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Sang-Mok Chang [a], Jong-Min Kim [a], Jeong-Soo Chang [b], Young-Soo Kwon [c], Hiroshi Muramatsu [d] & Tatsuaki Ataka [d]

[a] Dept. of Chemical Eng., Dong-A University, Pusan, Korea

[b] Dept. of Elec. Eng., Kyung Pook San Up University, Kyungsan, Korea

[c] Dept. of Electrical Eng., Dong-A University, Pusan, Korea

[d] Research Lab. for Adv. Tech., Seiko Instruments. Inc., Chiba, Japan

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DYNAMIC ELECTROCHROMATIC BEHAVIORS OF POLYPYRROLE THIN FILM USING Q.C.A. AND UV SPECTROSCOPY

SANG-MOK CHANG[1], JONG-MIN KIM[1], JEONG-SOO CHANG[2] YOUNG-SOO KWON [3], HIROSHI MURAMATSU[4], TATSUAKI ATAKA[4]

[1]Dept. of Chemical Eng.,, Dong-A University, Pusan, Korea

[2]Dept. of Elec. Eng., Kyung Pook San Up University, Kyungsan , Korea

[3]Dept. of Electrical Eng., Dong-A University, Pusan, Korea

[4]Research Lab. for Adv. Tech., Seiko Instruments. Inc., Chiba, Japan

Abstract This paper shows that the electrochemical mass transport in polypyrrole (Ppy) thin film deposited electrode, involves the rheological change and electrochromatics of the Ppy. These changes can be detected by measuring the resonant frequency, resonant resistance, and UV spectrum of a Ppy deposited quartz crystal.
A Ppy deposited quartz crystal is used and measured the cyclic voltammograms in $KClO_4$ electrolyte solution. The changes of the resonant frequency and resonant resistance showed that mass trasport and viscoelastic changes occur in the Ppy film. The absorption change means that the electrochromatics change occurs also in the Ppy film.

INTRODUCTION

The principle of the use of the quartz crystal is based on the relation between the mass change of surface elastic films and the resonant frequency changes of the quartz crystal. It was reported that the quartz crystal can be used in contact with aqueous solution at 1980, and this widened the application of the quartz crystal in the field of chemical analysis. In particular, the quartz crystal has been used as an effective analytical tool in electrochemistry[1-5]. Furthermore, the viscosity effect of liquids or solutions in contact with quartz crystal has been studied widely, and equations for the resonant frequency change and for the resonant resistance of the

quartz crystal have been derived.[3-4] These results were immediately applied to analytical applications such as the viscosity monitoring of bioprocess and coagulation factor assays.[6-8]

In the field of electrochemical analysis, the quartz crystal technique was used to study electrochemical deposition of organic films and redox reactions in the films. But it should be considered that the relation of mass and resonant frequency change is valid only for elastic films, and some organic films have insufficient rigidity to use Sauerbrey's equation.

The rigidity of the films can be estimated by measuring the impedance (or resistance) of the quartz crystal. As the resonant frequency change includes information about the mass, elasticity and viscosity of the coating film and the resonant resistance change reflects the viscosity and density changes in the film, we have shown that the resonant frequency - resonant resistance diagram (F-R diagram) can clarify the mass and viscoelastic changes of coated films. The results of this measurement showed that the viscosity of the polypyrrole films increased according to the increase of film thickness, and especially, swelling caused a large viscosity increase.

In this work, Ppy deposited quartz crystal is used to study electrochemical mass transport and micro-rheology changes in the Ppy films, since the Ppy films can be polymerized electrochemically. The absorption of Ppy film during cyclic voltammetry, is also analyzed by UV spectroscopy, because the electrochromatics of Ppy film changes during cyclic voltammetry process. The mass transport and micro-rheology changes can be clarified by the in situ measurement of the resonant frequency and resonant resistance.

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. 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 F-R diagram by plotting the relation of the resonant frequency and resonant resistance.

EXPERIMENTAL

Material

9 MHz, AT cut quartz crystal is formed ITO electrode by sputtering method, and used as working electrode with a specially designed plastic resin cell (Figure 1) for optical analysis.

