

A Study on Electrochemical Behavior of Polypyrrole Films In Differently Concentrated NaCl Electrolytes

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Abstract

Polypyrrole films doped with large surfactant anion dodecyl benzene sulfonate, PPy (DBS), have been electro polymerized in galvanostatic condition and characterized in highly concentrated NaCl aqueous solution (5 M) using Cyclic voltammetry, electrochemical microbalance (EQCM) and UV-visible absorption spectroscopy. In order to compare (property) similar experiments were carried out in 0.1 M NaCl (aq) electrolyte, as well. The EQCM studies show that the mass change occurring in the film during the first cycle, in 0.1 M electrolyte, is comparatively higher than that is observed in the 5 M electrolyte. This is because of many water molecules go in and out of the polymer accompanying the counter ions, when PPy(DBS) film cycled in dilute electrolytes, due to osmotic effect. On the other hand, during the redox process in highly concentrated electrolytes, the mass change is mainly due to moving counter ions where there is less amount of water molecules present in the electrolyte. A large number of continuous cycles were carried out to test the cycling stability of PPy(DBS) films. Cyclic voltammograms are almost unchanged after first few cycles in both higher and lower concentrations. But, on further cycling, the shape and capacity of the cyclic voltammograms change significantly in 0.1 M NaCl (aq) electrolyte while only a minor change is observed in 5 M NaCl (aq) electrolyte. It reflects that the PPy(DBS) films have better cycle life in concentrated electrolytes. The optical absorption spectra obtained at various reduction potentials in both electrolytes looks most identical to each other. This results shows that the PPy(DBS)films do not undergo any noticeable structural or conformational changes during the redox processes.

Key words: polypyrrole cyclic voltammetry, electropolymerization.

Introduction

The electrochemical characteristics of polypyrrole/dodecylbenzenesulphonate, PPy(DBS), films during the redox process depend significantly on many conditions, for instance, the type of counter ions and concentration of cycling electrolyte [1]. Short cycle life in aqueous electrolytes limits the applications of PPy based conducting polymers in practical devices. Using ionic liquids as cycling media resolves the above problem to some extent [2], however they cost too much. The aim of this study is to investigate whether concentrated electrolytes can be used to improve the cycling stability of PPy/DBS film.

In this paper we report the electrochemical characterization of PPy(DBS) films cycled in highly concentrated (5 M) NaCl(aq) solution using electrochemical quartz crystal microbalance (EQCM) and UV-visible absorption spectroscopy. The results were compared with those obtained in a dilute electrolyte solution having a concentration of 0.1 M. Tests on electrochemical stability of the PPy/DBS films also are reported.

Experimental

PPy(DBS) films were prepared using the galvanostatic electropolymerization technique. The 0.05M sodium dodecylbenzenesulphonate (SDBS) aqueous solution containing 0.05 M pyrrole, was used as the synthesis electrolyte. For the EQCM experiments, films were prepared on the gold electrode (area 1.37 cm²) on AT-cut 5 MHz quartz crystals, to have a thickness corresponding to a charge of 32 mC cm⁻² (calculated thickness 0.2 μm). A Stanford research systems (SRS) QCM-200 crystal analyzer in combination with a potentiostat (μAutolab Type III PGSTAT) was used for combined mass and redox cycling experiments. The cycling electrolyte (5 M and 0.1 M NaCl(aq) solution) was purged with nitrogen gas to remove dissolved oxygen. A Pt sheet was used as counter electrode and Ag/AgCl (3 M KCl) as a reference electrode. UV-visible optical absorption study was performed on films prepared, as described above, on ITO coated glass (Current density = 0.1 mA cm⁻²) using an Agilent 8453 UV-visible spectrometer. The film thickness is corresponding to a charge of 40 mC cm⁻².

Results and discussion

EQCM studies

Figure 3.1 shows that the first cyclic voltammograms and simultaneously obtained frequency (mass) changes of a PPy/DBS film cycled in (a) 5 M and (b) 0.1 M NaCl (aq) electrolytes. The sharp peak at around -0.5 V during the first reduction and a

broad anodic peak centered at -0.45 V are the usual first cyclic characteristic of the PPy(DBS) films and these peaks represent insertion and expulsion of cation (Na^+), respectively. Regarding the changes in the cyclic voltammograms in the two cycling electrolytes, only a slight shift in the reduction peak position was observed. However, frequency changes during the cathodic sweep differ by a large amount. The mass increase occurring in 0.1 M electrolyte is higher than that in 5 M electrolyte.

