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# Biomimetic Sensing – Actuators Based on Conducting Polymers

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#### 1. Introduction

Thirty years after the discovery of conducting polymers (CP) and their electrochemical behavior (Chiang et al. 1977; Shirakawa et al. 1977), CP have been proven to be useful for applications in a variety of areas such as batteries and supercapacitors, photovoltaics, memory devices, light emitting diodes, artificial muscles (actuators), biomedical devices, biosensors, corrosion protection etc., thanks to their unique physical and electrochemical properties. Their physical characteristics are similar to those of commodity polymers; but unlike commodity polymers, CP can be subjected to oxidation and reduction just as in the case of metals and inorganic semiconductors. These reactions yield a complex material combination: polymer-ions-solvent.

In the field of actuators, conductive polymers have been used with great success. During its oxidation/reduction the volume of the CP film changes. The volume variation can be used to perform a linear movement or an angular movement. The first CP actuators date back to 1992 (Baughman & Shacklette 1991; Otero et al. 1992a; Pei & Inganäs 1992b). Since then, much progress has been achieved in materials generation and design and characterization of devices. Different configurations have been designed and studied, and different models were proposed to understand the properties and to improve the performance of those devices. In addition, due to the electrochemical nature of the actuation, any variable acting on the reaction will be detected and quantified by the actuator response; it means that working under constant current, the potential evolution will detect the change. This is a unique device: artificial muscles based on conducting polymers are also sensors, while working, of the environmental variables (Otero 2009). They are sensors of temperature, electrolyte concentration and the current flowing through them. Since they are capable of detecting an obstacle along its route and moving it to performing a work, they possess tactile properties (Otero & Cortes 2003).

These unique features, coupled with the easy construction of actuators in many different sizes, from macro to microscopic devices, constitute a technological challenge. Some multinational companies, like Bayer, became involved in this new technology after acquisition of startup companies. The European Union is supporting the European Scientific

Network for Artificial Muscles (ESNAM). Development of new actuators is an ongoing active topic of research for the ESA and NASA, the European and American space agencies.

#### 2. Electrochemical reactions in conducting polymers

Much of the importance of these materials emanates from the fact that they can be oxidized and/or reduced from its neutral state, with the entry/exit of ions and solvent (reactions 1 and 2). The chemical reaction starting from the neutral polymer promotes an increase of the electrical conductivity and a change of material composition. With the change in composition, many other properties also change (they are the reactive properties or electrochemical properties), as can be seen in Table 1 (Otero 1999; Otero 2000).

Property	Action	Inspired organ
Electrochemomechanical	Change of volume	Muscles
Electrochromic	Change of color	Mimetic skins
Charge storage	Current generation	Electric organs
Chemical or	Chemical modulation	Glands
pharmacological storage	or chemical dosage	
Electron/neurotransmitter	Channel V action	Nervous interface
Electroporosity	Transverse ionic flow	Membrane
Electron/ion transduction	$\Delta V$ (Chemical/Physical properties)	Bio-sensors

Table 1. Biomimetic properties of conducting polymers driven by the electrochemical reaction, the mimicked biological functions and the related organs.

The reactive material is composed of reactive macromolecules, ions and solvent: this composition mimics dense reactive gels in the living cells, becoming reactive material models for biological reactions. The reverse variation of the magnitudes of biomimetic properties driven by the reverse electrochemical reactions envisages the development of devices and products like artificial muscles, biomimetic (electrochemical) electrochromic windows, mirrors or screens (Dyer & Reynolds 2007; Mortimer et al. 2006; Rosseinsky & Mortimer 2001), polymeric batteries (Irvin et al. 2007; Novak et al. 1997), and/or supercapacitors (Peng et al. 2008; Snook et al. 2011), smart drug delivery devices (Abidian et al. 2006; Kontturi et al. 1998; Pernaut & Reynolds 2000; Zinger & Miller 1984), nervous interfaces (Cui et al. 2001; Ludwig et al. 2006; Schmidt et al. 1997), smart membranes (Ariza & Otero 2007; Burgmayer & Murray 1982; Pellegrino 2003) or smart surfaces (Isaksson et al. 2006; Isaksson et al. 2004; Teh et al. 2009). A breaking technological border has appeared giving rise to reactive biomimicking materials and reactive devices based on properties whose magnitude changes along with the progress of material reaction or along the device actuation.

The reactions that we describe below are simplified expressions and initial approach to real processes. Any film of a CP acts as a polymeric membrane. As for any other membrane inside a liquid electrolyte, a physical equilibrium is stated between the film and the electrolyte: solvent, anions and cations getting a distribution between the polymer and the electrolyte. Then, an interchange of ions and solvent starts with the beginning of the electrochemical reactions (Hillman et al. 1989; Inzelt 2008). For most of the polymers one of the two ionic exchanges prevails carrying over 90% of the balancing charge (Orata & Buttry 1987; Torresi & Maranhao 1999).

