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ION-SELECTIVE ELECTRODES BASED ON BILAYER FILM COATING

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ABSTRACT

The electrode characteristics of ion-selective electrodes (ISEs) for K^+ , Na^+ , NH_4^+ , and Ca^{2+} based on bilayer film coatings, where the inner layer films are electroactive electropolymerized ones and the outer layer films are composed of conventional ion-sensitive materials, have been examined. These ISEs of the coated-wire electrode type have no conventional internal reference solution and reference electrode, but the inner films may be considered to function as the "internal standard solution." The ion selectivity coefficients and the activity range showing Nernstian response were almost comparable to those of conventional liquid-membrane electrodes. The bilayer-coated ISEs showed insensitivity to O_2 and CO_2 , long-term stability, and little drift. It was also found that the electrode performance is practically unchanged after sterilization in an autoclave. The results demonstrate that the bilayer-coated ISEs examined are promising for the determination of K^+ , Na^+ , NH_4^+ , or Ca^{2+} activity in biological and environmental systems.

INTRODUCTION

Coated-wire ion-selective electrodes (CWISEs), which consist of a metallic conductor directly coated with an ion-sensitive membrane without the conventional internal reference solution and reproducible reference electrode, have attracted considerable attention since they were inspired by the work of Hirata and Date in 1970 [1]. As can be expected from the structural specificity, the CWISEs have some significant advantages over conventional liquid-membrane ISEs and pH glass sensors, i.e., simple construction, low cost, easy fabrication, capability of extreme miniaturization, easy sterilization, etc. [2]. The "ion-selective field effect transistors (ISFETs)," which have been of considerable recent interest because it is envisaged that a single miniaturized solid-state chip could contain multiple gates and be used to sense several ions simultaneously, may be considered as a logical extension of the CWISEs [3].

However, the CWISEs still have problems to be resolved for practical use, such as large drift of the electromotive force; sensitivity to O_2 , CO_2 , and some redox species; slow response; etc. With a view to improvement of the properties of CWISEs, we [4] have recently demonstrated a new type of potentiometric pH sensor based on graphite microelectrodes directly coated with two-layer polymer films: the inner film functions as an "internal standard solution" and the outer one, which is composed of a conventional H^+ ion-sensitive membrane, as a H^+ ion-sensitive layer. In this case, electroactive electropolymerized films (e.g., poly-(1-pyrenamine) film) were employed as the inner film. The most interesting feature of this type of sensor is that it does not need any internal reference solution, which raises the possibility of fabricating a microsensor. Along this line, we extended the same idea to the development of potentiometric sensors for ions other than H^+ (i.e., K^+ , Na^+ , NH_4^+ , and Ca^{2+}). The results obtained are reported in this paper.

EXPERIMENTAL

Reagents

Ion-sensitive materials used included valinomycin (Sigma Chemical Co.), bis[(12-crown-4)methyl] dodecylmalonate (Wako Chemical Co.), bis[di(*n*-octylphenyl)phosphate] calcium (Fluka Chemical Co.), and monactin (Sigma Chemical Co.). All were of the highest reagent grade and used without further purification. Powdered poly(vinyl chloride) (PVC, Kanegafuchi Chemical Industry Co.), plasticizer dioctyl sebacate (DOS, Kyowa Hakko Kogyo Co.), and the impedance-moderating additive potassium tetrakis(4-chlorophenyl)

borate (KTPCIPB, Fluka Chemical Co.) were all used as received. Tetrahydrofuran (THF, Wako Chemical Co.) of reagent grade was used as the membrane casting solvent. Solutions were made up with distilled deionized water of resistivity greater than $6 \text{ M}\Omega \cdot \text{cm}$.

Basal-plane pyrolytic graphite (BPG) disks (Union Carbide Co.) were used as electrode substrates. The side of the disk electrode was sealed with heat-shrinkable polyolefin tubing. All electrodes used had an exposed geometric area of 4.9 mm^2 . Precinorm U (Boehringer Mannheim Co.) was used as a standard human serum. All other chemicals were reagent grade and were used as received.

