



# A formal representation of the anodic voltammetric response of polyaniline

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## ABSTRACT

It is presented a formal representation of the oxidation of Polyaniline (Pani) films that allows fitting the experimental voltammetric current-potential response of Pani modified electrodes. The model includes interactions between the redox centers and takes into account both the faradaic and the capacitive current contributions to the total voltammetric response. Although the separation of both contributions is not possible by just voltammetric techniques, the present formalism allows completely characterizing the voltammetric anodic behavior of conducting polymers. Its suitability is proved to represent the current-potential response of Pani films of different thickness in 3.7 M H<sub>2</sub>SO<sub>4</sub> solutions.

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## 1. Introduction

The electrochemistry of conducting polymers (CPs) is a complex subject; the charge transfer is associated to a number of processes of different nature [1]. Thus, together with the electron transfer process, there are changes in the degree of binding of the polymeric chains, ingress and egress of protons and coions, changes in the state of swelling (deformation) of the polymer matrix (reduced and oxidized), and so on. Moreover, there are oxidized and reduced domains within the polymer that grow or decrease according the polymer is being oxidized and reduced, respectively. Besides, many of these states and properties (deformation, swelling and redox potential) are coupled among them in the sense that changing one of them makes the others to change [2,3]. Furthermore, it is known that the voltammetric response of CPs such as Polypyrrole [4], Polyaniline (Pani) [5] and Polythiophene [6] contains both a faradaic and a capacitive contributions to the total current. The capacitive contribution is proportional to the amount of oxidized polymer. Despite the large amount of work related to the voltammetric response of CPs, only a few works consider this fact [7–15]. Two possible explanations refer to the origin of the capacitive current in the voltammetric response of CPs. One considers that it is mainly due to the fact that as the polymer is partially oxidized it becomes an electronic conductor, with metal-like properties and the interphase polymer/solution becomes charged as it is polarized [7]. The other one considers that it is due to ions deep trapped inside the polymer [8]. Whatever the facts may be, the capacitive current distorts the voltammetric

response of these CPs and the characteristic peak parameters, potential and current, do not have their usual meaning for a reversible electrochemical process [16]. So, the analysis of the voltammetric response of CPs should be done taking into account the capacitive current. However, it must be keep in mind that, no unambiguous separation of the total current into its capacitive and faradaic contributions can be made, unless the faradaic charge or the potential of zero charge of the oxidized polymer are measured by other methods.

In this work, it is presented an analysis of the voltammetric response of the oxidation process of Pani films, of different thickness, in acid media. Initially, it is taken into account previous considerations about the capacitive and faradaic currents [7], associated with the voltammetric switching of CPs films between the insulating and the conducting states. In the present paper, the analysis is extended, including the possibility of interactions between the redox centers. The formalism is deduced on the basis of lattice statistics [17], and the expressions for the peak parameters are obtained. Experimental data about the voltammetric response of Pani in the experimental conditions mentioned above are presented. The results prove the suitability of this model to represent the voltammetric oxidation behavior of CPs, what allows fitting the experimental data to the model.

A word of caution has to be given when considering the present experiments. It is well known that Pani films in the reduced state undergo a transformation process called ageing [18], memory effect [19], relaxation [20] or first cycle effect [21]. This process is characterized by a linear dependence of the extent of the ageing with the logarithm of the time expended at the reduction potential. Then, the  $j/E$  response depends on this ageing time. Therefore, care should be taken to maintain reproducible conditions when

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studying the voltammetric oxidation response of these polymers. At short times spent at the reduction potential ( $0 \text{ s} < t < 100 \text{ s}$ ), depending on the film thickness and proton concentration in the external solution [22], both the ageing process and the reduction of the polymer occur simultaneously. In this work, the  $j/E$  oxidation response is analyzed under stationary cycling conditions. The experimental results (Figs. 1–4), do not show any interference of the ageing process on the voltammetric response.

The formalism presented in this paper is devoted to evaluate just the anodic process of Pani. The main reason is related to the fact that the ageing process is evaluated by the features of the anodic peak during the first anodic scan after the ageing of the film has taken place. The understanding of the changes in the voltammetric behavior after the ageing requires a formal representation of the voltammetric response. Besides, the anodic and cathodic voltammetric response of Pani shows a hysteretic behavior for which, at the moment, there is no sound explanation.

