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POLYPYRROLE/ DODECYLBENZENESULPHONATE BASED ARTIFICIAL MUSCLES AND THEIR BEHAVIOR

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ABSTRACT

Conducting polymers can be easily synthesized by electrochemical oxidation of the corresponding monomer. During electrochemical synthesis, they tend to form freestanding and mechanically cohesive films over the electrodes. These films can be electrochemically oxidized and reduced in a continuous, reversible way. This process accompanies movement of ions and solvents into and out of the conducting polymer which results in conformational changes in the polymer. Artificial muscles that are based on reversible stress gradients linked to these reversible conformational changes were constructed in the form of conducting polymer/non-conducting polymer bilayers using polypyrrole/dodecylbenzenesulphonate (DBS) conducting polymer and polyimide. Simultaneous cyclic voltammetry and force measurement studies of these artificial muscles showed that force changes are associated with the main peaks of the cyclic voltammograms and almost all the force is generated in a narrow potential range.

Keywords: Conducting Polymer, Polypyrrole, Artificial muscles

1. INTRODUCTION

Systems that are capable of converting electrical energy into mechanical energy can be defined as actuators, or more specifically in the case of softer materials, artificial muscles. Since the beginning of the interest on artificial muscle, various types of materials have been used with interesting performances. Some of the materials considered were piezoelectric and electrostrictive in nature. The basic principle behind artificial muscle is its movements as a result of volume expansion/contraction. However the above mentioned materials have a common drawback of exhibiting slight movements under high applied voltages. These drawbacks encouraged researchers to find alternative materials. One such alternative is to use conducting polymers (CP). Conducting polymers are considered to be the most promising candidates for artificial muscles since they show both electronic and ionic conductions [1]. These materials could show considerable dimensional changes upon doping or dedoping [2]. It has been reported in literature that artificial muscle made with conducting polymers performed quite analogous to natural muscles. This was demonstrated by Pei *et al* with the help of a simple bilayer muscle [3]. In this paper we report the behaviour of artificial muscles based on polypyrrole (PPy), a conducting polymer that has been studied extensively by West *et al* [4]. The artificial muscles studied were prepared in the form of bilayer strips and were characterized using deflection and force measurements.

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2. EXPERIMENTAL

Fabrication of bilayer muscles was done on a polyimide film (Kapton-Dupont) having a thickness of 25 μm. To get the electrical contacts, the polymer film was coated with a 250 μm thick gold layer. A rectangular strip cut from the polyimide film to the size of 2.5 cm long and 0.5 cm wide was used as the base to deposit the PPy film. Deposition of PPy was done (electrochemically using 0.05 M sodium) dodecylbenzenesulphonate (Aldrich) electrolyte containing 0.05 M pyrrole monomer and a constant current density of 1 mA cm^{-2}. The configuration of the muscle is shown in Fig. 1.

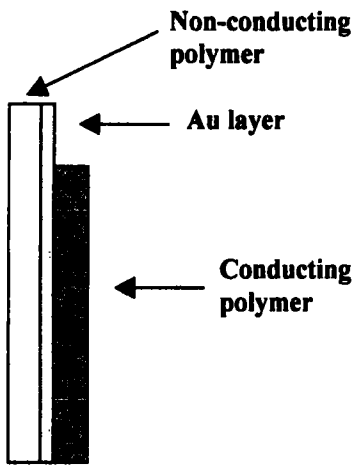


Fig.1 Schematic diagram of a bilayer artificial muscle.

Cycling experiments of the bilayer was carried out in a three electrode electrochemical cell in the potential range -0.85 to 0.60 V vs SCE with the sweep rate of 50 mV/s. Cycling electrolyte was 0.1 M sodium perchlorate (Aldrich). SCE and a Pt wire electrodes served as the reference and counter electrodes, respectively. While the bilayer was subjected to cycling, deflection measurements were obtained (in mm) with the help of a centimeter scale, which was fixed to the electrochemical cell.

