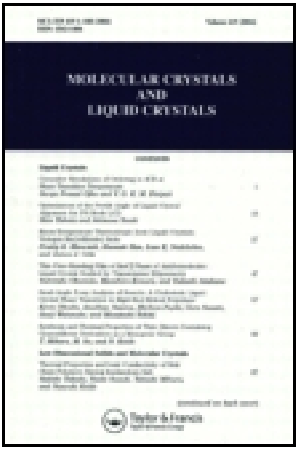

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Dynamic Behaviors of Electrochemically Polymerized Polypyrrole Thin Film During Deposition Process Using Q.C.A.

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DYNAMIC BEHAVIORS OF ELECTROCHEMICALLY POLYMERIZED POLYPYRROLE THIN FILM DURING DEPOSITION PROCESS USING Q.C.A.

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Abstract An advanced measuring system was developed using quartz crystal analyzer (Q.C.A.) for the in-situ measurement of the resonant frequency and resonant resistance of the polypyrrole deposited Q.C.A. with electrochemical reaction. The system was used to monitor polypyrrole deposition by the constant current method. In the electrochemical deposition, not only the resonant frequency change but also the resonant resistance increase was observed. The elastic film is formed at first stage of polymerization, but transformed to viscoelastic film later and this procedure is repeated in the process of polymerization.

INTRODUCTION

The first report on the oscillation of a quartz crystal in contact with liquid was presented in 1980[1)]. Several papers have been published with respect to the case of a crystal in contact with liquid, and equations derived for the resonant frequency and resonant resistance. The quartz crystal has been used as a viscosity sensor and several papers have also been presented describing its use with viscoelastic film coatings.[2-5)]

Since the discovery of electrochemical polymerization of conducting polymers, much attention has been paid to electrochemically polymerized conducting thin films with respect to their physical chemistry, and potential applications to electochromatic displays, batteries, and electro- chemical sensors, etc. Many studies have been performed focused on the synthesis of conducting polymers, such as polyacetylene, polypyrrole, polythiophene and their derivatives. Among them, polypyrrole can be obtained readily its conducting form by electrochemical oxidation of pyrrole.

The application of quartz crystal to electrochemical measurement started in 1985.[6] The first application was for monitoring metal ion deposition or oxidation on an Au electrode. It was also applied to monitor corrosion or electrochemical deposition.[7,8] In one of these papers, a mechanism of polypyrrole deposition was also considered.

In this paper, we describe the interpretation of the viscoelastic property using the contrast of the resonant frequency and resonant resistance. We developed an apparatus for the in-situ determination of the resonant resistance using an oscillating circuit and a measuring circuit for amplitude of high frequency voltage. The system was applied to monitor the electrochemical deposition of polypyrrole.

PRINCIPLE OF QUARTZ CRYSTAL ANALYZER

The well-known equation of the resonant frequency change for mass change of elastic film has been presented by Sauerbrey.[2] The equation for the frequency change in contact with liquid has been derived by Kanazawa et al..[3] The resonant resistance of the quartz crystal is the resistance included in the electrical equivalent circuit of the quartz crystal. The resonant resistance for the quartz crystal in contact with liquid has been derived by us.[4]

The typical cases of film properties on the vibrating quartz are expressed in terns of mass loading and energy loss effects. It is known that the resonant frequency of the quartz crystal reflects the substantial surface mass change, and the resonant resistance reflects the energy loss on the surface of the vibrating quartz plate.

In the case of the elastic film coating, the mass change of the film is reflected completely in the resonant frequency change and there is no energy loss on the surface of the quartz plate.

In the case of a viscoelastic film coating, the resonant frequency change with film deposition reflects the mass increase, and also the resonant resistance increases with film deposition reflecting the viscosity of the film.
This relation is expressed quantitatively in Figure. 1 by plotting the relation of resonant frequency and resonant resistance.

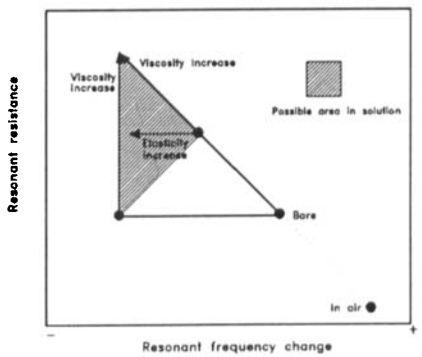

Fig 1. F-R model with same electrolyte.

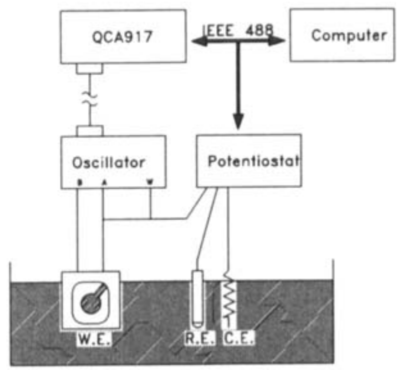

Fig 2. Schematic diagram of system.