Apparatus

In the testing system, the outputs up to 10 electrodes at a time could be sequentially acquired (NEC PC-9801 VM-2 computer) with a multiplexed high-impedance voltage follower in combination with an integrating digital voltmeter. Data were stored on disk and retrieved for interpretation and/or plotting at a later time (NEC PC-9801 VM-2 disk and HP 7470A plotter). Computer-controlled changes of concentrations of K^+ , Na^+ , NH_4^+ , or Ca^{2+} were performed by KCl , NaCl , NH_4Cl , or CaCl_2 additions from an automatic titrator (Metrohm Dosimat E535) into well-stirred and thermostated solutions (typically $37.0 \pm 0.3^\circ\text{C}$). The K^+ -, Na^+ -, NH_4^+ -, or Ca^{2+} -selective electrodes were stored in KCl , NaCl , NH_4Cl , or CaCl_2 solutions (1 mM), respectively, between measurements. A sodium chloride saturated calomel electrode (SSCE) reference was used for all potential measurements. The activity coefficients of the ions in aqueous solutions were calculated according to the Debye-Hückel approximation: $\log \gamma_i = -0.523Z_i^2 I^{1/2} / (1 + 0.331aI^{1/2})$ (at 37°C), where I is the ionic strength, Z_i is the charge of ion i , and a is the mean ionic diameter of ion i [5, 6].

Preparation of Ion-Selective Electrodes Based on Bilayer Film Coating

Figure 1 shows the schematic construction of the CWISEs employed in this study. The BPG electrode substrates were directly coated with two kinds of polymeric films in a bilayer fashion. The inner layers were electroactive electropolymerized films, and the thickness was typically $1\text{--}10 \mu\text{m}$. The polymeric films used were those of poly(*p,p'*-biphenol) (PBP), poly(1-pyrenamine) (PPA), or a 3,3',5,5'-tetramethyl-4,4'-diphenylquinone/2,2',6,6'-tetramethyl-1,1'-biphenol mixture (PDMP). They were prepared on BPG electrodes by the anodic oxidation of the corresponding monomers (i.e., *p,p'*-

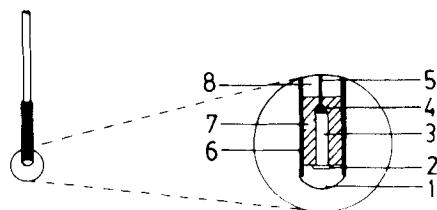


FIG. 1. A schematic construction of bilayer film-coated ion-selective electrodes. 1, outer layer membrane (PVC matrix); 2, inner layer film (electropolymerized film); 3, BPG electrode; 4, silver paste; 5, lead wire; 6, heat-shrinkable tubing; 7, epoxy resin; 8, insulator tube.

biphenol, 1-pyrenamine, or 2,6-dimethylphenol), as previously reported [7-9]. The detailed electrochemical behavior of these films has already been reported elsewhere [7-9].

The polymeric film-coated electrodes thus prepared were soaked repeatedly in each of the stock solutions (solvent: THF) for the preparation of K^+ , Na^+ , NH_4^+ , and Ca^{2+} -selective membranes, and then the bilayer film-coated electrodes were prepared by evaporating the solvent at room temperature. The stock solutions were composed of PVC, conventional ion-selective materials (i.e., valinomycin for K^+ [10], bis[(12-crown-4)methyl] dodecylmalonate for Na^+ [11], bis[di-(*n*-octylphenyl)phosphate] calcium for Ca^{2+} [12], or monactin for NH_4^+ [13]), DOS, and KTpClPB [14]. The thickness of the outer layer films was 300-700 μm . In every ion-sensitive membrane, the weight ratio of DOS (as a plasticizer) to PVC (as a membrane matrix) was kept at 2.0 and KTpClPB (as an impedance-moderating additive) of 0.6 wt% was imbedded in the PVC matrix. The concentrations of the ion-sensitive materials in the PVC matrix were 1.0-3.0 wt% (see Table 1).

Calculation of Potentiometric Selectivity Coefficients (K^{Pot})

K^{Pot} can be calculated from the equation

$$E = \text{constant} + \frac{2.303RT}{Z_i F} \log [a_i + K^{Pot} (a_j)^{z_i/z_j}],$$

where E is the experimentally observed cell potential; a_i and a_j are the activities of a primary ion i and an interfering ion j , respectively, in the sample solution; z_i and z_j are integers with sign and magnitude corresponding to the charge of ions i and j , respectively; and F , R , and T have their usual meanings.

