

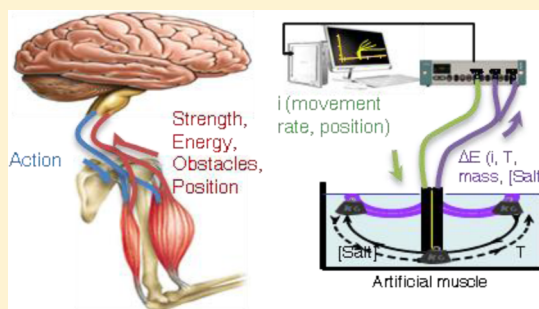
Biomimetic Dual Sensing-Actuators: Theoretical Description. Sensing Electrolyte Concentration and Driving Current

Jose G. Martinez and Toribio F. Otero*

Universidad Politécnica de Cartagena, ETSII, Center for Electrochemistry and Intelligent Materials (CEMI), Paseo Alfonso XIII, Aulario II, 30203 Cartagena, Spain

S Supporting Information

ABSTRACT: Here we present the theoretical (electrochemical and polymeric) description of chronopotentiometric responses (under driven constant current) from reacting conducting polymers both, as films or taking part of electrochemical devices, that sense driving current and electrolyte concentration during reactive actuation. The attained sensing-actuation equations describe the potential, or the consumed electrical energy, evolution as a function of working and environmental variables: driving current, temperature, electrolyte concentration, or mechanical conditions. Good agreement between theoretical and experimental results is attained here by using polypyrrole films under flow of different currents or in different electrolyte concentrations. Being a general theoretical description, any reactive device based on the electrochemistry of conducting polymers or carbon based reactive compounds is expected to sense working and environmental conditions being described by those equations as tactile artificial muscles do. Only two connecting wires contain actuating (current) and sensing (potential) signals that are detected, simultaneously and at any actuating time, by the computer as mammals brains do.



INTRODUCTION

The electrochemistry of conducting polymers includes reactive macromolecules exchanging ions and solvent with the electrolyte. Those dense reactive gels are the simplest material model mimicking biological materials and reactions in cells.^{1,2} Material properties, such as volume, color, stored charge, stored chemicals, or permselectivity, change under electrochemical control in a reversible way following the reversible electrochemical reactions.^{1–4} They mimic similar changes in natural muscles, mimetic skins, electric organs, glands, or membranes, giving similar mimetic artificial devices: they are biomimetic properties giving biomimetic reactive devices.^{2,3,5–7} New reactive devices as artificial muscles,^{1–3,5–8} smart windows,^{9,10} smart membranes,^{11–13} batteries and supercapacitors,^{14–16} smart chemical dosage,^{17,18} electron/ion transduction at very low overpotential and nervous interfaces^{19,20} are being developed.

From several years ago, our research group has probed that artificial muscles are faradic soft and wet electrical motors^{21–24} that sense, while moving driven by electrical currents, either working and surrounding variables. Movement rate and position are controlled, through faradic equations, by the flowing current and by the consumed charge.^{2–4,23–26} The muscle potential, or the consumed electrical energy, was empirically proved to depend linearly on the flowing current or semilogarithmically with the electrolyte concentration during the movement of the muscle.^{1–3,23,24,26–35} The driving current is the acting variable, and the material response (its potential

evolution) is the sensing function of working and environmental variables. Electrolyte concentration, temperature, driving current, and film volume (and through this volume the mechanical variables like pressure, strain, or stress) are the sensed variables. The actuating-sensing duality is a common characteristic of artificial muscles fabricated with conducting polymer that exchange, for charge balance, anions^{1,2,24,27–33} or cations^{3,23,26,34,35} with the electrolyte during actuation. This dual property is kept whatever the dimensions or structure (freestanding film,^{3,34} bilayer,^{3,23,27,32,35} triple layers,^{29,33} several bilayers³¹ or several triple layers,²⁶ interpenetrated networks,²⁷ or coated fibers²⁹) of the device. Any obstacle located in the way of the muscle movement produces a step of the muscle potential evolution (an increase of the consumed energy) at the contact time proportional to the opposed mechanical resistance: they are tactile muscles sensing obstacles in its way, giving information about the mechanical resistance and if the muscle is able to produce the required mechanical energy to shift the obstacle, or not.^{32,35} Those dual actuating-sensing devices constitute a new technological paradigm including several in one device without physical separation. The device is one actuator and several sensors all of them driven and controlled simultaneously by the same electrochemical reaction of the constituent material. Only two connecting wires contain,

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simultaneously and at any actuating time, actuating and sensing signals. The computer follows, simultaneously and at any time, the driving current (determining movement rate and position) and the sensing potential (temperature, reactant concentrations, pressure, strain, stress) signals. Today's technologies require one motor and several sensors each connected to the computer entrance through two different connecting wires per device: the computer requires time and software to read, alternatively, each device signal and to integrate those values for taking decisions. A new paradigm of dual or multi systems (sensing-actuators or actuating-sensors) including all the system information in only two connecting wires is emerging, opening a new world for development of biomimetic robots and devices.