To measure the force, which arises as a result of conducting polymer contraction, the free end of the muscle was connected to a microbalance with the help of a hook. The experimental setup consisted of an electrochemical cell with the muscle as the working electrode, a Pt wire as the counter electrode and SCE as the reference electrode. Force variation with respect to the applied potential (-0.85 to 0.30 V) and the cyclic voltammograms were simultaneously recorded in a computer.

3. RESULTS AND DISCUSSION

Bending in the bilayer muscles arises due to a rather complicated process. When PPy films are made with large surfactant anions (DBS), the anions were supposed to go into the polymer during polymerization and get bound in the polymer structure. When the muscle is cycled in an electrolyte containing a salt (M^+X^-), PPy gets neutralized during the reduction, by absorbing electrons while cations (M^+) are inserted into the film to maintain the charge neutrality. In addition to above, a considerable amount of solvent (water) also accompany the inserted cations. All these movements ultimately result in expansion of the polymer. Since the PPy is attached to the Kapton film having a fixed volume, the muscle starts to bend into a convex arc. But, no significant bending was observed during the very first reduction. We believe that this is due to conformational changes occurring in the film. Even though cation insertion takes place, these conformational changes may have counterbalanced the volume increase. But, a different idea was suggested by Pei *et al* [5]. They believe that the initial delay in bending is due to expulsion of DBS^- ions from the outer surface of the PPy layer. This is contradictory to what we have observed in our Electrical Quartz Crystal Microbalance(EQCM) studies in which no mass loss from the film was observed.

During the next oxidation, cations (M^+) start to move out of the PPy film along with water molecules, at lower potentials. In EQCM studies, it has been observed that water removal is not as fast as insertion. When the PPy film is subjected to high potentials, anions (X^-) in the electrolyte also tend to move into the film. However, the volume change in the polymer matrix due to cation and water expulsion is higher than that due to anion insertion. The net result is the contraction of the muscle, which will make the muscle to come back to its initial position. Thereafter, during the next reduction, both processes

of anion expulsion at higher potentials and cation and water insertion at lower potentials will occur causing expansion of the PPy film giving the final result of bending in the opposite direction. Since cations and anions are moving in opposite directions, both species affect the bending of the muscle. Figure 2 illustrates the deflection measurements done simultaneously with the cyclic voltammetry measurements. Cycling was started at the reduced state of the polymer at which the muscle has bent towards the Kapton film (convex shape). For the deflection measurements, this position was taken as the zero position. Then, during the oxidation, PPy film gets contracted and shows a deflection. The resultant deflections in mm measured at different potentials are indicated by squares in Figure 2. As the potential is increased from –0.85 to 0.30 V vs SCE, large deflections occurred and on further increase, the deflection remained almost constant for a while and started to decrease. This result shows that two different processes occur during oxidation. The decrease in the bending at higher potential may be due to anion insertion. During the reduction, the deflection almost follows the cyclic voltammogram. However, it is seen that the deflection does not come back to its initial value. This can be attributed to conformational changes that can occur in the polymer matrix during cycling. The muscle can be held with a certain bending by fixing the applied voltage [6].

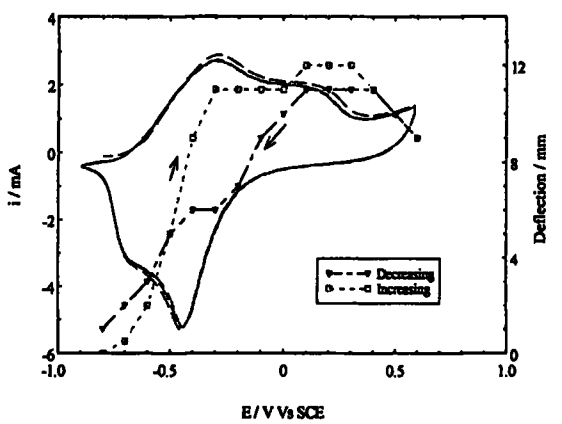


Fig.2 Simultaneous deflection measurements with the cyclic voltammogram of a bilayer artificial muscle. Sweep rate 10 mV s^{-1}. (□-□) indicates deflections during oxidation and (∇-∇) during reduction.