TABLE 1. Electrode Characteristics of the Bilayer Film-Coated Ion-Selective Electrodes

Electrodes	Inner layer films	Ion-sensitive materials ^a	Nernstian response range, mM	Response time, b s	Selectivity coefficients, $-\log K^{pot}$			
					Na ⁺	K ⁺	NH ₄ ⁺	Ca ²⁺ Mg ²⁺
K ⁺ -ISE	PDMP	I (1.0)	0.1-200	<30	2.0	—	2.7	4.0
K ⁺ -ISE	PBP	I (1.0)	0.001-200	<30	2.0	—	2.7	4.0
Na ⁺ -ISE	PDMP	II (2.5)	1-200	<60	—	2.0	2.7	4.0
Ca ²⁺ -ISE	PPA	III (3.0)	0.1-30	<60	3.1	—	—	3.3
NH ₄ ⁺ -ISE	PDMP	IV (2.5)	0.1-70	<90	2.5	1.0	—	—
H ⁺ -ISE ^c	PPA	V (1.0)	10 ⁻⁸ -1	<4	10.7	10.5	—	9.9

^aThe numbers in parentheses shows the wt% of ion-sensitive materials imbedded in the PVC matrix. I: Valinomycin. II: Bis[(12-crown-4)methyl] dodecylmalonate. III: Bis[di-(*n*-octylphenyl)phosphate] calcium. IV: Monactin. V: Tri-*n*-dodecylamine.

^bCorresponding to 95% response.

^cFrom Ref. 4.

RESULTS AND DISCUSSION

Figure 2 shows the typical electromotive force (emf) response of the bilayer film-coated ISE's. As shown in Fig. 2, the response is linear over the activity range of 0.1-200 mM for K^+ , 1-200 mM for Na^+ , 0.1-70 mM for

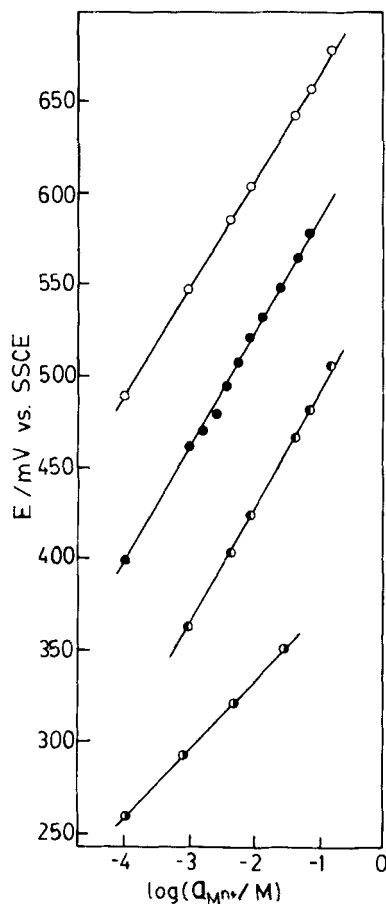


FIG. 2. Typical electromotive force response of the bilayer film-coated ISE's at 37°C. (○) K^+ -ISE (inner film: PDMP); (●) NH_4^+ -ISE (PDMP); (●) Na^+ -ISE (PDMP); (○) Ca^{2+} -ISE (PPA). The activity ($a_{M^{n+}}$) of K^+ , NH_4^+ , Na^+ , or Ca^{2+} ion was varied by the addition of KCl, NH_4Cl , NaCl, or $CaCl_2$ solution to unbuffered aqueous solutions.

NH_4^+ , and 0.1–30 mM for Ca^{2+} , with nearly Nernstian slopes of 57.9, 60.6, 63.5, and 31.7 mV per activity decade for K^+ , Na^+ , NH_4^+ , and Ca^{2+} , respectively, at 37°C. For the PBP (inner film)/ K^+ -sensitive membrane-coated electrode, a nearly Nernstian response was obtained in the range of K^+ activity of $\sim 10^{-6}$ –0.2 M. A Nernstian response was also obtained in standard human serum solutions.

The potentiometric selectivity coefficients (K^{Pot}) for K^+ , Na^+ , NH_4^+ , or Ca^{2+} relative to other ions were estimated by the fixed-interference method [15] and are listed in Table 1. These are almost the same as those previously obtained for liquid membrane electrodes [10–14], indicating that the inherent ion selectivity of the ion-sensitive membranes themselves is retained in the bi-layer-coated ISEs as well.