The system (computer/potential-galvanostat/artificial muscle) mimics muscles-brain actuating-sensing systems with instantaneous feedback communication (Figure 1) of the

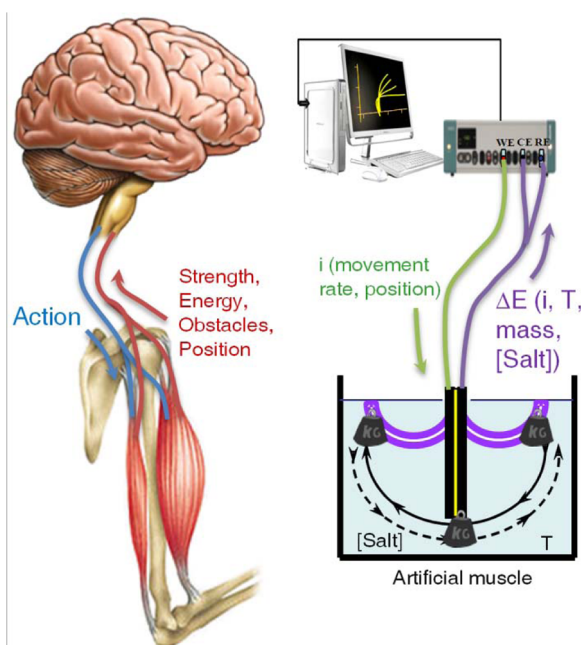


Figure 1. Brain-muscle feedback communication and scheme of the mimetic computer-generator/sensing artificial muscle system.

relative location, movement rate, concentration, temperature, current, or mechanical conditions. If we extend an arm in the dark (to avoid confusing visual messages) taking an object up our brain receives back information, at any time, about the exact energy required to translate the object, the rate of the movement, and the relative (to our body) position of the object: this is a conscious actuating-sensing system.

The terms electrochemical actuators, acting functions, or sensing-actuators are used in this paper in a broad sense including any device based on the electrochemical reaction in conducting polymers (from individual chains, to nanostructures, micro- or macrostructures; as films, powders, or bricks). Thus, molecular motors, artificial muscles, batteries, smart membranes, smart windows and mirrors, electron-ion transducers, artificial synaptic systems, and any other electrochemical device based on conducting polymers are here considered as electrochemical actuators.

Recently, we have developed, based on chemical, electrochemical, and polymeric principles, a theoretical description of

the chronopotentiometric responses to driving constant currents of conducting polymers and artificial muscles.³⁶ The evolution of the material potential between two different oxidation states results as a function of the working variables: driving current, temperature, electrolyte concentration, and volume variations. Only reversible slow redox processes taking place in the polymer film are considered. The oxidation/reduction processes are assumed to occur under chemical kinetic control. Conformational relaxation kinetic control, or counterion diffusion kinetic control, was avoided in this initial approach. Irreversible parallel processes, as overoxidation or degradation reactions or electrolyte discharge, are not included in this stage of the theoretical development. A good agreement was attained for different temperatures between experimental results and the theoretical description.³⁶ Here the theoretical description will be compared with the electrochemical responses of self-supported polypyrrole films for different values of a working (current) variable and of a surrounding (electrolyte concentration) variable. Similar empirical results from the literature for sensing and tactile artificial muscles will be analyzed and discussed.

EXPERIMENTAL SECTION

Experimental conditions, reactants, and equipments and the obtention of self-supported polypyrrole films have been described in a previous paper.³⁶

Every self-supported polypyrrole electrode was now submitted in 0.1 M LiClO₄ aqueous solution to potential sweeps (five consecutive cycles) between -1.0 and 0.6 V versus Ag/AgCl at 5 mV s^{-1} in order to obtain stationary electrochemical responses. The potential cycling was stopped every time after the last reduction sweep at -1.0 V. Then, the chronopotentiometric responses were obtained by applying five consecutive square waves of current: oxidation by flow of 0.75 mA for 30 s , then reduction by flow of -0.75 mA for 30 s . Stationary chronopotentiograms were attained after two consecutive square waves. The procedure is repeated for every studied electrolyte concentration. The experimental oxidation and reduction chronopotentiograms used to check the theoretical descriptions were taken from the fourth consecutive square wave for every concentration. The procedure guarantees transitions between the same two oxidation states (initial reduced and final oxidized for the oxidation reaction by consumption of the same charge) every time, as required for the theoretical development.

When the influence of the driving current is studied, in order to maintain the same initial and final states, oxidation and reduction times must guarantee the same oxidation and reduction charges. For every experimental current, anodic and cathodic polarization times were calculated from the oxidation/reduction charge: $q = it = 0.75 \text{ mA} \times 30 \text{ s} = 2.25 \text{ mC}$ for the electrolyte concentration influence, so $t = 2.25/i$ seconds.