#### 2.1 p-doping

P-doping, generally known as oxidation, involves the extraction of electrons from the polymer chains, generating positive charges, or holes, along the polymer chains, which are compensated by ions coming from the electrolytic medium in contact with the polymer. This type of doping is the most common in CP (Huang et al. 1986; Tsai et al. 1988). The transformation from a neutral material to an oxidized material can occur through two different ways:

- **Prevailing anion exchange**: During oxidation, stimulated conformational movements on the polymeric chains generate free volume and anions penetrate from the solution to balance the positive charges along the chains. The high concentration of charges inside the oxidized material induces the entrance of solvent from the solution required to maintain the osmotic pressure. The volume of the material increases during oxidation. Reverse processes and a volume decrease is observed during neutralization, as observed in reaction (1):

where the different sub indexes mean: s, solid and aq, solution,  $Pol^0$  represents the reactive centres along the chains where a charge can be stored and A- represents the anions. Volume changes and the transition, promoted by the reaction, from a packed solid state to a gel are illustrated in Fig. 1. The polymer film acts as a three dimensional gel electrode at the molecular level. Inside the swelling film every chain constitutes a molecular one-dimensional electrode. All the chains have the same chemical potential  $(\mu)$  at any electrical potential.

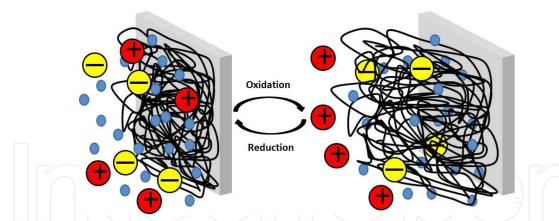


Fig. 1. Complex polymer structure, showing volume changes (swelling/shrinking) produced during p-doping of polypyrrole film. Anions go inside the film during oxidation and are released during neutralization. Blue circles represent solvent molecules.

- **Prevailing cation exchange**: If the polymer film is generated in presence of a big enough macro anion, this anion remains trapped inside the polymer matrix whatever may be the oxidation state. In this case when the polymer is oxidized, balancing cations are expelled as shown in Eq. 2. The material shrinks during oxidation and swells during reduction.

$$\left[ \left( Pol^{0} \right) \left( MA^{-} \right)_{n} \left( C^{+} \right)_{n} \right]_{s} \longleftrightarrow \left[ \left( Pol^{n+} \right) \left( MA^{-} \right)_{n} \right]_{s} + n \left( C^{+} \right)_{aq} + n \left( e^{-} \right)_{metal}$$

$$Neutral \text{ chains}$$
Oxidized chains
$$(2)$$

where MA- represents any macroscopic anion (organic, polymeric or inorganic) trapped inside the CP during polymerization and C+ represents a cation. Whether macroanions during reaction (2) remain trapped inside the film by its relative dimensions with the interchain distances in the network, or by strong intermolecular Van der Waals interactions between the macroion and the polymer is an unsolved point. The role of the solvent molecules in this case is not clear due to the presence of ionic species in the material, having strong interactions with the solvent dipole, whatever their oxidation state would be.

#### 2.2 n-doping

Some CP such as PEDOT (Ahonen et al. 2000; Skompska et al. 2005), 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, enabling them to store 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 reaction (3). The material swells during reduction and shrinks during neutralization.

$$(Pol^{0})_{s} + n(C^{+})_{aq} + n(e^{-})_{metal} \longleftrightarrow [(Pol^{n-})_{s}(C^{+})_{n}(Solv)_{m}]_{gel}$$
Neutral chains

Reduced chains

#### 3. Macroscopic dimensional changes

Though the polymer chains could be an example of molecular motors (Balzani et al. 2005; Davis 1999) due to their change in length (conformational changes) during oxidation or reduction, it is not yet possible to exploit this phenomenon because we are not able to connect each end of the chain to a nanoscopic contact taking advantage of that anisotropic linear expansion. Only three dimensional films of CP, giving three dimensional changes of volume are available. By chemical or electrochemical polymerization we produce films of branched, partially cross-linked and partially degraded materials. This entanglement of molecular motors swells or shrinks under electrochemical stimulation of the conformational movements of the electroactive part of the chains. The result is a quite isotropic three dimensional change of volume to produce mechanical properties. In order to generate macroscopic machines from the isotropic volume changes in the film we must induce anisotropy.

#### 4. Classification of actuators: Type of movement

The actuators made of CP can be classified in several ways, one of them is based on the device design to produce different types of macroscopic movements.

