

Poly-3,4-dihydroxybenzaldehyde Modified with 3,4-dihydroxybenzoic acid for Improvement of Electrochemical Activities

Seong-Keuck Cha[†]

Department of Chemistry Kyungnam University, Masan, 631-701, Korea

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Abstract : 3,4-dihydroxybenzaldehyde(3,4-DHB) was oxidatively electropolymerized on glassy carbon (GC) electrodes to prepare GC/p-3,4-DHB type electrodes, which were subsequently modified with 3,4-dihydroxybenzoic acid(3,4-DHBA) using 0.05M HCl as a catalyst. The esterification reactions were performed between -OH sites on the polymeric film surface of the p-3,4-DHB and the -COOH sites within the 3,4-DHBA molecules in solution. These reactions had a rate constant value of $1.18 \times 10^{-1} \text{ s}^{-1}$ for the esterification step as obtained from the first-order rate constant in the solution. The electrochemical responses of the GC/p-3,4-DHB-3,4-DHBA electrodes exert an influence upon the buffer solution, its pH and applied potential ranges. The redox process of the electrode was more easily controlled by charge transfer kinetics than that of the GC/p-3,4-DHB. The modified electrodes had redox active sites that were 10 times more active than those present before modification. The electrical admittance of the modified electrodes was also three times higher than that of the unmodified electrodes. After being annealed in ethanol for 20 hrs the electrodes brought about a 3.3 times greater change of water molecules in the redox reaction. The modified electrodes are stable in the potential range of 0.4 to 0.55 V.

Key words : 3,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, Electropolymerization, quinone, and esterification

1. Introduction

There are various ways of making polymer modified electrodes(PME). One of them involves the direct electropolymerization of electrode surface, which has the advantage of producing a homogeneous surface morphology with easy control of the extent of polymer. Phenol¹, aniline², pyrrole³ were anodically polymerized and the olefin could be reductively polymerized⁴. Those polymers containing a redox couple, such as ferrocene⁵ and $[\text{Ru}(\text{v-bpy})_3]^{2+,6}$ are polymerized using a reduction procedure. One of the non metallic redox polymers⁷ is 3,4-dihydroxybenzaldehyde(3,4-DHB)⁸, which has an o-quinone moiety that is known to be very active in electrochemistry, having a formal potential of *ca* 0.20 V vs. Ag/AgCl. Also, the presence of the o-quinone moiety gives this polymer catalytic ability for the oxidation of NADH at the glassy carbon electrode with the result that it is frequently used in enzymatic reaction⁹.

In this work, 3,4-DHB was electropolymerized on the glassy carbon electrode. The resulting polymer was subsequently modified with 3,4-dihydroxybenzoic acid(3,4-DHBA) to enhance the electroactive sites on the polymeric film by the esterification reaction of the -OH group on the surface of the polymer and the COOH group of the modifier. The catalyst was hydrogen chloride, which is known to have the highest catalytic constant in this reaction¹⁰. As in the reaction shown in

scheme I below, the reaction was accomplished in multiple steps under acidic catalysis. The extent of the reaction could be regulated by controlling the reaction time and the concentrations of the 3,4-DHBA. The electrochemical properties of the polymer modified electrodes were studied in both acetate and phosphate buffer solution and at several pH of values.

2. Experimental

2.1. Instruments and reagents

Electrochemical experiment was performed using EG & G 273A potentiostat/galvanostat with 270/250 software. A scan rate of 50 mVs^{-1} was employed in cyclic voltammetry(CV) experiment. The potential was measured in the range from -0.4 to 0.70 V in comparison with a silver-silver chloride reference electrode (Ag/AgCl). CV was used to evaluate the characteristics of the polymer modified electrodes(PME) and the ion association during the redox reaction. Glassy carbon (diameter = 0.2 cm) was inserted in a teflon tube which was polished successively with sand paper(1000 cp) and diamond paste (Struers, Denmark; 1 m) and then rinse with water-acetone. In those cases where activated electrodes were employed, the polished electrodes were placed in 1.0 M NaOH solution and potential was held at 1.20 V for 5 min followed by the potential cycling from 0.2 to +1.0 V in buffer solution for 5 min. The electrode was then rinsed with water, and used for polymerization⁹. An EG & G OP-amp(model 5210) with M398 software was employed for the measurement of the electro-