RESULTS

Any electrochemical device made of CP is based on the reversible reactions occurring in those materials exchanging anions, or cations, with the electrolyte.^{2,3} Here oxidation (main paper) and reduction (Supporting Information) reactions with prevalent exchange of anions between the polymer film and the electrolyte (reaction 1) will be considered.⁵⁻⁷

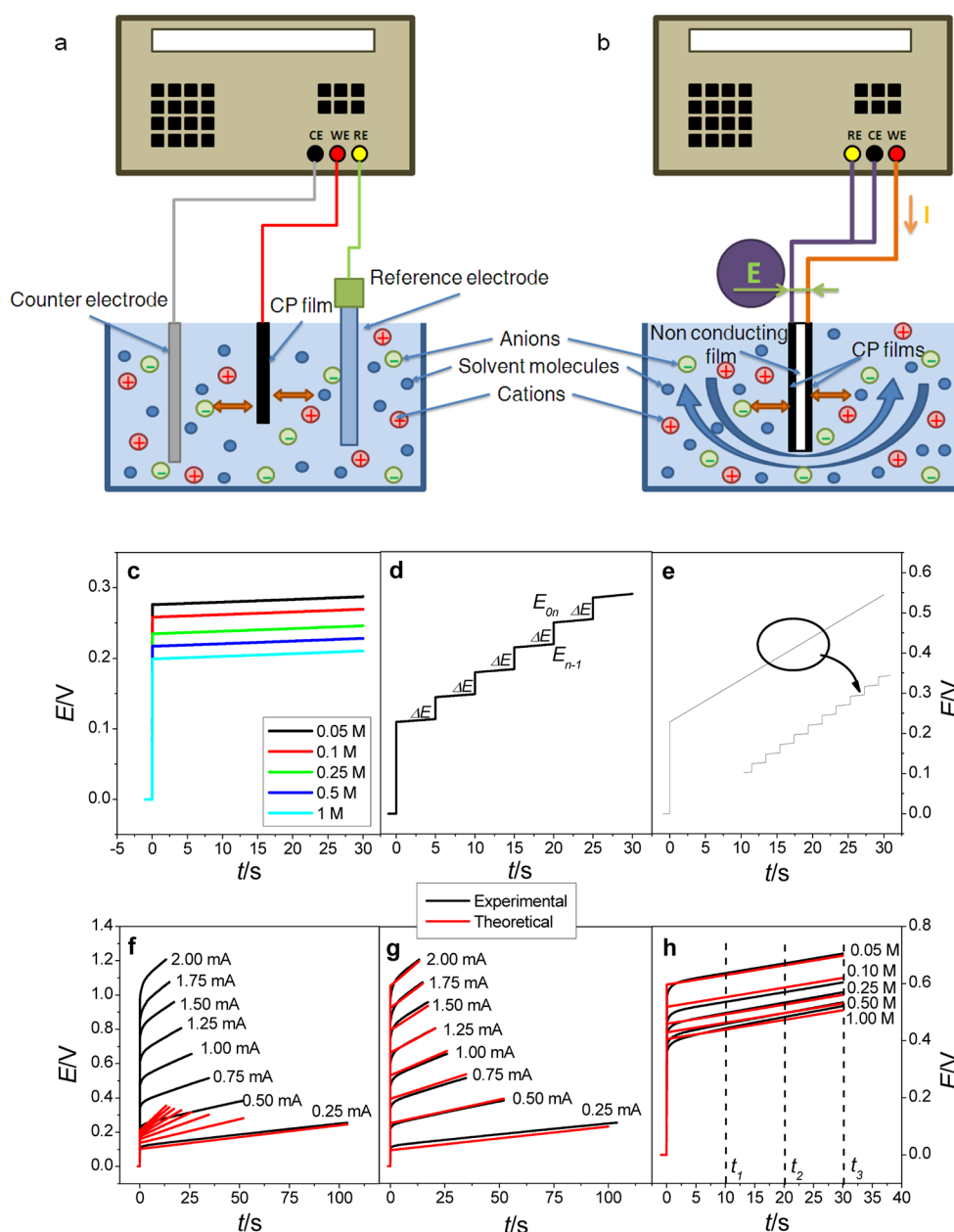
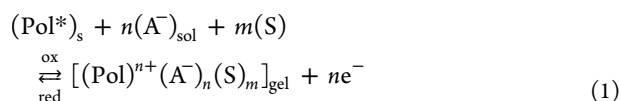


Figure 2. (a) Experimental setup for the electrochemical control of the reactive materials. (b) Experimental setup for the electrochemical control of artificial muscles. (c) Simulation of the polypyrrole potential evolution from eq 3 for different concentrations of electrolyte, starting every time from the same reduced state, by flow of a constant current of 0.75 mA through the polypyrrole film (1 cm length, 2 cm width, weighting 1.6 mg, density = 1540 g L⁻¹); by flow of constant anodic currents; being [Pol*] (the initial concentration of active centers in the film) 2 mol L⁻¹; assuming $\alpha = 0.5$ and $n = 1$ and at 25 °C. (d) Simulation attained from eq 5, being $E_n(t)$ defined by eq 4, when six electrons are extracted through six consecutive steps of one electron from every polymeric chain of a monodisperse polypyrrole film using constant values from part b. (e) Similar simulation for 190 consecutive steps of one electron per step. (f) Experimental (black) and simulated (red, through eqs 5 and 6, without impedance correction) anodic chronopotentiograms under flow of different constant anodic currents through the polypyrrole film in 1 M LiClO₄ aqueous solution at room temperature, being 190 the number of electrons extracted per chain. (g) Experimental (black) and simulated (red, through eqs 5 and 8) anodic chronopotentiograms, being 77 Ω the impedance of the system. (h) Experimental (black) and simulated (red, through eqs 5 and 7) anodic chronopotentiograms obtained by flow of 0.75 mA in different electrolyte concentrations.



where the different subindexes mean the following: s, solid; sol, solution; Pol*, the active centers in the polymer film (understood as those points on the polymeric chains where a positive charge will be present after oxidation); A⁻, the anions

exchanged between the polymer film and the solution to keep the film electroneutrality; S, solvent molecules exchanged for osmotic pressure balance forming a dense polymer gel (indicated by the subindex gel) film. The theoretical treatment should be similar, getting the same final equations, for conducting polymers with a prevalent exchange of cations during reaction. For subsequent developments, the permanent presence and exchange of both ions (anions and cations)

during reaction will be considered, even if one of them participates in a minor percentage.

