

## Supporting information

# Biomimetic Dual Sensing-Actuators Based on Conducting Polymers. Galvanostatic Theoretical Model for Actuators Sensing Temperature.

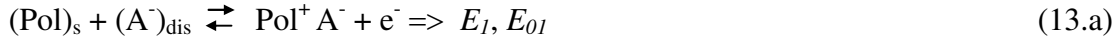
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At the oxidation potential onset,  $E_1$ , one electron is extracted from every polymeric chain by flow of a very low anodic current, reaching the first equilibrium state.

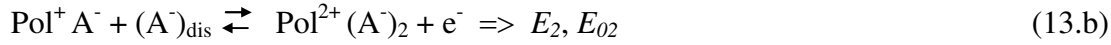
For  $n = 1$ :



The number of the equation, 13.a, is the same that in the main text.

Where  $E_1$  is the first equilibrium potential and  $E_{01}$  is its standard potential. When all the  $m$  chains of the film store a positive charge, the potential steps to the value required to extract a second electron from every chain attaining a new equilibrium state.

For  $n = 2$ :



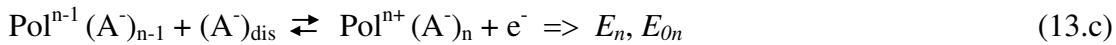
$E_2$  and  $E_{02}$  (equilibrium and standard potential) are more anodic potentials than  $E_1$  and  $E_{01}$  ( $E_2 > E_1$ ).

The oxidation goes on passing through  $n$  consecutive equilibrium intermediate states at increasing equilibrium potentials:

$$E_1 < E_2 < E_3 < \dots < E_{n-1} < E_n;$$

being  $E_{01}, E_{02}, \dots, E_{0n}$ , the standard potentials for the concomitant equilibria.

For the  $n^{\text{th}}$  equilibrium (extraction of the  $n^{\text{th}}$  electron from each of the  $m$  chains):



Each equilibrium potential,  $E_1, E_2, \dots, E_n$ , and concentrations there involved are linked by the Nernst equation:

$$E_1 = E_{01} + \frac{RT}{F} \ln \frac{[\text{Pol}^+ \text{A}^-]}{[\text{Pol}][\text{A}^-]} \quad (15.a)$$

$$E_2 = E_{02} + \frac{RT}{F} \ln \frac{[\text{Pol}^{2+} (\text{A}^-)_2]}{[\text{Pol}^+ \text{A}^-][\text{A}^-]} \quad (15.b)$$

.....

$$E_n = E_{0n} + \frac{RT}{F} \ln \frac{[Pol^{n+}(A^-)]_n}{[Pol^{(n-1)+}(A^-)]_{n-1} [A^-]} \quad (15.c)$$

For a galvanostatic oxidation the potential must go, from the initial reduced state, through the  $n$  consecutive anodic potential steps defined by equations 15. From equation 15.a, the concentration of the generated product can be obtained as a function of the reactants concentration:

$$\ln [Pol^+ A^-] = \frac{F}{RT} (E_1 - E_{01}) + \ln [Pol^*] + \ln [A^-] \quad (S1)$$

From the second equilibrium potential  $E_2$ , and using S1:

$$\ln [Pol^{2+}(A^-)_2] = \frac{F}{RT} (E_2 + E_1 - E_{02} - E_{01}) + \ln [Pol^*] + 2 \ln [A^-] \quad (S2)$$

Using the same procedure we get a general expression of the concentration of the product generated by the  $n^{\text{th}}$  equilibrium: steps:

$$\ln [Pol^{n+}(A^-)_n] = \frac{F}{RT} (E_n + E_{n-1} + \dots + E_2 + E_1 - E_{0n} - E_{0(n-1)} - \dots - E_{02} - E_{01}) + \ln [Pol^*] + n \ln [A^-] \quad (S3)$$