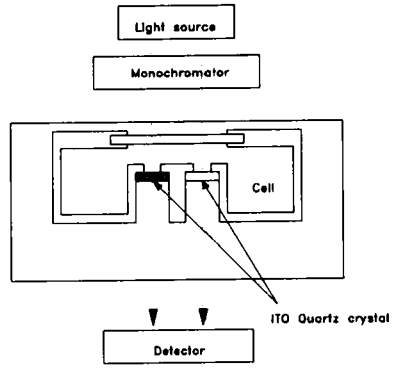
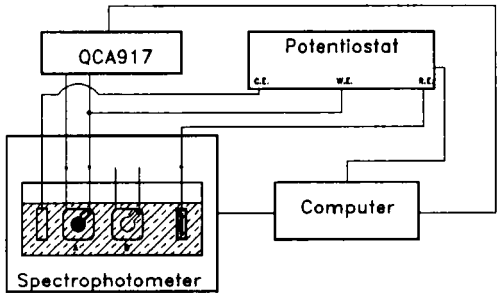


Fig 1. Cell structure of UV/Q.C.A. system

The area of 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. PPy coated ITO for working electrode
B. Bare ITO for optical reference

Fig 2. Schematic diagram of UV/Q.C.A. system

A potentiostat (Solartron, Model 1286), Q.C.A. analyzer (Seiko EG & G QCA 917), UV/vis spectrophotometer (Hitachi 340) 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 is performed by the constant current method with 0.1mA for 250 sec. Electrochromatic change is performed by cyclic votammetry with sweep range of -400 to 600 mV vs. Ag/AgCl and scan rate 50 mV/sec in 0.1 M $KClO_4$ solution after 17 μg Ppy deposition.

RESULTS AND DISCUSSION

Figure 3 shows the current-potential curve, resonant frequency-potential curve, resonant resistance-potential curve, and absorbance-potential curve during cyclic voltammogram of the 17 μg Ppy deposited quartz crystal ITO electrode. The electrochemically polymerized Ppy thin film is stable between -400 mV and 600 mV vs. Ag/AgCl from Figure 3 (a), and this result is obtained after 20 cycles of

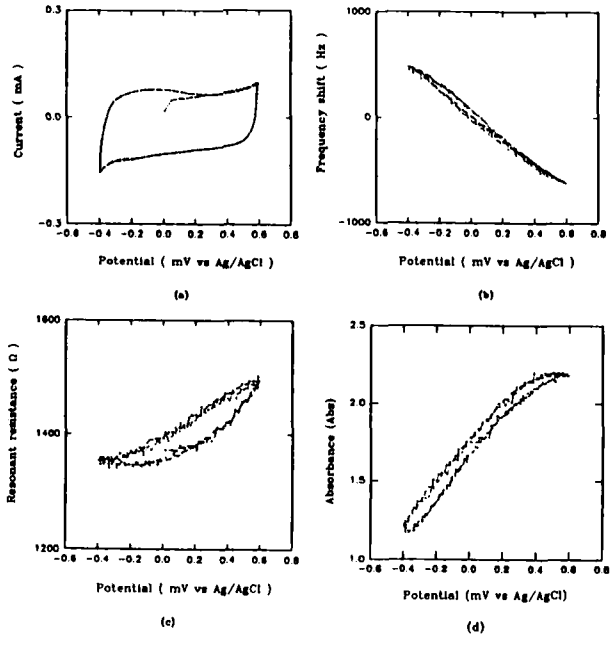


Fig 3. Synthesis variables during redox process.

cyclic voltammogram. The resonant frequency decreases in the 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. Anion doping on the Ppy film would caused a mass increase of the film, and anion dedoping from the Ppy film would caused a mass decrease of the film. This can explain the subsequent resonant frequency increase and decrease in the process of cyclic voltammogram.

The resonant resistance change of the Ppy deposited quartz crystal during the cyclic voltammetry, means that the anion transport induces a viscoelastic change in the Ppy film. Ppy film behaves as elastic films at negative potential, but viscoelastic film at positive potential. This result means that anion increases the viscosity and cation increases rigidity. The absorbance change of the Ppy deposited quartz crystal during the cyclic voltammetry, means that the anion transport induces a electrochromatic change in the Ppy film. Ppy film becomes bright at negative potential, but dark at positive potential. This result can be certified by naked eyes.

Figure 3(b) and (c) show that the resonant resistance changed differently from the resonant frequency change. The relationship between the resonant resistance and resonant frequency change can be clarified by plotting them in the F-R diagram. From F-R diagram, these results can be analyzed more detail.

CONCLUSIONS

The resonant frequency, resonant resistance, and absorbance changes are observed during the cyclic voltammogram of a Ppy deposited quartz crystal with ITO electrode, which clarify the rheological change and electrochromatic change of the Ppy film by the anion transport. These results show that F-R diagram is a useful technique with which to study the rheology and mass transport phenomenon on the thin film deposited electrodes.

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