Solution–Membrane Equilibrium at Metal-Deposited Cation-Exchange Membranes: Chronopotentiometric Characterization of Metal-Modified Membranes

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Copper- and lead-deposited interpolymer cationic membranes have been prepared by electroless plating by an ion-exchange method and characterized by chronopotentiometry and cyclic voltammetry. The parameters such as transition time (τ), $I\tau^{1/2}$, the potential drop (E_0) across these membranes immediately after the application of constant current (I), and the height of the potential jump (ΔE) across the membrane at τ have been measured by chronopotentiometry and compared with those of plain membranes. The approximate percentage of metal coverage and the number of ionic sites masked by the deposited metal in terms of NaCl concentration have been estimated from the differences in $I\tau^{1/2}$ values of plain and metal-deposited membranes. The quantity of metal deposited in a unit area of the membrane surface was measured by differential pulse polarography. The oxidation and reduction peak potentials corresponding to Cu(0)/Cu(II) and Pb(0)/Pb(II) couples were identified by cyclic voltammetry at pH 2.8 and 4.5 of 0.2 M $CH_3COONa–H_2SO_4$. © 1999 Academic Press

Key Words: **cation-exchange membrane; metal deposition; chronopotentiometry; transport phenomena; permselectivity.**

INTRODUCTION

Ion-exchange membranes such as Nafion with suitable metal catalysts entrapped in the body have been found applications in fuel cells, water electrolysis, and also electroorganic synthesis (1–5). They offer advantages like enhanced reaction rates and prevention of unwanted side reactions in electroorganic synthesis (6, 7). The interpolymer cation-exchange membranes that have been developed in this laboratory and used in electrodialysis units for versatile industrial applications (8–13) are highly conductive, thermally stable, and chemically inert. Development of metal composites from these membranes and the measurements of ion-exchange properties of such modified membranes by voltammetric techniques such as chronopotentiometry have great importance.

In the continuation of our earlier work (14), we describe here the changes in the chronopotentiometric responses and thus the

transport phenomena across the membrane–solution interface with the gradual growth of the metal film on a cation-exchange membrane. The chronopotentiometric data relevant to NaCl solutions has been measured for metalated membranes with different times and compared with those of the plain membrane. The approximate percentage of metal coverage and the number of ionic sites masked by the deposited metal in terms of molar concentration were evaluated. The peak potentials corresponding to Cu(0)/Cu(II) and Pb(0)/Pb(II) couples of these modified membranes were also studied.

EXPERIMENTAL

Materials

The interpolymer cation-exchange membrane used in these investigations was prepared by the procedures reported earlier (15). The membrane was based on an interpolymer of polyethylene and styrene-divinylbenzene copolymer having sulfonic acid as a functional group. Reagent grade copper sulphate, lead acetate, and hydrazine hydrate were procured from S. D. Fine Chemicals and were used as such. All other chemicals employed were also of reagent grade.

Circular pieces of cation-exchange membrane 5.8 cm in diameter, were equilibrated successively with 0.1 M HCl and 0.1 M NaOH and then thoroughly washed in distilled water before use. Such a conditioned membrane was found to have resistance in air of 1.5 Ω cm^{-2}, an ion-exchange capacity of 1.80 m equiv/g, and a moisture content of 29.8% after drying.

Preparation of Metal-Deposited Membrane

Metal (copper or lead) deposition on the conditioned membrane was carried out by electroless plating by an ion-exchange method (16). The membrane was mounted at the bottom of the inner compartment in a two-compartment cell. A solution of 0.1 M $CuSO_4$ or $Pb(CH_3COO)_2$ in the inner compartment and the solution of 8% (v/v) hydrazine hydrate in the other compartment were equilibrated for a specific time. The metal ions were allowed to pass across the membrane by ion exchange
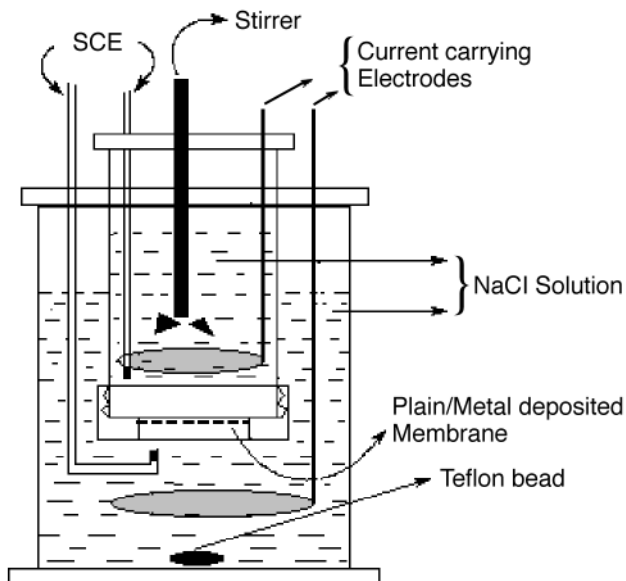
FIG. 1. Chronopotentimetric cell.

