

Influence of the Electrolyte Salt on the Electrochemical Polymerization of Pyrrole. Effects on *p*-Doping/Undoping, Conductivity and Morphology

M. A. del Valle ^{1,*}, A. M. R. Ramírez², F. R. Díaz¹, M. A. Pardo¹, E. Ortega¹, F. Armijo¹

¹ Pontificia Universidad Católica de Chile, Laboratorio de Electroquímica de Polímeros (LEP), Av. V. Mackenna 4860, 7820436-Macul, Santiago, Chile.

² Universidad Mayor, Núcleo Química y Bioquímica, Facultad de Estudios Interdisciplinarios, Laboratorio de Electroquímica, Av. Alemania 0281, 4801043-Temuco, Temuco, Chile.

*E-mail: mdvalle@uc.cl

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The relationship between the *p*-doping/undoping process (charge, stability and reversibility) and the nucleation and growth mechanisms concerning the influence of the type of electrochemical perturbation of the system during the electropolymerization of pyrrole (PPy) by oxidation of the monomer, is reported in the presence of different salts (LiClO₄, TBAClO₄, TBAPF₆, TEAPF₆, LiTFMS or TBATFMS), in acetonitrile. The characterization is conducted *in situ* by cyclic voltammetry or constant potential, complemented by conductivity measurements, using the four-point method, and morphological analysis employing SEM and AFM. The direct correlation between the *p*-doping/undoping process and the volume of the anion of the supporting electrolyte utilized for the electrosynthesis is thus established, in addition to the type of perturbation applied to the system (there are charge variations of up to 60% among electro-obtained PPy deposits under different experimental conditions). Furthermore, the *p*-doping/undoping process is evaluated after 1000 successive voltammetric cycles in 0.10 mol L⁻¹ LiCl aqueous solution, which allows verifying that PPy obtained by potentiodynamic method has greater stability, reversibility and charge. In summary, it is demonstrated that the electrochemical technique, under the working conditions, as well as the size of the anion and cation from the supporting electrolyte, determine the morphology of the deposited polymer and possess an intrinsic relationship with the *p*-doping/undoping process, responsible for the macroscopic properties of these materials, *e.g.* conductivity. This allows the experimental conditions to model according to the required properties to the application that will be given to the polymer deposit.

Keywords: Polypyrrole, electrosynthesis of polypyrrole, morphology and conductivity of polypyrrole, properties of conducting polymers.

1. INTRODUCTION

Since its discovery, conducting polymers (CP) have attracted much attention due to their electronic properties [1-3]. These properties, along with their stability in environmental conditions [4-6], have led to their varied utility in different applications, *e.g.* biosensors, capacitors, screens, rechargeable batteries, photo diodes, photovoltaic cells, among others [3,7-10]. However, one of the fundamental applications, aimed at the advancement of clean technologies to take care of the environment, has been the development of energy storage devices [11] and the extraction of polluting compounds from aqueous matrices [10,12], based on the doping/undoping process found in this kind of materials.

The electrochemical stability of the CPs is vital for this process to take place [13-21], since, for example, the application of a doping overpotential causes over-oxidation of the polymer chain, an irreversible process that results in a capacity decrease of the charging/discharging process [22].

Polypyrrole (PPy) is one of the CPs that has attracted much attention, since enables its electropolymerization, either by cyclic or constant potential voltammetry, from aqueous and/or organic electrolytic media. Therefore, it is important to take into account that the conditions used during the electro-obtention directly influences the charging/discharging process, as a result of the variation of the obtained chain length [21].

Likewise, it has been observed that, in general, the type of perturbation applied has a close relationship with the adhesiveness, conductivity and stability of the polymeric deposit on the surface of the working electrode [23]. All this implies the impossibility of establishing a single general optimum condition applicable to electropolymerization, consequently it is essential to study each system individually, optimizing the experimental conditions depending on the use that you want to give to the CP modified electrode.

To this purpose, the polymer electrosynthesis must be optimized according to the electrochemical perturbing of the system and in the presence of a variety of supporting electrolytes, generating fundamental information that improves the doping/undoping process and adhesion to the electrode surface. In this sense, our group has demonstrated the correlation between experimental variables and the nucleation and growth mechanism (NGM), which results in a direct effect on the PCs morphology [24-31].

In this new work a systematic study is proposed to establish the correlation between the different experimental variables used during the PPy electro-synthesis process (type of electrochemical perturbing, time of perturbation, applied potential or potential window, number of voltammetric cycles, and so on.) and the *p*-doping/undoping process, in the presence of different supporting electrolytes.

This should enable, besides correlating the morphology (roughness) and conductivity with the PPy NGM, establishing the effect of the size of the different anions and cations coming from the supporting electrolyte, on the *p*-doping/undoping process (or charging/discharging) of this polymer.

2. EXPERIMENTAL

Pyrrole monomer (Py, 98%) was purchased from Aldrich, stored in dark and, prior to use, double-distilled under argon atmosphere. 99.9% tetrabutylammonium trifluoromethylsulfonate (TBATFMS), lithium trifluoromethylsulfonate (LITFMS), lithium perchlorate (LiClO_4), tetrabutylammonium perchlorate (TBAClO₄), tetrabutylammonium hexafluorophosphate (TBAPF₆) or tetraethylammonium hexafluorophosphate (TEAPF₆), purchased from Sigma-Aldrich, were used as supporting electrolyte in acetonitrile (CH_3CN , 99.9%, Merck). The aqueous solutions were prepared with lithium chloride (LiCl , Riedel-Haen 99.9%) in milli-Q ultra-pure water.

The electropolymerization was conducted in a three compartment anchor-type cells, using a platinum coil of large area (20 times larger than the working electrodes) as counter-electrode; all potentials quoted in this paper are referred to an $\text{Ag}|\text{AgCl}$ electrode in tetramethylammonium chloride to match the potential of a saturated calomel electrode (SCE) at room temperature (20 °C) [32]. A 0.07 cm^2 geometric area platinum disc was utilized as working electrode. This electrode was polished to a mirror-like finish with a 0.3 μm alumina slurry on a polishing pad.

