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Communications

Changes in Viscoelasticity of Polypyrrole during Electrochemical Growth in Aqueous Potassium Bromide Electrolyte Solutions Probed by *in situ* Electrochemical Quartz Crystal Oscillator Method

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Since the first successful demonstration of electrochemically preparing coherent polypyrrole (ppy) films on the electrode surface and of lifting the highly conducting material from it was reported by Diaz *et al.*,¹ a large number of works were published to understand the electrochemical growth of ppy on conducting substrates in aqueous as well as in nonaqueous solutions.^{2,3} Recently most research with ppy has tended to be directed toward technological applications including electromagnetic shielding, electrochromics, controlled drug delivery, chemical separation, environmental remediation and secondary rechargeable battery,⁴⁻⁷ but not all the fundamental physical and chemical properties of ppy are fully investigated. For example, microrheological property of ppy has been largely neglected until the advanced electrochemical quartz crystal microbalance technique which can measure the resonant frequency and resonant resistance simultaneously in real time during electrochemical deposition of ppy was introduced by Muramatsu *et al.*⁷ In that study, it was shown that ppy in aqueous potassium nitrate solutions grew relatively elastic in the beginning but that it became viscoelastic with the film thickness increased. We have established for the first time the cost-effective *in situ* electrochemical quartz crystal oscillator (EQCO) system which consist-

ed of Pine RDE4 and Seiko QCA 917 interfaced to a personal computer. In this first report, we demonstrate that the viscoelastic behavior of ppy can vary significantly as ppy films grow at the electrode/electrolyte interface.

We probed the changes in viscoelasticity during electrochemical deposition of ppy at gold electrode surfaces in aqueous potassium nitrate and potassium bromide electrolyte solutions. The potassium nitrate was chosen to test the capability of our experimental setup, because viscoelastic property of ppy during electrochemical deposition has been recently examined in the electrolyte solution by Muramatsu *et al.*⁷ Bromide anions were selected firstly because they are simple anions, secondly because they are known to strongly adsorb on the electrode surface, thirdly because they have been used to form insoluble organic films of electrode surfaces⁸ and fourthly because ppy films formed in bromide solutions were expected to grow in viscoelasticity different from those grown in nitrate media. The present results show that electrochemically prepared ppy can have a significantly different viscoelastic property with the seemingly minor change of a simple replacement of electrolyte from potassium nitrate to potassium bromide. In the following we avoid presenting the experimental data reproduced on the electrochemical growth of ppy in potassium nitrate media, unless they are required for the purpose of our work.

For the quartz crystal oscillator in contact with the aqueous pyrrole solutions,

$$\Delta F = \frac{-F^2}{(\mu\rho_Q)^{1/2}} \left(\frac{\Delta m}{A} + \left(\frac{\rho_L \eta}{\pi F} \right)^{1/2} \right) \text{ and } R = \frac{(2\pi F \rho_L \eta)^{1/2} A}{k^2}$$

are assumed to be held, where ΔF is the resonant frequency shift, F is the resonant frequency, Δm is the surface mass load, μ is the shear modulus of the quartz crystal, ρ_Q is the density of the quartz crystal, A is the surface area of the quartz crystal, ρ_L is the density of the electrolyte, η is the viscosity of the electrolyte, R is the resonant electrical resistance, and k is the electromechanical coupling factor. Detailed derivation and discussion on the above relationships can be found elsewhere.⁷ In presenting the data, we took the resonant admittance versus resonant frequency plot instead of the resonance resistance versus resonant frequency one because in the former format the two quantities of reso-

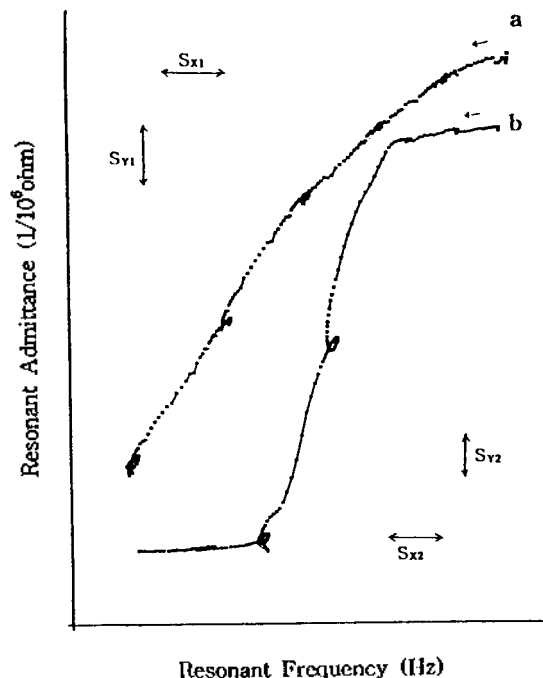


Figure 1. Plot of resonance admittance versus resonance frequency observed during electrochemical deposition of PPy from aqueous 0.2 M pyrrole (pH 7; 30 mM phosphate) in 0.1 M KNO_3 (a) and 0.1 M KBr (b) solutions. $S_{x1}=2000$, $S_{y1}=50$ for (a). $S_{x2}=5000$, $S_{y2}=100$ for (b).

