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A Cyclic Voltammetry Study on Bi Layer and Multi Layer Conducting Polymer Films

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Abstract: Polypyrrole (PPY) is a prime candidate for a polymer actuator; but has the disadvantage that the electronic conductivity decreases by two or three orders of magnitude as the polymer is reduced. This reduces the actuator performance. A Standard way of overcoming this problem is to add Au or Pt layers as thin patterns or as helices on the polymer. The present work is an attempt to use a second more highly conducting polymer, poly(3,4-ethylenedioxythiophene), (PEDOT), to enhance the electronic conductivity.

Bilayer and multilayers with PEDOT and PPY, each containing dodecyl benzenesulfonate (DBS) as immobile dopant species were synthesized and their electrochemical behaviour was investigated using cyclic voltammetry, optical absorption spectroscopy and electrochemical quartz crystal microbalance (EQCM) techniques. Bilayer results show combined characteristics of each individual polymer. In trilayer films, the reduction of inner and outer PPY layers takes place at two different potentials. The oxidation occurs at one potential only. The pentalayer film confirmed this: three reduction peaks were observed. The separation between the two reduction peaks depends on the thickness of PEDOT layer, the scan rate and the concentration of cycling electrolyte. This separation becomes smaller with the number of cycling, indicating the enhancement of ion diffusion through the PEDOT layer. The optical spectra of the trilayers show clearly distinguishable peaks belonging to PEDOT and PPY polymers, confirming the independent behaviour of the PEDOT in the system. Two important conclusions of relevance for actuator performance were reached: it is possible to make bilayer and multilayer films that do not delaminate –

the two polymers are compatible; and both polymers are active in the redox process. Ionic diffusion in the trilayer which is responsible for the actuation can be controlled by choosing appropriate thicknesses for the three layers.

Keywords: Polypyrrole, PEDOT, actuators, EQCM, cyclicvoltammetry

Introduction

In recent years, poly(3,4-ethylenedioxythiophene) (PEDOT) has emerged as one of the most important materials in the field of conducting polymers. PEDOT is highly insoluble in almost every solvent, exhibits quite a high conductivity, changes in colour depending on the applied potential, is practically transparent in the form of thin oxidized film, is very stable in the doped state and exhibits a low reduced band gap (ca. 1.6-1.7 eV) [1]. All these properties make this conducting polymer useful for many applications. On the other hand, polypyrrole (PPy) has been used as a prime candidate in the field of polymer actuators since it shows great volume changes during the redox cycling. But PPy 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 actuator performance; since only a small part of the polypyrrole film will then be actively contributing to the actuation [2]. A standard solution to this problem involves the addition of an extra electron conductor on the surface of the polypyrrole film, e.g. Au or Pt as helices or as thin patterns [3,4]. The use of a corrugated gold layer on PPy improved the performance of the actuator [5].

The present work is an attempt to solve the conductivity problem by using a second, more highly conducting polymer, PEDOT to enhance the electronic conductivity. Generally, mechanical properties of conducting polymers such as length and stiffness vary as ions from a cycling electrolyte moves in and out of the polymer during cycling. An exact knowledge of the nature and amount of ionic motion is therefore crucial to understanding and controlling the actuation process of these combined actuator system. In this paper, we report the preliminary characterization of the bilayer and multilayer systems having two conducting polymers of PEDOT and PPy using cyclic voltammetry, electrochemical quartz crystal microbalance (EQCM). Both polymers are doped electrochemically with dodecyl benzenesulfonate (DBS) anions to have homogeneous dopants in the film. Different thickness combinations in bilayer and trilayer configurations were tested, and were compared with those of pure PEDOT and PPy films.

Experimental

Pyrrole (Aldrich 98%) monomer was distilled under nitrogen and stored in a freezer in sealed vials prior to use. EDOT monomer (Aldrich 98%) was used without any further purification. Other chemicals, sodium dodecyl benzenesulfonate (NaDBS) (Aldrich) and NaCl (Merck) were used as received. Both PEDOT(DBS) and PPy(DBS) layers were formed by galvanostatic electropolymerization with a current density of 1 mA cm^{-2} . Bilayer PEDOT/PPy films were obtained by electropolymerization of PEDOT on the pre-prepared PPy films. Similarly tri-layer PPy/PEDOT/PPy films were obtained by electropolymerization of PPy on the pre-prepared PPy/PEDOT films. After synthesis, each layer was rinsed thoroughly in distilled water before the preparation of the next layer. 0.05M SDBS aqueous electrolyte containing 0.05 M pyrrole or 0.02 M EDOT was used for the synthesis of PPy(DBS) and PEDOT(DBS) layers respectively. For the cyclic voltammetric experiments films were prepared on Pt wire (10-mm length, 0.5 mm diameter). Nickel foil and Ag/AgCl in 3 M KCl were used as counter and reference electrodes respectively. The cycling

electrolyte (NaCl) was purged with nitrogen gas to reduce the oxygen concentration.