The Le Chatelier principle states that a system at equilibrium, when subjected to a perturbation, responds in a way that tends to minimize its effect.³⁷ Here, according to the Nernst equation, any increase of temperature or electrolyte concentration will promote a decrease of the potential (the Nernst equation defines and quantifies concentration and temperature sensors under equilibrium conditions). Considering the increase of volume from the reduced (shrunk state of a polymer exchanging anion) to the oxidized (swollen) state, any pressure, stress, or strain applied to the polymer film will promote the potential increase (mechanochemoelectrical sensor).³⁸

That means that those variables affect the equilibrium constant (K) by influencing both the oxidation (k_{ox}) and the reduction (k_{red}) reaction kinetic constants ($K = k_{\text{red}}/k_{\text{ox}}$). The influence of the experimental variables on the reaction kinetic constant is expected to remain on the evolution of the material potential during anodic (oxidation) or cathodic (reduction) direct reactions driven by current flow, outside the equilibrium. If the conducting polymer takes part of one of the above reactive devices, those devices are expected to behave as actuating-sensing devices. Founded on those basic principles, sensing and tactile artificial muscles have been empirically developed.^{27,28,35} Since the material potential is an intensive property, the simultaneous sensing/actuating duality must expand from molecules to nano-, micro-, and macroscopic structures.

The basic Butler–Volmer equation of the electrochemical kinetics correlates actuating (current), sensing (potential), chemical (concentration), and environmental (temperature and pressure) variables.³⁹ When applied to complex reactions including more than one reactant during the electron transfer from, or to, the polymer chain in the film (reaction 1), the basic equation becomes⁴⁰

$$i_a = FV k_{a0} [A^-]^d [\text{Pol}^*]^e \exp\left(\frac{(1-\alpha)nF(E-E_0)}{RT}\right) \quad (2)$$

where the subindex a indicates an anodic process; i_a is the anodic current passing through the electrode; F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$); V is the volume of the film; k_{a0} is the oxidation rate constant (see Supporting Information S.2), or rate coefficient, for $E = E_0$; E is the potential; E_0 is the standard potential; $[A^-]$ is the concentration of anions in solution; $[\text{Pol}^*]$ is the concentration of active centers in the film; d and e are the reaction orders; α is the symmetry factor for the electron transfer; n is the number of electrons removed (by oxidation) from every polymeric chain; R is the universal gas constant ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$); and T is the experimental temperature.

During oxidation by flow of an anodic current i_a , the active centers of the chains in the film are consumed. Its concentration variation with time (t) is defined by the evolution of the consumed charge, $Q = i_a t$, which determines the number of moles of electrons extracted from the film ($n = Q/F$) equal to the number of counterions penetrating from the solution into the film for charge balance. The concentration variation of active centers, or counterions, in the film volume (V) is $[\text{Pol}^*] = Q/FV$. By including this concentration variation in eq 2, the evolution of the material potential with time as a function of working and surrounding variables is attained:

$$E(t) = E_0 + \frac{RT}{(1-\alpha)nF} \left\{ \ln\left(\frac{i_a}{FV}\right) - d \ln[A^-] - e \ln\left([\text{Pol}^*]_{\text{initial}} - \frac{i_a t}{FV}\right) - \ln k_{a0} \right\} \quad (3)$$

Equation 3 describes the material potential evolution during reaction as a function of both acting and sensing variables (i , T , $[A^-]$, V). Equation 3 is the basic actuating-sensing function.

Figure 2 shows the electrochemical setup used for the experimental control of either free-standing films of conducting polymers (Figure 2a) or electrochemical devices as three-layer artificial muscles (Figure 2b). Figure 2c presents the theoretical evolution from eq 3, of the potential of a polypyrrole film during oxidation under flow of an anodic current of 0.75 mA, for an initial concentration of active center, $[\text{Pol}^*] = 2 \text{ mol L}^{-1}$; being $\alpha = 0.5$, $n = 1$, a film length of 1 cm, a film width of 2 cm, a film mass of 1.6 mg, and a film density of 1540 g L^{-1} , for different electrolyte concentrations $[A^-]$ (0.05, 0.1, 0.2, 0.5, and 1 mol L^{-1}) at ambient (25°C) temperature, for $d = 0.7$, $e = 1.2$, and $k_{a0} = 1.0142 \times 10^{-10}$, obtained by determination of the empirical oxidation kinetics of polypyrrole.⁴¹ For increasing electrolyte concentrations, the potential evolution shifts to lower potentials as expected from both the Nernst expression for equilibrium conditions or from eq 3 under reaction. The bad news is that a very low potential increment during the oxidation time is observed along the oxidation time in every theoretical chronopotentiogram; meanwhile, fast linear increase of the potential with time occurs (Figure 2h) in experimental results.

