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Simultaneous Smart Actuating-Sensing Devices Based on Conducting Polymers

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1. Introduction

Towards the end of 1970s new artificial organic materials, conducting polymers (CP), were discovered (Chiang et al., 1977; Inzelt, 2011; Shirakawa et al., 1977). Since then, most of the scientists working on CP became interested by the fact that their conductivity can shift, in a reversible way, over several orders of magnitude by oxidation/reduction (also called doping/dedoping) processes. The availability of these new organic semiconductors has opened up possibilities to rebuild electronics and microelectronics producing flexible devices (Guo et al., 2010; Klauk, 2006; Perepichka & Perepichka, 2009; So, 2010).

Besides conductivity other properties such as stored charge, stored chemicals, volume, porosity or colour also change during doping/dedoping, under electrochemical control, in parallel with the material composition (counterion content) along the redox reactions (Otero, 2008). Any intermediate oxidation state determines a chemical equilibrium characterized by an equilibrium potential. Any physical (temperature, pressure, applied current) or chemical (electrolyte concentration) magnitude affecting the chemical equilibrium modifies the electrical potential of the material that therefore can be used as a sensor of that magnitude (Otero, 2009).

These properties, whose value changes with the material composition, are allowing the development of different devices (Onoda et al., 1999a; Otero et al., 1992a; Otero et al., 1992c; Pei & Inganäs, 1992a). Volume variations driven by oxidation/reduction reactions are being used to generate new electrical motors having different configurations of the polymeric actuators (Alici et al., 2007; Smela et al., 1993; Wu et al., 2005).

We will present devices constructed with conducting polymers based on an electrochemical reaction and working, simultaneously, as an actuator and as several sensors of the surrounding conditions. During the movement they store and release charge working as a battery: they are multifunctional devices.
2. Electrochemical reactions in conducting polymers

Once generated (chemical or electrochemically), conducting polymers can be considered as both, classical unreactive materials having either a constant composition and a constant value of the magnitude of its physical and chemical properties; or new reactive materials varying their composition (polymeric chains, ions and solvent in different ratios) and properties along several orders of magnitude in a reversible way under electrochemical reaction (Otero, 1999), or promoted by redox agents present in solution (Kuttel et al., 2009).

2.1. p-doping

When the polymer chains are oxidized, consecutive electrons are removed from each chain generating an excess of positive charges (holes) along the chains. This excess of positive charges (lack of electrons) promotes the repulsion between the polymeric chains and the generation of free volume between them. This free space is occupied by anions arriving from the solution to compensate the emerging positive charges (keeping the electroneutrality) and solvent molecules to keep osmotic pressure balance (Huang et al., 1986; Otero, 1999; Tsai et al., 1988).

When the polymer is generated in the presence of small anions, they can be exchanged by other small anions present in solution by electrochemical reactions so a prevailing exchange of anion occurs during reaction:

\[
\left( \text{Pol}^0 \right)_s + n \left( A^- \right)_\text{sol} + m \left( \text{Solv} \right)_\text{gel} \leftrightarrow \left( \text{Pol}^{+n} \right)_s \left( A^- \right)_\text{sol} \left( \text{Solv} \right)_\text{gel} + n \left( e^- \right)_{\text{metal}}
\]  

(1)

where the different subscripts mean: \(s\), solid; \(s\), in solution; \(gel\) indicates that the material is a gel formed by oxidized polymeric chains (Pol\(^{+n}\)) generated after the extraction of \(n\) electrons (\(e^-\)) through the metal (indicated by subscript \(metal\)) from neutral polymer chains (Pol\(^0\)), \(n\) anions (\(A^-\)) coming from the solution to keep the gel electroneutrality and \(m\) molecules of solvent (Solv) required to keep osmotic pressure balance.

When the polymer is generated in the presence of a macroanion, due to its volume and the interaction with polymer chains, this macroanion cannot be exchanged by the electrochemical reaction keeping trapped inside the polymer film. So, in order to keep the electroneutrality, smaller cations are exchanged with the solution during the reaction:

\[
\left( \text{Pol}^0 \right)_s \left( \text{MA}^- \right)_s \left( \text{C}^+ \right)_\text{sol} \left( \text{Solv} \right)_\text{gel} \leftrightarrow \left( \text{Pol}^{+n} \right)_s \left( \text{MA}^- \right)_s \left( \text{C}^+ \right)_\text{sol} \left( \text{Solv} \right)_\text{gel} + n \left( \text{C}^+ \right)_\text{sol} + m \left( \text{Solv} \right)_\text{gel} + n \left( e^- \right)_{\text{metal}}
\]  

(2)

where MA\(^-\) is the macroanion trapped inside the polymer film and \(C^+\) are cations exchanged in order to keep the electroneutrality.

