SO<sub>4</sub><sup>-2</sup> polymers [31] which are attributed to low mobility, size and charge of SO<sub>4</sub><sup>2-</sup> ions [28,29,31]. However, in this research it was found that depending on the potentiostatic conditions used for Ppy-SO<sub>4</sub><sup>-2</sup> polymerization, other behaviors can be found.





**Figure 4.** Variation of the Ppy-SO<sub>4</sub><sup>2-</sup>-GCE modified electrode potential immersed in an aqueous solution containing different [Na<sub>2</sub>SO<sub>4</sub>]. The experimental condition for Ppy-SO<sub>4</sub><sup>2-</sup> film synthesis were those shown in Figure 3.

From the evaluation of all the different experiment conditions, some electrosynthesis boundaries can be established to induce experimentally the different potentiometric responses; this is shown in Table 2. The maximum experimental slopes found for each response type are shown in Table 3, for the anionic response a theoretical value of -29.60 mV per decade of SO<sub>4</sub><sup>2-</sup> concentration was expected, while for the cationic response, which corresponds to the diffusion of the Na<sup>+</sup> ion, a slope of 59.14 mV per decade of sodium concentration was expected (25 °C), as subnernstian slopes are found in all cases.

**Table 2.** Boundaries where the potentiometric response types can be induced for the Ppy-SO<sub>4</sub><sup>2-</sup>.

	Anionic	Cationic	Anionic-Cationic
E / V	0.86 – 0.96	0.80 – 1.00	0.52 – 0.86
t / min	10.8 – 15.0	6.0 – 10.0	4.00 – 15.0
[Py] / mol L <sup>-1</sup>	0.28 – 0.40	0.05 – 0.40	0.05 – 0.225
[SO <sub>4</sub> <sup>2-</sup> ] / mol L <sup>-1</sup>	0.35 – 0.54	0.005 – 0.50	0.005 – 0.35

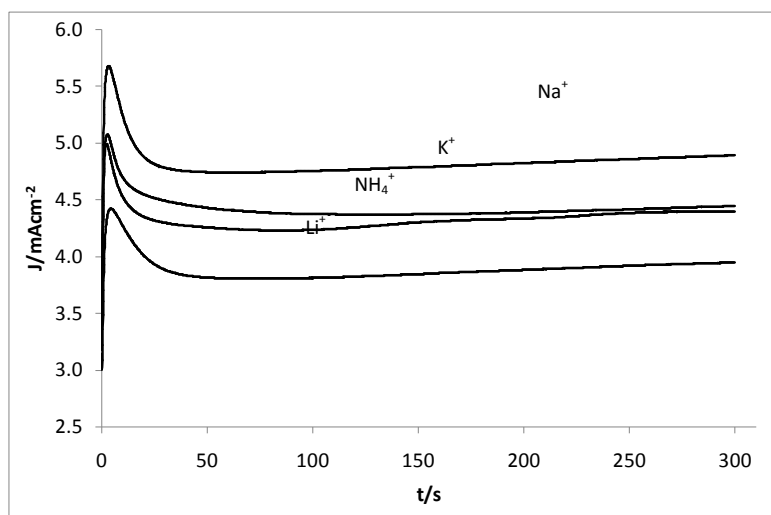
**Table 3.** Maximum slope values found for Ppy-SO<sub>4</sub><sup>2-</sup> synthesized with Na<sub>2</sub>SO<sub>4</sub>.

Response	Slopes maximum (mV per decade)
Anionic	-16.2
Cationic	9.2
Anionic - cationic	-14.2 and 6.7

### 3.1.4 Influence of the cation nature of the sulphate salt

#### 3.1.4.1 Current transients

Figure 5 shows a set of experimental current-density transients obtained at experimental conditions where the anionic – cationic potentiometric response of the Ppy-SO<sub>4</sub><sup>-2</sup> film was observed. The only difference among them was the type of salts used as sulphate source.



**Figure 5.** Experimental current-density transients recorded in the system GCE / 0.10 M Py, 0.10 M Cat<sub>2</sub>SO<sub>4</sub>, applying a potential step of 0.80 V. The cation, Cat, used for the sulphate salt is indicated in the Figures.

