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Pyrolytic carbon film deposit as an electrochemical interface.

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A pyrolytic carbon (PC) film was grown on planar substrate (graphite rods) by chemical vapor deposition from gaseous feed of methane using a vertical hot-wall deposition reactor. Scanning electron microscopy was used to study the surface structure. The PC film was also characterized by cyclic voltammetry technique to evaluate the background current, stability and the electrochemical response using ascorbic acid, $\text{Co(phen)}_3^{2+/3+}$ and $\text{Fe(CN)}_6^{3-/4-}$ redox couples and compared to glassy carbon (GC) electrode. High degree of electrochemical activity and the enhanced signal to background (S/B) ratio demonstrated that the PC film might be an attractive electrode material for electroanalytical measurements.

1. Introduction :

Development of new carbon electrode materials has been of interest to many researchers. Presently, carbon film electrodes fabricated from the techniques such as chemical vapor deposition [1 - 4] and physical vapor deposition [5 - 7] methods are widely used in electrochemical applications and it is found that the creation of specific carbon film structures with enhanced electrode activity is possible through these methods.

Pyrolytic carbon (PC) films are the deposits formed by the pyrolysis of a gaseous hydrocarbon depositing carbon onto a preformed hot substrate such as polycrystalline graphite [8 - 10]. Due to their interesting properties such as good strength, wear resistance and durability, they are used in wide industrial applications such as coating nuclear reactor fuel particles [11], in medical applications such as artificial heart valves [12 - 14]. However, in spite of their unique properties relevant to electrochemistry such as reversible electron transfer kinetics [3 - 4, 15 - 17] and enhanced signal to background (S/B) ratio [15], there are very few detailed studies. We have recently described the effects of anodization at high oxidation potentials (up to 2.1 V vs. Ag/AgCl) in a different article [15]. In this paper, electrochemical characteristics of PC electrodes are described. Study of the PC film electrodes can lead to greater understanding of the surface chemistry and electrochemical applications of new carbon film electrodes.

2. Experimental :

PC film was fabricated on graphite rod substrates in a

furnace at 1100 °C. The precursor was methane under the atmosphere pressure. The pyrolysis condition has been described in more details in Reference [15]. The PC film was used without any surface pretreatment other than a rinse with methanol for 10 min and then with deionized water for 5 min. To compare the cyclic voltammograms, a glassy carbon (GC) electrode (No. 6.1204.110, Metrohm) was used. Polishing was done by successively smaller grades of alumina slurry (1.0, 0.3, and 0.05 μm) on a glass plate. The electrode was rinsed thoroughly with deionized water for 5 min after each polishing step. The electrochemical anodization consisted of - applying the constant oxidation potential for 3 min. in 1 M KNO_3 solution followed by the reduction at -0.1 V vs. Ag/AgCl [15, 18]. Measurements were made in a one-compartment voltammetric cell containing a graphite rod auxiliary electrode and an Ag/AgCl (3 M NaCl) reference electrode. Voltammetric experiments were carried out using a μAutolab potentiostat (PGSTAT30) controlled by GPES 4.5 software. The redox systems used in this experiment were as follows : 1 mM ascorbic acid (Aldrich) in 0.1 M H_2SO_4 solution; 1 mM Fe(CN)_6^{4-} in 1 M KCl solution made from $\text{K}_4\text{Fe(CN)}_6$ (Merck); 2 mM Co(phen)_3^{2+} in 1 M KCl solution made from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck) and 1,10-phenanthroline (Merck). Scanning electron micrograph study was performed with a Cambridge-S360 scanning electron microscope (SEM).

3. Results :

3.1. Surface topography :

The scanning electron micrograph of the surface of the PC film is shown in Figure (1A), in which on the micrometer scale, the surface consists of globular features that do not have uniform size and sharp distribution.