Usually, the real redox process is not as easy as expressed by reactions (1) and (2): anions and cations are exchanged simultaneously (Hillman et al., 1989; Inzelt, 2008). Usually one of the previous interchanges prevails supporting the greater percentage of charge balance (Kim et al., 2010; Lyutov et al., 2011; Orata & Buttry, 1987; Torresi & Maranhao, 1999).
2.2. n-doping

Some CP such as PEDOT (Ahonen et al., 2000), polythiophene (Arbizzani et al., 1995) or polyfluorenes (Ranger & Leclerc, 1998) have an electronic affinity high enough to allow transitions from the neutral state to a reduced state, storing negative charges (by electron injection) on the chains at high cathodic potentials. In this case, very stable solvents and salts are required, as electrolytes, to perform this redox reaction:

\[
\text{Pol}^0 + n(c^-) + m(Solv) + n(e)_{\text{sol}} \rightleftharpoons \left[ \text{Pol}^{n+}(c^-) \text{(Solv)} \right]_{\text{sol}}
\]

where Pol\(^n^\) represents the reduced polymer chains after insertion of n electrons. Here, in an analogous way compared to reaction (1), an excess of negatives charges promotes repulsion between polymeric chains generating the free volume that will be occupied by cations (exchanged with solution to keep electroneutrality) and solvent (exchanged with solution to keep pressure and osmotic balance).

2.3. Double doping

Some conducting polymers can be doped both, by p-doping and by n-doping. Thus, from their neutral state they can be reduced (suffering n-doping) or oxidized (suffering p-doping). In those polymers the energy difference between both processes is the electrochemical bandgap (Arias-Pardilla et al., 2010; Otero et al., 2011).

3. Reversible change of the electrochemical properties

Electrochemical reactions 1, 2 and 3 are reversible reactions moving through n consecutive oxidation states (Otero et al., 2012) having different content of the counterion. The value of the magnitude of those properties being a function of the material composition (electrochemical properties) can also be shifted in a reversible way under faradic control. As previously indicated, conducting polymers can be oxidized and/or reduced from their neutral state, with the entry/exit of ions and solvent. The most studied electrochemical properties of conducting polymers are: volume, colour, stored charge, stored chemicals, porosity or permselectivity, sensing responses or wetability, among others. The progressive and reversible variation of the value of these electrochemical properties allows the development of different devices and products. The change in volume will be reviewed in detail below: this is the most important property of conducting polymers for the development of actuators or artificial muscles.

3.1. Volume variations

A chain of conducting polymer in solution can be considered as an electrochemical molecular motor (Balzani et al., 2005; Davis, 1999; Otero, 2011): movements are produced by reversible conformational changes in chains originated by oxidation/reduction reactions.
The reversible conformational movement from a coil like structure to a rod like structure is produced by extraction (oxidation) or injection (reduction) of \( n \) electrons through \( n \) consecutive steps of one electron per step, together with movement of balancing counterions. This results in length variation of a free polymer chain in solution but, in polymer films three dimensional changes of volume are observed. The entanglement of the polymer chains in the film gives reversible swelling or shrinking changes of volume under reversible electrochemical stimulation (Fig. 1).

Some mechanical test machines have been developed following length or thickness variations produced by submitting the film to different potential (Bay et al., 2003; Kiefer et al., 2007; Mazzoldi et al., 1998; Spinks et al., 2002) or current (Otero et al., 2006; Otero et al., 2007c) programs. In situ Atomic Force Microscopy (AFM) technique follows film thickness variation during reverse oxidation/reduction processes (Bierkowski et al., 2011; Cho et al., 2011; Smela & Gadegaard, 2001). In this way, it has been possible to measure a volume difference between reduced and oxidized state up to 35% (Smela & Gadegaard, 1999). The volume change depends on multiple factors such as type of polymer, synthesis conditions (potential or current applied), electrolyte and solvents used.

4. Simultaneous sensing and actuating properties in conducting polymers

The driving reversible electrochemical reaction supports the development of simultaneous sensing and actuating properties by conducting polymer materials and by any electrochemical device based on those materials. The electrochemical working device (based on the electrochemical reaction) senses changes of any physical or chemical variable acting on the polymer reaction rate while working. This is the Le Chatelier principle applied outside equilibrium conditions (Smith, 2004). Therefore, for increasing values of the electrolyte concentrations or of the temperature working under flow of a constant current (constant reaction rate), lower values of the device potential are observed (the reaction is easier) during the transition between the same initial and final oxidation states of the materials. When a
greater mechanical work is required (moving faster, applying a higher current, or a higher mechanical stress is needed to move the actuator) the reaction gives increasing potential when the device moves between the same initial and final oxidation states.