A typical emf response of the NH_4^+ -ISE to a change in the concentration of NH_4^+ ion after injection of NH_4Cl solution is shown in Fig. 3. The 95% response times for all the electrodes examined (summarized in Table 1) are within ~ 30 , 60, and 90 s for the K^+ -ISEs, the Na^+ (or Ca^{2+})-ISE, and the NH_4^+ -ISE, respectively, and these values are much larger than that of the H^+ -ISE reported previously [4]. Figure 4 shows the response time required for a stable emf of the Na^+ -ISE just after the immersion of the electrode,

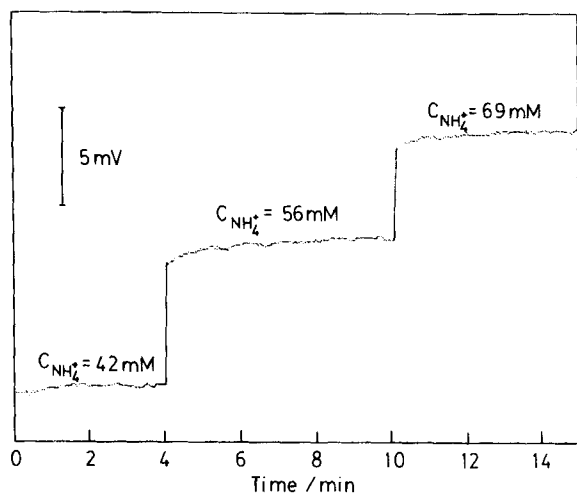


FIG. 3. Electromotive force response of the NH_4^+ -ISE with the PDMP inner film with changes in the concentration of NH_4^+ ion in aqueous NH_4Cl solutions at 36.7°C.

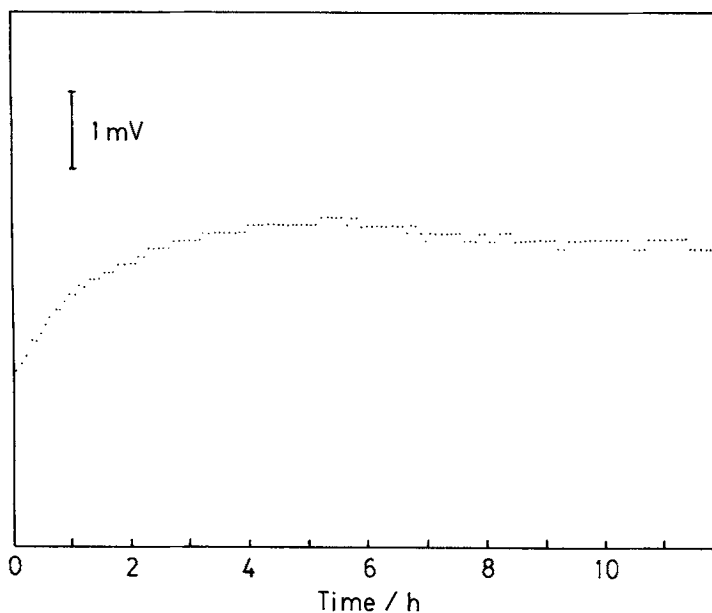


FIG. 4 A typical electromotive force-time profile of the Na^+ -ISE with the PDMP inner film in saline solution at 37°C . The abscissa shows the time elapsed after the immersion of the electrode, which had been soaked in a saline solution overnight, in fresh saline solution.

which has been soaked in a saline solution overnight, in fresh saline solution. It took ~ 4 h to obtain a constant emf value, and after that the emf drift was within 0.2 mV/h. In this case, so long as the electrode was not taken out of the solution, the response times of the emf response to a change in the activity of Na^+ ion were less than 30 s.

