

Polyimide-matrix Chemical-selective Membranes

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Abstract

Preliminary work using polyimide (PI) as the polymer matrix for permselective membranes is reported in this paper. The excellent adhesion of polyimide may be helpful in extending solid-state chemical sensor lifetimes. Electrochemical performance and adhesion to Si_3N_4 of these membranes is compared to that of conventional PVC-based membranes.

Introduction

Poly(vinylchloride) (PVC) is the most commonly used matrix for permselective polymeric membranes on solid-state ion sensors. One of the primary causes of failure in these microsensors has been poor adhesion of this organic membrane to the chip surface, leading to electrolyte shunts around the membrane which render the sensor inoperative [1]. Improvements by others to membrane adhesion have included modification of PVC for binding to hydroxyl-bearing surfaces [2, 3], several methods for mechanically attaching membranes [4–7], and use of other materials [8–10], some of which have improved adhesion but inferior electrochemical performance compared to PVC.

Our research is concerned with both extending sensor lifetime and with achieving mass-fabrication of sensors. These goals have led to development of permselective membranes which use polyimide as a matrix. As demonstrated by Blackburn's suspended-mesh method of attaching membranes of ISFETs [4], polyimide compounds have excellent adhesion to integrated circuit surfaces. Polyimides are also compatible with semiconductor processing, being commonly used as surface protection layers and as dielectrics between metal interconnect layers in integrated circuits. Polyimide films are strong, flexible and insoluble. Conventional polyimide curing (imidization) requires temperatures from 300 to 400 °C, which would

evaporate or destroy the ionophore and plasticizer needed to give a membrane the desired electrochemical properties. Fortunately, preimidized polyimide is now commercially available; curing of this material (removal of the solvent) can be accomplished at low temperatures.

Development of polyimide membranes has required particular attention to plasticizers and lipophilic additives. The challenge is to achieve acceptable potentiometric ion response and selectivity while retaining the adhesion properties of polyimide. While the polyimide work is preliminary at this point (membranes have so far been tested electrochemically only in ion-selective electrode bodies), based on initial results, we are optimistic about their use in solid-state ion sensors, the target application.

Experimental

Apparatus

For all the potentiometric measurements, membranes were mounted in Phillips electrode bodies (IS-561) (Glasblaserei Möller, Zurich). The external reference electrode was an Orion sleeve-type double junction Ag/AgCl electrode (Model 90-02). Electrodes were connected through a high impedance amplifier to a Zenith Z-100 PC computer equipped with an analog to digital converter (DT 2801, Data Transaction, Inc., Malborough, MA).

Reagents

Poly(vinyl chloride) high molecular weight (PVC), dibutyl sebacate (DBS), *o*-nitrophenyl octyl ether (*o*-NPOE), nonactin, calcium ionophore II (ETH 129), and potassium tetrakis(*p*-chlorophenyl)borate (KTpCIPB) were obtained from Fluka (Ronkonkoma, NY). Polyimide (PI; fully imidized and polymerized), and plasticizer sample kit 301 (90 different plasticizers; including dimethyl phthalate (DMP) and diethylene glycol dibenzoate (DGD)) were purchased

from Scientific Polymer Products, Inc. (Ontario, NY). Anhydrous tetrahydrofuran (THF; water content < 0.005%) and *N,N*-dimethylformamide (DMF; water content < 0.005%), were obtained from Aldrich Chemical Co. (Milwaukee, WI); dipentyl phthalate (DPP) from Eastman Kodak (Rochester, NY); and Pyralin LTP (PI-2590-D; preimidized polyimide encapsulant) from DuPont Co. (Wilmington, DE). All other chemicals used were analytical-reagent grade. Standard solutions and buffers were prepared with deionized water.

Preparation of Ion-selective Membranes

Polyimide-based ion-selective membranes

Polyimide (PI) powder was dissolved in DMF (25%, wt./wt.) by heating the solution to 120 °C. Various membranes having different compositions were then prepared by mixing the PI solution with membrane active components (i.e. ionophore, plasticizer and lipophilic additive) and applying the mixture dropwise to a glass plate. The solvent (DMF) was allowed to evaporate for 2 days under vacuum. On the other hand, PI-2590-D polyimide encapsulant was directly mixed with the membrane active components and applied to the glass plate. In this case, longer evaporation periods (4–5 days) were employed due to the high boiling point of the solvent (*N*-methyl-2-pyrrolidone) used in PI-2590-D.