nant admittance and resonant frequency shifts have the same tendency in representing *viscosity* and *mass with viscosity* changes, respectively. Pyrrole was distilled under vacuum and other chemicals used were the best analytical grade available. All the experiments were performed under nitrogen atmosphere with conventional three electrode configuration. 9 MHz quartz crystal oscillators were used throughout.

Figure 1 shows resonant admittance versus resonant frequency changes observed during electrochemical deposition of ppy on gold electrode surfaces in the aqueous 0.2 M pyrrole (pH 7.0; 30 mM phosphate) and 0.1 M potassium nitrate (a) or 0.1 M potassium bromide (b) solutions for the first five potential cycles between 0 V and +1.0 V vs SCE at 25 mV/s. In both cases of (a) and (b), the base capacitive current gradually increased with the number of voltammetric scan increased, as is shown in Figure 2(a), indicating that ppy grew continuously on electrode surfaces. Cyclic voltammograms observed in the presence of 0.2 M pyrrole solution and 0.1 M potassium nitrate were reported elsewhere.⁷ It should be noted from the first scan of Figure 2(a) that bromide anions are not significantly oxidized in the aqueous pyrrole solutions in the present experimental conditions. In the case of ppy growth in potassium nitrate solutions, resonant admittance and resonant frequency decrease in the beginning and do gradually increasingly as ppy films become thicker, which agrees with a previous observation that ppy film grew relatively elastic in the beginning and became viscoelastic in the further deposition from resonant resistance versus resonance frequency measurement at the scan rate of 50 mV/s in the similar medium.⁷ Apparently a slower scan rate of 25 mV/s used in the present study caused the grow-

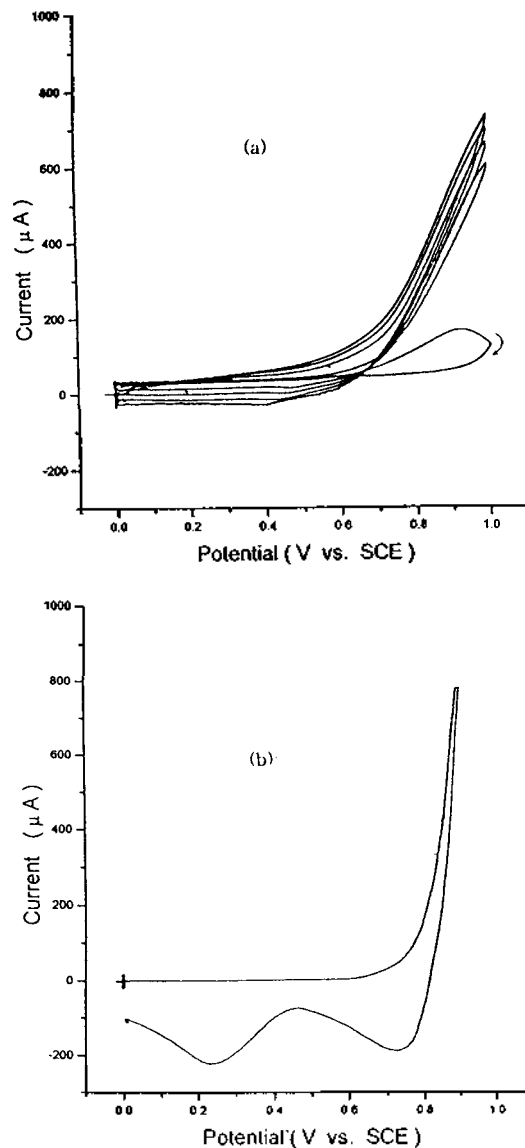


Figure 2. Cyclic voltammograms at gold electrode in aqueous 0.1 M KBr solutions (pH 7; 30 mM phosphate) in the presence (a) and in the absence (b) of 0.2 M pyrrole. Electrode area: 0.20 cm^2 , Scan rate: 25 mV/s.