This initial approach supposes that the n electrons removed from the polymeric chains are equivalent: they are removed at the same ionization potential, and only one equilibrium state and one standard potential E_0 should exist.

Coming back to the polymer science by accepting, as initial hypotheses, that the polymer film is constituted by m ideal and lineal polymeric chains having the same length (monodisperse material), the extraction of n electrons from every polymeric chain during current flow must occur through n consecutive steps of one electron each at n ionization potentials of increasing energies. That means that n consecutive chemical equilibrium states can be attained by polarization at increasing potentials. The oxidation, under flow of a constant anodic current, goes on through n consecutive steps initiated at increasing standard potentials: $E_{01} < E_{02} < E_{03} < \dots < E_{0n-1} < E_{0n}$ until oxidation completion.³⁶ The potential evolution during every intermediate step, that means during the time required to extract the n th electron from each chain, is given by

$$E_n(t) = E_0 + (n-1)\Delta E + \frac{RT}{(1-\alpha)F} \left\{ \ln\left(\frac{i_a}{FV}\right) - d \ln[A^-] - e \ln\left([\text{Pol}^*]_{\text{initial}} - \frac{i_a t}{FV}\right) - \ln k_{a0} \right\} \quad (4)$$

The evolution of the material potential during the time required for a full oxidation is attained by linking the n consecutive steps (eq 4 for consecutive values of n) through a unitary pulse function, to give a stair function:⁴²

$$E(t) = \sum E_n(t) p_n(t) = E_1(t) p_1(t) + E_2(t) p_2(t) + \dots + E_n(t) p_n(t) \quad (5)$$

where $E_n(t)$ is given by eq 4 for each of the consecutive n steps and $p_n(t)$ is the unitary pulse function, taking a unitary value in the considered n interval and being zero outside this interval.

By simulating now the new stair eq 5 for $n = 6$ (six electrons are removed by consecutive steps of one electron each from every polymer chain), the result (a stair) is shown in Figure 2d.

When the number of consecutive oxidation states is high enough, an almost straight line (Figure 2e), having a constant slope, is attained, giving a good correlation with experimental results.

At the moment, the number of polymer chains (m) in the polymer film, their length distribution, or the number of electrons (n) that can be removed from every polymeric chain are unknown magnitudes. Assuming a monodisperse polymer film, the number of electrons removed from every polymeric chain (n) can be attained by mathematical adjustment of eq 5 to an experimental chronopotentiogram giving 190 electrons per chain. This value remains constant for the simulation under different values of the studied experimental variables. The theoretical description becomes, at the moment, semiempirical.

In order to clarify the multisensing possibilities of eqs 4 and 5, different variables are being checked, at this initial stage, as independent sensors: by changing the values of a variable every time and keeping the rest constant. In a previous paper, temperature sensing ability of both materials and artificial muscles was proved.³⁶ Here the influence of the anodic current and that of the electrolyte concentration will be checked separately.

Starting from the same reduced state the polypyrrole film was oxidized by flow of a different anodic current every time until the same final state. That means by consumption of either the same constant charge (the time of current flow was varied) and the same concentration of active centers in the polymer film for every experiment. Figure 2f shows experimental and theoretical results from eq 5 keeping the same value of the constants stated for Figure 2c (experimentally measured), being 190 the number of electrons (one by step) extracted from every chain.

As expected, the film potential evolves during reaction at higher potentials for higher anodic currents. Theoretical slopes fit the experimental ones. Nevertheless, the initial theoretical and experimental potentials (at $t \rightarrow 0$ s) are different, indicating that electrical resistances in the system during current flow, other than the reaction resistance, were not considered by the theoretical treatment. The interfacial ionic (polymer/solution) and electronic (polymer/metal) transfer processes on both electrodes and the electric flow through the electrolyte are considered in electrochemistry as electrical resistances opposing to the current flow. By defining the system impedance (Z) as a result of all those resistances, a new term of the potential can be described by Ohm's law, $E_z = i_a Z$, and

$$E_n(t) = E_0 + i_a Z + (n - 1)\Delta E + \frac{RT}{(1 - \alpha)F} \left\{ \ln\left(\frac{i_a}{FV}\right) - d \ln[A^-] - e \ln\left([Pol^*]_{\text{initial}} - \frac{i_a t}{FV}\right) - \ln k_{a0} \right\} \quad (6)$$

Equation 6 is the multisensing-actuating function (actuator and current sensor through i_a ; electrolyte sensor, through $[A^-]$, temperature sensor, through T ; mechanical sensor, through V and k_{a0}). By including this new term in the potential evolution

(eq 5) and by adjusting the resulting theoretical description (eq 6) to one of the experimental results, a value of 77Ω was attained for Z . This value is very close to the ohmic resistance measured in the conducting polymer film. Using this value for the theoretical description, a good agreement (Figure 2g) is attained between theoretical and experimental chronopotentiograms for the oxidation of polypyrrole films by flow of different anodic currents.

