Artificial muscles: Non-Stoichiometry Nature, Sensing and Actuating Properties and Tactile Sensibility

T.F. Otero*, J.J. López-Cascales* and G. Vázquez-Arenas*

Abstract- Electro-chemo-mechanical devices or artificial muscles based on conducting polymers (CP) are presented as bilayers, CP/adhesive polymer, or as triple layers, CP/adhesive polymer/CP. Those soft and wet materials, working in aqueous solutions of a salt, mimic the composition of most organs from animals. Under electrochemical control, so working as new electrical machines, they produce continuous, reverse and elegant bending movements, mimicking those produce by animal muscles. By means of the current a perfect controls of the movement rate is attained giving soft and continuous movements. Muscles able to sense the chemical and mechanical conditions of work or muscle having tactile sense, as will be presented here, are being developed. All of them are founded on the non-stoichiometric nature of the soft and wet materials.

Keywords: Artificial muscles, conducting polymers, polypyrrole, non-stoichiometry, moleculardynamics

1. Introduction

Natural muscles are elegant actuators developed by nature through millions of years of evolution to transform chemical energy into mechanical energy and heat, triggered by an electric pulse. New electrical machines, mimicking natural muscles, include electric pulses, chemical reactions, conformational movements of polymeric chains, interchange of ions and changes of volume. Considering similitudes they are named artificial muscles. The basic materials for those new electrical machines are conducting polymers.

The non-stoichiometric nature of any oxidized conducting polymer is an important chemical and technological fact, present in the background of the literature related to conducting polymers for years. A common milestone related to conducting polymers is the fact that their conductivity can be changed by several orders of magnitude by doping, opening the way for the obtention of soft and flexible electronic components. But it is not a so common point in the literature that the composition of a conducting polymer also can be changed by several orders of magnitude in a continuous and reverse way under electrochemical control [1,2]. Continuous and reverse changes only are possible if the material is non-stoichiometric. Under those condictions any property of the material linked to the composition also will change in a continuous, reverse and infinitesimal way.

* T.F.Otero, J.J. López-Cascales, and G. Vázquez-Arenas are with the Laboratory for Electrochemistry and Intelligent Materilas and Devices, Universidad Politécnica de Cartagena, Campus Alfonso XIII, 30203 Cartagena, Spain.(toribio.fotero@upct.es, javier.lopez@upct.es, gemma.vazquez@upct.es).
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The basic property for the development of artificial muscles is the change of volume during the oxidation process. A soft and elegant muscle will require a continuous and infinitesimal and reverse change of volume under control of electrical currents.

Any film of a basic conducting polymer, as established Otero et al. [3] is mainly constituted by an amorphous entanglement of lineal, branched and crosslinked polymeric chains bearing positive charges and counterions required for charge balance. The result is an amorphous salt of the oxidized conducting polymer. The electrochemical reduction of this material in an electrolyte basically promotes the compensation of the positive charges along the chains, the expulsion of counterions and the shrinking of the material by progressive decrease of volume. During oxidation reverse processes occur with an electrochemical driven increase of volume[2-4].

According to the Electrochemically Stimulated Conformational Relaxation Model (ESCRM) [4-6] when a conducting polymer, such as polypyrrole, is reduced the polymer shrinks and the diffusion of counterions towards the solution becomes more and more difficult, so reduction it is necessary to apply high cathodic polarizations, which provide energy enough to expel the entrapped counterions by conformational movements of the chains. The polymer/solution interface of the compacted films is not uniform having points of greater mobility of the polymeric chains. So the oxidation begins at those points where the polymeric entanglement is not so dense. The nuclei growth and progress on the reduced material, until their colalescence[7,8] as shows figure 1. We will use this property to show the non-stoichiometric nature of our oxidized polymers, their suitability to generate muscles giving soft and elegant

movements.