It has been reported that the bending speed of PPy / DBS bilayer muscles is larger than that of PPy / ClO_4 muscles [7]. This implies that the cation movement in PPy/DBS films is the dominating part in the redox process. If anion movement is responsible for the fast actuation, PPy / ClO_4 muscles should show faster movements.

Figure 3 shows the force measurement curve of a PPy / DBS muscle as a function of potential with the corresponding cyclic voltammogram. Force is kept negative during the experiment since the experimental setup only allows pulling forces rather than pushing forces. The theory behind the force generation and the mechanical behavior of these bending actuators are given elsewhere [8]. Cycling was started at -0.85 V where the polymer was in its reduced state. During the first positive half cycle of the cyclic voltammogram, PPy is subjected to an oxidation process in which cation and water move out of the film resulting in contraction of the film. Due to this contraction, the artificial muscle tends to bend downwards giving an increase in the force. During the next half cycle (at higher potentials), anion insertion takes place as explained earlier and hence the force decreases. This is because anions are moving in the opposite direction to that of the cations. This means that anion insertion produces a reduction in the measured force of these muscles.

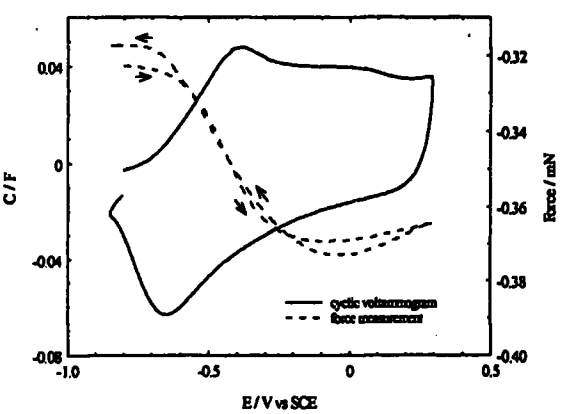
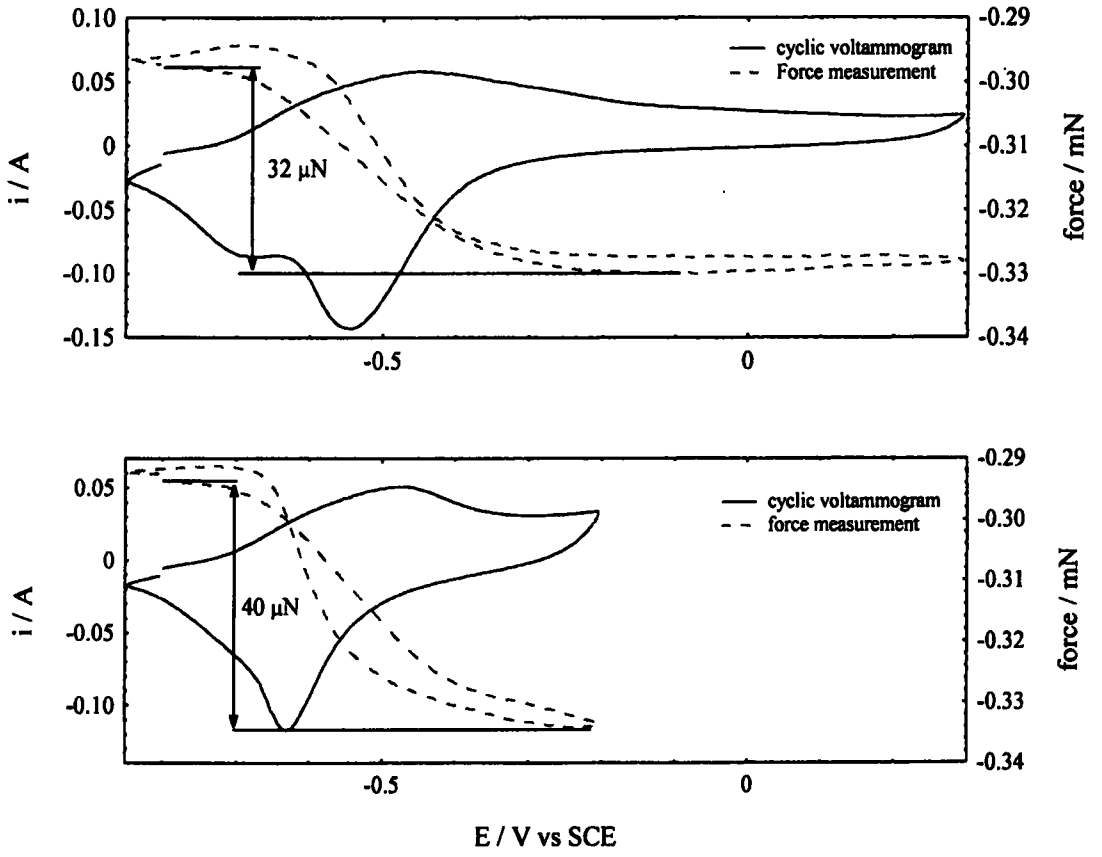


