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Microgravimetric study of the influence of the solvent on the redox properties of polypyrrol modified electrodes

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Abstract

The redox behavior of the polypyrrole films in the presence of LiClO_4 salt in different solvents like propylene carbonate (PC), *N,N*-dimetilformamide (DMF), methanol (MetOH), ethanol (EtOH), acetonitrile (ACN) and water was investigated using simultaneous electrochemical quartz crystal microbalance and cyclic voltammetry experiments. Both charge and mass changes during redox processes were rationalized in terms of multiple regression considering some solvent parameters and ionic transport characteristics. The electroactivity of PPY modified electrodes increase in the sequence $\text{PC} < \text{DMF} < \text{EtOH} < \text{MetOH} < \text{ACN} < \text{water}$. Also the mass gains in the sequence $\text{PC} < \text{water} < \text{EtOH} < \text{DMF} < \text{MetOH} < \text{ACN}$, showing clearly the influence of the solvent physico-chemical nature on the electroactivity and electroneutralization processes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: EQCM; Solvent influence; Polypyrrol

1. Introduction

Although a great deal of work has been devoted to the study of the electrochemical behavior of electronically conducting polymers (ECP) such as polyaniline, polypyrrol and polythiophene, a central problem is related to the nature of species (ions and solvent) that cross the film/electrolyte interface during the redox process [1]. Since the first investigation of conducting PPY films by Diaz and Kanazawa [2], many researchers have studied this behavior using several techniques [3–7] and have brought a better understanding of the role of redox properties and consequently, specific applications of this class of materials [8].

Considering the nature of ECPs to storage charge, one of the most important questions to be deeply studied is the solvent influence on their ability to storage charge. Recently Varela and Torresi [9] have shown that the polyaniline films growth in aqueous media are more active in acetonitrile solutions than in propylene carbonate ones. In that work, authors have attributed this difference in the charge storage features only to the dielectric constant effect. However, this kind of analysis is appropriate only if few solvents are compared, since it is necessary to take into account other

solvent properties in order to check the individual weight on the polymer redox process features. Specifically considering applications such as in a cathodic material in secondary lithium batteries, the role-played by the solvent during electroneutralization process presents a very important point since it is closely related to the mass attained in both charged and discharged states.

The solvent properties can be divided into two types: physical quantities (like vapor pressure, density, refractive index, for example) and chemical ones (polarity, ability to form hydrogen bonds, etc.). In order to relate such properties, solubility and rates of reactions [10], linear free energy relationships (LFER) or linear energy relationships (LSER) have been proposed. Otero et al. [11] reported the use of the Kamlet–Taft [12] expression to relate charge storage ability in polypyrrol films to some solvent parameters. The authors used cyclic voltammetry experiments and did not mention the mass change in the polymeric modified electrode during the redox process.

In this work, electrochemically obtained polypyrrol cycling features were studied in solutions of LiClO_4 in six different solvents, using simultaneous electrochemical quartz crystal microbalance (EQCM) and cyclic voltammetry (CV) experiments. Both charge and mass change during redox processes were rationalized in terms of multiple regression considering some solvent parameters and ionic transport characteristics.

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2. Experimental

2.1. Reagents and solutions

N,N-dimethylformamide (DMF, Mallinckrodt), propylene carbonate (PC, Aldrich) and acetonitrile (ACN, Merck) were distilled prior to use. Methanol (MeOH, Merck) and ethanol (EtOH, Merck) were used as received. Water was purified in an ultra pure Milli-Q (Millipore system). Anhydrous lithium perchlorate (LiClO_4) was purchased from Aldrich and used as received. Electrolytic solutions were prepared with 0.1 M LiClO_4 in different solvents.

