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Investigation of oxygen electroreduction on polyvinylferrocene coated glassy carbon electrodes

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Abstract

The electroreduction of O_2 has been investigated at a bare glassy carbon (GC) electrode and a polyvinylferrocene (PVF) coated glassy carbon electrode (PVF-GC) in both 0.1 M $NaClO_4$ solution and phosphate buffer solutions of various pH values by using cyclic voltammetry and chronoamperometry. Two well-defined reduction peaks were observed at about −0.55 and −0.80 V versus SCE at PVF-GC electrode while one reduction peak was observed at about −0.85 V versus SCE at GC electrode in 0.1 M $NaClO_4$ solution and phosphate buffer solutions of pH >6. Two peaks at PVF-GC electrode indicated a two-step four-electron pathway of O_2 in these mediums. The first peak was ascribable to the two-electron reduction of O_2 to H_2O_2, while the second peak was assigned to the reduction of H_2O_2 to H_2O. The electrocatalytic effects of PVF matrix for the reduction O_2 and the reduction of H_2O_2 were observed. The effects of the film thickness, O_2 concentration, pH and potential scan rates were investigated.

Keywords: Polyvinylferrocene; Oxygen electroreduction; Electrocatalytic effect

1. Introduction

Oxygen electrochemistry is a highly interesting field in electrocatalysis due to its high importance especially in fuel cells and biosensors. Several electrode materials; such as gold [1–3], Pt [4], copper [5], iron [6,7], various composite materials [8,9], with or without modifications have been suggested as cathodes for the reduction of O_2 in different media. The electrochemical reduction of oxygen on carbon electrodes is the subject of continuous interest because of the application of high surface area carbon materials as noble metal catalyst supports in fuel cells. Oxygen reduction to hydrogen peroxide is a two-electron reaction and the four-electron reduction leads to the formation of water [10]. The kinetics and mechanisms of oxygen reduction have been investigated on bulk carbon electrodes [11,12]. Many researchers have been reported that oxygen could be reduced electrocatalytically on modified carbon electrodes. Composite membrane modified electrodes prepared by electrochemical deposition of platinum particles in polymer film coated glassy carbon electrodes exhibited catalytic activities towards the reduction of oxygen and hydrogen peroxide [13]. Mediated reduction of oxygen at poly (phenosafranine) [14] or poly (nile blue) [15] modified electrodes were studied. Chemically modified carbon or glassy carbon electrodes to be used for oxygen reduction were prepared with the quinones [16–20], metal–porphyrin complexes [21–24], metal–phthalocyanine complexes [25,26], sodium montmorillonite-methyl viologen [27], calyx [6] arene-methyl viologen [28], vanadium-doped zirconias [29], Co-based catalysts [30], manganese oxide catalysts [31] as the modifier, and the construction of chemically modified electrodes was rather complicated and time-consuming.

The redox polymer polyvinylferrocene (PVF) gives rise to some interesting electrochemical results when used as a layer on electrode surfaces. PVF is insoluble in most solvents and so that electrode can easily be coated with this polymer by deep coating method. The oxidation of PVF films involves the conversion of ferrocene to ferrocenium units. In addition to its own electroactivity that is caused by this redox pair, diffusion of other electroactive species through the film and subsequent charge transfer at the metallic surface underneath can also take place [32]. The redox centers in the structure can also act as mediator for the charge transfer from substrate to some depolarizers. It was observed that PVF has attracted interest with regard to

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applications as electrocatalysis for electroreduction and electrooxidation of anthracene and some of its derivatives [33–35] and electrooxidation of hydrogen peroxide [36].

In this study we present the results of the electrochemical reduction of oxygen on bare glassy carbon (GC) and PVF-GC electrodes in aqueous solution containing 0.1 M $NaClO_4$. The results obtained from modified and unmodified electrodes are compared. The electrocatalytic effect of the PVF modified electrode was presented and the mechanism of the electrocatalytic process was discussed. The effect of the pH on the catalytic reduction of oxygen on GC and PVF-GC electrodes was also studied in various pHs of phosphate buffer solutions.

2. Experimental

PVF was prepared by chemical polymerization of this monomer, vinylferrocene (Aldrich), at 70 °C [37]. The glassy carbon electrode was immersed in a solution of PVF in methylene chloride for a certain time period and the solvent was then evaporated. The surface was rinsed with triple distilled water before use. A yellow PVF film was coated on the glassy carbon surface after this procedure. The average thickness of the dry film was estimated from the charge, *Q*, consumed during complete electrooxidation of the film by stepping the potential from 0.0 to 0.70 V versus SCE in 0.1 M $NaClO_4$ solution as described by Bard [32].

