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"In-situ" Quartz Crystal Microbalance Responses and Electrochemistry Regarding Langmuir–Blodgett Film of Viologen Polyion Complex on the Electrode Surface

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The electrochemical behavior and the response of the quartz crystal microbalance(QCM) for the Langmuir–Blodgett(LB) viologen film have been examined. LB monolayers employed are prepared by electrostatically fixing the viologen monolayer containing the alkyl chain moiety on the poly(potassium 1-sulfatoethylene). The number of monolayers accumulated on the polycrystalline Au electrode of a piezoelectric quartz crystal was controlled by changing the general vertical dipping times. The QCM frequency response for the first reduction scan of viologen dication (V^{2+}) to monocation radical ($V^{+\bullet}$) shows extremely large frequency increase, qualitatively indicative of mass loss, viscoelasticity decrease, or mechanical stress decrease during the reduction. A frequency increase during the second reduction scan is also observed, although not as large as for the first scan. The frequencies increase continuously with increasing number of scans and the steady-state responses can only be obtained after many repetitive potential scans. The results of the conductance spectra measurements of the quartz crystal/LB film composite resonator are interpreted as break-in and/or an increase of aggregation of the orientated structure during potential scans. The cyclic voltammetric wave obtained in the potential range 0 to −0.7 V vs. sodium chloride saturated calomel electrode has the characteristics of a simple, one electron transfer between V^{2+} and $V^{+\bullet}$, being chemically reversible process. The subsequent cyclic voltammogram responses obtained after the first cycle of potential scan are nearly identical for some hours, in contrast to the responses of the QCM. It is shown that structural change of the organized film dose not have a significant influence on the shape of the electrochemical response but does have an effect on the frequency response of the QCM.

Recently, the in situ technique of the electrochemical quartz crystal microbalance (EQCM) has received great attention as a high-sensitive probe to perform the measurement of mass, viscoelasticity and/or mechanical stress changes that accompany redox processes in both monolayer and multilayer films on electrodes. In several systems including inorganic films, polymer metal complex films, conducting polymers, and organic redox polymer films, both ion and solvent transports have been measured during redox reactions.[1—3] Although the possibility of nonrigid viscoelastic film behavior exists for organic polymers, we reported that for the amorphous film of osmium bipyridyl polymer the rigid-layer approximation is valid.[4]

As a part of our ongoing research to characterize the behavior observed in the electrochemistry of geometrically organized thin films containing redox active sites,[5] we are interested in the examination of how the ion migration and swelling processes can influence the activities of redox groups in such films in which solvent and ionic species are incorporated. Previously, a peculiar odd-even effect of alkyl chain connection among viologen groups, the polyion complex films of which were prepared from viologen polymers and anionic bilayer membrane, was found in the diffusion coefficients of the charge transport process.[5] In this paper we examine the electrochemical behavior, the frequency response of the EQCM and the conductance spectra response obtained with the Langmuir–Blodgett (LB) film of viologen, which was prepared by electrostatically fixing the viologen monolayer having alkyl chain moiety on a poly(pottasium 1-sulfatoethylene) monolayer. We will evaluate the mass change and/or the viscoelasticity change in the films during the course of charge propagation as a function of amount of redox cycling between V^{2+} to $V^{+\bullet}$.

Experimental

Apparatus and Procedure. 5 MHz AT cut quartz crystals of 13 mm diameter (Toyo Kurafuto) were coated on both faces with Au (ca. 300 nm) using a Cr adhesion underlying layer (2 nm) by vacuum deposition.[6] An asymmetric keyhole electrode arrangement was used in which the piezoelectrically active area (0.28 cm^2) was smaller than the area of the working electrode face (0.64 cm^2). This arrangement has a mass sensitivity of 5.65×10^7 Hz cm^2 g^{-1}.