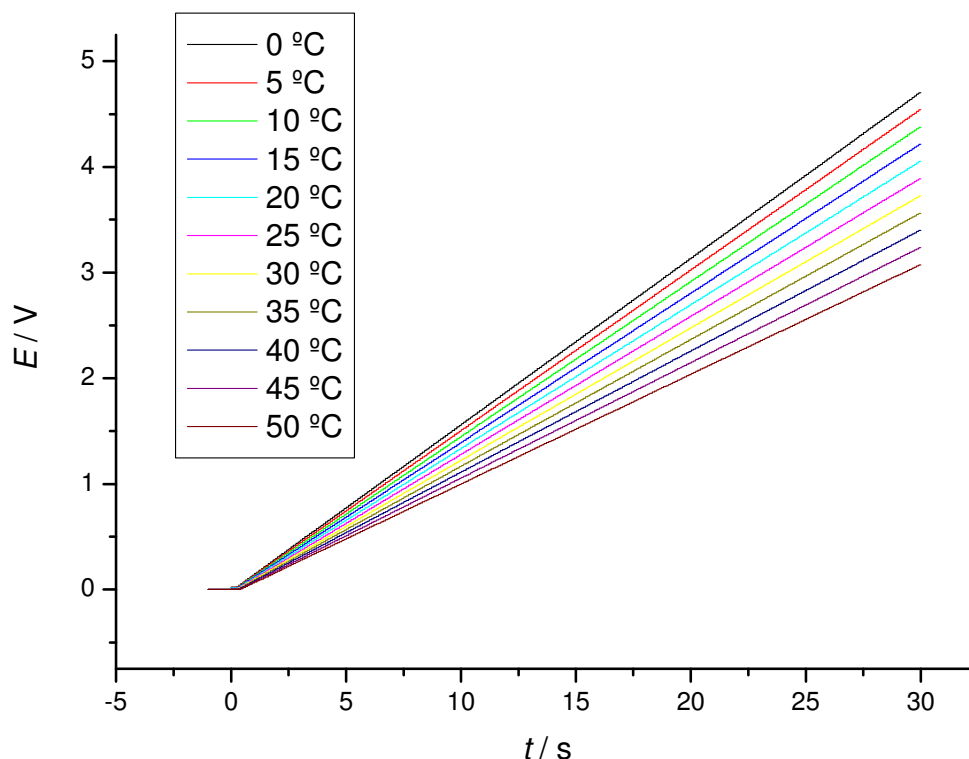
By using equations S1, S2, ..., S3, it is possible to express the potential evolution at every intermediate state, from equations 12 of the main text, as a function of the reactants concentrations. When a current is applied, a transition from an oxidation state,  $n$ , to the next oxidation state,  $n+1$ , will occur, giving a different potential evolution for the anodic processes of the consecutive steps:

$$E_{a1}(t) = E_{01} + \frac{RT}{(1-\alpha)F} \left\{ \ln \left( \frac{i_a}{FV} \right) - \ln [A^-] - \ln \left( [Pol^*]_{initial} - \frac{i_a t}{FV} \right) - \ln k_{a0} \right\} \quad (S4)$$

$$E_{a2}(t) = E_{02} + \frac{1}{1-\alpha} (E_1 - E_{01}) + \frac{RT}{(1-\alpha)F} \left\{ \ln \left( \frac{i_a}{FV} \right) - 2 \ln [A^-] - \ln \left( [Pol^*]_{initial} - \frac{i_a t}{FV} \right) - \ln k_{a0} \right\} \quad (S5)$$

$$E_{an}(t) = E_{0n} + \frac{1}{1-\alpha} (n-1) \Delta E + \frac{RT}{(1-\alpha)F} \left\{ \ln \left( \frac{i_a}{FV} \right) - n \ln [A^-] - \ln \left( [Pol^*]_{initial} - \frac{i_a t}{FV} \right) - \ln k_{a0} \right\} \quad (S6)$$

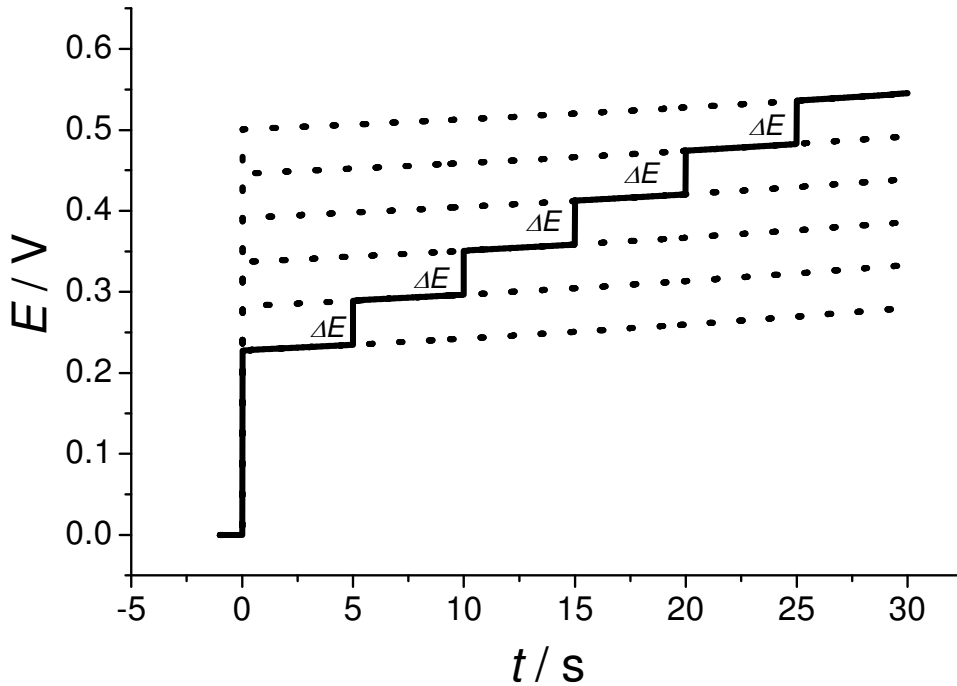
Simulating equation S6, for different temperatures and different intermediate states, when all the other experimental variables were kept constant ( $n=300$ , at room temperature (25°C), passing a current ( $i_a$ ) of 10 mA, being the initial concentration of active center,  $[Pol^*] = 1.3 \text{ mmol g}^{-1}$ ; electrolyte concentration  $[A^-]=1 \text{ M}$ ; assuming  $\alpha = 0.5$ , for a polymeric film which length = 1 cm, width = 0.5 cm, weight = 1.6 mg, density =  $1540 \text{ g l}^{-1}$ ) results shown in Fig. S1 are attained.