[†]E-mail: chask@kyungnam.ac.kr

chemical impedance along with a Philip model 8043 from Philips x-y recorder. A quartz crystal analyzer(Seiko-EG & G: QCA-917) was employed for the EQCM experiments. The electrochemical impedance spectra(EIS) was measured by potentiostat(273A), 5210 lock-in amplifier and 276 interface (EG & G). A EIS curve was then constructed by constant potential a.c.-impedance spectrometry from the initial frequency of 100 kHz to the final one of 1 mHz.

High-quality deionized water was obtained from a Millipore Mili-Q system. 3,4-DHB and 3,4-DHBA(Aldrich) were first dried and recrystallized in ethanol/water three times, then further dried at reduced pressure for 48 hrs at 75°C. All others chemicals were purchased from Aldrich and used as received.

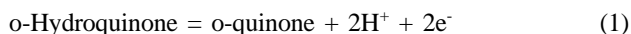
2.2. Preparation and measurements of PME

The 3,4-DHB was polymerized at a fixed 0.25 V with an electrochemical cell consisting of a working electrode/1.0 mM 3,4-DHB, 0.1 M phosphate buffer(pH=7.1)/Pt, which was electrochemically annealed in the buffer solution using CVs ranging from 0.2 to 0.30 V with a scan speed of 0.05 V/s until constant figure was obtained. The well formed PME was immersed in 1.0 mM 3,4-DHBA/0.05 M HCl solution for 1 hr in order to obtain doubly modified electrodes, namely the GC(or Au)/p-3,4-DHB-3,4-DHBA type electrodes. The electrodes were subsequently immersed in ethanol for the purpose of annealing the polymeric film.

3. Results and Discussion

3.1. Polymerization and its associated CVs

Fig. 1A shows CVs for electropolymerization of 3,4-DHB on a glassy carbon electrode in 0.1 M phosphate buffer (pH=7.1) containing 1 mM 3,4-DHB, which demonstrates the growth pattern of the polymer. The peak current increased continuously with increasing CVs, but the rate of increase gradually decreased. The resultant G.C./p-3,4-DHB type electrode was rinsed with water and transferred to a fresh 0.1 M phosphate buffer(pH=7.1) solution. The PME shown in Fig. 1B exhibited excellent reversibility in redox process with values of $E^0 = 0.30$ V and $\Delta E_p = 0.05$ V. The redox reaction involving the quinone moiety of the PME can be represented by the following equation:



The films exhibited two waves of reversible and well-defined for electrons transfer and those of weak and unstable for deprotonation at the potential ranges, where the CVs were more precisely shaped for the each redox procedure in the acidic acetate buffer solution. The waves at the PME gave quite well defined CVs, as shown in Fig. 2A, which correspond to those obtained in 0.1 M acetate buffer(from top, pH=4.5, 5.2 and 7.2). The presence of a relatively high concentration of proton could minimize the extent of the nucleophilic attack by the solvent at the ortho position of the cathecol ring, thereby favoring the reaction between the oxidized quinone and the functional groups present at the surface of the PME. How-