2.2. Polypyrrol modified electrodes

In order to minimize the role of morphological differences of PPY films, all electrodes in this study were obtained in the same conditions and used only one time in each solvent. Electrosynthesis of PPY films was carried out in potentiostatic conditions in a 53 mM PPY+0.3 M LiClO_4 electrolyte solution. A potential of 0.7 V was applied for 130 s. The current attained at this time was close to 0.8 mA cm^{-2} , and the total mass deposited onto working electrode was $40 \pm 2 \mu\text{g cm}^{-2}$ of PPY and it is equivalent to a film thickness of about 100 nm. So, these formed films are very thin and its behavior can be considered rigid and one can assume that there are no viscoelastic changes during redox processes [13]. In addition, the electropolymerization mechanism was found in agreement with that previously reported, taking into consideration both film formation and oxidation as reported by several authors [14–17].

2.3. Electrochemical and EQCM measurements

After film formation, electrodes were placed in a conventional three-compartment cell containing solutions of 0.1 M LiClO_4 in each solvent. A platinum wire was used as counter electrode and all potentials are referred to Ag/Ag^+ reference electrode. Working electrodes were 6 MHz overtone polished AT-cut quartz crystals of 26 mm diameter (Valpey-Fisher). Both sides of the quartz crystals were coated with thin (ca. 200 nm thickness) gold films over a ca. 5 nm Cr adhesion layer, but only one of the faces (working electrode) was exposed to the electrolyte solution (active area of 0.2 cm^2). The resonance frequency shift was measured with a HP-5370B Universal Time Counter. These shifts can be used to calculate mass changes using the Sauerbrey equation [18–20]. Electrochemical measurements were performed with a FAC 2001 potentiostat/galvanostat. The experimental details for EQCM measurements have been discussed previously [20].

3. Results and discussions

3.1. Voltammetric charge analysis

Fig. 1 shows j/E and $\Delta m/E$ potentiodynamic profiles for PPY in each solvent. In all cases, the potential range was the

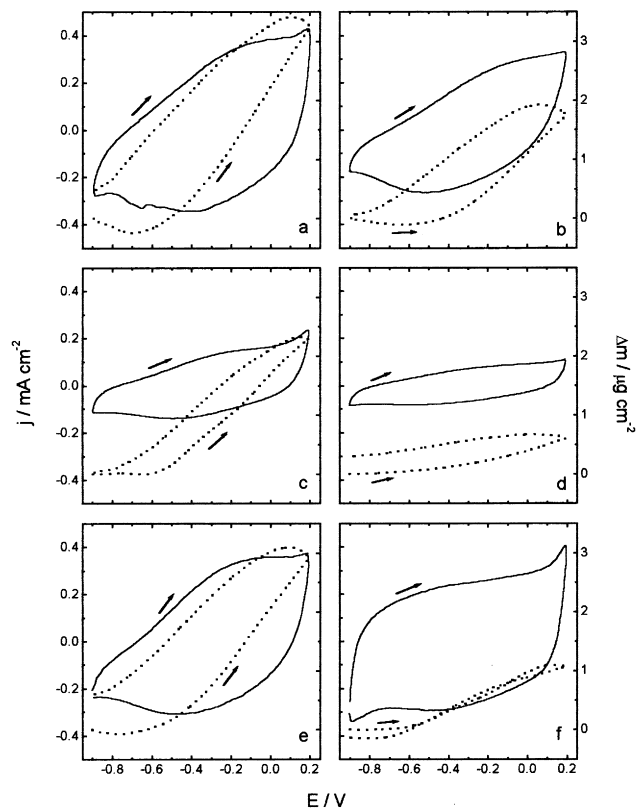


Fig. 1. Potentiodynamic j/E (full line) and $\Delta m/E$ (dotted line) profiles for PPY films in 0.1 M LiClO_4 using the following solvents: (a) ACN, (b) EtOH, (c) DMF, (d) PC, (e) MeOH and (f) water. $v=0.05 \text{ V/s}$.

same, including both oxidation and reduction current peaks. The voltammogram shapes are similar in all cases, with no appreciable differences in potential values for both current peaks (oxidation and reduction). The anodic and cathodic charges are similar for each solvent, but are different in comparison among them, due to the solvent influence in charge storage features. Focusing on the $\Delta m/E$ profile, a mass gain during the positive going scan and a mass loss in the reverse scan is observed, evidencing a charge compensation process dominated by anion insertion/expulsion, in oxidation/reduction processes, respectively. This anionic domain is given in a mass basis, since the molar mass for anion and cation are very different (99 and 7 g mol^{-1} , for perchlorate anion and lithium cation, respectively).

