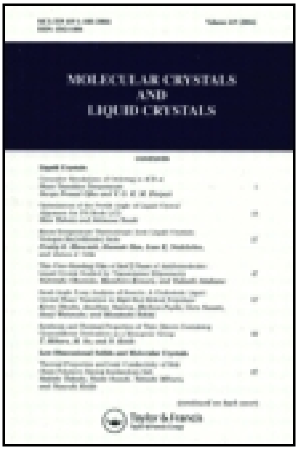

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Electrochemical Properties of a Conducting Polymer Composite P3HT/PSS

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Version of record first published: 24 Sep 2006

To cite this article: Dong-Kyu Kim, Jong-Moon Jin, Youngkwan Lee & Yongkeun Son (1997): Electrochemical Properties of a Conducting Polymer Composite P3HT/PSS, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 294:1, 233-236

To link to this article: http://dx.doi.org/10.1080/10587259708032290

Mol. Cryst. Liq. Cryst., 1997, Vol. 294, pp. 233–236
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ELECTROCHEMICAL PROPERTIES OF A CONDUCTING POLYMER COMPOSITE P3HT/PSS

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Abstract A conducting polymer composite of P3HT/PSS was prepared. Its electrochemical properties were investigated by using CV, EQCM, and UV/VIS spectroscopy. Cation transport properties of the composite films were discussed.

INTRODUCTION

There have been many research papers about charge/discharge properties of conducting polymers. Most of them are dealing with electrochemically prepared conducting polymers because of their lack of processability.[1] In case of Li ion secondary battery application, it is necessary for the conducting polymers having Li ion transport as well as processability. In this work, we prepared a soluble conducting polymer composite(P3HT/PSS) using poly(3-hexylthiophene) and poly(styrenesulfonate), and investigated their redox properties during electrochemical potential cycles.

EXPERIMENTAL

Most chemicals were purchased from Aldrich and used as received. Tetrahydrofuran (THF) and acetonitrile(ACN) were distilled and stored under N_2 before use. P3HT was synthesized following the reported way.[2] The PSS has 10 mole % of sulfonate group.[3] The composite solution was prepared by dissolving P3HT and Li-PSS in THF at 36% of composition ratio (number ratio of -SO_3Li units in PSS to thiophene rings in P3HT).

Composite films were spin-casted onto GC, Au, and ITO plates and used as working electrodes in a cell having an ACN solution of 0.1M $LiClO_4$ or Bu_4NClO_4 (tetrabuthyl ammonium perchlorate). A Pt plate counter electrode and a Ag/Ag^+ (0.01M $AgNO_3$ in ACN) reference electrode was used. Cyclic voltammograms(CV) of the composite films were determined by using a BAS 100W(BAS, USA) potentiostat. N_2 purging was done on the cell for ~10 min before any electrochemical measurements.

An electrochemical quartz crystal micro balance (EQCM) used to verify the mass variation of the composite films during redox process. The crystal used in this machine is a disk shaped 10 MHz AT-cut quartz with concentric Au electrodes of $0.2cm^2$ area on both sides. UV/VIS spectra of the films on ITO(Samsung Corning, Korea) were recorded with a HP 8453 (Hewlett-Packard, USA) spectrophotometer. Conductivites of free standing films were measured at room temperature using four-prove method.

RESULTS AND DISCUSSION

Characterization of the P3HT used in this study has been published elsewhere in detail.[3] The polymer has mostly head-to-tail linkage with negligible cross linking. Molecular weights are M_n=24,258 and M_w=107,417 (polystyrene standards). UV/VIS spectra of the polymer films show a band for π-π^* transition at 472 nm. CV's of the films show $E_{p,ox}$ at ~0.65V and $E_{p,red}$ at ~0.55V.

CV's of the composite films in two different electrolytes are appearing in Figure 1. The electrochemical redox response in a $LiClO_4$ electrolyte (a) looks similar to that of pure P3HT film in the same electrolyte. On the other hand, the composite electrode in a Bu_4NClO_4 electrolyte having large cation (Bu_4N^+) shows a continuous shifting of oxidation peak position (b). The peak shifting may be attributed to the continuous growing of oxidation overpotential that came from the retardation in cation transport and the conformation change of PSS in the composite: PSS intrinsically exists as a self-entangled form due to the strong ionic interactions, however, the entangled form is changed the a relaxed form when cations are removed by the E_{ox}.[6] On the reduction cycle, cations are easily inserted into the relaxed PSS from the electrolyte by the E_{red}. Therefore the reduction peaks are all at the same potential region in (b). In the reduced state PSS changed to the entangled form again, thus more overpotential due to sluggishness of the cation movement is appearing.[7]