## 2. Experimental

The polymer was obtained by electropolymerization on Au electrodes by cycling the potential at  $\nu = 0.1 \text{ V s}^{-1}$ , between  $-0.2 \text{ V}$  vs. SCE, and the potential corresponding to that of the beginning of the oxidation of the monomer, around  $0.8 \text{ V}$  vs. SCE, as described before [22,23]. The films were grown until the desired voltammetric charge was reached. The synthesis solutions were  $0.5 \text{ M}$  in the monomer in aqueous solution of  $3.7 \text{ M H}_2\text{SO}_4$ . The area of the working electrode was  $0.154 \text{ cm}^2$ . The voltammetric charge of the films employed in this work,  $Q_T(0.45)$ , was determined from the integration of the  $j/E$  profiles of the voltammetric response in the potential range comprised between  $-0.2$  and  $0.45 \text{ V}$  vs. SCE. Although the film thickness could be derived from correlations between the anodic voltammetric charge and film thickness, previously established by ellipsometry for these types of polymers, for the reasons stated in previous works the anodic charge corresponding to the first anodic peak,  $Q_T(0.45)$ , integrated between  $-0.2$  and  $0.45 \text{ V}$  vs. SCE, will be quoted as a measure of the film thickness [22]. The polymer films charges were in the range  $3 \text{ mC cm}^{-2} < Q_T(0.45) < 92 \text{ mC cm}^{-2}$ .

The electrolyte solutions were prepared from  $\text{H}_2\text{SO}_4$  (97%) (Backer, p.a.); aniline (Fluka-Guarantee, puriss. p.a.) and Milli-Q® water. The monomer was employed as received.

The experimental set-up for the voltammetric measurements was a three-electrode glass cell as described elsewhere [22,23]. The auxiliary electrode was a cylindrical Pt foil. The reference electrode was a Saturated Calomel Electrode (SCE). All potentials in the text,  $E$ , are referred to this electrode.

Conventional voltammetry was performed using a Teq-03 potentiostat at different sweep rates,  $\nu$ , ranging from  $10^{-3}$  to  $0.5 \text{ V s}^{-1}$  and covering a potential region between  $-0.2 \text{ V}$  and  $0.45 \text{ V}$ . All experiments were carried out in  $3.7 \text{ M H}_2\text{SO}_4$  solutions.

The ohmic resistance was previously obtained from the impedance response by extrapolating the real component to infinite frequency [23,24]. It resulted to be smaller than  $0.5 \Omega$ . These impedance measurements were performed with a PARC 309 impedance measurement system.

## 3. Results

The sweep rate dependence of Pani films is shown in Fig. 1. The well known features of the linear dependence of the peak current on the sweep rate and the independence of the peak potential on the sweep rate are shown in Fig. 2. The data in Fig. 1 are very similar in shape to those reported in reference [25], even though those were made with chemically synthesized Pani.

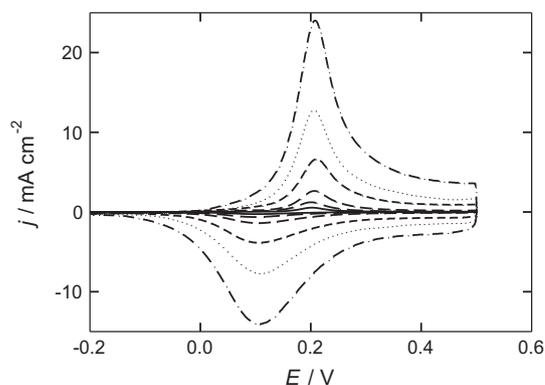


Fig. 1. Voltammetric current-potential relationship for a Pani film at different sweep rates,  $\nu$ . Electrolyte:  $3.7 \text{ M H}_2\text{SO}_4$ .  $Q_T(0.45) = 32.0 \text{ mC cm}^{-2}$ . (—)  $0.002 \text{ V s}^{-1}$ , (---)  $0.005 \text{ V s}^{-1}$ , (- - -)  $0.01 \text{ V s}^{-1}$ , (· · ·)  $0.025 \text{ V s}^{-1}$ , (— · —)  $0.050 \text{ V s}^{-1}$ , (— · — · —)  $0.1 \text{ V s}^{-1}$ .