All electrochemical measurements were performed under Ar atmosphere at room temperature (20 °C).

The electropolymerization was conducted on a CH Instruments 900B potentiostat/galvanostat using cyclic voltammetry (CV): five successive cyclic voltammetry scans ($n = 5$) between -1.200 V and an optimum switching potential for each supporting electrolyte, at a potential scan rate ν of 0.100 V s^{-1} .

In addition, it was also potentiostatically perturbed (FP), mainly to determine NGM, in a range between $0.950 < E < 1.160$ V.

The electrolytic solution consists of 0.10 mol L^{-1} of the X salt ($X = \text{LiClO}_4$, TBAClO₄, TBAPF₆, TEAPF₆, LITFMS or TBATFMS) and 0.01 mol L^{-1} Py, in acetonitrile.

The stability study of the different modified electrodes is accomplished by cyclic voltammetry in 0.1 mol L^{-1} LiCl aqueous solution, at $\nu = 0.100 \text{ V s}^{-1}$ and $n = 1000$.

Finally, conductivity measurements were conducted on a four-point probe Multi Hight Probe (Jandel) conductimeter, and the morphology of the electrodes modified with the polymer deposit was visualized by SEM and AFM using respectively NEW Jeol IT300 and a CS Instruments Nano Observer equipment controlled by a Nano-Solution software.

3. RESULTS AND DISCUSSION

The electropolymerization of Py on a Pt disk was accomplished by CV in the conditions described in the experimental. It must be borne in mind that the potential windows become modified by the use of different salts, making necessary to increase or decrease the switching potential. For instance, as seen in Table 1, electropolymerization in LiClO_4 has a switching potential 0.150 V lower than that used in LITFMS, the same difference obtained in the presence of TBAClO₄ and TBATFMS, although in all cases the appropriate initial potential was -1.200 V.

It is noteworthy that the optimal potential window is chosen to consider two important phenomena, with respect to the switching potential: i) at lower potentials, no homogeneous or very poor growth exist ii) at very high potentials, over-oxidation of the deposit takes place, which manifests itself through erratic responses.

In addition, it must be borne in mind that over-oxidation generates a decrease of the current density corresponding to the polymer growth, leading finally to a decrease of its conductivity [22]. In this way, the chosen optimum potential considers a constant increase of the current density, as a function of the corresponding voltammetric cycles, which accounts for an appropriate growth on the Pt electrode.

The foregoing is illustrated, by way of example, in Fig. 1, where voltammetric profiles recorded during the Py electropolymerization in the presence of LiClO_4 are shown in two potential windows, corresponding to the respective ranges depicted in Table 1.

Table 1. Experimental conditions for Py electropolymerization on Pt by CV (5 successive cycles).

Sample	Supporting Electrolyte	Potential Window (V vs. SCE)	Sample	Supporting Electrolyte	Potential Window (V vs. SCE)
S-1	LiClO_4	-1.200 - 1.500	S-7	TEAPF_6	-1.200 - 1.500
S-2	LiClO_4	-1.200 - 1.300	S-8	TEAPF_6	-1.200 - 1.400
S-3	TBAClO_4	-1.200 - 1.500	S-9	LiTFMS	-1.200 - 1.500
S-4	TBAClO_4	-1.200 - 1.350	S-10	LiTFMS	-1.200 - 1.450
S-5	TBAPF_6	-1.200 - 1.500	S-11	TBATFMS	-1.200 - 1.500
S-6	TBAPF_6	-1.200 - 1.400			

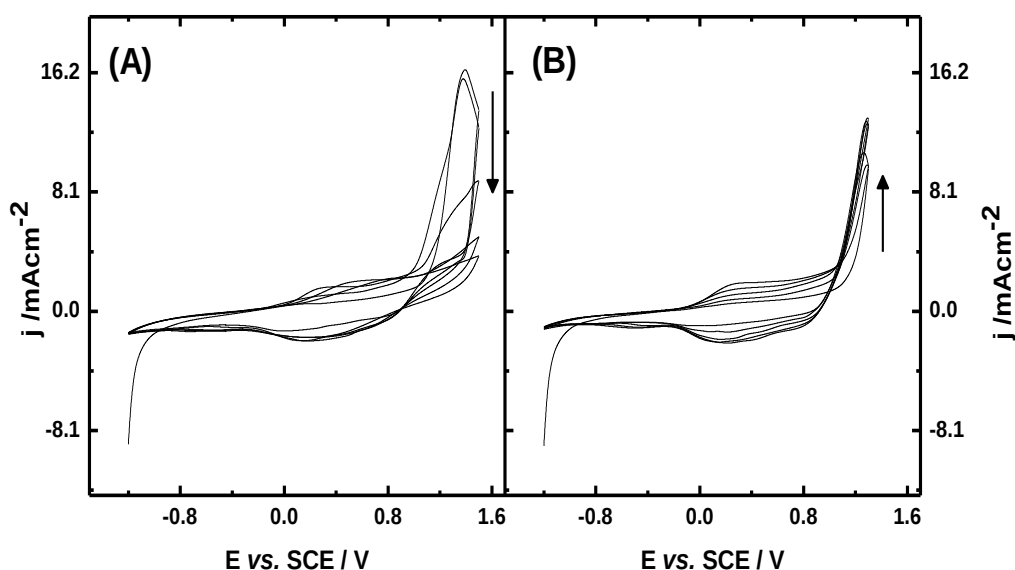


Figure 1. Voltammetric profiles during 5 cycles of Py electropolymerization on Pt at $\nu = 0.100 \text{ V s}^{-1}$ from $1 \cdot 10^{-2} \text{ mol L}^{-1}$ Py and $1 \cdot 10^{-1} \text{ mol L}^{-1}$ salt in CH_3CN , at the optimum potential window: (A) S1; (B) S2.

