Available online at www.sciencedirect.com

SCIENCE DIRECT®

Sensors and Actuators B 99 (2004) 525–531

SENSORS AND ACTUATORS B CHEMICAL

www.elsevier.com/locate/snb

Conducting polymer electrochemical actuator made of high-strength three-layered composite films of polythiophene and polypyrrole

Gaoyi Han [a,b], Gaoquan Shi [a,*]

[a] Laboratory of Organic Optical Electronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, PR China
[b] Institute of Molecular Science, Shanxi University, Taiyuan 030006, PR China

Received 7 September 2003; received in revised form 26 November 2003; accepted 8 January 2004

Abstract

Tri-layer conducting polymer composite films of polypyrrole/polythiophene/polypyrrole have been electrochemically synthesized by successive oxidation of pyrrole in aqueous solutions and thiophene in boron trifluoride diethyl ether (BFEE) solution, respectively. One of the polypyrrole layers was doped by a small anion of perchlorate (PPy (ClO_4)) and the other one was doped by a large anion, dodecylbenzene sulfonate (PPy (DBS)). The tri-layer film was deformed by electrochemical reduction and oxidation of polypyrrole layers. The polythiophene (PTh) layer provided a high strength conductive polymeric support for the actuator. A 0.4 mg composite film can reversibly raise a 10 mg material (e.g. a copper wire) from the position of 0° to the position of ∼±90° at ±1. 0 V (versus saturated calomel electrode (SCE)), respectively, while the bi-ionic film of PPy (ClO_4)/PPy (DBS) with the same weight can raise the 10 mg copper wire to only a position of ∼±25°. The movement rate of the tri-layer film was also higher than that of the bi-ionic polypyrrole film.

Keywords: Polypyrrole; Polythiophene; Actuator; Raman spectroscopy

1. Introduction

In the last decades, several soft actuators with the change in volume of intrinsically conducting polymers during redox process have been studied extensively [1,2]. This volume change can be expressed as electrochemomechanical deformation.

Most of the actuators have a bilayer or a tri-layer configuration [3–5]. In unimorph bilayers, a single actuating film is affixed to a second, electromechanically inert layer. Bimorgh actuators use two conjugated polymer films attached to either side of a passive film, such as an adhesive tape. In these configurations, the electrochemically inert layer can increase the strength, however, also provides extra weight and volume of the actuator. Recently, Takashima and coworkers [6,7] reported a bi-ionic actuator (BIA) consists of only two layers of polypyrrole films, which is driven by cooperative bending associated with the anion driven (anodic expansion) and the cation driven (anodic contraction). Although the bending actuation of the actuator has been enhanced because of bi-ionic contributions, the mechanical strength of the conducting polymer films was relatively weak. Furthermore, during the redox process, the ions and solvent molecules were inserted and de-inserted into the film repeatedly and changed the morphology of the film of a compact film into a porous one. As a result, the mechanical strength of the actuator decreased dramatically.

In this paper, we report an actuator consists of three layers of conducting polymer films with a configuration of PPy (DBS)/PTh/PPy (ClO_4). The two layers of polypyrrole act as bi-ionic driving layers for actuation. The polythiophene (PTh) layer is electrically conductive and acts as a current collector. Furthermore, the polythiophene layer was electrochemically synthesized by direct oxidation of thiophene in boron trifluoride diethyl etherate (BFEE) solution, and it had an excellent high tensile strength (∼130 MPa) and good flexibility [8]. Thus, the polythiophene layer provided the actuator with an excellent mechanical support.

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 cm × 3.0 cm and 2.0 cm × 3.0 cm, respectively) and

---

[*] Corresponding author. Tel.: +86-10-62773743;
fax: +86-10-62771149.
E-mail address: gshi@tsinghua.edu.cn (G. Shi).

