Poly (3,4-ethylendioxithiophene) (PEDOT) oxidation. Activation energy and conformational energy.

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Abstract. The oxidation kinetics of films of the conducting polymer PEDOT-ClO₄ after electrochemical reduction by polarization at increasing cathodic potential was studied by potential steps. The response i/t presents a maximum at intermediate oxidation times. At the maximum the reaction occurs under chemical kinetic control following the expected current variations from the Chemical and Electrochemical Kinetics, when reactant concentrations or temperatures are changed. The obtained activation energy of the oxidation present two ranges as a function of the cathodic potential of prepolarization: constant values after prepolarization at low cathodic potentials and a linear variation after prepolarization at increasing high cathodic potentials. According with the conformational relaxation model during electrochemical reduction the polymer shrinks, closes and packs the conformational structure. The activation energy for the subsequent oxidation includes two terms: the constant chemical activation energy and the conformational energy required to relax the packed polymeric structure. The conformational energy only appears after prepolarization at more cathodic potentials than the closing potential where more packed conformations were obtained. The conformational activation energy accounts the energetic requirements to relax and unfold the polymeric chains generating the required free volume to lodge balancing counterions;
meanwhile the chemical activation energy accounts the energetic requirements for the electrochemical reaction to occur.

Keywords: pedot, oxidation, kinetics, reaction coefficients, activation energy, conformational energy.

1. Introduction
Conducting polymers, when submitted to electrochemical reactions, can be considered as reactive gel. Reverse electrochemical reactions promote swelling and shrinking (figure 1) processes [1, 2]. Changes of volume are linked to the continuous shift of the polymeric composition. The packed molecular structure of a neutral polymer due to strong polymer-polymer Van der Waals interactions changes during oxidation. Electrons are extracted from the chains and as a consequence of the double bonds redistribution to lodge the positive charges, conformational movements are induced generating the required free volume to balancing counterions coming from the solution. Solvent molecules also penetrate from the solution. Devices as artificial muscles or smart membranes are based on the conformational structure attained under electrochemical control [3-7]. Conformational movements mean energetic changes on the polymeric chains. So, the conformational energy defines, moreover traditional sensing abilities of the polymer, actuating possibilities to produce artificial muscles or membranes.

Both composition and volume variation are mimicking, at molecular level, events that occurring in natural muscles and in other living organs, during actuation: a chemical reaction is triggered by an electric pulse arriving from brain and promoting conformational movements on biopolymers. The question arising now is whether the Chemical Kinetics can be applied to those dense gels and if so, which kind of information can we obtain about those reactive materials so close to those constituents of the living organs and, the most important, if the involved energy during reaction includes the conformational energy. If so, a way should be open to subsequent characterization of primary, secondary, tertiary or quaternary structures [8] and their conformational energy components.

2. Experimental
Acetonitrile (ACN) (Lab Scan) and anhydrous lithium perchlorate (LiClO₄) (Fluka) were used as received, and 3, 4-ethylenedioxythiophene from (Merck) was distilled under vacuum before use. The working electrode was a platinum sheet having 1 cm² surface area. The counter electrode was a stainless steel sheet, an Ag/AgCl in 3M Cl⁻, supplied by Crison Instruments being the reference electrode. A one-compartment electrochemical cell was used. The experiments were carried out under
nitrogen atmosphere. The electrochemical techniques were applied by an Eco Chemistry Autolab potentiogalvanostat.

PEDOT films were electrochemically obtained from 0.1 M LiC104 and 10 mM 3, 4-ethylenedioxythiophene acetonitrile solution, by chronopotentiometry passing constant current density (2 mA) through the Pt working electrode versus Ag/AgCl, obtaining a constant total charge (300 mC cm-2). After polymerization the coated electrodes were rinsed with acetonitrile and dried before use. The weight of the dried films (0.3582 ± 0.0599 mg) was obtained from a Sartorious SC2 balance having a precision of 10-7 g.

The films were checked by cyclic voltammetry (control voltammograms) after every experimental series. When the oxidation charge of the control voltammogram decreases around 10%, related to that of the just electrogenerated film, a new film is electrogenerated and checked to go on the kinetic study.