Those sensing abilities are intrinsic properties of the reaction. They are characteristics of the material reaction and of any device based on this electrochemical reaction. So, the dual and simultaneous sensing-actuation property is expected to be quantified from electrochemical equations.

The evolution of the conducting polymer film potential with time $E(t)$ during the movement from the same initial oxidation/reduction state to the same final oxidation/reduction state driven by flow of a constant anodic current is given by a stair function (Otero et al., 2012).

$$E(t) = \sum E_n(t)p_n(t) = E_1(t)p_1(t) + E_2(t)p_2(t) + \ldots + E_n(t)p_n(t)$$  \hspace{1cm} (4)

where:

$$p_n(t) = u(t - t_n) - u(t - t_{n+1})$$  \hspace{1cm} (5)

Being $t_n$ the time while the $n^{th}$ electron is removed from every polymeric chain and $E_n(t)$:

$$E_n(t) = E_0 + (n-1)\Delta E - \frac{RT}{(1-\alpha)F} \left\{ \ln \left( \frac{n}{FV} \right) - d \ln \left( \frac{A^{-}}{\alpha} \right) - e \ln \left( \left[ A_{\text{POL}} \right]_{\text{an}} - \frac{iF}{FV} \right) - \ln k_{a0} \right\}$$  \hspace{1cm} (6)

where $E_0$ is the standard potential, $i_a$ is the applied current; $n$ is the number of consecutive electrons extracted from a chain; $\Delta E$ is the increment observed in the potential when a new electron is extracted from a polymeric chain, $R$ is the universal gas constant ($R = 8.314$ J K$^{-1}$ mol$^{-1}$); $\alpha$ is the symmetry factor; $F$ is the Faraday constant ($F=96485$ C mol$^{-1}$); $V$, the volume of the film; $\left[ A^{-} \right]$ the concentration of anions (counterion) in solution; $t$, the time of current flow; $T$ is the experimental temperature; $d$ and $e$ are the reactions orders related with the concentration of anions in solution or to that of the active centres $\left[ \text{POL}^* \right]$ in the film (sites of the polymer where a positive charge will be stored after oxidation) and $k_{a0}$ is the rate constant or rate coefficient for $E=E_0$.

Therefore, Eqs. 4 and 6 are the sensing equations: the evolution of the device potential during actuation is a function of either, driving (current) and working (temperature, electrolyte concentration and film volume) variables.

Being electrical machines, by integration of Eq. 6 the evolution of the electrical energy consumed by the electrochemical device ($U_a$) during the actuation time is attained:

$$U_a(t) = i_a \int E(t)dt = i_a \left\{ E_0 + (n-1)\Delta E \right\} + \frac{RTi_a(t)}{(1-\alpha)F} \left\{ \ln \left( \frac{i_a}{FV} \right) - d \ln \left( \frac{A^{-}}{\alpha} \right) - \ln k_{a0} \right\} +$$

$$\frac{RTVe}{(1-\alpha)} \left\{ \ln \left( \left[ A_{\text{POL}} \right]_{\text{an}} - \frac{iF}{FV} \right) - 1 \right\} \left( \left[ A_{\text{POL}} \right] - \frac{iF}{FV} \right)$$  \hspace{1cm} (7)
The consumed energy ($U_a$) after any constant time ($t$) of current flow is also a sensing function of the same variables. Fig. 2 shows the good agreement between experimental and theoretical results for the consumption of three different charges (from the same initial oxidation/reduction state, three different final oxidation/reduction states are obtained) at different experimental temperatures by flow of a constant anodic current for three different times of current flow.

**Figure 2.** a) Anodic and cathodic experimental (full lines) and theoretical (dotted lines) chronopotentiograms obtained by flow of ±0.75 mA through a 1.6 mg pPy film (10.77 mm x 5.09 mm x 19 μm) at different temperatures (black line: 5ºC; red line: 10ºC; green line: 15ºC; blue line: 20ºC and cyan line: 25ºC) in 1 M LiClO$_4$ aqueous solution. b) Achieved potential after different times of anodic (positive) or cathodic (negative) current flow. c) Consumed electrical energy after the same times of current flow. Reproduced from (Otero et al., 2012), with permission of American Chemical Society).