0925-4005/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2004.01.001

placed 1.5 cm apart. All potentials were referred to a saturated calomel electrode (SCE). Raman spectra were recorded on a RM 2000 microscopic confocal Raman spectrometer (Renishaw Company) with an excitation of 632.8 nm laser light at 0.5 mW, and were accumulated three times for 30 s each. The spectra were recorded with a charge coupled device (CCD) camera. The composite membrane was cut vertically into two pieces and the laser light spot was focused on the newly formed cross-section.

PPy films were deposited from the aqueous solution of pyrrole at a constant current density of 2 mA cm^{-2} and the PTh films were electrochemically synthesized by direct oxidation of thiophene in freshly distilled BFEE at a constant potential of 1.3 V (versus SCE). 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-layer composite films used for actuations as follows. First, 2.0 C cm^{-2} PPy (DBS) layer electrodeposited from the aqueous solution containing 0.1 M freshly distilled pyrrole monomer and 0.1 M dodecylbenzene sulfonate soldium (DBS) at pH 3–4 (adjust by 0.1 M dodecylbenzene sulfonic acid). Secondly, after drying in air for 24 h, 3.5 C cm^{-2} PTh layer was deposited on the PPy (DBS) layer surface from the BFEE solution containing 30 mM thiophene. Lastly, 2.1 C cm^{-2} PPy (ClO_4) layer was deposited on the PTh layer surface from the aqueous solution containing 0.1 M freshly distilled pyrrole monomer and 0.1 M $LiClO_4$ at pH 3–4 (adjust by 0.1 M $HClO_4$ solution). The bi-ionic PPy film PPy (DBS)/PPy (ClO_4) was also prepared in the corresponding aqueous media described above for comparison to the tri-layer composite film.

The movements of the bilayer or tri-layer composite films were investigated in a one-compartment cell by the use of 1 M $LiClO_4$ aqueous solution as the electrolyte. The working electrode was the polymeric film, counter electrode was a stainless steel (AISI 304) sheet and the potentials were referred to a saturated calomel electrode.

3. Results and discussion

The structure of a PPy (DBS)/PTh/PPy (ClO_4) tri-layer composite film and its bending movements during redox process in electrolyte solution are illustrated in Fig. 1. During reduction of the PPy (ClO_4^-) film, electrons are injected into the chains and positive charges in the polymer chains are compensated. In order to maintain overall charge neutrality, counterions are expelled towards the solution, and the film shrinks. In contrast, during oxidation of the film, the electrons are extracted from polymeric chains, positive charges are stored along the chains. In order to maintain the electron neutrality inside the film, counter anions and water molecules from the solution are incorporated into the film, and the film swells [9–11]. Otherwise, the PPy film doped with large anions (immobile counterions, e.g. DBS) showed an opposite electrochemomechanical behavior [12,13]. Thus, during reduction of the composite film, the film bends to the direction of the PPy film doped with small anions, and during oxidation, the film bends to the direction of the PPy doped with immobile large anions.

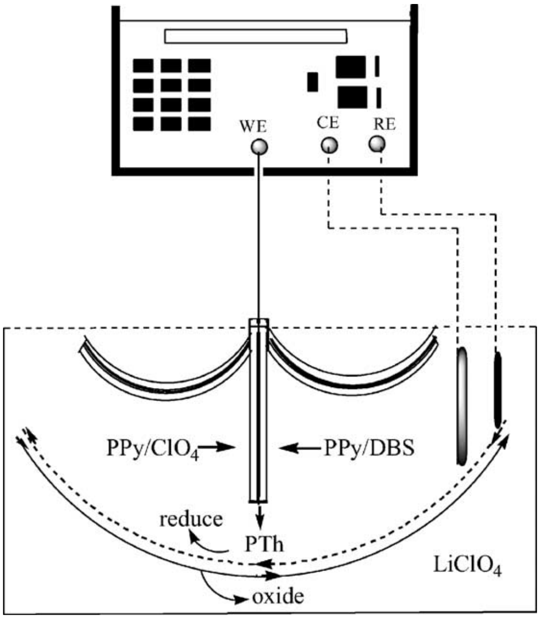

Fig. 1. Electrochemical equipment, electrical contact and the structure of the composite film of PPy (DBS)/PTh/PPy (ClO_4) and its movements during redox process.

