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Mechanism of the Amperometric Response of a Proposed Glucose Sensor Based on a Polypyrrole-Tubule-Impregnated Membrane

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13. ABSTRACT *(Maximum 200 words)*

Nolte et al recently proposed a new type of amperometric glucose sensor. This sensor is based on a microporous membrane that contains polypyrrole tubules within the pores of the membrane. The procedure for preparing these polypyrrole tubules was developed in this laboratory. Nolte et al claim that glucose oxidase can be irreversible adsorbed to the inside walls of these polypyrrole tubules and that the resulting device functions as a glucose sensor. Indeed, they claim that this device functions via direct electron transfer from the reduced enzyme to the polypyrrole tubule. We have recently explored the response characteristics of this proposed new sensor. Our results suggest that this sensor does not function in the manner proposed by Nolte et al. Instead, our results indicate that the device operates by direct electrochemical oxidation of glucose at the metal (Pt) film that is coated onto one face of the membrane. This is proven by the fact that the sensitivity of the device is improved when polypyrrole and glucose oxidase are not present in the membrane.

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Mechanism of the Amperometric Response of a Proposed Glucose Sensor Based on a Polypyrrole-Tubule-Impregnated Membrane

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ABSTRACT

Nolte et al. recently proposed a new type of amperometric glucose sensor. This sensor is based on a microporous membrane that contains polypyrrole tubules within the pores of the membrane. The procedure for preparing these polypyrrole tubules was developed in this laboratory. Nolte et al. claim that glucose oxidase can be irreversibly adsorbed to the inside walls of these polypyrrole tubules and that the resulting device functions as a glucose sensor. Indeed, they claim that this device functions via direct electron transfer from the reduced enzyme to the polypyrrole tubule. We have recently explored the response characteristics of this proposed new sensor. Our results suggest that this sensor does not function in the manner proposed by Nolte et al. Instead, our results indicate that the device operates by direct electrochemical oxidation of glucose at the metal (Pt) film that is coated onto one face of the membrane. This is proven by the fact that the sensitivity of the device is improved when *polypyrrole and glucose oxidase are not present in the membrane.*

Introduction

Considerable research effort is currently being devoted to the development of amperometric glucose sensors based on the enzyme glucose oxidase.[1-20] Glucose oxidase catalyzes the two-electron, two-proton oxidation of glucose, and the electrons and protons are transferred to the cofactor flavin adenine dinucleotide (FAD) which is buried within the enzyme. Unfortunately, the FAD cannot be reoxidized by direct electrochemistry at an electrode. Hence, most sensors of this type make use of an electron accepting species which can reoxidize the FAD and then shuttle the electrons to a nearby anode. Electron acceptors employed include O_2[2-5] and various synthetic oxidizing agents such as quinones[6-8] and derivatives of ferricinium.[9-17] Developing methods for immobilizing both the enzyme and the electron acceptor at an electrode surface to produce a compact, reproducible and reliable sensor remains one of the most challenging aspects of this research effort.

Nolte et al. have recently made a potentially interesting and important contribution to this research effort.[18-20] They used a procedure developed in our laboratories to prepare microscopic tubules composed of the electronically conductive polymer polypyrrole.[21,22] These tubules are prepared by synthesizing polypyrrole within the pores of a microporous membrane. Electrical contact can be made to the tubules by simply sputtering a metal film onto one face of the tubule-containing membrane (see Figure 1). Nolte et al. prepared "tubule-based electrodes" like that shown in Figure 1. They claim that glucose oxidase can be irreversibly adsorbed to the inner walls of the tubules and that the resulting electrode functions as a glucose sensor *without the need for an electron acceptor.* Indeed, they claim that this device functions by direct electron-transfer between reduced FAD and the polypyrrole tubules.[18-20]

If this is correct, it is an interesting and potentially important result. Because we developed the procedure for preparing these tubules[21,22] and because we have an interest in glucose sensors,[17] we decided to look at this proposed new sensor in our laboratory. Our results suggest that this sensor does not function in the manner proposed by Nolte et al.[18-20] Instead, we have found that the device operates by direct electrochemical oxidation of glucose at the metal (Pt) film that is coated onto one face of the membrane (see Figure 1). This is proven by the fact that the sensitivity of the device is improved when *polypyrrole and glucose oxidase are not present in the membrane*. We describe the results of these investigations in this paper.

Experimental

Materials and Equipment. Pyrrole (99%, Aldrich) was twice distilled under N_2 prior to use. Purified water was obtained by passing house-distilled water through a Milli-Q water purification system (Millipore). $FeCl_3$ (Aldrich), glucose oxidase from Aspergillus Niger (Type II, Sigma), and microporous polycarbonate membranes (Nuclepore, 0.6 μm-pore diameter) were used as received. Indium/tin oxide-coated glass (ITO) was obtained from PPG. Electrochemical experiments were conducted using an EG&G Model 273 potentiostat. Metal films (Pt and Au) were deposited using an Ar-plasma metal sputtering apparatus (Technics, Hummer).

Sensor Fabrication. Polypyrrole microtubule-based sensors were prepared by immersing a ca. 5 cm^2 section of the microporous polycarbonate membrane into 10 mL of an aqueous solution that was 0.2 M in pyrrole monomer. Oxidative polymerization was initiated by adding 10 mL of an aqueous solution that was 0.5 M in $FeCl_3$ and 0.5 M in p-toluenesulfonic acid to the pyrrole solution. We have shown that when polypyrrole is oxidatively polymerized in the presence of the polycarbonate membrane, polymer preferentially nucleates and grows on the pore walls and faces

of the membrane.[21,22] Because of the preferential growth on the pore walls, polypyrrole tubules are obtained.

The thickness of the tubule wall can be varied by varying the polymerization time.[21,22] In these studies we systematically varied the polymerization time over a range from 30 sec. to 10 min. After polymerization, a platinum film (ca. 100 nm-thick) was sputter-coated onto one face of the tubule-impregnated membrane (see Figure 1). This film blocks the pores at the membrane surface (Figure 1). Hence, these membranes have a blocked Pt-film-coated face and an open polypyrrole-tubule face. The tubules were exposed to glucose oxidase following the procedure used by Nolte et al.[18,20] The tubule-containing membrane was immersed for 1 hr into 50 mL of phosphate buffer (pH = 7.0) containing 300 units of glucose oxidase and then dried overnight at ca. 4° C in a refrigerator. The phosphate buffer was prepared by adding a small quantity of 4.0 M KOH to a 0.5 M solution of KH_2PO_4.