and were reduced to the metallic form by hydrazine on the other side under constant stirring. Deposition to different extents was obtained by fixing the reaction time ranging from 30 min until maximum coverage was reached over the entire membrane surface. The membranes thus modified were then thoroughly washed with distilled water and equilibrated in 1 M NaCl for subsequent studies.

Measurements

The quantity of metal in such membranes was estimated by differential pulse polarography (DPP). In these studies, the deposited metal was leached out by immersing the membranes in 10 ml of concd HNO_3 followed by successively washing with an excess of concd HNO_3 and distilled water so that all the metal (Cu^{++}/Pb^{++}) ions in it were replaced by protons. The resulting solution was dried on a water bath and diluted to 10 ml. The composition of metal in 1 ml of this solution was determined by running a differential pulse polarogram in 10 ml of 0.2 M ammonium citrate buffer at pH 3.0. The peak currents at -0.06 V for Cu(0)/Cu(II) and -0.48 V vs a saturated calomel electrode (SCE) for Pb(0)/Pb(II) were compared with those of standard samples and the contents of the respective metals were calculated (9).

The electrical responses of the plain and metal-deposited membranes were recorded in dilute NaCl solution using a Perspex cell (14), as shown in Fig. 1. The cell had two compartments (inner and outer) separated by a circular plain or metal-deposited membrane 5.8 cm in diameter. A constant current was applied across the membrane using two large titanium electrodes coated with precious metal oxides, placed one above and other below the membrane by employing an EG&G PAR Model 174 potentiostat/galvanostat. A high pre-

cision EG&G PAR Model 0089 X-Y recorder in conjunction with the PAR Model 174A was used to record the variations in the potential (E_t) versus time across the membrane under static conditions. The direction of the current in all of these studies was set in such a way that the counterion should move vertically upward from the outer to the inner compartment with minimal perturbations caused by natural convection. The effective membrane area facing the two electrodes was 12.5 cm². The potential difference across the membrane under static conditions was measured by using two saturated calomel electrodes (SCEs). The solutions of both the outer and inner compartments were stirred vigorously between two successive measurements to ensure the return of equilibrium conditions in the two solution–membrane interfacial zones.

Cyclic voltammetric studies were performed using an EG&G PARC Model 273A potentiostat/galvanostat (M270 electrochemistry software) coupled to a three-electrode cell assembly and a Gateway 2000 (4DX2-66) computer (17, 18). The metal-coated cationic membrane (1 cm $\times$ 3 cm) was mounted on a single-surfaced Pt plate. The supported membrane and its edges were wrapped with a Teflon tape leaving about 0.25 cm² of membrane exposed for experimental purposes. All potentials were measured with reference to Ag/AgCl (0.222V vs NHE) in 3 M NaCl. A platinum wire separated from the analytical solution by a Vycor tip bridge served as a counter electrode. A 0.2 M acetate–H_2SO_4 (pH 2.8 or 4.5) mixture was used as the electrolyte solution. All of the experimental solutions were thoroughly deoxygenated with Ar.