Equations 5 and 6 were now used to describe the potential evolution of the reactive polypyrrole film (self-supported or taking part of any electrochemical device) by flow of a constant anodic current of 0.75 mA in aqueous solution of different electrolyte concentrations (dual actuating-concentration sensor equations); being 190 the number of electrons extracted per polymer chain. The impedance of the system 77Ω must be now corrected by the concentration influence on the electrolyte conductivity (see the Supporting Information, eq S7):

$$E_n(t) = E_0 + i_a \left(C_1 + \frac{C_2}{\sqrt{[A^-]}} \right) + (n - 1)\Delta E + \frac{RT}{(1 - \alpha)F} \left\{ \ln\left(\frac{i_a}{FV}\right) - d \ln[A^-] - e \ln\left([Pol^*]_{\text{initial}} - \frac{i_a t}{FV}\right) - \ln k_{a0} \right\} \quad (7)$$

where $C_1 = 77 \Omega$ was empirically adjusted above and $C_2 = 0.02 \Omega \text{ mol}^{1/2} \text{ L}^{-1/2}$ (adjusted empirically as in the case of C_1) is a constant that represents the variation in the system impedance when the concentration of the electrolyte changes in 1 mol L^{-1} . The term, $C_1 + (C_2[A^-]^{-1/2})$, ranges between 77.09Ω in 0.05 M solutions and 77.02Ω in 1 M solutions: it can be considered equal to C_1 in this initial approach. Under those conditions, a good agreement is attained, Figure 2h, between theoretical and experimental evolutions of the film potential.

Looking into the sensing properties of reaction 1, eqs 5 and 6 state that for the extraction of the n th electron (after consumption of a constant charge, $q = i_a t$) from every chain of the film, a linear variation is expected between the applied current (in this initial approach, the logarithmic terms are low and can be included in the origin ordinate) and the potential of the conducting polymer film.

$$E_n(i_a, t) = E'_n(i_a, t) + Zi_a \quad (8)$$

Equation 8 is the linear current sensing equation: the polymer films or any based electrochemical device behave, in an initial approach, as a resistance. Results were checked for the different currents after consumption of three different constant charges (8.87, 17.73, and 26.60 mC) from the same initial state every time. Figure 3a shows a good linear dependence whatever the consumed charge and a good agreement between experimental and predicted theoretical results. Parallel linear variations were attained after consumption of different charges. Slopes represent the sensitivity of the current sensor, 0.58 and 0.59 V A^{-1} , for the theoretical and experimental, respectively, anodic currents and -0.52 or -0.54 V A^{-1} for the theoretical and experimental, respectively, cathodic currents. Equation 8 also fits the empirical results from the literature obtained for different artificial muscles^{26,28} and sensing hybrid materials or fibers including a conducting polymer.^{29,34}

By keeping constant all the other variables, eqs 5 and 7 predict, for a constant consumed charge (a constant time of

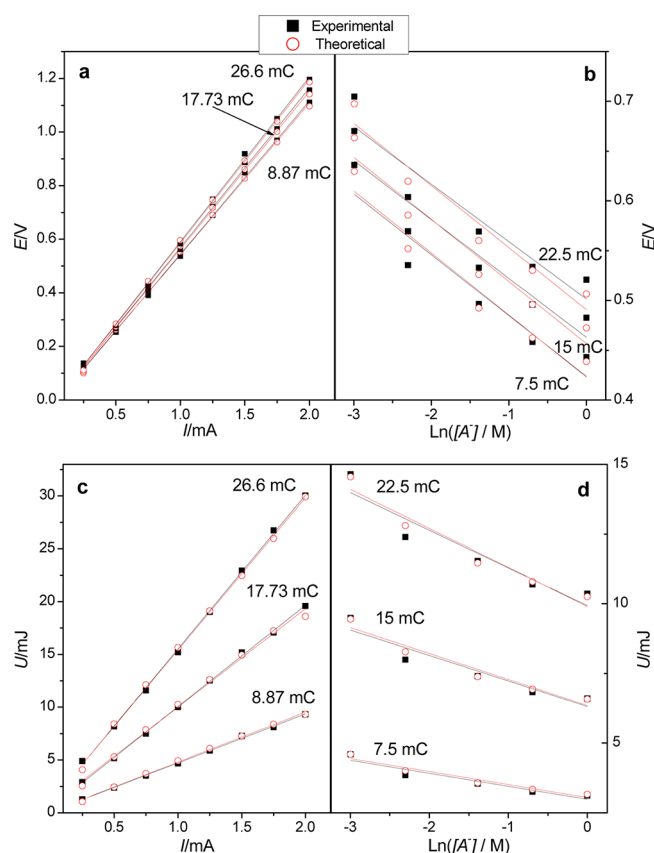


Figure 3. Experimental control of the sensing eqs 8, 9, 11, and 12 after consumption of the same oxidation charges, that means during extraction of the n th electron from every chain: (a) Experimental (Figure 2g) and theoretical, from eq 8, potentials attained by flow of different currents. (b) Experimental (Figure 2h) and theoretical, eq 9, potentials attained in different electrolyte concentrations. (c) Experimental and theoretical, eq 11, electrical energy consumed after flow of the same anodic charge by flow of different constant currents. (d) Experimental and theoretical, eq 12, electrical energy consumed in different electrolyte concentrations.

current flow), a semilogarithmic dependence of the film potential from the electrolyte concentration.