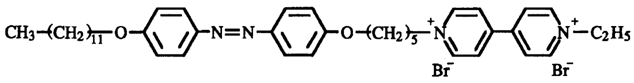
The resonant frequency was determined with the crystal as the active element of an oscillation circuit using a Hewlett Packard 5334B universal counter and its response is stable at the level of ±0.1 Hz. The conductance spectra of the quartz crystal/polymer film/solution composite resonators were measured with a Hewlett Packard 4192A impedance analyzer interfaced to a PC-9801 (NEC) using a GP-IB interface. The conductance was measured under condition (0.0 V vs. a saturated sodium chloride calomel electrode (SSCE)) of potentiostatic control of the cell. Electrochemical measurements were conducted with the working electrode at ground in an operational amplifier based potentiostat/galvanostat (Polarization Unit PS-06, Toho Technical Research) in an earthed Faraday cage. A Pt wire was used as the counter electrode in a glass frit separated compartment and an SSCE was used in aqueous electrolytes as the reference electrode. All chemicals used were of guaranteed reagent grade. All experiments were carried out in 0.2 M $NaClO_4$ solutions (1 M=1 mol dm^{-3}) at room temperature (25±1°C). The solutions were deaerated with prepurified nitrogen.

The LB films were allowed to dry for 1 d under ambient conditions before attachment of the crystal to the side arm of an electrochemical cell using silicone rubber. The geometric area of the film exposed to solution, not covered with silicone, was determined accurately for each case and was typically 0.5 cm^2.

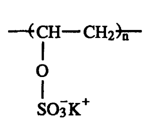
Preparation of Langmuir–Blodgett Film. Bilayer-forming viologen having the azobenzene functional group was deposited on the electrode surfaces by the LB technique reported previously.[8,9] Insoluble monolayer of viologen **1** in Fig. 1 used in LB film deposition was formed at the interface of air-aqueous solutions by formation of polyion complexes between viologen dication and the negatively charged polymer of poly(potassium 1-sulfatoethylene) **2** dissolved in water. The spreading solvent of **1** was a 9 : 1 (by volume) mixture of chloroform and ethanol. The concentration of **2** was approximately 10 mg dm^{-3}. The water used as the subphase was purified by Milli-Q system.

A fully computer-controlled film balance and a film lift (FSD-20 and 21, Sanesu Keisoku, Japan) was used for measurements of surface pressure-area isotherms (π–A curves) and for preparation of LB films, and the experimental data were analyzed by a personal computer (NEC PC 9801 Vm II). A typical example of the surface pressure-area curves is shown in Fig. 2(a). Each monolayer was deposited on the quartz crystal electrode at 25 mN min^{-1} at 20±0.5°C and the dipping and lifting speeds were 10 and 100 mm min^{-1}, respectively. Figure 2(b) shows a proposed structure in the resultant LB film on the electrode surface.[9]

The Au electrodes were subjected to Ar etching treatment for the purpose of changing the originally hydrophobic Au surface to a hydrophilic surface. The π–A curve did not change for the first dipping process using the Au electrode with no Ar treatment. Here, the formation of a film layer on the electrode was justified from the surface pressure-area curves.[9]



1 : $C_{12}AzoC_5EV^{2+}$



2 : poly(pottasium 1-sulfatoethylene)

Fig. 1. Viologen ($C_{12}AzoC_5EV^{2+}$) having azobenzene functional group and poly(potassium 1-sulfatoethylene) used for the LB-film preparation.

Results and Discussion

Cyclic Voltammetric Measurements. Figure 3 shows typical steady-state cyclic voltammetric responses of a surfactant of alkylviologen coated on the quartz crystal Au electrodes in 0.2 M $NaClO_4$ aqueous solution at a potential scan rate 10 mV s^{-1}. The responses obtained for variation of the number of viologen layers coated on the electrode surface through successive dipping are shown. The results are typical with three trials carried out for the same number of LB layers. Several interesting features to note exist in the CV responses. The peak current increased with the deposition of each additional monolayer. This means that packing defects are present allowing the electron trans-