PVC-based ion-selective membranes

Ammonium- and calcium-selective membranes were prepared by incorporating nonactin and ETH-129, respectively, into PVC membranes as described elsewhere [11–13].

Evaluating Potentiometric Response

Small disks were punched from the membranes formed on glass plates, and mounted in Phillips electrode bodies. In the case of the polyimide membranes, a sharp razor was used to detach the membrane from the glass. The inner filling solution varied, depending on which ion-selective membrane was being evaluated: 0.1 M NH_4Cl for NH_4^+ -selective membranes; and 0.01 M CaCl_2 for Ca^{2+} -selective membranes. The calibration plots were obtained from additions of standard solutions to 250 ml of background electrolyte (0.05 M Tris-HCl, pH 7.2) at room temperature. Selectivity coefficients were determined by the separate solution method [14].

Evaluating Adhesion Characteristics

Adhesion characteristics were evaluated using the method described by Moody *et al.* [3]. For each membrane type, ten membranes were formed by dispensing drops of membrane mixture onto a silicon wafer coated with 10 000 Å of plasma-

deposited silicon nitride. In the case of PI membranes, an adhesion promoter (VM-651, DuPont Co., Wilmington, DE) was applied to the wafer before casting the membranes. After the membranes were cured, the wafers were immersed in an ultrasonic bath (Branson Cleaning Equipment, Smithkline Co., Shelton, CN). The time to detachment was recorded for each membrane.

Results and Discussion

In our initial work with polyimide-matrix membranes, it was found that the plasticizers frequently used for the preparation of PVC-based ion-selective membranes (e.g., DBS, DOA, *o*-NPOE, etc.) were not compatible with polyimide. Among more than 90 plasticizers tested for incorporation in polyimide matrices, only two, dimethyl phthalate (DMP) and diethylene glycol dibenzoate (DGD), resulted in transparent, flexible, yet mechanically strong membranes. Incorporating these plasticizers into the polyimide matrix appeared to have little effect on the excellent adhesion properties of the resulting membranes toward glass surfaces. These membranes cannot be pulled free from the glass, but must be cut from the plate with a razor blade.

In order to examine the feasibility of using polyimide as the matrix of ion-selective membranes, nonactin (2 mg) was incorporated into polyimide matrix membranes (75 mg of PI) along with a plasticizer DMP or DGD (130 μl). Figure 1 illustrates the potentiometric response of the resulting PI-based membranes toward ammonium ions. As can be seen, the PI membrane prepared with DGD exhibited better response characteristics (i.e. lower detection limit) than that prepared with DMP. However, the response characteristics of the PI/DGD-based ammonium-selective mem-

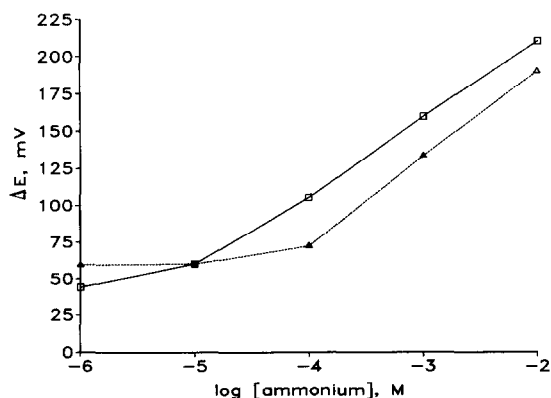


Fig. 1. Potentiometric ammonium response of PI-based membranes prepared by using DGD (□) and DMP (Δ), respectively, as the plasticizer.

brane, with a slope of 50 mV per decade for 10^{-5} to 10^{-2} M NH_4^+ , were inferior to those of PVC-based membranes.

