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High-response tri-layer electrochemical actuators based on conducting polymer films

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Abstract

Sandwich structured tri-layer films of polypyrrole/gold/polypyrrole have been electrochemically synthesized by successive oxidation of pyrrole in aqueous solutions and sputtering deposition of a thin gold layer, respectively. One of the polypyrrole layers was doped by a relatively large anion, dodecylbenzene sulfonate (PPy(DBS)) and the other one was doped by a smaller anion, benzenesulfonate (PPy(BS)). The tri-layer film could be deformed quickly by electrochemical reduction and oxidation of polypyrrole layers. The thin gold layer provided a highly conductive support for actuation. The tri-layered film could move from a position of 0° (vertical) to a position of $+90^{\circ}$ (oxidation) or -90° (reduction) at potentials higher than 0.7 V or lower than -0.7 V (vs. saturated calomel electrode (SCE)), respectively. The movement rate of the tri-layer film was $\sim 260^{\circ}$ /s at potentials of ± 1.2 V vs. SCE, which was five times that of a PPy(DBS)/PPy(BS) bi-layer film. Furthermore, the tri-layer film could be driven at potentials as low as ± 0.2 V vs. SCE. The bending motion rate of the tri-layer film increased quadratically with the increase of driving potential, while the motion rate of the bi-layer film, PPy(DBS)/PPy(BS), increased linearly with an increase of driving potential. © 2004 Elsevier B.V. All rights reserved.

Keywords: Polypyrrole; Tri-layer film; Gold layer; Actuator

1. Introduction

In recent decades, several soft actuators functioning by volume changes of intrinsically conducting polymers during redox processes have been studied extensively [1,2]. This volume change can be expressed as electrochemomechanical deformation. Most of the actuators have a bi-layer or a tri-layer configuration [3–5]. In the bi-layer actuators, a single actuating film is affixed to a second, electromechanically inert layer (e.g., a nonconducting adhesive tape). The tri-layer actuators usually consist of two conducting polymer films attached to either side of a passive film (e.g., a non-conducting flexible double-sided adhesive tape). In these tri-layer actuators, one of these conducting polymer films acts as the working electrode and the other acts as the counter and reference electrodes [4]. In the configurations described above, the electrochemically inert layer can increase the strength of the actuator. Recently, a highstrength tri-layer actuator based on polypyrrole and high-strength polythiophene has also been investigated [6]. However, the bending and response ability of these actuators were not satisfactory. Recently, Takashima et al. [7.8] reported a bi-ionic actuator (BIA) consisting of only two layers of polypyrrole films, which was driven by a combination of the anodic expansion of one PPy layer and the anodic contraction of the other layer. Although the bending movement of the actuator was enhanced through bi-ionic contributions, the response rate was not improved. This is because the conductivities of the polymer films were relatively low, which meant that the doping ions could not be inserted or removed quickly. In order to obtain efficient charge transfer and quick actuation response, spiral-wound metal wire was integrated into the conducting polymer tube device, which enabled linear movement [9,10].

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In this paper, we report an actuator consisting of three layers of films with a configuration of PPy(DBS)/Au/PPy(BS), which bends in electrolyte solution. The anodic shrinking film, PPy(DBS), and the anodic swelling film, PPy(BS), act as cooperative driving layers for actuation. The gold layer acted as a charge collection electrode to accelerate the redox reaction of the polypyrrole film. As a result, an actuator with high response and high bending ability was obtained. The movement behavior of the actuator has also been investigated.

2. Experimental

Electrochemical syntheses and examinations were performed in a one-compartment cell with the use of a Model 283 potentiostat–galvanostat (EG&G Princeton Applied Research) under computer control. The working and counter electrodes were stainless steel (AISI 304) sheets $(1.0 \times 3.0$ and 2.0×3.0 cm, respectively), and were placed 1.5 cm apart. All potentials are referred to a saturated calomel electrode (SCE).

PPy films were deposited from an aqueous solution of pyrrole at a constant current density of 2.0 mA cm^{-2} . All solutions were de-aerated by bubbling dry nitrogen, and maintained at a light overpressure during the experiments. The procedure for preparation of the tri-laver composite films used for actuation was as follows. First, a PPy(DBS) layer was electrodeposited from the aqueous solution containing 0.1 M freshly distilled pyrrole monomer and 0.1 M dodecylbenzene sulfonic acid for a charge density of 2.0, 3.0 or 4.0 C cm⁻². Secondly, after drying in air for 48 h, a gold layer about 250 nm thick was evaporated onto the surface of the PPy(DBS) layer under vacuum. Lastly, a PPy(BS) layer was deposited on the gold layer surface from an aqueous solution containing 0.1 M freshly distilled pyrrole monomer and 0.1 M benzene sulfonic acid for a charge density of 2.0,

3.0 or 4.0 C cm⁻². After the films were washed with water, they were peeled off from the substrates with a knife and dried in air. Free-standing PPy(DBS) (2.0 C cm^{-2}) and PPy(BS) (2.0 C cm^{-2}) films were also synthesized for CV measurements. A free-standing bionic PPy(DBS) (2.0 C cm^{-2})/PPy(BS) (2.0 C cm^{-2}) film was also prepared for comparison by the same procedure described above. Before CV and movement measurements, the tri-layered or bi-ionic films were cut into pieces with areas of $25 \times 2 \text{ mm}^2$ and the thickness of the films was measured by the use of a thickness monitor (CH-1-ST, Shanghai China).