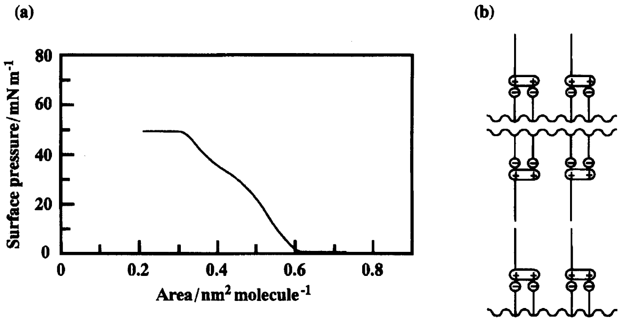


Fig. 2. (a) Surface pressure–molecular area isotherm (π–A curve) of $C_{12}AzoC_5EV^{2+}$/poly(1-sulfatoethylene) at 20±1°C and (b) the structure of $C_{12}AzoC_5EV^{2+}$/poly(1-sulfatoethylene) polyion complex LB films.

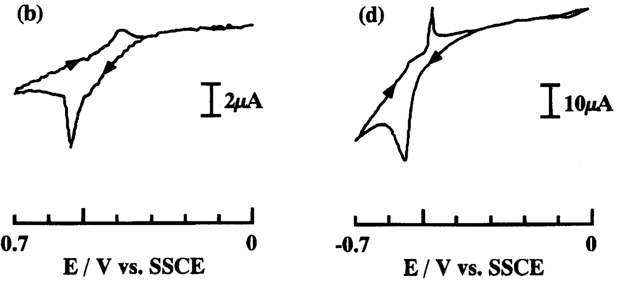


Fig. 3. Steady-state current-potential curves of $C_{12}AzoC_5EV^{2+}$/poly(1-sulfatoethylene) LB film coated QCM electrodes: (a) bare (b) 2-monolayer (c) 5-monolayer (d) 20-monolayer in 0.2 M $NaClO_4$ aqueous solution. Scan rate; 10 mV s^{-1}.

fer reaction to occur and that viologen centers between different layers are connected, because the large separation distance between the active redox layers in a multilayer assembly and the distance between two neighboring layers of viologen would hinder the electron transfer reaction at the electrode/film interface. Packing defects and/or breakage of the layered structure which produce the electron transfer path are promoted by the first potential scan of the viologen reduction, as being deduced from the large difference between the peak potentials of the first and the second reduction peaks shown in Fig. 4. The reduction peak current for the first scan was obtained at slightly more negative potential than that obtained for the second scan. In general, after several potential scans, steady-state cyclic voltammograms which have the same magnitude of peak current and a constant peak potential of oxidation–reduction of viologen, could be obtained for several hours. Film defects and/or structure breakage which are created due to the charge imbalance and solvation change during the electrochemical reduction and oxidation reactions contribute to permit facility of the electron transfer reaction and their contributions to the electron transfer process apparently become constant after several potential scans. As demonstrated in Fig. 5, although the peak currents observed increase with increasing number of viologen layers, the absolute peak currents which would be expected from the surface coverage of viologen are suppressed. The suppression is likely the result of a slowdown in the electron transfer process across the viologen layer and/or the slowdown of the mass transfer process of counter ion movement for neutralization within the film.

With thick films i.e. more than 5 monolayers of a surfactant of viologen, the peak currents are almost proportional to the square root of scan rates ranging from 10 to 500 mV s^{-1}, as would be expected for a reversible diffusion-controlled voltammogram.$^{10,11)}$ However, note that the surface coverages estimated from the integration of the CV were smaller than those expected from the molecular area (0.48 nm^2/molecule) of the LB isotherm at the pressure of 25 $mN\,m^{-1}$ by factors of 0.5—0.8. This indicates that not all the viologen of the coating are electroactive. It means that there exists a hydrocarbon layer resulting in a distance barrier to the electron transfer and/or a hydrophobic region in the films where the viologen moiety is aggregated, thereby hindering the solvation of the viologen and the access of the supporting electrolyte to viologen. This explanation seems to be reasonable from the fact that a large portion of the viologen is the hydrophobic moiety composed of alkyl chain. A similar behavior has been observed for other viologen coatings.$^{11)}$