The variation of the potential window as a function of the size of the anion coming from the supporting electrolyte, used in the oxidative electropolymerization, can be explained; for example, TFMS^- is 1.5 times bulkier than ClO_4^- [33]. Thus, if the potential window amplitude is increasingly sorted out, the same order as the volume of the respective anion is obtained: $\text{ClO}_4^- < \text{PF}_6^- < \text{TFMS}^-$. This sequence has also been reported for PEDOT electropolymerization [34].

In addition, and as already reported [34], it was observed that the presence of larger cations also affects the amplitude of the interval. Although the synthesis consists of oxidative electropolymerization, in which the cations do not participate directly in the mechanism, they do contribute as a function of their volume, exerting a barrier effect, which prevents the free diffusion of the monomer towards the electrode/solution interface. Consequently, it is possible to relate the size of these cations to the potential window amplitude increase, classifying themselves in an increasing way as follows: $\text{Li}^+ < \text{TEA}^+; \text{TBA}^+$.

On the other hand, in Fig. 2 voltammograms of electrodes modified according to conditions for S-1 and S-2 (Table 1), scanning between -0.270 and 1.000 V, are shown in solution containing no monomer. In both cases a peak is seen by scanning in the positive direction, at 0.824 V for S-1 and 0.469 V for S-2. This behaviour is mainly ascribed to chain length of the deposited polymer. Heize [21] pointed out that, to a lesser extent of the range of electrosynthesis potential, the chain length is up to 64 units, while for larger potential intervals, they would present a difference of up to 50 units less, which would explain why the *p*-doping/undoping process occurs at lower potential.

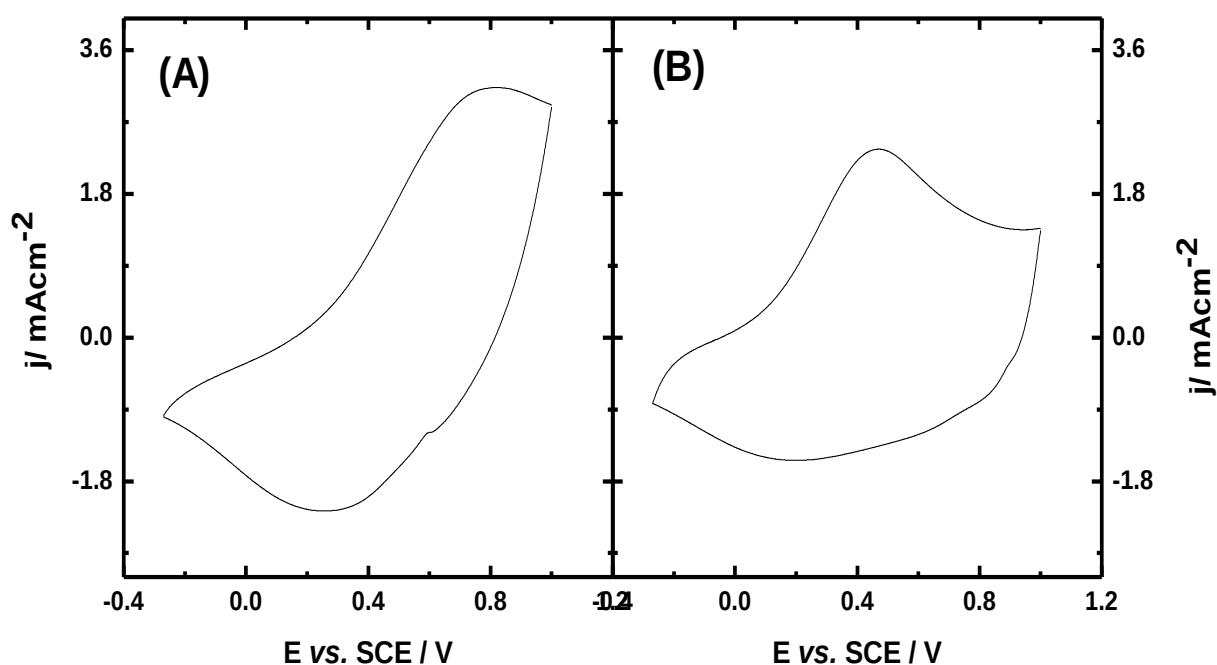


Figure 2. Voltammetric response of Pt|PPy modified electrodes in $0.10 \text{ mol L}^{-1} \text{ TBAClO}_4$ in CH_3CN prepared by (A) S1; (B) S2.

Table 2 summarizes the values of the *p*-doping/undoping charges obtained from the cyclic voltammetry response of the Pt|PPy modified electrode in the electrolytic solution without monomer, scanned within the respective potential windows. These values are all measured after the fifth scanning cycle of the Pt|PPy modified electrode. Thus, an excellent chemical reversibility of all the modified electrodes was verified, since the coefficient between the *p*-doping process and the respective *p*-undoping one is practically unity.

Furthermore, it can be observed that the electropolymerization in TBAPF₆, affords a charge up to 60% higher than that of electrodes modified in LiClO₄, pointing out that the synthesis in this salt would generate longer chains polymeric deposits and, consequently, with higher conductivity.

From the corresponding voltammograms, the optimum potential regions for nucleation and growth were selected, to record the Py electro-oxidation process at fixed potential, FP. To this purpose, a systematic study, according to the different salts used as supporting electrolyte, analogous to that performed by CV, will be conducted in order to also analyse the effect of the kind of perturbing applied to the system.

Consequently, it is important to emphasize first that, when using the same salt for electropolymerization at fixed potential, an inversely proportional relationship is generated by increasing the system perturbing potential, *i.e.* a decrease of the induction time, τ , is produced, corresponding to the duration time of the exponential decay of the current after the initial jump generated by the applied potential. After this τ time, the current increase occurs once again, now produced by the nucleation and subsequent growth of the polymer deposit on the electrode surface, if the applied potential is suitable for it.

