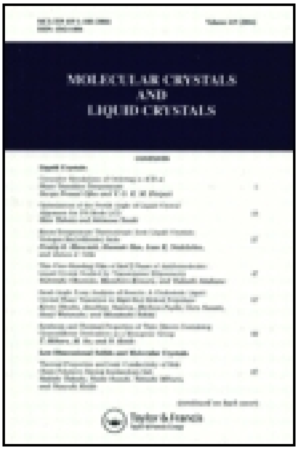

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In this work, the in-situ viscoelastic characteristics of electro-polymerized polypyrrole (Ppy) thin film were investigated in the electrolyte solution of $KClO_4$, $LiClO_4$ and $NaClO_4$ using quartz crystal analyzer (QCA). One side of quartz crystal electrode was used as a working electrode mounted in a specially fabricated QCA electrochemical cell. The resonant frequency and resistance diagram was utilized to interpret the viscoelastic behavior of Ppy thin film. The larger the size of cation is, the more distinct the viscoelastic change is due to the cation penetration into the polypyrrole thin film. The cyclic voltammetry, using Ppy deposited AT-cut quartz crystal electrode, suggests that the swelling of Ppy film reduces the conductivity of the Ppy film.

Keywords: QCA; polypyrrole; viscoelasity; cation effect

INTRODUCTION

The quartz crystal microbalance (QCM) has been widely used to analyze the mass change of working electrode by measuring the change of resonant frequency. Drata and Buttry[1] stressed a great advantage of the QCM in electrochemical analysis.

Up to date, however, few reports have been published about analysis of the viscoelastic property of thin film utilizing quartz crystal. Muramatsu *et al.*[2] expanded the application of quartz crystal in the analytical science inducing the concept of resonant resistance. Lately, Chang *et al.*[3] also reported that resonant resistance is an excellent tool to describe the change of phase transition phenomena. Resonant resistance corresponds to the resistance in electrical equilivalent circuit derived by Muramatsu[2]. The resonant resistance is simply measured with a home-made peak hold circuit[3]. The rheological changes occurred on the film coated quartz crystal can be explained by drawing the diagram of resonant frequency shift (ΔF) and resonant resistance (R). If two different phenomena occur simultaneously, the changes in the F-R diagram are represented by the sum of F-R vectors [4].

EXPERIMENTAL

Figure 1 shows an experimental layout employed in this work. Pyrrole (Wako Pure Chem. Co.) was purified by the vacuum distillation and stored in a dark room at low temperature. The compounds of $KClO_4$, $LiClO_4$, $NaClO_4$ and other materials of analytical grade were used as purchased. An Au electrode sputtered on a bare quartz crystal was used as a working electrode. Polypyrrole was polymerized at constant current density for 180 seconds. The solutions of 0.1 M $KClO_4$, $LiClO_4$ or $NaClO_4$ were used as electrolyte.

RESULTS AND DISCUSSION

Figure 2 shows the effect of cation on the polypyrrole deposition with constant current density of 0.1 mA/cm^2 for 180sec. The resonant frequency decreases slowly for the first 60 sec, steeply after 60 sec and slowly again after 120 sec. Whereas the resonant resistance is constant in the first stage, it increases after 60 sec with the penetration of the electrolyte solution into partly polymerized Ppy film which arises mass loading effect and the frequency decreases suddenly. The resonant resistance changes in the order of $LiClO_4$, $NaClO_4$ and $KClO_4$ according to hydrated cation size. As the polymerization proceeds, the electric conductivity of Ppy film lowers and polymerization rate reduces which leads to the decrease of the change of resonant frequency after 120 sec.

Figure 3 shows the cyclic voltammogram of a polypyrrole film deposited quartz crystal with -600~+600 mV (vs. Ag/AgCl) scan range and 50 mV/sec scan rate in 0.1 M $LiClO_4$ electrolyte solution. The electrochemically polymerized Ppy film is stable between -600 mV and +600 mV (vs. Ag/AgCl). This result is obtained after 30 cycles of C. V.

The resonant frequency decreases in positive potential sweep and increases in the following negative potential sweep. These resonant frequency changes can be explained by the mass transport of anion doping and dedoping.

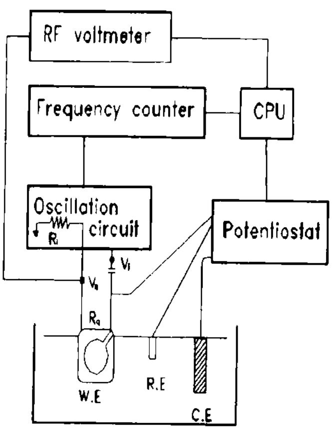

FIGURE 1 Schematic diagram of QCA measuring system coupled with electro-chemical analyzer.

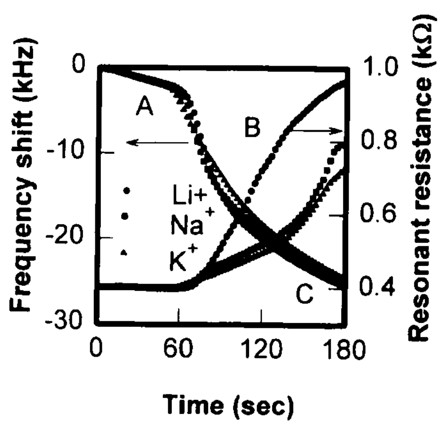

FIGURE 2 The effect of cation on the resonant frequency shift and resonant resistance during Ppy deposition for 180 seconds.

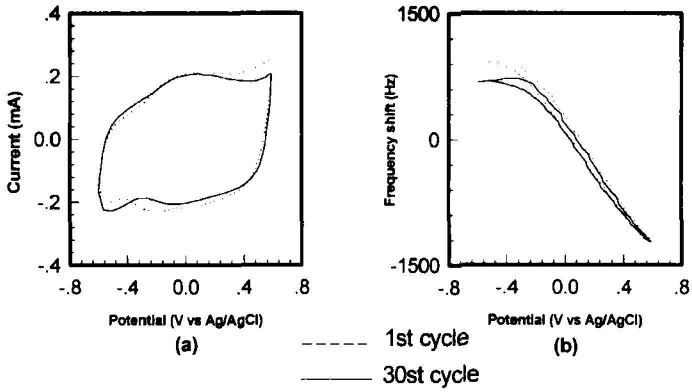

FIGURE 3. Cyclic voltammetry of Ppy film deposited AT-cut crystal in 0.1 M $KClO_4$ solution and cycled in 0.1M $LiClO_4$ solution (............ 1st cycle, ——— 30th cycle)

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