We call an electrode prepared in this way an s-Pt/PC/PPy/GOD electrode. The prefix "s" in s-Pt denotes the sputtered Pt film. The prefix "s" is used because we will show that these sputtered Pt films have higher electrochemical activity than Pt electrodes made in the conventional way from Pt foil. PC stands for the polycarbonate host membrane, PPy stands for the polypyrrole tubules present in the membrane, and GOD stands for the glucose oxidase (if any) within the tubules.

The s-Pt/PC/PPy/GOD electrode was used as the working electrode in the electrochemical cell shown in Figure 2. Electrical contact was made to the membrane by clamping the s-Pt-film-coated face against an ITO electrode. As indicated in Figure 2, the polypyrrole-tubule face of the membrane contacted an electrolyte solution (the pH = 7.0 phosphate buffer). A Pt mesh counter electrode and an Ag/AgCl reference electrode (in sat. KCl) were immersed into this solution. The O-ring used provided a working electrode surface area of 2.5 cm^2.

Three types of control sensors were also prepared and evaluated. The first was a membrane that was prepared exactly as described above but not exposed to glucose oxidase. This device is referred to as an s-Pt/PC/PPy electrode. Obviously, this electrode will allow for an assessment of whether glucose oxidase is a necessary component in the proposed[18,20] glucose sensor. The second control device was prepared by sputtering a Pt film onto a polycarbonate membrane that contained no polypyrrole or glucose oxidase. This device (referred to as an s-Pt/PC electrode) will allow for an assessment of the role played by polypyrrole and glucose oxidase in the response of the sensor. The final type of control sensor was prepared by sputtering a Pt film (ca. 100 nm-thick) onto the surface of an ITO electrode. We refer to this electrode as an s-Pt electrode. The s-Pt electrode is the simplest electrode investigated as it contains no polycarbonate, no polypyrrole and no glucose oxidase. Finally, we also investigated the electrochemical response of sputtered-Au (s-Au) electrodes. This type of electrode was prepared by sputtering Au films (100 nm-thick) onto the surface of an ITO electrode.

Amperometric measurements. The methods used were analogous to those employed by Nolte et al.[18,20] The cell (Figure 2) was charged with ca. 15 mL of the phosphate buffer and the potential of the working electrode (i.e. the s-Pt/PC/PPy/GOD, s-Pt/PC/PPy, s-Pt/PC or s-Pt electrode) was potentiostated at 0.35 V vs. Ag/AgCl. After background currents decayed to a constant value,[18,20] the phosphate buffer was spiked with a measured volume of a stock glucose solution (2.0 M in pH = 7.0 phosphate buffer), and the solution was stirred for 30 sec. As was observed by Nolte et al.[18,20] injection of glucose caused an increased anodic current to flow. The current was monitored until a plateau value was reached. Another aliquot of glucose solution was then injected and the process was repeated.

In this way, calibration curves of anodic current vs. glucose concentration were obtained.

In their work, Nolte et al have used both pH =7.0 phosphate buffer[18] and "phosphate-buffered saline solution"[20]. However, they have shown that NaCl lowers the amperometric response of their device to glucose[18]. Since NaCl proved detrimental to their amperometric response, we have chosen to use phosphate buffer that does not contain saline for these studies. It is well know that Cl^- inhibits glucose oxidation kinetics[23].

It is conceivable that the amperometric response reported here is due to oxidation of H_2O_2 generated from the reaction of O_2 with the reduced form of the enzyme. To eliminate this as a possibility, all solutions were purged with N_2 for one hour prior to electrochemical measurements and were blanketed in N_2 during measurement. Furthermore, to unequivocally prove that this procedure eliminated the possibility of H_2O_2 production and oxidation we ran several calibration curves in the presence and absence of 500 units of dissolved catalase. Catalase catalyzes the decomposition of H_2O_2 to O_2 and H_2O. If a fraction of the amperometric current was due to H_2O_2, the oxidation current would be smaller in the presence of catalase. The calibration curves in the presence and absence of catalase were identical.

Finally, it is conceivable (although highly unlikely) that glucose oxidase is not enzymatically active in the buffer used here. To eliminate this as a possibility, we assayed for glucose oxidase activity in this buffer. The solutions used were 5 mM in glucose, 50 μM in the electron acceptor 2,6-dichlorophenol-indophenol[24], and contained 1 mg per mL of glucose oxidase. The enzyme activity can be assessed from the rate of disappearance of the absorbance of the oxidized form of DPIP at 602 nm. These studies showed that the enzyme has higher activity in the 0.5 M ionic strength buffer used here than in the same buffer with an ionic strength of 0.05 M.

Results and Discussion

Figure 3 shows anodic current at an s-Pt/PC/PPy/GOD electrode after spiking the buffer with an aliquot of glucose solution. As was observed by Nolte et al.,[18,20] anodic current flow increases until a plateau is reached. Figure 4 shows a plot of plateau current vs. glucose concentration. A nonlinear calibration curve, analogous to that observed by Nolte et al,[20] was obtained.

The origins of the electrochemical response shown in Figures 3 and 4 can be elucidated by investigating the magnitude of the plateau current for s-Pt/PC/PPy/GOD electrodes having polypyrrole tubules of differing wall thickness. As was discussed above, the wall thickness of the polypyrrole tubules within the membrane can be controlled by varying the polymerization time.[21,22] The shortest polymerization time used here (30 sec.) gave tubules with walls that are ca. 100 nm-thick. The longest polymerization time used (10 min) gave solid polypyrrole fibers, rather than hollow tubules.

Figure 5 shows plateau currents at s-Pt/PC/PPy/GOD electrodes as a function of polypyrrole polymerization time. The sensitivity of the s-Pt/PC/PPy/GOD electrode decreases as the tubule walls become thicker. Nolte et al. observed an analogous trend and suggested that the amount of glucose oxidase immobilized was higher for the thin-walled tubules.[20] This explanation cannot, however, account for the first data point in Figure 5. This point was obtained from an electrode that contained no polypyrrole and no glucose oxidase (i.e. an s-Pt/PC electrode). Figure 5 shows that the s-Pt/PC electrode has greater sensitivity than all of the s-Pt/PC/PPy/GOD electrodes.