Table 2. *p*-doping/undoping (Q_{pd} , Q_{pu}) charges during the voltammetric response in electrolytic solution without monomer, over the optimal potential windows for PPy electrosynthesis by CV, through 5 successive cycles, in the presence of different salts.

Sample*	$Q_{pd} / \text{mC } \mu\text{g}^{-1}$	$Q_{pu} / \text{mC } \mu\text{g}^{-1}$	$Q_{pd} \cdot Q_{pu}^{-1}$
S-2	0.3841	0.3818	1.01
S-4	0.5377	0.5037	1.05
S-6	1.0003	0.9861	1.01
S-8	0.7540	0.7250	1.04
S-10	0.6514	0.6352	1.03
S-11	0.5760	0.5488	1.05

* Described in Table 1.

Hence, it is important to firstly emphasize that, when using the same salt for electropolymerization at fixed potential, an inversely proportional relationship is generated by increasing the system's perturbing potential, *i.e.* a decrease in the induction time, τ , is produced corresponding to the duration time of the exponential decay of the current after the initial jump generated by the applied potential. After this τ time, the current increases once again, now produced by the nucleation and

subsequent growth of the polymer deposit on the surface of the electrode, when the applied potential is suitable for it.

This phenomenon can be explained by the increase of energy applied to the system, generating a faster formation of nuclei on the Pt surface generating, as a result, the formation of a deposit at a shorter time. However, this occurs up to an optimum value for each deposit. If the potential increases above this value, over-oxidation of the deposit takes place, which, as in the case of CV polymerization, manifests itself through erratic and irreproducible responses. In contrast, within the region of adequate potential, the recorded profiles are fully reproducible. This behaviour has been previously observed and was now corroborated in the presence of all the salts used as supporting electrolyte in the current study.

Therefore, just as when perturbed by CV, it is possible, depending on the salts used as supporting electrolyte, to appreciate a variation of the electropolymerization optimum potential when FP is utilized. Figure 3 shows j/t transients corresponding to the effect of the anion and the cation of the supporting electrolyte, being also possible in this case to ascribe the variation to the volume of the anion coming from the supporting electrolyte. Likewise, the presence of bulky cations generates a hindrance towards the monomer diffusion to the electrode/solution interface, as inferred from the results obtained from Py electropolymerization by CV method.

By way of example, j/t transients recorded during the PPy potentiostatic growth at 1.020 V are shown in Fig. 3, in the presence of each of the tested salts. Thus, when the cation is kept constant, it is noted that the variation of the anion generates two phenomena *i)* change of the τ value, and *ii)* charge increase due to the deposit growth and doping processes.

On the other hand, by keeping the cation constant, it was observed that these two phenomena also occurred, however, the influence of the size of the anion is much more significant than that showed by large cations. As pointed out, this was ascribed to the fact that although obtaining these deposits is performed by an oxidative polymerization mechanism of the monomer, where the cation has no participation, in any case these bulky ions provoke a decrease of monomer diffusion to the electrode/solution interface, delaying the oxidation process and subsequent formation of oligomers that give rise to the high density oligomer region, HDOR.

Table 3 summarizes the *p*-doping/undoping values of electrogenerated PPy deposits at different fixed potentials, where again the same general behaviour observed for CV growth is verified, *i.e* in the presence of TBAPF₆ the charge of the *p*-doping/undoping process is greater. This may be ascribed to the faster deposit growth, thanks to the greater basicity of PF₆⁻, as has been described in the literature for thiophene electropolymerization[25].

Comparison of the charges obtained for analogous deposits generated by the two different perturbations usually shows that deposits electrosynthesized by CV present higher charge, independent of whether the *p*-doping/undoping process be always reversible. That is, when comparing the *p*-doping/undoping charge values of electrosynthesized PPy using FP and CV, an important increase for the same salt in the supporting electrolyte stands out: deposits prepared by potentiodynamic perturbing exhibit between 15 and 60% more charge than those synthesized using potentiostatic perturbing.

This behaviour is mainly explained by considering that when applying a fixed potential to the system an uncontrolled increase of oligomers generation takes place, which translates into a rapid increase of the HDOR. Consequently, the precipitation of the nuclei over the surface of the electrode is

performed in a more disorderly manner, from oligomers of various chain lengths. On the other hand, the deposits prepared by CV are generated from a perturbing controlled by the variation of the applied potential, that allows different processes during the electropolymerization, among which the reordering of the structure during the undoping process is included, generating thus a more orderly deposition [35,36].