The temperature of the cells was maintained by means of two Julabo F25 cryostats. Activation energy was obtained from experiments performed at different temperatures. Two electrochemical cells were used containing the working solution. One cell was maintained at 25ºC, the second was adjusted at different temperatures for every different experimental series. The Pt coated electrode was reduced and packed by prepolarization for 30 s at ambient temperature every time, and then it was translated to the second cell where the oxidation experiments were performed.

3. Basic theoretical considerations for the experiments

The electrochemical oxidation-reduction of PEDOT films in acetonitrile can be written, after the ESCR model, as:

\[
\begin{align*}
\text{[PEDOT}^{a+}(A^-)_a + n (A^-)_{\text{org}} + m (ACN) \leftrightarrow [(\text{PEDOT}^{(a+a)}(A^-)_{n+a} (ACN)_m]_{\text{gel}} + (n e^-)_{\text{metal}} \end{align*}
\]

where s means solid and org organic solution and the number of positive charges on the reduced chain, a, increases with cathodic potential of polarization. We consider the reactants are anions (A-) from the acetonitrile (ACN) solution and active centres (AC), understood as those points on the polymer chains able to store a positive charge after oxidation (PEDOT+).

According to the Electrochemical Stimulation of Conformational Relaxations (ESCR) model [9-15], the reduction of an oxidized and swollen polymer promotes the polymer shrinking under kinetic control of the counterions diffusion towards the solution. The structure closes under partial oxidation and the reduction, and polymeric packing, goes on under kinetic control of the conformational movements of the chains that open the ions way towards the solution. The subsequent potentiostatic oxidation of a packed (reduced ahead the closing point) polymer starts by nucleation of the oxidized material under conformational relaxation kinetic control. Using thin and electrochromic films of conducting polymer the nucleation process can be visually followed [14, 15]. The chronoamperometric current rises meanwhile the nuclei grow, passing through a maximum when the nuclei coalesce. After the maximum the oxidation is completed and the current drops under diffusion control of the counterions inside the polymer.

The model allows a good description of the influence of the different chemical or physical variables on the evolution of the oxidation time at the chronoamperometric maxima, but the fit of the current at the maximum is not so good.

The question now is whether the current at the chronoamperometric maximum (in between the two inflexion points) is under kinetic control of the chemical reaction, and if so, how the empirical kinetics should be influence if we use different conformational packed states of the polymer film as initial states for the potentiostatic oxidation. Those different conformational packed states can be attained by cathodic polarization (reduction), for a constant time, at different cathodic potentials; or by cathodic polarization at a constant potential for different polarization times. Here we will explore the first possibility.

So, if the oxidation around the maximum occurs under chemical kinetic control, the current at the maximum will follow the Butler-Volmer equation:

\[
i = k \Pi c_f^{\beta f} \exp (\alpha zF \eta/RT)
\]
the current at the maximums (i), changes as a function of the product (Π) of the concentrations (c) of the reactants (j), being β, j the concomitant reaction orders; k is the rate constant or rate coefficient, α is the electronic transference coefficient and η is the oxidation overpotential.

And the reaction (1), under chemical kinetic control involves that the oxidation rate can be defined from the consumption rate of active centres along the time: R = - d [PEDOT*]/dt. As every consumed active centre requires the flow of one electron, the empirical equation kinetics is:

\[ \frac{dQ_{ox}}{dt} = i = k [\text{ClO}_4^-]^\alpha [\text{AC}]^\beta \]  

(dQ_{ox}/ dt(mC cm^{-2} s^{-1})= i(mA cm^{-2})), being Q_{ox} the oxidation charge at every time after the potential step for each anodic potential step, α and β are the reaction orders related to counterions concentration in solution and the active centres concentration in the polymer, respectively, and k is the rate constant or rate coefficient. [ClO4^-] and [AC] means counterions in solution and polymeric active centres concentrations, respectively.