In order to compare charge and mass gain for oxidation of PPY films, Fig. 2 shows the bar graphics for these amounts as a function of solvent. The electroactivity of PPY modified electrodes increase in the sequence $\text{PC} < \text{DMF} < \text{EtOH} < \text{MeOH} < \text{ACN} < \text{water}$ solvent. The obtained electroactivity sequence is different to that observed previously for PPY films growth in ACN solutions at 0.8 V [11] onto Pt surface, this fact is associated to different electrosynthesis conditions [21] employed. The mass gain increases in the sequence $\text{PC} < \text{water} < \text{EtOH} < \text{DMF} < \text{MeOH} < \text{CAN}$. So, through simple inspection, one can observe that there are no direct relations between charge and mass gain. This fact presents a key point

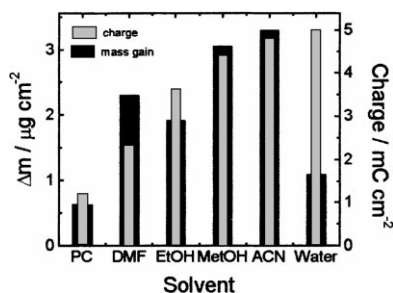


Fig. 2. Bar graphics for charge and mass gain as a function of solvent.

to be explored in this work, in other words, which properties may be used to estimate these two amounts?

As discussed in Section 1, in order to describe the linear solvation energy relationships (LSER), the Kamlet–Taft expression was chosen. The main parameters used are: α (hydrogen bond donation, HBD, ability of the solvent), β (hydrogen bond acceptance, HBA, or electron pair donation ability to form a coordinative bond), π^* (polarity/polarizability parameter) and ϵ (relative permittivity or dielectric constant). The terms α and β are solvatochromic properties of the solvents and are determined by the energies of the longest wavelength absorption peaks of certain carefully selected probe solutes in the required solvent. The parameter π^* describes a combination of properties, the polarity and the polarizability of the solvents. The hydrogen bond donation (HBD) can also be expressed by the acidity [10]. In the same way, basicity serve to express the parameter π^* , and measures the ability of the solvent to stabilize a charge or a dipole due to its dielectric effect. Some parameters and properties for solvents are shown in Table 1, as given by Marcus [22].

In order to obtain an expression for charge storage ability in PPY films as a function of solvent parameters, the procedure suggested by Otero et al. [11] was adopted and multiple regression processing was carried out by using the Origin[®] package, version 5.0. The multiple correlation coefficients were obtained and the adjustment quality was checked through the R^2 term [23] and the uncertainties for the calculated coefficients. The equation for charge (normalized by the deposited PPY mass) considering α , β , π^* and ϵ terms, can be written as

$$q_N = 127.75 + 79.5\alpha - 197.25\beta + 228.50\pi^* - 3.15\epsilon \quad (1)$$

Table 1
Selected solvent properties for the charge multiple regression

Solvent	ϵ	α	β	π^*	Acidity	Basicity
ACN	36.6	0.19	0.40	0.75	0.39	0.86
PC	66.1	0.00	0.40	0.83	0.24	0.83
DMF	47.2	0.00	0.76	1.00	0.30	0.93
EtOH	25.3	0.86	0.75	0.54	0.66	0.45
MetOH	33.0	0.98	0.66	0.60	0.75	0.50
Water	80.1	1.17	0.47	1.09	1.00	1.00

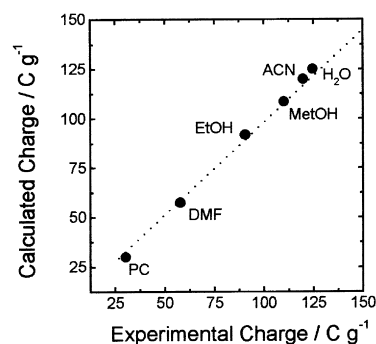


Fig. 3. Calculated charge (using Eq. (1)) as a function of the experimental charge (oxidation process) for the different solvents. The experimental charge was obtained by integration of the voltammograms of Fig. 1.