The solution contained 0.1 M $NaClO_4$ (Merck) was prepared using triple distilled water as the supporting electrolyte. The buffer solutions were prepared using NaH_2PO_4 (Analar BDH) and NaOH (Merck). Methylene chloride (Merck) was used to prepare PVF solutions. The purification of methylene chloride was accomplished according to the method proposed in literature [38].

Electrochemical measurements were carried out in a three-electrode cell. A Pt foil and SCE electrode were used as counter and reference electrode, respectively. Glassy carbon electrode (diameter 2 mm, CH Instruments) was used as working electrode. Before each experiment, the working electrode was polished with electrode polishing kit (CH Instruments). Then the electrode was washed in triple distilled water and dried in air. Prior to each electrochemical experiment, O_2 gas (99.99%) was bubbled directly into the cell for 30 min to obtain an O_2 saturated electrolyte solution and during the measurements O_2 gas was flushed over the cell solution. Electrolyte solutions were, if necessary, deaerated by bubbling N_2 gas (99.99%) for at least 30 min prior to electrochemical measurements. All the measurements were performed at room temperature. The electrochemical measurements were accomplished with CHI 660 A Electrochemical Analyzer (CH Instruments) equipped with a personal computer.

3. Results and discussion

3.1. Electrochemical behavior of the modified electrode

The cyclic voltammogram in Fig. 1 is characteristic for a PVF coated glassy carbon electrode in deoxygenated 0.1 M $NaClO_4$ solution. In the first cycle, the oxidation peak of PVF appears at about +0.38 V versus SCE, corresponding to a reverse reduction peak of PVF^+ with a peak potential of +0.24 V versus SCE. The cathodic peak was broader and less intense than the anodic peak. Neutral PVF polymer takes counter ions into its structure when oxidized and swells. Deswelling occurs upon the reduction of the oxidized polymer as the counter ions are expelled from the structure. Swelling and deswelling kinetics of the polymer are not identical, which is the main reason for asymmetry of the anodic and cathodic peaks. In presence or absence of O_2, the modified electrode was found to remain stable and reproducible after several repetitive cyclic voltammograms.

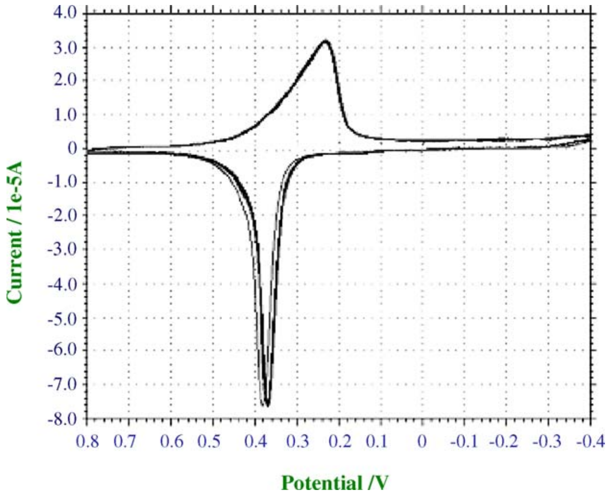

Fig. 1. Multisweep cyclic voltammogram of 1.37×10^{-7} mol cm^{-2} of PVF coated glassy carbon electrode in N_2 saturated 0.1 M $NaClO_4$ solution. Potential scan rate: 100 mV s^{-1}.

3.2. Electrocatalytic reduction of O_2 at PVF-GC electrode

Fig. 2 shows the cyclic voltammograms for the reduction of O_2 with GC and PVF-GC electrodes in O_2 saturated 0.1 M

