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Plasma-Polymerized 4,4′-Methylenedianiline Membrane Formed on Platinum as Chemically Modified Electrode for pH

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4,4′-Methylenedianiline was plasma-polymerized on a platinum plate; the monomer was sublimated, followed by discharging for polymerization. The emf between the platinum plate covered with the plasma-polymerized film and Ag/AgCl electrode was measured, and it was found that a nearly Nernstian response to pH (slope of $-60\,\mathrm{mV\ pH^{-1}}$) was given over the range 4 to 10. The film was characterized with scanning electron microscope and Fourier-transform infrared spectroscopy.

Keywords plasma-polymerized 4,4′-methylenedianiline; pH-sensitive electrode; chemically-modified electrode; plasma-polymerization

Introduction

Plasma-polymerization has recently been used to produce ultra-thin films on a variety of substrates, and this technique can easily modify the surface characteristics of a material.(2) The coating film adheres strongly to the substrate, and is highly resistant to chemical and physical treatment. For normal plasma-polymerization, monomers are limited to those that are volatile and must therefore be liquids or gases.

One method to give higher sensitivity, more convenience and a longer lifetime to a chemically modified electrode (CME) or an ion-selective electrode (ISE) is the stable immobilization of an ion-exchange material.(3,4) Indeed, some papers have reported that ion-exchangers were immobilized covalently on the polymer skeleton of the membrane(5,6) or that membrane formed on metal wire by the electropolymerization of 1,2-diaminobenzene(7) or 4,4′-diaminobiphenyl(8) worked as pH sensors.

Many ion-exchangers used for CMEs or ISEs are non-volatile,(3,4) so plasma-polymerization is not applicable to immobilization. We have reported, however, that modification of the method developed by Osada and colleagues(9,10) enabled immobilization of ion-exchangers on a membrane filter and permitted the construction of a long-life lipophilic cation-selective electrode(11) or drug electrode.(12) We found that the essential features of the monomer were unchanged after polymerization. The method developed by Osada *et al.*(9,10) is as follows: solid monomers are sublimed in a polymerization chamber, followed by discharge for the formation of films on the substrate.

We prepared a pH-sensitive plasma-polymerized membrane, choosing 4,4′-methylenedianiline as the solid monomer, since the aromatic ring is easily polymerized and since the amino group may act as a pH-sensitive group. Characterization of plasma-polymerized 4,4′-methylenedianiline (ppMDA) films was carried out by scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FT-IR). The ppMDA-coated platinum plate electrode [ppMDA (Pt)] exhibited the Nernstian pH response from pH 4 to 10.

Experimental

Materials Platinum plates (Pt) were obtained from Nilaco Co., Japan (purity 99.98%, 30×10×1.0 mm). Reagents used were of analytical or certified grade, and were purchased from Wako Pure Chemicals, Ltd. (Osaka). Water was prepared with Milli-Q (Millipore Ltd.) and its specific resistance was more than 18 MΩ·cm.

Plasma-Polymerization Pt was chosen as a substrate because of its strong physical resistance under the high temperature of the sublimation conditions. The apparatus and procedure for the plasma-polymerization of solid monomers were essentially as described previously.(9,13) Pt was washed twice with ethyl alcohol, followed by thorough rinsing in pure water using an ultrasonic bath. The Pt (30×10×1 mm) was fixed below the upper electrode (80 mm in diameter). The distance between lower and upper electrodes was 35 mm. Five mg of the solid monomer was placed in a crucible. The system was evacuated to 1.33 Pa (0.01 Torr) using a rotary vacuum pump. The reactant was heated by means of an internal heating unit, then controlled sublimation was performed by adjusting the voltage of heater. Electric discharge was carried out using 100 W of 13.56 MHz to continue plasma polymerization for a predetermined period. During the discharge, the pressure was manually controlled at 45 Pa (0.34 Torr) by opening and closing a needle valve controlling the evacuating speed of the pump. A film of about 100 nm thickness was formed on the Pt surface.

Characterization of the Film Membrane thickness was measured by a multi-interference thickness meter.(14) The Pt and ppMDA (Pt) surfaces were examined by a SEM (Hitachi S-430). FT-IR was carried out with a Nicolet 5DX-FTIR using the technique of reflection absorption spectroscopy, RAS: The film was formed on a flat aluminum plate and was 100 nm of thick.

pH Response of ppMDA (Pt) The potentiometric response of ppMDA (Pt) was measured in the following manner: the ppMDA (Pt) was so clamped between a Lucite trough of 5 cm^3 and a Lucite block that the plasma-polymerized film was in contact with the solution in the trough. A buffer solution of pH 6.86 was added to the trough and left overnight to condition the membrane.

