Artificial Muscles Based on Conducting Polymers

Short communication

Artificial muscles based on conducting polymers ☆

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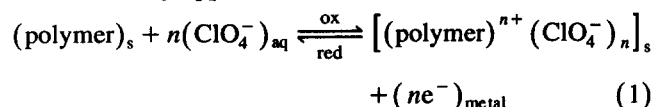
Abstract

A general description of artificial muscles based on the reversible electrochemical oxidation/reduction reactions in conducting polymers and the concomitant reversible change of volume is presented. The construction of bilayers and multilayers of conducting polymer/flexible adherent polymer is presented. The reproducibility of the macroscopic movement was very high using bilayers showing deviations < 5%. When the device was charged with a mass some 20 times the polymer mass, the reproducibility of movements had a higher average deviation of 20%. A bilayer trailing a steel sheet over 180° is shown. Variations of time, energy and power for uncharged and charged films, working under different constant currents are described.

Keywords: Artificial muscle model; Conducting polymers; Polymer movement; Oxidated polymer

1. Introduction

A muscle can be considered as an electrochemomechanical device: an electric pulse comes from the brain, through the nervous system and triggers chemical reactions in the muscle which promote a change of volume and concomitant mechanical work.

Conducting polymers are fascinating new materials which can be electrochemically oxidized and reduced in an electrolytic media by flow of anodic or cathodic currents, respectively [1–4, and refs. therein]. During electrochemical oxidation in a solution containing a salt, electrons are lost from the polymeric backbone and positive charges are generated along the chains. Those positive charges are radical cations (polarons) or bications (bipolarons). To keep the electroneutrality, counterions (anions) have to penetrate from the solution through the polymeric entanglement. In order to allow this penetration, channels open in the polymer; the solid increases in volume. The rate of the change of volume has to be related to the rate of the oxidation process, which is controlled by means of the current density applied to the system:

$$(polymer)_s + n(ClO_4^-)_{aq} \underset{red}{\overset{ox}{\rightleftharpoons}} \left[(polymer)^{n+} (ClO_4^-)_n\right]_s$$

$$+ (ne^-)_{metal} \qquad (1)$$

The volume of the reduced polymer (V_1) is lower than that of the oxidized polymer (V_2).

During the electrochemical reduction the reverse process takes place: electrons are injected into the polymer, positive charges along the chains are neutralized and counterions are expelled to the solution. At the same time the channels are closed and the volume of the film decreases. The diminution rate of the volume has to be proportional to the cathodic current density applied to the polymer.

These facts have been known since the beginning of eighties and such polymers were applied as actuators able to change in a few micrometers its length to close or open an electrical circuit [5].

To transform this molecular movement into a macroscopic movement we developed a bilayer structure: conducting polymer/nonconducting, flexible, adherent elastic film [6–10]. In this paper we will study new aspects of the device such as reproducibility, energy consumption, energy transformation and developed power.

2. Experimental

Polypyrrole films were electrogenerated from 0.2 M pyrrole and 0.1 M LiClO₄ acetonitrile + 2% water solutions. As working electrodes AISI 304 stainless steel sheets having dimensions 3.0×1.5 cm² were used. As counterelectrodes two stainless steel sheets were also used. Polymerizations were carried out by application of consecutive
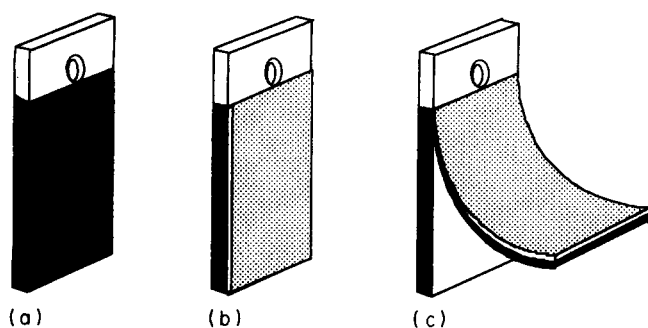
Fig. 1. (a) Stainless steel electrode partially coated with an electrogenerated polypyrrole film. (b) Adhesion of the nonconducting polymeric film on one side of the electrode. (c) The bilayer being removed from the surface.

square wave potentials of − 300 mV (vs. SCE) for 2 s and 850 mV for 8 s. This method has being optimized to obtain homogeneous, flexible, good quality polypyrrole films.

