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PLASMA THIN FILMS PREVENTING CHLORIDE LONS FROM INTERFERING WITH THE NERNSTIAN pH-RESPONSE OF PLATINUM ELECTRODE SURFACE

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ABSTRACT

The plasma-deposited polymer thin films at platinum surface were investigated as materials blocking access of chloride ions to the platinum surface and preventing their interference with the Nernstian responce of platinum. In the presence of chloride ions, the pH response of a naked platinum was remarkably affected. By comparison of pH responses of coated and uncoated platinum-wire electrodes immersed in solutions with chloride ions, it was found that toluene and ethylbenzene plasma films could improve the pH response of platinum. The pH response of coated platinum electrodes may be explained by the ability of protons, by virtue of their small size, to move through the polymer matrix to the platinum surface.

INTRODUCTION

Recently, there has been interest in the use of chemically modified electrodes as potentiometric sensors[1-3]. Platinum is worth notice as an electrode material for producing pH-sensing devices because it intrinsically shows the Nernstian potential response to pH of a solution[4]. However, there is a problem that pH-response reactions at platinum surface is apt to be subject to interference of redox systems, especiallly chloride ions coexisting in the solution[5]. One breakthrough to overcome the limitation and to develop ultramicro-pH-sensing devices[6] composed of platinum involves interference-preventing polymer films at the platinum surface. In this study, the plasma-deposited thin films at platinum surface were investigated as materials blocking access of chloride ions to its surface and preventing their interference with the Nernstian responce of platinum. In the presence of chloride ions, the pH response of a naked platinum was remarkably affected. By comparison of pH reponses of coated and uncoated platinum-wire electrodes immersed in solutions with chloride ions, it was found that oluene andethylbenzene plasma films could improve the pH response of platinum. Those results and their significance in regard to sensor development will be discussed.

EXPERIMENRAL

Fabrication of plasma-film-coated platinum electrodes were carried out with an ap paratus shown in Figure 1[7]. A naked platinum wire (0.5-mm diam.x 5-cm length) was

fixed at the tip of a Pyrex glass rod and inserted into the apparatus to be put at a position of a, b or c. A Pyrex reactor tube (45㎜ diameter × 80㎜ length) was connected to a vacuum system. a copper coil tubing was wound around the reactor tube. The coil was connected to a 13.56 MHz radiofrequency(rf) generator. After evacuation, a monomer vapor was introduced into the reactor from the reservoir vessel. The flow rate of the vapor(r_M) was estimated from the reduced weight of the reservoir and the elapsed time. The vapor pressure was $10-10^2$ Pa. The monomer plasma was generated by the inductively coupled discharge. Plasma polymer grown in the gas-phase was deposited on the surface of the platinum wire. It was kept room temperature and not heated during the fabrication. The thickness of the so-obtained plasma film was estimated by a scanning electron microprobe. Used momo-mers were toluene (TOL), p-xylene (p-XY), ethyl-benzene(EB), styrene(SR), Methyl methacrylate (MMA) and so on, which were preliminary degased by freeze-pump-thaw method. Table 1 shows typical conditions for fabrication of plasma-film coated platinum electrodes used in this work.

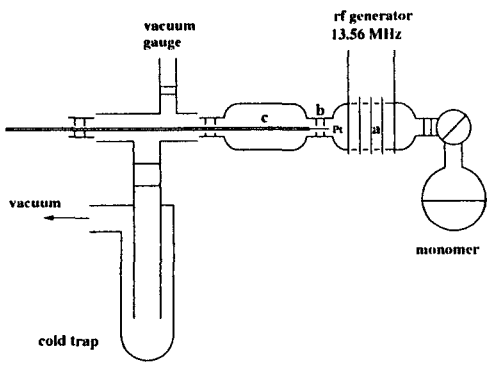

Fig. 1 Apparatus for fabrication of plasma-film-coated platinum-wire electrodes.

Table 1 Typical Fabrication conditions of Plasma Film -Coated Electrodes

Coated Pt	Monomer	Pa (W)	rM[b] (mmol min^{-1})	τ[c] (min)
TOL-	Toluene	50	0.111	1.0
EB-	Ethylbenzene	50	0.081	1.0
SR-	Styrene	50	0.104	1.0
p-XY-	p-Xylene	50	0.122	1.0
MMA-	Methylmeth-acrylate	50	0.136	1.0

[a]Plasma power. [b]Flow rate of monomer. [c]Coating time.