This equation is a general empirical kinetic equation from reaction (1) indicating the experimental methodology that will be followed to check if, at the chronoamperometric maximum the current occurs under chemical kinetic control. In that case:

3.1. Working at constant temperature (k=constant) and constant concentration of active centres (potential step to the same anodic potential), and changing the electrolyte concentration, the current at the chronoamperometric maxima must fit:

\[ \log i = \log k'' + \alpha \log [\text{ClO}_4^-] \]  

3.2. Working at constant temperature (k=constant) and constant concentration of counterions in solution, and changing the concentration of active centres by changing the oxidation potential, the current at the chronoamperometric maxima must fit:

\[ \log i = \log k''' + \beta \log [\text{AC}] \]  

3.3. Working under constant concentration of counterions in solution, and constant concentration of active centres in the polymer (constant oxidation potential) and by changing the working temperature for the oxidation process, the current at the chronoamperometric maxima must fit:

\[ \log i = \log k + \log [\text{ClO}_4^-]^\alpha + \log [\text{AC}]^\beta = \log A - \frac{E_a}{RT} + \log [\text{ClO}_4^-]^\alpha + \log [\text{AC}]^\beta \]

\[ \log i = \log K - \frac{E_a}{RT} \]

So, we have three experimental methodologies to check if there exists a chemical kinetic control for the oxidation of those reactive and swelling gels at the chronoamperometric maximum. In that case, from the obtained variations, the reaction orders (α and β), the kinetic coefficients, k, and the activation energy, Ea, can be obtained as a function of the initial conformational packing state of the film.

4. Results and discussion.

After prepolarization of PEDOT films for 30s at increasing cathodic potentials -200, -400, -600, -800, -1000, -1500, -2000, -2500 and -3000 mV vs. Ag/AgCl sat. in 0.1 M LiClO4 acetonitrile solutions, chronoamperometric responses (figure 2A) show a maximum at rising oxidation times when the initial states were obtained by polarization at increasing cathodic potentials, that means from initial states presenting more reduced chains with more packed conformations.
Figure 2. A. Chronoamperometric responses of a PEDOT coated platinum electrode in 0.1 M LiClO₄ acetonitrile solution, submitted to potential steps from different cathodic potentials, indicated on the figure, maintained for 30s, to 400 mV versus Ag/AgCl in 0.1M LiClO₄. The current at the maxima give the oxidation rates under chemical kinetic control.

Figure 2. B. Chronocoulograms obtained by integration of the experimental chronoamperograms. The slopes of the tangents at the induction time give the initial oxidation rate under chemical kinetic control.

By integration of the chronoamperograms to give chronocoulograms Q/t (figure 2B), which shows the same oxidation kinetics from figure 2A as reactions having an induction time, a most usual representation in books of Chemical Kinetics. The more packed was the initial conformational state of the film, the higher was the induction time. For those kinetics having an induction time the initial rates were the slopes at the inflexion points (dQ/dt), which is the current (i) at the original chronoamperometric maxima (figure 2A). So, ahead we will take currents at the experimental chronoamperometric maxima as initial rates to check if they follow equations (4, 5 or 6).

The concentration of active centres, [AC], represents those places along the chains that will store a positive charge, [PEDOT+], after electrochemical oxidation. Every active centre involved in the reaction requires the flow of one electron. So, the concentration of active centres is obtained from the consumed charge (Qox mC-1), which is obtained by integration of the experimental chronoamperogram and calculated from equation (7) using the polymer weight (0.3582 ± 0.0599 mg) and the polymer density (1.46 g cm-3) [16]:

\[
[\text{PEDOT}^+] (\text{mol L}^{-1}) = [\text{AC}] (\text{mol L}^{-1}) = \frac{[Q_{\text{ox}} (\text{C})/96485 (\text{C mol}^{-1})]}{W (\text{g})/ \rho (\text{g L}^{-1})} \tag{7}
\]
Figure 3. Double logarithmic plots, from Equations 4 or 2, of the oxidation rates (current at the chronoamperometric maxima) of PEDOT films submitted to potential steps between -2000 mV, kept for 30s every time, and 500 mV in different concentrations of LiClO$_4$ acetonitrile solutions: 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 and 1M. The procedure was repeated for different anodic potentials, indicated on the figure.

Figure 3 (lg i vs. lg [ClO$_4$-]) shows the experimental double logarithmic relationship expected from equation (4). As a preliminary conclusion this figure corroborates the chemical kinetic control of the reaction at the chronoamperometric maximum. Slopes from Figure 3 are, according to equation (4), the reaction order $\alpha$ ($0.3 \leq \alpha \leq 0.6$), being independent of the both initial packing state and the oxidation potential limit ($E_c$).