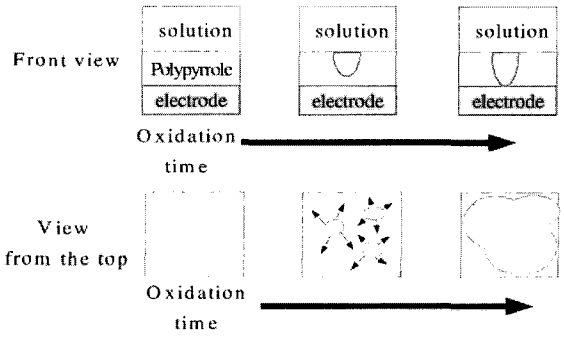

Fig. 1: Scheme of oxidation and coalescence of nuclei of a conducting polymer on an electrochromic film during the oxidation process.

2. Experimental

2.1. Generation of polypyrrole films.

Thin polypyrrole electrochromic films were synthesized by electrochemical generation on a 1 cm^2 mirror polish platinum electrode [1] in a one-compartment electrochemical cell. The films were electrogenerated at a constant potential of 700 mV, applied by means of a PAR 273A potentiostat/galvanostat, by flow of a polymerization charge of 50 mC through a 0.2M $LiCLO_4$ and 0.1M pyrrole acetonitrile solution. Two platinum sheets having a surface area of 4 cm^2 were used as counter electrodes and placed side by side of the working electrode. A saturated calomel electrode (SCE) was used as reference electrode. These polypyrrole films present reverse electrochromic changes when are submitted, in the background electrolyte, to consecutive square potential waves.

For preparation of different artificial muscles the polypyrrole films also were electrogenerated using a one compartment electrochemical cell and a monomeric solution as above. Now the polymerization process is driven by square potential waves between –0.322V, kept for 2 s, and 0.872V, kept for 8 second. As working electrode, and two couterelectrodes, 3.5 cm^2 AISI 304 stainless steel sheets were used []. This methodology allow us the obtention of films that can be removed from the metallic electrode and showing a flat morphology and a good flexibility. The electro-generation takes place in a in 0.2M pyrrole (Aldrich, 95%)+ 0.1M $LiClO_4$ (Fluka, 98%) acetonitrile solution (containing a 2% vol. of water), consuming a polymerisation charge of 26±1 C. A Ag/AgCl electrode was used as reference electrode. When the polymerisation was finished the working electrode was coated with two polypyrrole films, each film having a surface area of 2 cm^2, a 12.5-14 μm thickness range, and weighing between 6 and 7.5 mg. The coated electrode was rinsed with acetonitrile and acetone and dried in air for several hours

2.2. Construction of artificial muscles.

Once the polypyrrole films were dried, we use a double-sided plastic tape to separate the film from the electrode. The tape was fixed to one of the films and peeled off from the electrode, and by the other side of the tape was fixed the second film of polypyrrole, resulting a triple layer: polypyrrole/ double-sided plastic tape/ polypyrrole. Triple layers constituted artificial muscles.

One of the polypyrrole film was connected to the working electrode output of the potentiostat-galvanostat and the second film was connected to the counter electrode sort-circuited to the reference electrode outputs, so working electrode, counterelectrode and reference electrode were included in the same polymeric film (Figure 2). So, we can follow the evolution of the muscle potential during work and none metallic counterelectrode is required outside the muscle. Artificial muscles were studied in 1M $LiClO_4$ aqueous solutions.

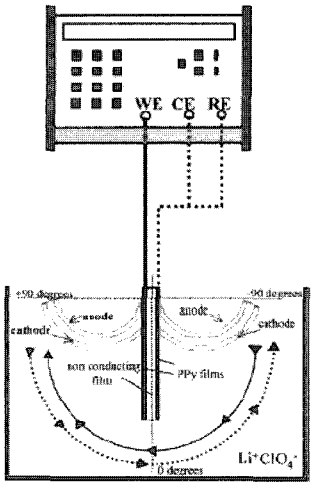

Fig. 2: Electrochemical equipment, electrical contacts and scheme of artificial muscle in his bending movement.

3. Results

3.1. Non-stoichiometry nature of conducting polymers.

The non-stoichiometric nature of the oxidized conducting polymers supports the reliability of any intermediate composition (polymer/counterion) of the material. This gives us the possibility to construct

muscles moving so elegant as natural ones.