Responses of Quartz Crystal Microbalance. Figure 6 shows the frequency responses as a function of redox cycling for the viologen coated on the Au electrodes. The EQCM frequency response for the first negative-potential scan over the potential showing reduction peak current shows extremely large frequency increase, qualitatively indicative of mass loss according to Sauerbray equation,$^{7,12—15)}$ a viscosity decrease,$^{16)}$ and/or stress release,$^{17)}$ during reduction. With the scan over the potential region of an anodic peak wave, the frequency decrease slightly, but the frequency change does not recover its initial value. Therefore, some of the irreversible processes contributing to the increase of the frequency at the potential of 0 V vs. SSCE still exist within the film after the charge propagation. The magnitude of frequency change (Δf) between initial scan and second scan at 20-monolayer coated electrode is +260 Hz which corresponds to the recovery of 13% against nearly 2000 Hz reduction obtained when the corresponding same electrode was soaked in an aqueous solution. In general, we investigated about 2000 Hz decrease in the resonant frequency response accompanying the exposure of the electrode to a bathing aqueous solution. This reduction of the frequency would be caused by the changes of the electrode surfaces and bulk liquid-phase properties such as density, viscosity, and conductivity et al., as described in the literature.$^{18)}$ Therefore, we notice that the increase of the frequency which is induced by electrochemical reaction not large compared with the value induced by the bathing process described above.

The frequency change during the second potential scan is smaller than that during the first potential scan, as seen from Fig. 6. The above-mentioned incomplete return of the frequency is not observed after a long time potential scan cycling; for example, it takes 90 min for the 20-monolayer coated electrodes as shown in Fig. 6(c) to reach the steady-state. On the other hand, a stable steady-state CV response can be obtained after a couple of potential scan and the magnitude of the peak currents of oxidation and reduction of viologen will not decay as shown in Fig. 4. Consequently, the behavior of the EQCM response suggests that an irreversible process involving loss of viologen is not present in the overall redox reaction. Possible origins other than viologen loss should be considered and may be changes of the LB membrane such as increased hydrophobicity$^{18e)}$ by aggregation, decreased mechanical stress,$^{6b)}$ et al. In the EQCM/CV experiments, it was found that the frequency–potential response depends largely on the number of monolayer coated on electrodes. The frequency change obtained during potential scanning increases with the increase of the number of monolayer as being found in a typical example of experiments shown in Fig. 6. In the case of the bare Au electrode, a very small frequency change during the reduction process is observed, being ascribed to a small amount of adsorption of the intermediate hydrogen atom and its frequency returns to the initial value after the oxidation process.$^{6)}$ After attainment of the stable EQCM responses, that is, when the complete

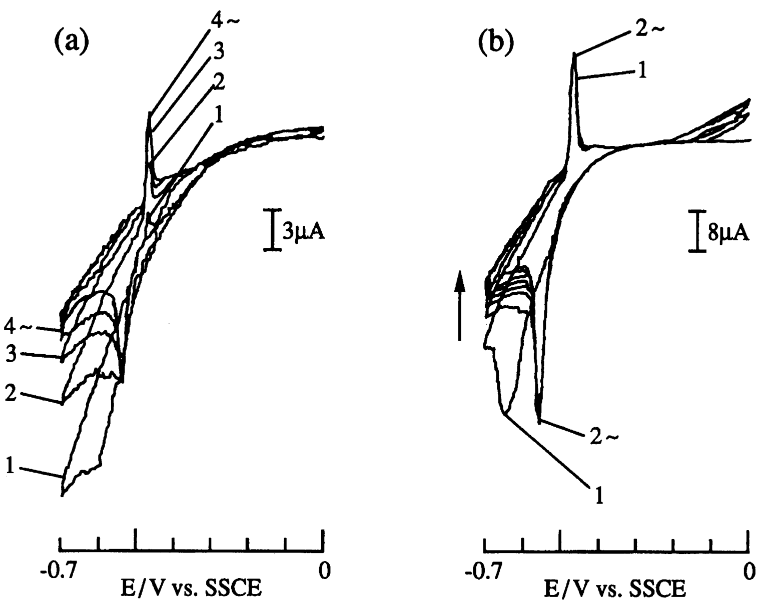


Fig. 4. Cyclic voltammograms obtained for successive potential scans (a) at 5-monolayer and (b) at 20-monolayer coated QCM electrode in 0.2 M $NaClO_4$ aqueous solution. Scan rate: 10 mV s^{-1}.