In an effort to improve the performance of the polyimide matrix membrane, several membranes were prepared by further incorporating lipophilic additives or other plasticizers in addition to nonactin and polyimide (this time, PI-2590-D encapsulant was used). Increasing the amount of lipophilic additive (KTpCIPB) in the membrane phase increased the response slope of the resulting PI-2590-D matrix membranes (see Fig. 2). The response was further improved when the membrane was prepared by using an additional plasticizer, dipentyl phthalate (DPP), previously used for the preparation of NH_4^+ -selective polymer membranes [15]. Although incorporating DPP into the PI-2590-D matrix led to a less transparent membrane, the resulting membrane retained its high mechanical strength and homogeneity. As seen in Fig. 2, the response of the membrane was greatly enhanced by using the mixed plasticizer (DGD/DPP; 50 $\mu\text{l}/50 \mu\text{l}$) and KTpCIPB (0.67 mg), along with nonactin (2 mg) and PI-2590-D (600 mg).

The potentiometric response of the optimized NH_4^+ -selective PI-2590-D matrix membrane was compared with those of PVC-based membranes. Figure 3 shows that PVC-based membranes prepared using DGD as the plasticizer had significantly degraded response toward NH_4^+ (slope of 47.25 mV per decade over the range 10^{-5} to 10^{-1} M NH_4^+). However, the optimized PI-2590-D membranes exhibited nearly the same response slope (56.5 mV per decade) as those found for the conventional PVC-based membrane (56.9 mV per decade). In addition, the selectivity coefficients ($\log k_{\text{NH}_4^+,j}^{\text{Pot}}$) obtained for the PI-2590-D matrix

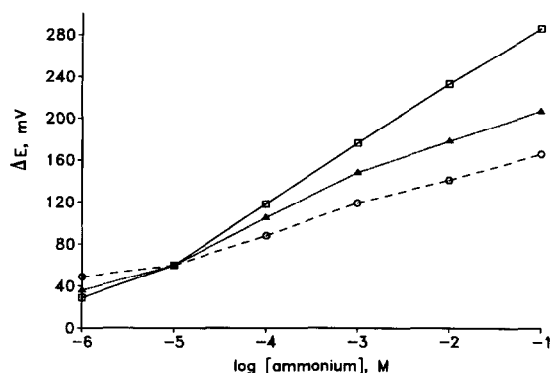


Fig. 2. Potentiometric ammonium response of PI-2590-D matrix membranes having three different compositions: (○) KTpCIPB (0.67 mg), DGD (100 μl); (Δ) KTpCIPB (1.34 mg), DGD (100 μl); (□) KTpCIPB (0.67 mg), DGD/DPP (50 $\mu\text{l}/50 \mu\text{l}$). Each membrane was prepared using 2 mg of nonactin and 600 mg of PI-2590-D polyimide encapsulant.

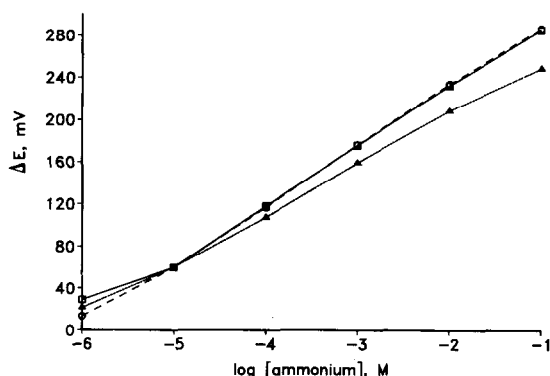


Fig. 3. Potentiometric ammonium response of PVC and PI-2590-D matrix membranes doped with nonactin: (Δ) PVC/DGD; (○) PVC/DBS; (□) PI-2590-D/DGD/DPP/KTpCIPB.

membrane (-0.9 for K^+ ; -2.7 for Na^+) were similar to those for PVC-based membranes (-0.9 for K^+ ; -2.9 for Na^+).