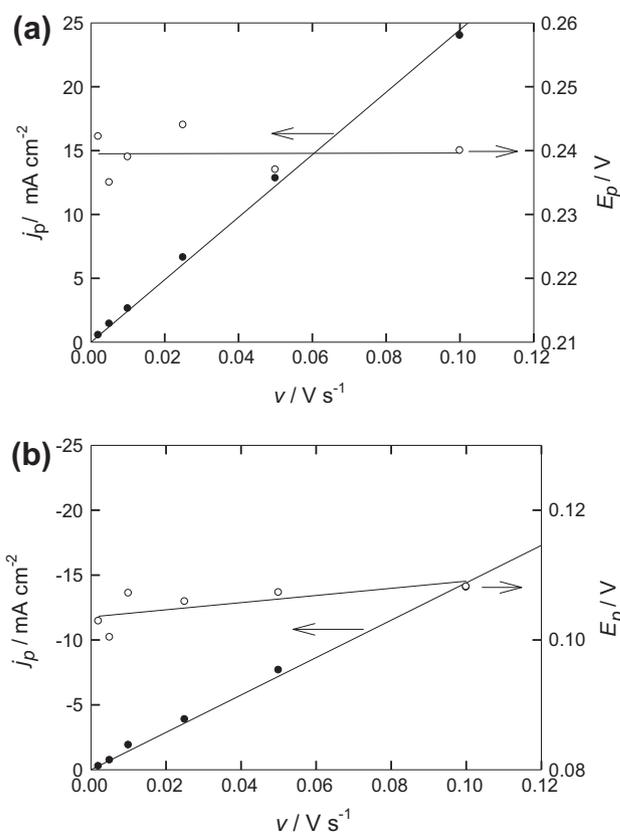
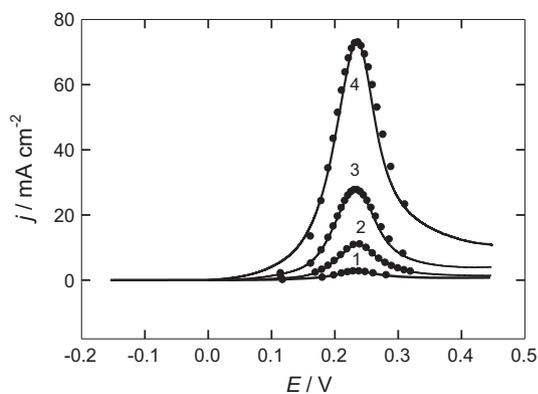


Fig. 2. Dependence of the peak current (left) and potential (right) on the sweep rate for the results shown in Fig. 1, (a) anodic sweep, (b) cathodic sweep.

In the range  $0.02 < \nu < 0.1 \text{ V s}^{-1}$ , the peak density of current,  $j_p$ , changes linearly with  $\nu$  and peak potential,  $E_p$ , is independent of  $\nu$ . From this sweep rate on (not shown in Figs. 1 and 2)  $j_p$  departs negatively from the linear relation and  $E_p$  slightly increases with  $\nu$ .

It is clear that the data of Fig. 1 show some sort of hysteresis, in the sense that the peak potentials for the forward and backward reactions do not coincide [26]. Otherwise, in the sweep range studied, the peak current and potential values, for both reactions fulfill, independently, the criteria for electrochemically reversible reactions. At the present time, there is no definitive explanation for this type of hysteresis. If it were due to kinetics reasons, it should be dependent on the time scale. However, it seems to depend on the nature of the counter ions present in the external electrolyte



**Fig. 3.** Voltammetric current-potential relationship for Pani films of different total charges,  $Q_T$  (0.45): (1)  $3.6 \text{ mC cm}^{-2}$ , (2)  $10.5 \text{ mC cm}^{-2}$ , (3)  $33.2 \text{ mC cm}^{-2}$ , (4)  $92.2 \text{ mC cm}^{-2}$ . Electrolyte:  $3.7 \text{ M H}_2\text{SO}_4$ ,  $\nu = 0.1 \text{ V s}^{-1}$ . (●) calculated with Eq. (27), the results of the fit are shown in Table 1.

[27]. For these reasons, in this work it will be consider just the oxidation reaction.

The current-potential responses of Pani films, of different voltammetric charges, are shown in Fig. 3. It is seen that the peak current increases linearly with the thickness, whereas the peak potential does not depend on it (Fig. 4).

In Fig. 5, the charges obtained from the voltammetric response presented in Fig. 3 are shown as a function of the potential. The characteristic feature of these plots is the linear dependence of the charge on the potential, in the potential range where the charge transfer process has finished. This is the potential range where the polymer, partially oxidized, has achieved its electronic conductivity, with metal-like properties and the interphase polymer/solution becomes charged as it is polarized.