RESULTS AND DISCUSSION

Chronopotentiometry of Plain Membrane

The electrical responses of the conditioned, plain, cation-exchange membrane were studied at low current densities between 0.10 and 0.96 mA cm^{-2} in 1–10 mM NaCl. The representative chronopotentiograms observed at 0.8 mA cm^{-2} in 10 mM NaCl and 0.1 mA cm^{-2} in 1 mM NaCl are shown in Figs. 2A and 2B(a), respectively, each one having two potential zones and one inflection at $t = \tau$. At $I = 0.8$ mA cm^{-2}, the inflection in 10 mM NaCl was at 46 s which is about 0.70 V in height (ΔE) spreading itself over 46 s on the time axis. Moreover, the two potential zones were nearly horizontal, and the potential drop (E_0) across the membrane at the beginning is 0.2 V. In 1 mM NaCl, the two potential zones, separated at 30 s, were nearly parallel to the abscissa maintaining the separation (ΔE) to about 0.54 V between them in a span of about 30 s. The E_0 in this case was found to be 0.25 V. The τ values measured at the midpoint of the inflections were 15–62 s in 1 mM NaCl and 39–90 s in 10 mM NaCl, and the $I\tau^{1/2}$ value in each case varied negligibly with the change in I in the above said range. These experimental features may be explained as follows.

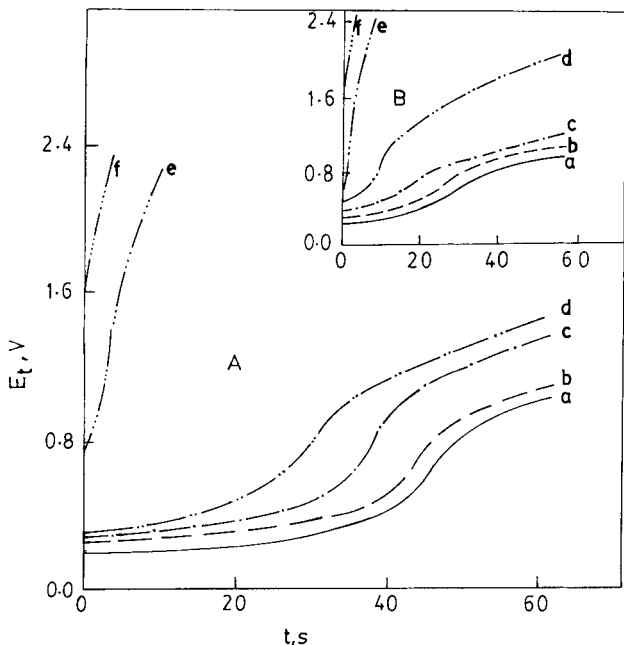When a constant current is applied in an electrolytic solu-

FIG. 2. Potential vs time characteristics of the (a) plain, (b) $\frac{1}{2}$-h, (c) 1-h, (d) 2-h, (e) 5-h, and (f) 7-h copper-deposited cation-exchange membranes in (A) 10 mM NaCl at $I = 0.8$ mA cm^{-2}; (B) 1 mM NaCl at $I = 0.10$ mA cm^{-2}.

tion, electrolysis starts instantly at the electrodes. If the electrodes are separated by an ion-exchange membrane, the rate of reaction at each electrode depends upon the counterion mobility in the membrane and the membrane permselectivity P, i.e., the case of counterion migration across the ion-exchange membrane which is defined for a cation-exchange membrane as

$$P = \frac{\bar{t}_+ - t_+}{1 - t_+}, \qquad [1]$$

where $\bar{t}_+$ and t_+ are the transport numbers of cations in the membrane phase and solution phase, respectively.

Assume that the membrane is placed in NaCl solution of strength C_0. Then, the Na$^+$, in the presence of an electric field, drifts across the membrane from the anode compartment to the cathode. As a result, a concentration gradient develops across the membrane–solution interfaces on account of the difference in Na$^+$ ion mobility in the solution and the membrane phase. The potential difference across the membrane remain constant initially as no concentration polarization has occurred, and it steadily increases when the concentration polarization starts to occur because of an additional voltage drop across the external diffusion zone. Eventually, a new steady state occurs when the concentration profile externally reaches a steady state, and the new steady voltage is the sum of the membrane and the diffusion layer potentials. Thus, a kind of S-type profile for the E_t–t plot with a fairly diffused inflection at the transition time $t = \tau$ may be obtained. The transition time τ in turn depends

upon the magnitude of applied current density I, the molar concentration of Na$^+$ in the bulk, the membrane permselectivity, and the solution phase transference number (t_+) as shown here (14):

$$I\tau^{1/2} = \frac{z_c F(\pi D_s)^{1/2}}{2(1 - t_+)P} C_0 \qquad [2]$$

where D_s is the diffusion coefficient of NaCl and $z_c = 1$ for Na$^+$. This holds very well for an ideal membrane whose surfaces are plain and fully conditioned.