The error in the coefficient determination (or uncertain) was less than 4% and R^2 was 0.99944. Similar results were obtained when acidity and basicity are used instead of the α and π^* terms, respectively. Fig. 3 shows plots of calculated charge using Eq. (1) and experimental oxidation charges for PPY modified electrodes in all solvents. The excellent confidence discussed is well seen in this figure.

Analyzing each term of Eq. (1), we can observe that the parameter α (or acidity) has a low contribution to the storage charge of PPY film. This term is related to the ability to accept an electron pair and since there are no negative charges being formed in the polymer chain and ClO_4^- anions are poorly solvated, so, low influence is expected for this parameter. The negative coefficient for β suggest an inverse influence: this term informs about donation of electron pairs capacity and it is equivalent to the interaction of the solvent with the positive charges created in the oxidized polymer chain. Therefore, for strong interaction between neutral molecules and polymer chain, these molecules occupy sites, blocking these sites for ClO_4^- anions, and, as a consequence, decreasing the charge. Solvents with high π^* (or basicity) present a high electric orientation and can force the polymer structure to expand, increasing the ionic diffusion inside the film, leading to a better charge storage features. Finally, high dielectric constant (ϵ) result in a low charge storage ability influencing the electric field inside the film and the swelling process as shown previously by Varela et al. [9].

3.2. Mass change analysis

The same procedure was used to relate mass gains during oxidation to solvent parameters. The obtained correlation was very poor in this case, with uncertainties of about 50% and $R^2=0.82524$. Plots for calculated and experimental mass gains are shown in Fig. 4. Note that there are no units in both mass gain axes, since these amounts were normalized by PPY film mass, in the same way of the charge. This result is expected if one focus attention in mass gain and charge values in Fig. 2.

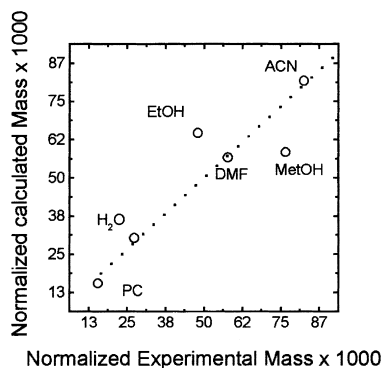


Fig. 4. Normalized calculated mass gain (obtained with the same set of parameters of calculated charge-Eq. (1)) as a function of the normalized experimental mass gain (oxidation process) for the different solvents. The experimental mass was the mass value at 0.2 V in the mass/potential profile of Fig. 1.

The mass gain can be related with the same parameters used for charge only if the electroneutrality is attained by the same ionic contributions in all solvents. In other words, if the individual amounts of cations and anions, which participate during charge compensation process, do not depend on the used solvent, so, in this case, differences in mass gain could be related only to the solvent participation. The next step is tried to investigate how the electroneutrality is attained in each solvent, take into consideration both j/E and $\Delta m/E$ profiles for PPY shown above.