### 3.1. Theory

The polymer is oxidized at the metal/polymer interface according to the reaction:



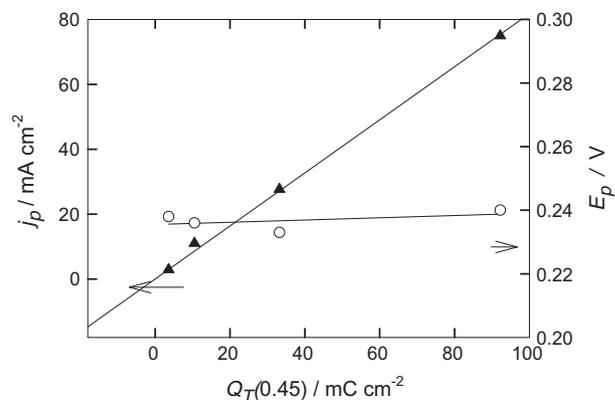
Then, charge must be transported across the film. At the polymer/solution interface, ionic charge transfer occurs by which ionic fluxes are established to maintain the polymer electroneutrality. Any of these processes, or combination of them, may be the rate determining step. In order to simplify the analysis we will assume that both charge transfer reactions are very fast and also that there no hindrance to charge transport within the polymer, so at each potential the polymer can be considered at equilibrium. Also, and in order to avoid the consideration of membrane potentials, it will be assumed that an infinitely supported situation can be achieved inside the polymer [28].

On the basis stated in reference [7], the total charge,  $Q_T$  can be written as the sum of the capacitive charge,  $Q_C$ , and that due to the charge transfer, that it will be called faradaic charge,  $Q_F$ .

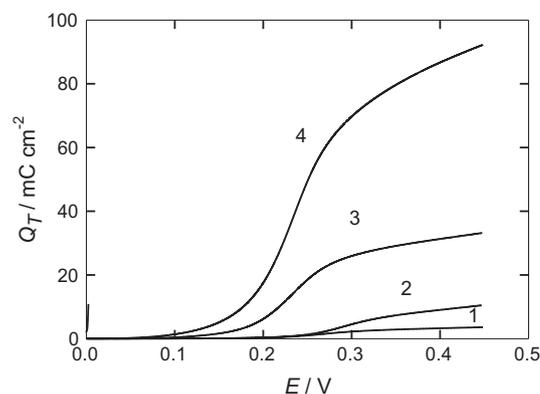
$$Q_T(E) = Q_C(E) + Q_F(E) \quad (2)$$

Eq. (2) is based on the following assumptions: (i) The integral capacitance of the polymer,  $K$ , is proportional to the faradaic charge. Thus,  $K = aQ_F$ , where  $a$  is a proportionality constant. Also, the integral capacitance can be written as  $K = Q_C/(E - E_z)$ , being  $E$  the applied potential and  $E_z$  the potential of zero charge of the oxidized material. (ii) The differential capacitance of the conducting form of the polymers is independent of the applied potential. (iii) The differential capacitance of the base electrode is negligible.

Assumption (i) allows writing the capacitive charge as:



**Fig. 4.** Thickness dependence of the voltammetric peak parameters,  $j_p$  and  $E_p$ . The conditions are the same as in Fig. 3.



**Fig. 5.** Voltammetric charge,  $Q_T$ , as a function of the applied potential for the same conditions as in Fig. 3.

$$Q_C(E) = a(E - E_z)Q_F(E) \quad (3)$$

So, the total charge,  $Q_T$ , can be written as:

$$Q_T(E) = (1 + a(E - E_z))Q_F(E) \quad (4)$$

From this equation the total current,  $j_T$ , can be obtained by differentiation with respect to the time:

$$j_T(E) = (1 + a(E - E_z))j_F + \nu aQ_F(E) \quad (5)$$

where  $\nu$  is the sweep rate,  $\nu = dE/dt = \text{constant}$ .