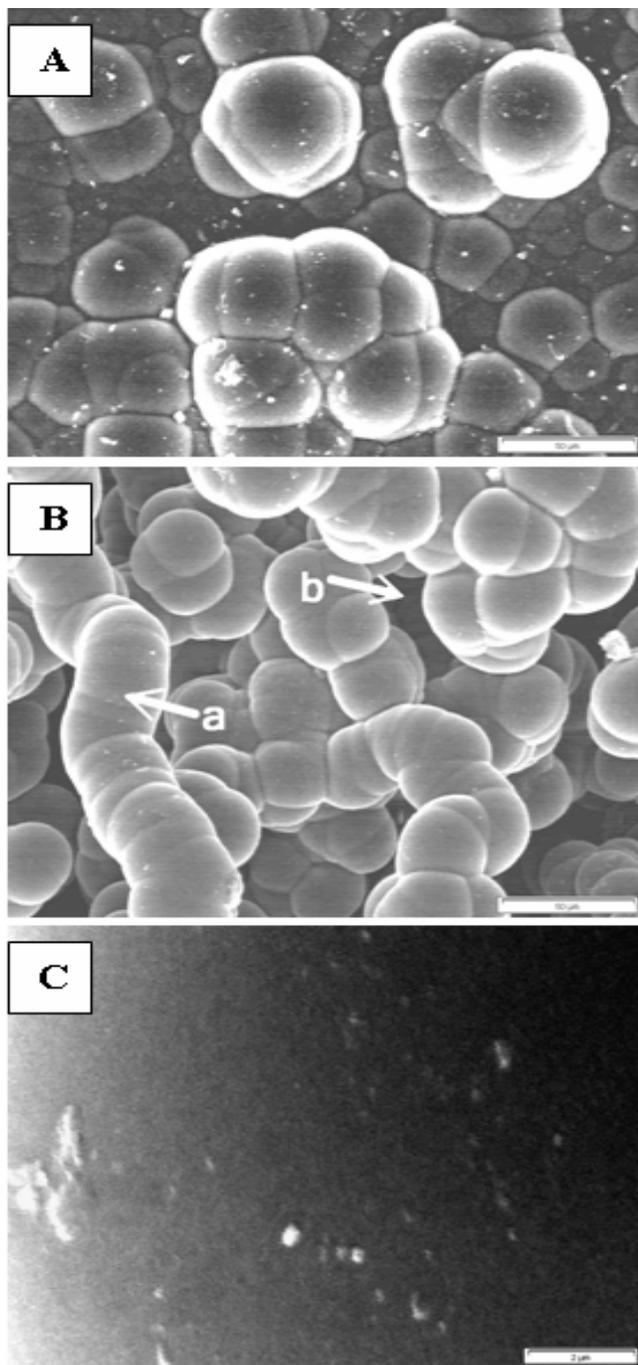


Figure (1) : Scanning electron micrographs of PC film at a magnification of 1000 (A and B) and 10000 (C).

During scanning the PC film surface with SEM, it was found that the topography of entire surface of the film was similar to micrograph presented in Figure (1A), in which all

the surface of graphite substrate was covered by the PC film. However, while scanning the surface, some of the area was observed with different topography. An example is shown in Figure (1B), in which globular or rounded features are successively agglomerated together to form long columnar features (indicated with narrow (a)). Also, in these areas, it is not certain that the dark or deeper zones (indicated with an arrow (b)) reach to the surface of graphite substrate. This may be attributed to the graphite substrate.

3.2. Background current :

Potential scans were carried out in 1 M KCl for graphite rod without and with the PC film. The voltammograms are shown in Figure (2) over a 1.2 V potential range (0 to 1.2 V vs. Ag/AgCl). Without carbon film deposits, the background current at graphite was very greater than those observed after deposition.