Potential measurements were performed by a system shown in Figure 2 with using a TOA Model PM-18U dc microvoltammeter. The pH of a test solution was changed by adding every 10-μl 0.5 M sulfuric or 1 M acetic acid to 100-ml 0.01 M NaOHaq. and was determined with a Horiba Model D-13 pH meter. Obtained potentials were values vs. a saturated calomel electrode(sce). All measurments were carried out at room temperature(22℃)

RESULTS AND DISCUSSION

When an uncoated platinum electrode was immersed in a 100-ml 0.01 M NaOH aq. to which small volumes of 1.0M sulfuric acid was added step by step so to change pH over a range of 12-2, the potential-pH response obtained was linear over a pH range of 3 to 11, the slope was ca.-57 mV/pH as shown in Table 2 and Figure 3. This result indicates that the pH response of the electrode is approximately Nernstian. The response time for potential formation at this electrode was

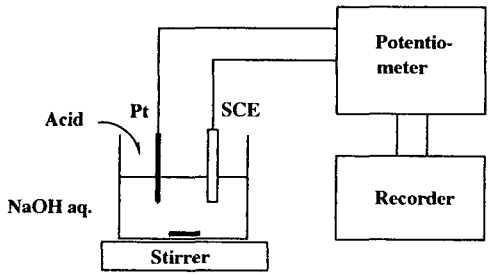

Fig. 2 System for potential measurements.

Table 2 Slopes of Typical pH response Curves

Acid	pH[a]	slope/mVpH^{-1}
H_2SO_4	3-11	-57
H_3PO_4	3-12	-53
HNO_3	2-12	-51
HCL	3-12	-42
Acetic acid	5-11	-56
	4-12[b]	-50[b]
	4-12[c]	-46[c]
	6-8[d]	-59[d]
Phthalate[e]	5-11	-54
Acetic anhydride	4-10	-48

[a]pH linear range. [b]Added 0.5M urea. [c]Added 1M urea. [d]Added L-ascorbic acid. [e]Potassium hydrogen phthalate.

rather long, taking approximately 15min to reach stable values(i.e., less than 0.10mV/min change). After being coated with plasma films, the platinum electrodesexhibited slopes similar to that observed for the uncoated platinum electrode and the response time roughly equal to that for the uncoated electrode in the same solution mentioned above.

The presence of chloride ions evidently affected the potential-pH response of the electrode.

By comparison of the responses shown in Figure 3 for the coated and uncoated electrodes in the presence f chloride ions, TOL and EB plasma films could improve well the pH response of platinum surface. it is evident that the values above pH 7 are roughly the same for both surfaces, while a significant difference between the two responses exists below pH 7. For the other platinum surfaces, a similar but less pronounced effect was noted, except that the curves for the coated and uncoated electrodes coincided more closely at alow pH than at high pH.

These studies indicate that, although a rather stavle plasma polymer film is present on the platinum electrode surface, the observed pH response of the system appears to be due principally th the platinum surface.

The response observed at platinum most probably involves an oxide layer on the platinum surface. The curvature in pH response observed at the coated electrodes is evidently due to the presence of the polymer films. This effect may involve some small pH response of the films themselves or may rflect some pH-dependent property of the films(e.g., molecular conformation).

It is interesting to speculate that the presence of the polymer coating may actually improve the performance(selectivity)of these electrodes by blocking access of larger redox systems to the electrode surface, whereas the response to protons through the polymer film could still occur.

In any event, these results indicate that the development of potentiometric sensors must take into account the properties of the substrate material employed in their construction.