If the oxidation occurs at the maximum under chemical kinetic control, the activation energy can be obtained from experiments at different temperatures as indicate equation (5). We try to follow the influence of the temperature on the oxidation process, without any influence of the temperature on the initial state. Two electrochemical cells were required: one allowing for reduces and pack the polymer at constant temperature, the second used to oxidize the packed film at a different temperature every time. One cell was maintained at 25ºC, the second was adjusted at different temperatures (-10, -5, 0, 5, 10, 15, 20, 25, 30, 35 and 40ºC) for every different experimental series. The Pt coated electrode was reduced and packed at 25ºC every time by prepolarization at a different cathodic potential every time (-0.2, -0.4, -0.6, -0.8, -1, -1.1, -1.2, -1.6, -1.7, -1.8 or -1.9 V) for 30 s. Then it was translated into the second cell were it was submitted to the same prepolarization potential for 1 second, stepping then the potential to the oxidation potential of 800mV for 30 s.
Figure 4. Temperature influence on the oxidation of PEDOT films: semi-logarithmic plot from equation (6). The coated electrode was reduced at the prepolarization potential and 25°C for 30 s in 0.1 M LiClO₄ acetonitrile solution. Then the electrode was switched off and translated into a new cell at the working temperature and submitted to a potential step from the prepolarization potential, kept for 1s, to 800 mV versus Ag/AgCl. The procedure was repeated for the different cathodic potentials of prepolarization and for the studied temperatures (-10, -5, 0, 5, 10, 15, 20, 25, 30, 35 and 40°C). Before and after every series the state of the film was checked by cyclic voltammetry, using a new film when the diminution of the voltammetric charge surpasses 10% the initial value. Finally we used a just electrogenerated film for every temperature.

As expected from equation (6), when a reaction occurs under chemical kinetic control, a semilogarithmic variation is obtained between the current at the maxima and 1/T (figure 4). Slopes are the activation energy. The obtained activation energies were plotted versus the cathodic potential of prepolarization; two domains (figure 5) were obtained. When the polymer was reduced by polarization at potentials higher than -0.8 V (the closing potential) the activation energy is constant and independent of the reduction potential. Rising cathodic prepolarizations from -0.8 V, a linear increase in the activation energy with cathodic potential was obtained. Similar results were obtained with polythiophene [17], PEDOT presenting a higher dispersion of the experimental results.

Figure 5. Evolution of activation energy (Eₐ), as a function of the cathodic polarizations for 30s. (line) Theoretical evolution according with equation (10) and the experimental zₜ. Two linear fits are obtained showing their regression coefficients (R²) on the figure.

The Electrochemical Kinetics predicts, by combination of equations (2) and (6), an exponential variation of the activation energy of an electrochemical oxidation with the anodic overpotential ($\eta$), but it does not exist any previous result where the activation energy is a function of a cathodic potential of prepolarization. In order to describe those unexpected results, we come back to the Thermochemistry where the activation energy of a reaction is defined as ($E_a = RT + \Delta H$). Considering that all the energetic terms linked to swelling, shrinking and packing processes in reactive conducting polymers are described by the electrochemical stimulation of conformational relaxations model (ESCR), where $\Delta H = \Delta H^* - z_\eta \eta + z_\eta \eta$.
\[ E_a = RT + \Delta H = RT + \Delta H^* - z_c \eta_c + z_r \eta_a \] (7)

This equation states that activation energy changes, under constant temperature (T) and for potential steps to the same anodic potential (constant \( \eta \)), as a function of the cathodic overpotential (\( \eta_c \)) of prepolarization:

\[ E_a = B - z_c \eta_c \] (8)

being \( B = RT + \Delta H^* + z_r \eta_a \) a constant, the “electrochemical activation energy” of the electrochemical reaction, and \( z_c \eta_c \) is the conformational packing energy.

Equation (8) describes two ranges for activation energy. When prepolarization potential is more anodic than the closing potential, \( \eta_c > \eta_s \) and \( \eta_c = 0 \), it doesn’t exist any conformational packing and the activation energy is a constant, \( E_a = B \), the electrochemical activation energy (E_{act \text{eq}}). The initial states obtained by prepolarization were open, relaxed and partially oxidized gels which subsequent oxidation occurs under diffusion kinetic control of the counterions inside the material. More cathodic prepolarization potentials than the closing potential give \( \eta_c < 0 \), and the activation energy increases linearly as a function of the cathodic potential of prepolarization, as obtained experimentally.

