A solid state artificial muscle based on polypyrrole and a solid polymeric electrolyte working in air

J. M. Sansiñena,[a] V. Olazábal,[a] T. F. Otero,[a] C. N. Polo da Fonseca[b] and Marco-A. De Paoli[b]

[a] *Laboratorio de Electroquímica, Facultad de Química, Universidad del País Vasco, Apd 1072, 20080 San Sebastián, Spain*
[b] *Laboratório de Polimeros Condutores, Instituto de Química, Unicamp, C. Postal 6154, 13081-970 Campinas, SP, Brazil*

A solid state artificial muscle based on polypyrrole(PPy) and poly(epichlorohydrin-co-ethylene oxide) [P(ECH-co-EO)]/ $LiClO_4$ (solid polymeric electrolyte) is developed; an angular movement in air with rate, direction and electrical control similar to those obtained in a liquid electrolyte (aqueous solution of $LiClO_4$) is registered when an electrical current was applied.

Conducting polymers like polypyrrole, polythiophene and polyaniline, can be electrochemically oxidized and reduced in a continuous and reversible way. Simultaneous changes in conductivity,[1] colour,[2] volume[3–5] and other parameters are observed. All these properties are linked to movement of ions and solvent inside and outside the conducting polymer. These movements are accompanied by conformational changes along the polymeric chains, driving the opening and closure of the polymeric entanglements. Artificial muscles based on reversible stress gradients linked to these reverse conformational changes have been developed in recent years.[6–14] All these prototypes are in the liquid configuration, usually a lithium salt dissolved in an aqueous solution.

In this work, we have investigated the construction of a new solid state artificial muscle, fully polymeric, based on two polypyrrole (PPy) film electrodes and a new polymeric electrolyte, poly(epichlorohydrin-co-ethylene oxide) [P(ECH-co-EO)]/$LiClO_4$.

Polypyrrole films were electrogenerated from 0.2 M pyrrole and 0.1 M $LiClO_4$ organic solutions (acetonitrile with a water content of 2%). Three AISI 304 stainless steel plates, having a surface area of 3.50 cm^2, were used as electrodes, one of them as the working electrode and the other two as counter electrodes. The electrogeneration was performed under an inert atmosphere of argon. Potential square waves were applied between -0.300 V (2 s) and 0.850 V (8 s) to control the morphology of the film and its adherence to the metal. A saturated calomel electrode (SCE) was used as reference electrode.

Polymer electrolytes were prepared from a tetrahydrofuran solution containing 2.5% (w/w) of [P(ECH-co-EO)] and $LiClO_4$. An elastomeric solid with high ionic conductivity is obtained after evaporation of the solvent (casting). Higher ionic conductivity was attained when the salt concentration, defined as $\eta = [O]/[Li^+]$, was fixed at $\eta = 6$.[15]

The artificial muscle prototype was prepared by dripping the electrolyte solution on two polypyrrole films (mass = 3 mg, thickness = 6 μm) grown on two different stainless steel electrodes, followed by evaporation of the solvent under atmospheric pressure at room temperature. Two [steel ∥ PPy ∥ P(ECH-co-EO)/$LiClO_4$] systems were obtained. The evaporation of the THF gives increasingly viscous and adherent films. Once the polyelectrolyte was viscous and adherent enough, the two electrodes covered by the polyelectrolyte film (thickness = 3 μm) were put in contact and a [steel ∥ PPy ∥ P(ECH-co-EO)/$LiClO_4$ ∥ PPy ∥ steel] system was performed. After 30 min the polyelectrolyte is dry and the triple layer [PPy ∥ P(ECH-co-EO)/$LiClO_4$ ∥ PPy] was then peeled off the stainless steel plates. The two films of polypyrrole were held at the top with a metallic clamp to allow independent electrical contract to the PPy films. One polypyrrole film was connected as working electrode and the other as counter electrode short-circuited with the reference electrode contact of the potentiostat. The movement of the triple layer was studied at room temperature with a controlled humidity (60%).