5. Artificial muscles

In general, artificial muscles are devices attempting to reproduce composition, characteristics and capabilities of natural muscles. Different materials have been used as piezoelectrics (PZT), shape memory alloys (SMA) (Ouyang et al., 2008), carbon based materials as nanotubes (Baughman et al., 1999) or graphene (Huang et al., 2012) and polymeric gels. Also the pneumatic approach has been studied with contractile or extensional devices operated by pressurized air (Daerden & Lefeber, 2002).

Natural muscles transform chemical energy into mechanical energy and heat. Their actuation involves: a) aqueous media, b) an electric pulse arriving from the brain to the
among the above-mentioned materials for artificial muscles, conducting polymers are the most similar to natural devices including: electric pulses, polymeric chains, chemical reactions, aqueous solutions (ions and water), volume variations, and strain and stress changes. Two families of electrical polymeric actuators can be differentiated (Otero et al., 2007a; Otero, 2000; Otero, 2007):

- **Electromechanical actuators**: the polymer responds to electric fields (E) and the polymer chains do not participate in chemical reactions (the structure of its intramolecular chemical bonds doesn’t change) during actuation. In this type of actuator the dimension variations are proportional to $E^2$ for electrostrictive actuators and to $E$ for electrostatic and electrokinetic (movement of ions and/or solvent molecules) actuators.

- **Electrochemomechanical actuators**: the polymer chains respond to electric currents and participate in electrochemical or chemical reactions, changing the structure of its chemical bonds, varying their composition and originating volume changes. In this case dimensional variations are under control of the electrochemical reaction becoming proportional to consumed charge. Conducting polymers can be used for the production of this kind of actuators. Whether carbon nanotubes and graphenes based actuators are electromechanical or electrochemomechanical is still under discussion (Gimenez et al., 2012; Mukai et al., 2011). Any electrochemically reactive material that can be laminated as stable films can be used as part of electrochemomechanical actuators.

From now on we will focus on electrochemomechanical actuators. These actuators have been built using different configurations as discussed below, always containing one or several films of conducting polymers, where reaction 1, 2 or 3 takes place. Volume variations generated by reactions 1, 2 or 3 are almost isotropic, while natural muscles are anisotropic devices. So to produce anisotropy, only volume changes following length variation of the films are used, with the consequent efficiency reduction.

### 5.1. Bending artificial muscles

Historically the first way to transduce reversible length variations in films of conducting polymers into macroscopic movements was through a bilayer, or bimorph structure, i.e. CP/passive layer (Otero et al., 1992b; Otero et al., 1992a; Otero et al., 1992c; Pei & Inganäs, 1992a) (Fig. 3). The variation of the mechanical stress gradient generated across the bilayer interface by swelling/shrinking processes induced by the electrochemical reactions in the conducting polymer film develops a macroscopic movement of the bilayer free end by the progressive bending of the device. The direction (clockwise or anticlockwise) of the movement depends on the prevalent ionic exchange (anions or cations) of the conducting polymer film. Conducting polymers with a prevalent exchange of anions swell by oxidation, pushing the bilayer free end meanwhile conducting polymers with prevalent cation...
exchange shrink during oxidation, trailing the device. Different materials have been used as passive layer, for example a tape (Otero et al., 1992b; Otero et al., 1992a; Otero et al., 1992c; Pei & Inganäs, 1992a), a sputtered metal (Jager et al., 2000a; Jager et al., 2000b; Smela et al., 1993), a piece of paper (Deshpande et al., 2005b), a non conducting plastic (Higgins et al., 2003), a solid state electrolyte film (Alici et al., 2011; Baughman, 1996) or a thin film of any flexible material which is metal coated (i.e. by sputtering) (Deshpande et al., 2005a).

In a similar way it is possible to obtain bending movement from asymmetrical monolayers of the same conducting polymer, having an internal asymmetry capable of producing asymmetric swelling or shrinking across the film under the same electrochemical process (Okamoto et al., 2000; Onoda et al., 1999a; Onoda & Tada, 2004; Onoda et al., 1999b; Shakuda et al., 1993; Takashima et al., 2003; Takashima et al., 1997; Wang et al., 2002). Here half of the film has a prevalent anionic exchange, while the second half experiences a prevalent cationic exchange. These asymmetrical monolayers are obtained in two separate stages of electrogeneration using different salts and the same monomer. Other ways are being studied to produce asymmetric monolayers by physical means, for example, by growing the conducting polymer on adsorbed and porous materials (Li et al., 2004), or by electrochemical means generating a film of conducting polymer with a counterion concentration gradient (Okuzaki & Hattori, 2003; Sansinena et al., 2003), conductivity (Nakano & Okamoto, 2001; Onoda et al., 2005) or morphology gradients (Han & Shi, 2006; Okamoto et al., 2001) by crosslinked networks.