It is possible to note that the kind of cation used does not change the general shape of the j-t plots, however, it is clear that the charge involved (the area under the j-t plots) in each case is different. Recently, Palomar-Pardavé et al., [39] have proposed a theoretical framework that describes j-t plots with a very similar shape to those shown in Figure 6. It is relevant to stress out that this model is not merely a mathematical description of the experimental current transients, because each parameter involved (see equations 3-6) has a clear physical meaning. According to them [39], this sort of j-t plots are obtained when a new phase is potentiostatically formed on the electrode surface by multiple hemispherical 3D nucleation and growth limited by the mass transfer reaction, simultaneously with another faradaic process, like an oxidation reaction, that is occurring on the growing surface of the new phase. The equation derived to describe this process is:

$$J_{total}(t) = J_{3D}(t) + J_{PO}(t) \quad (1)$$

Where the overall current density-time transient,  $J_{total}(t)$ , is given by the sum of the contributions due to the growth of the polypyrrole deposit,  $J_{3D}(t)$ , and that due to the pyrrole oxidation,  $J_{PO}(t)$ , on polypyrrole surface.



Equation (1) can be parameterized as follows, see [39]:

$$J_{total}(t) = (P_1 + P_4 t^{-1/2}) \left( 1 - \exp \left\{ -P_2 \left[ t - \frac{1 - \exp(-P_3 t)}{P_3} \right] \right\} \right) \quad (2)$$

with

$$P_4 = \frac{zFD^{1/2}c_0}{\pi^{1/2}} \quad (3)$$

$$P_2 = N_0 \pi k' D \quad (4)$$

$$k' = (8\pi c_0 / \rho)^{1/2} \quad (5)$$

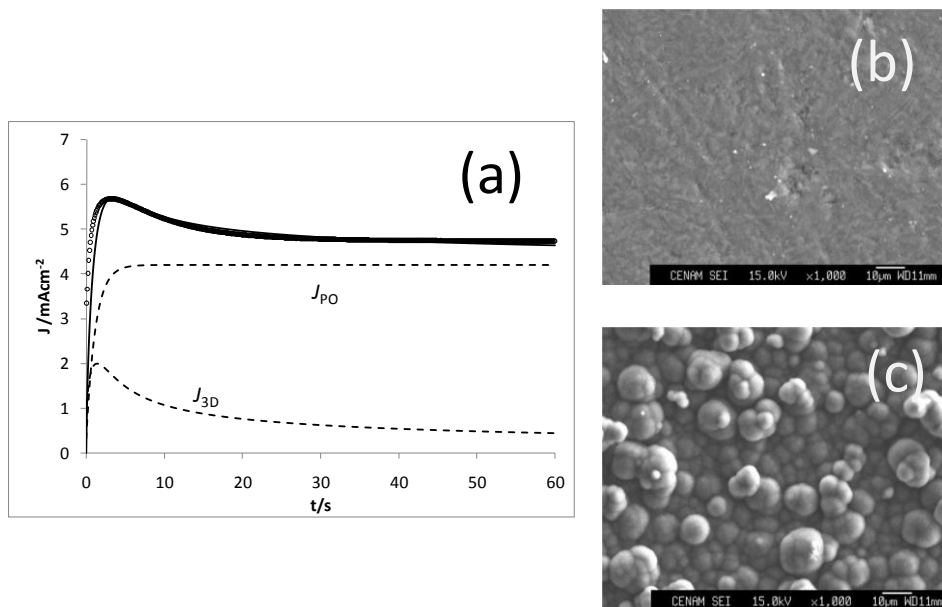
$$P_3 = A \quad (6)$$

$$P_1 = \left( \frac{2c_0 M}{\pi \rho} \right)^{1/2} z_{PO} F k_{PO} \quad (7)$$

Where, in our case,  $c_0$  is the pyrrole concentration of the bulk of the solution,  $F$  is the Faraday constant,  $\rho$  is the density of the deposit,  $M$  is its molar mass,  $z_{PO}F$  is the molar charge transferred during the pyrrole oxidation process,  $k_{PO}$  is the rate constant of the pyrrole oxidation reaction on the polypyrrole surface,  $D$  is the pyrrole diffusion coefficient,  $A$  is the polypyrrole nucleation rate,  $N_0$  number density of active sites for polypyrrole nucleation on the electrode surface.