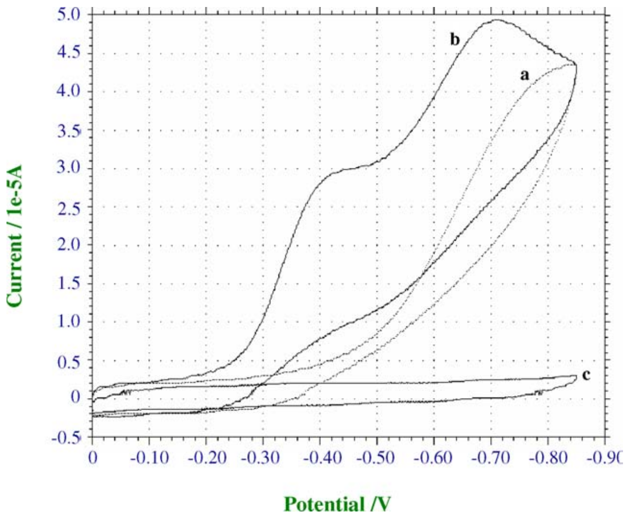

Fig. 2. Cyclic voltammograms for the O_2 reduction (a) GC; (b) PVF-GC electrodes (1.37×10^{-7} mol PVF cm^{-2}) in O_2 saturated 0.1 M $NaClO_4$ solution. The line (c) is the blank response at both of GC and PVF-GC electrodes, in N_2 saturated 0.1 M $NaClO_4$ solution. Potential scan rate: 100 mV s^{-1}.

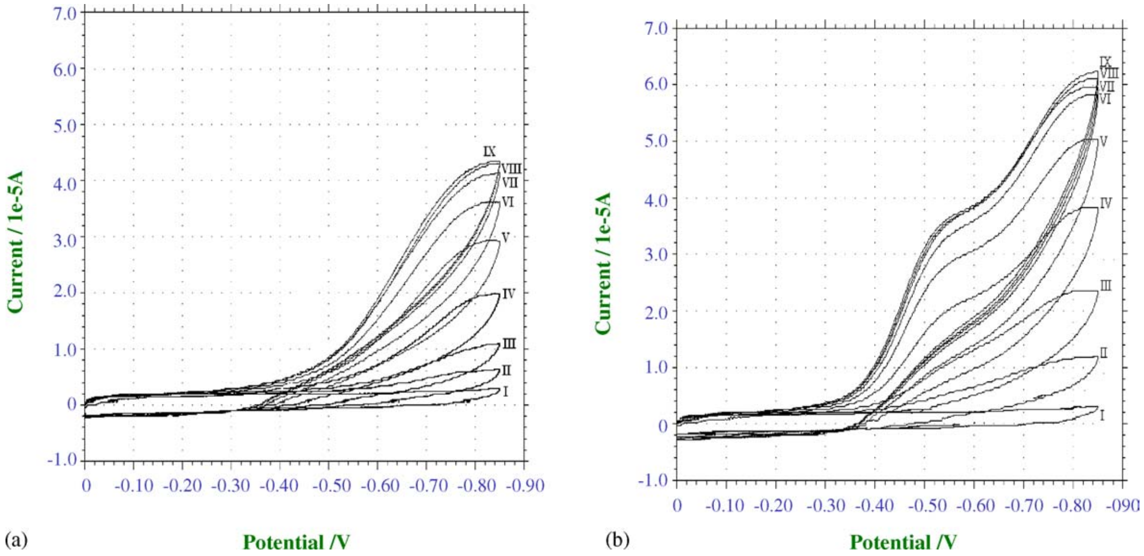

Fig. 3. Cyclic voltammograms of (a) GC and (b) PVF-GC electrodes 1.37×10^{-7} mol PVF cm^{-2} in 0.1 M $NaClO_4$ solution with increasing concentration of O_2. The oxygen times are (I) 0 s (saturated with N_2), (II) 40 s, (III) 100 s, (IV) 220 s, (V) 400 s, (VI) 640 s, (VII) 940 s, (VIII) 1120 s, (IX) 1360 s. Potential scan rate: 100 mV s^{-1}.

$NaClO_4$ solution. This figure reflects two important catalytic features of the PVF-GC electrode, i.e., (i) a significant positive shift and splitting of the O_2 reduction peak from −0.85 V (in the case of the GC electrode) to −0.55 and −0.80 V (at the PVF-GC electrode) and (ii) an increase in the peak current.

The effect of the PVF film on the glassy carbon electrode surface was examined. The thickness of the PVF film varied between 9.3×10^{-8} mol cm^{-2} of PVF and 1.6×10^{-7} mol cm^{-2} of PVF, when the oxygen concentration was kept constant (saturated O_2 solution). The oxygen reduction peak current values increased with polymer thickness up to a value corresponding to 1.37×10^{-7} mol cm^{-2} of PVF after which it decreased slightly. The thickness of the PVF film was kept constant at this value for all measurements.