$$E_n([A^-], t) = E_n''(t) - \frac{RT}{(1-\alpha)F} d \ln[A^-] \quad (9)$$

Equation 9 is the concentration sensing equation. Figure 3b corroborates this semilogarithmic dependence, showing the good fit between theoretical and experimental results after consumption of 7.5, 15, or 22.5 mC. Parallel linear variations were attained after consumption of different charges. Slopes represent the sensitivity of the concentration sensor: -62.20 and -59.20 mV M^{-1} from the theoretical and experimental, respectively, anodic chronopotentiograms and 48.40 and 49.40 mV M^{-1} from the theoretical and experimental, respectively, cathodic chronopotentiograms. Equation 8 also fits the empirical results from the literature obtained for different artificial muscles and sensing hybrid materials or fibers including a conducting polymer.²⁹

The evolution of the electrical energy, $U(t)$, consumed by the film during extraction of the n th electron from every chain of the film by flow of a constant anodic current is attained by integration of its potential evolution, eq 6, giving:

$$\begin{aligned} U(t) &= i_a \int E dt \\ &= E_0 i_a t + Z i_a^2 t + (n-1) \Delta E i_a t + \frac{RTVe}{(1-\alpha)} \\ &\quad \left\{ \ln \left([\text{Pol}^*]_{\text{initial}} - \frac{i_a t}{FV} \right) - 1 \right\} [\text{Pol}^*]_{\text{initial}} \\ &\quad - \frac{i_a t}{FV} \left\{ + \frac{RT}{(1-\alpha)F} i_a t \ln \left(\frac{i_a}{FV} \right) - \frac{RT}{(1-\alpha)F} i_a t \right. \\ &\quad \left. \ln k_{a0} - \frac{RT}{(1-\alpha)F} d i_a t \ln[A^-] \right\} \quad (10) \end{aligned}$$

Equation 10 is a multiactuating-sensing function. It describes the consumed electrical energy as a function of the experimental variables: applied current (i_a), time of current flow (t), temperature (T), film volume (V), and electrolyte concentration ($[A^-]$). This is a sensing equation, and the consumed electrical energy $U(t)$ is the sensing magnitude. After consumption of a constant oxidation charge ($q = i_a t$), this equation predicts linear, eq 11, or semilogarithmic, eq 12, variations of the consumed electrical energy with the applied current (in this initial approach, the terms including $\ln i_a$ are considered low and included in the constant) or with the electrolyte concentration.

$$U_a(i_a, t) = U_a'(i_a, t) + QZi_a \quad (11)$$

$$U_a(t) = U_a''(t) - \frac{RT}{(1-\alpha)F} dQ \ln[A^-] \quad (12)$$

After integration of the experimental and theoretical chronopotentiograms from Figure 2g for three different consumed charges, 8.87, 17.73, and 26.60 mC, results presented by Figure 3c depict the linear variations (theoretical and experimental) of the consumed electrical energy with the applied currents. The obtained lines are not parallel because U_c' is time dependent (see the Supporting Information). Slopes represent the sensitivity of the current sensor. The system is most sensitive, presents higher slopes, for higher consumed energies, which means for a higher number of electrons extracted from every chain (Table 1). Equation 11 also fits empirical results from the literature obtained for different artificial muscles^{26,28} and sensing hybrid materials including a conducting polymer.^{29,34}

Figure 3d shows the semilogarithmic variations (theoretical and experimental) with the electrolyte concentration for the oxidation charges of 7.5, 15, and 22.5 mC, respectively. There exists an excellent agreement between experimental results and theoretical predictions. The obtained lines are not parallel because U_a'' is not constant with time. Slopes represent the sensitivity of the current sensor. The system is most sensitive, presents higher slopes, for higher consumed energies, which means for a higher number of electrons extracted from every chain (Table 1). Equation 12 also fits the empirical results from the literature obtained for different artificial muscles and sensing hybrid materials including a conducting polymer.^{29,34}

Arrhenius plots for temperature sensing³⁶ and resistances (electrochemical cell resistance here) used to sense currents, as eqs 8 and 11, could be considered as physical sensors. Nevertheless, the simultaneous inclusion of the semilogarithmic concentration dependence, eqs 9 and 12, only can be explained by chemical (electrochemical) processes. Equations 7 and 10 are multiactuating-sensing (several sensors and one actuator)

Table 1. Upper Part, Slopes (Sensitivities) Obtained from Figure 3c under Flow of Different Anodic (Oxidation) or Cathodic (Reduction) Currents Keeping Constant the Rest of the Experimental Variables; Lower Part, Slopes (Sensitivities) Obtained from Figure 3d for Different Electrolyte Concentrations during Oxidation or Reduction Processes, Keeping Constant the Rest of the Experimental Variables^a

Q (mC)	current			
	anodic		cathodic	
	theoretical (mJ A ⁻¹)	experimental (mJ A ⁻¹)	theoretical (mJ A ⁻¹)	experimental (mJ A ⁻¹)
8.87	4.73	4.64	4.62	4.61
17.73	9.31	9.61	9.25	9.45
26.60	14.45	14.59	13.90	13.84

Q /mC	electrolyte concentration			
	anodic		cathodic	
	theoretical (mJ M ⁻¹)	experimental (mJ M ⁻¹)	theoretical (mJ M ⁻¹)	experimental (mJ M ⁻¹)
7.5	-0.47	-0.47	-0.36	-0.36
15.0	-0.93	-0.92	-0.73	-0.73
22.5	-1.40	-1.35	-1.09	-1.10

^aTheoretical current and concentration sensitivities were calculated from eqs 11 and 12, respectively.

equations for the description of chemically reactive materials and devices.