The 632.8 nm excited Raman spectra of the cross-section of an as-formed PPy (DBS)/PTh/PPy (ClO_4) composite film is illustrated in Fig. 2. These spectra showed a weak 'fluorescence' background and high signal-to-noise (S/N) ratios, while the film was black in color. We set one edge of the cross-section of the composite film as the start point, and Raman spectra were recorded by focusing the laser spot (1 μm in diameter) at certain distances along the cross-section of composite film. In agreement with previous reports [14–16], the assignments of the Raman bands of PPy and PTh are listed in Table 1. Here, the intensity of the 1452 cm^{-1} band, which is attributed to C=C symmetric stretching, can be regarded as a measurement of PTh content, and that of the band at ca. 1586 cm^{-1} as a measurement of PPy content in the film. As shown in Fig. 2, the 1452 cm^{-1} band emerged in the spectra recorded at the points more than 8 μm from the edge of PPy (DBS) layer, while the 1586 cm^{-1} band decreased gradually and finally disappeared as the laser spot moved for 14 μm along the cross-section. The 1586 cm^{-1} band emerged again when the laser spot moved to the position of 32 μm, while 1452 cm^{-1} band became weaker and weaker gradually and finally disappeared as the laser spot move to the position of 38 μm. The spectroscopic phenomena described above imply that the composite film cannot be simply divided into two PPy parts and a PTh part. It has four composition zones: zone of pure PPy (DBS) (∼8 μm), an overlap zone of both PPy (DBS) and PTh (∼6 μm), a zone of pure PTh (∼17 μm),

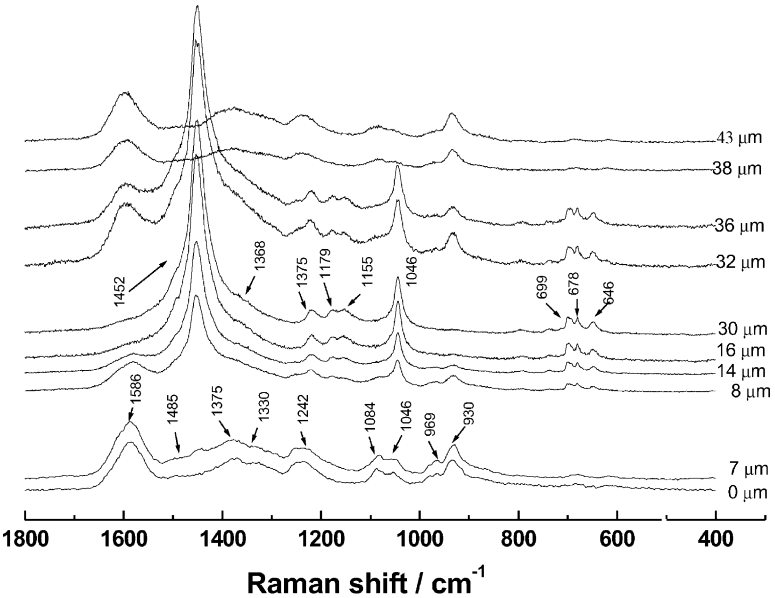

Fig. 2. Raman spectra of the cross-section of an as-grown tri-layer composite film of PPy (DBS)/PTh/PPy (ClO_4).

Table 1
The band assignments (cm^{-1}) of the Raman spectra of the tri-layer film of PPy (DBS)/PTh/PPy (ClO_4)

Assignment	PPy band (cm^{-1})	Assignment	PTh band (cm^{-1})
C=C ring stretching	1586	C=C ring stretching	1452
Skeletal band	1485	C–C inter-ring stretching	1368
C–N stretching	1375, 1330	C–C stretching	1217
C–H in-plane bending	1242	Kinks	1179
C–H in-plane bending associated with dication	1084	Kinks	1155
C–H in-plane bending associated radical cation	1046	C–H bending	1046
Ring deformation associated with radical cation	969	Ring deformation C–S–C	699
Ring deformation associated with dication	930	Kinks	678
		Kinks	646

another overlap zone of Pth and PPy (ClO_4) (~6 µm) and the zone of pure PPy (ClO_4) (~6 µm).