Cyclic voltammograms of GC and PVF-GC electrodes in 0.1 M $NaClO_4$ solution containing varying concentrations of oxygen are shown in Fig. 3(a) and (b). As can be seen from these curves, there is an increase in the cathodic peak current with increasing time of oxygen bubbling into the solution on both types of electrodes up to bubbling times of about 1120 s, after which saturation occurs. The bubbling times for oxygen were used as 1800 s in all of the experiments.

At the bulk GC electrode, the reduction peak at −0.85 V is due to the two-electron reduction of O_2 to H_2O_2 and the further reduction of H_2O_2 to H_2O has not been observed under the present experimental conditions, since the H_2 evolution has occurred predominantly and in addition the reduction of H_2O_2 on GC is very slow. For the PVF-GC electrode, on the other hand, two reduction peaks at −0.55 and −0.80 V are believed to correspond to the two-step four-electron reduction of O_2, i.e., the first reduction peak at −0.55 V is due to the reduction of O_2 to H_2O_2, while the second peak at −0.80 V, the reduction of H_2O_2 to H_2O takes place. To confirm that mechanism, H_2O_2 has been added to the O_2-saturated solution with gradually increasing amounts and after each addition cyclic voltammograms have been recorded at the GC and PVF-GC electrodes (Fig. 4a, b). It is clear from Fig. 4b that the addition of H_2O_2 to the O_2-saturated solution resulted in an increase in the reduction peak current at −0.80 V, while the peak current at −0.55 V was not affected at PVF-GC electrode. On the other hand, the reduction peak current at −0.85 V was not affected significantly from the addition of H_2O_2 at the GC electrode (Fig. 4a).

The following mechanism has been proposed for the reduction of O_2 on carbon electrodes in the literature [39]

$$O_2 + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_{2\,\mathrm{ads}}^- \tag{1}$$

$$O_{2\,\mathrm{ads}}^- + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HO_2 + OH^- \tag{2}$$

$$HO_2 + O_{2\,\mathrm{ads}}^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HO_2^- + O_2 \tag{3}$$

or

$$HO_2 + e^- \rightleftharpoons HO_2^- \tag{4}$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \tag{5}$$

The product of the first electron transfer O_2^- may be strongly bound through its radical structure to paramagnetic centers, or microscopic regions of the surface [11]. Relatively mobile adsorbed O_2^- ions on the remainder of the surface may migrate either to “trapped” O_2 ions, or to other active sites at which the disproportionation reaction (2) occurs. Reaction (2) is the protonation of $O_{2\,\mathrm{ads}}^-$, and proposed that k_2 are increased relative to their solution values by adsorption. Two important conclusions are available at PVF-GC electrode. First, the PVF coating must increase the rate of O_2 reduction to superoxide (k_1). Second, adsorption is critical to increasing the reduction rate by accelerating protonation of O_2^-. Increases in $O_{2\,\mathrm{ads}}^-$ from PVF coating