The following electrochemical cell was constructed:

ppMDA (Pt) | sample solution | KCl (saturated) | AgCl; Ag

The electromotive force, E was measured with an electrometer (Model TR-8651, Takeda Riken Co., Tokyo). Sample solutions of different pH values were prepared using 0.1 M phosphate buffer. The solution was stirred at 360 rpm while the temperature was kept at 25±1 °C.

Results and Discussion

Characterization of the Plasma-Polymerized Films The film obtained was not dissolved in ethyl alcohol or ether, which are good solvents for the monomer. The film appeared yellowish and glossy, and the thickness was approximately proportional to the period of polymerization; a formation rate of 10 nm/s was observed. The SEM photographs at a magnification of 10000 showed that the ppMDA (Pt) was flat and smooth in comparison with the Pt plate used as a substrate (data not shown).

The assignments of FT-IR data are: absorption at 3350 and 3220 cm^{-1} (N–H stretching in aromatic amine or amide), 2900 (C–H stretching), 1610 cm^{-1} (N–H bending in aromatic amine or amide), 1510 cm^{-1} (N–H bending),

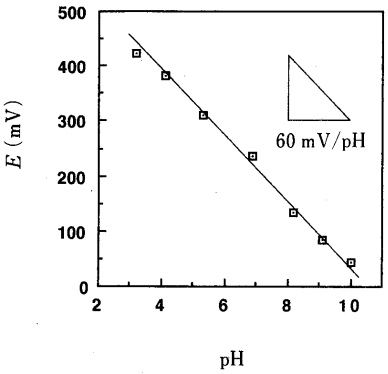

Fig. 1. Plots of the Electromotive Force of ppMDA(Pt) *versus* pH in the Test Solution

Here, ppMDA(Pt) denotes the plasma-polymerized 4,4′-methylenedianiline film formed on a platinum plate. Temperature, 25 °C.

1300 cm^{-1} (C–N stretching in aromatic groups). The FT-IR results suggest that the film may include the amine or amide groups that are linked to the aromatic ring, implying that the essential feature of the monomer remained after the polymerization.

This membrane electrode was stable and reproducible; the same electromotive force (± 1 mV) was obtained every time (at least 3-times). The calibration curve was shown in Fig. 1. The resulting CME gave the Nernst response (a slope of -60 mV pH^{-1}) in the pH range of 4—10. The response time was about 10 min when the test solution was changed to one of a different pH. The lifetime of the membrane electrode was more than 1 week when it was stored in buffer (ionic strength, $I = 0.10$, pH 6.86). The electrical properties of ppDMA (Pt) are probably the result of the protonation of amine linkages in the polymer. The poor potential response at pH 3 could be due to the saturation of protonation sites on the polymer. This tendency was also reported in the electropolymerized 1,2-diaminobenzene used as a pH sensor.[6)]

As described above, electropolymerization is a physical method of immobilization of an ion-exchanger material and differs from the present plasma-polymerization. For electropolymerization, the choice of monomer is limited to materials that can be oxidized or reduced by an electrode. The ordinary plasma-polymerization requires the monomer to be in the gaseous state, but the Osada method allows solid monomers. Plasma-polymerization has s wider scope in terms of monomer selection than electropolymerization, although there remains the problem of whether the functional group of the monomer is remained or not after polymerization.

Other monomers containing amino groups and polyene are also candidates for ion-exchangers in addition to 4,4′-methylenedianiline. We tried 1,2-diaminobenzene as a monomer: The plasma-polymerized membrane from this material obtained using the present method swells when immersed in electrolyte solutions and fails to work as a pH sensor. Although there is a possibility that a membrane could be formed under different conditions, this material is not really suitable. The reason for this difference between 4,4′-methylenedianiline and 1,2-diaminobenzene is not known at present.

Conclusion

4,4′-Methylenedianiline was plasma-polymerized on a flat Pt. The film formed was yellowish and glossy. The film may include amine or amide groups that are attached to the aromatic ring. The compound, ppMDA (Pt), was effective as a potentiometric electrode. The pH response of ppMDA (Pt) was nearly Nernstian between pH 4 and 10. Preparation of a plasma-polymerized membrane that shows both good stability and quick pH response is our next aim.

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