2.1. Construction of a bilayer

Once the polypyrrole film had been electrogenerated on the steel sheet, the coated electrode was extracted from the solution in the oxidized state: the potential pulses were stopped under anodic polarization. The polypyrrole film (Fig. 1(a)) from one side of the steel sheet was stuck to a commercially available double-sided plastic tape (Fig. 1(b)). The bilayer was removed from the stainless steel (Fig. 1(c)).

Once the plastic tape had been removed, the bilayer obtained was used as an electrode in the background solution (aqueous $LiClO_4$). Electrical contact between the polypyrrole layer and the current source was made through a platinum-coated clamp. Voltages and currents were applied from a PAR 273 potentiostat/galvanostat. Two platinum sheets (4 cm^2 surface area) were used as the counterelectrode.

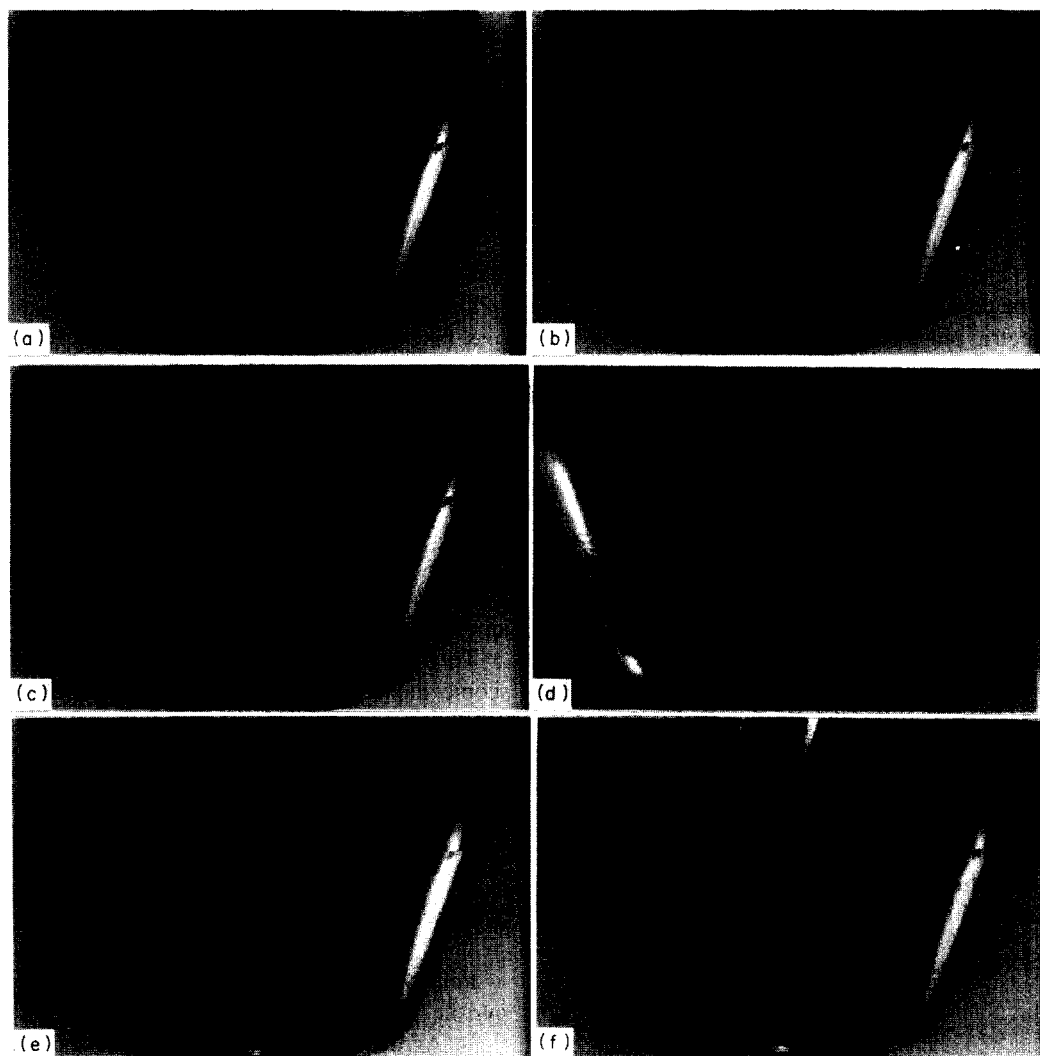

Fig. 2. (a) The bilayer polypyrrole (black)/nonconducting polymer (white) during oxidation of the conducting polymer. (b)–(f) A movement of 180° is described by the attached steel when a cathodic current passes through the conducting polymer.