As a consequence of the existence of a capacitance, the voltammetric current is not zero at high potentials, even when the faradaic process has finished. Then, at high enough potentials,  $E > E_L$ , where  $j_F = 0$ ; the current is only capacitive and it follows that:

$$Q_F(E > E_L) = Q^0 \quad (6)$$

where  $Q^0$  is the maximum faradaic charge,

$$j_T(E > E_L) = \nu aQ^0 \quad (7)$$

and

$$Q_T(E > E_L) = Q^0(1 - aE_z) + aQ^0E \quad (8)$$

As a consequence of these equations, at high enough potentials, the total charge depends linearly with the applied potential and the current is constant (Figs. 5 and 1, respectively). The product  $aQ^0$  is then obtained from the slope of the linear portion in Fig. 5, and  $(E_z - a^{-1})$  from the ordinate.

It is interesting to point out that neither  $Q^0$  nor  $E_z$  can be separately obtained from the voltammetric experiments. To evaluate these magnitudes a different procedure would be required.

### 3.1.1. The voltammetric response in the presence of interactions between the redox sites

In the presence of interactions, the Bragg–Williams approximation [17] may be employed, in the same way as it is done in Van Laar model for regular solutions [17]. Here it will be considered that the polymer film contains  $N_{Ox}$  and  $N_{Red}$  redox centers, the total number of them,  $N = N_{Ox} + N_{Red}$  is constant. The conversion of Red to Ox occurs through reaction 1. This process can be visualized as an electron binding process by which  $n$  electrons are added to Ox to form a Red center and *vice versa*. The problem will be analyzed within the framework of lattice statistics, and  $N_{Ox}$  will be chosen as the independent variable [17].

Let us suppose that each redox center can interact with  $c$  neighbor centers. It will be considered only pair wise interactions between next neighbor centers. The oxidized neighbor centers interact with energy  $\varepsilon_{OO}$ , the reduced ones with energy  $\varepsilon_{RR}$ , and the interaction energy for a reduced-oxidized pair is  $\varepsilon_{OR}$ . At this point, it will be shown only the final results. The details of the deduction procedure are shown in Appendix A.

The formal redox potential,  $E^0$ , results:

$$E^{0'} = E^0 - \frac{RT}{nF} [(\zeta_{Ox} + \zeta_R)x - \zeta_R] \quad (9)$$

where  $x$  is the fraction of oxidized polymer and the dimensionless interaction energies,  $\zeta_{Ox}$  and  $\zeta_R$  are given as by:

$$\zeta_R = -\frac{cN_{Av}(\varepsilon_{RR} - \varepsilon_{OR})}{RT} \quad (10)$$

And

$$\zeta_{Ox} = -\frac{cN_{Av}(\varepsilon_{OO} - \varepsilon_{OR})}{RT}$$

The potential results as:

$$E = E^0 - \frac{RT}{nF} [(\zeta_{Ox} + \zeta_R)x - \zeta_R] + \frac{RT}{nF} \ln\left(\frac{x}{1-x}\right) \quad (11)$$

In the present case, the formal potential depends linearly on the fraction of oxidized centers. It is interesting to point out that this result is equivalent to that obtained from the models of Laviron [29], Brown and Anson [30] and Murray and co-workers [31], deduced from thermodynamic basis or the Frumkin isotherm.

The faradaic current for a linear potential sweep,  $j_F$ , can be obtained from the derivative of the charge with respect to the time. Taking into account the definition of  $v = dE/dt$ , then  $j_F = v dQ_F/dE$ . On the other hand, the faradaic charge can be written as  $Q_F = nFN_{Ox} = nFNx = Q^0x$ . Then,  $j_F$  can be obtained from the derivative of  $x$  with respect to  $E$ :

$$\frac{dx}{dE} = \frac{nF}{RT} \left[ \frac{(1-x)x}{1 - (\zeta_{Ox} + \zeta_R)(1-x)x} \right] \quad (12)$$

And  $j_F$  results

$$j_F = vQ^0 \frac{dx}{dE} = vQ^0 \frac{nF}{RT} \left[ \frac{(1-x)x}{1 - (\zeta_{Ox} + \zeta_R)(1-x)x} \right] \quad (13)$$

This equation is also equivalent to that obtained by previous workers [29–31].