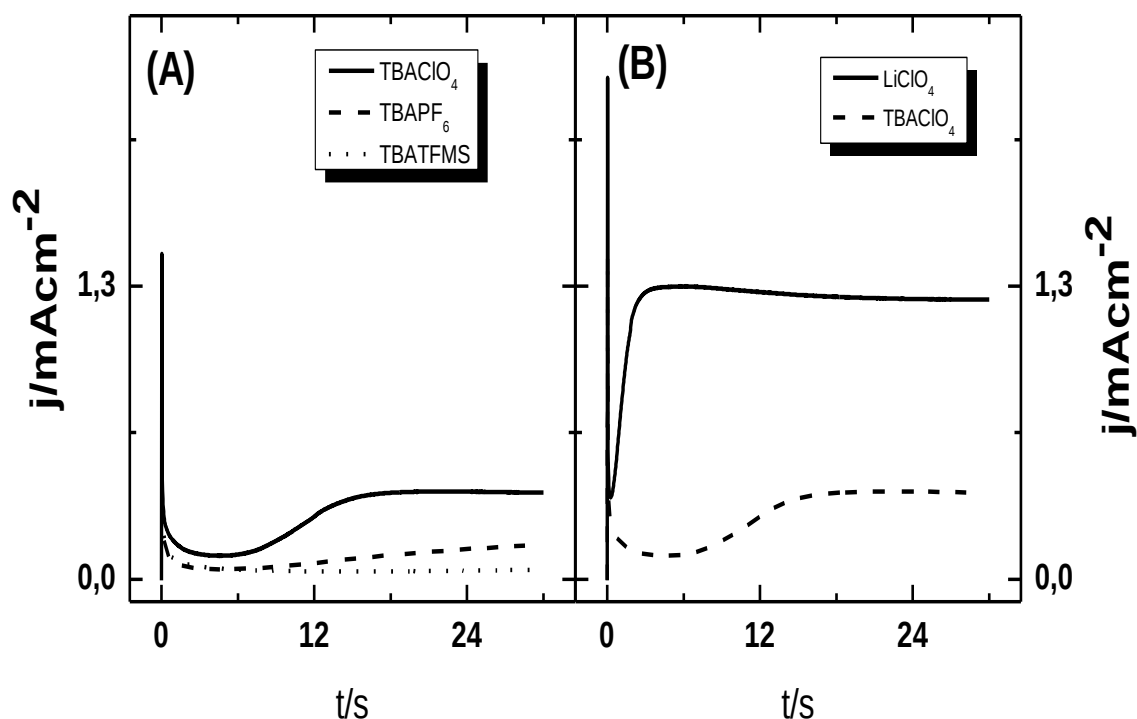


Figure 3. j/t transients during Py electropolymerization on Pt from 0.01 mol L^{-1} Py + 0.10 mol L^{-1} supporting electrolyte (salts in the inset), at $E = 1.020 \text{ V}$. (A) Anion size effect; (B) cation size effect.

Table 3. PPy p -doping/undoping (Q_{pd} , Q_{pu}) synthesized by FP, obtained from responses recorded within the optimum potential windows of the electrodeposits.

Supporting Electrolyte	E_p / V	$Q_{\text{pd}} / \text{mC } \mu\text{g}^{-1}$	$Q_{\text{pu}} / \text{mC } \mu\text{g}^{-1}$	$Q_{\text{pd}} \cdot Q_{\text{pu}}^{-1}$
LiClO ₄	1.020	0.2436	0.2334	1.04
TBAClO ₄	1.060	0.6247	0.5923	1.05
TBAPF ₆	1.110	0.9905	0.9687	1.02
TEAPF ₆	1.090	0.2767	0.2695	1.03
LiTFMS	1.100	0.3807	0.3595	1.06
TBATFMS	1.120	0.2822	0.2711	1.04

The facts described and discussed are corroborated through conductivity measurements of different electrogenerated polymeric coatings. Thus, for a deposit prepared using the same salt and potentiodynamic perturbing, a conductivity 53 % greater than that of a PPy deposit obtained under the same conditions, but using a potentiostatic perturbing.

Thus, it was verified that PPy prepared in TBAPF₆ employing CV presents higher conductivity (25.91 S cm⁻¹), while the lowest conductivity was recorded for PPy obtained by FP in LiClO₄ (9.83 S cm⁻¹). Therefore, for electropolymerization, it is likely to sort them out, according to decreasing conductivity, as a function of the anion and independent of the perturbing in the following order: PF₆⁻ > TFMS⁻ > ClO₄⁻. It should be noted, however, that in all cases the conductivity of PPy is in the same order of magnitude, but it should be borne in mind that two or three times increase in conductivity can make important differences, depending on the practical used to be given to the modified electrode.

On the other hand, from the *j/t* transients recorded during the potentiostatic growth, it is possible to determine the effect of the cation and the anion in the PPy NGM electrogenerated on Pt, to establish its correlation with the *p*-doping/undoping process. Thus, from τ that, as was observed for the growth of PPy, corresponds to the contribution by diffusion during the oxidation of the monomer [37,38], new coordinates *j*(0,0) are designated, to determine the PPy NGM in the working conditions utilized herein. This was done using the conventionally known equations for electro-obtained metallic deposits, which have also proved valid for polymeric electrosynthesis, with errors under 2% being achieved when the respective *j/t* transients are deconvolved by combinations of two or more of those equations [7,24-31,37,38]. In this case, the proposed mechanism is represented by Eq. 1:

$$j = at^2 \exp^{-bt^3} + ct^{-0.5} [1 - \exp^{-dt^2}] \quad (1)$$

Equation 1 presents two contributions, where the first term corresponds to a process of instantaneous nucleation with two-dimensional growth, IN2D, and the second, to progressive nucleation and 3D growth under diffusion control, PN3Ddif. In this equation, the variables *a*, *b*, *c* and *d* correspond to:

$$a = \frac{2\pi M k^2 n F h A N_0}{\rho} \quad (2) \quad b = \frac{\pi A M^2 k^2 N_0}{3\rho^2} \quad (3)$$

$$c = \frac{\pi F D^{1/2} C_\infty}{\rho^{1/2}} \quad (4) \quad d = \frac{A' k \pi D}{2} \quad (5)$$

where *F*, *M* and ρ are known and usually used, *N*₀ is the number of nuclei formed at *t* = 0, *k* is the nuclei growth rate constant, *D* and *C*_∞ are, respectively, the diffusion coefficient and the monomer concentration in the bulk solution. Finally, *A'* and *k* are described by another mathematical algorithm, represented by:

$$A' = A N_{dif} \quad (6) \quad y \quad k = \frac{3}{4} \left(\frac{8\pi C_\infty M}{\rho} \right)^{1/2} \quad (7)$$

where N_{dif} is the number of nuclei formed at $t = 0$, growing under diffusion control, and A is the nuclei formation rate constant.

In Fig. 4A it can be seen, by way of example, the detailed deconvolution of a transient using Eq. 1, with its respective independent contributions, for PPy electropolymerization. It is observed that the electropolymerization mechanism of PPy is governed from the beginning by NP3D_{diff}, overlapping the IN2D contribution.