The solid polymeric electrolyte provided the ionic contact between the two polypyrrole electrodes with a face to face

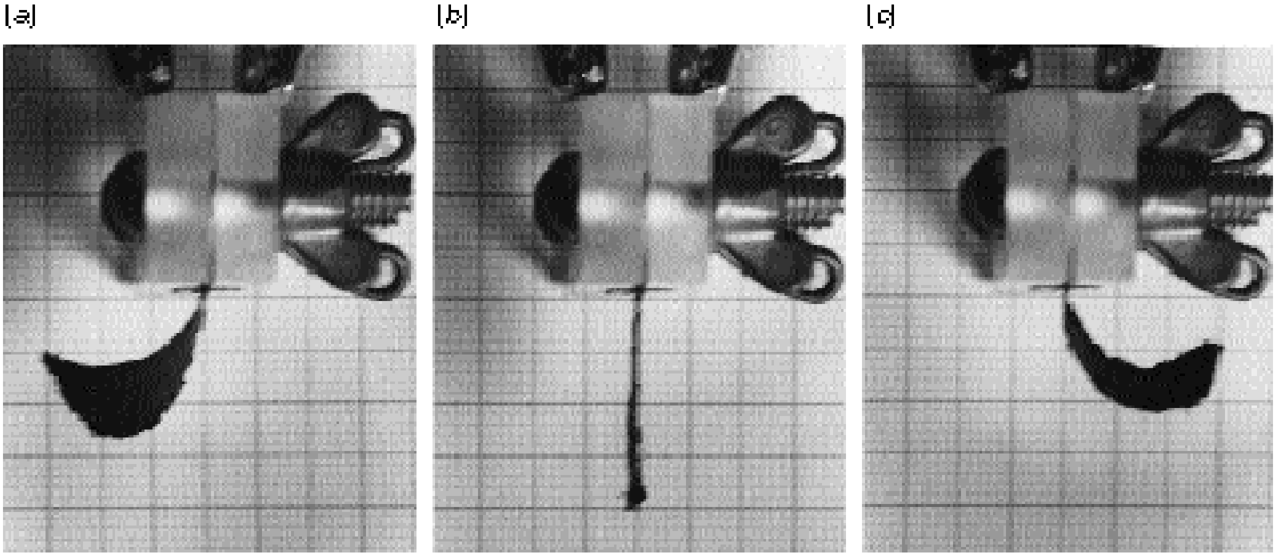

Fig. 1 Movement of the solid artificial muscle during the application of an electric current: (*a*) position after 108 mC of reduction charge, (*b*) position at neutral electrical state and (*c*) position after 108 mC of oxidation charge

configuration. All experiments began from the vertical position as can be seen in Fig. 1(*b*) with the two PPy films in a semi-oxidised state (250 mV *vs.* SCE). The right face of the triple layer was the working electrode and the left side worked as a counter electrode.

The flow of a constant current through PPy films promotes an angular movement of the free end of the triple layer. An anodic current applied to the PPy film connected as working electrode produced an angular movement of the free end in the direction of the counter electrode, Fig. 1(*c*). A movement in the opposite direction was observed when a cathodic current was applied, Fig. 1(*a*). The triple layer bent in the direction of the working electrode. Under a constant current of 20 mA the free end of the artificial muscle delay 5.4 s to cross 90°.

The angular movement in air was similar to that obtained in a liquid medium.[10–12] The direction of the movement during the oxidation or reduction of the working electrode was the same to that obtained when a liquid electrolyte ($LiClO_4$ aqueous solution) was used. In this liquid electrolyte, ClO_4^- anions enter into the PPy film during the oxidation process and the volume of PPy increases. These anions leave the film during reduction and the film volume decreases. In the solid configuration the flow of the current between both PPy films is supported by ionic movements inside the polymer electrolyte.

On the other hand, the electrical charge consumed during the movement of the solid state artificial muscle to cover 90° (36 mC per mg of PPy) was the same as that consumed when an aqueous $LiClO_4$, solution was used.

Taking into account that the covered angle depends directly on the volume change of the PPy film,[11,12] the PPy volume variation (covered angle) was the same for a similar electrical charge consumed when an aqueous $LiClO_4$ solution or a solid polymeric electrolyte (containing $LiClO_4$) was used.

The movement rate was also recorded. This parameter remained constant while the electrical current applied did not change. A linear relationship between movement rate and applied electrical current (similar to that showed in liquid configuration) was obtained [eqn. (1)].

$$\text{Movement rate rad s}^{-1} = 0.042\ I/\text{mass (mA mg}^{-1}) \quad (1)$$

Under these conditions both rate and direction of the angular movement are controlled by the intensity and direction of the current flow, respectively.

All the results obtained in this work show the feasibility of electrochemomechanical devices based on polypyrrole and a solid polyelectrolyte P(ECH-co-EO)/$LiClO_4$ film able to work in air. This fact starts a new development toward actuators and microrobotic applications.

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Footnotes and References

* E-mail: qppfeott@sq.ehu.es

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