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PEDOT and PPy conducting polymer bilayer and trilayer actuators

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ABSTRACT

Actuators based on conducting polymers are attracting increasing interest due to their desirable features such as large mechanical stress generated, sufficient maximum strain values, high reversibility, good safety properties and the possibility of precise control using small voltages. Many attempts have been made to improve the actuator performance. We report electromechanical measurements on actuators of bilayer and trilayer free standing films prepared with polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) conducting polymers. Both types of conducting polymer are pre-doped during synthesis with dodecyl benzenesulfonate (DBS). These multilayer films were prepared electrochemically so that the PEDOT layer is very thin compared to that of the PPy layer. In the trilayer film, the PEDOT layer is sandwiched between two PPy layers.

The films were characterized electromechanically and the results compared with those of PPy single layer film. Bilayer films show a significant increase in the strain measured at higher scan rates (>100 mV s^{-1}). The force difference generated between the reduced and oxidized states is much higher for trilayer films and higher for bilayer films than that in a single layer of PPy. Trilayer films are both stronger and faster than a single layer PPy film of half the thickness.

1. Introduction

The oxidation and reduction of conducting polymers are associated with volumetric changes [1]. The volume changes of conducting polymers are induced by charge compensating ions and solvent molecules flowing in and out of the polymer during the reduction and oxidation processes [2,3]. This electro–chemo-mechanical property can be used to produce micro- and macroactuators [4–6]. Actuators based on conducting polymers remain a very actively pursued research goal due to their desirable features such as large mechanical stress generated, possible large maximum strain values [7], high reversibility and safety (low voltages).

Polypyrrole (PPy) is a prime candidate for a conducting polymer actuator, but has the disadvantage that the electronic conductivity decreases by two or three orders of magnitude as the polymer is reduced. This causes a decrease in performance; since only a small part of the polymer film will then be actively contributing to the actuation [8]. This is one of the reasons for the difficulty in reaching high actuation speeds, which is a main limitation of performance [9]. A standard solution to this problem involves the addition of an extra electron conductor, e.g. Au, Pt or W as thin patterns, corrugated thin layers or helices [10–12].

This introduces the potential problems of delamination and contact resistance, since the interfacial and other mechanical properties of metals differ strongly from those of conducting polymers. If the actuators are to be used in an application requiring many cycles (PPy actuators have reached up to a million cycles [13]), this represents a very tough challenge. Several sophisticated attempts have been made to solve the problem by chemical or physical means [14,15].

The present work is an attempt to solve the conductivity problem of PPy by using a second, more highly conducting polymer, instead of a metal, to enhance the electronic conductivity. The material chosen for this purpose is poly(3,4-ethylene dioxythiophene), PEDOT, which can achieve a very high conductivity [16]. The cyclic voltammograms as well as the UV–vis spectra of PEDOT and PPy are very different, pointing towards the possibility of being able to separate the two polymer contributions experimentally, even when combined in a single film of different layers.

In our previous work, several important conclusions were reached: It is possible to make a bilayer film of PPy and PEDOT that does not delaminate, the two polymers are compatible and both polymers are active in the redox process as ions are able to move through the PEDOT layer and penetrate into PPy and vice versa [17]. Building on these results, we report here electromechanical measurements on actuators of bilayer and trilayer free standing films

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prepared with PPy and PEDOT conducting polymers. These multi layer films were prepared so that the PEDOT layer is very thin compared to the PPy layer, in order to retain the advantageous actuator properties of PPy. Both polymers were doped electrochemically with dodecyl benzenesulfonate (DBS) anions to have a homogeneous dopant level in the film. It has proven difficult to measure a reliable figure for the conductivity of pure PEDOT(DBS) film, but it is probably lower than that obtained with smaller anions [16]. The use of DBS as an immobile anion means that the primary mechanism of expansion during reduction is the insertion of Na^+ ions and H_2O molecules. Different thickness combinations were tested, and were compared with those of pure PEDOT and PPy films.

2. Experimental

PPy(DBS) or PEDOT(DBS) films were electrodeposited galvanostatically from an aqueous solution containing 0.05 M SDBS and either 0.05 M pyrrole or 0.02 M EDOT. Cyclic voltammetry was performed on ca. 1 μm films deposited on a 0.5 mm diameter Pt wire. Free-standing actuator films were formed on the surface of a polished stainless steel electrode using an oxidation current density of $1\ \mathrm{mA\,cm^{-2}}$. Bilayer PEDOT(DBS)/PPy(DBS) composite films were obtained by electropolymerization of PEDOT on the pre-prepared PPy films. Similarly trilayer PPY(DBS)/PEDOT(DBS)/PPy(DBS) composite films were obtained by electropolymerization of PPy on the pre-prepared PEDOT/PPy films. The as-prepared films are peeled off from the steel electrode and dried in air for 1 day prior to the measurements. The thickness of the PPy(DBS) films is controlled by the charge passed during the polymerization and the charge of $1.6\ \mathrm{C\,cm^{-2}}$ corresponds to a film thickness of 10 μm [18]. The thickness of PEDOT(DBS) layers are difficult to estimate, but a charge of $0.32\ \mathrm{C\,cm^{-2}}$ was used, which would correspond to a 2 μm film using the same relation as for PPy(DBS). Thicker PEDOT(DBS) layers relative to PPy(DBS) resulted in poorer actuator performance.