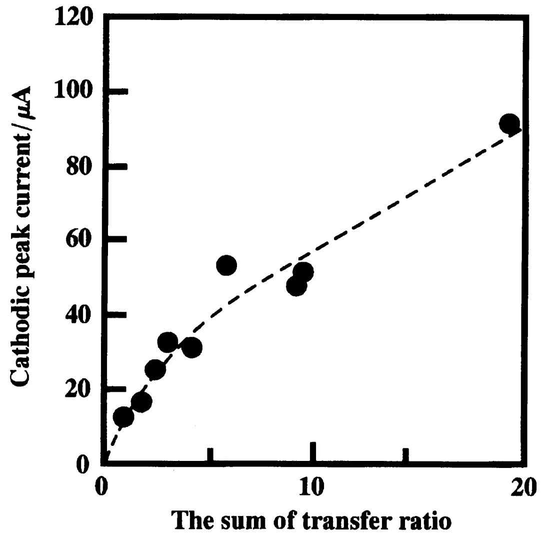


Fig. 5. Dependence of cathodic peak currents upon the sum of transfer ratio for each C_{12}Azo-C_5EV^{2+}/poly(1-sulfatoethylene) LB films coated on QCM electrode. These data were obtained from cyclic voltammograms at scan rate of 50 mV s^{-1} in 0.2 M $NaClO_4$ aqueous solution.

frequency returning is achieved, we could observe that the reduction of viologen induces a frequency increase and the oxidation of the monocation radical accompanies the recovery of the frequency. In the case of the 20-monolayer coated electrode, as being shown in Fig. 7, the value of Δf obtained with the steady-state EQCM responses means that a change in mass of 98 g per mol of viologen species occurs during the reduction process, if the Δf occurs as a result of only the mass change in the film. This result indicates that the reduction of a viologen accompanies the ejection of one unsolvated ClO_4^- anion (molecular mass, 99 g mol^{-1}). The steady-state EQCM response for 0.2 M $NaClO_4$ can be mainly explained by the anion doping and undoping processes and is typical of permselective anion mass transport in analogy with the mass transport process in the thin film of $[Os(bpy)_2PVP_{10}Cl]^+$ during the redox reaction of the $Os^{2+/3+}$ couple (bpy=2,2′-bipyridyl; PVP=poly(4-vinylpyridine)) reported previously.[4] This means that the charge imbalance induced by the oxidation–reduction of the $V^{+\bullet}/V^{2+}$ couple is compensated by anion movement, since the charge of poly(1-sulfatoethylene) in the film is fixed.

As pointed out above, the EQCM frequency response for the first potential scan shows extremely large frequency increase and its magnitude is more than ten times that of the steady-state response. The frequency continued to increase but it's magnitude becomes gradually smaller for each of the potential scan cycles. As mentioned by Battry et al. recently,[16] the results in Fig. 6 are sometimes expected for organic films. Battry has examined the solvent swelling influences for thin films of nitrated polystyrene and pointed out that a measure of how the extent of swelling changes with scanning can be obtained by monitoring frequency change versus the number of scans. The present system consists of LB monolayers of viologen prepared by electrostatically fixing the viologen containing an alkyl chain moiety on the poly (pottasium 1-sulfatoethylene) and thus the regularly oriented bilayer membrane will be a semi-stable situation having mechanical stress. The charge propagation by the oxidation–reduction reaction of viologen induces structure breaking of a part of the oriented film by solvent swelling or ionic aggregation, and/or incorporation of ionic species from the support-