Nucleation process was used to probe the non-stoichiometric nature of the oxidized conducting polymers. Due to the electrochromic nature of conducting polymers the material color once reduced and compacted is a pale-yellow color (figure 3a). Under oxidation the materials shows a dark blue color. During the oxidation different nuclei of dark-blue oxidized polypyrrole are formed and expand on the reduced film as shown in figure 1. The polypyrrole films were compacted at room temperature in LiClO4 acetonitrile solution by cathodic polarization at –1200 mV for 60 sconds, and after that the potencial was stepped to 100mV. The formation dark blue oxidized nuclei start. By switching off the polarization after 3 seconds the growth of the nuclei was interrupted. If a stoichiometric oxidized material is formed either, number, shape and colour of the nuclei will remain unchanged with time when the polarization is switched off. Nevertheless after switching off the potential (figure 3c), a partial oxidation of the reduced film is observed, so the colour of the reduced material become more dark, at expenses of a partial reduction (bleaching) of the oxidized nuclei. These study proportionate the mechanism to obtain any intermediate uniform oxidation, depending of the oxidation time, proving by this way the non-stoichiometric nature of the oxidized material.

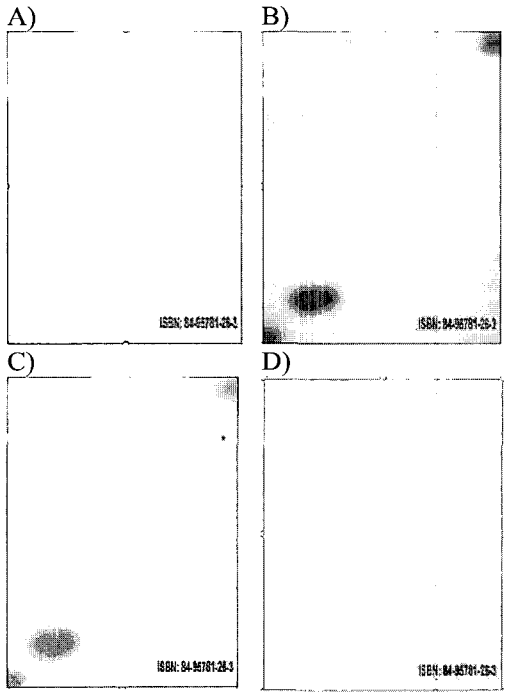

Fig. 3. Oxidation of an electrochromic polypyrrole film in 0.1M $LiClO_4$ acetonitrile solution at room temperature. Polypyrrole film was compacted at –1200 mV for 60 seconds, after that the polymer was oxidized by a potential step to 100 mV and switching off the process after 3 s. Photos were taken at the switching off time and 6 and 9 second after this time, to follow the evolution of the nuclei (dark blue) on the reduced polymer (yellow).

On this base, any infinitesimal increment (positive, or negative) of this composition is also possible. That means that any property of the material, as their volume, and any device based on this property, as artificial muscles, can move in a continuous and reverse way, mimicking so elegant movements as those from natural muscles.

These composition changes have been simulated by Classical Molecular Dynamics Simulation [12,13]. Thus Fig. 1.a depicts how the system shows a compact structure and a well-defined interface in the reduced state compared with Fig. 1.b where a swelling of the polymer can be observed in its oxidized state. In this regard, counterions and water penetrate into the core of the polymer to balance the net charge emerging during the polymer oxidation. In this case, the polymer resembles a gel state.

