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### ► To cite this version:

D. Giménez-Romero, P.R. Bueno, Claude Gabrielli, C. Castaño, Hubert Perrot, et al.. Mass/charge balance as a tool to estimate dimensional change in polypyrrole-based actuators. *Electrochemistry Communications*, 2006, 8 (1), pp.195-199. 10.1016/j.elecom.2005.11.007 . hal-04163610

**HAL Id: hal-04163610**

**<https://hal.science/hal-04163610>**

Submitted on 24 Mar 2024

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# Mass/charge balance as a tool to estimate dimensional change in polypyrrole-based actuators

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The deconvolution of the voltammograms of polypyrrole electrochemistry has proved to be possible through the electrochemical quartz crystal microbalance data using the  $F(dm/dQ)$  function. This deconvolution allows the evolution of the thickness of the polypyrrole films during their redox processes to be estimated and therefore, the mechanical contraction/decontraction of this polymer as a function of the ionic exchange processes can be evaluated.

*Keywords:* Polypyrrole; EQCM; Thickness change

## 1. Introduction

Conducting polymers represent an entirely new class of functional material whose unique properties are facilitating the development of intelligent material systems [1]. Among several modified conducting polymers, polypyrrole was optimized to display properties that draw near some of the performance characteristics of natural muscle. When such kind of polymer is subjected to an electric field in an appropriate electrolytic medium, the polymer contracts like a muscle; when the field is removed, the polymer relaxes similarly to an artificial muscle [2–4]. The result is a polymer actuator material that flexes like a muscle providing dimensional changes [2–4]. The demand for actuators featuring biomimetic properties, such as linearity, high power density and compliance, is growing in microrobotics and bioengineering. It exploits the electromechanical phenomena of  $\pi$ -electron conjugated conducting polymers, occurring when ionic species are exchanged with the

surrounding medium, i.e., solid or liquid electrolyte. From both scientific and technological point of view, it is important to design new methodologies to study the relationship between dimensional changes and charge injection in conducting polymers which are capable of acting as artificial muscles.

The main goal of the present work is to develop a methodology to estimate the dimensional change during electron transfer in polymer actuators. The methodology is based on the knowledge of the electron transfer mass/charge balance process that can be evaluated by using electrochemical methods, such as electrochemical quartz crystal microbalance (EQCM). EQCM technique was used here as a tool to obtain information on the exchanged mass during the electrochemical processes involved in the operation of the device (polymer acting as an artificial muscle). As it shall be demonstrated below, the proposed approach can be used to estimate the dimensional variation of the polymer-based actuator as a function of the mass/charge balance process involved in the operation of the actuators.

To start to describe the mentioned approach it is first important to describe the use of combined EQCM and

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traditional cyclic voltammetry (CV) techniques as a tool to obtain an estimation of the molecular mass of the species involved in the electronic transfers by means of the mass /charge ratio [5], as following:

$$F \frac{dm}{dQ} = \sum \alpha_i \frac{z_i}{x_i} MW_i v_i \pm \text{mass changes due to uncharged species} \quad (1)$$

where  $x_i$  is the charge of the exchanged species. Furthermore, in the expression of Eq. (1),  $\alpha_i$  is assumed to be  $-1$  when an exchange of cationic species (the guest species is positively charged) occurs with the host and  $+1$  when an exchange of anionic species (the guest species is negatively charged) exists. Therefore, the sign indicates the direction of the anionic or cationic movement during the ionic exchange process.  $F$  is the Faraday constant (96484.56 C/mol),  $dQ$  the electric charge which crosses the polymer-based actuator and  $dm$  is the concomitant mass change.  $MW_i$  and  $z_i$  represent the molecular mass of the charged species and the number of electrons involved in  $i$ th faradaic process, respectively.  $v_i$  represents the percentage of the electrical charge balanced by the participation of the ion involved in the global electrochemical process. In some situations, it is also important to consider uncharged species, such as the solvent molecules that likely participate in the electrochemical process. In such a case, a mass change occurs but its movement does not cause any electrical charge flux and consequently, no faradaic current is associated to the solvent molecule movement. Nonetheless, the participation of these species modifies the mass/charge ratio. The function represented in Eq. (1) will be named throughout this text as the  $F(dm/dQ)$  function.

## 2. Experimental

The electrochemical experiments were carried out in a typical three electrode cell, where a gold electrode of the quartz crystal microbalance (CQE, Troyes, France) of about 25 mm<sup>2</sup> was the working electrode, a platinum plate the counter electrode and a saturated calomel electrode (SCE) the reference electrode. All experiments were carried out by using a homemade UPR15/RT0100 oscillator of 9 MHz, a TC 110 Yokogawa frequency meter and an AUTOLAB potentiostat.