3. Results and discussion

3.1. Electrochemistry

The polypyrrole film grown from an aqueous or acetonitrile solution of $LiClO_4$ (PPy(ClO₄)) was found to be brittle and weak. Furthermore, it adhered weakly to the thin gold substrate. Thus, we constructed a trilayer film of PPy(DBS)/Au/PPy(BS) instead of PPy(DBS)/Au/PPy(ClO₄). Fig. 1 shows the typical successive cyclic voltammograms (CV) of free-standing asgrown PPy(BS), the bi-ionic film of PPy(DBS)/PPy(BS) and the tri-layer composite film of PPy(DBS)/Au/ PPy(BS) in 1 M LiClO₄ aqueous solution at a potential scan rate of 20 mV s⁻¹. The as-grown PPy(BS) film exhibited cathodic expansion when it was reduced [11–14]. However, the doped anion, BS⁻, was gradually replaced by the electrolyte anion, ClO_4^- , during the redox process. As a result, the initial few CV cycles are unstable as is shown in Fig. 1. The replacement of BS⁻ by ClO₄⁻ is an irreversible process. Thus, the BS⁻ would be completely replaced by ClO_4^- after several CV cycles. Finally, the PPy(BS) film has electrochemomechanical properties similar to those of a $PPy(ClO_4)$ film.

The typical stable CVs of PPy(DBS), PPy(BS), the biionic film of PPy(DBS)/PPy(BS) and the tri-layer com-



Fig. 1. Successive cyclic voltammograms of an as-grown PPy(BS) film (a), a PPy(DBS)/PPy(BS) bi-layer film (b), and a tri-layer composite film PPy(DBS)/Au/PPy(BS) (c) in 1 M LiClO₄ aqueous solution. Potential scan rate: 20 mV s⁻¹.

posite film of PPy(DBS)/Au/PPy(BS) in 1 M LiClO₄ aqueous solution are illustrated in Fig. 2. The PPy(DBS) film showed an *n*-doping (reduction) wave at ca. -0.54 V and a dedoping (oxidation) wave at ca. -0.025 V (Fig. 2(a)). The potential difference between the oxidation and reduction current peaks (ΔE_p) was as large as 0.52 V. On the other hand, the film of PPy(BS) showed a oxidation wave at ca. -0.24 V and a reduction wave at ca. -0.50 V (Fig. 2(b)). The ΔE_p was relatively small (~ 0.26 V), indicating that the redox process was relatively reversible. However, for the PPv(DBS)/ PPy(BS) bi-ionic film, only a broad reduction wave at -0.79 V was observed, while the oxidation wave was not obvious. In the case of the tri-layer composite film PPy(DBS)/Au/PPy(BS) (Fig. 3(d)), a pair of well-resolved redox waves with much higher current densities than that of PPy(DBS)/PPy(BS) were observed at -0.59and -0.17 V, respectively. This indicates that the trilayer film has quicker and stronger electrochemomechanical deformation responses than those of the bi-layer film.

3.2. The bending motions of the films

Because the as-deposited PPy(BS) film exhibited cathodic expansion when it was reduced, the measurement of the bending motions of the bi- and tri-layer films were performed after 10 CV scans in 1 M LiClO₄ aqueous electrolyte for ion exchange. The structure of a



Fig. 3. Schematic presentation of the electrical instrument, and the structure of the composite film of PPy(DBS)/Au/PPy(BS) and its movements after 10 CV scans at a potential scan rate of 100 mV s⁻¹ during the redox process.

PPy(DBS)/Au/PPy(BS) tri-layer composite film and its bending movements (after 10 CV scans) during the redox process in electrolyte solution are illustrated in Fig. 3. In this structure, the tri-layered film acted as the working



Fig. 2. Stable cyclic voltammograms of a PPy(DBS) film (a), PPy(BS) film (b), PPy(DBS)/PPy(BS) film (c) or a PPy(DBS)/Au/PPy(BS) film (d) recorded after 10 CV scans in 1 M LiClO₄ aqueous solution at a potential scan rate of 20 mV s⁻¹.



Fig. 4. Photographs of bending motions of a PPy(DBS)/Au/PPy(BS) tri-layer actuator which is held with the PPy(DBS) layer to the right. (a) The film bent from 0° (vertical) position to the position of 90° , (b) the film curled after moving to the position of 90° at a potential of ± 0.7 V, left hand photographs are at negative potentials and right hand photograph are at positive potentials.