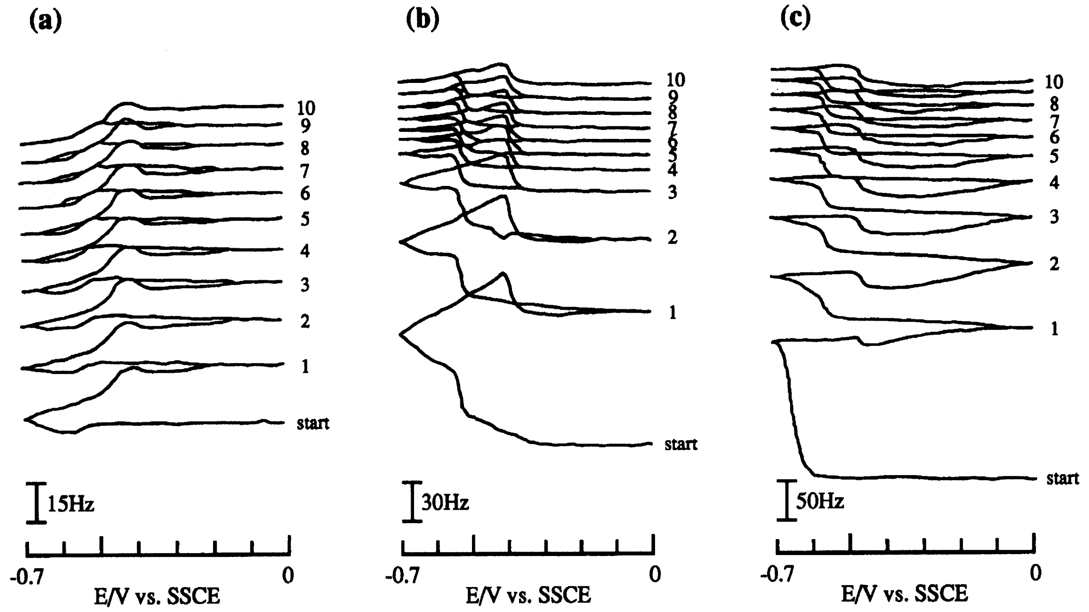


Fig. 6. Potential–frequency curves obtained for successive potential scans (a) at 1-monolayer, (b) at 5-monolayer and (c) at 20-monolayer coated QCM electrodes in 0.2 M NaClO$_4$ aqueous solution. Scan rate: 10 mV s^{-1}.

ing electrolyte solution into the film. The large frequency changes at the initial stage of the potential cycles seem to be due to the factors of viscosity change of the film, ionic aggregation in the film, and release of mechanical stress as mentioned above.

Conductance Measurements. The relationship between frequency and mass given by $\Delta f = -K_f \Delta m$, where K_f is a constant, is satisfied for some of thin films of organic polymers, i.e., poly(vinylferrocene),[19—21] polyaniline,[5,14,22] polypyrrole[23—25] and the film of [Os(bpy)$_2$PVP$_{10}$Cl]Cl during redox of the Os$^{2+/3+}$ couple (bpy = 2, 2′-bipyridyl; PVP = poly(4-vinylpyridine)).[4] The relationship of $\Delta f = -K_f \Delta m$ holds only for rigid films and in these systems mentioned above the film was concluded to exhibit rigid layer behavior. However, this is not to be generally expected and thus the question of whether or not rigid layer behavior prevails must be addressed for each individual system. One straight forward way to distinguish whether the present system exhibits rigid layer behavior or frequency dependent viscoelastic behavior is to measure the conductance spectrum of the EQCM/polymer film composite resonator.[26] The conductance of the EQCM electrode coated with viologen film is measured as a function of frequency, and, from this, the influence of viscoelasticity in the film on the resonance frequency is determined. The extent of viscoelasticity is determined by the ratio (R) of the resonant frequency f_0 to the full width at half height $\Delta f^{w}{}_{1/2}$ of the conductance. The conduc-

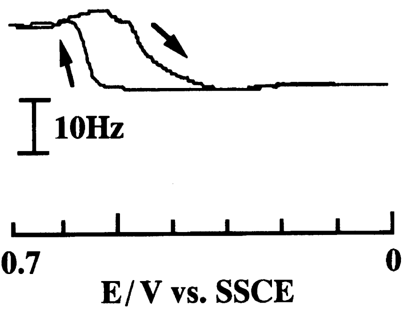


Fig. 7. Steady-state potential–frequency curves obtained at 20-monolayer coated QCM electrode after more than 90 min in 0.2 M NaClO$_4$ aqueous solution. Scan rate; 10 mV s^{-1}.