Figure 6a shows a comparison of a experimental  $j-t$  plot recorded during polypyrrole nucleation and growth, see Figure 5, and a theoretical current density transient generated by non-linear fit of eqn. (2) to the experimental data. It is possible to note that the theoretical model represented by eqn. (1) can describe adequately the whole current density transient recorded when  $\text{Na}_2\text{SO}_4$  was used as sulphate source. In a similar way, the other transients depicted in Figure 5 were analyzed. From this analysis the kinetics parameters,  $A$  and  $N_0$  were obtained, see Table 4. From Table 4 it results clear that the nature of the cation used, as sulphate source, during the electrochemical formation of the Ppy- $\text{SO}_4^{-2}$  film does not change the nucleation rate, however the number density of active site is affected. This fact can be explained in terms of the different adsorption energies of the cations on the electrode surface that provoke a change on the surface electronic distribution as shown by Mendoza-Huizar et al., [39,40]. The SEM images taken before, Figure 6b, and after the current transient, Figure 6c, depict the bare surface of the electrode and the resulting morphology of the Ppy deposit. From Figure 6c one could clearly note that Ppy deposition actually occurs over most of the electrode surface by multiple nucleation of hemispheres as the theoretical model used for the analysis of the current transients

required. It is important to stress out that during the Ppy chemical polymerization, Sharmal et al [45] found alike morphologies.



**Figure 6.** a) Comparison between an experimental current-density transient recorded in the system GCE / 0.10 M Py, 0.10 M  $\text{Na}_2\text{SO}_4$ , applying a potential step of 0.80 V (ooo) and a theoretical current density transient ( — ) generated by the non-linear fitting of eqn. (2) to the experimental data. Individual contributions due to  $J_{PO}$  and  $J_{3D}$  are also shown. b) SEM image of the bare GCE,  $t = 0$ ) and c) SEM image of the GCE taken after the current density transient.

**Table 4.** Kinetics parameters gathered from the analysis of the experimental current density transients shown in Figure 6 using equation (2).

Cation	$\text{A} / \text{s}^{-1}$	$10^{-5} N_0 / \text{cm}^{-2}$
$\text{Li}^+$	100	3.65
$\text{Na}^+$	100	5.72
$\text{K}^+$	100	5.95
$\text{NH}_4^+$	100	6.85

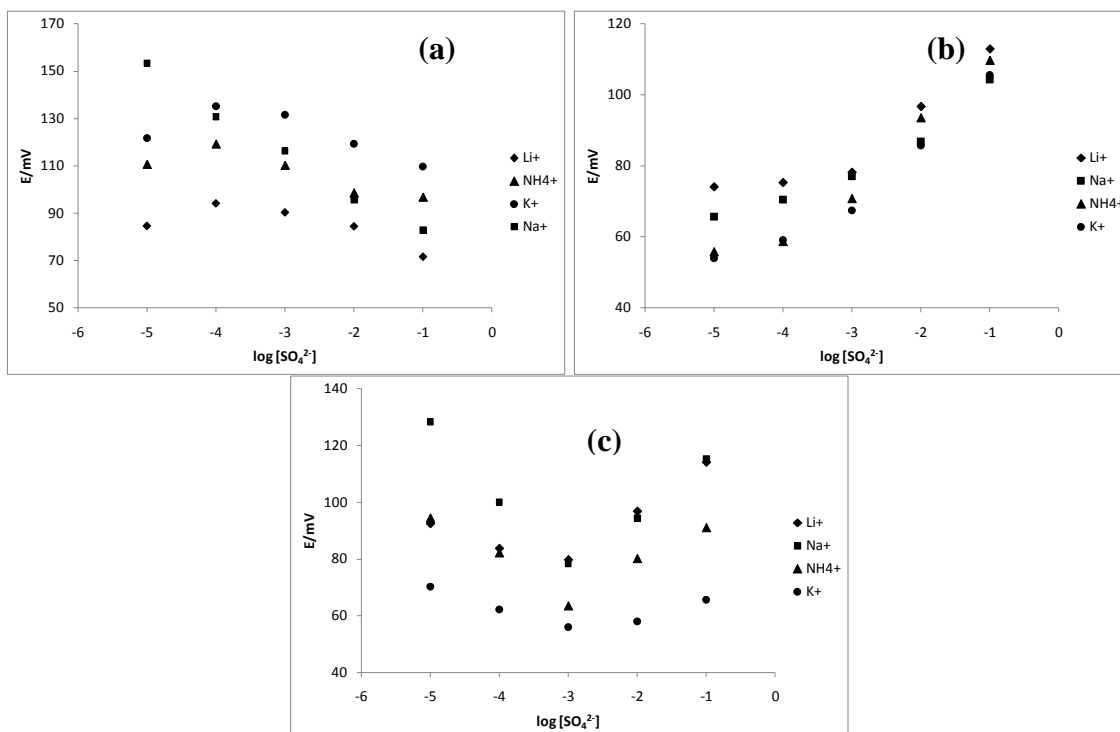
### 3.1.4.2 Potentiometric evaluation of the $\text{Ppy-SO}_4^{-2}$ films.