The use of EQCM data to extract the contributions of anions and cations to the observed mass changes during a given EQCM voltammetric scan have been previously described elsewhere [24,25], and will be simplified here. The treatment starts from the global mass and charge balances during the charge compensation process. And the fluxes of Li^+ and ClO_4^- ions with a contribution from solvent, as a function of the current density and mass flux are given by

$$\frac{d\left(\hat{I}_{\text{Li}^+(\text{E})} + \frac{W_s}{W_{\text{LiClO}_4}} \hat{I}_{\text{s}(\text{E})}\right)}{dt} = \frac{1}{W_{\text{LiClO}_4}} \frac{d(\ddot{A}m(\text{E}))}{dt} - \frac{W_{\text{ClO}_4^-} j(\text{E})}{W_{\text{LiClO}_4} F} \quad (2)$$

and

$$\frac{d\left(\hat{I}_{\text{ClO}_4^-(\text{E})} + \frac{W_s}{W_{\text{LiClO}_4}} \hat{I}_{\text{s}(\text{E})}\right)}{dt} = \frac{1}{W_{\text{LiClO}_4}} \frac{d(\ddot{A}m(\text{E}))}{dt} + \frac{W_{\text{Li}^+} j(\text{E})}{W_{\text{LiClO}_4} F} \quad (3)$$

where F is the Faraday' constant, j is the current density, W is the molar mass of lithium, perchlorate ions or solvent molecules (s) and \hat{I} is the number of moles of cations, anions or solvent molecules undergoing transport. Negative flux values refer to ejection and positive values to incorporation of species in the film. Note that both fluxes contain contribution from solvent; this is because the set of simul-

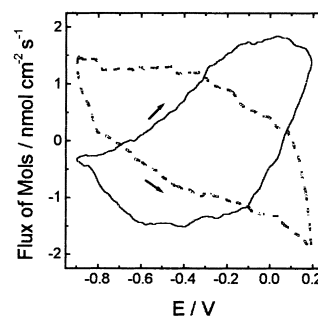


Fig. 5. Fluxes of cation+solvent (full line) and anion+solvent (dotted line) for PPY films in LiClO_4 -EtOH solution. $v=0.05$ V/s. Data calculated from Fig. 1b.

taneous expressions for charge and mass is non-determined [24].

Fig. 5 shows fluxes of cations (dotted line) and anions (full line) for PPY modified electrodes in LiClO_4 -EtOH solution. The flux for anion+solvent profile is similar to the voltammogram shape showed in Fig. 1b, but cation+solvent flux is very important to the electroneutralization process, considering both maximum values attained at about oxidation peak potential.

Cation and anion participation in the electroneutralization process as reported by Kaufman and Kanazawa [26] in the first study of PPY modified electrodes using EQCM technique. As a result, for poorly solvated film some perchlorate anions tend to stay trapped inside the film, decreasing the mass gain during cycling and in the reduced state, ClO_4^- resides inside the film as $\text{Li}^+ + \text{ClO}_4^-$ pairs [26,27].

Nevertheless, keep in mind that the separation between ionic and neutral species fluxes is not an easy task, a way to estimate and compare the Li^+ participation in different solvents studied is to calculate a transport number for Li^+ . Since there is no possibility to neglect the solvent contribution for this flux, it is possible to obtain an 'apparent' lithium transport number, $t_{\text{Li}^+\text{ap}}$. So, this amount can be calculated using the following equation

$$t_{\text{Li}^+\text{ap}} = \frac{d\left(\hat{I}_{\text{Li}^+(\text{E})} + \frac{W_s}{W_{\text{LiClO}_4}} \hat{I}_{\text{s}(\text{E})}\right)}{dt} \times F \quad (4)$$

Eq. (4) shows the contribution of lithium cations+solvent to the charge transport. Even in this case, considering the solvent contribution, the apparent lithium transport number is inversely proportional to the total mass gain. Since, the $t_{\text{Li}^+\text{ap}}$ is related to the mass leaving the film during oxidation process.