This point is reinforced by the calibration curves shown in Figure 6. Figure 6 compares calibration curves for an s-Pt/PC/PPy/GOD electrode, an s-Pt/PC/PPy electrode, and an s-Pt/PC electrode. The responses of the s-Pt/PC/PPy and s-

Pt/PC/PPy/GOD electrodes are essentially identical. This unequivocally proves that glucose oxidase is not a necessary component in this device. Furthermore, the s-Pt/PC electrode shows the highest sensitivity. This unequivocally shows that polypyrrole is also not a necessary component. Indeed, its presence is detrimental to the electrochemical response.

The data presented thus far indicate that the electrochemical response observed must be attributed to either the s-Pt film that is sputtered onto the back of the membrane (Figure 1) or to the ITO electrode that acts as the current collector (Figure 1). We eliminated the ITO electrode as a possibility by looking for glucose oxidation currents at ITO electrodes that had not been coated with Pt. Glucose oxidation currents could not be observed at such naked ITO electrodes. Therefore, the sputtered Pt film must be responsible for the electrochemical response observed here and by Nolte et al.[18-20]

There have been a number of investigations of electrochemical oxidation of glucose at conventional Pt and Au electrodes.[23,25-28] (By conventional we mean Au or Pt electrodes prepared from bulk samples of the metal. This may be contrasted to the *sputtered electrodes* studied here.) The general observation with the conventional electrodes has been that while glucose can be oxidized at such electrodes, the electrode surface ultimately fouls due to adsorption of intermediates.[26,28,29] To our knowledge there has been no prior investigation of glucose oxidation at s-Pt or s-Au electrodes. Figure 7 shows cyclic voltammograms for glucose at s-Pt and s-Au electrodes. These voltammograms show that electrochemical oxidation of glucose is possible at these sputtered metal electrodes and that s-Pt has higher catalytic activity than s-Au. Analogous results were obtained at conventional Au and Pt electrodes. [23,25-28] Analogous results (i.e. that higher

currents were obtained when the membrane was sputtered with a Pt film than with an Au film) were also obtained by Nolte et al.[18,20]

Figure 8 compares the amperometric response at a conventional Pt electrode and an s-Pt electrode. (Note that the y-axis is current density, i.e. current normalized for the geometric areas of the electrodes.) Figure 8 illustrates several important points. First, the current density at the s-Pt electrode is 130 times higher than at the conventional Pt electrode. One of the problems noted for glucose sensors prepared from conventional Pt electrodes was low sensitivity, especially in neutral solutions.[25] The data in Figure 8 suggest that s-Pt electrodes can solve this sensitivity problem. The higher apparent activity of the sputtered electrode is undoubtedly attributable to a higher real electroactive surface area.

Figure 8 also addresses the issue of fouling of these electrodes. As indicated in Figure 8, the solution was stirred during the first four minutes after spiking the solution with glucose. During this time interval, the current at both the conventional and s-Pt electrodes remained relatively constant, suggesting that convection helps prevent adsorption and fouling of the electrode surface. Two effects were observed after the stirring was turned off. First, there is an immediate drop in current due to the loss of convective mass transport of glucose to the electrode surface. More importantly, however, there is a slow decay in current with time due to fouling of the electrode surface. This effect is observed at both the conventional and s-Pt electrodes. Hence, fouling of the electrode surface remains a problem for oxidation of glucose at any kind of metal electrode.

Figure 9 compares calibration curves for an s-Pt/PC electrode and an s-Pt electrode. Again, the current has been normalized for the geometric area of the electrodes. At the s-Pt/PC electrode, the glucose solution can only access the s-Pt film through the pores in the polycarbonate membrane. Because the porosity of such

membranes is very low, the true active electrode area is significantly smaller than at the s-Pt electrode. This accounts for the lower sensitivity of the s-Pt/PC electrode. These data reinforce the point that the electrochemical response is due to the s-Pt film and not due to other components of the device proposed by Nolte et al.[18,20]

Finally, Nolte et al. also investigated the selectivity of their s-Pt/PC/PPy/GOD electrodes.[18,20] They found that species such as fructose, citrate, lactate, urea, uric acid, gluconate, and pyruvate do not interfere, *when tested separately,* even when they were present at millimolar concentrations.[20] Table I shows results of experiments of this type at an s-Pt electrode. In complete agreement with the data from Nolte's s-Pt/PC/PPy/GOD electrodes,[20] we find that the glucose oxidation current at the s-Pt electrode is much larger than the current obtained for any of the potentially-interfering species. This, however, does not mean that the s-Pt electrode will function as a selective sensor for glucose. It is well known that if these other species (Table I) are present in solution with glucose, they will adsorb to the Pt surface and thus decrease the glucose oxidation current.[26,28,29] This was proven for the s-Pt electrode by making analogous measurements in a solution that was 5 mM in glucose and 5 mM in each of fructose, citrate, lactate, urea, gluconate, and pyruvate; the solution was also 1.2 mM (saturated) in uric acid. The glucose oxidation current in this solution was 9.8 $\mu A\ cm^{-2}$ as opposed to 32.9 $\mu A\ cm^{-2}$ for the solution that contained only 5 mM glucose.

Conclusions

We have shown that of the electrodes investigated here (s-Pt/PC/PPy/GOD, s-Pt/PC/PPy, s-Pt/PC, and s-Pt) the highest sensitivity to glucose is observed at the simplest - the s-Pt electrode. We have also shown that the polypyrrole and glucose oxidase present in the other types of electrodes are not responsible for the observed electrochemical response. Rather, the s-Pt film at the back of the polycarbonate

membrane is responsible for the glucose oxidation currents. Finally, while the s-Pt electrode shows high activity for glucose oxidation, it cannot serve as a selective glucose sensor because other species (e.g. Table I) act as interferants by adsorbing to the electrode surface.

Acknowledgments

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Figure Captions

Figure 1. Schematic diagram of procedure used to prepare the proposed glucose sensor. The pores in a microporous polycarbonate membrane (A) are used as templates to synthesize polypyrrole tubules (B). As indicated in (B), this occurs because polypyrrole preferentially grows on the faces and pore walls of the membrane. One face of the membrane is then sputter-coated with a Pt film (C).

Figure 2. Schematic diagram of electrochemical cell used in these investigations. The glass tube was 1.8 cm in diameter.

Figure 3. Current density vs. time for an s-Pt/PC/PPy/GOD electrode after the solution was made 10 mM in glucose. Electrolyte solution was pH = 7.0 phosphate buffer. The s-Pt/PC/PPy/GOD was prepared with polymerization time of 1 min.