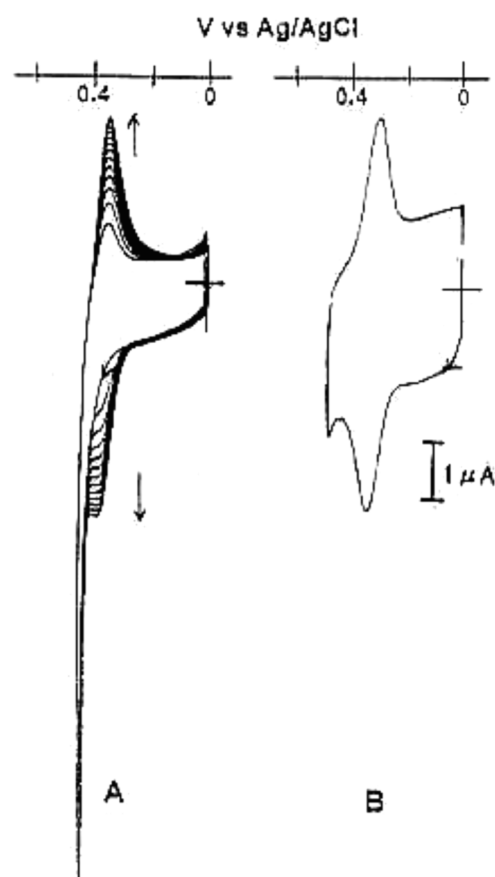


Fig. 1. Cyclic voltammograms of electropolymerization for 3,4-dihydroxybenzaldehyde on glassy carbon (A) and the polymeric film electrode(B) in phosphate buffer(pH=7.10); (scan rate: 0.1 V/s, electrode area: $7.5 \times 10^{-2} \text{ cm}^2$)

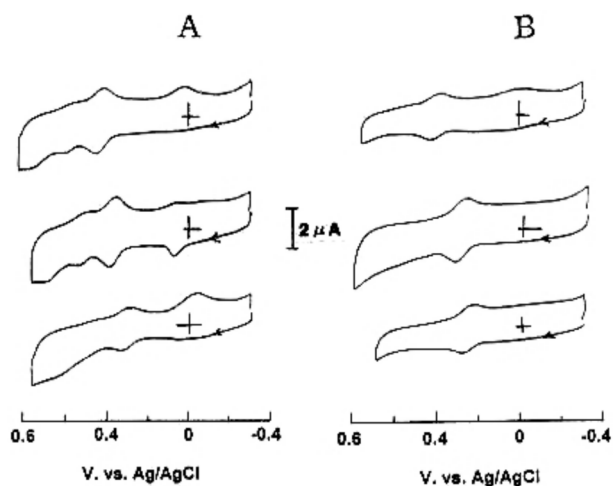


Fig. 2. Cyclic voltammograms of GC/p-3,4-DHB electrode in 0.1 M acetate buffer at pH=4.5, 5.2 and 7.2 from top(A) and 0.1 M phosphate buffer from top pH=5.5, 7.1 and 8.0(B). (scan rate: 50 mV/s, electrode area: $7.5 \times 10^{-2} \text{ cm}^2$)

ever, at basic pH, the presence of a higher concentration of OH^- , which acts as a strong nucleophile, enhances the reaction with the active functional groups on the surface. The CVs

shown in Fig. 2B obtained in 0.1 M phosphate buffer (from top, pH=5.5, 7.1 and 8.0). The phosphate ions act as a stronger nucleophile than acetate ions, thereby increasing the strength of the attack, which hinders the oxidation reactions¹¹. Based on these results, it was decided all subsequent experiments would be done in acidic acetate buffer solution (pH=5.2).

3.2. Esterification reaction of 3,4-DHBA

The cyclic voltammetric responses of the GC/p-3,4-DHB electrode and the GC/p-3,4-DHB-3,4-DHBA electrode before and after annealing in ethanol for 20 hrs in acetate buffer (pH=5.2) are shown at Fig. 3A, Fig. 3B and Fig. 3C, respectively. The 3,4-DHBA, which contains both carboxyl and hydroxyl groups, reacted with the hydroxyl groups on the GC/p-3,4-DHB electrode during the first step, which then led to a polymerization reaction take place, because the reacting 3,4-DHBA molecules, contain both groups. In the solution, most of the monomer molecules were self-polymerized, but a small portion of them participated in the esterification reaction on the PME surface. Also, some of the monomer molecules might have reacted on the film in the oligomer state.