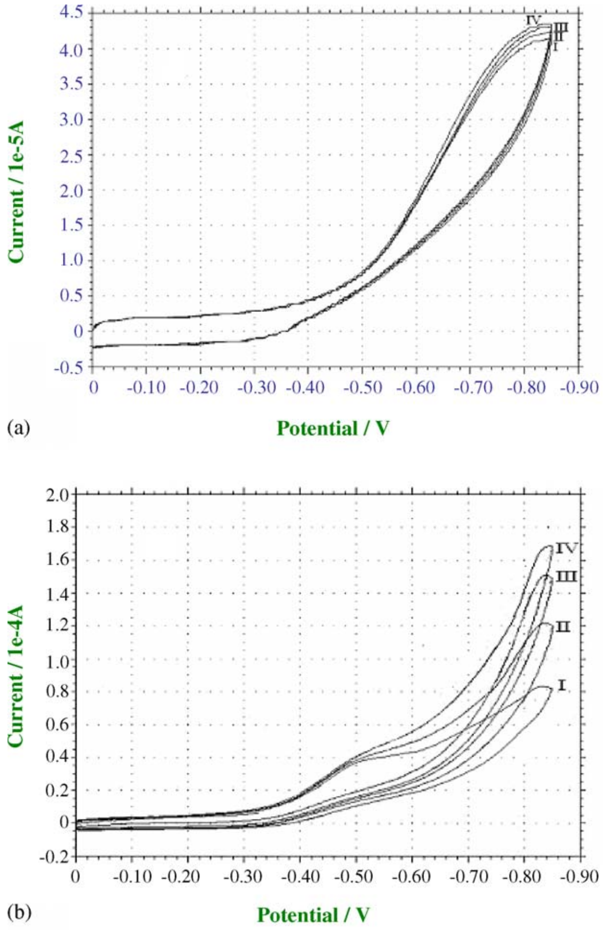

Fig. 4. Cyclic voltammograms of (a) GC and (b) PVF-GC electrodes for various concentration of H_2O_2: (I) 0 mM, (II) 1.5 mM, (III) 3.0 mM, (IV) 6.0 mM in oxygen saturated 0.1 M $NaClO_4$ solution. Potential scan rate: 100 mV s^{-1}.

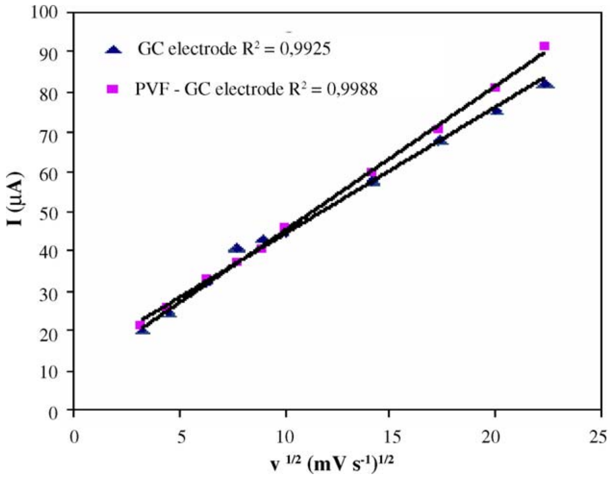

Fig. 5. Plots of reduction peak currents, *I*, (µA) vs. square root of scan rates, $\upsilon^{1/2}$, $(\mathrm{mV\,s^{-1}})^{1/2}$ for (▲) GC and (■) PVF-GC electrodes in O_2 saturated 0.1 M $NaClO_4$ solution. Potential scan rate: 100 mV s^{-1}.

can be caused either by formation of new adsorption sites or by increases in microscopic surface area. Observed changes in O_2 reduction voltammetry by surface modification can be explained by changes in $O_2{}^-$ adsorption and rate of $O_2{}^-$ generation from O_2.

The cyclic voltammograms of the GC and PVF-GC electrodes in 0.1 M $NaClO_4$ solution saturated with O_2 were recorded at various scan rates. The currents of oxygen reduction are increased with the increase of scan rates. Plots of reduction peak current versus the square root of scan rate for oxygen reduction are shown in Fig. 5. As is seen from Fig. 5, there is a linear correlation between the reduction peak current and the square root of the scan rate, and this result demonstrates that the electrocatalytic reductions are controlled by mass transport of oxygen from the bulk solution to the electrode surface.The reduction of O_2 at GC and PVF-GC electrodes were also studied by chronoamperometry. The chronoamperograms in the absence and presence of O_2 are recorded. The net electrolysis current was obtained by subtraction of the background current using the point-by-point subtraction method. The current for the electrochemical reaction (under mass transport control) of an electro active material (O_2 in this case) is described by the Cottrell equation

$$I = \frac{nFAD^{1/2}C}{\pi^{1/2}t^{1/2}} \tag{6}$$

where *D* is diffusion coefficient ($\mathrm{cm^2\,s^{-1}}$) and *C* is the bulk concentration ($\mathrm{mol\,cm^{-3}}$) of O_2. *A* is effective electrode area ($\mathrm{cm^2}$), *n* is the number of electrons transferred and *F* is Faraday constant.

