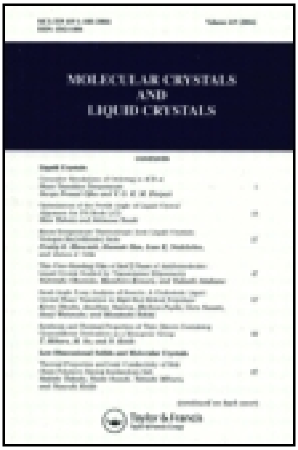

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In-Situ Measurement of Surface Tension During Electrochemical Doping of Polypyrrole Films

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In-Situ Measurement of Surface Tension During Electrochemical Doping of Polypyrrole Films

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We have performed in-situ measurement of surface tension during the electrochemical oxidation-reduction process of polypyrrole films by using Wilhelmy's plate technique with specially designed electrochemical cell. Polypyrroles were synthesized on a platinum plate electrode with various dopants and placed in the electrochemical cell. Dynamic contact angle was measured by using the Wilhelmy plate technique while the electrochemical potential was applied. Polypyrrole showed the changes in contact angle during the electrochemical oxidation-reduction process. Effects of dopants and the redox potential on the contact angle was studied.

Keywords: in-situ electrochemical measurement; surface tension; polypyrrole

INTRODUCTION

In-situ methods of characterization are most appropriate for the measurement of intrinsic properties of conducting polymers in relation with their tendency to change their physical and/or chemical properties in different environments as described in a recent review.[1] However, some of their intrinsic natures such as surface properties have not been explored in relation with the electrochemical doping-dedoping process. Surface tensions via contact angle measurement can provide information on the solvent-polymer interactions which are inherent for all processes occurring at polymer-solution interfaces and are likely to be responsible for the dynamic behavior of conducting polymers. Recently, Wallace et al.[2] reported a characterization of conducting polymers by measuring dynamic contact angle using Wilhelmy's plate technique. However, in their research only the intrinsic surface properties of doped polymer have been investigated, which in turn gave no informations on the dynamic properties in relation with the electrochemical redox reaction of conducting polymers. In this paper, we report our recent results on the in-situ measurement of surface tension during the electrochemical oxidation-reduction process of polypyrrole films. Dynamic contact angle (DCA) was measured in-situ by using the Wilhelmy plate technique[3,4] with simultaneously applying the electrochemical potential on the polypyrrole electrode through the electrochemical cell.

EXPERIMENTALS

Reagents and Materials

The polypyrrole film (ca. 7~10 μm thick) was deposited on a platinum working electrode using electochemical oxidation of pyrrole (Aldrich, 97%) by applying cyclic potential (-0.3 ~ 0.9 V vs. Ag/AgCl) with sweep rate of 50 mV/s for 25 min from acetonitrile polymerization solution containing 0.06 M of pyrrole and 0.1 M of electrolyte salt.

Instrumentation and Measurement

The working electrode was a platinum plate (1 × 2 cm) with a platinum wire hook for contact with DCA sample holder which was connected with CV-27 cyclovoltameter (BAS) by a copper coil (d = ca. 0.05 mm). The dynamic contact angle measurements were carried out using a Cahn DCA 322 Dynamic Contact Angle Analyzer interfaced with an IBM-compatible computer. The platform speed was 21 μm/s for all experiments.

RESULTS AND DISCUSSION

The Wilhelmy plate technique enables the measurement of an effect of surface tension due to the Archimedean upthrust of the solution on the apparent weight of a partly immersed plate. Fig. 1(a) shows a typical diagram of DCA measurements in which the measured force is plotted against the immersion depth.

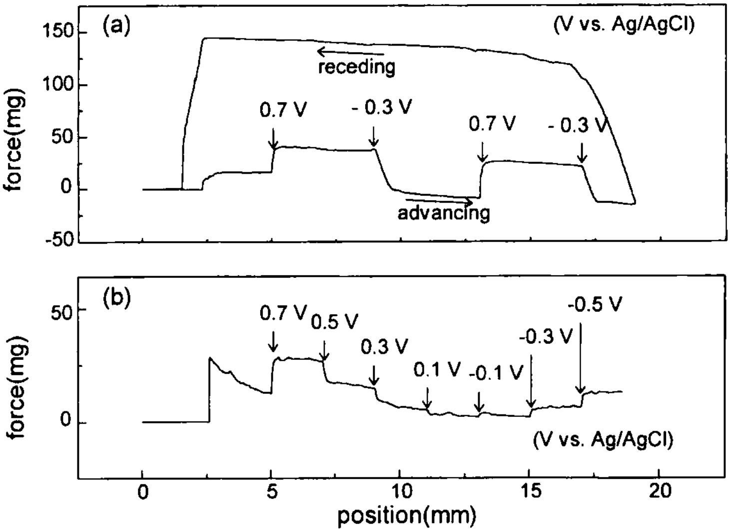

FIGURE 1. (a) Force-immersion depth plot for polypyrrole doped with $(CH_3CH_2)_4NBF_4$; (b) Force-immersion depth plot for polypyrrole doped with $LiClO_4$ at different oxidation level.

After the plate was partially immersed in aqueous electrolyte solution, a potential of 0.7 V (vs. Ag/AgCl) was applied to oxidize the polypyrrole, which resulted in the immediate increase of measured force. This can be attributed to the fact that as the polypyrrole is oxidized, positive charges are developed along the polymer chain and the counter-ions (anions) move into the polymer as a dopant. This process makes the polymer more polar, and in consequence, the interfacial attraction force between liquid and the plate is increased. When the polymer was reduced to -0.3 V (vs. Ag/AgCl), a slow decrease of the measured force was observed, which is to be considered as a reverse process of the above explanation. The absolute value of force differences between the oxidized and reduced states probably seemed to depend on the type of dopants as well as the surface porosity of the film. The effect of dopant types on the surface tension was not clear and requires further investigation. Effects of oxidation potential on the contact angle was examined as shown in Fig. 1(b). As the applied potential decreased step-wisely, the surface tension decreased until 0.1 V (vs. Ag/AgCl) then increased again. The depth of decrease was also slowly decreased until the minimum has reached and then slowly increased. The changes in contact angle with respect to the applied potential seemed to be related with the electrochemical double layer of conducting polymer chain surrounded by the electrolytes[5,6] as well as the redox potential (E_p) of polypyrrole. Cyclic voltammogram of polypyrrole in the same electrolytic medium showed its E_p at around -0.1 ~ 0.1 V (vs. Ag/AgCl) where the minimum of measured force was found.

Further works and detailed results will be published elsewhere.

Acknowledgments
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