By replacing the expression of the faradaic current into Eq. (5) it is obtained the current in dimensionless form as [14]:

$$\frac{j_T}{a v Q^0} = \frac{nF}{RT} \frac{(\Delta E - \Delta E^*)(1-x)x}{[1 - (\zeta_{Ox} + \zeta_R)(1-x)x]} + xp \quad (14)$$

where

$$\Delta E = E - E^0 \quad (15)$$

and

$$\Delta E^* = E_z - E^0 - a^{-1} \quad (16)$$

An expression for the peak potential,  $E_p$ , is obtained from Eq. (11) by replacing  $x$  by  $x_p$ , the oxidation fraction at the peak potential.

$$E_p = E^0 - \frac{RT}{nF} [(\zeta_{Ox} + \zeta_R)x_p - \zeta_R] + \frac{RT}{nF} \ln\left(\frac{x_p}{1-x_p}\right) \quad (17)$$

The expression for the total peak current,  $j_p$ , is obtained by replacing  $E$  by  $E_p$  and  $x$  by  $x_p$  in Eq. (14).

$$\frac{j_p}{a v Q^0} = \frac{nF}{RT} \frac{(\Delta E_p - \Delta E^*)(1-x_p)x_p}{[1 - (\zeta_{Ox} + \zeta_R)(1-x_p)x_p]} + x_p \quad (18)$$

### 3.1.2. The peak parameters

The peak parameters are obtained by deriving Eq. (14) with respect to the potential and equating to zero. The following implicit expression for the oxidized fraction at the peak potential,  $x_p$ , is obtained:

$$x_p = \frac{1}{2} + \frac{RT}{nF} \frac{[1 - (\zeta_{Ox} + \zeta_R)(1-x_p)x_p]^2}{(\Delta E_p - \Delta E^*)} \quad (19)$$

This is a fourth grade equation for  $x_p$ . Moreover, unless a reasonable guess is made on  $x_p$  or  $(\zeta_{Ox} + \zeta_R)$  it is not possible to separate both quantities. If it is assumed  $x_p = 0.5$  (no capacitive current), this value may be employed to obtain an initial estimate of  $(\zeta_{Ox} + \zeta_R)$ , by using Eq. (14). With this estimate it is obtained a new value of  $x_p$  from Eq. (19) and so on. Once  $x_p$  and  $(\zeta_{Ox} + \zeta_R)$  are known,  $\zeta_R$  it is obtained from Eq. (17). The resulting values for different  $Q_T$  are assembled in Table 1. The parameters  $aQ^0$  and  $(E_z - a^{-1})$ , were obtained directly from the experiments applying Eq. (8) to the straight line portion of the plot of  $Q_T$  vs.  $E$  (Fig. 5). The value of  $=0.191$  V vs. SCE, used for Pani in this acid media, was estimated from spectroelectrochemical measurements [32].

### 3.2. Analysis of the experimental results

Now, it will be demonstrated that the current-potential response, during the voltammetric half-oxidation of Pani, can be represented by the model. Following the method proposed above, it is obtained  $(\zeta_{Ox} + \zeta_R)$ , and then  $\zeta_{Ox}$  and  $\zeta_R$ . All these data are assembled in Table 1 for different film thicknesses. The comparison of some experimental curves with those obtained with the fitted parameters and  $n = 2$  [21,33], is shown in Fig. 3. As it can be seen the agreement is satisfactory.

For the same film, the product  $aQ^0$  is a constant independently of the sweep rate. So, it is possible to conclude that both  $a$  and  $Q^0$  are constants. Furthermore, for electrodes with different film thicknesses the product  $aQ^0$  changes linearly with  $Q_T$  (0.45) (Fig. 6).

It is interesting to enquire how the parameter  $(E_z - a^{-1})$  depends on the total charge. The data presented in Table 1 show that, in general, it becomes more negative as the charge increases.  $a$  must be greater than zero and, presumably, independent of the

**Table 1**  
Peak parameters at different thicknesses (see Fig. 3 for conditions).

$Q_T$ (0.45) (mC cm <sup>-2</sup> )	$j_p$ (mA cm <sup>-2</sup> )	$E_p$ (V)	$aQ^0$ (mC V <sup>-1</sup> cm <sup>-2</sup> )	$E_z - a^{-1}$ (V)	$\zeta_R$	$\zeta_{Ox}$
3.6	2.9	0.238	7.4	-0.041	1.06	-3.85
10.5	11.0	0.236	20.5	-0.106	1.05	-3.90
33.2	27.7	0.233	41.1	-0.360	1.04	-4.46
92.2	74.9	0.240	123.3	-0.301	0.91	-4.62