The other two terms influencing the mass gain are the molar mass (or volume) of the solvents and charge. In order to obtain dimensionless parameters after multiple regression, volume and the molar mass was normalized by the terms for the largest solvent molecule, PC (102 g mol^{-1}), and charge was normalized by the charge for PPY film in

Table 2
Selected parameters for the mass gain multiple regression

Solvent	M/M_{PC}	V/V_{PC}	$t_{Li^+_{ap}}$	q/q_{water}
ACN	0.40	0.171	0.24	0.96
PC	1.00	1.000	0.41	0.24
DMF	0.72	0.541	0.20	0.46
EtOH	0.45	0.250	0.47	0.73
MetOH	0.31	0.112	0.31	0.88
Water	0.18	0.017	0.73	1.00

water solution (about 5 mC cm^{-2}). Table 2 summarizes all terms used in multiple regression processing for mass gain. The resulting equation for normalized mass gain, mg_N , was

$$mg_N \times 1000 = 103.6 - 126.6t_{Li^+_{ap}} + 28.1 \frac{q}{q_{water}} - 43.5 \frac{M}{M_{PC}} \quad (5)$$

The uncertainties in each obtained coefficient were less than 11% and R^2 was found to be 0.99450. Fig. 6 shows the obtained results for calculated and experimental data. The linear behavior attests the good quality for the regression processing.

Eq. (5) shows that the cation transport through film/solution interface has an inverse influence on the total mass gain during cycling. The term $t_{Li^+_{ap}}$ can be associated to the polymer solvation, since ionic diffusion is more difficult when the polymer film is poorly solvated and Li^+ cations can diffuse faster than ClO_4^- [28]. So, $t_{Li^+_{ap}}$ is inversely related to the polymer solvation. The normalized charge was found to be proportional to the mass gain, since it is related to the ionic population inside the film. The normalized molar mass, present an inverse influence on the mass gain, this term can be understood considering the solvent radius, so, large solvent molecules do not diffuse easier to the polymer matrix. In fact, using normalized volume instead molar mass, a good correlation can be also obtained, and equation

can be written as

$$mg_N \times 1000 = 84.7 - 118.1t_{Li^+_{ap}} + 33.3 \frac{q}{q_{water}} - 30.0 \frac{V}{V_{PC}} \quad (6)$$

In this case, results for the uncertainties in each obtained coefficient and R^2 value were less than 13% and 0.99404, very similar to that observed when molar mass is used.

Finally, analyzing Eqs. (5) and (6), it is observed that the ratio q/q_{water} include all parameters used in Eq. (1) and, other terms were included in order to rationalize the experimental results for mass gain during oxidation. With this purpose, $t_{Li^+_{ap}}$ and solvent molar mass (or volume) were included. The $t_{Li^+_{ap}}$ informs about the nature of the compensating ions considering the differences in electroneutralization process for each solvent. Both solvent molar mass and volume provide information about the incorporation of neutral species inside the film and, consequently, about the mass gain during oxidation. So, through this approach it was possible to relate both charge storage and mass gain during oxidation process to the selected solvent parameters and experimental data from EQCM experiments.

4. Conclusions

Through simultaneous EQCM and CV experiments, the behavior of polypyrrol modified electrode was studied in the presence of $LiClO_4$ salt in different solvents. The film electroactivity increased in the order: $PC < DMF < EtOH < MetOH < ACN < water$. Mass gained in the order: $PC < water < EtOH < DMF < MetOH < ACN$. The charge storage was discussed as suggested by Otero et al. [11], while, the mass gain during oxidation was rationalized considering the charge storage, apparent lithium transport number and molar mass (or volume) of the solvent, using multiple regression analysis.

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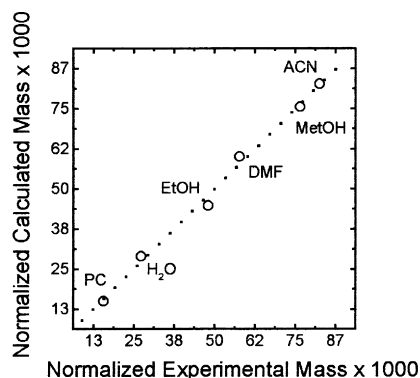


Fig. 6. Normalized calculated mass gain (using Eq. (5)) as a function of the normalized experimental mass gain (oxidation process) for the different solvents. The experimental mass was the mass value at 0.2 V in the mass/potential profile of Fig. 1.

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