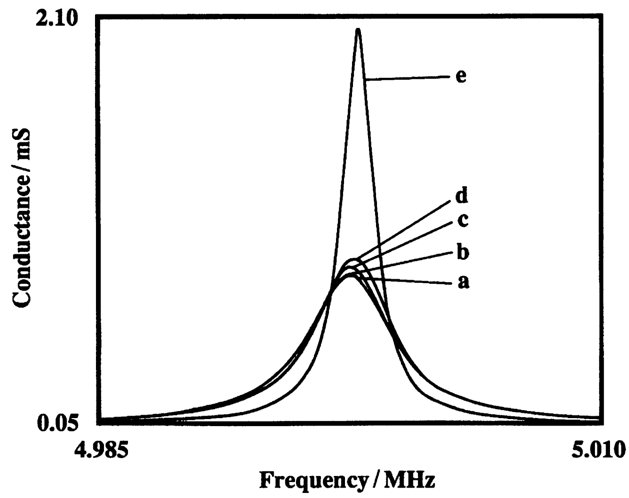


Fig. 8. Conductance–frequency characteristics of the LB film (3 layers) coated QCM electrode obtained (a) before electrochemistry, (b) after 1 scan, (c) after 5 scans, and (d) after 10 scans and the characteristics of (e) was obtained at a bare Au electrode.

tance spectra behavior of an LB film coated electrode soaked in 0.2 M $NaClO_4$ aqueous solution is shown in Fig. 8, being obtained before and after performing potential scan cycles in the range of potential 0.0 V to −0.7 V vs. SSCE. The value of R becomes significantly smaller after fixing the electrode to the cell and soaking the electrode in the solution. It can be considered that these changes in R are caused by a source independent of that caused by film viscoelasticity. The value of $\Delta f^{w}{}_{1/2}$ for the film coated electrode before any potential scans is 5038 Hz which depends upon how to fix the electrode to the experimental cell. After one potential scan the $\Delta f^{w}{}_{1/2}$ is 5028 Hz. The difference of the $\Delta f^{w}{}_{1/2}$ between before and after of one potential scan is small, although the resonant frequency change is relatively large (65 Hz) as justified from Fig. 6. Therefore, the resonant frequency change in the initial potential scan cycle may be mainly attributable to the release of the mechanical stress of an LB film. After 10 scans, $\Delta f^{w}{}_{1/2}$ becomes 4404 Hz. On the other hand, the value of $\Delta f^{w}{}_{1/2}$ for the bare electrode which is fixed to the cell and soaked in the aqueous solution is 1866 Hz and keeps constant after several potential cycles. That the value of $\Delta f^{w}{}_{1/2}$ obtained with the bare electrode is significantly smaller than that obtained with the film coated electrode is good evidence of viscoelastic behavior for the film coating, which causes broadening of the conductance spectra due to viscous loading by the film. Furthermore, these data demonstrate that $\Delta f^{w}{}_{1/2}$ decreases during the redox cycling, that is, viscosity of the film is decreased by the redox cycling. This probably means that the ionic aggregation is promoted by the charge propagation of the oxidation–reduction reaction of the viologen at local regions within the film.

Conclusions

This work demonstrates that in situ EQCM measurement can provide fruitful information regarding the changes of film morphology during the course of charge propagation as a function of potential cycling. It became apparent that the observed frequency changes versus the potential scan do not simply correspond to doping and undoping processes of the counter ion into and from the film but exhibit a viscoelastic behavior of the film and a change of mechanical stress. During the charge propagation through the film, oriented LB bilayer membranes which are prepared by electrostatically fixing the electroactive species on the ionic polymer are subject to large frequency changes but do not significantly influence the shape of the electrochemical responses. A detailed estimation of morphology changes is now in progress.

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References

1) C. Lu and A. W. Czanderna, "Methods and Phenomena, Vol. 7, Applications of Piezoelectric Crystal Microbalance," Elsevier, New York (1984).

2) J. Janata, "Principles of Chemical Sensors," Plenum Press, New York (1988) Chap. 3.