Figure 4. Glucose calibration curve for an s-Pt/PC/PPy/GOD electrode. The s-Pt/PC/PPy/GOD was prepared with polymerization time of 30 sec.

Figure 5. Plot of current density for glucose oxidation vs. polymerization time used during tubule synthesis for s-Pt/PC/PPy/GOD electrodes and for an s-Pt/PC electrode (first point). The thickness of the tubule wall increases with polymerization time (see text). Solution as per Figure 2.

Figure 6. Glucose calibration curves for s-Pt/PC, s-Pt/PC/PPy and s-Pt/PC/PPy/GOD electrodes. The s-Pt/PC/PPy and s-Pt/PC/PPy/GOD were prepared with polymerization time of 30 sec.

Figure 7. Cyclic voltammograms for glucose at s-Au and s-Pt electrodes. Solution was 10 mM in glucose (pH = 7.0 phosphate buffer). Scan rate = 10 mV sec^{-1}. Geometric area of the electrodes was 2.5 cm^2.

Figure 8. Comparison of amperometric response of an s-Pt electrode (top) and a conventional Pt electrode (bottom). Solution as per Figure 2.

Figure 9. Glucose calibration curves for an s-Pt electrode and an s-Pt/PC electrode.

Table 1 Oxidation current density (at 0.35 V vs. Ag/AgCl) obtained at an s-Pt electrode when immersed into a solution that was 5 mM in the indicated speces.

Molecule	Current ($\mu A/ cm^2$)
Glucose	32.9
Fructose	0.59
Citrate	1.11
Lactate	0.52
Urea	1.78
Uric acid[a)]	0.19
Gluconate	1.22
Pyruvate	0.78

a) 1.2 mM (saturated).

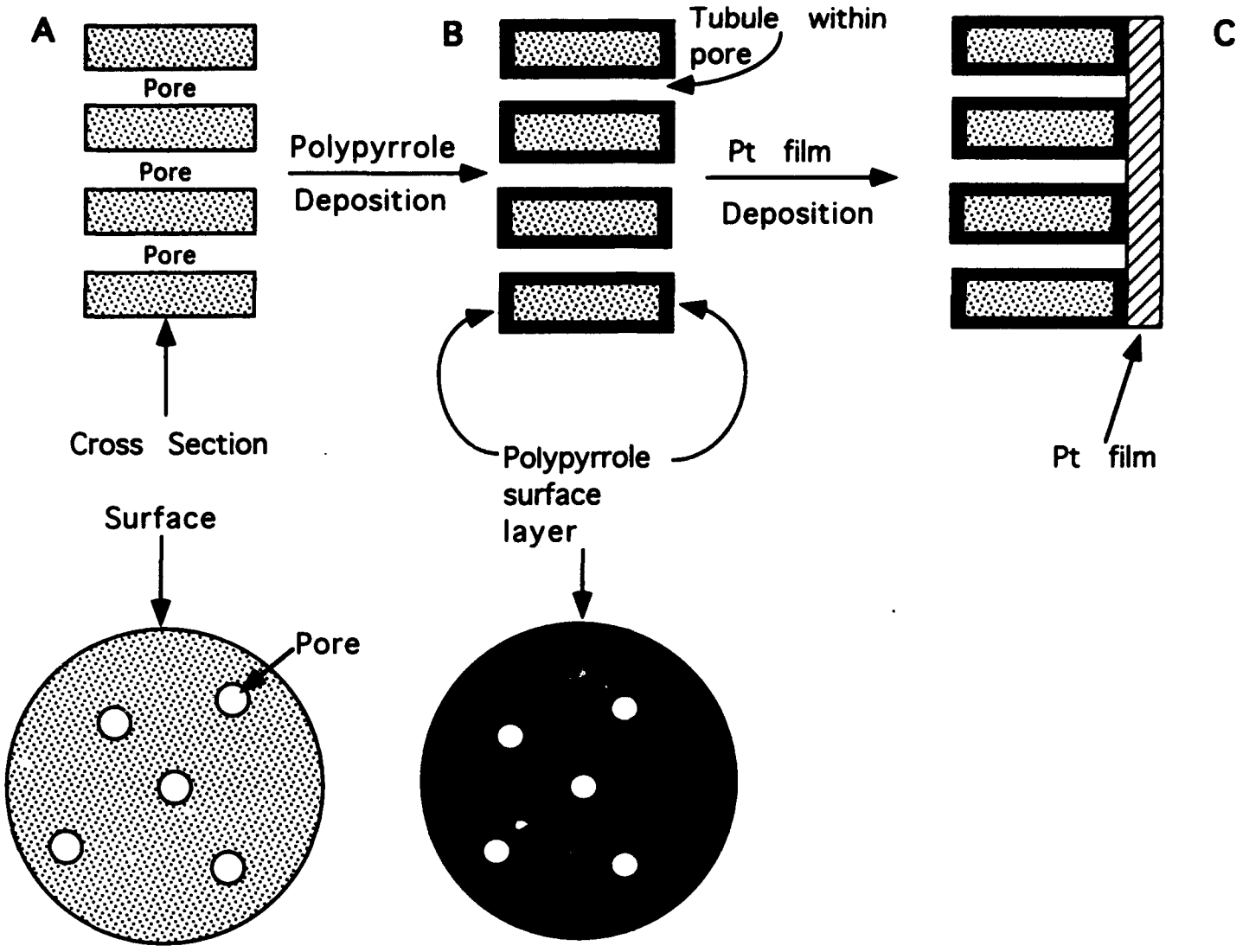
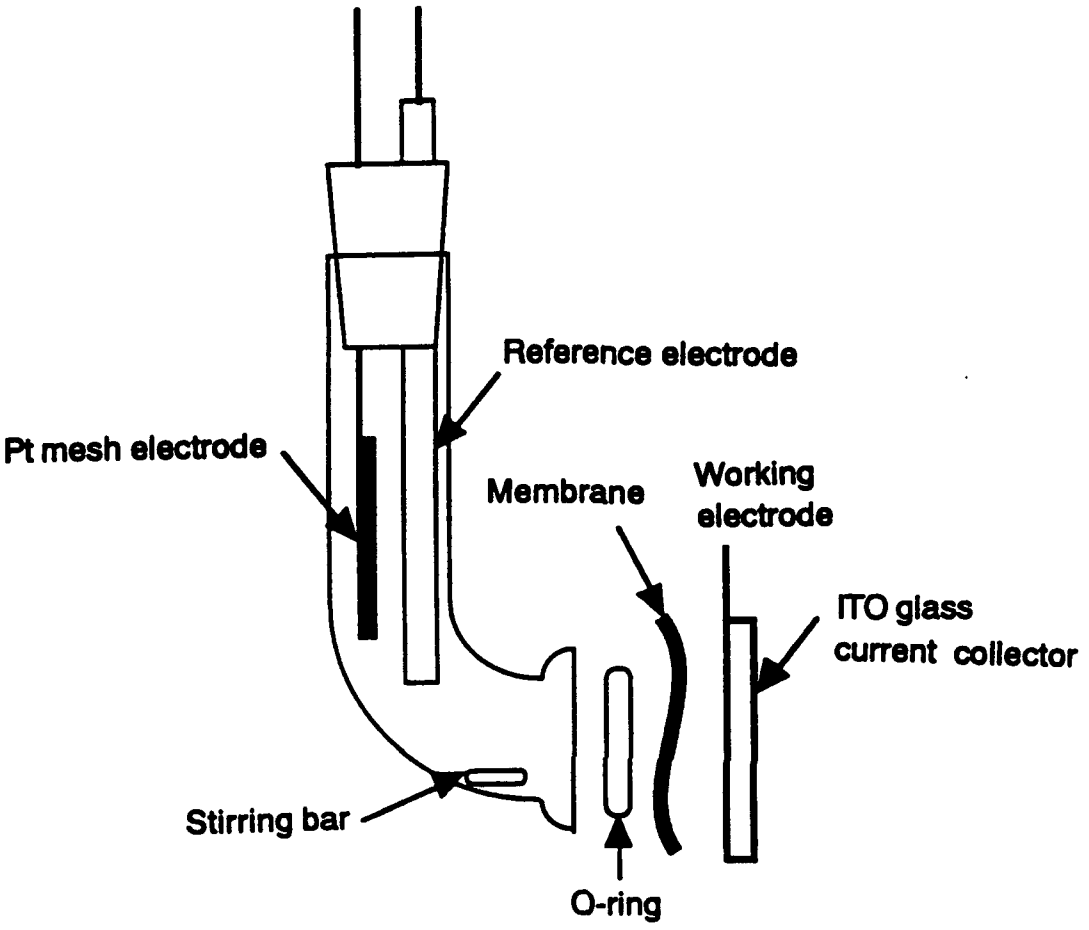