Fig. 3 shows the typical cyclic voltammograms (CV) of PPy (ClO_4), PPy (DBS), bi-ionic film of PPy (DBS)/PPy (ClO_4) and tri-layer composite film of PPy (DBS)/PTh/PPy (ClO_4). The films were electrochemically active, and each demonstrated a couple of oxidation and reduction waves. It can be seen clearly from this figure that the PPy (ClO_4) film showed a *p*-doping (oxidation) wave at ca. 0.17 V and a dedoping (reduction) wave at ca. −0.26 V (Fig. 3a). The potential difference between the oxidation and reduction current peaks (ΔE_p) is relatively small (~0.43 V), indicating the redox process is relatively reversible. On the other hand, the PPy (DBS) film showed an *n*-doping (reduction) wave at ca. −0.88 V and a dedoping (oxidation) wave at ca. +0.25 V (Fig. 3b). The ΔE_p of the process was as large as 1.13 V. However, the PPy (DBS)/PPy (ClO_4) bi-ionic film shows only a broad reduction wave at −0.48 V and an oxidation wave at +0.51 V (Fig. 3c). This is possibly due to the overlap of the redox waves and the increase of iR drops of the film because of the film thickness increase. The tri-layer composite film PPy (DBS)/PTh/PPy (ClO_4) (Fig. 3d) showed a

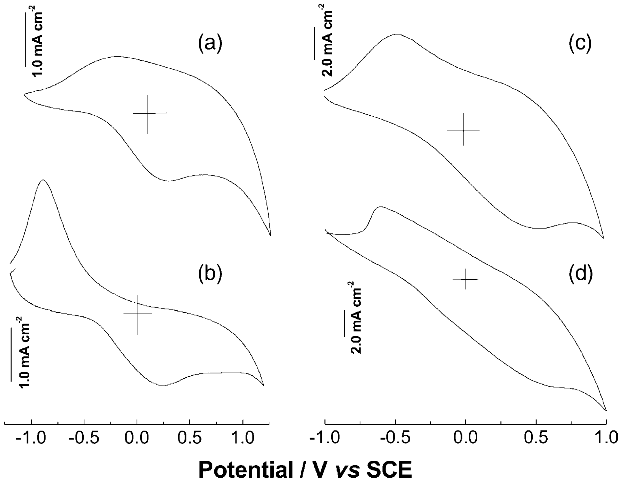

Fig. 3. Cyclic voltammograms of the PPy films, bi-ionic PPy film and tri-layer composite film in 1 M $LiClO_4$ electrolyte solution at a potential scan rate of 20 mV s^{-1}: (a) PPy (ClO_4), (b) PPy (DBS), (c) PPy (DBS)/PPy (ClO_4), (d) PPy (DBS)/PTh/PPy (ClO_4).