### 4.1 Bending structures

#### 4.1.1 Bilayer

This was the first type of CP actuator that was developed in 1992 by the construction of bilayers constituted by a tape adhered to a film of a CP (Fig. 2) (with prevalent anion exchange, or cation exchange) electrogenerated on a metallic electrode (Otero et al. 1992b; Otero et al. 1992a; Otero et al. 1992c; Pei & Inganäs 1992b). The mechanical stress gradient generated across the bilayer interface by swelling /shrinking processes induced by the

electrochemical reactions develops a macroscopic movement of the bilayer free end by the device bending. Films of CP having a prevailing exchange of anions swells by oxidation, pushes the bilayer free end and stays at the convex side of the bended device. CP having cation prevailing exchange suffer shrinking processes during oxidation trailing the device and staying at the concave side of the bended device. Different materials have been used to prepare bilayer devices as CP/metal (Jager et al. 2000a; Jager et al. 2000b; Smela et al. 1993), CP/solid state electrolyte(Baughman 1996), CP/CP (Han & Shi 2004a; Takashima et al. 2003a), CP/plastic(Higgins et al. 2003), CP/paper (Deshpande et al. 2005b) or CP/thin film of any flexible material which is metal coated (i.e. by sputtering) (Deshpande et al. 2005a). In these devices, a metallic counter electrode is required to allow the current flow. A major fraction of the consumed electrical energy is wasted to produce electrochemical reactions on this counter electrode (such as solvent dissociation, which requires a high overpotential). Moreover, those reactions result in pH variations and new chemicals, which migrate towards the muscle promoting the progressive deterioration of the actuating film.

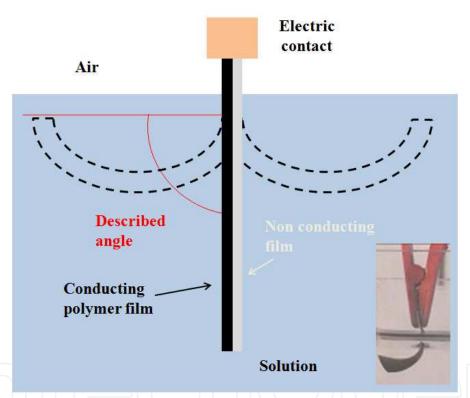


Fig. 2. Bilayer device scheme in solution, formed by a conducting polymer film and a non-conductive film. A real device is shown in inset.

#### 4.1.2 Three-layer structure

This configuration evolves from the bilayer, trying to avoid the metallic counter electrode (Fig. 3) getting higher efficiencies by using the same current twice to produce opposite volume changes. This is produced by using a two sided polymeric tape and two films of the same, or different, CP which are allowed to stick on both sides of the tape (Otero et al. 1992c). The triple layer is immersed in an electrolyte allowing the current flow. One of the CP films acts as the anode, swelling (for preferential anionic interchange during the reaction) and pushing the device while the second CP film acts as the cathode, shrinking and trailing the device (John et al. 2008; Yao et al. 2008).

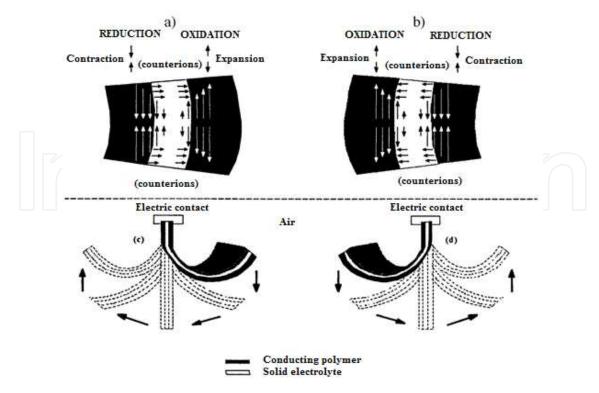


Fig. 3. A scheme of ionic interchange, induced stress gradients and generated angular movements during current flow of a trilayer device (Reproduced from (Otero 2000), with permission of Elsevier).

But unlike the bilayers, three-layer devices can move outside a liquid electrolyte media using an ionic conducting membrane separating the two films of CP. 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): the two films of CP are generated by chemical polymerization on the external part of the film membrane.

#### 4.1.3 Asymmetrical monolayers

It is possible to obtain bending movement from asymmetrical monolayers of the same CP, having an internal asymmetry capable of producing asymmetric swelling or shrinking across the film under the same electrochemical process (doping or de-doping) (Okamoto et al. 2000; Onoda et al. 1999a; Onoda & Tada 2004; Onoda et al. 1999b; Shakuda et al. 1993; Takashima et al. 2003b; Takashima et al. 2003b; Wang et al. 2002): one half of the film has a prevalent anionic exchange, while the second half experiences a prevalent cationic exchange. This can be achieved in two separate stages of electrogeneration using different dopants for the same polymer. A metallic counter electrode is required.

Other possibilities are being explored to produce asymmetric monolayers by physical means, for example, by growing the CP on adsorbed and porous materials (Li et al. 2004), or by electrochemical means generating a film of CP with a counterion concentration gradient (Okuzaki & Hattori 2003; Sansiñena et al. 2003; Shakuda et al. 1993; Wang et al. 2002), conductivity (Nakano & Okamoto 2001; Onoda et al. 2005) or morphology gradients (Han & Shi 2006; Okamoto et al. 2001; Onoda & Tada 2004) by crosslinking network, or by generating a bilayer of the conducting polymer with a macroanion (shrinks by oxidation)

and then of the same conducting polymer with a small anion (swells by oxidation) (Han & Shi 2006; Takashima et al. 2003a), or even placing a metal sheet between both films (Han & Shi 2004b). As in the case of bilayer devices, asymmetric films also need an electrolyte and a metallic counter electrode in order to allow the flow of the current and to produce the bending movement.