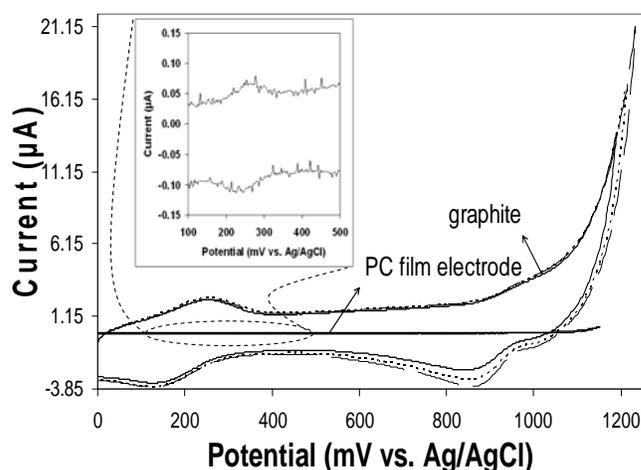


Figure (2) : The positive background cyclic voltammograms of graphite electrode before and after PC film deposition in 1 M KCl solution. Scan rate = 50 mV s^{-1} . The positive potential limit was 1.19 V (solid lines), 1.21 V (dotted line) and 1.23 V (dashed line).

The apparent electrode area calculated from the outer dimensions of the electrode was 0.07 cm^2 but the real surface area available could be greater due to high porosity that causes high background current. A reversible peak-couple observed at 0.25 V vs. Ag/AgCl at the voltammogram of graphite electrode can be attributed to the faradaic charge of surface quinines redox couples [19, 20]. Probably, because of the lower surface area of the PC film and smaller amount of oxygen functional groups on its surface [15, 21], the height of this peak is very low as shown by the inset in Figure (2). Also, during the cathodic sweep, the irreversible peak observed at ca. 0.85 V vs. Ag/AgCl may be attributed to the reduction of a little amount of dissolved Cl_2 gas produced during the anodic sweep and remained in the pores of graphite. This peak was not observable at the voltammogram of PC film. The low background current of PC film is important for possible analytical applications and represents contributions both from double-layer capacitance and surface redox reactions.

The low density of redox active surface groups such as quinines causes the reducing of the faradaic contribution to observed background current. Also, the smooth surface of PC film must be at least partly responsible for its low background current. In spite of the roughness on micrometer scale [see Figure (1A) and (B)], the SEM micrograph at higher magnification showed that the surface may be smooth on the sub-micrometer scale. Micrograph in Figure (1C) obtained at the higher magnification of 10000 indicates that the globular features observed in micrographs (A) and (B) probably have a smooth surface on the sub-micrometer scale.

3.3. Redox systems :

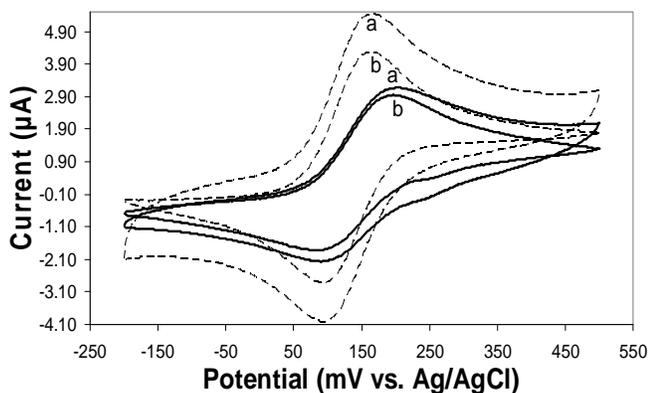


Figure (3) : Cyclic voltammograms for 2 mM $\text{Co(phen)}_3^{2+/3+}$ in 1 M KCl at GC (dashed lines) and PC film electrode (solid lines) before (a) and after (b) background correction. Scan rate = 50 mV s^{-1} . Uncorrected iR drop.