Fig. 5. Photographs of the bending motions of the PPy(DBS)/Au/PPy(BS) tri-layer actuator which was held with the PPy(DBS) layer to the right at different driving potentials: (a) -0.5 V; (b) -0.3 V; or (c) -0.2 V; (d) 0.3 V; (e) 0.1 V; or (f) 0.0 V.

electrode, and a platinum plate and a saturated calomel electrode were used as the counter and reference electrodes, respectively. PPy(BS) acted as an anion-driven layer [15–17] and PPy(DBS) acted as a cation-driven [14,18] layer. Thus, during reduction of the composite film, the film bends in the direction of the PPy(BS), and

during oxidation, the film bends in the direction of the PPy(DBS).

The bending motions of the bi-ionic film, PPy(DBS)/ PPy(BS), and the tri-layer composite film, PPy(DBS)/ Au/PPy(BS), were investigated electrochemically in 1 M LiClO₄ aqueous solution. Both the bi-ionic PPy film and tri-layer composite films can easily bend from a position of 0° (vertical) to +90° (oxidation) and -90° (reduction) at potentials of ± 0.7 V vs. SCE initially, and subsequently, the films were curled as shown in Fig. 4(b). The bending capacity of the tri-layer composite film was also investigated in 1 M LiClO₄ aqueous solution at various potentials. A tri-layer composite film, PPy(DBS)/Au/ PPy(BS), with a mass of 1.4 mg and a size of $25 \times 2 \times 0.03$ mm could bend reversibly from a position of 0° (vertical position) to a position of $\sim \pm 45^{\circ}$ (Fig. 5(c) and (f)) at a potential of 0 V or -0.2 V vs. SCE, respectively, and could bend to $\sim \pm 65^{\circ}$ (Fig. 5(b) and (e)) as the film was oxidized at a potential of 0.1 V or reduced at a potential of -0.3 V vs. SCE, respectively. Furthermore, as the oxidation potential was made higher than 0.3 V or the reduction potential was made



Fig. 6. The movement rates of PPy(DBS)/Au/PPy(BS) films with different thicknesses in 1 M LiClO₄ aqueous solution under various galvanostatic conditions (a), and plots of the charge consumed vs. the applied electrical current during the oxidation process (b).

lower than -0.5 V, the film bent more than 90° and started to curl (Fig. 5(a) and (d)).

3.3. The movement properties of the films

The movement properties of the tri-layer composite film and the bi-ionic film in 1 M LiClO₄ solution were also investigated according to a previously reported method [19,20]. The angular movement of the free end of the film was referred to the vertical position as 0° . The movement rate (deg/s), the electrical energy consumed (mJ) and the electrical charge consumed (mC) in the actuation can be defined as follows:

Movement rate = angle/time.

Electrical energy consumed = $\int (IV) dt$.

Electrical charge consumed = $\int I dt$.

The movements of the tri-layer films with different thickness were studied under various conditions. The experimental results are demonstrated in Figs. 6 and 7. From Fig. 6, we can see that the bending rates of the trilayer film with different PPy thickness increase linearly with the increase of applied current density. Furthermore, at a given driving current density, the bending rates of the tri-layer composite film increase with decrease of the film thickness. Furthermore (from Fig. 6(b)), thicker films consumed more electrical charge in moving to the same position. However, for a given trilayer film, the charge consumed for the film to bend to a constant angle is a constant and independent of the value of the driving current density.

Fig. 7 illustrates the bending motion of the bi-ionic and tri-layer films of the same size and mass at different driving potentials. The tri-layer film PPy(DBS)/Au/ PPy(BS) has a bending rate of ~260°/s at a driving potential of 1.2 V vs. SCE, which is five times that of the bi-ionic film PPy(DBS)/PPy(BS) at the same potential. The bending motion rate of the film PPy(DBS)/PPy(BS) increases linearly with increase of the applied driving potential in the range of $-1.2 \sim +1.2$ V vs. SCE. Otherwise, the bending motion rate of the tri-layer film PPy(DBS)/Au/PPy(BS) increases quadratically with the



Fig. 7. The bending motion rates of the bi-ionic and tri-layer films at different driving potentials in 1 M LiClO₄ solution: PPy(DBS)/PPy(BS) (a); PPy(DBS)/Au/PPy(BS) (b).



Fig. 8. The plots of energies consumed for bending at a certain angle for a bi-ionic (A) and a tri-layer film (B) with the same area and thickness vs. the driving current density during the oxidation processes.

increase of applied driving potential in the range of $-1.2 \sim +1.2$ V vs. SCE. Furthermore, in comparison to the bi-ionic film PPy(DBS)/PPy(BS), the tri-layer film PPy(DBS)/Au/PPy(BS) consumed less energy in bending to a constant angle (Fig. 8).

4. Conclusions

Tri-layer composite films of PPy(DBS)/Au/PPy(BS) and bi-ionic PPy films of PPy(DBS)/PPy(BS) have been electrochemically synthesized by successive oxidations of pyrrole in aqueous solutions. The bending responses and capacity of the tri-layer film were found to be much higher than those of the bi-ionic film, mainly due to the gold nano film, which provided a high conductive layer. Therefore, under given driving conditions, the movement rate of the tri-layer composite film was much higher than that of the bi-ionic polypyrrole film.

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