The CVs shown in Fig. 4 had the expected wave shape for a surface-immobilized redox center with a small ΔE_p value.

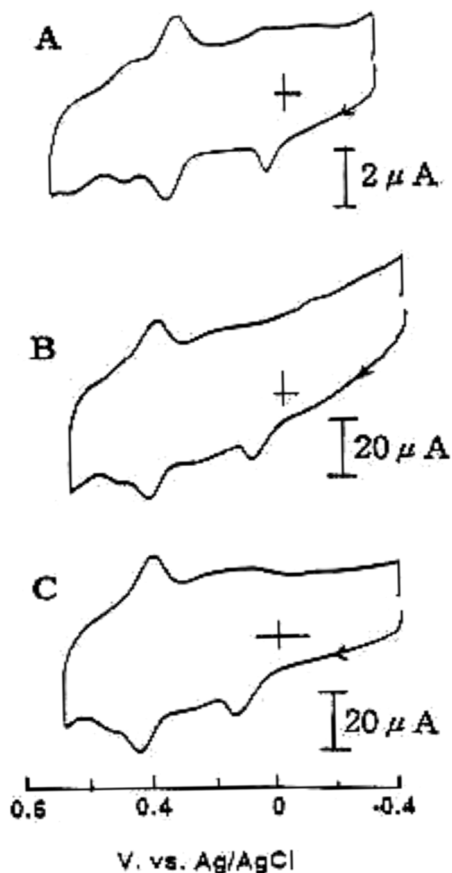


Fig. 3. The cyclic voltammograms in 0.1 M acetate buffer (pH=5.2) for the GC/poly-3,4-DHB electrode (A), GC/poly-3,4-DHB/3,4-DHBA electrode (B) and after annealing of electrode (B) for 20 hrs in ethanol (C).

In addition, the current was directly proportional to the rate of potential sweep over the range of 10 to 500 mVs⁻¹ for the GC/p-3,4-DHB electrode: (Fig. 5A) and 10 to 300 mVs⁻¹ for the GC/p-3,4-DHB-3,4-DHBA electrode: (Fig. 5B) in acetate buffer (pH=5.2), which has more reactive in reaction suggesting

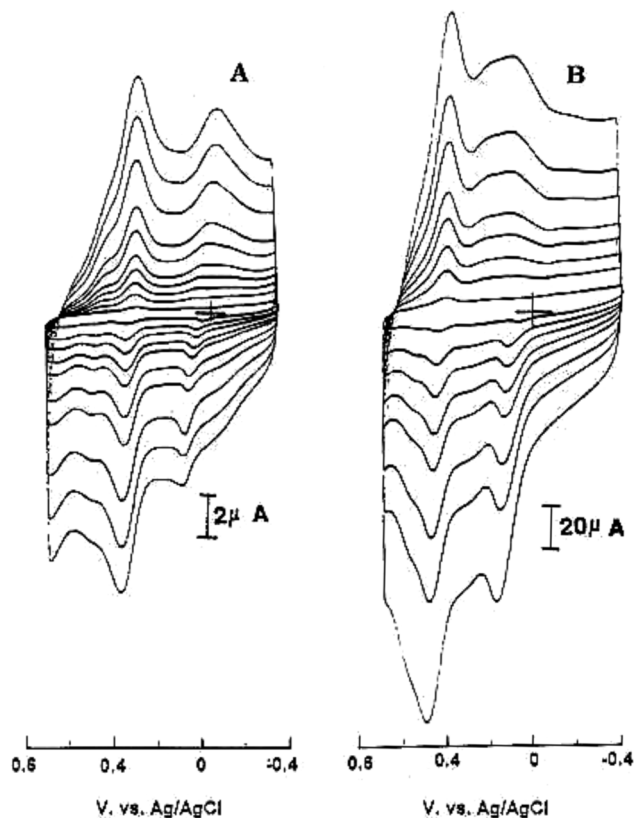


Fig. 4. Cyclic voltammograms of GC/p-3,4-DHB in 0.1 M acetate buffer (pH=5.2) (A) and 0.1 M phosphate buffer (pH=5.2) (B) at scan rate of 0.01, 0.03, 0.05, 0.075, 0.1, 0.2, 0.3, 0.4 and 0.5 V/s, electrode area: $7.5 \times 10^{-2} \text{ cm}^2$