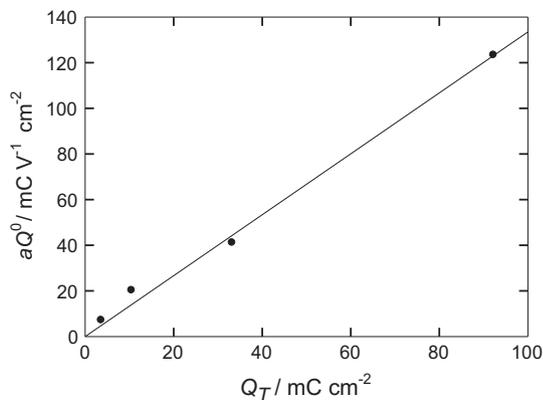


Fig. 6. Charge dependence of the parameter  $aQ^0$ . Same conditions as in Fig. 3.

charge; so, it is possible to conclude that  $E_z$  decreases with charge. However, for the smaller charges the long extrapolation to  $E = 0$  may lead to errors in the ordinate. So, the values of  $(E_z - a^{-1})$  for the smaller charges should be taken with caution.

It is important to remark that in systems which have an important capacitive contribution to the total current, after the faradaic current has decreased to zero, the integrated charge increases linearly with the potential (Fig. 5). For this reason it is not enough to quote the charge of the anodic current wave, but it is also necessary to specify at which potential this charge is referred. Moreover, to use the charge–thickness relationships by other techniques such as ellipsometry [34] or electron microscopy [10], it is important to employ charge values determined at the same potential at which these charges were originally measured. On the other hand, it is observed that the difference  $(\zeta_R - \zeta_{Ox})$  is positive for all films. According to Eq. (10), this implies that  $\varepsilon_{OO} - \varepsilon_{RR} > 0$ , which means that the interaction between oxidized centers is less attractive (or more repulsive) than the interaction between reduced ones. The mixing energy  $\Delta\varepsilon_m = -(1/2)RT(\zeta_R + \zeta_{Ox})$  results to be positive, indicating that the existence of pairs Ox–R is energetically favorable ( $\varepsilon_{OO} + \varepsilon_{RR} > 2\varepsilon_{OR}$ ).

#### 4. Conclusions

The present formalism can be satisfactorily employed to represent the current–potential response of the anodic voltammetric process of conducting polymers.

The capacitive response is characterized by three parameters:  $a$ ,  $Q^0$  and  $E_z$ . However, from the voltammetric response can be obtained only two combinations of them (e.g.  $aQ^0$  and  $(E_z - a^{-1})$ ). This means that the separation of the faradaic and capacitive contributions to the total voltammetric current response cannot be achieved by just voltammetric experiments. Fortunately, the total charge depends only on these two combinations of the capacitive parameters (Eqs. (5) and (14)). So, the faradaic parameters  $\zeta_{Ox}$  and  $\zeta_R$  can be effectively obtained from the experimental data. The determination of the parameters  $\zeta_{Ox}$  and  $\zeta_R$ , allows concluding that in the present formal representation of the oxidation process, the interaction between the oxidized centers is less attractive (or more repulsive) than between reduced ones.

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#### Appendix A

In the presence of interactions, the canonical partition function for this system,  $Q(N, N_{Ox}, T)$ , can be written as [2,17]:

$$Q(N, N_{Ox}, T) = \frac{N!}{(N - N_{Ox})!N_{Ox}!} (p_{Ox})^{N_{Ox}} \left( \exp\left(-\frac{\varepsilon_{OO}}{kT}\right) \right)^{P_{OO}} (p_R)^{N - N_{Ox}} \left( \exp\left(-\frac{\varepsilon_{RR}}{kT}\right) \right)^{P_{RR}} \left( \exp\left(-\frac{\varepsilon_{OR}}{kT}\right) \right)^{P_{OR}} \quad (A.1)$$

where  $P_{ij}$  is the number of neighbor pairs  $i$ – $j$ ;  $p_{Ox}$  and  $p_R$  are the internal partition functions of the oxidized and reduced centers respectively when no interaction is considered [17]. Within the Bragg–Williams approximation the number of neighbor pairs is calculated as

$$P_{OO} = \frac{c(N_{Ox})^2}{2N} \quad (A.2)$$

$$P_{RR} = \frac{c(N - N_{Ox})^2}{2N} \quad (A.3)$$

$$P_{OR} = \frac{c(N - N_{Ox})N_{Ox}}{N} \quad (A.4)$$

So, the partition function results

$$Q(N, N_{Ox}, T) = \frac{N!}{(N - N_{Ox})!N_{Ox}!} \left( p_{Ox} \exp\left(-\frac{c\varepsilon_{OO}}{2kT}\right) \right)^{N_{Ox}} \left( p_R \exp\left(-\frac{c\varepsilon_{RR}}{2kT}\right) \right)^{N - N_{Ox}} \left( \exp\left(\frac{\Delta\varepsilon_m}{RT}\right) \right)^{N_{Ox}(N - N_{Ox})/N} \quad (A.5)$$

where it is defined,

$$\Delta\varepsilon_m = \frac{1}{2}N_{Av}c(\varepsilon_{OO} + \varepsilon_{RR} - 2\varepsilon_{OR}) \quad (A.6)$$