A potential of −0.85 V was used for GC electrode in chronoamperometric studies. The chronoamperometric curve in the presence of O_2 for GC electrode and the corresponding plot of net current versus $t^{-1/2}$ are shown in Fig. 6(a). The number of electrons transferred in the reduction of O_2 is obtained from the slope of this plot. The diffusion coefficient, *D*, and the concentration of O_2, *C*, were obtained from the literature. The diffusion coefficient and the concentration of O_2 were taken $1.67 \times 10^{-5}\ \mathrm{cm^2\,s^{-1}}$ and $1.38 \times 10^{-6}\ \mathrm{mol\,cm^{-3}}$, respectively [40]. The number of electrons transferred in the reduction of O_2 at GC electrode was calculated as 2.04. The reduction of O_2 at GC electrode is a two-electron process, which indicates the formation of H_2O_2 by the reduction of O_2. To determine the number of electrons transferred in the reduction of O_2 at PVF-GC electrode, chronoamperometric curves were recorded at −0.55 (Fig. 6(b)) and −0.80 V (Fig. 6(c)). The number of electrons involves in each step for the O_2 reduction were calculated as 2.02 and 2.91 for −0.55 and −0.80 V, respectively. The calculated *n* values shows that the first reduction peak is assigned to the two-electron reduction of O_2 to H_2O_2, while the second reduction peak is the subsequent two-electron reduction of H_2O_2 to H_2O on PVF-GC electrode. Although the two peaks of curve b (in Fig. 2) represent a two-electron + two-electron reduction of O_2, the first peak current is higher than the second one. Furthermore, the number of transferred electrons at −0.80 V was calculated as 2.91 that this value is smaller than 4.0. This may be due to the catalytic decomposition of H_2O_2 by the PVF matrix on the GC electrode [27]

$$\mathrm{2PVF + H_2O_2 + 2H^+ \rightarrow 2PVF^+ + 2H_2O} \tag{7}$$

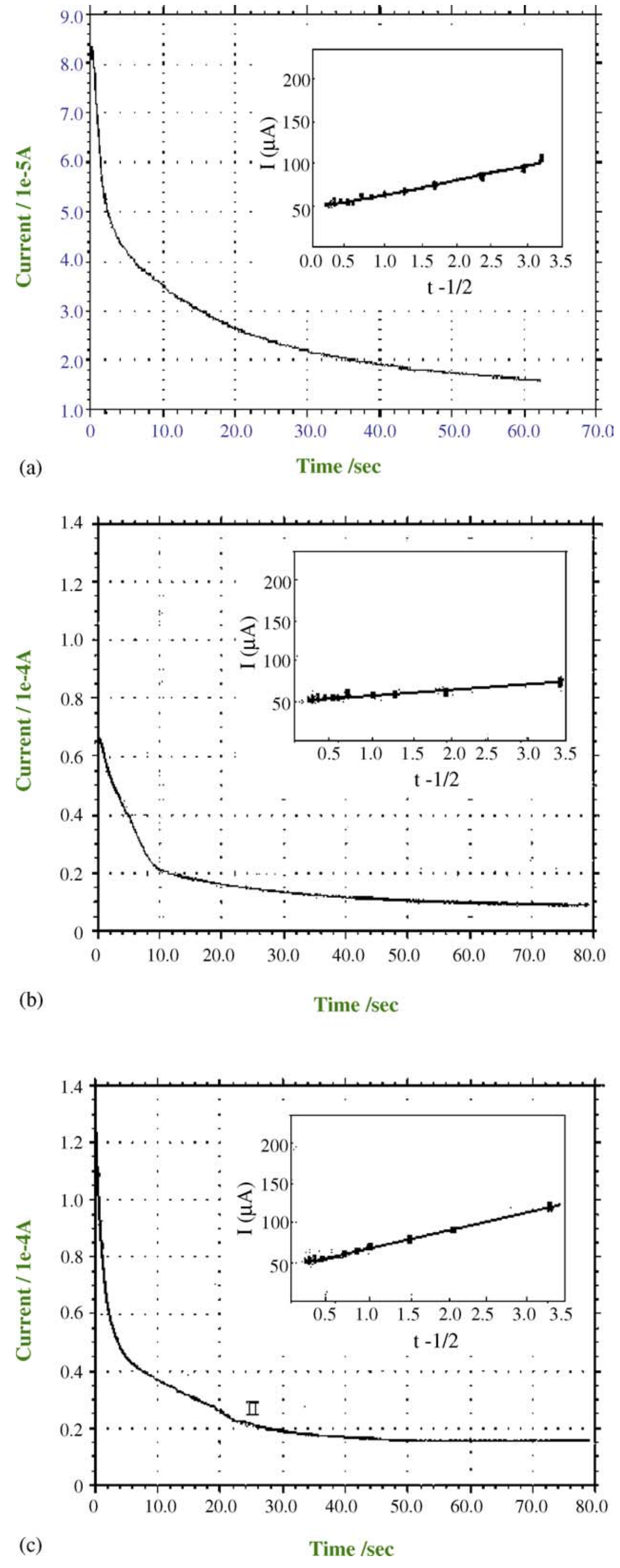

Fig. 6. Chronoamperometric responses in O_2 saturated 0.1 M $NaClO_4$ solution obtained at a potential of (a) −0.85 V vs. SCE for GC electrode, (b) −0.55 V vs. SCE for PVF-GC electrode, (c) −0.80 V vs. SCE for PVF-GC electrode. The insets show the corresponding Cottrell plots I (μA) vs. $t^{-1/2}$ ($s^{-1/2}$). Potential scan rate: 100 mV s^{-1}.