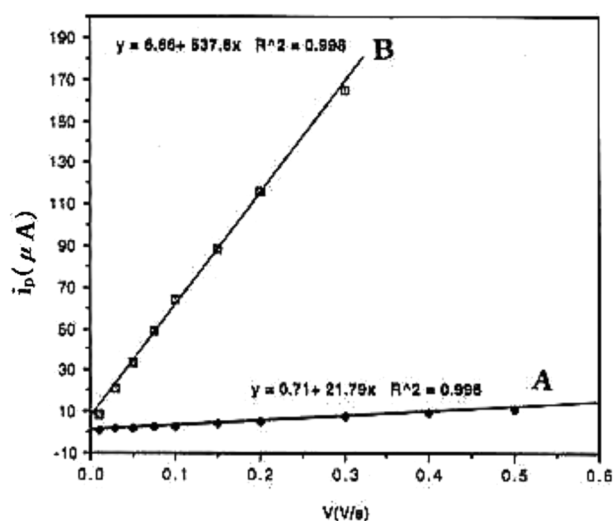


Fig. 5. Sweep rate dependence of the cyclic voltammetric response for the electrodes consisting of GC/p-3,4-DHB (B) and GC/p-3,4-DHB/3,4-DHBA (A) in acetate buffer (pH=5.2).

facile charge transfer kinetics than that. Laviron equation¹², which is as equation (2), was used to determine the rate constant of charge transfer,

$$(E^0 - E_p) = RT/\alpha nF \{ \ln(\alpha nF/k_s RT) \} + RT/\alpha nF \{ \ln v \} \quad (2)$$

where, E^0 , E_p , k_s , α , and v are formal potential, peak potential, the charge transfer rate constant, charge transfer coefficient and scan speed, respectively. From the intercept of Laviron plot, $(E^0 - E_{pa})$ and $(E^0 - E_{pc})$ vs. $\log v$, the k_s was found to be $9.5 \times 10^{-8} \text{ s}^{-1}$ for the GC/p-3,4-DHB electrode (Fig. 6A) $4.7 \times 10^{-3} \text{ s}^{-1}$ for the GC/p-3,4-DHB-3,4-DHBA electrode (Fig. 6B). Thus the electron transfer process for the latter film in the acidic acetate buffer solution appears to be a few thousand times faster than that for the former one. Fig. 7 shows the frequency-time curve for the reactions on the Au(QCA)/p-3,4-DHB electrode containing $1.98 \times 10^{-5} \text{ g cm}^{-2}$ of p-3,4-DHB, which were plotted with the first order reaction equation of $\ln(M_0 - M) = -10.0 + 0.118t$ for the initial step. These equation imply that the reaction has the rate constant corresponding to the esterification reaction, which is $1.18 \times 10^{-1} \text{ (s}^{-1}\text{)}$. The quantities of 3,4-DHBA was calculated by means of the Sauerbrey equation¹³, which is as follow:

$$\Delta m = \Delta F \times 9.107 \times 10^{-8} \text{ g Hz}^{-1} \quad (3)$$

3.3. EIS results

The electrochemical admittance values (Fig. 8) were measured for the three electrode types GC:(a), GC/p-3,4-DHB:(b) and GC/p-3,4-DHB-3,4-DHBA after annealing in ethanol for 20 hrs: (c). The electrodes had electrochemical admittance values of 3.45×10^{-3} , 1.32×10^{-3} and $6.78 \times 10^{-3} \text{ S}$ in 0.1 M acetate buffer (pH=5.2) respectively. It is very important to modify and anneal the electrodes, in order to improve their electrochemical responses, as shown in the electrochemical