**Figure S1.** Simulation of equation S6, for different temperatures and extraction (oxidation) of  $n$  consecutive electrons from every polymeric chain (the number of oxidation states,  $n=300$ ), when all the other experimental variables were kept constant, at room temperature (25°C) passing a current of 0.75 mA, being the initial concentration of active center,  $[Pol^*] = 2 \text{ mol l}^{-1}$ ; electrolyte concentration  $[A^-]=1\text{M}$ ; assuming  $\alpha = 0.5$ , for a polymeric film which length = 1 cm, width = 0.5 cm, weight = 1.6 mg, density =  $1540 \text{ g l}^{-1}$ ).

The simulated chronopotentiograms  $E(t)$  are very different than the experimental ones (Fig. 6 from the

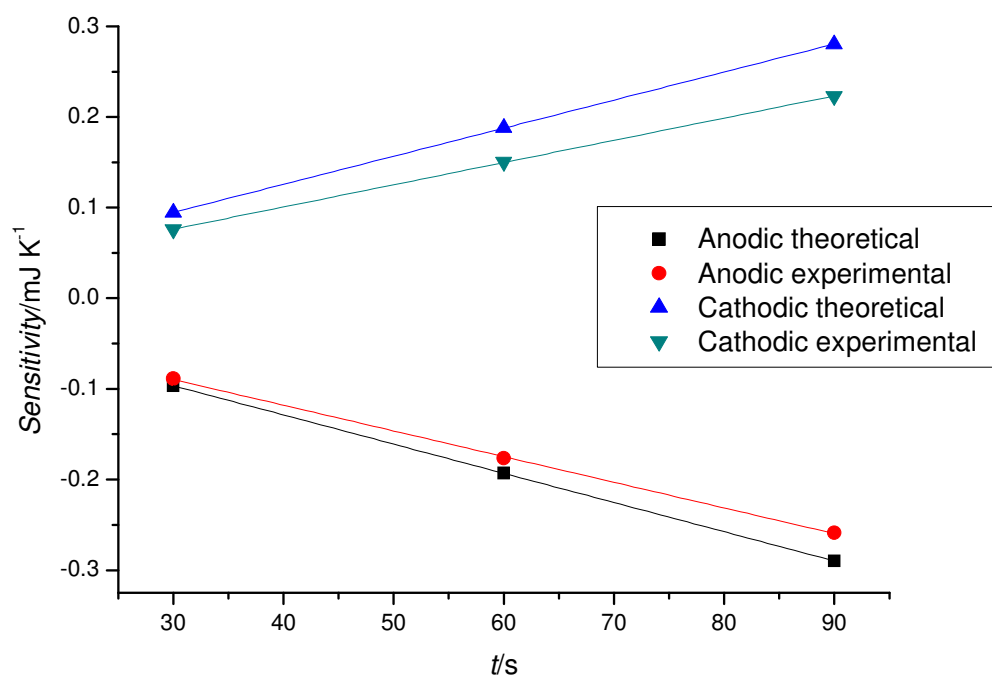
main text). There the potential evolutions range is 0.8V, the potential range here is 70V; slopes for different temperatures are similar there and different here. Equations S4 to S6 define a different coefficient (reaction order),  $n$ , of the electrolyte concentration for every oxidation stage. That means that the consecutive oxidation steps moreover having a different oxidation potential:  $E_{0n}+(n-1)\Delta E$ , they have a different potential evolution inside each the stage. That means that the different states are not equivalent from a kinetic point of view. The Polymer Science was developed assuming the same reaction kinetics for the incorporation of a monomeric unit to the growing polymer chain, whatever the length of this chain (from 1 monomeric unit to  $n$  monomeric units). By analogy we can assume here that the oxidation kinetics for the extraction of each of the consecutive  $n$  electrons is equivalent. So, assuming that the  $\Delta E$  between different oxidation states are equivalent and that the oxidation kinetics inside every stage also are equivalent, the step function (Eq. 22) from the main text is obtained. The potential evolution of the step function for 6 steps (consecutive extraction of 6 electrons from the chain) keeps inside the experimental potential range.



**Figure S2.** Simulation of equation 22 from the main paper considering all the oxidation states as equivalent states ( $\Delta E$  between different oxidation states is constant, and the kinetics inside every oxidation stage is defined by the same equation Eq. 19.a and 19.b for oxidation and reduction processes, respectively).

**Changes in sensitivity with the reaction time when the consumed electrical energy is studied at different temperatures.**

It is possible to obtain the sensitivity (slope) in Fig. 8 (main paper) as a function of the reaction time, or time of current flow, as can be seen in Fig. S3. The sensitivity increases for increasing oxidation, or reduction, states of the polymer: increasing number of electrons were extracted, or injected, respectively in each chain.



**Figure S3.** Variation of the sensitivity with the reaction time, obtained from Fig. 8 in the main paper.