A
Pore
Pore
Pore
Cross Section
Surface
Pore
B
Tubule within pore
Polypyrrole
Deposition
Polypyrrole surface layer
Pt film
Deposition
C
Pt film

Fig. 1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Pt mesh electrode
Membrane
Working electrode
ITO glass current collector
Stirring bar
O-ring

Fig 2

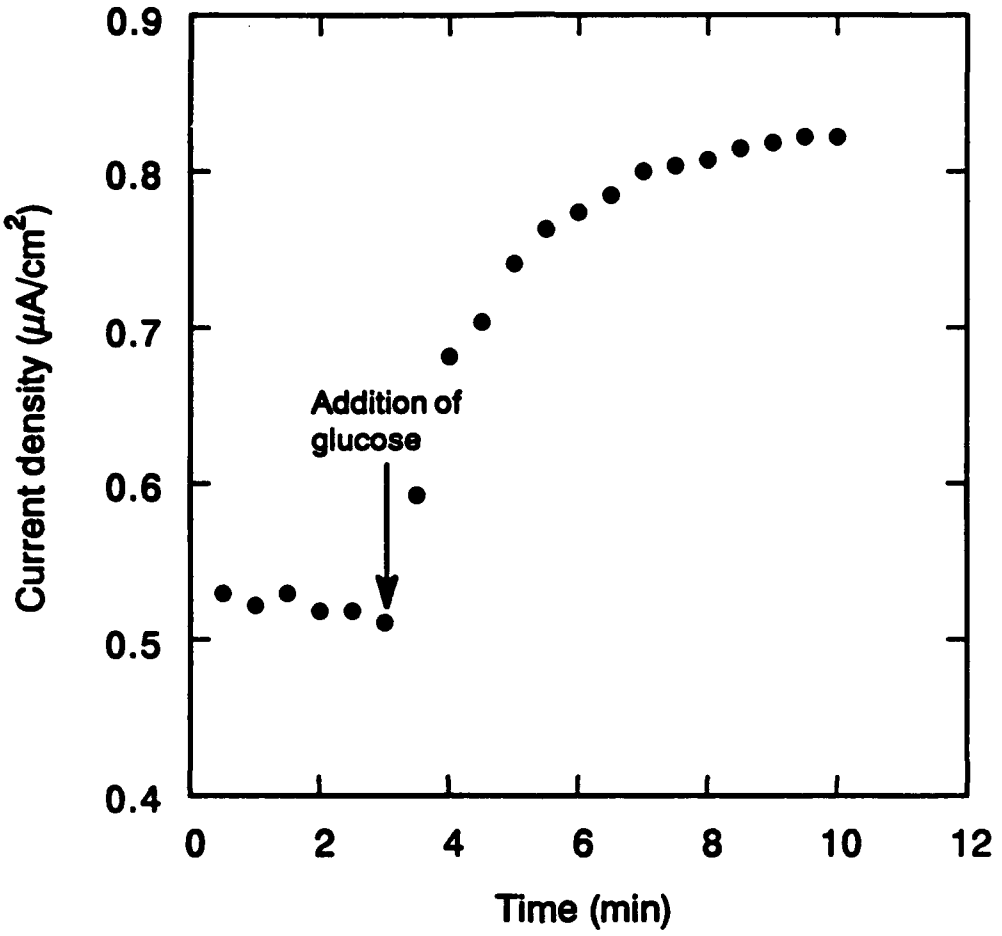
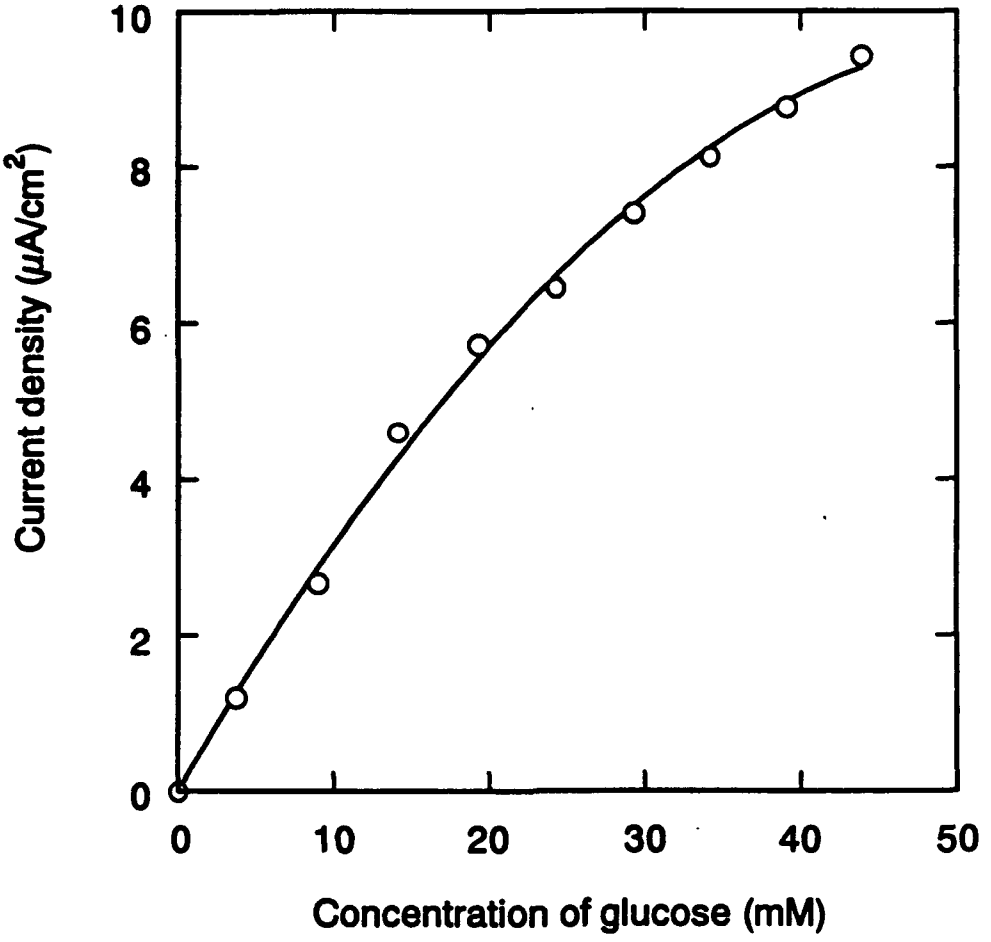