An Electrochemical Quartz Crystal Microbalance setup using 1 cm, 10 MHz crystals with 0.2 cm^2 gold electrodes controlled by a Hewlett-Packard E4916A crystal analyzer in combination with a potentiostat (Autolab PGSTAT 30) was used to measure the change of mass during polymerization and cycling.

Results and Discussion

Cyclic voltammograms (CVs) of PEDOT(DBS) and PPy(DBS) are different in shape and size as shown in figure 1 (note that the current scales are very different). The CV of the pure PPy(DBS) film exhibits strong and well defined reduction and oxidation peaks. In the PPy film, the reduction takes place in a narrow potential while the oxidation occurs over a range of potentials. On the other hand, the PEDOT(DBS) has a capacity-like current and the redox peaks are barely distinguishable. Furthermore, the capacitance which is proportional to the area covered by the CV is much smaller in PEDOT compared to that in PPy. This is not surprising since it is well known that a PPy film is much compact than a PEDOT film. It has been reported that PEDOT forms a highly porous structure in aqueous solution and therefore electrochemical redox reactions are fast in this material [6].

As shown in figure 2, when these two polymers are combined as a bilayer system, CVs are mostly similar to that of a single PPy film without much changes in the main features of the CV. This reveals that PPy seems to play a dominant role in the bilayer system, and this also indicates that PEDOT does not diminish the PPy response. However, PEDOT does influence the CV, especially at lower potentials ($< 0.7 \text{ V}$). This is more clearly observed with bilayers having a thinner layer of PPy. This shows that both PEDOT and PPy take part in the redox process. EQCM results obtained for the PEDOT/PPy bilayer (outer layer is PPy) are shown in fig. 3.

In this experiment, the total thickness of the bilayer is less than $1 \mu\text{m}$. For comparison, the results obtained for single PEDOT(DBS) and PPy(DBS) layers

are plotted in the same figure. Results (Fig. 3) show that the electrode mass change is small in the single PEDOT(DBS) film compared to that results obtained for the PEDOT/PPy bilayer (outer layer is PPy) are shown in fig. 3. In this experiment, the total thickness of the bilayer is less than 1 μm . For comparison, the results obtained for single PEDOT(DBS) and PPy(DBS) layers are plotted in the same figure. Results (Fig. 3) show that the electrode mass change is small in the single PEDOT(DBS) film compared to that of the PPy(DBS) during both the cathodic and anodic parts of the cycle and this may be due to the fact that

the PEDOT(DBS) may have less tendency to accommodate both ions and solvent. However, the sum of the frequency changes of the pure films is almost equal to the frequency change observed for the bilayer film during reductive/oxidative cycling. This indicates the active participation of the inner PEDOT layer in the redox process of the bilayer film. This is in good agreement with results reported by Y. Syritski *et al.* [7]. They claimed that the bilayer structure is redox active and that PEDOT influences redox processes even after complete coverage with PPy suggesting the formation of a three dimensional electrode.

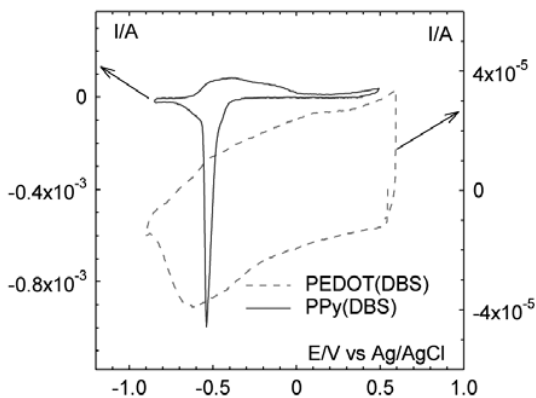


Fig. 1: Cyclic voltammograms of PPy(DBS) and PEDOT(DBS) films in 2 M NaCl electrolyte. Scan rate 10 mV s⁻¹. Current scales are different.

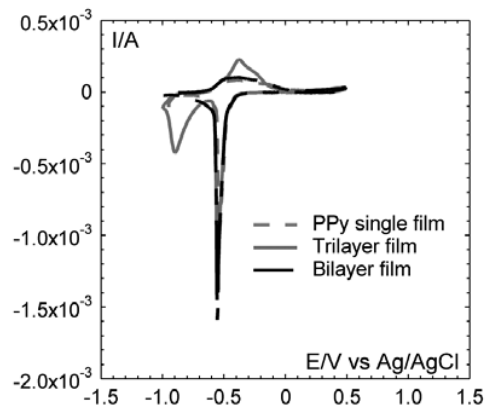


Fig. 2: Cyclic voltammograms of PPy, bilayer and trilayer films in 2 M NaCl electrolyte. Scan rate 10 mV s⁻¹.

