BILAYERS AND MULTILAYERS OF POLYPYRROLE AND POLY(3,4-ETHYLENEDIOXYTHIOPHENE) FOR CONDUCTING POLYMER ACTUATORS

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BILAYERS AND MULTILAYERS OF POLYPYRROLE AND POLY(3,4-ETHYLENEDIOXYTHIOPHENE) FOR CONDUCTING POLYMER ACTUATORS

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Polypyrrole (PPy) is a prime candidate for conducting polymer based actuators, 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 the actuator performance. Thus, there is a need to improve the conductivity of PPy in its reduced state. The present work aims to improve the actuator performance of PPy by using a second, more highly conducting polymer poly(3,4-ethylenedioxythiophene), (PEDOT), as two-component conductive polymeric systems (bilayer and trilayer). In this regard, understanding the electrochemical behaviour of individual PPy and PEDOT films, and multilayer films is essential to use these films as a combined system. Systematic studies on the preparation and characterization of PEDOT single layer and PEDOT/PPy multilayer films are reported in this thesis.

PEDOT doped with dodecyl benzene sulfonate (DBS) films were prepared electrochemically with constant currents and characterized using cyclic voltammetry, electrochemical quartz crystal microbalance (EQCM) and optical absorption spectroscopy techniques. Films were prepared at different current densities to choose a suitable preparation current to produce films with optimum properties. With suitable films, influence of ions present in the electrolyte and its concentration on redox process of PEDOT/DBS films were investigated systematically. The investigations show that large DBS^- anions are immobile and stay in the polymer matrix during redox cycling and cation movement dominates the charge compensation process. The redox behaviour is found to depend on the type of ions (both cations and anions) present in the electrolyte and the concentration of the electrolyte.

The cyclic voltammetric studies on PEDOT/DBS films show that the main oxidation and reduction peaks assigned to the cation movement shifts gradually towards more negative potentials with the increasing size of the cations. The influence of different anions is more clearly seen in the EQCM responses rather than in cyclic voltammograms. It is found that ions like SO_4^{2-} has a greater difficulty to enter the polymer matrix, whereas the Cl^- and Br^- ions seem to move in and out of the film easily. The EQCM results also reveal that anion transport becomes more prominent with increasing concentration of the cycling electrolyte in the ionic exchange process. The EQCM responses also show indication of water movement taking place during the redox process, but in a smaller scale compared to water movement occurring in PPy/DBS films under similar conditions.

The UV-visible absorption spectral studies have shown that the band gap for a typical PEDOT/DBS film is 2.1 eV. In the oxidized state, absorption spectrum has a peak centred at 1.3 eV, which can be assigned to the bipolaron electronic transition.

Bilayer and trilayer films were prepared electrochemically with PPy and PEDOT conducting polymers, both doped with DBS^- anions. In trilayer films, the PEDOT layer is sandwiched between the PPy layers. These multilayer films were characterized using the same techniques used for single layer films. The voltammetric and EQCM results obtained for bilayer films show combined characteristics of individual polymer. Thus, both PPy and PEDOT polymers are active in the redox process in the bilayer films. The redox behaviour is highly dependent on the thickness of each layer. In trilayer films, the reductions of inner and outer PPy layers take place at two different potentials. The results on a pentalayer film confirmed this with the occurrence of three such reduction peaks. The main oxidation peaks in trilayer films appeare to occur at one potential only. It is also found that the separation between the two reduction peaks depends on the thickness of the middle PEDOT layer, the scan rate and the concentration of cycling electrolyte. The reduction peak separation becomes smaller and smaller and finally vanishes on repeated cycling. This indicates a gradual enhancement of ion diffusion through the middle PEDOT layer. The optical absorption spectra obtained for multilayer films at different redox potentials show clearly distinguishable peaks belonging to

PEDOT and PPy polymers, confirming the independent behaviour of the PEDOT layer in multilayer films.

Electro-chemo-mechanical behaviour of multilayer films was investigated using the force displacement setup. The actuator strain has been found to be large for bilayer and trilayer films compared to that of single PPy layer at faster scan rates. Creep in multilayer and single layer films is found to be rather high during the first few cycles and it gradually disappears after nearly 50 continuous cycles. This indicates that around nearly 50 initial cycles is necessary in cases where actuator operation is required with minimum creep. The force differences between oxidized and reduced states in single and multilayer films are found to vary with scan rates. When the scan rate is increased from 0.01 to 10 V s^{-1} force difference increases until it reaches maximum value at about 1.75 V s^{-1} and then the force difference decreases for higher scan rates. Larger force difference is obtained for trilayer and bilayer films compared to that observed in a PPy single layer. This shows that there is a significant improvement in the force generation when a thin PEDOT layer is added to PPy layers so as to form multilayer films.

Young's moduli of bilayer, trilayer and single layer actuator films are found to depend on the films' redox states. For single and multilayer films, the Young's moduli are found to drop nearly to one fifth of the values in the oxidized state, when the films are reduced.

The main conclusion from these studies can be summarized as follows: The multilayer actuators fabricated with PEDOT and PPy conducting polymers function qualitatively like a single PPy/DBS layer actuator. No negative effects or delamination has been observed. Hence the performance of PPy based actuators can be improved significantly by incorporating a thin layer of PEDOT/DBS. This points the way towards the use of such multilayer film assemblies for fabricating polypyrrole based actuators with better performance.