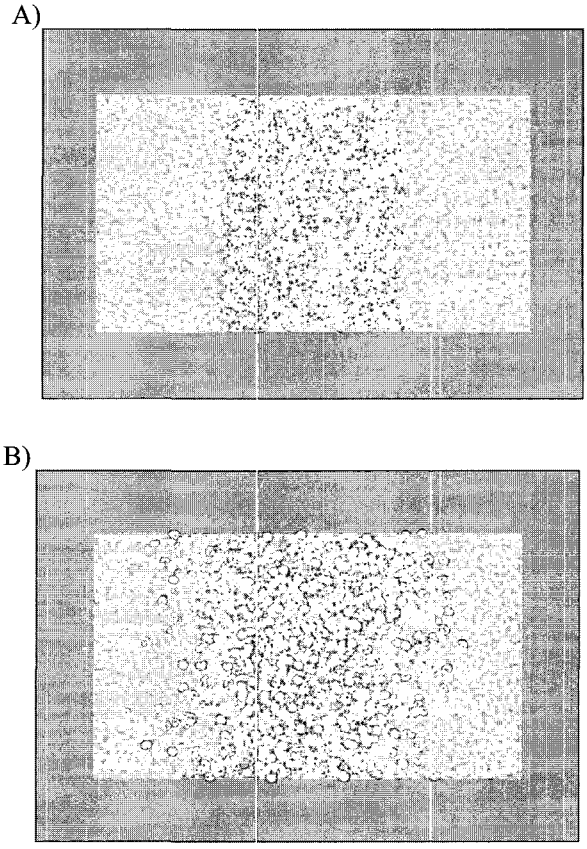

Fig. 4. A) polypyrrole/water structure in its reduced state. B) Polypyrrole/ion chloride/water structure in its oxidized state.

3.2. Sensors and actuators.

An artificial muscle based on polypyrrole is an electrochemical device able to transform electrical eneergy into mechanical energy including ionic movements and conformational movements of polymeric chains under electrochemical stimulation. So when the bilayer are checked in aqueous electrolytes, the flow of an anodic constant current promotes a bending movement of the bilayer (see figures). The folw of a cathodic current allows to recover the original position. Working under constant current we follow the muscle potential and the consumed electrical energy is:

$$E_e = i\int E \cdot dt \qquad (1),$$

This energy is a linear function, through i, of every one of working variables, such as: concentration of electrolyte, current density, temperature or mechanical variable.

The triple layer is immersed in 1M $LiClO_4$ aqueous solution and we characterized the movement of the devices under a constant current flow of 10 mA, describing the bottom of the device an angular movement of 90°. If we repeat the same procedure but changing the current flow, the movement rate increases when the current rises. Also rises the lectric potential of the muscle (figure 5a). Similar potential changes were observed for different variables. For any of then the consumed electrical energy is a linear function of the studied variable (figure 5b): this is a sensor.

A new paradigm of the electrical machines has been stated here. Using only two connecting wires (figure 2) the actuator is submitted to a driving current promoting the movement of the device, which give us an answer through the same two connecting wires (the muscle potential) indicating, in this case, the temperature of work. The device is, at the same time, an actuator and a sensor of the different chemical or physical variables, including the trailed weight (figure 5 a and b).

Whatever the used current the same consumed charge produces the same angular movement: the electrochemical reaction produce the same change of the film volume. We have a perfect control of the device movement and position.

Instead of loading the devices with .a weight, an obstacle was located in the way of the muscle movement. So, we start the current flow and the device starts to move free. After a few seconds the muscle meets the obstacle and pushes it. The response of the muscle potential (potential difference between the two polypyrrole films) shows some differences related to that obtained by trailing of different weights attached to the muscle.

Figure 6.a and 6.b show how the artificial muscle is able to push the obstacle. The obstacle is several time

