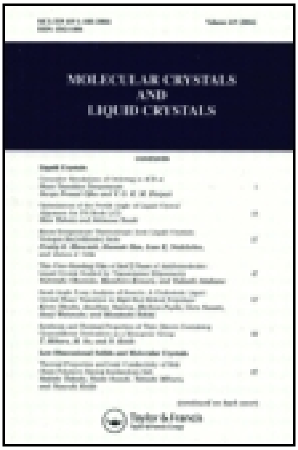

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Changes in Viscoelasticity of Polyaniline during Electrochemical Growth in Aqueous Solutions Probed by In Situ Electrochemical Quartz Crystal Oscillator Method

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Changes in Viscoelasticity of Polyaniline during Electrochemical Growth in Aqueous Solutions Probed by *In Situ* Electrochemical Quartz Crystal Oscillator Method

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In situ electrochemical quartz crystal oscillator method was applied to aqueous acid electrolyte solutions of aniline to investigate changes in viscoelasticity of polyaniline during electrochemical growth. Changes in both resonant frequency and resonant admittance were in the order H_2SO_4 > HNO_3 > HBr > HCl > $HClO_4$ ≥ H_3PO_4 ≥CF_3COOH Thus decreases in resonant frequency during electrochemical deposition of polyaniline included contribution from not only mass but also viscosity and the polyaniline film deposited on electrode surface should be considered to be viscoelastic.

Keywords : viscoelasticity ; polyaniline ; quartz crystal oscillator

INTRODUCTION

Polyaniline has been considered as one of the most promising organic conducting materials, since it can be easily prepared chemically or electrochemically from aniline-containing solutions, is cheap and stable in air and has good conductivity at ambient temperature.[1-14] It has been applied for a high energy density rechargeable lithium batteries, photocorrosion protection, capacitors, electrochemical sensors, electrochromic devices and electromagnetic shielding.

Although a large number of works were performed to understand the electrochemical growth of polyaniline on conducting substrates in synthetic and kinetic aspects, it is true that many fundamental physical and chemical properties of polyaniline formed electrochemically on electrode surfaces are unknown but they are necessary information for successful application of this useful material. For example, microrheological property of polyaniline has been completely neglected. In this work we wish to describe changes in viscoelasticity of polyaniline observed during electrochemical growth by employing *in situ* electrochemical quartz crystal oscillator method in commonly used aqueous electrolyte solutions.

EXPERIMENTAL

All chemicals used in this work were of the best quality available from Aldrich and were used without further purification except aniline, which was purified by distilling under reduced pressure to produce colorless liquid. Solutions were made up with Milli-Q grade water.

Polyaniline was grown by sweeping the potential applied to the electrode between -200 and to 900 mV vs. sodium chloride saturated calomel electrode (SSCE) in solutions of 0.1 M aniline and 1 M acids. For sulfuric acid, 0.5 M aqueous solution was used. All the experiments were performed under argon atmosphere. An electrochemical set-up of three electrode cell was used as before.[5]

RESULTS AND DISCUSSION

Figure 1 shows changes in resonant frequency (a) and in resonant admittance (b) during electrochemical deposition of polyaniline on gold electrode surfaces in the aqueous 0.5 M sulfuric acid solution of 0.1 M aniline for the first six potential cycles between -0.2 and +0.9 V vs. SSCE at 25 mV/s. Cyclic voltammograms simultaneously recorded agreed with those reported in the literature[7,13,14]. As the potential was cycled starting from -0.2 V, resonant frequency decreased and the frequency decrease per cycle increased, indicating that oxidized product of aniline was continuously accumulating on the electrode surface with potential cycles and polymerization reaction was faster on polymer than on gold. Frequency increase in negative sweep observed in the sixth cycle arises from degradation of polyaniline[9-13] and therefore only six potential cycles were applied for the present work. The decrease in resonant frequency does not originate solely from the increase in polyaniline film mass on electrode because resonant admittance simultaneously measured at the same quartz crystal oscillator decreases during the potential sweeps and the changes in resonant admittance or resonant resistance are directly related to material viscosity.[5,14] Decreases in both resonant frequency and resonant admittance imply that polyaniline film on gold electrode surfaces grows viscoelastically during cyclic voltammetric scans in sulfuric acid solutions of aniline.

Resonant admittance versus resonant frequency observed during electrochemical growth of polyaniline in sulfuric acid solutions and those in other acid electrolyte solutions are plotted in Figure 2. Concentration of acids was adjusted to 1 M for comparison purpose. Anions in electrolyte solutions strongly influence the rate of polyaniline growth and results in differentiated decrease in resonant frequency. Tshe present

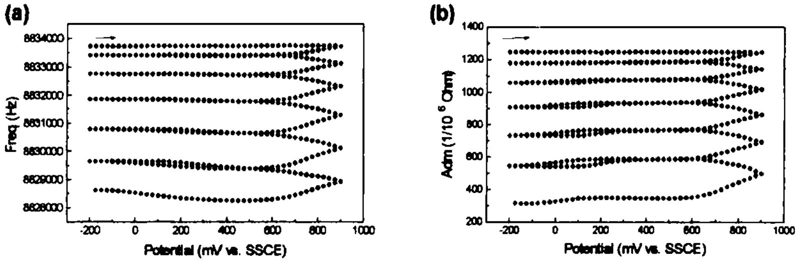

FIGURE 1. Plots of resonant frequency and resonant admittance versus potential during potential cycles in 0.5 M H_2SO_4 and 0.1 M aniline at 25 mV/s.

results show that growth rate is H_2SO_4 > HNO_3 > HBr > HCl > $HClO_4$ ≥ H_3PO_4 ≥ CF_3COOH, in agreement with the literature.[7]

Important message from Figure 2 is that both resonant frequency and resonant admittance decreased during electrochemical growth of polyaniline in all acid solutions investigated in the present work, indicating that polyaniline grows viscoelastically, not elastically, on electrode surfaces. Polyaniline formed in sulfuric acid solution was the largest in inelasticity.

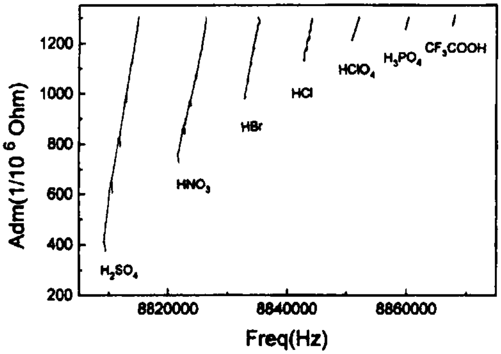

FIGURE 2. Plots of resonant admittance versus resonant frequency during cyclic voltammetric growth of polyaniline. Initial points were shifted for display.

Acknowledgments

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