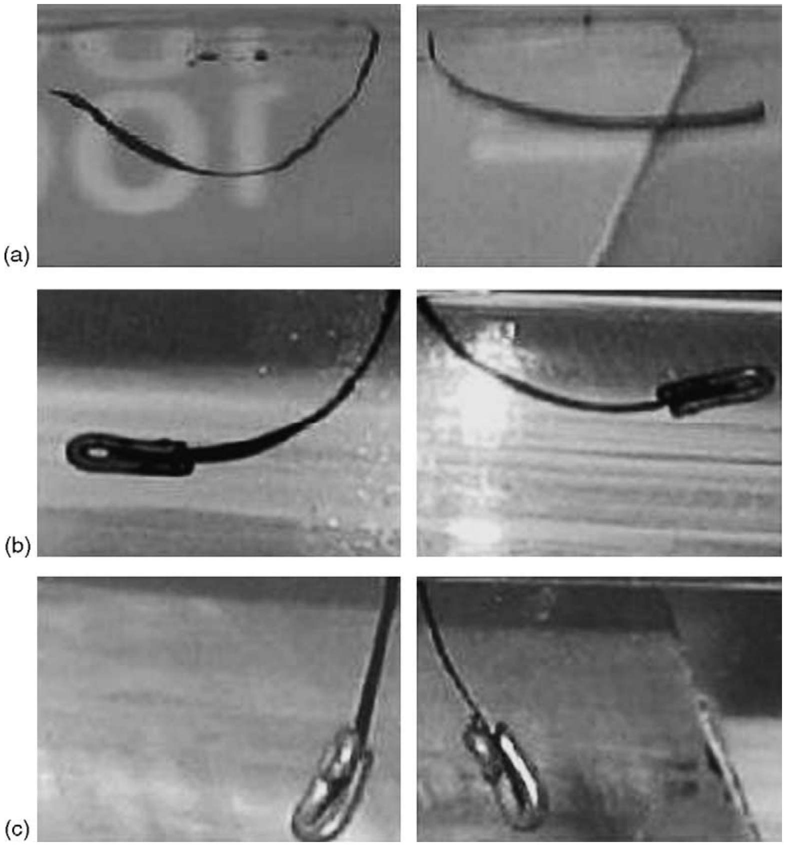

Fig. 4. Photographs of bending motion of PPy (DBS)/PTh/PPy (ClO_4) tri-layer actuator which is held as PPy (DBS) layer in right: (a) free state; (b) a 10 mg or (c) a 25 mg copper wire attached to the free end of the composite film; left photographs are at negative potentials and right photograph are at positive potentials.

similar CV diagram to that of the bi-ionic PPy film (Fig. 3c), implied the PTh layer nearly had no contribution to the redox reactions.

The bending motions of bi-ionic film PPy (DBS)/PPy (ClO_4) and tri-layer composite film PPy (DBS)/PTh/PPy (ClO_4) were investigated electrochemically in 1 M $LiClO_4$ aqueous solution. Both the bi-ionic PPy film and tri-layer composite films in free states exhibited a large bending motion at the potential of −0.7 or 0.7 V. In these cases, the free ends of the films traced over 180° in a single potential cycle as shown in Figs. 4a and 5a.

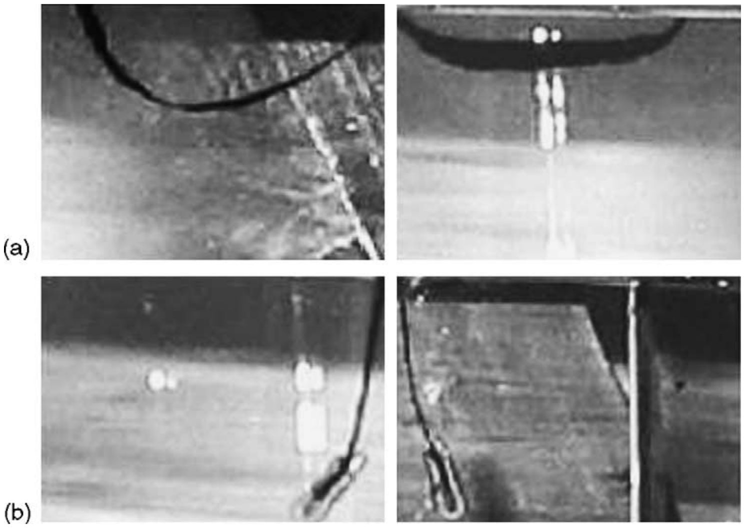

Fig. 5. Photograph of bending motion of PPy (DBS)/PPy (ClO_4) bi-ionic actuator which is held as PPy (DBS) layer in right: (a) free state; (b) a 10 mg copper wire attached to the free end of the bi-ionic film; left photographs are at negative potential and right photograph are at positive potential.