When the polypyrrole layer was obtained by applying a square wave potential for 90 min, an overall charge of 25 C was consumed. The weight of the polypyrrole layer (from one side of the steel electrode) used to prepare the device was 6 mg. The mass of the adhesive film (a cellulose film with a rubber adhesive, 0.13 mm thick) was 45 mg. The overall mass of the device was 51 mg, being 2.5 cm long and 1.5 cm wide.

An area of 3 cm² was introduced to the solution, keeping the contact clamp out of the solution. The device was then checked at constant potential and constant current. To quantify the ability of the device to develop mechanical energy, a glass rod weighing 0.1 g with volume 0.039 cm³ was attached to the bottom of the device. The density of the background solution was 1.0534 g cm⁻³.

Fig. 3. Time required to cross 90° from vertical during oxidation of the conducting polymer in aqueous 1 M LiClO₄ (density 1.0534 g cm⁻³), as a function of the anodic current.

2.2. Reproducibility of the experiment

In order to test the reproducibility, four different devices were checked in 1 M LiClO₄ aqueous solution. When a potential of 1000 mV was applied, the oxidation process of the conducting film promoted the expansion of the polymer with penetration of counterions, and the bottom of the bilayer was bent as the polypyrrole film pushed the plastic tape. When the bottom had described an angle of 90° relative to the vertical position and was closer to the water surface the potential was changed to −1000 mV. Electrochemical reactions and consequent direction of movement were now reversed. The bottom of the device described a movement of 180 degrees.

The average times (for the four devices) required to describe 90° and 180° during the oxidation process were 4.5 ± 0.31 s, and 11.21 ± 0.54 s, respectively. The final part of the movement was slower. Under reduction (polarization at −1000 mV) movements were faster: 2.56 ± 0.05 s reach 90° and 6.09 ± 0.46 s to describe 180°. The reproducibility is good being the higher deviation of movement through 180°, under reduction. When the glass rod was attached to the bottom of the dispositifs and these were submitted to oxidation/reduction processes the time required to describe 90° under oxidation was 5.32 ± 0.95. To describe 180°, 13.95 ± 2.76 s was needed. All results were averaged over the four different devices. Under reduction processes times of 2.27 ± 0.41s were employed to reach 90° and 12.2 ± 1.75 s, to go over 180°. The reproducibility when carrying a weight is lower and deviations are around a 20%.

2.3. Movement under weight

Fig. 2 shows the different positions under the reduction process under weight. The glass rod was replaced by a piece of steel. The maximum expansion of the black polypyrrole film was produced and the free end of the
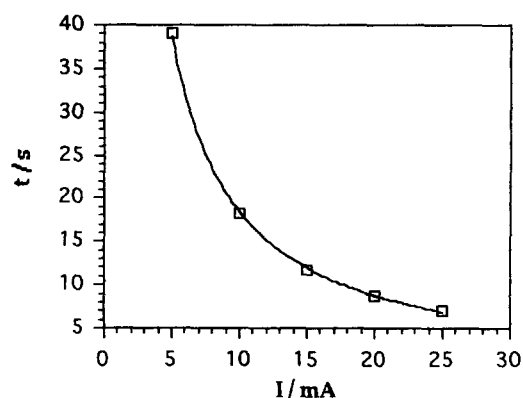
bilayer was pushed from the bottom until a position of +90° had been reached (Fig. 2(a)).

During reduction, counterions are expelled from the polypyrrole film. A progressive decrease of volume takes place. The steel sheet attached to the bottom described a movement of − 180°. This movement can be seen in Figs. 2(a)–2(f). During oxidation the opposite movement takes place.