0.9
0.8
0.7
0.6
0.5
0.4
Current density (μA/cm²)
Addition of glucose
0
2
4
6
8
10
12
Time (min)

Fig. 3


Current density (μA/cm²)
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8
6
4
2
0
0
10
20
30
40
50
Concentration of glucose (mM)

Fig 4

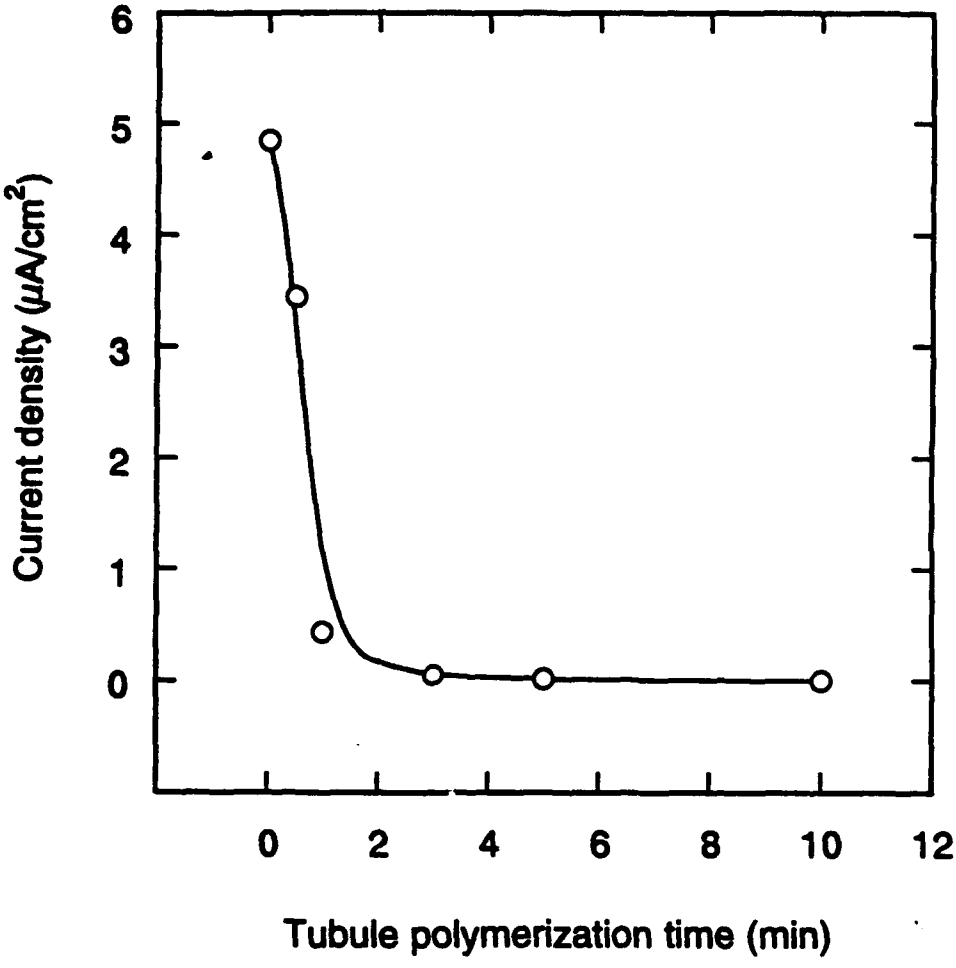
Current density (μA/cm²)
6
5
4
3
2
1
0
0
2
4
6
8
10
12
Tubule polymerization time (min)