### 4.2 Structures giving lineal movements 4.2.1 Films and fibers

A freestanding CP film is the simplest lineal actuator possible (DellaSanta et al. 1997a). Its actuation principle is based on longitudinal expansion and contraction of the polymer during the insertion and de-insertion of ions although expansion and contraction occur in all three dimensions, as indicated earlier. Different strategies were used to improve the performance of these actuators, like depositing platinum on CP to increase conductivity (Hutchison et al. 2000); although the resulting films are very brittle and difficult to handle. To overcome these problems multilayered actuators were proposed, in which several thin laminations of CP films and an electrolyte (ionic liquid-soaked paper) are used to develop a compact and scalable linear CP actuator with a high work output (Ikushima et al. 2009). Also folded films with Origami shapes provide good linear movements (Okuzaki 2008). Different methods are being used to obtain fibers of CP. One of them is extrusion through a spinneret of a polymer soluble organic solution (normally dimethylpropylene urea (DMPU) or N-Methyl-2-pyrrolidone (NMP)), followed by a couple of stages, first being an immersion in water followed by immersion in doping bath (Mazzoldi et al. 1998). Another method is chemical polymerization over a fiber-shaped substrate (Lu et al. 2002). This substrate can be a hollow fiber 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. Bundles of films or fibers were investigated to produce vertical displacements of weights (Lu et al. 2002). Different models have been proposed to describe mechanical behaviour (DellaSanta et al. 1997b; DellaSanta et al. 1997c; Qi et al. 2004) or electro-chemomechanical deformations (Kaneto et al. 2000; Pandey et al. 2003; Zama et al. 2004) of these devices. When individual fibers or bundles are used as working electrodes, a metal counter electrode is required to allow the current flow generating similar effects described above for bending asymmetric films.

#### 4.2.2 Tubes and films with metal support

A different approach consists of electropolymerization of a CP on springs and helical metallic wires until the generation of a tube (Ding et al. 2003; Hara et al. 2003; Hara et al. 2004b; Spinks et al. 2003b), or on zigzag metal wires (Hara et al. 2004a) to generate films. The supporting metal wire should guarantee a uniform potential and current distribution, greater strain and length variation rates under electrochemical reactions.

#### 4.2.3 Combination of bending structures

Another way to obtain a linear displacement is the combination of different bending structures as bilayers (Otero & Broschart 2006) or trilayers (Otero et al. 2007; Otero et al. 2002) capable of achieving a longitudinal displacement of up to 60% of their original longitude. In the case of longitudinal displacements where small bending angle lower than a 20% is required, the films suffer low mechanical fatigue.

#### 5. Conducting polymer actuator applications

While the investigation of these devices is still mainly in academic laboratories, some companies dedicated to the development of actuators based on conjugated polymers have emerged in recent years. MicroMuscle AB based in Sweden which was later acquired by Creganna Tactx Medical, Artificial Muscles from California acquired by Bayer MaterialScience and EAMEX from Japan are actively working on actuators for biomedical and electronics applications. Also Santa Fe Science and Technology, USA, has produced continuous spun polyaniline fibres and demonstrated their use as linear actuators. Many different applications can be found in literature. The following is a summary of a few of them, both macroscopic and microscopic.

#### **5.1 Propulsion or locomotion systems**

Biomimetic systems based on tri-layer polymer combination of actuators are proposed for swimming devices (Alici et al. 2007), where undulatory movements were employed to create enough thrust for propulsion. Bending actuators like cilia can be used in biological systems to produce movement in mini-robotic systems capable of performing applications like pipe inspection, search inspection and data gathering in confined spaces (Alici & Gunderson 2009).

#### 5.2 Braille displays

CP is one of the technological materials explored to develop low-cost, efficient, and refreshable displays for Braille text. Producing a full-page Braille display is difficult because it requires packing of many small actuated dots into a small, closely-spaced arrangement without interferences. Actual displays are close to performing at the required specs; challenges still limit their commercial viability such as short cycling life (Ding et al. 2003; Spinks et al. 2003a).

#### **5.3 Steerable microcatheters**

Two CP films around a passive catheter and a fast ionic conductor solid polymer electrolyte are used to control the movement of the catheter tip, transforming passive catheter to an active and steerable one. Such devices are typically expected to produce a bending angle of at least 20° (Santa et al. 1996; Shoa et al. 2008). CP are also being used in Optical Coherence Tomography fast scanning catheters to enable high-resolution 3-D imaging (Lee et al. 2009).

#### 5.4 Integrated cell sensors

Cell-based sensors are being developed to harness the specificity and sensitivity of biological systems for sensing applications, from smell detection to pathogen classification (Jager et al. 2002; Smela et al. 2007). These integrated systems consist of CMOS chips containing sensors and circuitry by means of which microstructures have been fabricated to transport, contain, and nurture the cells. The structures for confining the cells are microvials that can be opened and closed using polypyrrole (pPy) bilayer actuators.