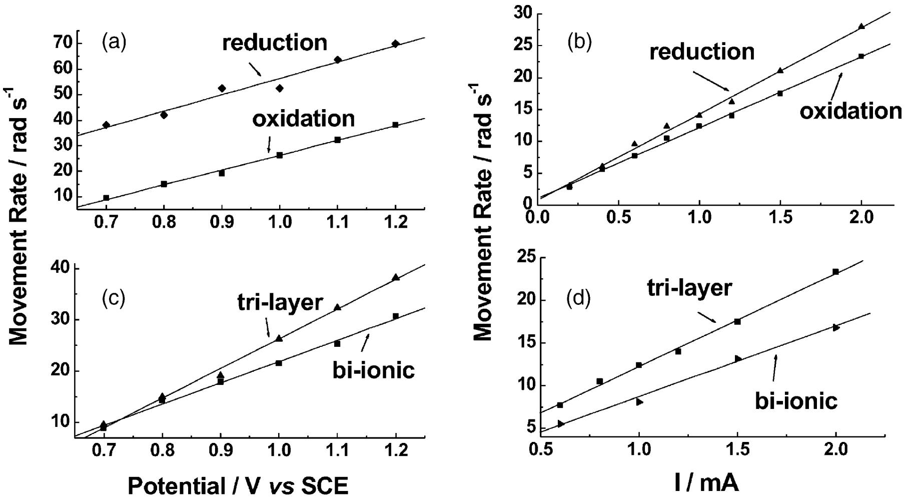

Fig. 6. The movement rates of the tri-layer composite film and bi-ionic polypyrrole film in free state measured in 1 M $LiClO_4$ aqueous solution at different galvanostatic condition. (a), (b) for tri-layer film and (c), (d) for tri-layer film and bi-ionic film during oxidation process. The potential and movement directions were ignored.

The loading capacity of bi-ionic PPy film and tri-layer composite film were also investigated in 1 M $LiClO_4$ aqueous solution (Figs. 4b, c and 5b). A tri-layer composite film of PPy (DBS)/PTh/PPy (ClO_4) with a weight of 0.4 mg, and a size of 10 mm × 1 mm × 0.04 mm can reversibly raise a 10 mg material (copper wire) from position of 0° (vertical position) to the position of ∼±90° (Fig. 4b), and raise a 25 mg material from position of 0° to the position of ∼±30° (Fig. 4c) when it was oxidized and reduced at potential 1.0 and −1.0 V, respectively. However, a bi-ionic PPy film with a weight of 0.4 mg, and a size of 10 mm × 1 mm × 0.05 mm cannot raise a 25 mg material. It can only reversibly raise a 10 mg material from the position of 0° to ∼±25° when the film was oxidized and reduced at potential 1.0 or −1.0 V (Fig. 5b), respectively. These results demonstrated that the PTh layer in the composite tri-layer film enhanced the strength of the composite film and the loading capacity of the composite film.

The movement properties of the tri-layer composite film either in free or in loading state and the bi-ionic film in free state were also investigated according to a previously reported method [17,18]. The angular movement of the free end of the film was referred to the vertical position as 0°. The movement rate (rad s^{-1}), the consumed electrical energy (mJ) and consumed electrical charge (mC) of actuation can be defined as follows:

$$\text{Movement rate} = \frac{\text{Angle}}{\text{Time}}$$

$$\text{Consumed electrical energy} = \int (IV)\,dt$$

$$\text{Consumed electrical charge} = \int I\,dt$$

From Fig. 6, we can see that the movement rates of the tri-layer film in free state increase linearly with the increase of applied potential during redox processes, and the movement rates during reduction process is higher than that during oxidation process (Fig. 6a and b). Furthermore, at a given driving potential or a driving current, the movement rates of tri-layer composite film in free state are higher than those of bi-ionic polypyrrole film (Fig. 6c and d). However, the consumed electrical charges to reach a constant angle (90°) remain constant for both the tri-layer film and bi-ionic film, independent of the value of driving current (Fig. 7).