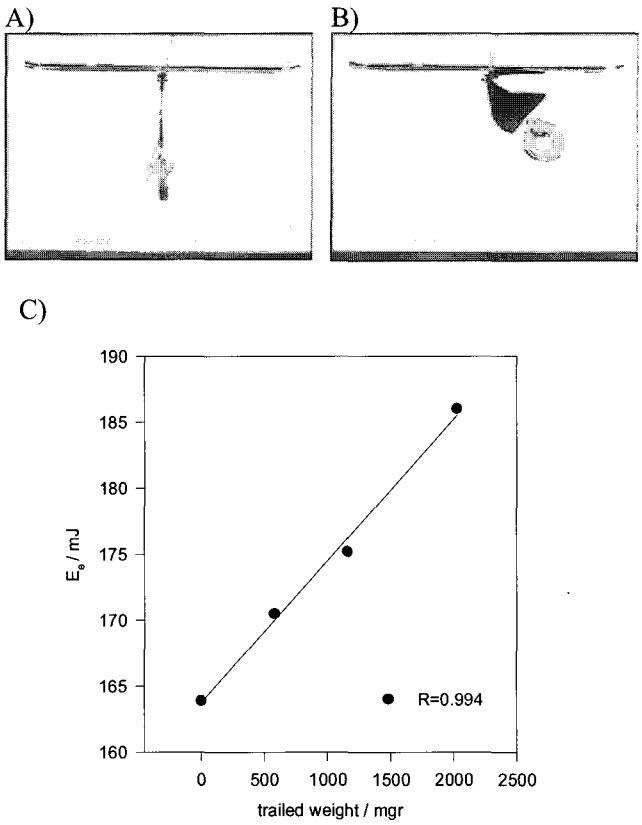

Fig. 5: A) and B) Scheme of movement of a triple layer loaded with stainless steel washers under a current of 10 mA flow through it in 1M $LiClO_4$ at room temperature. C) Evolution of electrical energy consumed by a artificial muscle at the same conditions of figure 5.a and 5.b, loaded with different trailed weight.

heavier than the device.

The evolution of the muscle potential follow that of the free muscle up to the touching moment. There a potential step is observed and the increase of the consumed electrical energy, related to that of the free muscle, is proportional to the pushed weight (table 1), that means to the mechanical resistance opposed by the obstacle

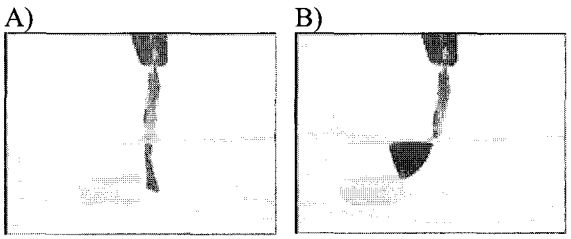

Fig. 6: Scheme of movement of an artificial muscle with an obstacle in its way. Surface area of the artificial muscle 2 cm^2, movement under a current flow of 5 mA in 1M $LiClO_4$ aqueous solution at room temperature.

Table 1. Electrical energy consumed by an artificial muscle of 2 cm^2 under the flow of 5 mA in 1M $LiClO_4$ aqueous solution sliding different obstacle in its way.

	Obstacle (mg)					
	1200	2400	3600	4800	6000	7200
Electrical Energy (mJ)	110.2	113	117.1	125.0	133.2	140.5

6. Conclusions

The oxidation of any electrochromic conducting polymer film, after reduction and compaction at high cathodic potentials (more cathodic than the closing potential of the polymer) occurs with formation and growth of nuclei of oxidized dark polymer on the reduced and clear film. The interruption of the nuclei growth allowed us to visualize the non-stoichiometric nature of the oxidized material: the composition of counterions into the polymer change in a continuous, reverse and infinitesimal way along several orders of magnitude.

So artificial muscles have been developed showing uniform, soft and elegant movement under control of the consumed charge. The electrochemical reaction, and the muscle potential, are so very sensitive to any chemical, physical or mechanical variable of the ambient. So artificial muscles work, at the same time, as actuators and sensors of mechanical conditions of work. Going ahead on the sensor abilities of the artificial muscles, the muscle potential indicates when a muscle touches an obstacle and the weight of the obstacle: this is a tactile muscle.

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Toribio Fernández Otero

He received the Master degree in chemistry from The Oviedo University in 1974 and its PhD from the Complutense Univ. of Madrid in 1978, obtaining the Chair of Physical Chemistry of the Univ. of the Basque Country in 1989 and that of the Polytechnic Univ. of Cartagena in 2000. His background includes Electrochemistry, Corrosion, metals electrodeposition and Polymer Science.

Jose Javier López Cascales

He received its degree in Chemistry from The University of Murcia, Spain in 1987 and its Phd from the same University in 1991. His interest includes mechanical characterization of conducting polymers and MD Simulations of polymers and biological assemblies.

Gemma Vázquez Arenas

She received the B.S. degree in industrial engineering from Universidad Politécnica de Cartagena in 2001. His interest includes nonlinear control, adaptive control, and system identification.