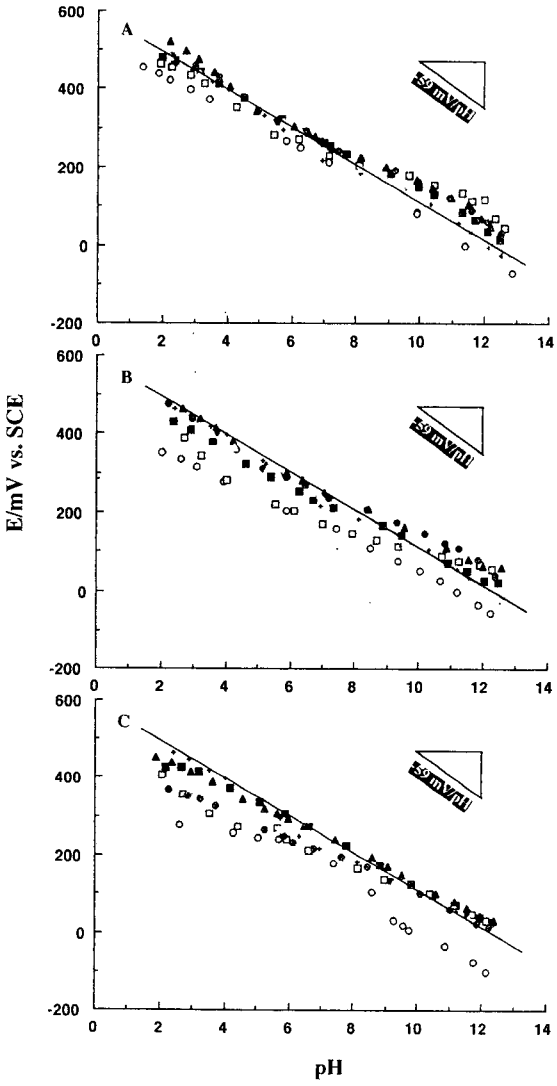

Fig. 3Effect of plasma thin films on chloride ions interfering with the Nernstian pH-response of platinum surface :
Three Figures show pH responses of electrodes of uncoated Pt(○), TOL-coated Pt(■), p-XY-coated Pt(□), EB-coated Pt(▲), SR-coated Pt(△), and MMA-coated Pt (●) in test solutions including chloride ions as follows :
A, 0.01M-NaOH aq. to which 1M-HCL was added;
B, 0.01M-NaOH aq. with 4% NaCl to whoch 0.5M-H_2SO_4 was added:
C, 0.01M-NaOH aq. with 16% NaCl to which 0.5M-H_2SO_4 was added.
symbolic+shows the pH-response of an uncoated electrode immersed in the solution including no chlordide ion: 0.01M-NaOH aq. to which 0.5M-H_2SO_4 was added, and solid lines show te averaged Nernstian pH-response.

CONCLUSION

In the presence of chloride ions, the pH response of a naked electrode was remarkably affected. By comparison of the responses for the coated and uncoated electrodes in the presence of chloride ions, it was found that TOL and EB plasma films could improve the potential-pH response of platinum surface. The response of coated platinum electrodes to pH may be explained by the ability of protons, by virtue of their small size, to move through the polymer matrix to the platinum surface. Since the response observed at platinum most probably involves an oxide layer on the platinum surface. it is interesting to speculate that the presence of the ploymer coating may actually improve the performance of these electrodes by blocking access of chloride ions to the electrode surface, whereas the response to protons through the polymer film could still occur.

The curvature in pH response observed at the coated electrodes is evidently due to the presence of the polyemer films. This effect

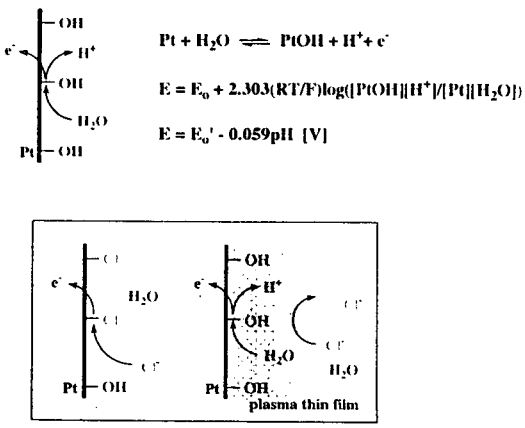

Fig. 4 Scheme of Nernstian response and interference of Cl.

may involve some small pH response of th films themselves or may reflect some pH-depenhdent property of the films(e.G., molecular conformation). In any event, these results indicate that the development of potentiometric sensors must take into account the properties of the substrate material employed in their construction.

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