The movement rate for the tri-layer composite film under loading increased linearly with the increase of driving potential or current, while decrease with the increase of loading weight as shown in Fig. 8. Furthermore, the energy consumed per degree angle increased with the increase of loading weight, and also increased linearly with the increase of driving potential and current as shown in Fig. 8c and d, respectively.

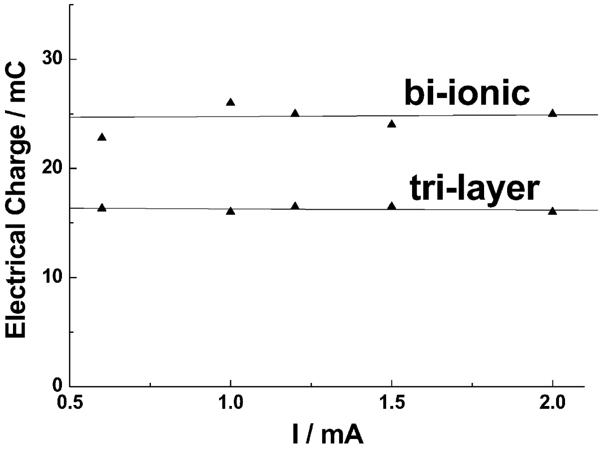

Fig. 7. Plots of the consumed charges vs. the applied electrical current for bi-ionic and tri-layer film during oxidation process.

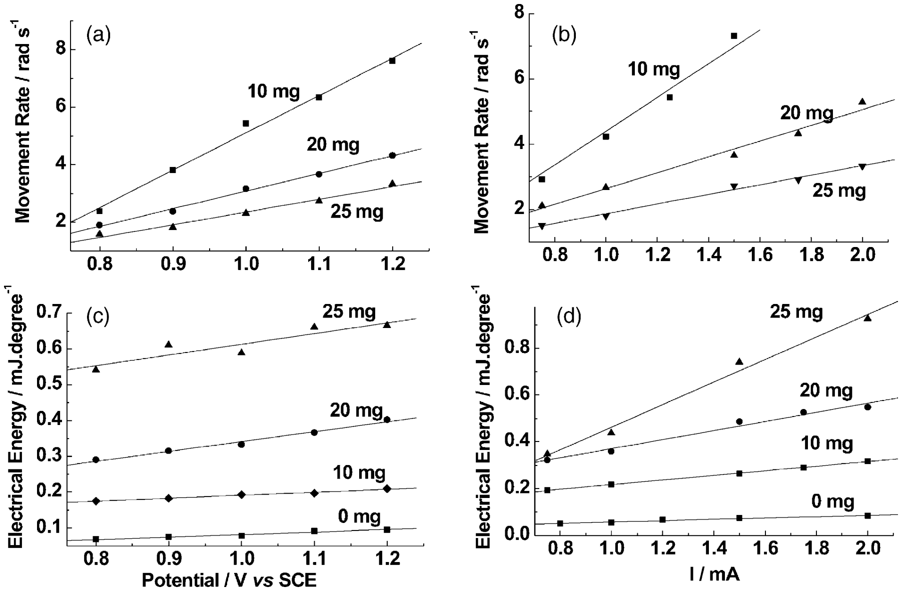

Fig. 8. Plots of the movement rates and consumed energy per degree of the tri-layer film with different loads to its free end vs. driving potential or current.

4. Conclusions

The tri-layer composite film of PPy (DBS)/PTh/PPy (ClO_4) and bi-ionic PPy film of PPy (DBS)/PPy (ClO_4) have been electrochemically synthesized by successive oxidation of pyrrole in aqueous solutions and thiophene in BFEE solution. The loading capacity of the tri-layer film was tested to be much higher than that of the bi-ionic film, mainly due to the polythiophene layer provided a strong mechanical support for the actuator and also enhanced its loading capacity. Furthermore, at a given driving condition, the movement rate of the tri-layer composite film is faster than that of the bi-ionic polypyrrole film. The energy consumed per degree for bending actuation increases linearly with the increase of loading weight, driving potential or current. The simple structure and easy electrosynthesis process of tri-layer composite conducting polymer film may be very promising for fabrication of the actuator with excellent high strength and loading capacity.