All these bilayer devices require a counter-electrode in order to close the electrical circuit allowing the current flow. In this electrode (usually a metal) different electrochemical reactions as solvent oxidation, must occur during current flow consuming a major fraction of the electrical energy, resulting in pH variations and generating new chemicals, which can deteriorate progressively the bilayer device.

Trying to avoid the counter electrode and its associated problems, a three layer structure was proposed (Otero et al., 1992c). Initially, it was produced by using a central passive film (two sides tape) each side coated with a conducting polymer film (Fig. 3). The triple layer was immersed in an electrolyte allowing the current flow. One of the conducting polymer films acts as the anode while the second film acts as the cathode (Garcia-Cordova et al., 2011; John et al., 2008; Yao et al., 2008). But using this configuration it is also possible to obtain movement outside a liquid electrolyte media using an ionic conducting membrane to separate the two films of conducting polymers. This membrane can be obtained by solvent evaporation and UV irradiation (Blonsky & Meridian, 1997; Heuer et al., 2002; Sansinena et al., 1997; Song et al., 2002), or by formation of interpenetrated networks (Cho et al., 2007; Plesse et al., 2005; Vidal et al., 2009; Vidal et al., 2003). In this case, the two conducting polymer films are generated by chemical polymerization on the external part of the membrane. Using this approach, multilayer devices were constructed and characterized (Ikushima et al., 2009; Zainudeen et al., 2008). The three-layer configuration provides greater efficiencies of the consumed energy: the same current is used two times to produce opposite electrochemical reactions and volume variations in the conducting
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polymer films; the anode swells and pushes the device and the cathode shrinks and trails the device.

Figure 3. Bilayer and three layer devices in solution, formed by conducting polymer films and non-conductive films. Described angle is also shown.

5.2. Longitudinal or linear artificial muscles

Freestanding conducting polymer films are the simplest longitudinal actuators (DellaSanta et al., 1997). Its actuation principle is based on longitudinal expansion and contraction of the polymer during ionic exchange, although expansion and contraction occur in all three dimensions, as previously indicated. To improve the performance of these actuators overcoming problems of fragility, multilayered actuators were proposed (Hara et al., 2006; Kaneto et al., 2008; Kaneto et al., 2009), in which several thin conducting polymer films and an electrolyte (ionic liquid-soaked paper) are used to develop a compact and scalable longitudinal actuator with a high work output (Ikushima et al., 2009). Also folded films with Origami shapes provide good linear movements (Okuzaki, 2008).

Fibres of conducting polymer also can be considered as longitudinal actuators. Fibres can be obtained by extrusion (Mazzoldi et al., 1998) or by chemical polymerization over a fibre-shaped substrate (Ismail et al., 2011; Lu et al., 2002), or hollow fibre solid polymer electrolyte (Plesse et al., 2010) making it possible to obtain two concentric CP films separated by the electrolytic medium, allowing its movement in air (Dobbelin et al., 2010; Plesse et al., 2009; Vidal et al., 2010; Vidal et al., 2009). Microrods (Cho et al., 2011) or nanorods (Park et al., 2009; Vlad et al., 2012) of conducting polymers and bundles of films or fibres were investigated to produce vertical displacements of weights (Lu et al., 2002). Also, conducting polymer tubes were generated using springs and helical metallic wires (Ding et al., 2003; Hara et al., 2003; Hara et al., 2005; Spinks et al., 2003b) or zigzag metal wires (Hara et al.,
as substrates, looking for uniform potential and current distribution. When individual fibres, bundles or tubes are used, a counter electrode is necessary, for the same reasons given above in the case of the bilayers.

Finally, it is possible to obtain linear displacement by combination of different bending structures as bilayers (Fuchiwaki et al., 2009; Naka et al., 2010; Otero & Broschart, 2006) or trilayers (Mutlu & Alici, 2010; Otero et al., 2007b) achieving longitudinal displacements over 60% of their original length.

6. Sensing and tactile muscles

As mentioned above, any reactive (electrochemical) device based on conducting polymers will sense every variable influencing the electrochemical reaction rate during actuation. Following this basic principle of the chemical kinetics sensing and tactile artificial muscles have been developed.