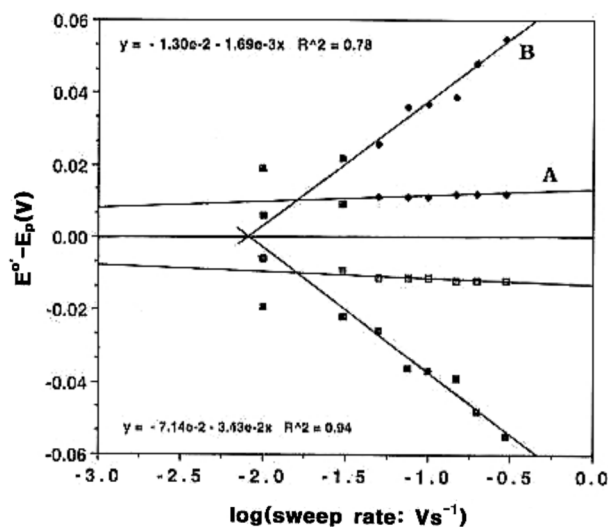


Fig. 6. Variation of peak potential difference ($E^0 - E_p$) as a function of $\log v$ (sweep rate: V/s) for the electrode consisting of GC/p-3,4-DHB(A) and GC/p-3,4-DHB-3,4-DHBA(B) in acetate buffer (pH=5.2).

impedance values of the latter two types of electrode.

3.4. QCA results

To determine the quantity of deposited the p-3,4-DHB and 3,4-DHBA, Au(QCA) electrode was employed. The measured frequency difference of this electrode during polymerization was 24.8 Hz, whereas the calculated value was $2.26 \times 10^{-6} \text{ g}$ according to equation (3). This frequency difference came from the deposited polymeric film was controlled to have 2-4 coverage by regulating the numbers of CVs¹⁴. Fig. 9A shows the EQCM result for the Au(QCA)/p-3,4-DHB electrode in

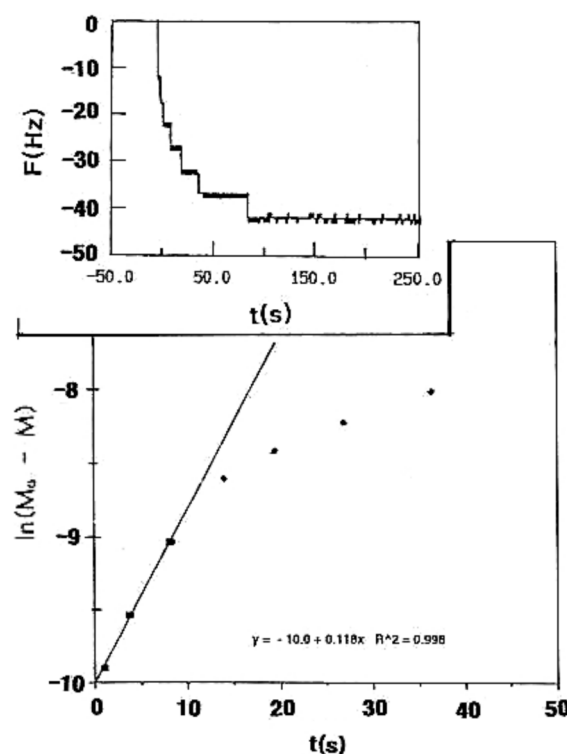


Fig. 7. Frequency-time curve for the esterification reaction of 3,4-DHBA on Au(QCA)/p-3,4-DHB electrode: (top) and plots for rate constant of first order reaction: (bottom)