Consumed PVF sites are catalytically regenerated at the applied potentials

$$PVF^+ + e^- \rightarrow PVF \tag{8}$$

We have shown in earlier study [36] that PVF^+ sites are act as a mediator for the oxidation of H_2O_2 according to

$$H_2O_2 + 2PVF^+ \rightarrow O_2 + 2PVF^+ + 2H^+ \tag{9}$$

H_2O_2 can be reduced chemically by the PVF sites and PVF^+ sites can be electroreduced at the applied potential. Furthermore, PVF^+ sites can also be reduced chemically by the H_2O_2. Catalytic regeneration of PVF sites occurs in competition with the chemical reduction of PVF^+ sites, resulting in the small peak current of the second wave relative to the first one, and the number of transferred electrons is smaller than 4.0.

3.3. The effect of the pH

The electrocatalytic reduction of oxygen may be affected by the pH value of the medium. The effect of the pH in the phosphate buffer solution on the current response was therefore examined, and the pH values were varied between 3.0 and 9.0. The number of electrons transferred in reduction of oxygen is obtained from chronoamperometric curves. Fig. 7 shows the typical voltammograms for oxygen reduction on the GC and the PVF-GC electrodes in phosphate buffer solution of various pH values. As can be seen from Fig. 7, the reduction potentials of oxygen to hydrogen peroxide are dependent on pH and shifts to more positive potentials with increasing pH.

The current values of oxygen reduction obtained with PVF-GC electrodes were substantially higher than those obtained with bare GC electrodes for all the working pH values. Furthermore, the reduction of oxygen at GC and PVF-GC electrodes were also studied by chronoamperometry in phosphate buffer solutions of various pHs. It was found that the reduction of oxygen on bare glassy carbon electrode is two-electron reduction process in both acidic and alkaline medium. The reduction of oxygen on PVF-GC electrodes are two-electron process in solutions at pH <6, while two-electron reduction followed by two-electron reduction process occurs in solutions at pH >6. The change in reaction pathway taken places in pH 6.

This experimental phenomenon can be explained in the following way: the amount of adsorbed $O_2{}^-$ on the surfaces plays a major role in the catalytic reaction. Ferrocene moieties in PVF matrix are a sandwich form contained Fe (II). Fe (II) is well known to coordinate O_2 in an "end-on" configuration in which a donor–acceptor type bonding occurs through a partial or even complete electron transfer from Fe (II) to O_2. If the electron transfer is complete, Fe (II) will be transformed into Fe (III) and O_2 molecules will be transformed into superoxide $O_2{}^-$ ions [7]. Ferrocene centers on PVF-GC electrode play two important roles. First, ferrocene centers must increase the rate of O_2 reduction to superoxide. Second, the amount of adsorbed superoxide must be increased by coordination of Fe (II) with O_2. Observed changes in O_2 reduction voltammetry by surface modification