The observations shown in Figs. 3A(a) and 3B(a) satisfy the validity of Eq. [2] for the plain membrane. The permselectivity P and counterion transport number $\bar{t}_+$ of the cation-exchange membrane are in the range of 0.95–0.97 and 0.92–0.97, respectively.

Chronopotentiometry of Metal-Deposited Membranes

The responses of the copper- and the lead-deposited membranes were studied in 1–10 mM NaCl solutions at low applied current densities ranging from 0.11 to 0.97 mA cm^{-2}. The representative data obtained with $\frac{1}{2}$-, 1-, 2-, 5-, and 7-h copper deposited membranes, with coated surfaces up in 10 mM NaCl at 0.8 mA cm^{-2} and in 1 mM NaCl at 0.1 mA cm^{-2}, are compared with those of a plain membrane in Fig. 2. The data revealed that the first potential zone reduced in length as the copper deposition progressed. As a result, the inflection point ($\tau = 46$ s in 10 mM and 30 s in 1 mM NaCl) observed with the plain membrane, moved toward the origin in the case of $\frac{1}{2}$-h to 5-h deposited membranes and finally overlapped with the potential axis in the case of a 7-h deposited membrane. This trend
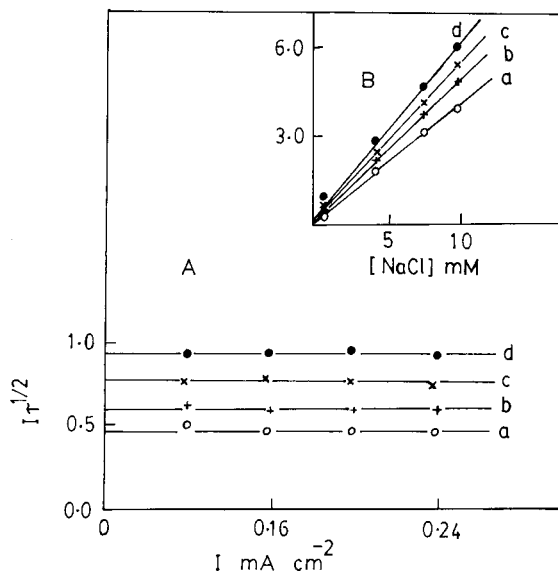

FIG. 3. Plots of (A) $I\tau^{1/2}$ vs I in 1 mM NaCl, (B) $I\tau^{1/2}$ vs [NaCl]. (a) plain and (b) $\frac{1}{2}$-h, (c) 1-h, and (d) 2-h copper-deposited ion-exchange membranes.

indicates that the concentration diffusion layer in the vicinity of the membrane surface on the dilute side develops with ease in a given electrolyte concentration because the deposited copper grew in size. Then, the absence of an inflection in the case of a 7-h deposited membrane in Figs. 2A(d) and 2B(d) is accounted for by the rapid growth of a diffusion layer in the interfacial zone at the inception. The shift in the inflection appeared to be almost regular in the first two hours and was rapid in the subsequent stages of copper deposition, as seen in Figs. 2A(b–d) and 2B(b–d). Similarly, the potential drop E_0 across the membrane at the very start increased with the increase in copper deposition due to masking of ion-conductive sites at the membrane surface in contact with the ionic solution. This is obvious because more of the ionic paths are blocked by the deposited metal which apparently reduces the ionic mobility in the interfacial zone. The drop in membrane potential E_0 was nearly uniform with the initial two-hour deposited membranes compared with others. The data in Fig. 2 also revealed that the slopes of the first and second potential zones were insignificant for plain and 30-min deposited membranes. They were, however, considerable in the case of 1-h and 2-h deposited membranes and quite remarkable in the case of 5- and 7-h deposited membranes. It seems that the change in potential drop with time was dominated by the resistance of the depletion layer having the highest resistance within the diffusion layer at the metalated surface where the lowest ion concentration exists. Then, for increasing values of constant current, the long time slopes of the chronopotentiograms have increasing slopes, compared with those of the plain membrane, because the higher current causes a steeper concentration profile with lower counterion concentration on the surface and higher resistance. In contrast, the potential separation (ΔE) between the two zones with $\frac{1}{2}$-h to 5-h deposited membranes, in both 1 mM and 10 mM NaCl, was negligibly affected by copper deposition, and its magnitude was almost comparable with that of the plain membrane in the respective medium. The τ values measured at midpoints of the inflections varied between 26–98 s for $\frac{1}{2}$-h, 24–68 s for 2-h, and 2–5 s for 5-h deposited membranes in 10 mM NaCl. They were found to be between 13–42 s for $\frac{1}{2}$-h, 6–28 s for 1-h, 3–19 s for 2-h, and 0.3–1.4 s for 5-h deposited membranes in 1 mM NaCl. These ranges are lower than the values obtained for the plain membrane. However, the product $I\tau^{1/2}$ for each of these deposited membranes in both the NaCl solutions was fairly constant, as depicted in Fig. 3A for 1 mM NaCl, and it decreased in the order plain $> \frac{1}{2}$-h $>$ 1-h $>$ 2-h $>$ 5-h deposited membrane. Further, the $I\tau^{1/2}$ values for each of these deposited membranes, like the plain one, appeared (Fig. 3B) to have linear dependence on [NaCl].