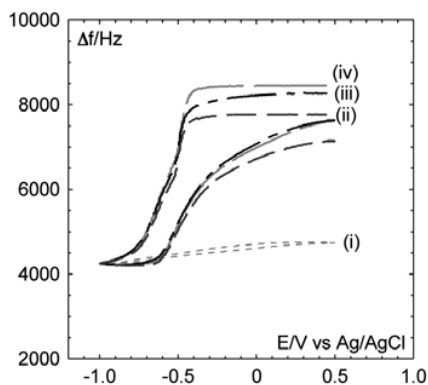


Fig. 3 mass change plots of (i) a PEDOT(DBS) film, (ii) a PPy(DBS) film and (iv) a PEDOT/PPy bilayer (outer layer is PPy) in 1 M NaCl aqueous solution. Scan rate 10 mV s⁻¹. Sum of the (i) and (ii) are indicated by (iii).

In trilayer films, PPy/PEDOT/PPy, the reduction of PPy seems to take place at two different potentials (Fig. 2) with two well separated peaks. The middle PEDOT layer is responsible for this separation. This was confirmed by keeping the PEDOT thickness same and changing the thicknesses of outer and inner layers of PPy. During reduction of the trilayer film, at first the outer PPy layer, exposed to the electrolyte, is reduced within a narrow potential range centered at around -0.55 V and then the reduction of the inner PPy layer occurs at around -0.95 V over a wider range of potentials. The pentalayer film reconfirmed this phenomenon where three reduction peaks corresponding to the three PPy layers were observed. The separation of reduction peaks is due to the partially blocking behaviour of the middle layer of PEDOT. On the other hand, in the trilayer film oxidation occurs at one potential (-0.38 V) only for both PPy layers with a peak current twice of that expected for a single layer. The observed peak current confirms further the coincidence of the two oxidation peaks at one potential. Furthermore, for a trilayer film with fixed inner and outer PPy layer thicknesses, the separation between the two reduction peaks depends on the thickness of PEDOT layer; the separation increasing as the thickness of PEDOT is increased as shown in Table 1. Evidently, the first reduction peak potential which corresponds to the outer PPy layer is independent of the PEDOT thicknesses and only the second peak position seems to shift to more negative potential as the thickness of PEDOT increases giving rise to the peak separation. Thus the blocking effect of the PEDOT film becomes larger as the thickness of the film increases. From Table 1, it can be concluded that the trilayer system with a thin PEDOT at the middle is preferable for use in actuators since there will be less interference from the PEDOT on the ionic motion. Moreover, interestingly the reduction peak of the inner PPy layer becomes a little broader with increasing thickness of PEDOT while that of the outer layer remains same. This shows slower kinetics taking place in the inner PPy layer due to the presence of PEDOT layer. However, after a number of consecutive cycles at a particular scan rate, the separation between the two reduction peaks becomes smaller and smaller and finally vanishes. This indicates the enhancement of ion

diffusion through the PEDOT layer with the number of cycles. Furthermore, it was found that the peak separation also depends on the scan rates and on the concentration of cycling electrolyte. The scan rate effect again suggests a kinetic explanation, whereas the concentration effect is more difficult to understand. At slower scan rates and lower concentrations of the electrolyte the separation becomes negligibly small, increasing with either increasing scan rates or increasing concentration as shown in Tables 2 and 3.

The CV and EQCM result obtained for a trilayer film are shown in figure 4. Corresponding results for a single PPy layer are also shown in the same figure for comparison. The reduction peak separation in the trilayer film is very small due to the thin nature of the PEDOT film used. Each frequency curve shows a steep drop exactly centered at the potential of the corresponding reduction peak maximum. Accordingly, there are two such steep drops seen clearly on the frequency curve observed for the trilayer film corresponding to the two peak maxima. This again confirms that reductions are taking place at two different potentials in the trilayer films. The total frequency changes during the cathodic and anodic processes are little higher in the trilayer film than those of the single PPy layer indicating some contribution of the PEDOT to the mass change of the trilayer system. In other words, the PEDOT layer is also active in the redox process and does not weaken the PPy response.

Conclusions

We have succeeded in making bilayer and multilayer films that do not delaminate with PEDOT and PPy conducting polymers by electrochemical technique. In multilayer configuration, it is found that the PEDOT polymer does not affect the PPy performance and thus these two polymers are compatible for use in actuator applications. In redox processes, both polymers of the multilayers are found to be active, however the thicker layer plays the dominant role. Ionic diffusion in the trilayer which is responsible for the actuation can be controlled by choosing appropriate thicknesses for the three layers.

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Table 1:
Different thickness of middle layer PEDOT

PEDOT thickness. (μm)	Peak separation (V)	Half width of the 1st reduction peak (V)	Half width of the 2nd reduction peak (V)
0.1	0.07	0.4	0.049
0.25	0.11	0.4	0.065
0.5	0.21	0.4	0.115
1.0	0.31	0.4	0.16
2.0	0.32	0.4	0.22

Table 2:
Different scan rate

Scan rate mV/s	peak separation (V)
1	0.050
2	0.067
5	0.187
10	0.305

Table 3:
Different concentration of cycling

Concentration of NaCl (M)	peak separation (V)
0.05	0.140
0.1	0.140
0.5	0.190
1.0	0.190
2.0	0.344
3.0	0.409
4.0	0.623