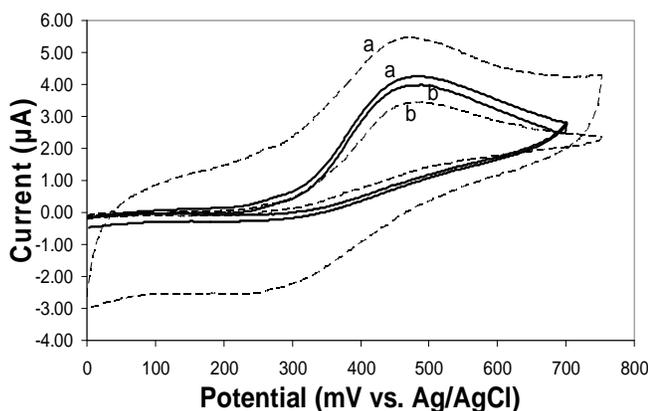


Figure (4) : Cyclic voltammograms for 1 mM ascorbic acid in 0.1 M H_2SO_4 at GC (dashed lines) and PC film electrode (solid lines) before (a) and after (b) background correction. Scan rate = 50 mV s^{-1} . Uncorrected iR drop.

The redox systems such as dopamine and hydroquinone whose electron transfer kinetics are expected to involve catalysis by the surface oxides [1, 22] showed a weak electron transfer at PC film [15, 21], presumably due to the lack of catalytic carbonyl groups. However, when a surface catalytic interaction was not involved, PC film showed a reversible response comparable to GC. For

example, the redox system such as $\text{Co(phen)}_3^{2+/3+}$ [Figure (3)] and ascorbic acid [Figure (4)] showed high electrode activity and subsequently, high (S/B) ratio.

In Figures (3) and (4), the cyclic voltammograms of $\text{Co(phen)}_3^{2+/3+}$ and ascorbic acid are shown and compared with the GC electrode. For $\text{Co(phen)}_3^{2+/3+}$, the ΔE_p value was about 108 mV and 74 mV at PC film and GC respectively. Figure (3) shows the total peak current and background corrected current for $\text{Co(phen)}_3^{2+/3+}$ at GC and PC film. For ascorbic acid, the value of $E_{1/2}$ was about 363 mV and 380 mV (vs. Ag/AgCl) at PC film and GC respectively [Figure (4)]. The very interesting observation was the enhanced (S/B) ratio. Because of the lower background current in PC film, the (S/B) ratio (calculated from $([i_{\text{total}} - i_{\text{bkd}}]/i_{\text{bkd}})$ and from the i_{ox}) was higher than GC, which was 11 and 15 respectively for $\text{Co(phen)}_3^{2+/3+}$ and ascorbic acid at PC film; and 3 and 6 at GC. The high (S/B) ratio at PC film electrode is the important and noticeable observation and shows the suitability of PC electrode material for future study in electroanalysis applications.

3.4. The stability :

After pyrolysis, the electrode can be hold even for several months in holding vessel and with no significant decline in electrochemical activity. In spite of this advantage, the electrochemical behavior of PC film suffers from the low stability of electrode with respect to air or solution exposure and in most case a dramatic deactivation was observed after one day of air exposure or overnight. In Figure (5), cyclic voltammogram is shown for the electrode exposed to air for overnight (dashed line).

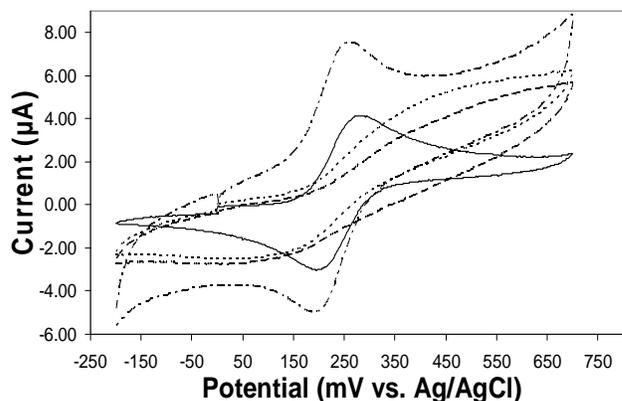


Figure (5) : Cyclic voltammograms for 1 mM $\text{Fe(CN)}_6^{3-/4-}$ in 1 M KCl at the fresh PC film (solid line), at the same electrode after air exposure for 12 h (dashed line) and after anodization at 1.9 V vs. Ag/AgCl (dotted dashed line) and at the fresh film after polishing (dotted line). Uncorrected for background current and iR drop. Scan rate = 50 mV s^{-1} .