While a current is applied to the artificial muscle, producing a mechanical work, it is possible to follow the potential achieved in the muscle at every time. Under flow of a constant current (constant reaction rate) the achieved potential is lower when a variable which favours the electrochemical reaction increases. This is the case for temperature (Garcia-Cordova et al., 2011; Ismail et al., 2011; Otero & Cortes, 2003b; Valero Conzuelo et al., 2010; Valero et al., 2010) or electrolyte concentration (Arias-Pardilla et al., 2011; Garcia-Cordova et al., 2011; Otero & Cortes, 2003b; Otero et al., 2007b; Valero Conzuelo et al., 2010). On the other hand, the potential shifts to higher values when a variable makes the reaction harder: the muscle moves larger masses (Garcia-Cordova et al., 2011; Otero et al., 2007b; Valero Conzuelo et al., 2010) or moves the mass faster by applying now rising currents (Garcia-Cordova et al., 2011; Ismail et al., 2011; Valero et al., 2011).

Being the potential evolution a sensor of the working variables, the electrical energy (U) consumed by the device during actuation and obtained by integration is also sensor:

\[ U(t) = \int E(t) I dt \]  

(8)

Where t is the elapsed time, E(t) is the potential evolution during the actuation time and I is the constant applied current.

When a free muscle moves driven by a constant current finds an obstacle, the potential steps to higher values, trying to produce more energy and to shift the obstacle. The potential increment detects the object and its mechanical resistance to be shifted. Related with this property, artificial muscles with tactile sensitivity have been developed too (Otero & Cortes, 2003a).

7. Multi-devices: Actuators-sensors-battery-electrochromic

As mentioned above, different properties can be tuned simultaneously and in a reversible way during electrochemical reactions in conducting polymers. Electrochemical devices
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created with conducting polymers may change several of those properties, such as volume, stored charge or color, at the same time. For example, using the same configuration, changing the quantity of conducting polymer used in the device, it's possible to obtain different optical or mechanical devices (Vidal et al., 2010).

Also, as the configuration of a three layer is the same of a battery with two conducting polymer films as electrodes, electrical charge is trapped in the actuator during electrochemical reaction. A way to recover that charge may be developed in order to recover that energy, acting now as a battery and moving the actuator in the opposite direction until a uniform oxidation state is attained in both polymer films (vertical position in Fig. 3).

8. Theoretical models

Several models have been proposed to characterize the electrochemomechanical behaviour of artificial muscles. At the moment, there exist different approaches from different fields as mathematics, physics or chemical-physics.

8.1. Faradic control of the movement

As mentioned above, artificial muscles are electrochemomechanical machines controlled by the electrochemical reaction occurring while actuating. As any electrochemical reaction, actuation in conducting polymers is controlled by the charge consumed during actuation. Volume changes are not an exception: according to reactions 1, 2 or 3, volume variations will be given by the number of extracted (or inserted) charges from (or to) the polymeric chains, promoting the swelling/shrinking and the ionic exchange during reaction.

For bending bilayer or trilayer artificial muscles, it has been experimentally proven that the described angle (α in rad) follows a linear relationship with the consumed charge (Q in C):

\[ \alpha(t) = kQ(t) \]  

where k is a constant (rad C\(^{-1}\)) depending on every actuator system: the device (conducting polymer and isolating tape) and the electrolyte where is moving.

By definition of the angular rate of the movement (ω):

\[ \omega(t) = \frac{d\alpha(t)}{dt} = k \frac{dQ(t)}{dt} = kI(t) \]  

This expression confirms the faradic control of the movement: the angular rate of the movement is a linear function of the applied current. Any increment of the current produces (immediately, without any relaxing time) a faster movement of the actuator, by stopping the current flow the movement stops (the driving reaction and the film volume variation stops). Eq. 9 also indicates that the actuator is a positioning device: the same charge produces the
same displacement and the charge consumed during description of a movement of one degree \((\alpha/Q = k)\) is constant (independent of the applied current).

The above expressions can be normalized by mass unit of active conducting polymer reacting during actuation. This allows predicting the behaviour of every artificial muscle moving in a known electrolyte made of the same material whatever the geometry of the device is (shape, thickness, surface area, etc.). That means that the same change of the specific composition (according with reactions 1, 2 or 3) per unit time produce the same angular rate in devices having different geometry. This means that experiments from one muscle are only required in order to obtain this faradic characteristic of the CP.

The faradic control of the movement has been checked with different artificial muscles made of different polymers, exchanging both anions (Otero & Cortes, 2004) or cations (Valero et al., 2011).