And  $N_{Av}$  is Avogadro's Number. Finally,

$$Q(N, N_{Ox}, T) = \frac{N!}{(N - N_{Ox})!N_{Ox}!} \times (p_{Ox}^*)^{N_{Ox}} (p_R^*)^{N - N_{Ox}} \left( \exp\left(\frac{\Delta\varepsilon_m}{RT}\right) \right)^{N_{Ox}(N - N_{Ox})/N} \quad (A.7)$$

With  $p_{Ox}^* = p_{Ox} \exp\left(-\frac{c\varepsilon_{OO}}{2kT}\right)$  and  $p_R^* = p_R \exp\left(-\frac{c\varepsilon_{RR}}{2kT}\right)$  being the internal partition functions of the interacting centers in the completely oxidized and reduced polymer, respectively.

In previous work [2] it was demonstrated that the redox potential for a mixture of redox centers can be obtained from the corresponding derivative of the canonical partition function,  $Q(N_{Ox}, N, T)$  of the system as:

$$E = -\frac{1}{e} \frac{\partial A}{\partial N_e} = \frac{N_{Av}}{nF} \left( \frac{\partial A}{\partial N_{Ox}} \right)_{T,N} = -\frac{RT}{nF} \left( \frac{\partial \ln Q}{\partial N_{Ox}} \right)_{T,N} \quad (A.8)$$

where  $e$  is the electron charge,  $F$  the Faraday's constant and  $n$  the number of electrons exchanged in the redox reaction.

By using the Stirling approximation and deriving the last equation with respect to  $N_{Ox}$ , it is obtained:

$$\left( \frac{\partial \ln(Q(N, N_{Ox}, T))}{\partial N_{Ox}} \right)_{T,N} = \ln\left(\frac{(1-x)}{x} \frac{p_{Ox}^*}{p_R^*}\right) + (1-2x) \frac{\Delta\varepsilon_m}{RT} \quad (A.9)$$

where  $x = \frac{N_{Ox}}{N}$  is the fraction of oxidized centers.

Replacing Eq. (A.9) into Eq. (A.8), the potential is obtained:

$$E = -\frac{RT}{nF} \ln\left(\frac{p_{Ox}^*}{p_R^*}\right) - \frac{RT}{nF} \ln\left(\frac{(1-x)}{x}\right) - \frac{\Delta\varepsilon_m}{nF} (1-2x) \quad (A.10)$$

Dimensionless interaction energies will be defined as:

$$\zeta_R = -\frac{cN_{Av}(\varepsilon_{RR} - \varepsilon_{OR})}{RT} \quad (\text{A.11})$$

And

$$\zeta_{Ox} = -\frac{cN_{Av}(\varepsilon_{OO} - \varepsilon_{OR})}{RT} \quad (\text{A.12})$$

So that

$$E = -\frac{RT}{nF} \ln\left(\frac{p_{Ox}}{p_R}\right) - \frac{RT}{nF} [(\zeta_{Ox} + \zeta_R)x - \zeta_R] + \frac{RT}{nF} \ln\left(\frac{x}{1-x}\right) \quad (\text{A.13})$$

The standard redox potential,  $E^0$ , will be defined as:

$$E^0 = -\frac{RT}{nF} \ln\left(\frac{p_{Ox}}{p_R}\right) \quad (\text{A.14})$$

And the formal redox potential,  $E^0$ , as:

$$E^{0'} = E^0 - \frac{RT}{nF} [(\zeta_{Ox} + \zeta_R)x - \zeta_R] \quad (\text{A.15})$$

The potential results

$$E = E^0 - \frac{RT}{nF} [(\zeta_{Ox} + \zeta_R)x - \zeta_R] + \frac{RT}{nF} \ln\left(\frac{x}{1-x}\right) \quad (\text{A.16})$$

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