#### 5.5 Micro pump

Volume change of CP can be used to develop a micro pump system capable of transporting fluids at a microflow rate with high precision. Micropumps are essential components of

microfluidic systems and biosensing systems. The energy consumption rate of these polymeric micro pumps is markedly lower than those of conventional micropumps (Naka et al.; Ramírez-García & Diamond 2007; Wu et al. 2005).

#### 5.6 Micro actuators

The electrochemical synthesis of CP films and their electrochemical actuation are suitable for the construction of elegant and imaginative 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 (Kiefer et al. 2008) using microelectronic technologies.

#### 6. Models for the characterization of the movement

Throughout the development of these new devices, researchers have proposed different models to characterize their movement, using different approaches, from physical and mathematical methods to others based on their physicochemical properties.

#### 6.1 Faradic control of the movement

All the above described artificial muscle structures can be considered as electrochemical devices working under faradic conditions. The volume changes between reduced and oxidized polymer films are under control of the used charge, either injected or extracted. This electrical charge controls the amount of counterions interchanged with the solution, and the volume change is related to the stress gradient variations at the polymer/non-conducting tape interface. Experimentally, different electrical charges (Q) applied to the device produce proportional movements ( $\alpha$ ) (Eq. 4). The constant, k, is a function of the nature of ions exchanged in the process.

$$\alpha (rad) = k (rad \cdot s^{-1} \cdot A^{-1}) * Q (A \cdot s)$$
(4)

From this equation, a linear relationship is obtained between applied current (I) and the rate of the angular movement,  $\omega$ , (Eq. 5).

$$\omega (\text{rad } \text{s}^{-1}) = k (\text{rad } \text{s}^{-1} \cdot \text{A}^{-1}) * I (A)$$
 (5)

Eq. 5 confirms that all these electrochemomechanical actuators are electrical machines, whose movement is under perfect control of the driving current (magnitude and sense of flow). Whatever the initial position of the device free end is, the charge required to produce an angular movement of one radian must be constant, and this amount is a characteristic magnitude of the tested system. Therefore, the movement can be accelerated using a higher current and retarded by current decrease. The movement stops when the current flow is halted, and the movement sense is reversed by changing the current sense.

The electrochemical nature of these devices allows to anticipate the response of different devices, having different surface areas, different shapes or including different polymer mass per device. The angular rate produced by interchange of the same number of moles of ions (cations or anions) per unit time and per unit mass of CP during actuation is the same and independent of the shape, surface area or amount of conducting polymer in the device. That means the same change of the specific composition (mol g-1) per unit time (s) produce the

same angular rate in different devices. From Eq. 5, changing the current by the specific current, we obtain:

$$\omega \text{ (rad s-1)} = k' \text{ (rad g s-1 · A-1)} * i \text{ (A · g-1)}$$
 (6)

where the new constant, k', is the angle described when the reactive polymer consumes one unit of charge per gram of CP. This means that experiments from one muscle are only required in order to obtain this faradic characteristic of the CP. Then Eq. 6 describes the dynamics of any device prepared from the same material.

#### 6.1.1 Prevailing anion exchange

Below are the results for a three-layer device consisting of pPy films, obtained using LiClO<sub>4</sub> as electrolyte, of dimensions 2 cm x 1.5 cm x 13 µm and 6 mg weight each. Such films have prevailing anion exchange. As anticipated, Fig. 4 shows the expected linear relationships between the current and the rate of the angular movement and electric charge and movement for a triple layer: the movement is under control of the current (Otero & Cortes 2004). Also a constant value of charge is consumed, irrespective of the amount of applied current, in agreement with the fact that the electrochemical reaction controls through the composition and the volume change of the polymeric films.

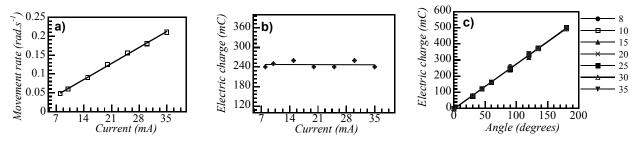


Fig. 4. a) Linear relationship between the applied current and the angular rate determined from the time required to describe an angular movement of 90° under 7 different currents. b) Electric charge consumed by the triple layer muscle to move through 90°. c) Electric charge consumed by the triple layer muscle to describe different angles (30, 45, 60, 90, 120, 135, and 180 degrees) under the different currents studied. Electrolyte: 1M LiClO<sub>4</sub> aqueous solution (From (Otero & Cortes 2004), with permission of the Royal Society of Chemistry).

Fig. 5 shows how different artificial muscles with prevailing anion exchange, having different surface area, constructed with pPy films having different thicknesses (different weight of pPy), produce the same angular movement rate under flow of analogous charge per unit time (current) and per unit weigh of CP (same variation of the oxidation).