Figure 5 indicates the sensitivity of the K^+ -ISE with and without the PBP inner film to O_2 or CO_2 dissolved in test solutions. This shows that, under the conditions studied, there is no influence of O_2 and CO_2 on the electrode performance of the bilayer film-coated electrodes, while the electrode coated with ion-sensitive membrane alone (i.e., without the PBP film) is sensitive to O_2 . Similar results were also obtained for the bilayer film-coated Na^+ , Ca^{2+} , and NH_4^+ -selective electrodes. The long-term stability of the bilayer-coated ISEs, compared with the ISEs without inner films, was also obtained. For example, in the case of the K^+ -ISE with the PBP film as an inner layer, Nernstian or

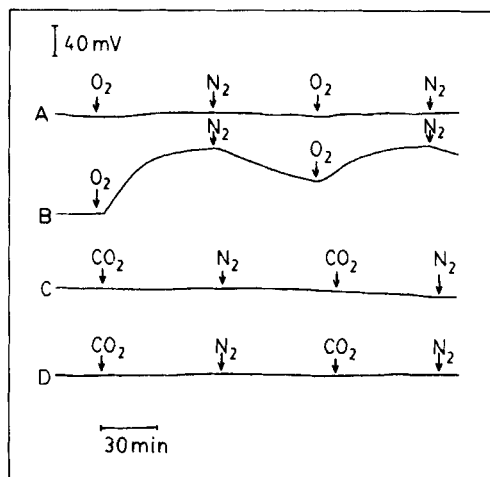


FIG. 5. Sensitivity of the K^+ -ISE's with (A, C) and without (B, D) the PBP inner film to O_2 or CO_2 dissolved in boric acid/sodium phosphate/citric acid-buffered solutions (pH 6.4, concentration of K^+ ion: 0.01 M) at 25°C. Thickness of PBP film: 6 μm . Thickness of outer layer of K^+ -sensitive membrane: 300 μm . O_2 pressure: 760 torr. CO_2 pressure: 100 torr.

sub-Nernstian response of ~ -50 to 60 mV per activity decade for K^+ ion activity 0.1-10 mM was obtained for a period of ~ 70 days, but in the case of the K^+ -ISE without an inner film for at most 40 days. Thus, the above-mentioned bilayer film-coated ISEs can be expected to be useful for the determination of K^+ , Na^+ , Ca^{2+} , or NH_4^+ activity in biological and environmental systems.

The sterilization of ISEs is an important process in practical use. The effect of the sterilization using autoclave (at 121°C for 20 min) on the coated-wire electrode performance was examined. A typical result is shown in Fig. 6, which demonstrates that the electrode performance is practically unchanged after sterilization, which is advantageous in clinical use.

As mentioned above, some improvements of the electrode performance were actually achieved by a bilayer film coating. This may be attributable to the electroactivity of the inner layer film [4]. The concentration of the electroactive sites in the film is very high (usually of the order of 1 M) [7-9]. Thus, it is expected that the redox couples in the film actually determine the potential level of the electrode surface. In other words, the inner film is con-

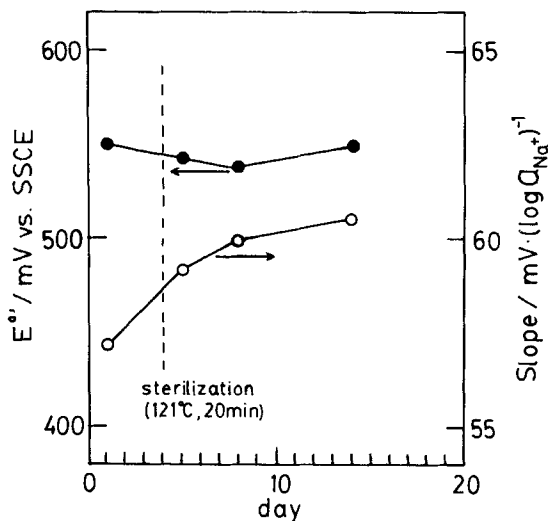


FIG. 6. Effect of sterilization on the electrode performance of the Na^+ -ISE with the PDMP inner film. The sterilization was carried out in an autoclave (at 121°C for 20 min). The filled symbols (left scale) show the potentials corresponding to $a_{\text{Na}^+} = 1 M$, estimated by extrapolation of the linear electromotive force- $\log a_{\text{Na}^+}$ plots to $\log a_{\text{Na}^+} = 0$. The slopes of these plots are shown by the open symbols (right scale).

sidered to function as an "internal standard solution," leading to the above-mentioned improvements in electrode performance. Further data, such as those concerning 1) potential and potential distribution at electrode/inner film, inner film/outer membrane, and outer membrane/solution interfaces; 2) potential and potential distribution in inner film and outer membrane; 3) charged species transport in inner film and outer membrane; etc., should be accumulated in order to fundamentally understand the function of the inner film as well as the potential response of the bilayer film-coated ISEs.

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