Acknowledgements

This work was supported by National Natural Science Foundation of China with grant numbers of 50225311, 20374034 and 50133010.

References

[1] E. Smela, Conjugated polymer actuators for biomedical applications, Adv. Mater. 15 (2003) 481–494.

[2] R.H. Baughman, Conducting polymer artificial muscles, Synth. Met. 78 (1996) 339–353.

[3] T.F. Otero, J.M. Sansinena, Soft and wet conducting polymers for artificial muscles, Adv. Mater. 10 (1998) 491–494.

[4] T.F. Otero, M.T. Cortes, Artificial muscle with tactile sensitivity, Adv. Mater. 15 (2003) 279–282.

[5] J.M. Sansinena, V. Olazabal, T.F. Otero, C.N. Polo da Fonseca, M.-A. de Paoli, A solid state artificial muscle based on polypyrrole and a solid polymeric electrolyte working in air, Chem. Commun. 22 (1997) 2217–2218.

[6] W. Takashima, S.S. Pandey, K. Kaneto, Bi-ionic actuator by polypyrrole films, Synth. Met. 135/136 (2003) 61–62.

[7] W. Takashima, S.S. Pandey, K. Kaneto, Investigation of bi-ionic contribution for the enhancement of bending actuation in polypyrrole film, Sens. Actuators, B. 89 (2003) 48–52.

[8] G.Q. Shi, S. Jin, G. Xue, C. Li, A conducting polymer film stronger than aluminum, Science 267 (1995) 994–996.

[9] T.F. Otero, H. Grande, J. Rodriguez, Reinterpretation of polypyrrole electrochemistry after consideration of conformational relaxation processes, J. Phys. Chem. B 101 (1997) 3688–3697.

[10] T.F. Otero, H. Grande, J. Rodriguez, A new model for electrochemical oxidation of polypyrrole under conformational relaxation control, J. Electroanal. Chem. 394 (1995) 211–216.

[11] H. Grande, T.F. Otero, Intrinsic asymmetry, hysteresis, and conformational relaxation during redox switching in polypyrrole: a coulovoltametric study, J. Phys. Chem. B 102 (1998) 7535–7540.

[12] M.R. Gandhi, P. Murray, G.M. Spinks, G.G. Wallace, Mechanism of electromechanical actuation in polypyrrole, Synth. Met. 73 (1995) 247–256.

[13] J.M. Davey, S.F. Ralph, C.O. Too, G.G. Wallace, Synthesis characterization and ion transport studies on polypyrrole/polyvinylphosphate conducting polymer materials, Synth. Met. 99 (1999) 191–199.

[14] M.X. Fu, F.E. Chen, J.X. Zhang, G.Q. Shi, Electrochemical fabrication of aligned microtubular heterojunctions of poly(p-phenylene) and polythiophene, J. Mater. Chem. 12 (2002) 2331–2333.

[15] G.Q. Shi, J.K. Xu, M.X. Fu, Raman spectroscopic and electrochemical studies on doping level changes of polythiophenes during electrochemical polymerization process, J. Phys. Chem. B. 106 (2002) 288–292.

[16] F.E. Chen, G.Q. Shi, M.X. Fu, L.T. Qu, X.Y. Hong, Raman spectroscopic evidence of thickness dependence of the doping level of electrochemically deposited polypyrrole film, Synth. Met. 132 (2003) 125–132.

[17] T.F. Otero, J.M. Sansinena, Bilayer dimensions and movement in artificial muscles, Bioelectrochem. Bioenerg. 42 (1997) 117–122.

[18] T.F. Otero, J.M. Sansinena, Artificial muscles based on conducting polymers, Bioelectrochem. Bioenerg. 38 (1995) 411–414.