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### Asymmetric Bilayer Muscles. Cooperative and Antagonist Actuation



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#### ABSTRACT

Thick films of polypyrrole-paraphenolsulfonic acid (PPy-HpPS), polypyrrole-dodecylbenzensulfonic acid (PPy-DBS) and a bilayer PPy-HpPS/PPy-DBS (asymmetric bilayer) were electrogenerated from aqueous solutions. Two bilayers: PPy-HpPS/tape and tape/PPyDBS were constructed. The angular displacement of those three bilayer muscles was characterized in NaCl aqueous solution by cyclic voltammetry and parallel video recording of the bending movement. The attained coulo-voltammetric (charge-potential), dynamo-voltammetric (angle-potential) and coulo-dynamic (charge-angle) responses until different cathodic potential limits were analyzed. The dynamo-voltammetric and coulo-dynamic responses from the PPy-HpPS/tape and tape/PPyDBS muscles inform about the reaction driven ionic exchanges in the two PPy films. Electrochemo-dynamical responses from the asymmetric PPy-HpPS/PPy-DBS bilayer muscles are explained using those reactions. Cooperative dynamic effects exist when both layers follow complementary reaction-driven volume changes (swelling/shrinking, or shrinking/swelling) due to complementary entrance/expulsion of ions. The cooperative amplitude of the angle described by the asymmetric bilayer muscle is one order of magnitude larger than those attained from each of the conducting polymer/tape bilayer muscles. Antagonist dynamic actuation occurs when the two films swell, or shrink, simultaneously originating narrower angular displacements. Improving cooperative actuation or eliminating antagonist actuation and creeping by suitable selection of polymers and electrolytes seem the way to get most efficient polymeric motors and industrial products.

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#### 1. Introduction

Films of conducting polymers exchange ions and solvent during electrochemical reactions for charge and osmotic balance [1–3]. Those reactive dense gels mimic, in its simplest expression (reactive macromolecules, ions, water and reaction-driven conformational movements of the conducting polymer chains) the intracellular matrix in cells. There reactions originate and support life and life functions [4]. Any biological cell is a complex chemical reactor in which most of the reactions cannot be described by nowadays-available chemical models. Those models were developed from reactions taking place in gaseous phase or in dilute solutions [5,6], quite far from the dense gel of the intracellular matrix where functional reactions occur.

Several biomimetic properties of the conducting polymer change with the polymer-counterion composition driven by the reaction. Each of those properties allow the development of a biomimetic reaction-driven device [1,2,7]. Among those devices,

artificial muscles are transducers of the reaction-driven volume variations, required to lodge or expel balancing counterions and solvent, into macroscopic linear [8-16] or bending movements from bilayer or multi-layer structures [17-29]. Thus, bending artificial muscles can be considered as polymeric Faradaic motors translating reaction-driven ionic and aqueous exchanges into large angular movements. Thinking in the opposite direction artificial muscles can be considered as useful tools for the identification and quantification of different processes linked to the electrochemical reaction. They are being used to clarity and quantify ionic and aqueous exchanges [30,31], osmotic and electrosomotic processes [32], creeping effects [33] and any other mechanical or chemical influence on the electrochemical reaction of the constitutive conducting polymer. During actuation a progressive variation of both, inter and intra-molecular interactions (polymer-polymer, polymer-ions, polymer-solvent and solvent-ions) occur inside the CP film. Thus, by changing the solvent, or the salt, the reaction can move from driving cation exchanges to anion exchanges, and vice versa [34,35]. The muscle can be proposed as a tool to quantify the evolution of the intra-molecular forces in reactive gels (artificial or biological) during reactions [4]. Similar variations during parallel biological reactions in functional cells defines health or illness [6].

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An electroactive material layer (conducting polymer, redox polymer, carbon nanotube, graphene, and so on) and a passive (from the electrochemical point of view) material layer (tape, plastic, metal, wood, and so on) constitute those bilayer muscles. The passive film, if essential to generate the transversal muscular stress gradient during actuation, consumes a fraction of the applied electrical energy to be bended. As a result the muscular energetic efficiency and the angular displacement, for the same consumed charge, decrease.