#### 6.1.2 Prevailing cation exchange

The linear relationships between electric charge and movement rate and applied current and movement rate are not exclusive of anion-exchange devices. Devices with prevailing cation exchange can also have the same properties. For example, a pPy-DBSA-ClO<sub>4</sub>-/non-conducting tape bilayer (Valero et al. 2011) also presents a linear relationship between angular rate and specific current for devices of different dimensions and weights, indicating that these are general properties of these materials, regardless of the type of material, device or species exchanged. (Fig. 6)

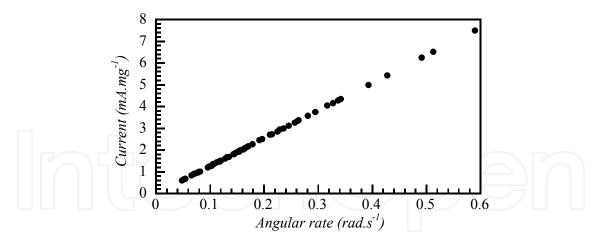


Fig. 5. Angular rate measured through a movement of 90 degrees using triple-layer muscle of polypyrrole (anion exchange) having different dimensions (including different weights of polypyrrole films: 8.3, 7.8, 7.4, 6, 5.5, 5.1, 5, 4, 3.7, 3.5, 3, 2.3 and 2 mg) and checked in 1M LiClO<sub>4</sub> aqueous solution under different currents (10, 15, 20, 25 and 30 mA) (From (Otero & Cortes 2004), with permission of the Royal Society of Chemistry).

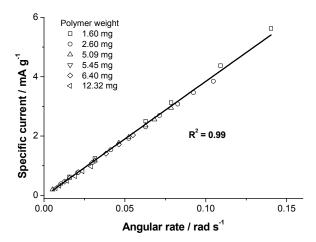


Fig. 6. Angular rate measured through a movement of  $\pi/4$  radians using bilayer muscles of pPy/DBS (interchanging cations) having different dimensions (1.2x2.4; 1.0x1.5; 1.65x0.7, and 1.5x0.8 cm) with different weights, indicated on the figure. R<sup>2</sup> is the square of the correlation coefficient (From (Valero et al. 2011), with permission of Elsevier).

In conclusion, the faradic nature of the movement allows a perfect control of both the movement rate (by the current) and the angular position (by the charge). It means that we have a machine capable of transforming electrical energy into mechanical energy using molecular motors as mechanical components: the electrochemically stimulated conformational movements of the polymeric chains. The electrical generators nowadays available are able to give very precise electrical currents and soft current variations; therefore very precise movement rates and soft rate variations can be produced using artificial muscles, mimicking elegant movements from biological beings.

#### 6.2 Other models

There are different methodologies that allow people working with artificial muscles to model their behaviour. Usually these methods are based on different aspects of the working principle of artificial muscles or they simply employ usual mathematical methods from different fields to develop the model.

#### 6.2.1 Bending beam method

The bending beam method (Gere & Goodno 2009; Timoshenko 1925) is related to the mechanical study of solid state beam bending. The use of this model to explain the behaviour of artificial muscles is based on the study of the forces generated at the interface between the non-conductive layer, keeping its volume constant and the conducting polymer film, varying locally its volume. This model assumes that: (I) the thickness of the beam is small compared to the minimum radius of curvature, (II) there is a linear relationship between stress and strain of the material, and (III) Young's modulus, E, and the actuation coefficient of expansion of the conducting polymer,  $\alpha$ , are constant and do not depend on spatial location inside each layer.

Pei and Inganäs (Pei & Inganäs 1993b; Pei & Inganäs 1993a; Pei & Inganäs 1992a) developed a model that correlates the local linear strain from a polypyrrole film and the curvature change suffered by an artificial muscle employing concepts from geometry and mechanics (Fig. 7). The actuator curvature radius ( $R_{\infty}$  is the radius at equilibrium and  $R_0$  is the initial radius) is related to Young's modulus (E') and thicknesses (h) of the conducting and the non-conductive films (indicated by subscripts 1 and 2 respectively), and to the volume changes locally produced at the interface between both films  $\alpha_{(t)}$ , in Eq. 7.

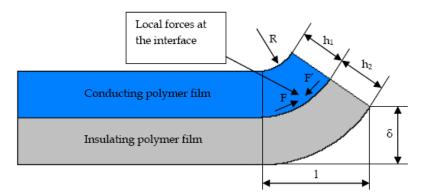


Fig. 7. Scheme of deformation during actuation used in the bending beam method.

$$\frac{1}{R_{\infty}} - \frac{1}{R_{0}} = \frac{6\alpha_{(t)}}{\frac{\left(E'_{1}h_{1}^{2} - E'_{2}h_{2}^{2}\right)^{2}}{E'_{1}E'_{2}h_{1}h_{2}\left(h_{1} + h_{2}\right)} + 4\left(h_{1} + h_{2}\right)} \tag{7}$$

Christophersen et al. (Christophersen et al. 2006) expanded the model by including strain and modulus variations along the direction of film thickness in order to obtain a tool to develop micro-actuators to achieve a specified radius of curvature. Also Alici et al. (Alici et al. 2006b) worked out in their approach, considering that the mechanical movements produced at a trilayer actuator were due to the charge transference occurring during redox reactions in conducting polymers. Actuator's position, rate of the movement and force generated by the actuator (Alici & Huynh 2006) were simulated. They applied this model to the study of a biomimetic device (propulsion fins) (Alici et al. 2007). Finally, Lee et al. (Lee et al. 2005) used this model for the movement of ionic polymer-metal composite actuators and

more recently, Du et al. (Du et al. 2010) developed a general model for a multilayer system (N layers) to link the actuation strain of the actuator to the bending curvature.