Figure 7 shows the different calibration plots for each type of potentiometric response [46] with different sulphate salts. Very similar behaviors to those observed with the sodium salt are found, but with different slope magnitudes, which are shown in Table 5.

The ammonium salt shows the higher cationic response: this can be attributed to the fact that the cation is significantly larger and so it cannot be easily hydrated; therefore ammonium ions mobility within the polymer matrix is favored, whereas the opposite is true for the lithium ion with a smaller size.

**Table 5.** Maximum slope values (mV per /decade) for the different Ppy-SO<sub>4</sub><sup>2-</sup> synthesized with different sulphate salts.

	Anionic	Cationic	Anionic-Cationic
Na <sub>2</sub> SO <sub>4</sub>	-16.2	9.2	-14.2 and 6.7
Li <sub>2</sub> SO <sub>4</sub>	-9.35	7.6	-6.35 and 17.2
K <sub>2</sub> SO <sub>4</sub>	-8.82	8.35	-7.1 and 4.75
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-10.35	17.61	-15.5 and 13.8



**Figure 7.** Variation of the Ppy-SO<sub>4</sub><sup>2-</sup>-GCE modified electrode potential immersed in an aqueous solution containing different [Cat<sub>2</sub>SO<sub>4</sub>].

#### 4. CONCLUSIONS

According to the results obtained for the diverse Ppy-SO<sub>4</sub><sup>2-</sup> films potentiostatically grown, different potentiometric responses were observed depending on the electrochemical variables used:

anionic, cationic and a anionic – cationic combination This is attributed to different polymerization kinetics, as demonstrated by the different current-density transients obtained. Therefore, there are morphological differences that have a direct influence on the diffusion of ions through the polymer matrix. In all cases the Ppy-SO<sub>4</sub><sup>2-</sup> films showed subnernstian slopes, the anionic had a maximum value of -16.2 mV per decade when using the sodium salt as supporting electrolyte; while the minimum value found was of -8.82 mV per decade for the Ppy-SO<sub>4</sub><sup>2-</sup> obtained from the potassium salt. The cation size of the counter ion sulphate salt has some influence in the potentiometric response, the larger-size cations move easier in the Ppy-SO<sub>4</sub><sup>2-</sup> matrix, because they are less hydrated, inducing a cationic response. The contrary effect is observed for smaller cations like lithium.

#### ACKNOWLEDGMENTS

TJLS is grateful to CONACYT for the stipend received for her Ph. D. studies. The authors are also grateful to CONACYT for the financial support given through projects 80058, 24658 and 82932 and to PROMEP for project 46481 and RED SIATA. G.A.A.R, M.P.P., C.A.G.V, M.E.P.H and M.R.R. gratefully thank the SNI for the distinction of their membership and the stipend received. M.P.P and M.R.R wish to thank the Departamento de Materiales, UAM-A, for the financial support given through projects 2261203, 2261204 and 2261205.

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