Fig. 5

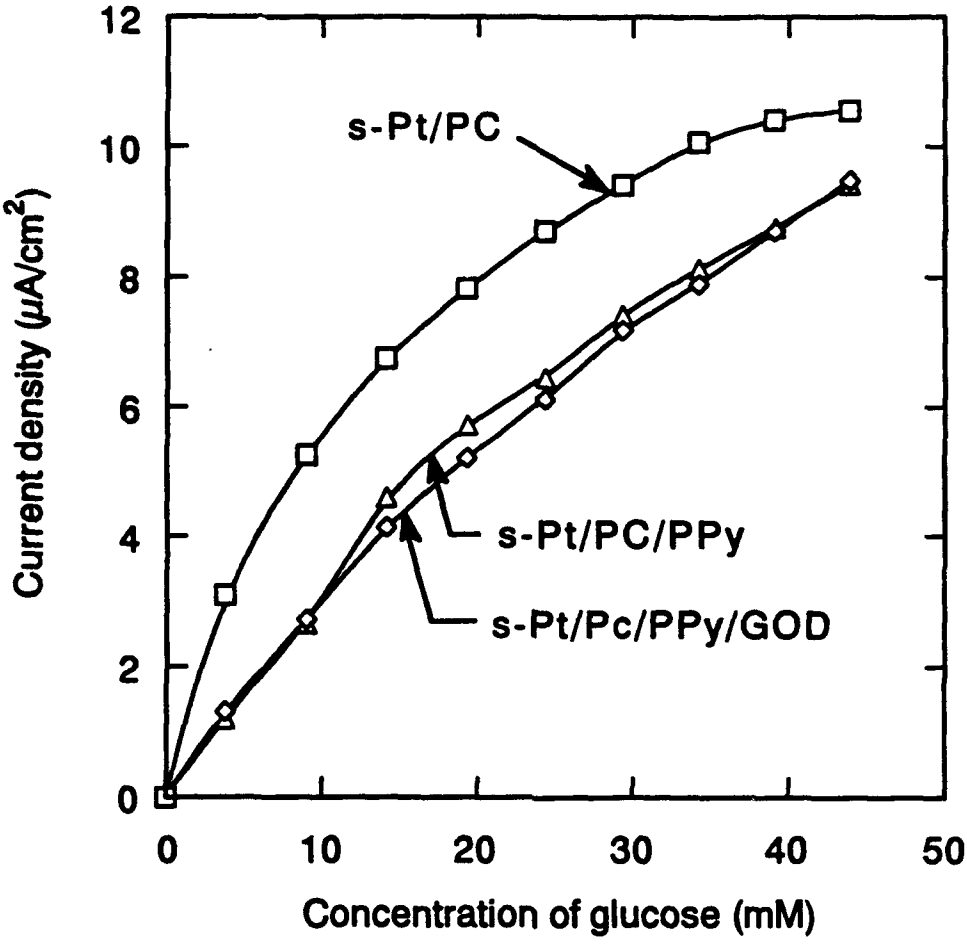
12
10
8
6
4
2
0
Current density (μA/cm²)
s-Pt/PC
s-Pt/PC/PPy
s-Pt/Pc/PPy/GOD
0
10
20
30
40
50
Concentration of glucose (mM)