3) M. R. Deakin and D. A. Buttry, *Anal. Chem.*, **61**, 1147A (1989), and references therein.

4) a) A. J. Kelly, T. Ohsaka, N. Oyama, R. J. Forster, and J. G. Vos, *J. Electroanal Chem.*, **287**, 185 (1990); b) A. J. Kelly and N. Oyama, *J. Phys. Chem.*, **95**, No.23, 9579 (1991).

5) M. Shimomura, K. Utsugi, J. Horikoshi, K. Okuyama, O. Hatozaki, and N. Oyama, *Langmuir*, **7**, 760 (1991).

6) H. Daifuku, T. Kawagoe, N. Yamamoto, T. Ohsaka, and N. Oyama, *J. Electroanal. Chem.*, **274**, 313 (1989).

7) G. Sauerbrey, *Z. Phys.*, **155**, 206 (1959).

8) M. Shimomura and T. Kunitake, *Thin Solid Films*, **132**, 243 (1985).

9) M. Shimomura, Y. Hamada, and T. Onosato, *Thin Solid Films*, **160**, 287 (1988).

10) N. Oyama and F. C. Anson, *J. Electrochem. Soc.*, **127**, 640 (1980).

11) N. Oyama, T. Ohsaka, H. Yamamoto, and M. Kaneko, *J. Phys. Chem.*, **90**, 3850 (1986).

12) S. Bruckenstein and A. R. Hillman, *J. Phys. Chem.*, **92**, 4837 (1988).

13) S. Bruckenstein, C. P. Wilde, M. Shay, A. R. Hillman, and D. C. Loveday, *J. Electroanal. Chem.*, **258**, 457 (1989).

14) D. Orata and D. A. Buttry, *J. Am. Chem. Soc.*, **109**, 3574 (1987).

15) S. J. Lasky and D. A. Buttry, *J. Am. Chem. Soc.*, **110**, 6258 (1988).

16) R. Borjas and D. A. Buttry, *J. Electroanal. Chem.*, **280**, 73 (1990).

17) G. T. Cheek and W. E. O'Grady, *J. Electroanal. Chem.*, **277**, 341 (1990).

18) a) G. G. Guilbault, in "Applications of Piezoelectric Quartz Crystal Microbalances: Methods and Phenomena. Their Applications to Science and Technology," ed by C. Lu and A. W. Czanderna, Elsevier, New York (1984), Vol. 7, p. 251; b) T. Nomura and M. Iijima, *Anal. Chim. Acta*, **131**, 97 (1981); c) S. Bruckenstein and M. Shay, *Electrochim. Acta*, **30**, 1295 (1985); d) K. K. Kanazawa and I. Gordon, *Anal. Chim. Acta*, **175**, 99 (1985); e) L. V. Rajakovic, A. B. Cavic-Vlasak, V. Ghaemmaghami, K. M. R. Kallury, A. Kipling, and M. Thompson, *Anal. Chem.*, **63**, 615 (1991).

19) P. T. Varineau and D. A. Buttry, *J. Phys. Chem.*, **91**, 1292 (1987).

20) A. R. Hillman, D. C. Loveday, and S. Bruckenstein, *J. Electroanal. Chem.*, **274**, 157 (1989).

21) M. Mizunuma, T. Ohsaka, H. Miyamoto, and N. Oyama, *Bull. Chem. Soc. Jpn.*, **64**, 2887 (1991).

22) D. Orata and D. A. Buttry, *J. Electroanal. Chem.*, **257**, 71 (1988).

23) C. K. Baker and J. R. Reynolds, *J. Electroanal. Chem.*, **251**, 307 (1988).

24) J. H. Kaufman, K. K. Kanazawa, and G. B. Street, *Phys. Rev. Lett.*, **53**, 2461 (1984).

25) K. Naoi, M. M. Lien, and W. H. Smyrl, *J. Electroanal. Chem.*, **272**, 273 (1989).
26) M. O'Donnell, L. J. Buses, and J. G. Miller in "Methods of Experimental Physics, Ultrasonics," ed by P. D. Edmonds, Academic Press, New York (1981), Vol. 13, Chap. 3.