The physical meaning is that rising cathodic prepolarization produce more stable (energetically) and more reduced initial states of the material, related to the relaxed and open gel. The stabilization is related to more packed conformations of the chains. The electrochemical oxidation only can be initiated if, simultaneously to the electrochemical activation energy, \( (E_{act \text{eq}}) \), energy enough is supplied to relax the packed polymeric conformations (conformational energy, \( (E_{act \text{conf}}) \) conf with generation of the required free volume to lodge coming counterions. So, the activation energy of reactive materials which reaction involves packed conformations and conformational changes of one of the reactants includes two components, the chemical (or electrochemical) activation energy and the conformational energy:

\[ E_{act} = (E_{act \text{eq}}) + (E_{act \text{conf}}) \] (9)

This conformational energy, required to initiate the reaction, must be added to the chemical activation energy (figure 6).
This increasing conformational energy stored by the system by cathodic prepolarizations for 120 s can be explicated working at constant temperature by Voltammetric oxidation. More packed conformations, and more stable initial states, require a higher energy to relax and open the structure in Figure 6.

**Figure 6.** Schema indicating swelling/shrinking and packing processes as a function of the potential of prepolarization. Conformational activation energy increase can be interpreted from voltammograms evolution obtained from a PEDOT film in 0.1 M LiClO₄ acetonitrile solutions, between different cathodic potentials (-800, -1000, -1200, -1400, -1600, -1800, -2000, -2500 and -3000mV), kept for 120s and the same anodic potential (800mV) vs. Ag/AgCl, at 0.1 Vs⁻¹ and 25ºC showing relaxation/swelling processes.

This increasing conformational energy stored by the system by cathodic prepolarizations for 120 s can be explicated working at constant temperature by Voltammetric oxidation. More packed conformations, and more stable initial states, require a higher energy to relax and open the structure in
order to start the oxidation process. As we are working now under constant temperature the only energetic source comes from the applied anodic potential sweep and the oxidation is expected to start at more anodic potentials, as experimentally shows figure 7: higher anodic overpotentials (higher electrical energy) are required to relax and open, under constant temperature, rising packed conformations.

![Chemical Activation Energy](image1.png)

**Figure 7.** The attained experimental activation energies for PEDOT oxidation by potential steps from different cathodic prepolarizations are constituted by two components: the constant electrochemical activation energy ($E_{act}$) and the energy required to relax the initial packed conformations of the folded chains ($E_{conf}$). The relaxation energy can be increased in a continuous way under control of the cathodic potential of polarization, for a constant polarization time.

Considering that tactile and sensing artificial muscles[1-2, 18-25] are devices based on those conformational movement of the chains, the way is now open to try a quantitative description of either actuating, sensing and tactile properties.

As conclusions, the potentiostatic oxidation of packed conformational states of conducting polymers starts under conformational relaxation kinetic control (rising currents on the chronoamperograms), go on under chemical kinetic control (at the chronoamperometric maximum) finishing under diffusion kinetic control of the counterions inside the polymer.

Methodologies from the Chemical and Electrochemical Kinetics can be applied to those reactive gels. The attained activation energy contains structural information including two terms: the constant activation energy and the conformational activation energy. This conformational energy is understood as the energy required for relaxing a packed conformational state generating free volume enough to lodge the balancing counterions.

Progressive packed conformational states are attained by prepolarization, for the same time, at rising cathodic potentials. Any of these packed (energetic) conformational states is erased by oxidation to a stationary state of. Any packed initial state is reproduced by the same cathodic prepolarization for the same polarization time. The way is open to lodge information (energy) by polymeric conformations that can be read and erased.

Experimental methodology, physical changes and resulting signals are analogous to those observed in nervous pulses through ionic channels [26], constituted by natural polymers that, under the influence of an electric field threshold generated by an ionic gradient, relax and swells allowing the ionic flow or shrinks and closes, in synaptic events. A way is opened to explore if some kind of memory is stored in brain by conformational states of those biological polymer chains in channels, each of the conformational states being read every time the channel is open and ions flow through the
channel. Electric pulses, conformational movements and chemical or electrochemical reactions also occur in most of the enzymatic processes requiring a new methodology to study the different way physical or chemical conditions influence the conformational energy acting on the reaction and the reaction kinetics in living ambient or under influence of different drugs.

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