The EQCM was calibrated by means of a galvanostatic Cu electrodeposition, which gave an experimental Sauerbrey constant equal to  $16.3 \times 10^7$  Hz g<sup>-1</sup> cm<sup>2</sup>. This calibration procedure has been commonly used [6,7].

Polypyrrole films were prepared from 0.1 M distilled pyrrole + 0.05 M sodium dodecyl sulphate (NaDS) (Rectapur<sup>®</sup>). This low NaDS concentration was chosen to avoid surfactant aggregates and to obtain films of good quality in term of mechanical properties [8]. From these solutions, a cyclic potential scan between 0 and 0.675 V versus SCE at a 10 mV/s rate was applied twice. These films were sufficiently thin (about 0.1 μm) to allow the Sauerbrey equation

[9] to be used without limitation coming from viscoelastic properties of the polymer film [10,11]. Other non-ideal contributions which could cause frequency shifts, like roughness, are not expected for very thin films [12].

Voltammetric experiments were carried out in the potential interval from  $-1.05$  to  $0.4$  V. The solution was composed of 0.25 M NaCl (A.R. Normapur<sup>®</sup>) and it was deaerated by bubbling N<sub>2</sub> (Air Liquide) during 5 min.

## 3. Results and discussion

It is possible to observe in Fig. 1 that the polypyrrole film-based actuators present two different electron transfer processes in the potential range of the experiment. These transfers can be due to the simultaneous synthesis of two different variants of polypyrrole in these deposit conditions [13]. Both electron transfer processes are clearly separated during the anodic scan (there are two electrochemical peaks) whereas they overlap during the cathodic scan (there is only one electrochemical peak in the anodic potential range, see Fig. 1).

Fig. 1 also shows the  $F(dm/dQ)$  function changes. The potential range between  $[0.50, \text{ and } -0.25]$  V is characterized by the movement of the anionic species and the  $F(dm/dQ)$  function has a value of about  $100 \text{ g mol}^{-1}$ , whereas the anodic region  $[-0.50, -0.25]$  V is characterized by the movement of the cationic species with the  $F(dm/dQ)$  function presenting a value of about  $-300 \text{ g mol}^{-1}$ . The other zones observed in the voltammogram are just transition regions where both ions are simultaneously exchanged. Consequently, the value of  $F(dm/dQ)$  function is not constant and it presents a potential dependence.

This result is corroborated in Fig. 2, since this figure shows the evolution of the voltammograms according to the anion present in solution. It is possible to see in this figure that, in the anodic region between  $[-0.50, \text{ and } -0.25]$  V, the current remains more or less constant when

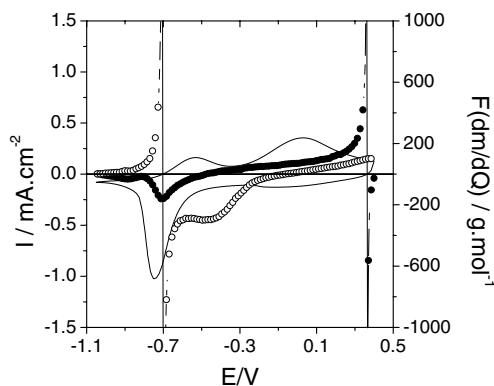


Fig. 1. Curves of  $F(dm/dQ)$  function versus potential during a linear scan of the polypyrrole film doped with NaDS. Experimental conditions were 0.25 M NaCl and scan rate 20 mV/s. The potential range was from 0.40 to  $-1.05$  V and the solution was deaerated by bubbling N<sub>2</sub> during 5 min. (●) is the  $F(dm/dQ)$  function during cathodic scan and (○) the  $F(dm/dQ)$  function during the anodic scan.

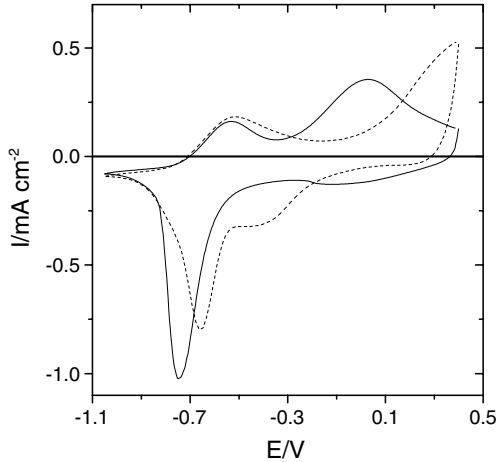


Fig. 2. Curves of current versus potential during the linear potential scan of the polypyrrole film doped with NaDS. The potential range was from 0.40 to  $-1.05$  V and the solution was deaerated by bubbling  $N_2$  for 5 min. The continuous line is the voltammogram in 0.25 M NaCl and the dashed line the voltammogram in 0.25 M NaAc at 20 mV/s.

the anion present in solution is changed. Therefore, it is possible to say that this potential interval is characterized only by the movement of the cations. However, the other potential intervals are very influenced by the anions present in solution and consequently, all these intervals involve the exchange of anions. Thus, the cation exchange occurs in the anodic region between  $[-0.50, \text{ and } -0.25]$  V, whereas the anion exchange occurs in the anodic region between  $[0.50, \text{ and } -0.25]$  V. Both ionic exchanges have been observed in the literature [13–15].