ing ppy film layers to swell more during cyclic scans, which is also supported by the fact that electrochemical deposition of ppy at smaller constant current mode grew less elastic in the early stage.⁷ Radically different from the one seen in the potassium nitrate solution was it observed when the identical experimental conditions were used except the anion replaced with bromide (b). Within the experimental range of ppy growth investigated, the film grew nearly elastic in the first stage, inelastic in the middle part and nearly elastic again in the last stage. Ribbons in the middle part of resonant admittance versus resonant frequency diagram may indicate the dynamic nature of movement of electrolytes and solvent molecules at the conducting polymer film electrode/electrolyte interface during potential scans. Further clear demonstration of changes in viscoelasticity of ppy film electrochemically deposited in the potassium bromide solu-

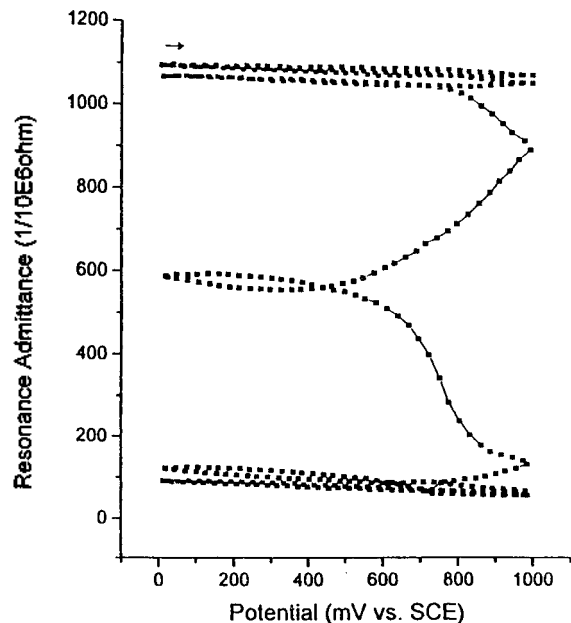


Figure 3. Change in resonance admittance observed during potential cycling in aqueous 0.2 M pyrrole (pH 7; 30 mM phosphate) and 0.1 M KBr solutions.

tion is shown in Figure 3, where resonant admittance shifts were plotted as the electrode potential was scanned cyclically. Sudden changes in resonant admittance are noticed between the nearly constant resonant admittance values observed during cyclic scans in the beginning and final stages. Similar changes in viscoelasticity of ppy were observed with longer scans when the potential scan was limited up to less positive potentials in the aqueous potassium bromide solution of pyrrole. For example, ten hours of continuous potential scans were required to observe the elastic to viscoelastic to elastic ppy films in the identical experiments except the potential window of zero to 0.65 V vs SCE. Thus three-stage evolution of viscoelasticity of ppy with films thicker is real in the presence of potassium bromide. We note that with platinum films deposited on mica by rf sputtering the three-stage evolution of platinum topography and crystallinity is evidenced for films of thickness between 20 and 1500 Å by scanning tunneling microscopy (STM).⁹ We believe that the present EQCO results on ppy in the potassium bromide electrolyte are the first example showing the viscoelastic or structural evolution of conducting polymer films with thickness increased at the electrode/electrolyte interface. Further studies are in progress to investigate the viscoelastic property of ppy growing in different electrolyte media and to characterize the possible evolution of surface topography by STM.

In conclusions, we have established the cost-effective *in situ* electrochemical quartz crystal oscillator system to probe changes in viscoelastic property during electrodeposition and demonstrated that the viscoelastic property of ppy film prepared in aqueous potassium bromide solutions is fundamentally different from that in aqueous potassium nitrate solutions and that it significantly vary as film thickness increased.

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Conformational Studies on the DNA Oligomer d[(CG)₃TA(CG)₃] Duplex Induced by Hexaminecobalt(III) Chloride

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The B-Z transition illustrates that the conformational properties of DNA depend on the nature of the bases, the DNA sequences, and the solvent environment.¹ Z-DNA has been formed for some sequences which contain A·T as well as G·C basepairs.² However, the consecutive insertion of A·T basepairs into (dC-dG)_n stretches in DNA oligomers strongly inhibits the formation of Z-form DNA. If two or more A·T basepairs, in an alternating purine-pyrimidine pattern, are inserted between stretches of alternating (dC-dG)_n, either the entire sequence may adopt a Z-DNA structure or only the (dC-dG)_n stretches may do so. This depends on the solution conditions, the length of the (dC-dG)_n stretches, and the number of A·T basepairs. For example, the oligomer duplex, d(CGCGTACGCG)₂, does not form a left-handed helix under any condition,³ but the Z-Z junction is formed in the d[(br⁵-CG)₂TTAA(br⁵-CG)₂] duplex.⁴ We have found that 2 mM Co(NH₃)₆Cl₃ converts the right-handed helix of the oligomer d(CG)₅ into a left-handed helix at room tempe-