In order to confirm the cation transport property of the composite film, EQCM analysis was carried out. The mass variations of P3HT and composite films are shown in

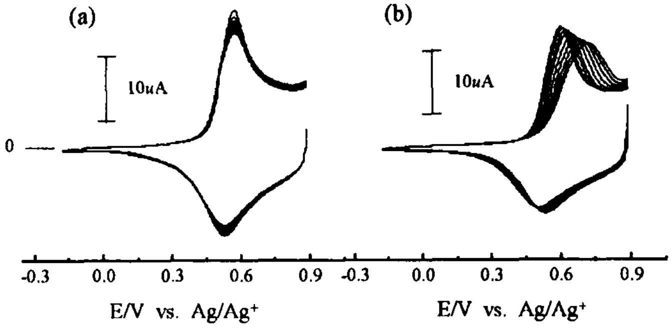

FIGURE 1. Cyclic voltammograms of P3HT/PSS composite films on GC electrodes in acetonitrile solutions of (a) 0.1M$LiClO_4$, and (b) 0.1M Bu_4NClO_4. Scan rate: 30mV/s.

Figure 2. The mass of P3HT is increasing for oxidation and decreasing for reduction (a) due to anion transport. On the other hand, the composite film shows completely revered process in (b). The reversed mass variation is attributed to the transport of dopant cation.

Furthermore, the composite shows interesting absorption properties in Figure 3. As the UV/VIS spectra show, the film is partially oxidized (b) even with the application of reduction potential. This is quite different optical behavior compared to that of P3HT/PS (a). The composite film has conductivity of 1.21×10^{-3}S/cm at reduced state. This could be explained by stabilization of cation radicals due to the interaction between sulfonate anions and radical cations on the P3HT formed during oxidation stage.

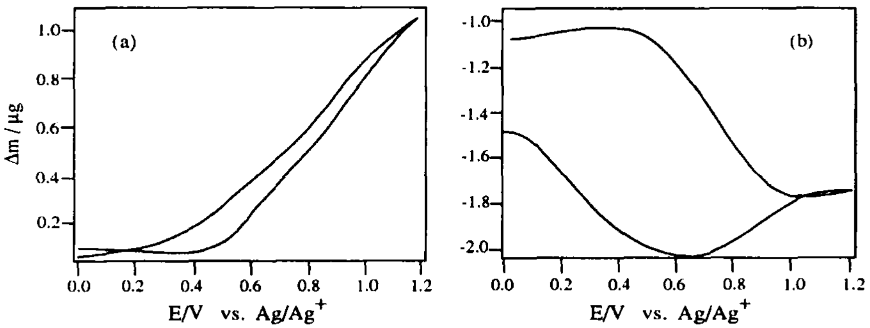

FIGURE 2. Mass variation during electrochemical redox cycles. (a) pure P3HT, and (b) P3HT/PSS composite films on EQCM electrode.

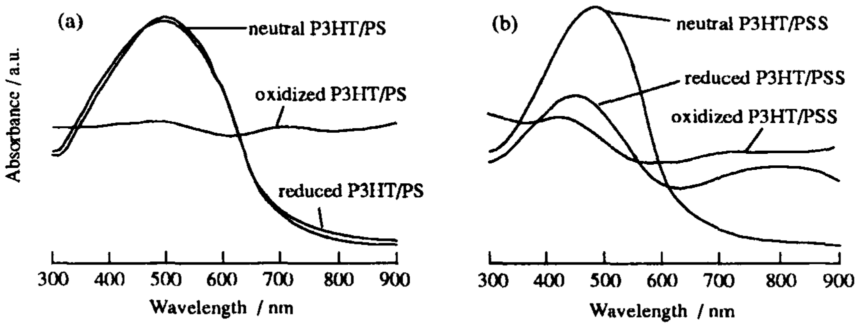

FIGURE 3. UV/VIS spectra of composite films (a) P3HT/PS, and (b) P3HT/PSS where PS is poly(styrene).

CONCLUSION

Conducting polymer composite of P3HT/PSS was prepared by solution blending method. The mass variation by EQCM shows that the cation, Li^+, behaves as a dopant in this composite. The discharged films show electrical conductivity in the range of 10^{-3} S/cm. Results of our investigation imply that the composite could be a good base material for a Li ion secondary battery system.

ACKNOWLEDGMENT

The authors are grateful for financial support provided by the Ministry of Education, Korea through BSRI 96-3421 and using ITO electrodes that were donated by Samsung Corning, Korea.

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