### 8.2. Bending beam method

The bending beam method (Gere & Goodno, 2009; Timoshenko, 1925) is based on the analogy existing between a bending artificial muscle and a solid-state bending beam: the study of the forces generated at the interface between the non-conductive layer, keeping its volume constant during actuation, and the conducting polymer film, varying its volume locally.

This mechanical model assumes several characteristics related with the study of traditional mechanical bending beam: (I) the thickness of the beam is small compared to the minimum radius of curvature, (II) a linear relationship exists between stress and strain of the material and (III) the Young’s modulus, \(Y\), and the actuation expansion coefficient of the conducting polymer, \(\alpha\), keep constant: they do not depend on spatial location inside each layer.

The actuator curvature radius \(R_\infty\) is the radius at the equilibrium and \(R_0\) is the initial radius) is related to either, the Young’s modulus \(Y\) and the thicknesses \(h\) of the conducting and non-conductive films (indicated by subscripts 1 and 2 respectively), and to the volume changes locally produced at the interface between both films \(\alpha(t)\) (Pei & Inganäs, 1993b; Pei & Inganäs, 1993a; Pei & Inganäs, 1992b):

\[
\frac{1}{R_\infty} - \frac{1}{R_0} = \frac{6\alpha(t)}{Yh_1h_2(4h_1 + h_2)} \left( Y_1h_1^2 - Y_2h_2^2 \right) \quad (11)
\]

Christophersen et al. (Christophersen et al., 2006) expanded the model by including strain and modulus variations along the direction of film thickness. Actuator’s position, rate of the movement and force generated by the actuator (Alici & Huynh, 2006; Alici et al., 2006b) were simulated and applied to the design of biomimetic device (propulsion fins) (Alici et al., 2007). Du et al. (Du et al., 2010) have developed a general model for a multilayer system (N layers) to link the actuation strain of the actuator to the bending curvature.
8.3. Finite element method

The finite elements methodology is a well known mathematical treatment for engineering designs that can be applied to solve the movement of the artificial muscles too. Alici et al. (Alici et al., 2006a; Metz et al., 2006) developed a model based on a lumped-parameter mathematical model for trilayer actuators employing the analogy between thermal strain and the real strain (due to the insertion/extraction of ions inside the polymeric film) in polypyrrole actuators actuating in air. An optimization of the geometry was required, in order to obtain the greater output properties from a determined input voltage. Shapiro et al. (Shapiro & Smela, 2007) developed a two dimensional model (along a full area) to obtain curvature and angular moment from bilayer and trilayer actuators. Thus, they combined the results from the previous method (bending beam method) with finite element method to attain a solution. Another example of the employment of this method was carried out by Gutta et al. who applied it to the study the movement of a cylindrical ionic-polymer metal composite actuator (Gutta et al., 2011).

8.4. Equivalent transmission line model

Electrochemical systems, as many other systems, can be assimilated to electrical circuits and electrochemomechanical actuators have been treated by the equivalent transmission line method. This resource is a practical tool due to the great number of facilities available to the study of electrical circuits through different steps or modules. Such treatments are employed by engineers and physicists, or electrochemists, in order to explain the claimed capacitive behaviour of CP (Albery & Mount, 1993; Bisquert et al., 2000; Paasch, 2000). Ren et al. (Ren & Pickup, 1995) proposed equivalent electrical circuits to model the electron transport and electron transfer in composite pPy-PSS films based on Albery’s works. Fang et al. (Fang et al., 2008; Yang et al., 2008) have developed a scalable method including dynamic actuation performance under a given voltage input, joining three different modules for different aspects of the actuator: electrochemical dynamics, stress-generation by charge and mechanical dynamics. Shoa et al. (Shoa et al., 2011) developed a dynamic electromechanical method for electrochemically driven conducting polymer actuators based on a 2-D impedance model using an RC transmission line equivalent circuit to predict the charge transfer during actuation. Besides, a mechanical model (based on the bending beam model) is considered after the equivalent circuit that simulates ion “diffusion” through the thickness and electronic resistance along the length (Shoa et al., 2010). If the angular movement is not linear along the full geometry of the actuator, the bending beam method has to be modified, for example for cantilever type conducting polymer actuators (Alici, 2009).

From all these kind of models, it is possible to employ only one or several of them at the same time in order to obtain the best required model (Woosoon et al., 2007).