It is also possible to observe the influence of the potential (Figs 4B-C), where the increase of the electropolymerization potential, E_p , favours the diffusion controlled process, mainly due to the fact that the IN2D contribution decreases its participation with respect to PN3D_{diff}. That is, if we consider the previously proven correlation between these NGMs and the morphology of the deposit [24,25,29-31], in the electropolymerization at 1,110 V the growth in the form of nuclei of analogous or uniform size (being an instantaneous nucleation), during the first 5 s of the process contributes less than 22% of the total charge, and then give way to the NP3D_{diff} contribution, now corresponding to time-dependent growth in the form of semi-spheres of varying sizes, since in this case the nucleation mechanism is progressive.

When the electropolymerization is performed at 1,110 and 1,120 V, both NGMs were identical, as evidenced for all the studied cases. Nevertheless, in what way the times at which each contribution predominates was monitored, in addition to the variation of their contribution, which is ascribed to the kinetics of growth as the potential increases: the IN2D contributes 17.54 and 11.15 % of the total charge, respectively.

At the same time, in the presence of the different salts and at optimum electropolymerization potentials, with TEAPF₆ at $t < 5$ s, NP3D_{diff} (88.04 % of the total charge) also predominates. Likewise, in the case of LiClO₄ and TBAClO₄ salts, there are, respectively, contributions to the total charge of 78.35 and 73.92 % of NP3D_{diff}.

In the case of salts whose anion has a greater radius (LiTFMS and TBATFMS), IN2D contributes even less, with charge percentages of 29.31 and 26.68 %, respectively. This behaviour has been ascribed to the kinetic cohesion of the nuclei, a greater roughness being expected for these deposits, because the HDOR's density would be greater than that generated in the presence of salts with smaller ionic radius.

Table 4 summarizes the values obtained for the constants of Eq 1, which allows deconvolution of each transient with an error < 2 %. It is perceived that c (from the PN3D_{diff} contribution), for the same salt, is independent of the potential applied to the system. This is because this variable is mainly substantiated on the diffusion coefficient, which is defined as a kinetic concept, while the former is thermodynamic. However, when the variation of the supporting electrolyte is observed, it is appreciated that this constant varies, which can be explained by the already mentioned two phenomena: i) the larger size of the anion hinders the cohesion of the nuclei, preventing this takes places at a shorter time and ii) the cation acts as a sort of barrier hindrance for the free diffusion of the monomer towards the electrode/solution interface.

In this manner, from Eq. 4, determination of the diffusion coefficient, D , in the different experimental conditions is allowed. Table 5 exhibits the obtained values, whose monomer diffusion decreases in the presence of large cations and anions is confirmed, although both ions are of larger size, a difference of an order of magnitude is reached.

In the case of parameter d , which is related to the number of nuclei formed on the electrode surface, it is noteworthy that the growth is under the diffusional regime of the monomer. As inferred from the values of d , the profiles of the different j/t transients are similar, emphasizing only the decrease of the charge after reached maximum, as a result of the increase of the applied potential. It should be observed that the magnitude remains practically constant, because the surface on which this polymer grows corresponds to the electrode already modified with the first polymer layer deposited on the substrate, *e.i.* once the first layer is formed, the deposit grows because the chains are lengthening.

Figs. 5A-B show respectively SEM micrographs of PPy, PF_6^- and PPy, TFMS^- modified electrodes obtained by CV. When the electropolymerization was conducted in PF_6^- as supporting electrolyte, a much more homogeneous and compact deposit was obtained, standing out the small semi-spherical structures, consistent with the type of growth predicted from the NGM of the deposit. In contrast, the deposit generated in the presence of TFMS^- is less homogeneous, with a rougher surface, also consistent with that predicted by the respective NGM and demonstrates that it is possible to correlate the morphology with the anionic radius.