2.4. Movement under constant current density

The movement of the device is related to the oxidation and reduction processes. The rate of those electrochemomechanical movements depends on the current density, the magnitude of which controls the rate of electron loss from the polymer. Times required for the free end of a bilayer to pass 90° during the oxidation of the conducting polymer in aqueous 1 M LiClO₄ decrease when the current is increased, as shown in Fig. 3. This corresponds to the equation

$$t_{ox} = 217 \, I^{-1.07}; \quad \text{regression} = 0.999 \qquad (2)$$

During reduction processes are faster and the time changes with current density as:

$$t_{red} = 194 \, I^{-0.94}; \quad \text{regression} = 0.998 \qquad (3)$$

When the polymeric bilayer was charged with a glass rod weighing 0.1 g, which volume was 0.039 cm³, the respective equations are:

$$t_{ox} = 241 \, I^{-1.08}; \quad \text{regression} = 0.999 \qquad (4)$$

$$t_{red} = 208 \, I^{-0.94}; \quad \text{regression} = 0.999 \qquad (5)$$

The electrical energies consumed (J) to move the free bilayer under different current densities follow the equations

$$E_{ox} = 0.068 + 0.006 \, I; \quad \text{regression} = 0.997 \qquad (6)$$

$$E_{red} = 0.020 + 0.009 \, I; \quad \text{regression} = 0.994 \qquad (7)$$
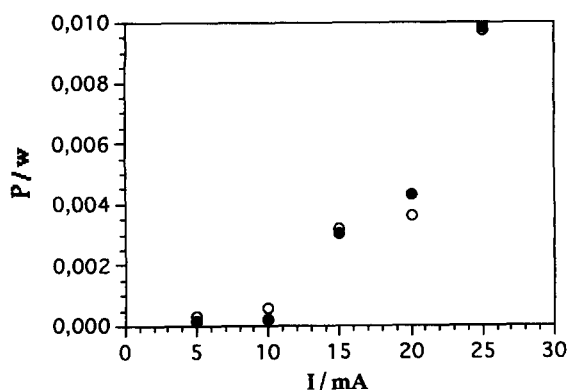
Fig. 4. (O) Difference in electric power between uncharged and charged bilayers during oxidation, as a function of the anodic current. (●) The same under reduction.

When the bilayer is charged, the electrical energies consumed are:

$$E_{ox} = 0.059 + 0.009\ I; \quad \text{regression} = 0.989 \tag{8}$$

$$E_{red} = -0.006 + 0.014\ I; \quad \text{regression} = 0.991 \tag{9}$$

Under those conditions the electric power consumed (P) during the movements promoted by the oxidation of the film under different anodic currents followed the equation:

$$P_{ox} = 0.00019\ I^{1.58}; \quad \text{regression} = 0.999 \tag{10}$$

and for the reduction process:

$$P_{red} = 7.5 \times 10^{-5}\ I^{1.82}; \quad \text{regression} = 0.999 \tag{11}$$

When the bilayer was charged with the glass rod the analogous equations for the power consumed were:

$$P_{ox} = 1.6 \times 10^{-4}\ I^{1.68}; \quad \text{regression} = 0.999 \tag{12}$$

$$P_{red} = 6.0 \times 10^{-5}\ I^{1.97}; \quad \text{regression} = 0.999 \tag{13}$$

The great similarity between power values for charged and uncharged bilayers indicates that only a small amount of the consumed power was spent to trail the glass rod. The differences under oxidation and reduction processes are depicted in Fig. 4.

3. Similarity to muscles

These devices can be considered as artificial muscles: an electric pulse promotes chemical reactions in the active

layer which produce a change of volume and hence mechanical movement. The process requires the presence of an electrolyte. Similarities between muscle and artificial muscle can be summarized:

- electric currents related to chemical reactions are involved;
- a change of volume is present during work;
- a mechanical movement is produced from chemical reactions without mediation of macroscopic mechanical components;
- an aqueous solution of ionic salts is required to allow muscles to work;
- ionic flows are present during muscle work.

Some differences are present as well:

- the driving power in muscles is the chemical energy, the electric pulse being a trigger;
- the driving power in artificial muscles is an electric current having the oxidation and reduction reactions of the polymer as mediators;
- muscles only work under contraction due to the irreversibility of the chemical reactions. Artificial muscles work both by contraction and by expansion, by virtue of reversible reactions depending on the direction of the current.

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