9. Actuators applications

The investigation of these devices is mainly performed in academic laboratories. Nevertheless a rising number of applications and products are emerging with pioneering
companies that are being incorporated by large multinationals. So Creganna Tactx Medical and Bayer MaterialScience recently acquired a pair of companies working in the field, indicating the potential of these technologies. Also EAMEX from Japan is developing actuators for biomedical and robotic applications. NASA and ESA space agencies consider polymeric actuators as preferential technologies, and the European Scientific Network for Artificial Muscles (ESNAM) has started funded by the European Union. Many different applications can be found in literature. The following is a summary of a few of them, both macroscopic and microscopic.

- **Smart electronic textiles**: Although different strategies have been used to overcome problems like short lifetimes and high response times (Carpi & De Rossi, 2005; De Rossi et al., 2009; Wallace et al., 2007), much work has to be done in order to endow textiles with efficient and reliable actuating functions.

- **Braille displays**: Conducting polymers is one of the materials explored to develop low-cost and efficient displays for Braille text. Actual displays are close to achieve the required specs, but they have to overcome short cycling life (Ding et al., 2003; Spinks et al., 2003a).

- **Micropump**: It is possible to find in literature different types of micropumps made with conducting polymer actuators able to transport fluids at a microflow rate with high precision with low energy consumption (Kiefer et al., 2008; Kim et al., 2008; Morita et al., 2010; Naka et al., 2010; Ramírez-García & Diamond, 2007; Wu et al., 2005).

- **Propulsion or locomotion devices**: Systems based on trilayer configuration were proposed in aquatic devices (Alici et al., 2007; James et al., 2007; McGovern & et al., 2009; McGovern et al., 2010) for creating enough thrust for propulsion. Also bending actuators like cilia can be used in mini-robotic devices (Alici & Gunderson, 2009).

- **Microcatheters**: By depositing two conducting polymer films around a passive catheter and using a fast conductor solid state electrolyte, it is possible to control the movement of the catheter tip (DellaSanta et al., 1996; Shoa et al., 2008). This kind of microcatheters can be used in Optical Coherence Tomography to enable high-resolution 3D imaging (Lee et al., 2009).

- **Microactuators**: The electrochemical synthesis of conducting films and their electrochemical actuation (Wilson et al., 2007) are suitable for the construction different microdevices (He et al., 2007; Jager et al., 2001; Pede et al., 1998; Roemer et al., 2002) and microtools constituted by bilayers (Jager et al., 2000a; Jager et al., 2001; Jager et al., 2000b; Jager et al., 1999; Smela, 1999; Smela & Gadegaard, 1999; Smela et al., 1995; Smela et al., 1993) or trilayers (Gursel et al., 2009; Kiefer et al., 2008) using microelectronic technologies. These microactuators can be integrated in CMOS chips containing all the elements required to transport, contain and nurture biological cells (Jager et al., 2002; Smela et al., 2007).

### 10. Published papers and patents evolution

An indication of the initiation and fast growth of the field is given by bibliographic and patents evolution. As can be observed, the literature related to conducting polymers
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actuators starts from 1990 (Fig. 4.a) reaching a maximum in 2006 with 45 papers, an excellent value for such a specific topic. After that, around 30 papers have been published every year. Fig. 4.b shows exponential evolution of citations with a value of almost 2000 in 2010. A similar evolution is observed in Fig. 4.c for patents, reaching a maximum in 2009 with 180 patents.

Figure 4. Evolution of a) published papers, b) citations and c) patents for “conducting polymer & actuator”, from the ISI web of Knowledge® and Scopus®.

11. Future and challenges

Although a hard work has been performed, it does not exist yet an uncontroversial model for the description of the new reactive polymers and devices based on these reactive polymer gels whose composition and properties mimic those from artificial organs in mammals. New models should include concepts from very different fields of knowledge as electrochemistry, mechanics, polymer science and thermodynamics. In those systems, electrochemical reactions produce structural (conformational) changes in the polymeric chains and macroscopic volume changes related to the composition change of the material. Those aspects are not considered in the classical chemical kinetic models. Conducting polymer films should be used as models for the study and quantification of chemical kinetics under structural control with the aim to develop a new structural chemical model, able to quantify conformational changes and structural information in conducting polymers and in biological reactions originating life in living cells.

This model will allow the synthesis of new conducting polymers providing a more precise control of structural changes and intermolecular forces (polymer-ion interactions) with the
reaction. Those materials should be used in a new generation of polymeric actuators able to overcome current limitations, opening possibilities for new applications.

Other factors, such as configuration, manufacture of the actuators, design of the electric contacts or electrolytic media (solid or liquid) are also very important for the improvement of the electrochemomechanical actuators. This is a multidisciplinary field, a lot of work performed by specialists from different disciplines is required in order to attain a good control and modelling of both, devices and soft robots.

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**12. References**


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