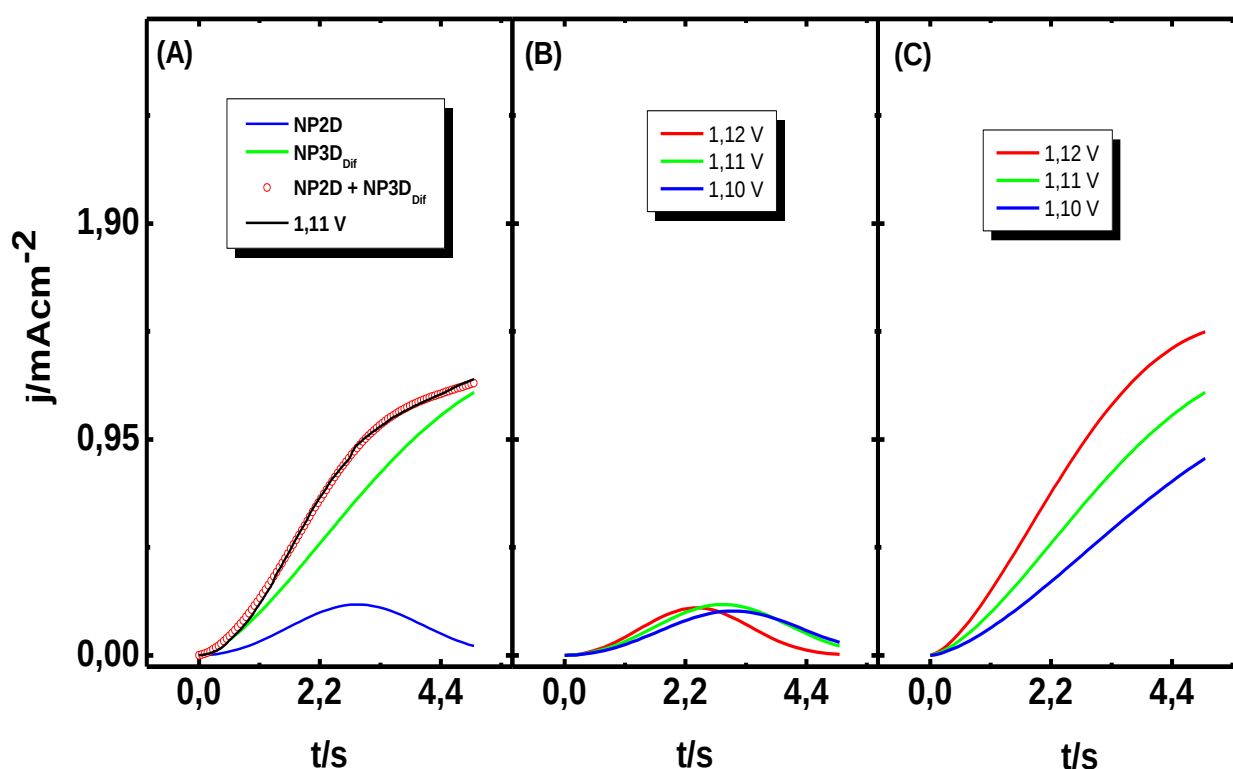


Figure 4. (A) j/t transient at $E_p = 1.110$ V, between $0 < t < 5$ s: (—) experimental and (---) fitted according to equation 1. Interface: $\text{Pt}[0.01 \text{ mol L}^{-1} \text{ Py} + 0.10 \text{ mol L}^{-1} \text{ TBAPF}_6, \text{CH}_3\text{CN}]$. (B) IN2D contribution vs. E_p . (C) PN3Ddif contribution vs. E_p .

In Fig. 5C, concerned to a SEM micrograph of the electrode modified with PPy, PF_6^- obtained at FP, a less homogeneous deposit is observed, which explains the lower charge of the p -

doping/undoping process and, with it, the lower conductivity of the deposits obtained by applying this perturbation.

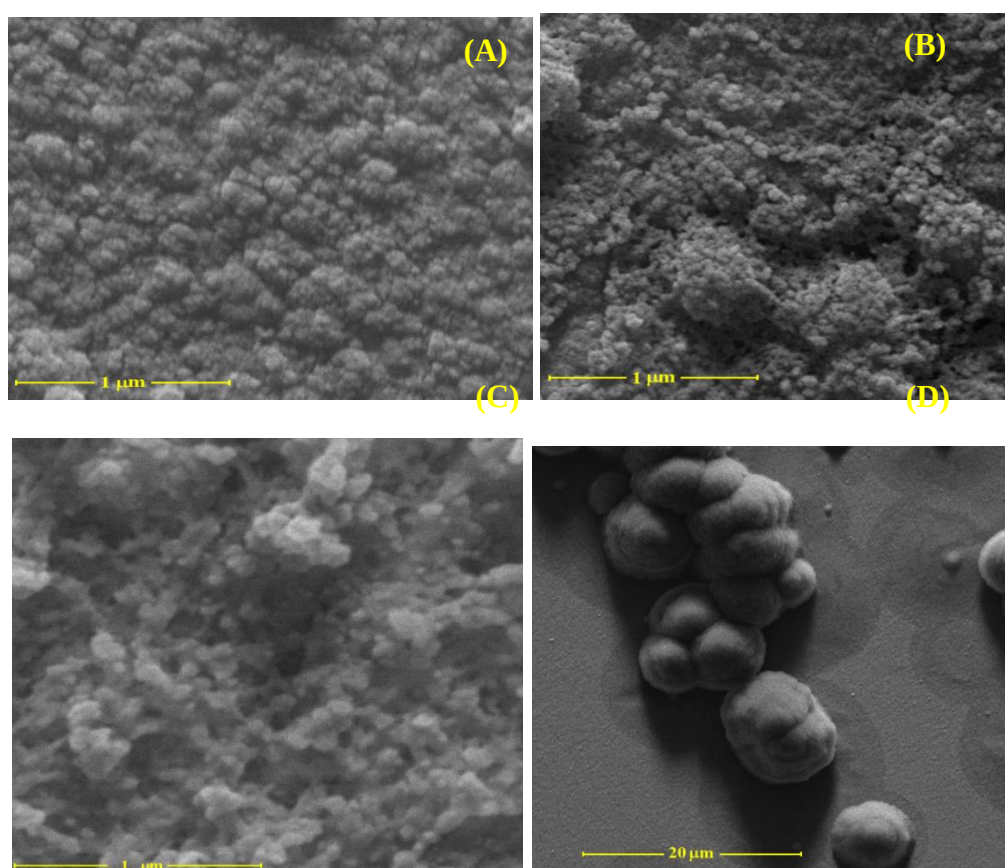
Finally, Fig. 5D shows a SEM micrograph of the nuclei obtained by FP electropolymerization, which demonstrates the possibility of correlating with the proposed NGM. It can be observed that the morphology responds mainly to semisphere-type growths of different sizes, consistent with the PN3D_{dif} contribution, as predicted by the NGM established from the deconvolved transients (Figs 4B-C). In this way, the morphological analysis also allows verifying the effect of the size of the dopant anion, since a more homogeneous morphology is observed when electropolymerized using TBAPF₆ in place of LiTFMS.

Table 4. Values of the numerical constants of Eq. 1, as a function of the electrosynthesis potential and the salt of the supporting electrolyte.