Only sodium cation ( $-23 \text{ g mol}^{-1}$ ) and chloride anion ( $35.5 \text{ g mol}^{-1}$ ) are the ions present in the ionic reservoir. Accordingly, it is possible to infer that these ions are the only ions exchanged to maintain the electroneutrality of polypyrrole-based films [14,15]. The fact that the  $F(dm/dQ)$  function values are higher than the molecular mass of the ions demonstrates that the exchange movement is accompanied by solvent molecules, which is in agreement to the major literature approach [15,16]. This solvent movement can be explained by the reversible 3D electrode transitions during the redox processes of the polypyrrole-based films [17–20].

The solvent exchange proposed by several authors [15,16] takes place at the same time that the ionic species exchange since it is associated to the ion movement and therefore, it is not a random movement. The  $F(dm/dQ)$  function behavior and values in potential ranges corresponding to that related to anodic peaks do not change significantly as a function of the electrochemical potential. This behavior is explained by the fact that the movement depends on the conformational changes which take place in association to other electron transfer processes (i.e., different ionic exchanges). On the other hand, this result is also corroborated by means of *ac*-electrogravimetry [14], since the solvent exchange takes place at intermediate frequencies whereas the experiments of cyclic voltammetry

have been carried out at low frequencies. Consequently, the solvent and the ion exchange are difficult to separate during the experiments of cyclic voltammetry in these experimental conditions.

Accordingly, the number of the water molecules that are exchanged between the polymer-based actuator and the ionic reservoir (electrolyte) due to the conformational changes can be easily calculated, by means of the experimental values of the  $F(dm/dQ)$  function, as following:

$$\left| F \frac{dm}{dQ} \right|_{\text{experimental}} = \left| F \frac{dm}{dQ} \right|_{\text{theoretical}}^{\text{ion}} + 18n \quad (2)$$

where  $n$  is the number of water molecules available to be exchanged due to polymer-based conformation. As a result, the chloride anion movement occurs associated together with about four water molecules (theoretical  $F(dm/dQ)$  about  $107.5 \text{ g mol}^{-1}$ ), whereas the sodium cation is exchanged together with 15 water molecules (theoretical  $F(dm/dQ)$  about  $-293 \text{ g mol}^{-1}$ ) due to the fact that the exchange of these ions takes place at the same time that the volumetric change of the polymer.

As a result, the voltammetric current can be deconvoluted by using the  $F(dm/dQ)$  function values (Fig. 3). Consequently, the total current,  $I$ , can be expressed as the sum of two currents:  $I_1$ , the current related to the anion exchange and  $I_2$ , the current due to the cation exchange.

$$I = I_1 + I_2, \text{ where } I_1 = v_1 I \text{ and } I_2 = (1 - v_1) I \quad (3)$$

At the same time, the experimental  $F(dm/dQ)$  function can also be written, for such a process, as following:

$$F \frac{dm}{dQ} \Big|_{\text{experimental}} = v_1 F \frac{dm}{dQ} \Big|_1 + (1 - v_1) F \frac{dm}{dQ} \Big|_2 \quad (4)$$

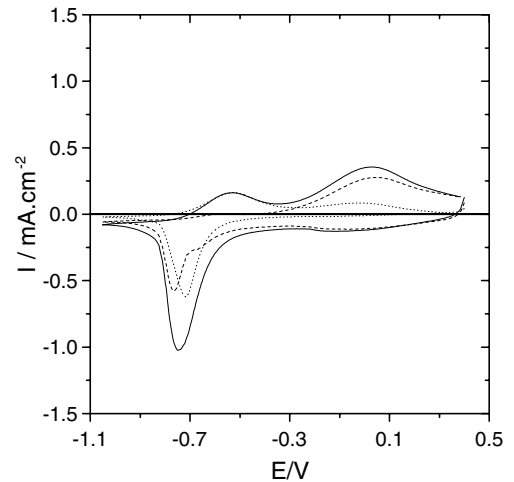


Fig. 3. Voltammogram deconvolution in the two electrochemical processes of the polypyrrole. The experimental voltammograms are showed in Fig. 1. Continuous line is the experimental voltammogram, dashed line the voltammogram due to the anions exchange and dotted line is the voltammogram due to the cations exchange.

where the values of the  $F(dm/dQ)$  function correspond to the molecular mass of the exchanged ions plus the number of water molecules which accompanies them, i.e.  $-293 \text{ g mol}^{-1}$  for the sodium cation and  $107.5 \text{ g mol}^{-1}$  for the chloride ion. This is due to the fact that the solvent exchange is mainly related to the dimensional changes of polypyrrole films which take place during its respective electrochemical processes and besides, due to the fact that the experiment is carried out at low scan rate. Consequently, both processes are not separated in the time.

