**PEDOT Electrochemical Reaction: Evolution Of Chemical And Kinetic Parameters.**

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Electrochemical reactions in conducting polymers involve progressive changes on inter and intra-molecular interactions among polymer chains, anions, cations and solvent in dense gels. Those reactive materials behave quite similarly to living systems involving chemical reactions, conformational changes and ionic interchanges: muscles, enzymatic reactions or membrane pumps or channels. Are the chemical and electrochemical kinetic models still valid to those reactive materials? The anodic chronoamperometric response of conducting polymers after prepolarization at high cathodic potentials shows a maximum (Figure 1), which is described in terms of conformational relaxation and diffusion kinetic control [1, 2]. Our aim here is to prove the presence of chemical kinetic control at the maxima. The Buttler-Volmer equation under chemical control: $\mathbf{i = k\ \Pi\ c_j^{\beta,\ j}}$, relates the current at the maximum with the reactant concentrations.
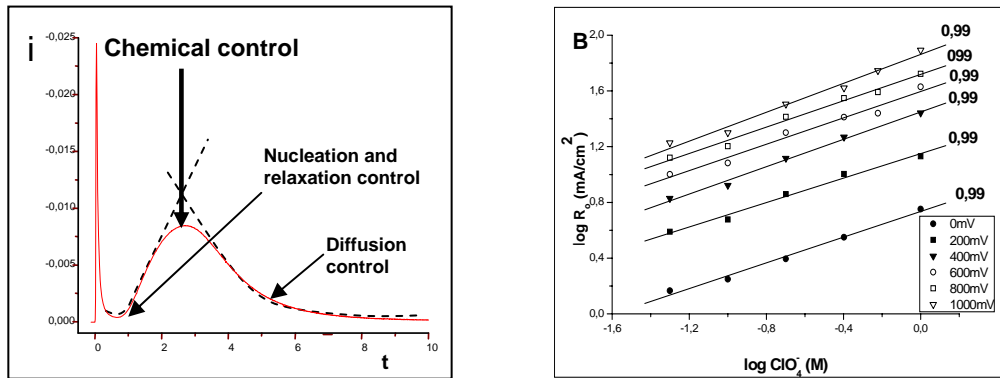
Figure 1. Chronoamperometric responses of a PEDOT film in 0.1M LiClO$_4$: a) prepolarization at -3000mV and stepped to 500mV, B) prepolarization at -2000mV and stepped to different anodic potentials for different electrolyte concentration **[ClO$_4^-$]**

The electrochemical reaction for PEDOT (poly (3, 4-ethylenedioxythiophene) can be written:

$$[PEDOT^{a+}(ClO_4^-)_a]_s + n(ClO_4^-)_{solv} + m(ACN) \leftrightarrow [(PEDOT^{(n+a)+})(ClO_4^-)_{n+a}(ACN)_m]_{gel} + (ne^-)_{metal} \quad (1)$$

the kinetic equation is described as: $\mathbf{R = i = dQ/dt = k\ [ClO_4^-]^\alpha\ [AC]^\beta}$ **(2)**
where **R** is the oxidation rate, i (mA cm^{-2}), at the maximum; **k** is the rate constant, or rate coefficient (**k= A exp (-E_a/RT)**), and **α** and **β** are the reaction orders related to the concentration of counterions and active centers (**AC**) on the polymer chains, respectively. Subindex s and solv means solid and solvated. Taking logarithms: **log i= log k + α log [ClO$_4^-$] +β log [CA]   (3)**
Eq, 3 indicates how to obtain α, β and k from experimental results by changing one variable every time. The attained result supports (Figure 1b) the chemical kinetic control of the process.

The kinetic magnitudes β and k are found to change as a function of cathodic reduction, and prepolarization, potential. The obtained activation energies include two components: chemical (constant) and conformational (increases with the cathodic prepolarization). So it includes structural information about conformational polymeric packing, as the ESCR model predicts. After higher cathodic prepolarizations, more time is required to relax and open polymeric structures giving rise to slower kinetics and lower k.

[1] T.F. Otero and E. Angulo. _Solid State Ionics_, **1993**, _63-65_, 803-809.
[2] T.F. Otero; H-J. Grande and J. Rodríguez. _J. Phys. Chem. B,_ **1997**, _101_, 3688-3697.