Py / mol·L ⁻¹	Supporting electrolyte	/ mol·L ⁻¹	E / V	τ / s	a / mA·cm·s ⁻²	b / s ³	c / mA·cm ⁻² ·s ^{-1/2}	d / s ⁻²
0.01	LiClO ₄	0.10	1.010	0.42	0.00325	5.25e-5	3.2666	0.01716
			1.020	0.26	0.02463	0.00425	3.2666	0.04665
			1.030	0.22	0.04284	0.00674	3.2666	0.06482
0.01	TBAClO ₄	0.10	1.050	0.92	0.03366	0.01076	3.56599	0.01593
			1.060	0.66	0.03923	0.02578	3.56599	0.05543
			1.070	0.48	0.06939	0.06240	3.56599	0.09055
0.01	TBAPF ₆	0.10	1.100	0.44	0.04033	0.02309	3.99215	0.02656
			1.110	0.42	0.05234	0.02778	3.99215	0.04176
			1.120	0.40	0.07055	0.04819	3.99215	0.06386
0.01	TEAPF ₆	0.10	1.080	0.32	0.07273	0.04179	4.69495	0.03986
			1.090	0.27	0.09483	0.05489	4.69495	0.05730
			1.100	0.24	0.18154	0.13388	4.69495	0.09507
0.01	LiTFMS	0.10	1.090	0.18	0.0188	0.00248	1.37547	0.51818
			1.100	0.16	0.02309	0.00340	1.37547	0.56999
			1.110	0.14	0.04883	0.00679	1.37547	0.92606
0.01	TBATFMS	0.10	1.110	0.36	0.01204	0.00256	1.8864	0.25721
			1.120	0.32	0.02307	0.00287	1.8864	0.49094
			1.130	0.26	0.03663	0.00455	1.8864	0.75053

Table 5. Py diffusion coefficient: effect of the cation and anion volume of the supporting electrolyte.

Supporting electrolyte	Volume cation/ $\text{\AA}^3$ [33]	Volume anion/ $\text{\AA}^3$ [33]	D/ $\text{cm}^2 \text{s}^{-1}$
LiClO ₄	25.25	57.09	$6.4 \cdot 10^{-3}$
TBAClO ₄	300.40	57.09	$7.1 \cdot 10^{-3}$
TEAPF ₆	164.34	71.35	$1.1 \cdot 10^{-3}$
TBAPF ₆	300.40	71.35	$1.2 \cdot 10^{-3}$
LiTFMS	25.25	85.20	$6.7 \cdot 10^{-4}$
TBATFMS	300.40	85.20	$7.8 \cdot 10^{-4}$

**Figure 5.** SEM micrographs of PPy electrosynthesized by CV using various salts: A) TBAPF₆; (B) LiTFMS and by FP: (C -D) TBAPF₆. In each case, the electrodeposits are prepared in the respective optimum conditions (optimum potential window or E_p , depending on the perturbing).

The morphological characterization by AFM of Figs. 6A-B shows AFM micrographs of electrodes modified with PPy electropolymerized in the presence of TEAPF₆ and LiTFMS, respectively.

It is worth noting that in all cases a compact and total coating of the electrode surface was obtained, with similar deposit thicknesses, over equal electrolysis times.

On the other hand, when calculating the average of the square of the roughness, R_q , of the different electrodes modified with PPy (Table 6), it was found that the values were all the same order of magnitude. However, a trend is observed that correlates with the volume of the different anions present in the solution used for electropolymerization. Thus, it is possible R_q to be sorted in ascending order, according to: $\text{ClO}_4^- < \text{PF}_6^- < \text{TFMS}^-$, in agreement with the other results obtained and discussed in the current paper.

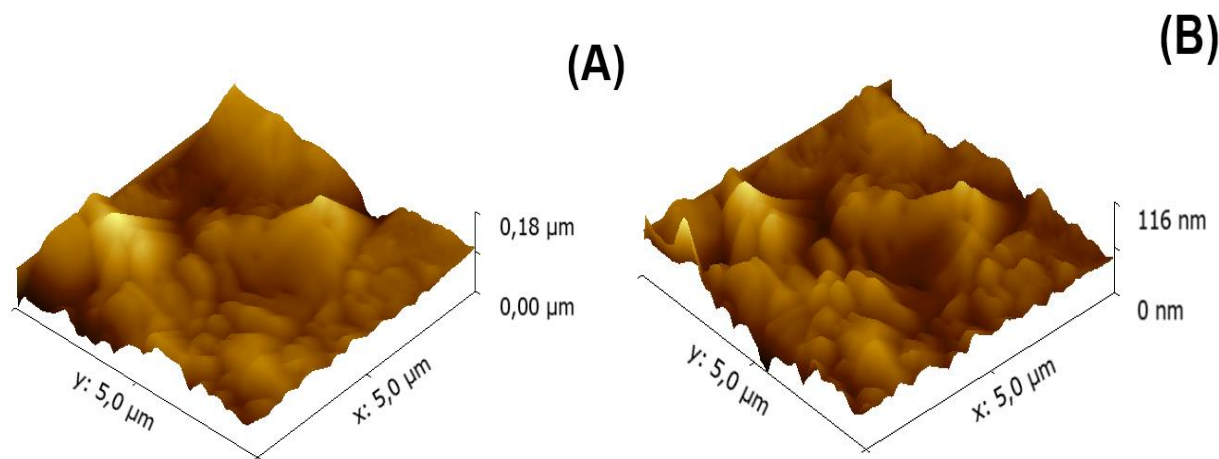


Figure 6. AFM micrographs of PPy electrosynthesized by CV (5 successive cycles), in the presence of: (A) TBAPF₆; (B) LiTFMS.

Table 6. Average of the square of the roughness calculated for PPy electrosynthesized by CV (5 successive cycles), in different salts.

Supporting electrolyte salt	R_q (μm)	Supporting electrolyte salt	R_q (μm)
LiClO ₄	0.031	TBAPF ₆	0.035
TBAClO ₄	0.033	LiTFMS	0.043
TEAPF ₆	0.033	TBATFMS	0.053

4. CONCLUSIONS

The electrochemical conditions of perturbation of the system, as well as the size of the anion and cation from the supporting electrolyte, determine the morphology of the polymeric deposit and have an intrinsic relationship with the *p*-doping/undoping process, responsible for the conductivity of these materials.

The greater stability of the *p*-doping/undoping process (or charging/discharging) of PPy, with excellent reversibility, is achieved when TBAPF₆ is used during its electrosynthesis by cyclic voltammetry.

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