Fig. 3 Force variation with cyclic voltammogram of a PPy / DBS artificial muscle. PPy film thickness corresponds to 360 mC cm^{-2}, sweep rate 10 mV s^{-1}.

During the next half cycle of the cyclic voltammogram, that is, during the reduction process of the film, anions move out of the film resulting in a

contraction while at more negative potentials, cations and water move into the film causing an expansion. Hence the muscle will move upwards and the microbalance will sense it as a reduction in force. As a result of this, we see that the force curve almost follows the original curve. But, as we can observe in Fig. 3, the force has not reached the initial value but stopped at a lower value. This may be due to two reasons. First the conformational changes occurring in the polymer structure may have affected the ion movement. Secondly, the oxygen present in the cycling electrolyte may have caused partial oxidation of the film. This in turn reduces the cation insertion. As a result, there will be a reduction in the measured force. This behavior is visible even in the cyclic voltammogram where the end potential is far below the starting potential.

It is important to note that the change in the force is associated with the peak positions in the cyclic voltammogram. It seems that almost all the force changes are connected with the main peaks and furthermore the force is generated in a rather narrow voltage interval (400 mV vs SCE).



(a) – 0.85 to 0.30 V and
(b) - 0.85 to –0.20 V vs SCE for a PPy / DBS bilayer artificial muscle.
PPy film thickness corresponds to 360 mC cm^{-2}. Sweep rate 10 mV s^{-1}.

Fig.4 Comparison of force variation in the potential ranges,

This has important implications since the small voltage range will be an advantage for practical applications as actuators. The occurrence of full force in a narrow potential window was verified by cycling a muscle made with a PPy / DBS film between a wide potential interval from -0.85 to 0.30 V vs SCE and a narrow potential interval from -0.85 to -0.20 V vs SCE .The results obtained are shown in Fig. 4.(a) and (b). The results clearly show that in the narrow potential range, the force change is slightly higher that in the wider range. This again clarifies our argument that anion movement reduces the mass change, deflection and the measured force.

4. CONCLUSION

Deflection of the PPy/DBS bilayer artificial muscles takes place in a two-step process corresponding to cation and anion movement. Force exerted by these muscles always follows the peak positions of the cyclic voltammogram. Almost all the force is generated in a rather narrow voltage interval.

5. ACKNOWLEDGEMENT

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