A Reinforced Oleophilic Anion-exchange Resin Membrane as a Sensitive Membrane of Anion-selective Electrodes

Akinori Jyo,*,† Toshihiko Imato, Hirofumi Kohno, and Nobuhiko Ishibashi
Department of Applied Analytical Chemistry, Faculty of Engineering, 36, Kyushu University, Fukuoka 812
(Received April 8, 1983)

Synopsis. Based on an impregnation technique for the preparation of ion-exchange resin membranes, a simple way was proposed for the preparation of a reinforced oleophilic anion-exchange resin membrane as an anion-selective electrode membrane with a chemically fixed site. The resulting exchange resin membrane is thin (*ca.* 25 μm) and flexible. It gives anion-selective electrodes with high performances.

We have developed anion-selective electrodes based on an oleophilic anion-exchange resin membrane, which is a homogeneous crosslinked polystyrene membrane with a chemically fixed benzyltrioctylammonium ion as the anion-exchange site.[1] The resin membrane performs almost the same as the sensitive membrane of a liquid membrane anion-selective electrode when it is impregnated with a water-immiscible organic solvent.[1] Since the membrane is based on a homogeneous crosslinked polystyrene matrix, it is hard and weak to bending. In addition, much experience and skill are generally required for the preparation of homogeneous ion-exchange resin membranes.[2,3] Thus from a practical point of view, it is desirable to develope a simple method of preparing a flexible membrane.

Based on an impregnation technique widely used in the preparation of usual hydrophilic ion-exchange resin membranes,[2] we have developed a simpler way to prepare an oleophilic anion-exchange resin membrane. The newly developed membrane is thinner and more flexible than the previously reported membrane. This note will describe the preparation of the membrane. The performances of anion-selective electrodes based on the membrane will also be presented.

Experimental

Preparation of the Oleophilic Anion-exchange Resin Membrane. A sheet of Duragard (macroporous film of polypropylene, thickness, 25 μm; Polyplastic Co.) was cut into appropriate squares (3 cm × 3 cm or 4 cm × 4 cm). They were immersed in a styrene–divinylbenzene mixture (20 ml : 0.5 ml) containing benzoyl peroxide (0.2 g) for 24 h. The sheets impregnated with the monomers were then inserted between piled glass plates. After the glass plates had been fastened, they were immersed in a hot solution of saturated sodium sulfate (70 °C) for 8—10 h in order to polymerize the monomers.[3] Although the original Duragard itself was opaque, a translucent membrane was thus obtained. After the membrane had been soaked in hot water for 1 h, it was washed with ethanol for 2 h and then with acetone for 30 min in a Soxhlet extractor. After drying in a vacuum desiccator, it was weighed. The increase in weight was 48% of the initial weight of the sheet. The membrane was then chloromethylated by the conventional method.[4] After the chloromethylated membrane had been soaked in a mixture of hydrochloric acid and ethanol (1 : 10) overnight, it was washed with acetone in a Soxhlet extractor for 20 h and then dried. After it had swollen in a trioctylamine–ethanol mixture (2 : 1) overnight at room temperature, the mixture was maintained at 80 °C for 30 h in order to effect the quaternization of the membrane with the amine. In this stage, the membrane expanded in every direction by 1.2 times, while no marked change in the size was observed before the quaternization process. The resulting anion-exchange resin membrane was washed with ethanol in a Soxhlet extractor for 30 h. The conditioning of the membrane and determination of the exchange capacity were performed by the previously reported procedures.[1]

Ion-selective Electrode Assemblies. The membrane was converted into the nitrate or perchlorate form according to the previously reported procedures.[1] As a solvent to be impregnated in the membrane, nitrobenzene was used. The fabrication of the electrode and the evaluation of the electrode performances have been reported in detail elsewhere.[1]

Results and Discussion

The exchange capacity of the membrane is 0.68 mequiv./g of resin, which is smaller than those of the previously reported homogeneous membranes (1.0—1.1 mequiv./g of resin).[1] This may be due to the fact that the present membrane contains polypropylene as a reinforcing material. The membrane is thin (*ca.* 25 μm) and flexible. It is strong for bending. In the case of the homogeneous membrane, it took more than a week to change its ionic form by means of ion exchange since it is relatively thick (0.2—0.5 mm). The thickness of the present membrane is reduced to about one-tenth of the previous one. Accordingly, the ion exchange could be easily finished within a week. The present membrane also showed the oleophilic property; it is easily wetted with organic solvents, but is hardly to wet with water.[5]

Nitrate and perchlorate ion-selective electrodes were fabricated by using the membranes in nitrate and perchlorate forms respectively. The results for electrode

Table 1. Performances of anion-selective electrodes based on oleophilic anion-exchange resin membranes

Membrane	Sensing ion of electrode	Slope[a] (mV/log *a*)	Lower limit of linear response/M
Present membrane	NO_3^-	−57	$10^{-4.3}$
(Reinforced membrane)	ClO_4^-	−59	$10^{-4.3}$
Previous membrane	NO_3^-	−57	$10^{-4.3}$
(Homogeneous membrane)	ClO_4^-	−58	$10^{-4.3}$

a) The solvent impregnated in the membrane is nitrobenzene. The electrodes were calibrated at an ionic strength of 0.3 (0.10 M Na_2SO_4).

† Present address: Department of Industrial Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860.

Table 2. Selectivity coefficients of nitrate ion-selective electrodes based on oleophilic anion-exchange resin membrane

Membrane	Selectivity coefficient ($\log K^{pot}_{NO_3,j}$)[a]			
	(j)	Cl^-	NO_2^-	CH_3COO^-
	Concn of j-ion/M	0.0050	0.0010	0.10
Present membrane		−2.1	−1.1	−3.6
Previous membrane		−2.0	−1.4	−3.4

a) The solvent impregnated in the membrane is nitrobenzene.

calibrations are summarized in Table 1. The performances are almost the same as those of the previously reported electrodes based on the homogeneous membranes.[1] Although the response of the present electrodes was also rapid within the concentration range of the linear response, a small oscillation of potentials was sometimes observed. This presents no serious problem, however, since the oscillation is less than ± 0.3 mV.

Table 2 gives the selectivity coefficients of the nitrate ion-selective electrode. They were determined by the mixed-solution method under fixed activity of an interferent ion.[6] No marked difference in selectivity is seen between the present and previous electrodes when a common solvent, nitrobenzene, is impregnated in the membranes. That is, no marked influence of polymer matrices on the electrode selectivity can be seen. This observation is in accordance with the view that the selectivity of anion-selective electrodes of the liquid membrane type is essentially governed by the solvent of the membrane.[7]

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