From Eqs. (3) and (4), it is possible to obtain  $I_1$  and  $I_2$  values (see Fig. 3). Therefore, the charge related to these partial currents allows the polypyrrole-based film thickness to be monitored as a function of the potential. Such relationship is possible due to the fact that the  $F(dm/dQ)$  function is a percentage value of the movement associated to the contribution of each electroactive state of the polypyrrole-based actuator. Therefore, if it is possible to obtain the amount of water molecules which is exchanged due to the conformation changes and by considering the films as being homogeneous, the following expression that relates the film thickness and the charges exchanged can be applied:

$$d = N_A \times \frac{V_{\text{H}_2\text{O}} (Q_{\text{anion}} n_{\text{H}_2\text{O}}^{\text{anion}} - Q_{\text{cation}} n_{\text{H}_2\text{O}}^{\text{cation}}) + Q_{\text{anion}} V_{\text{anion}} - Q_{\text{cation}} V_{\text{cation}}}{FA_{\text{electrode}}} \quad (5)$$

where  $d$  is the estimated increment of the polypyrrole film thickness,  $N_A$  the Avogadro number,  $V_i$  is the volume of the molecule  $i$ ,  $Q_i$  the electrical charge due to the movement of the species  $i$ ,  $A_{\text{electrode}}$  is the working electrode surface and  $n_{\text{H}_2\text{O}}^i$  is the number of water molecules which are exchanged at the same time that the species  $i$ . Due to the non-additiveness of the volume into the polymeric matrix, the calculated value in the Eq. (5) is only the maximum value of the thickness increment that this film can reach during their redox processes.

Fig. 4 shows the estimation of the evolution of the polypyrrole film thickness with respect to the applied potential. This result is in agreement with the evolution of the film thickness as a function of potential calculated by means of an atomic force microscope by Smela et al. [21]. Thus, the small difference between the values estimated by means of the Eq. (5) and the experimental values can be used to quantify the kind of interactions which take place into the polymeric matrix. Nonetheless, it is possible to estimate the dimensional values of polymer-based actuators from the appropriate use of the mass/charge balance that arises from the combined EQCM and CV techniques.

In conclusion, it was shown in this paper that, from the  $F(dm/dQ)$  function, it was possible to estimate the thickness change of the polypyrrole-based films during ionic exchange processes. This leads to a quick and easy method to estimate the thickness increment of electroactive films during a redox process. At the same time, in this paper, a

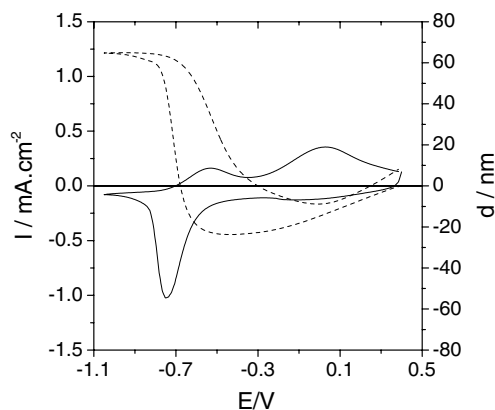


Fig. 4. Estimated curve showing the evolution of the polypyrrole-based film thickness as a function of potential. Continuous line is the experimental voltammogram and the dashed line is the estimated increment of the polypyrrole-based film thickness. For this calculus (Eq. (5)), the value of  $V_{\text{H}_2\text{O}}$  is equal to  $2.99 \times 10^{-29} \text{ m}^3$ ,  $V_{\text{cation}}$  is  $3.94 \times 10^{-29} \text{ m}^3$  and  $V_{\text{anion}}$  is  $3.77 \times 10^{-29} \text{ m}^3$ .

voltammetric method was proposed to calculate the number of water molecules exchanged during the charge compensation process occurring in a redox reaction from the  $F(dm/dQ)$  function.

## Acknowledgments

This work has been supported by FEDER-CICyT project CTQ 2004-08026/BQV. J.D. Giménez-Romero acknowledges a Fellowship from the Generalitat Valenciana, Post-Doctoral Program. Paulo R. Bueno acknowledged São Paulo state research funding institution (FAPESP) by the project under No. 02/06693-3. J. García-Jareño acknowledges their position to the Ramon y Cajal Program (Spanish Ministry of education and science).

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