#### 6.2.2 Finite element model

Several authors have worked out models using the finite element method well known in engineering.

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 pPy actuators actuating in air, more difficult for simulation than thermal phenomena. The bending angle and the moment were solved by using finite element method and ANSYS software. An optimization of the geometry was performed as well, in order to obtain the greater output properties from a determined input voltage.

Shapiro and Smela (Shapiro & Smela 2007) developed a two dimensional model (along a full area) to obtain curvature and angular moment of bilayer and trilayer actuators (metal, polymeric buffer, non actuating but conducting, and polymeric actuator). Thus, they combined the results from the previous model (bending beam method) with finite element method to obtain the solution.

#### **6.2.3 Equivalent transmission line model**

This model is based on the development of electrical equivalent circuits giving similar electrical responses to that of the actuator. This resource is a very useful tool to develop models due to the great number of facilities available to study electrical circuits (they are easy to study in different steps or modules). Such models are employed in engineering and physics, or in electrochemistry in order to explain the capacitive behaviour of CP (Albery & Mount 1993; Albery & Mount 1994; Bisquert et al. 2000; Buck & Mundt 1999; Paasch 2000; Vorotyntsev et al. 1994).

Ren and Pickup (Ren & Pickup 1997) proposed equivalent electrical circuits to model the electron transport and electron transfer in composite pPy-PSS films based on the works of Albery. Also, Fang et al. (Fang et al. 2008; Yang et al. 2008) developed a scalable model (valid for different sizes of the actuator) including dynamic actuation performance under a given voltage input, joining three different modules that model three different aspects of the actuator: electrochemical dynamics, stress-generation relating transferred charges to internal actuation stress and mechanical dynamics. Finally, Shoa et al. (Shoa et al. 2011) developed a dynamic electromechanical model 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.

#### 7. Simultaneous sensing capabilites

The electronic levels for the different compositions of those wet and reactive polymers are expected to respond very fast to the change of any external physical or chemical variable. These electronic levels are in fast equilibrium with electronic levels in the connecting metal, so the modification of the device potential, whatever maybe its origin, will be detected by the potentiostat simultaneously to the change of the variables. These fast events allow

developing actuators able to sense the ambient conditions, during actuation (Otero 2008; Otero 2009). For example, the flow of a constant anodic current through a trilayer device under constant ambient conditions gives a progressive increase of the electrodic potential. (Otero & Cortes 2000; Otero & Cortes 2001).

Fig. 8 shows the evolution of device potential for different values of the surrounding variables: electrolyte concentration, temperature, different applied current or different weights attached to the bottom of the trilayer. As expected, rising electrolyte concentrations and rising working temperatures promote a shift of the device potential evolution while working, towards lower potentials. Rising weights attached to the device at the bottom require higher energies to keep a constant movement rate, under constant current, giving increasing device's potential. The flow of rising currents, assuming constant resistances (electrolyte, anodic and cathodic reactions), produces higher potentials and requires shorter times to flow the same charge describing the same angle.

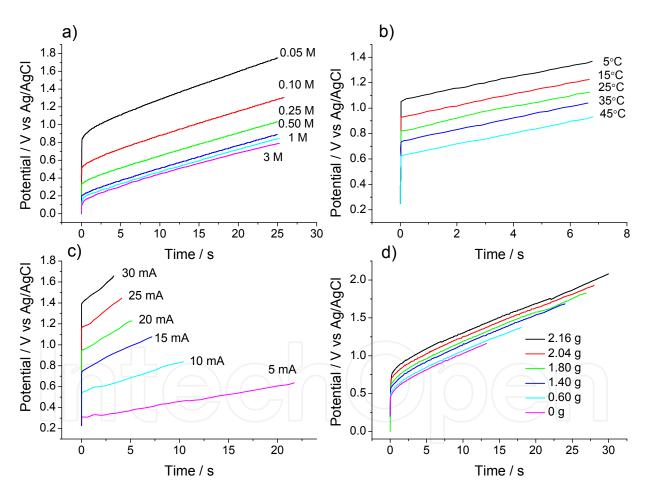


Fig. 8. Chronopotentiograms obtained when a triple layer (2 x 1.5 cm², 12 mg of pPy) describes 90° angular movement a) in aqueous solutions of LiClO<sub>4</sub> (3, 1, 0.5, 0.25, 0.1, and 0.05 M) under a constant current of 10 mA, b) in 0.1 M LiClO<sub>4</sub> at different temperatures: 5, 15, 25, 35 and 45 °C. c) under flow of different currents: 5, 10, 15, 20, 25, and 30 mA and d) shifting different attached steel weights: 0.6, 1.4, 1.8, 2.04, and 2.16 g with a device of 12 mg of polymer weight (Adapted from (Otero & Cortes 2000; Otero & Cortes 2001), with permission).

