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Analysis of the Morphology and Characteristics of Ppy Thin Film Using QCA and AFM

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In this work, the in-situ viscoelastic characteristics of electropolymerized polypyrrole (Ppy) thin film were investigated in the electrolyte solution of $NaClO_4$, $LiClO_4$ and $KClO_4$ using quartz crystal analyzer (QCA) and AFM. One side of quartz crystal electrode was used as a working electrode mounted in a specially fabricated QCA electrochemical cell.

The result suggests that the Ppy film polymerized onto the crystal behaves as a rigid elastic layer at the initial stage of electropolymerization, while the film becomes a viscoelastic layer as the polymerization proceeds further. At the same time, the film thickness increases and some morphological changes take place due to the penetration of electrolyte solution into the film.

Keywords: polypyrrole; AFM; morphology; viscoelasticity; QCA

INTRODUCTION

The application principle of quartz crystal in the characterization of polymer film is based on the relation between the mass change of surface elastic film and the resonant frequency change of the quartz crystal[1-2]. The quartz crystal has been utilized as an effective analytical tool in electrochemistry[3-4]. Furthermore, the viscosity effect of liquid and solution in contact with quartz crystal has been widely studied, and equations for the resonant frequency change and for the resonant resistance of the quartz crystal have been obtained[5]. The viscoelasticity of the film can be estimated by

measuring the resistance of the quartz crystal. As the change of resonant frequency includes information on the mass, elasticity and viscosity of the coated film and the change of resonant resistance reflects the variations of viscosity and density in the film, we have shown that the resonant frequency-resonant resistance diagram (F-R diagram) can clarify the relation of mass and viscoelastic changes of the coated film. This relation is quantitatively represented in Figure 1.

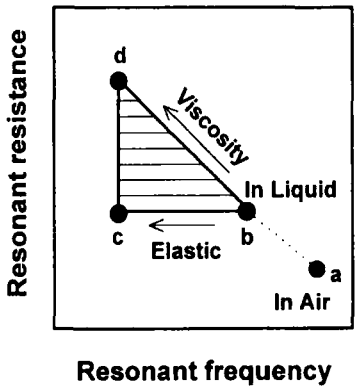


FIGURE 1. The quantitative relation and changes in resonant frequency and resonant resistance.

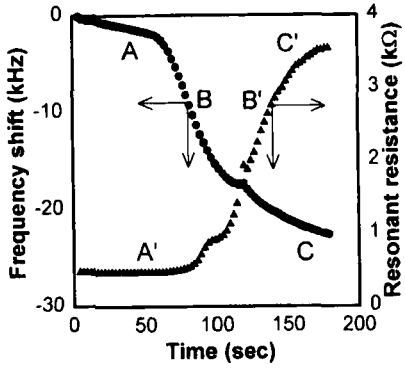


FIGURE 2. Changes in resonant frequency and resonant resistance during Ppy deposition.

EXPERIMENTAL

A potentiostat (Solartoron, Model 1286) is used and the terminal for the working electrode is connected to the terminal of electrode of quartz crystal. A 9 MHz AT-cut quartz crystal is converted into an Au electrode by sputtering method and employed as a working electrode in a plastic resin cell exposing only one side of the electrode. The area of working electrode is 0.2 cm^2. Polypyrrole is polymerized with constant current density on the Au electrode for 180 seconds. The 0.1 M solutions of $LiClO_4$, $KClO_4$ and

$NaClO_4$ are used as electrolyte.

RESULTS AND DISCUSSION

Figure 2 shows examples of the resonant frequency and resonant resistance on the electrochemical deposition of polypyrrole in the solution of 0.1 M $KClO_4$ with a constant current of 0.1 mA/cm^2 for 180 sec. As expected the resonant frequency is decreased but the resonant resistance is increased with polymerization time, which means that the formation amount of Ppy rises with time. The resonant frequency decreased with time, but the resonant resistance remains constant until the resonant frequency changes by 103 kHz. The result suggests that the Ppy film polymerized onto the crystal behaves as a rigid elastic layer at the initial stage of electopolymerization, while the film behaves as a viscous medium when the polymerization proceeds further. Also film thickness increases and some morphological changes take place due to the anion doping and the penetration of electrolyte solution into the film. This phenomenon can be confirmed from AFM image as shown in Figure 3.

Figure 4 shows the cyclic voltammogram of Ppy film with -600 ~ 600 mV (vs. Ag/AgCl) scan range and 50 mV/sec scan rate in 0.01 M and 0.5 M

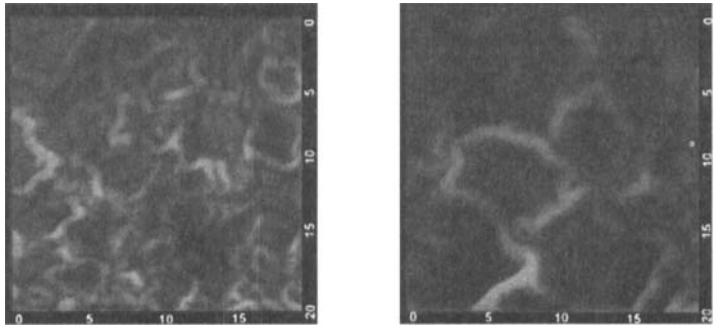
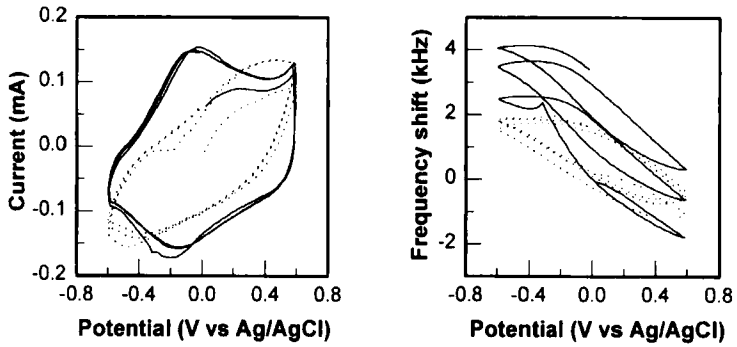


FIGURE 3. AFM photograph of polypyrrole thin film.(20 x 20 μ m)
(a) polymerized for 50 sec.; (b) polymerized for 180 sec.

$NaClO_4$ electrolyte solutions. The redox peaks are clearly observed when Ppy film is polymerized in higher concentration solution than electrolyte concentration, but those are not clear when polymerized in lower concentration solution than electrolyte concentration. The electrolyte solution transportation with potential sweep become more distinct at higher concentration, which induces continuous resonant frequency decrease.



(a) (b)

FIGURE 4. The effect of electrolyte concentration on the cyclic voltammetry of Ppy thin film prepared in 0.1 M $NaClO_4$ solution.
(····· in 0.01 M $KClO_4$, —— in 0.5 M $KClO_4$)
(a) potential-current; (b) potential-frequency shift

Acknowledgments

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