The polyimide matrix was further evaluated by preparing Ca^{2+} -selective membranes. For this, ETH 129 (2 mg) was incorporated with KTpCIPB (1.2 mg), DGD (66 μl), and polyimide (PI; 66 mg). Figure 4 compares the response of the PI matrix membrane to those of conventional PVC and commercial Orion liquid-type Ca^{2+} -selective electrodes. The performance of these electrodes is seen to be comparable except for a slightly higher detection limit for the polyimide matrix membrane.

As expected, the PI membranes exhibited much better adhesion to the silicon nitride surface than did PVC membranes (see Fig. 5). Detachment of the ten PVC membranes occurred over a range of 25 to 60 min, with the median time being 31 min. Five PI membranes detached almost in unison between 9 h 37 min and 9 h 40 min, and the remaining five remained intact when the test was

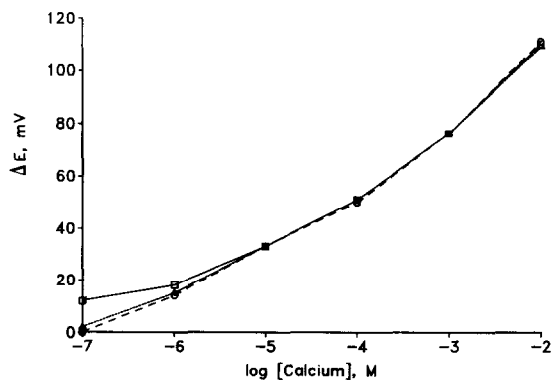


Fig. 4. Potentiometric calcium response of PI and PVC matrix membranes doped with ETH129, and an Orion calcium-selective electrode: (□) PI; (Δ) Orion, (○) PVC.

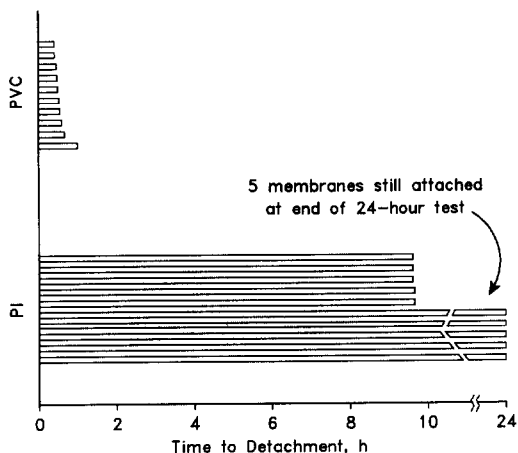


Fig. 5. Accelerated adhesion test of conventional PVC matrix and polyimide matrix membranes on Si_3N_4 , showing time to detachment for ten membranes of each type.

terminated after 24 h. The median PI membrane lifetime in this test was, therefore, more than 25 times longer than that of PVC membranes.

In evaluating a variety of membrane materials in the ultrasonic bath accelerated lifetime test, we have observed a correlation between adhesion time and compliance of the membrane. The ultrasonic vibrations are more effective at detaching rigid membranes which are able to absorb the ultrasonic energy through elastic deformation. Comparisons of dissimilar membrane materials with this method, therefore, will favor the softer material. Since PI membranes are harder than PVC membranes, the comparison given can be considered as worst-case for PI membranes. Future studies will evaluate true membrane lifetimes, including degradation of electrochemical properties through such effects as ionophore loss.

Conclusions

This work has demonstrated the feasibility of using polyimide as the polymer matrix of ion-selective membranes. Two plasticizers have been identified which are compatible with polyimide. Membrane compositions for ammonium- and calcium-selective membranes are reported, for which potentiometric slope and selectivity are comparable to those of PVC-based membranes at ion concentrations above 1 ppm. The potentiometric response of PI matrix membranes has been tested only in electrode bodies. Our ongoing work involves development of a wafer-level deposition process for such PI membranes, and evaluation of these membranes on solid-state sensor chips.

We have also confirmed the expected improvement in adhesion of plasticized PI membranes compared to PVC membranes; it is hoped that this characteristic will help extend the lifetimes of chemical microsensors. Further studies are needed for complete evaluation of these membranes. Based on this preliminary work, though, polyimide should be considered as one of the material alternatives for making permselective membranes on solid-state chemical sensors.

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