One of the strategies followed trying to eliminate those two adverse effects getting more robust and efficient polymeric motors is by using asymmetric bilayer muscles. Two layers of the same conducting polymer, here polypyrrole (PPy), constitute an asymmetric bilayer muscle. One PPy layer is expected to swell during oxidation by entrance of anions pushing the bending movement. The second PPy layer must shrink during oxidation (simultaneously) by expulsion of cations pulling the bending movement. Reverse ionic exchanges, volumetric changes and bending movements should occur during reduction of the asymmetric bilayer. On this way both films are simultaneously active and larger angular movements are expected by consumption of the same charge, or of the same energy, than using polypyrrole/tape bilayers.

Thus, for a good design of most efficient polymeric motors we must select two compatible conducting polymers: bilayers can be constructed by consecutive electrogeneration. The two layers should present asymmetric volume changes during reaction. For the first layer we have selected a polypyrrole blend electrogenerated in presence of the large dodecylbenzenesulfonic acid (HDBS), the second was generated in presence of the shorter paraphenolsulfonic acid (HpPS) [36]. The two organic ions, DBS and pPS, generate very compatible films giving a uniform interpenetrated bilayer.

Here we will explore the parallel electro-chemo-dynamical characterization of the asymmetric bilayer muscle (PPy-HpPS/PPy-DBS) and each of the PPy-HpPS/tape [37] or PPy-DBS/tape [38] bilayers muscles in NaCl aqueous solutions. The aim is to characterize the three selected bilayer muscles, identifying any reaction-driven effect as ionic exchanges or intermolecular interaction changes, cooperative and antagonist dynamic effects, creeping effects, and so on. Advantages and disadvantages of using

asymmetric bilayer muscles for the development of industrial products will be discussed.

#### 2. Experimental methods

Either chemicals, methodologies and video recording of the bending movement under electrochemical control have been described in a previous work [39].

## 2.1. Preparation of Polypyrrole-paraphenolsulfonic acid/tape (PPy-HpPS/tape) bilayer muscle

PPy-HpPS films were electrogenerated from 0.2 M pyrrole and 0.05 M HpPS aqueous solutions (50 mL). The working electrode was a stainless steel plate having 6.6 cm<sup>2</sup> of surface area. Two similar stainless steel electrodes were used as counterelectrodes CE, one by WE side at a distance of 1.0 cm in order to get a uniform electric field. The reference electrode was Ag/AgCl (3 M KCl) from Metrohm. Potentials in this work are referred to this electrode. A constant current density of 0.5 mA cm<sup>-2</sup> was applied to the WE during 1 hour at 0 °C. After water rinsing the coated electrode was dried in air for 24 hours. The electrode borders were scrapped and two PPy-HpPS films were peeled off and weighed using a microbalance, 20 µm thick and 4.8 mg mass. Those freestanding films were cut into  $20\,\text{mm} \times 1\,\text{mm}$  strips. After determining its mass, each strip was attached under pressure to a double-sided tape from 3 M. A paint (Max Effect, MAXFACTOR) strip from 5.0 mm to 12.0 mm of the upper border avoids the direct contact between the electrolyte (by capillarity) and the metallic clamp that allows the electrical contact (Fig. 1a). The final bilayer muscle inside the solutions was 8 mm long.

# 2.2. Preparation of tape/Polypyrrole-dodecylbenzenesulfonic acid (PPy-DBS/tape) bilayer muscle

A similar procedure was used to electrogenerate on a stainless steel electrode a Polypyrrole-dodecylbenzenesulfonic acid (PPy-DBS) film from 0.15 M pyrrole and 0.25 M DBSA aqueous solution (50 mL). Two PPy-DBS film (one by side), 20  $\mu$ m thick and 22 mg mass, were attained, cut in small pieces and attached to a tape getting the final tape/PPy-DBS bilayer.

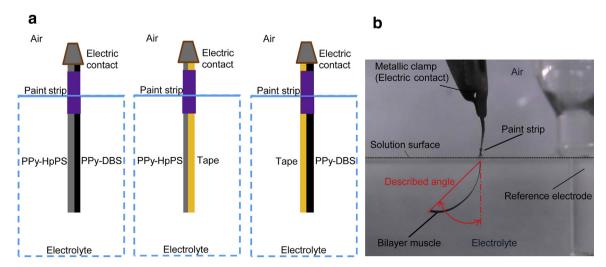


Fig. 1. (a) Scheme of the PPy-HpPS/PPy-DBS, PPy-HpPS/tape and PPy-DBS/tape bilayer artificial muscles with the relative position of the two constitutive layers as in the checked muscles, transversal paint strip and alligator metal electric contact. (b) A picture of a bilayer muscle in the cell and determination of the described angle.

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