A force–displacement setup described elsewhere is used to measure the mechanical properties and the length change when actuator film is oxidized and reduced electrochemically [19]. Typical dimensions of the exposed, active part of the strips were 5 mm (length) × 3 mm (width). The film was immersed in cycling electrolyte (unless otherwise stated 0.1 M NaCl aqueous solution was used) which is continuously bubbled with nitrogen gas to lower the amount of dissolved oxygen. The potential was measured against an Ag/AgCl reference electrode. In all cases, a final actuator device will require sealing the system against oxygen, and also against moisture if non-aqueous electrolyte is to be used.

3. Results and discussion

The redox behaviours of single, bilayer and trilayer films were examined using cycling voltammetry, and the results are shown in Fig. 1. CVs obtained for bilayer films are very similar to that of a single PPy film. PPy seems to play a dominant role for the bilayer system current, and this also indicates that PEDOT does not diminish the PPy response, with the sharp reduction peak at −0.55 V being a diagnostic PPy(DBS) feature. However, PEDOT does influence the CV, especially at lower potentials (<−0.7 V). This is more clearly observed with bilayers having a relatively thinner layer of PPy (not shown). This shows that both PEDOT and PPy take part in the redox process. In trilayer films, PPy(DBS)/PEDOT(DBS)/PPy(DBS), the reduction of PPy seems to take place at two different potentials with two well separated peaks. The middle PEDOT layer is responsible for this separation. During reduction of the trilayer film, at first the outer PPy layer, exposed to the electrolyte, is reduced within the typical narrow potential range centered at around −0.55 V and then the reduction of the inner PPy layer occurs later at around −0.95 V, and over a wider range of potentials. The larger width of the peak may be caused by diffusion broadening after the ions have penetrated the PEDOT(DBS) layer. All three layers are thus redox active, and current response from the two different PPy(DBS) layers (inner and outer) can be clearly separated and identified by this method.

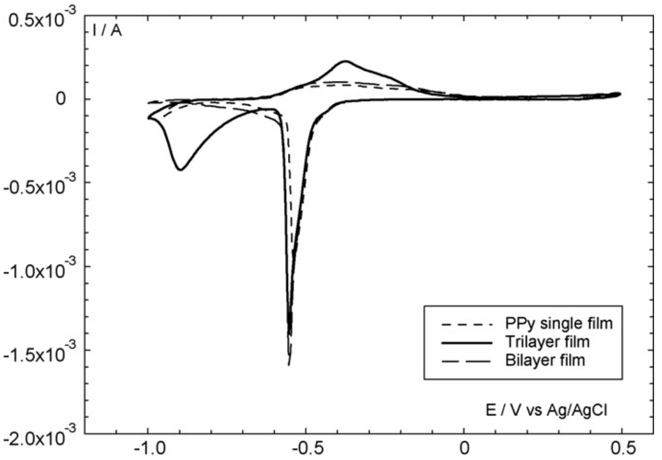

Fig. 1. Cyclic voltammograms (between −1.0 and +0.5 V) of 1 μm PPy(DBS), a PEDOT(DBS)/PPy(DBS) 1 μm/0.2 μm bilayer and a PPy(DBS/PEDOT(DBS)/PPy(DBS) 1 μm/0.2 μm/1 μm trilayer film on Pt in 2 M NaCl electrolyte. Scan rate $10\ \mathrm{mV\,s^{-1}}$. The single and bilayer traces are almost identical.

Conversely, the oxidation in the trilayer film occurs centered at one potential only (−0.38 V) for both PPy layers. The peak current is about twice that for a single layer, as expected if the two PPy(DBS) layers are oxidized at the same potential.

The linear expansion and contraction of trilayer and bilayer films during the electrochemical cycling was systematically investigated using the force–displacement setup, and compared with that of pure PPy films. Fig. 2(a) shows the length change of the stabilized trilayer film as response to linear cycling at three different, slow scan rates. The trilayer consisted of a total of 20 μm PPy(DBS) (each PPy layer is 10 μm) and a middle PEDOT layer (∼2 μm). The active, actuating dimension of the strip was 3 mm × 5 mm. The actuator was kept under a constant load corresponding to 1.5 g during the entire measurement, and was cycled within the potential range +0.4 to −1.0 V against Ag/AgCl in aqueous 0.1 M NaCl solution. The first two cycles shown have a period of 300 s ($10\ \mathrm{mV\,s^{-1}}$), subsequently changed to 1500 s ($2\ \mathrm{mV\,s^{-1}}$), and finally to 600 s ($5\ \mathrm{mV\,s^{-1}}$). The largest strain (3%) was achieved during the slowest scan rate.

Fig. 2(b) shows the actuator strain at different scan rates. The data indicate a significant decrease in the strain with increasing scan rate, as expected because limitations caused by both ionic diffusion and by drift in an electric field occur [20–22]. The most important conclusion is the fact that the presence of the PEDOT layer and the more complicated assembly of the trilayer do not influence the strain response in any negative way. The bilayer film even shows a slight improvement in the strain response compared to that of pure PPy film at faster scan rates. Of notice is the encouraging fact that the trilayer film is not inferior to the single PPy layer even though it has more than double the thickness.

A alternative method of achieving actuation at higher frequencies is to keep the length of the actuator constant, and then utilizing the change in force generation under tension caused by faster processes, perhaps changes in Young's modulus and in the electronic configuration of the backbone. This method has been shown to extend the useable frequency range significantly, and the possible explanations are described in Refs. [23–25]. Fig. 3(a) shows the