Carbon electrodes are prone to adsorb impurities from the solution or air [23], which cover the active site on the surface. When we applied the polishing procedure described in experimental section, there was no significant improvement in the response. Polishing the fresh electrode has also the same effect to inactivate the electrode as shown with dotted line voltammogram in Figure (5). For the

electrode such as GC, abrading the surface after polishing can remove the impurities and expose the new surface [24]. But for PC film, it was not a successful treatment method perhaps because of the high mechanical characteristic and hardness of these carbon layers. As shown with the dotted line voltammogram in Figure (5), polishing can inactivate even a fresh surface, which may be attributed to sticking a little amount of alumina particles into the fossate or deeper zones or the slits between the rounded features that come forward on the surface.

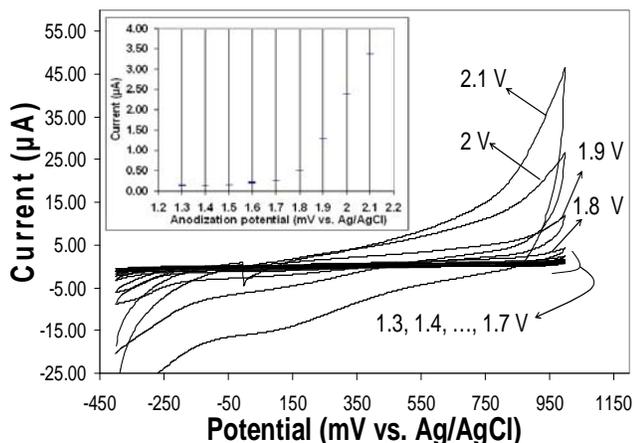


Figure (6) : Cyclic voltammetry experiment for PC film after anodization at 1.3, 1.4, ..., 2.1 V (vs. Ag/AgCl). The solution was 1 M KCl and was not degassed with nitrogen. The scan rate was 50 mV s^{-1} . The inset plot shows the background currents at 0.2 V (vs. Ag/AgCl) versus oxidation potentials.

To reactivate the electrode, we examined the effects of anodization and it was found that anodization at the oxidation potential lower than 1.8 V have not significant effect on reactivation of electrode but applying the voltage greater than 1.8 V reactivates the electrode as shown by the cyclic voltammogram for the electrode anodized at 1.9 V vs. Ag/AgCl (dotted dashed line) with a ΔE_p of about 68 mV.

The background current level was observed to be very sensitive to the anodization at high oxidation potential. In Figure (6), the background current of the carbon film are shown after anodization at the successive oxidation potentials of 1.4, 1.5... 2.1 V. The anodization procedure has been described in the experimental section. As shown in Figure (6), the amount of background current level increases with increasing the anodization potential. Also, as indicated in the inset in Figure (6), there was an extreme increase in the background current level after anodization at the oxidation potentials greater than 1.8 V vs. Ag/AgCl. This can be attributed to the extreme increase in the surface oxide due to the high oxidation potential which is sufficiently positive to cause gas evolution and to get the surface covered with a film of oxide [15], which mechanically can remove the physisorbed surface impurities.

Conclusions :

The Pyrolytic Carbon film was deposited by chemical vapor deposition method and the electrochemical response and stability were evaluated. The electrode had good electrochemical activity for ascorbic acid, $\text{Co(phen)}_3^{2+/3+}$ and $\text{Fe(CN)}_6^{3-/4-}$ redox couples but a dramatic deactivation was observed after one day of air exposure. The electrochemical anodization by applying the voltage greater than 1.8 V vs. Ag/AgCl was a successful treatment method to reactivate the electrode. The smooth surface of electrode and low density of redox active surface groups might be responsible for low background current and capacitance.

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