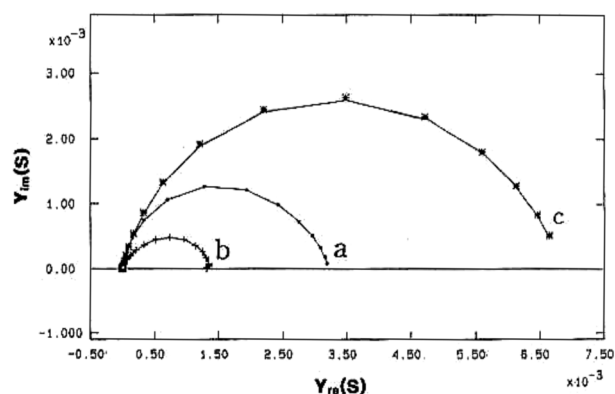


Fig. 8. Electrochemical impedance spectra of admittance presentation for GC(a), GC/p-3,4-DHB(b) and GC/p-3,4-DHB-3,4-DHBA(c) electrode in 0.1 M acetate buffer (pH=5.2). The frequency range is 100 kHz to 1 mHz.

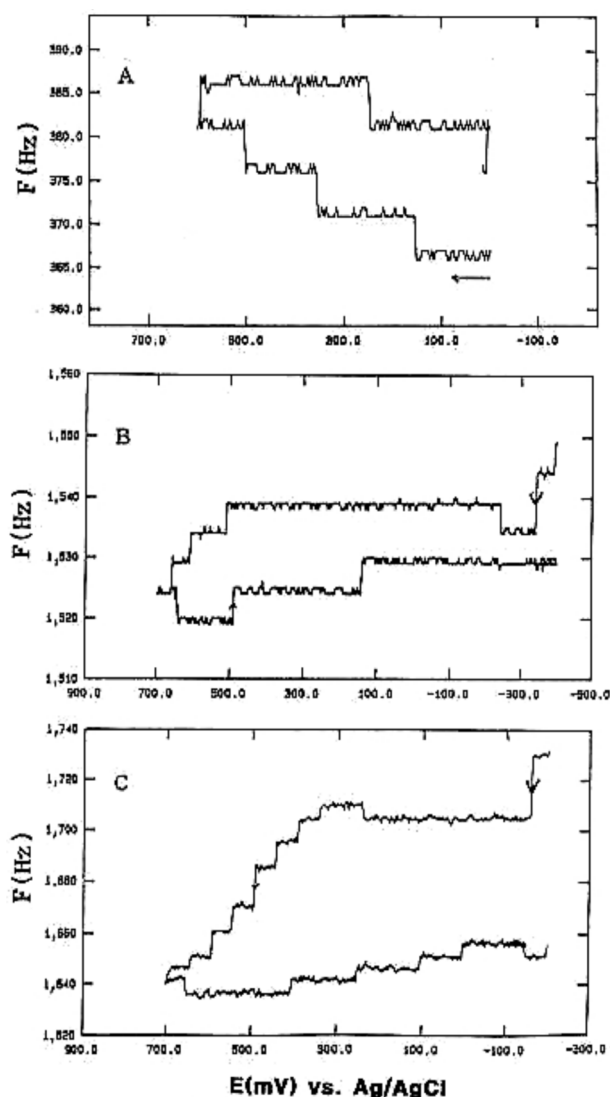


Fig. 9. The frequency changes vs. potential curve of Fig.3 in 0.1 M acetate buffer solution (pH=5.2) for the GC/poly-3,4-DHB electrode (A), GC/poly-3,4-DHB-3,4-DHBA electrode (B) and after annealing of electrode (B) for 20 hrs in ethanol (C). ($f^0=8,878,000$ Hz, scan rate = 50 mV/s, electrode area = 0.3 cm²) respectively.

0.1 M acetate buffer (pH=5.2) at standard frequency of 8.862,000 Hz. The frequency change was only 20 Hz for the redox process. Fig. 9B and 9C show the EQCM curves for the Au(QCA)/p-3,4-DHB-3,4-DHBA electrode before and after annealing in ethanol, for which the frequency differences were 20 and 74 Hz, respectively. These corresponded to the respective CVs shown in Fig. 3 respectively. The bigger frequency difference for the annealed polymeric film, which coincided with the difference in the hydration number between the two states, implies that the well ordered surfaces, having a quinoidal structure, have more sites for hydration, so as to increase the hydration number from 87 to 288 molecules¹³. As can be seen in Fig. 9A, the oxidation reaction causes an increase in frequency, corresponding to a decrease in the mass contained on the p-3,4-DHB film, while in Fig. 9B and 9C, the frequency is decreased, corresponding to an increase