EXPERIMENTAL

Material

9 MHz, AT cut quartz crystal is formed ITO electrode by sputtering method, and used as working electrode with a plastic resin cell to expose only one side of the electrode. The working electrode area is 0.2 cm^2. An Ag/AgCl electrode is used for the reference electrode and a Pt electrode is used for the counter electrode. Pyrrole is obtained from Wako Pure Chemicals and other chemicals were of analytical grade.

Experimental Procedure

The measuring system is shown in Figure. 2. A potentiostat (Solartoron, Model 1286) is used, and the terminal for the working electrode is connected to the terminal of the electrode of the quartz crystal. Pyrrole(C_4H_4NH)(0.1 M) in 0.1 M $KClO_4$ solution is used for the electrochemical deposition of the polypyrrole. Electrochemical deposition was performed by the constant current method with 100 A.

RESURTS AND DISCUSSION

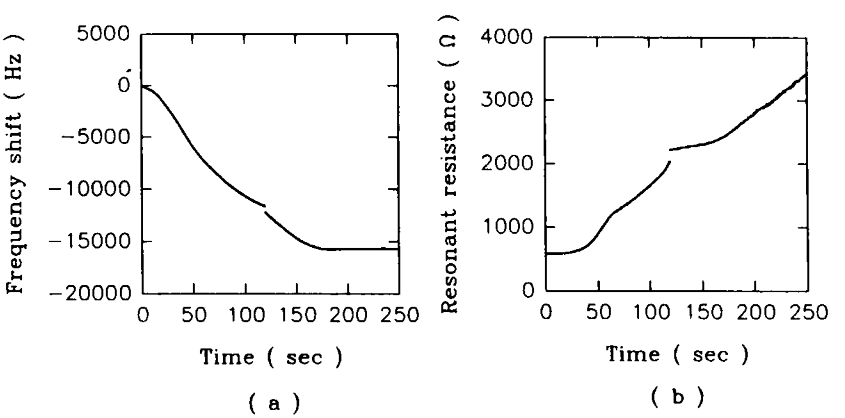

Fig 3. Resonant frequency and resistance response of Ppy polymerization.

Figure 3 shows examples of the resonant frequency (a) and resonant resistance (b) on the electrochemical deposition of the polypyrrole with a constant current of 100 A for 250 sec. Figure 3 (a) shows that the resonant frequency decreases in the first 100 sec and decreases again followed by sudden jumping, and reaches steady state after 160 sec, then the frequency change is 17kHz. This means that electrochemical polymerization is terminated when 17μg polypyrrole is deposited on the quartz crystal working electrode, because of lower activated cite of ITO electrode compared with other electrode such as platinum or gold. Whereas the resonant resistance shows no change in the first stage, but the resonant resistance increases simultaneous with the decrease of frequency. The resonant resistance increases even if the resonant frequency reaches steady state. This suggest that swelling of the film occurred in the solution.

These relations are represented as F-R diagram using the contrast of the resonant frequency and resonant resistance for the detailed consideration of microrheology on the polymerized polypyrrole. Figure 4 shows the relation of the resonant frequency change and resonant resistance of Figure 3 Figure 4 shows that the elastic film is deposition in the initial stage, but the film changes viscoelastic film. The characteristic change of deposition film in the deposition process, may be considered detailly by using the relation of resonant frequency and resonant resistance.

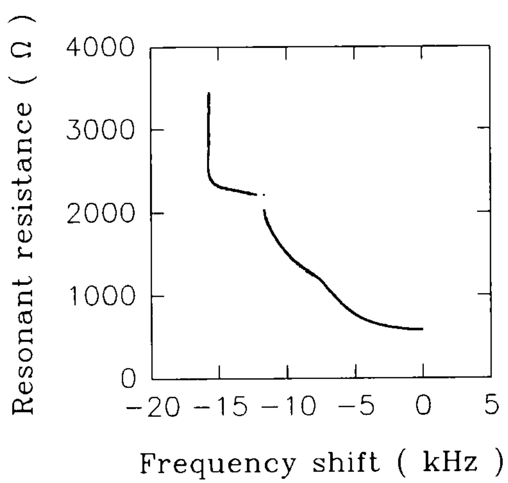

Fig 4. F–R diagram for Ppy deposition.

CONCLUSION

We have developed an advanced measuring system for in-situ measurement of electrochemical deposition. The system was applied successfully to polypyrrole deposition in the constant current method. The resonant frequency change and resonant resistance change showed that the film is deposited elastic film in initial stage, but the film changes viscoelastic and that swelling of the film is occurred. These phenomena are depending on the condition of deposition. The consideration of the resonant resistance change will help the interpretation of result of the study of the film deposition.

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