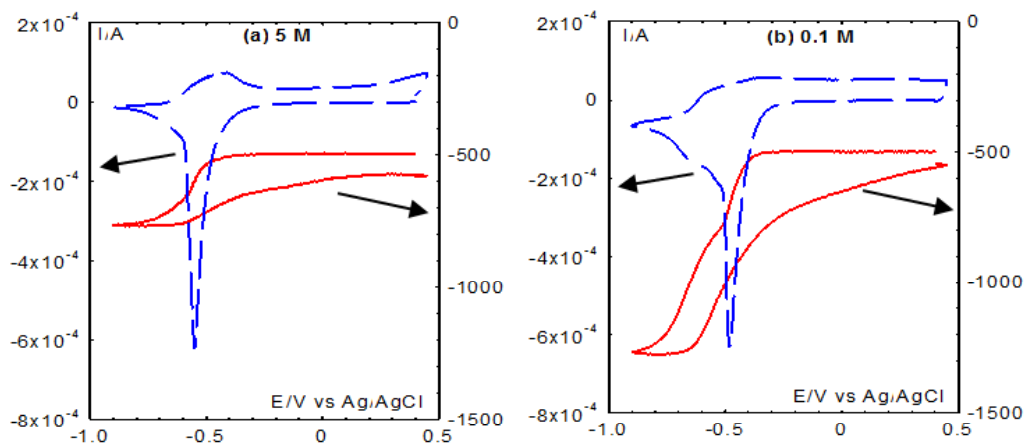


Figure 3.1: Cyclic voltammograms and frequency curves of the PPy/DBS film cycled in (a) 5 M and (b) 0.1 M NaCl solution

This is because of more water molecules can enter the film accompanying the counter ions due to osmotic effect when the film is cycled in dilute electrolyte. Similar observation can be seen during the anodic scanning, as well.

To investigate the cycling stability of the PPy(DBS) films, about 300 continuous cycles were carried out in electrolytes having both higher and lower concentrations. The Cyclic voltammograms were found to be almost unchanged after first few cycles up to about 50 cycles in both cases. However, on further cycling, shape and capacitance of the cyclic voltammograms change significantly in the dilute electrolyte while only a minor change was observed in the cyclic voltammograms in the 5 M electrolyte. Figure 3.2 shows the capacity variation of the cyclic voltammograms obtained in both electrolytes as a function of cycle numbers. For easy comparison of the variations, the ratio of C_n/C_{10} versus cycle number was shown in Fig.3.2, here C_n and C_{10} corresponds to the capacities of the n th and 10th cyclic voltammograms. Figure 3.2 clearly shows that the PPy/DBS films have better stability in the highly concentrated electrolyte.

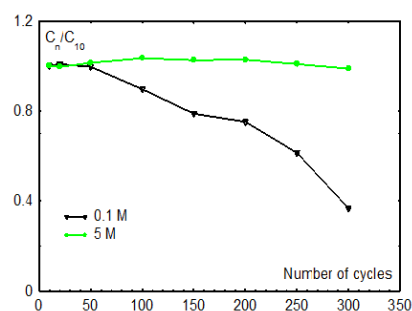


Figure 3.2: Electrochemical stability of PPy(DBS) films in (a) 5 M and (b) 0.1 M NaCl as a function of number of cycles. C_n : capacitive of n th cycle, C_{10} : capacitive of 10th cycle

UV-visible absorption studies

Fig.3.3 (a) and (b) show the UV-Visible absorption spectrum of PPy(DBS) films obtained at different potentials during the steady state (after 10 cycles) reduction of the film in 5 M and 0.1 M NaCl(aq) solutions, respectively. Both sets of spectra look identical except for slight difference in the amount of absorption. However, no change in the peak positions corresponding to

π - π^* (3.0 eV), polar on (2.2 eV) and bipolar on transition were observed. These results indicate that the PPy/DBS films do not undergo any noticeable structural or conformational changes during the steady state redox process in the lower concentration electrolyte in spite of considerable water movement taking place.

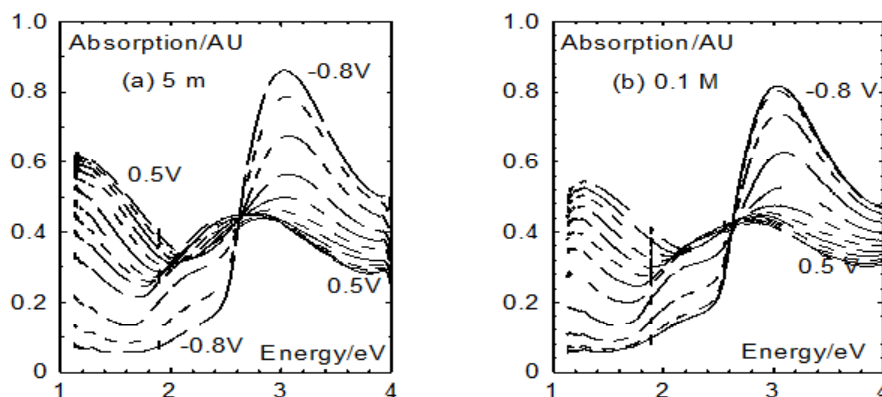


Figure 3.3: Optical absorption of PPy/DBS stable film as a function potential during the reduction in (a) 5 M and (b) 0.1 M NaCl

Conclusion

The electrochemical stability of PPy/DBS films in aqueous NaCl electrolyte solution depends highly on the concentration of the electrolyte. While the cycling capacity in 0.1 M electrolyte solution decreases significantly after about 50 cycles, the capacity remains same even at 300th cycle in 5 M electrolyte solution indicating that the films are more stable in concentrated electrolytes. Comparatively large amount of water are moving in and out of the film, during the redox process in dilute electrolytes and this water movement may be responsible for the low cycling stability of the films. However, the optical absorption spectra obtained in both electrolytes do not show any significant changes, indicating that there are no significant structural or conformational changes taking place in the PPy/DBS films when cycled in dilute electrolytes in spite of the large water movement.

References

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