in the mass contained on the p-3,4-DHB-3,4-DHBA film. These changes in frequency can be mainly influenced on an incorporation of anion and water upon oxidation, and their subsequent ejection when reduction occurs across the film and solution interface, because the oxidized and reduced polymeric film have different morphologies. The surface of the p-3,4-DHB film electrode, which loses protons during the oxidation reaction, is covered with carbonyl groups, resulting in its having reduced mass. On the other hand, the surface of the p-3,4-DHB-3,4-DHBA electrode has a more extensive surface area, with the result that the added carboxyl group gave the reversed pattern in the EQCM experiment. The annealing of the surface resulted in the presence of well ordered catechol moieties, as shown on scheme II, which resulted in a greater difference in frequency, due to the hydration and dehydration of the annealed surface.

4. Conclusions

3,4-Dihydroxybenzaldehyde was anodically electropolymerized on glassy carbon electrodes previously activated in alkali solution. The polymer modified electrodes gave better CV responses in 0.1 M acetate buffer solution (pH=5.2) than in 0.1 M phosphate one. The PME was esterified with 3,4-dihydroxybenzoic acid to GC/p-3,4-DHB-3,4-DHBA type electrodes. It is suggested that the reaction is multi-step, with the initial step proceeding by esterification, which subsequently leads to polymerization. These modified electrodes exhibited electrical admittances that were 5 times higher and currents that were over 20 times larger than the unmodified electrodes in terms of their CV responses. The well ordered polymeric film and the enhanced electroactive sites of the GC/p-3,4-DHB-3,4-DHBA electrode resulted in there being a 3.3 times greater change in water molecules in the EQCM experiment than with the GC/p-3,4-DHB electrode. The film electrodes are stable at the sweep potential range of 0.4 V to +0.55 V. This reaction could be applied to the electrode containing of hydroxyl and carboxylic group material for conductive one.

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References

1. M.-C. Pham, P.-C. Lacaze, and J.-E. Dubois, *J. Electroanal. Chem.*, **99**, 91 (1979).
2. A. F. Diaz and J. A. Logan, *J. Electroanal. Chem.*, **111**, 111 (1980).
3. K. K. Kanazawa, A. F. Diaz, and R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Rabolt, and G. B. Street, *J. Chem. Soc. Chem. Commun.*, 854 (1979).
4. P. Denisevich, H. D. Abruna, C. R. Leidner, T. J. Meyer, and R. W. Murray, *Inorg. Chem.*, **21**, 2135 (1982).
5. P. J. Pearce, and A. J. Bard, *J. Electroanal. Chem.*, **114**, 6641 (1980).
6. S. K. Cha, and H. D. Abruna, *Anal. Chem.*, **2**, 274 (1990).
7. C. Degrand, and L. L. Miller, *J. Electroanal. Chem.*, **117**, 267

- (1981).
8. M. K. Campbell, Biochemistry, Holt, Rinehart and Winston Inc., Orlando, 1991.
9. Q.Wu, G. D. Storrier, F. Pariente, Y. Wang, J. P.Shapleigh, and H. D. Abruna, *Anal. Chem.*, **69**, 4856 (1997).
10. W. J. Moore, Basic Physical Chemistry; Prentice Hall, Inc. pp311, 1983.
11. F. Pariente, F. Tobalina, M. Darder, E. Lorenzo, and H. D. Abruna, *Anal Chem.*, **68**, 3135 (1996).
12. E. Laviron, *J. Electroanal. Chem.*, **101**, 19 (1979).
13. D. A. Buttry, and M. D. Ward, *Chem. Rev.*, **92**, 1355(1992).
14. S. K. Cha, *J. Polymer Sci. part B*, **35**, 165 (1997).