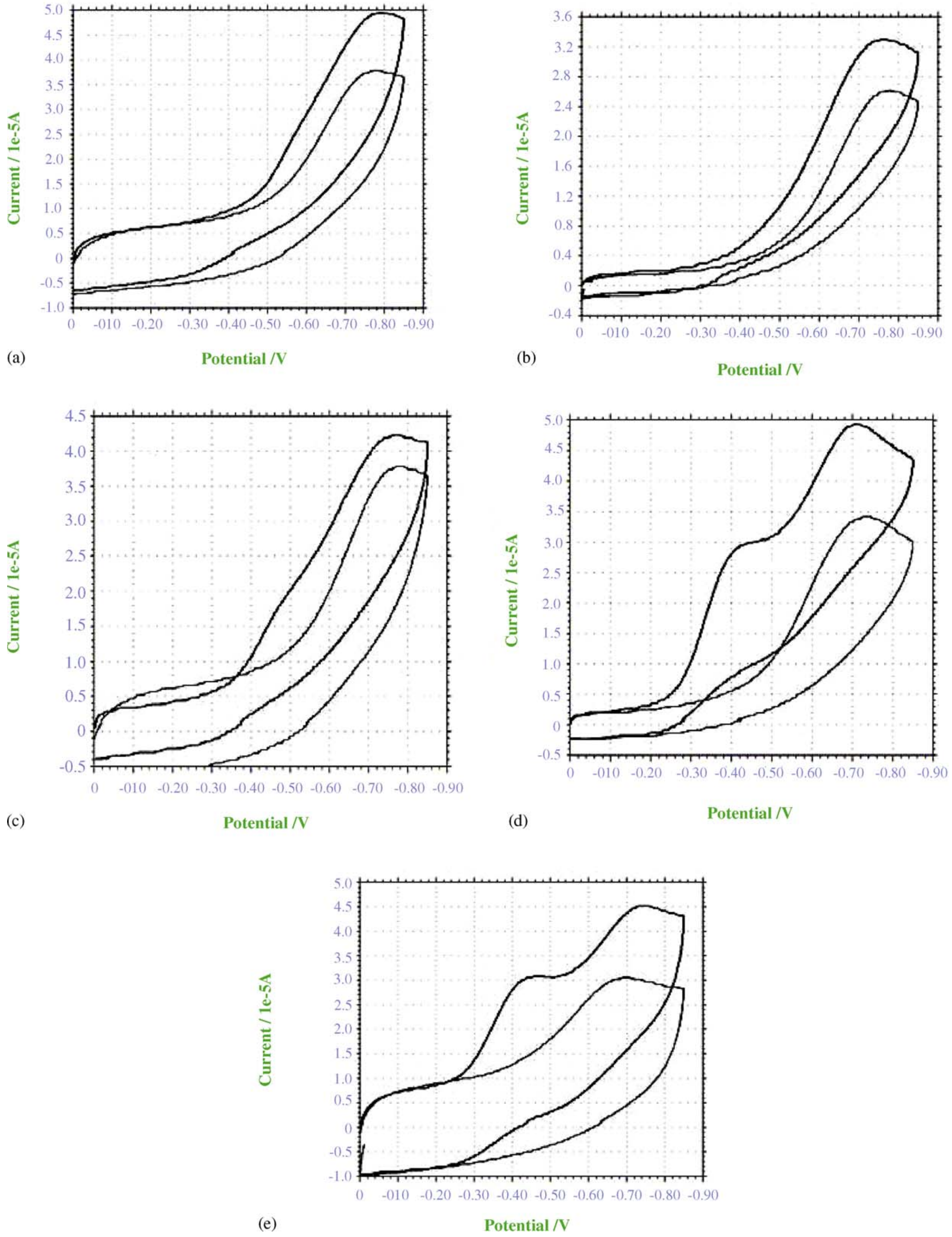

Fig. 7. Cyclic voltammograms of (—) GC, (—) PVF electrodes in oxygen-saturated phosphate buffer solutions (a) pH 3, (b) pH 5, (c) pH 6, (d) pH 7, (e) pH 9. Potential scan rate: 100 mV s^{-1}.

can be explained by changes in $O_2{}^-$ adsorption and rate of $O_2{}^-$ generation from O_2. It is well known that Fe (II) is not stable enough at acidic medium and it is not coordinate O_2 completely. Furthermore, pK_a value for HO_2 is 4.8 approximately [12]. The protonation rate of $O_2{}^-$ increases in solutions at pH ≤ 5 while the amount of adsorbed superoxide decreases. Thus, the catalytic effect of modified surface on oxygen reduction decreases with increased acidity.

4. Conclusion

The effects of PVF modification of GC electrode were examined on the O_2 reduction in both 0.1 M $NaClO_4$ solution and phosphate buffer solutions. Some interesting features were observed:

- The reduction pathway of O_2 was altered from one-step two-electron reduction to two-step four-electron reduction upon PVF modification of GC electrode in both 0.1 M $NaClO_4$ solution and phosphate buffer solutions of pH >6.
- A significant positive shift of the reduction peak potentials and concurrent increase of the peak current were achieved.
- A significant catalytic effect for the H_2O_2 reduction was also obtained.
- The catalytic effect of the modified surface increases with decreasing acidity.

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