Fig. 6

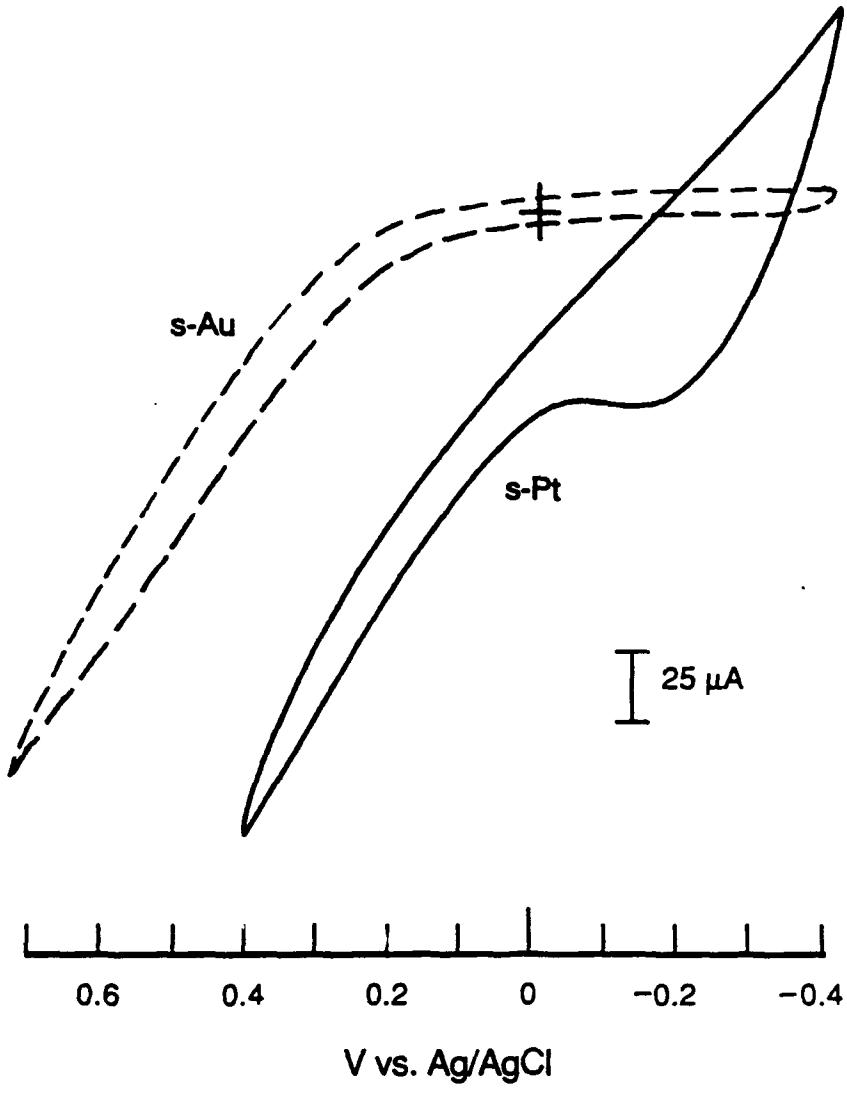

Fig 7

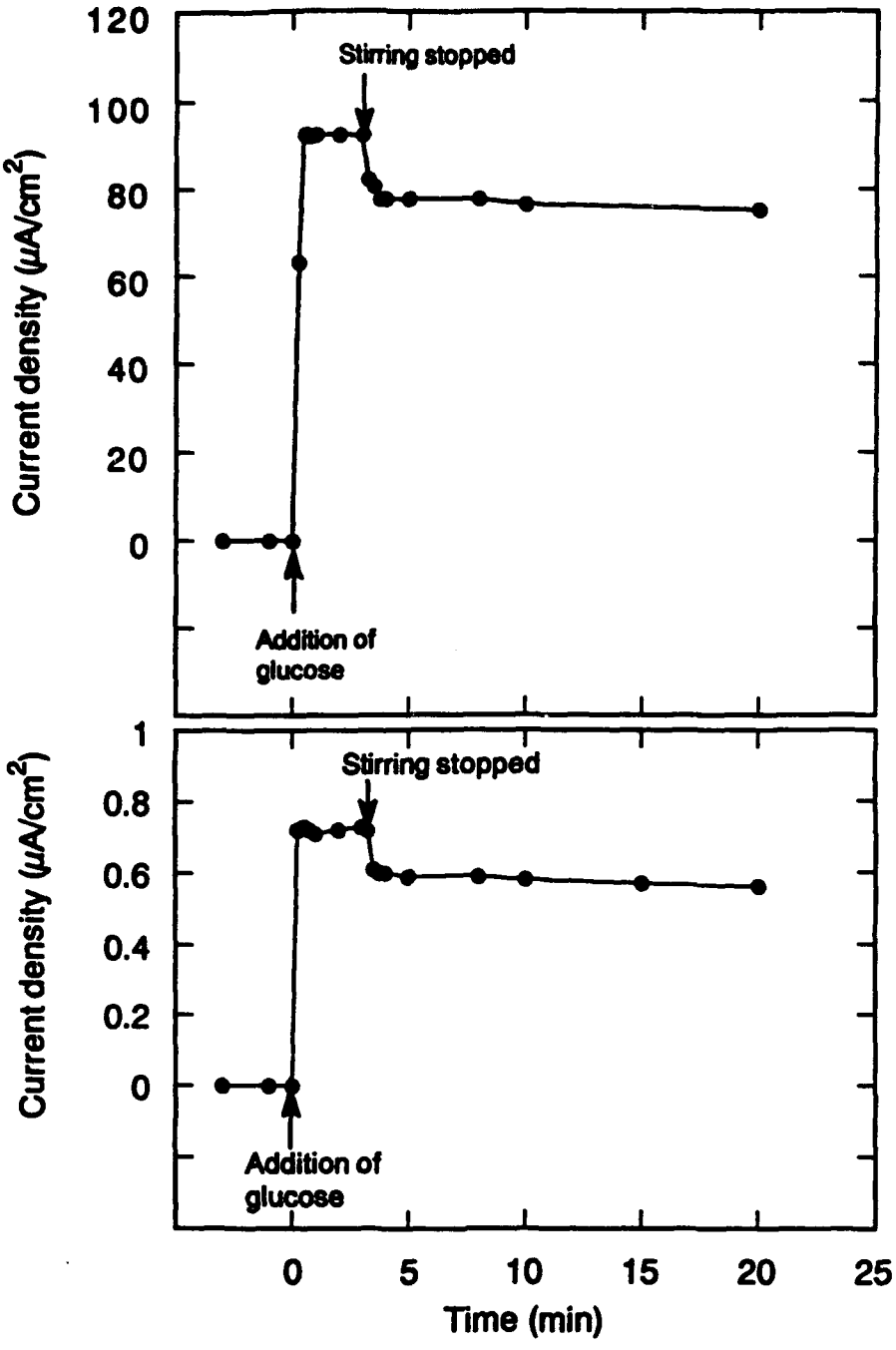
120
100
80
60
40
20
0
Current density (μA/cm²)
Stirring stopped
Addition of glucose
1
0.8
0.6
0.4
0.2
0
Current density (μA/cm²)
Stirring stopped
Addition of glucose
0
5
10
15
20
25
Time (min)

Fig. 8

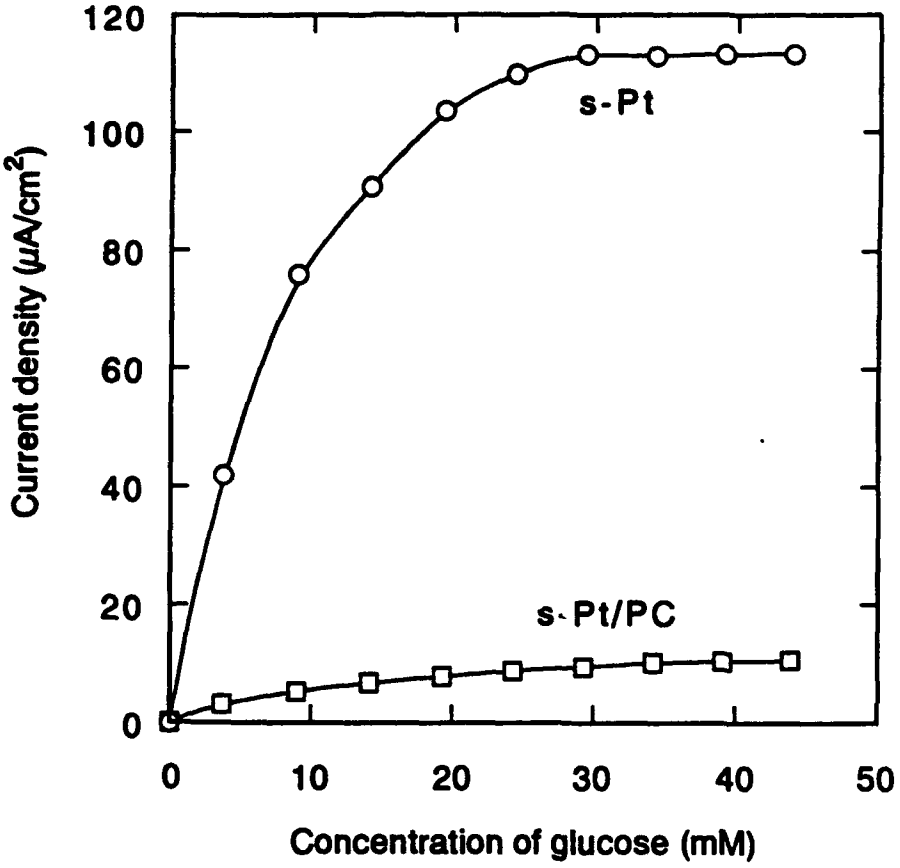
120
100
80
60
40
20
0
Current density (μA/cm²)
s-Pt
s-Pt/PC
0
10
20
30
40
50
Concentration of glucose (mM)

Fig9