The theoretical description also provides a way for the specific discrimination between capacitive and faradic assignment of the consumed charges. If the high slope depicted by the experimental chronopotentiograms is due to capacitive charges, the same slope is expected to go on until the water discharge potential is attained. Nevertheless, if this slope has a faradic origin, the potential is expected to step, after oxidation completion, until the beginning of the water discharge, as batteries do after charge completion. Figure 4 corroborates the faradic experimental origin of the polypyrrole oxidation and how eqs 5 and 6 simulate this evolution, despite the assumed monodispersity of the chains in the film.

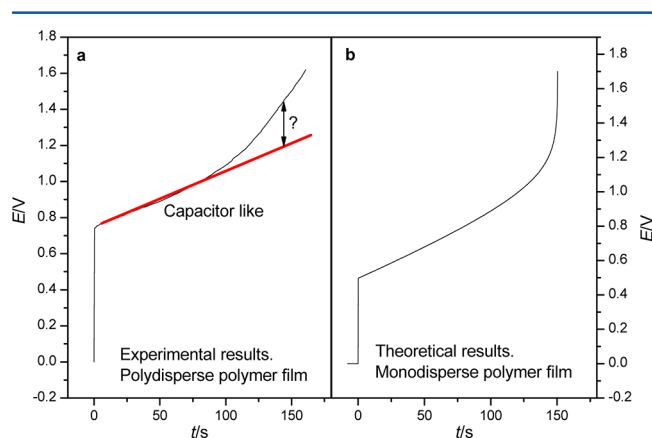


Figure 4. (a) Experimental chronopotentiogram obtained by flow of 0.75 mA for a time long enough to overcome the oxidation completion. (b) Theoretical description through eqs 5 and 6 for a polypyrrole film constituted by ideal lineal and monodisperse polymeric chains.

CONCLUSIONS

The basic electrochemical kinetics, eq 2, states a good theoretical base for describing the galvanostatic response of polymer films (self-supported or taking part of any electrochemical device) by eq 6, and for the evolution of the consumed electrical energy with time, eq 10. The theoretical chronopotentiometric responses are stair functions, eq 5, including the n consecutive electron transfer steps per chain. Those equations are quantitative relationships between actuating (i) and sensing (T , V , and electrolyte concentration) variables: they are multiactuating-sensing equations.

Changing one variable every time and keeping a constant value for each of the other variables, eq 5 gives dual sensing-actuating functions. Here it was probed that the theoretical description fits experimental results when different anodic currents flow through a polypyrrole film or in different electrolyte concentrations. The same functions also describe chronopotentiometric results from artificial muscles moving under the influence of the same variables. Equations 8, 9, 11, and 12 also describe the empirical results at different oxidation states from artificial muscles whatever the shape, dimension, bilayers, triple layers, or multilayers during muscle's work and for muscles made of conducting polymers exchanging anions or cations.

The attained actuating-sensing equations are based on reaction 1, so any electrochemical device based on conducting polymers, fullerenes, carbon nanotubes, graphenes, or any electrochemically reactive carbon based organic material also will give simultaneous sensing-actuators. Batteries, smart windows and mirrors, smart membranes, drug delivery devices, or electron-ion transducers are expected to sense working and environmental variables while working. At any moment of the device actuation, as it occurs during muscle actuation (Figure 1), the connecting wires contain, and the computer reads, the driving current and the potential response. Any change of the potential communicates a variation on the driving current or of the electrolyte concentration (as independent variables). The system mimics brain–organs feedback communications (Figure 1): this is the simplest biomimetic and dual sensing/actuator device.

Equations 5, 6, and 10 describe several sensors and one actuator: those are multisensing-actuating functions. The sensitivity of the reaction is different for each of the studied variables, being defined by the slope of the linear or semilogarithmic variations. The simultaneous change of two or more variables will be studied in the near future for checking the multisensing-actuating description of the attained equations.

Intelligent actuating-sensing devices announce a new biomimetic technological world of gel robots and gel tools. Dynamic³ and actuating-sensing electrochemical equations solve the engineering problem of activeness⁴³ and deformability⁴⁴ uncertainty for gel robots. After quantitative descriptions, uncertainties related to the surrounding influence on gel devices, gel tools, and gel robots⁴⁵ disappear.

As a side conclusion, a full faradic nature of the galvanostatic responses of conducting polymers was described.

ASSOCIATED CONTENT

Supporting Information

Theoretical description of the cathodic process, evolution of the concentration of active centers in the film, evolution of the

electrolyte concentration, effect of the electrolyte concentration on the system impedance, relationship between concentration of reactants and products, evolution of the potential during reduction by flow of a constant cathodic current, unitary pulse function, evolution of the consumed electrical energy during reduction, theoretical and experimental results for different concentrations of electrolyte or different applied currents, the potential at the same reduction state is a sensor of the flowing current, the potential at the same reduction state is a sensor of the electrolyte concentration, the consumed electrical energy between two reduction states is a linear function of the current. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Phone: +34 968 325519. Fax: +34 968 325915. E-mail: toribio.fotero@upct.es.

Notes

The authors declare no competing financial interest.

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