Fig. 9 shows the linear evolution of the electrical energy consumed by the artificial muscle as a function of the studied experimental variables. Rising driving currents, or increasing shifted weights, produces higher overpotentials consuming greater electrical energy. Rising electrolyte concentrations, or temperatures, require lower overpotentials consuming lower electrical energies during the movement. Those results underline the simultaneous sensing capabilities of the device during the actuation process under reactive conditions and outside the chemical equilibrium. This is a general property for any device working by electrochemical reaction of conducting polymers such as batteries, smart windows, smart membranes, artificial muscles, electron-ion transducers, etc.

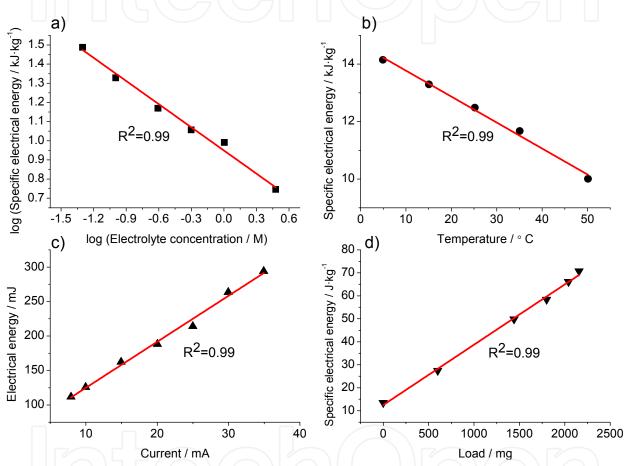


Fig. 9. Consumed electrical energy by the device in Fig. 8 as a function of the different studied variables: (a) electrolyte concentration, (b) temperature, (c) current, and (d) shifted weight (Adapted from (Otero & Cortes 2000; Otero & Cortes 2001), with permission).

#### 8. Tactile sensitivity

By trailing increasing weights by the muscle we obtain increasing device potentials. If a trilayer or bilayer device moves freely and meets an obstacle, it must touch, push and shift the obstacle if possible. As observed in Fig. 10, at the beginning of the movement, the muscle moves freely until it touches the obstacle: the evolution of the muscle potential must be the same as that of the muscle moving freely, without any hanging weight or without any obstacle in its way. When the muscle touches the obstacle it feels a mechanical resistance and the muscle produces an extra energy drain by raising the muscle potential (Otero et al.

2004a; Otero & Cortes 2003; Otero et al. 2004b). The response is a potential step, proportional to the obstacle weight.

When the mechanical resistance of the obstacle exceeds the mechanical energy produced by the device, the muscle is unable to shift the obstacle and the muscle potential steps to very high values at the moment of the contact. The system indicates when a muscle, or the mechanical tool driven by the muscle, touches an obstacle how much mechanical resistance the obstacle opposes.

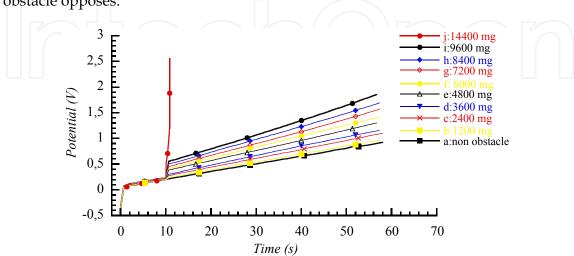


Fig. 10. Chronopotentiograms obtained from a triple layer device composed of two polypyrrole films [ $2 \text{ cm x } 1.5 \text{ cm x } 13 \text{ } \mu\text{m}$ ] weighing 6 mg each, under flow of 5 mA in 1 M LiClO<sub>4</sub>. The muscle moves freely, meeting an obstacle after 10 s and sliding it for 3.5 s, overcomes its border and continues with a full angular movement. Obstacles weighing 1.2, 2.4, 3.6, 4.8, 6.0, 7.2, 8.4, 9.6 mg were slided, but the muscle was unable to push and slide an obstacle weighing 14.4 g (From (Otero & Cortes 2003), with permission of John Wiley & Sons).

#### 9. Conclusions

Artificial muscles from reactive conducting polymers provide another unique property: simultaneous actuation and sensing. Both signals (driving current and sensing potential) are simultaneously incorporated in the two connecting wires. New scientific and technological challenges and borders are stated. Those borders require new theoretical models. Tentative electrochemical, mechanical, mathematical models are being developed for helping engineering designs and predictions. An integrated model is expected for those reactive dense and biomimetic materials and their applications in biomimetic devices.

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