The τ, E_0, and ΔE data corresponding to the chronopotentiometric responses which are shown in Fig. 2A and 2B for copper-deposited membranes are compared in Table 1 with those of the plain membrane. The τ data showed that the extent of copper deposition on membranes has been found to be similar in nature in both NaCl concentrations. However, the

TABLE 1
The Measured τ, E_0 and ΔE Data of Plain and Metal-Deposited Cation Exchange Membranes at 0.10 mA cm^{-2} in 1 mM and 0.80 mA cm^{-2} in 10 mM NaCl

Membrane	1 mM NaCl			10 mM NaCl		
	τ (s)	E_0 (V)	ΔE (V)	τ (s)	E_0 (V)	ΔE (V)
Plain	30	0.25	0.54	46	0.19	0.70
			Cu-deposited			
$\frac{1}{2}$ h	28	0.33	0.50	43	0.25	0.68
1 h	23	0.40	0.42	39	0.28	0.65
2 h	12	0.43	0.42	31	0.30	0.64
5 h	2	0.57	0.40	3	0.73	0.63
7 h	UD[a]	1.73	UD[a]	UD[a]	1.62	UD[a]
			Pb-deposited			
$\frac{1}{2}$ h	12	0.42	0.44	33	0.35	0.69
1 h	8	0.45	0.32	30	0.74	0.64
2 h	UD[a]	2.20	UD[a]	UD[a]	1.42	UD[a]

[a] UD = undetected under the present set of experimental conditions.

rate of decrease in τ value with the deposition time in a given NaCl solution as relatively slow within the two-hour deposition and rapid at longer times. Conversely, the E_0 values increased unevenly as the deposition time increased. Besides these variations, a negligible change in the ΔE was noted among the different copper-deposited membranes indicating the formation of a uniformly thick diffusion layer with respect to the given NaCl concentration.

The results obtained with the $\frac{1}{2}$-, 1-, and 2-h lead-deposited membranes and that of plain membrane in 10 mM NaCl at 0.8 mA cm^{-2} are shown in Fig. 4, and the relevant data for 1 mM and 10 mM NaCl are incorporated in Table 1. As in the case of the copper-deposited membranes, the inflection at $\tau = 46$ s with the plain membrane shifted to 33 and 30 s in 10 mM NaCl and 28 and 26 s in 1 mM NaCl with 30-min and 1-h deposited membranes, respectively. However, the inflection with the 2-h deposited membrane, unlike the copper-deposited membrane, completely drifted toward the origin and overlapped the potential axis, as seen in Fig. 4. This indicates that the total surface covered by the deposited metal over the membrane in a given period is relatively higher for lead than copper. Paradoxically, the potential drop E_0 across the membrane rose to a considerable extent in the case of all lead-deposited membranes (Table 1). The magnitude of variation in E_0 (about 0.49 to 1.17 V in 1 mM NaCl and 0.23 to 2.01 V in 10 mM NaCl) given in Table 1 is more than those (0.15 to 0.18 V in 1 mM NaCl and 0.06 to 0.11 V in 10 mM NaCl) observed with the corresponding copper-deposited membranes, proving that the resistance of the metal-deposited membrane varies with the nature of the metal as well as the extent of surface coverage by the metal on the membrane surface. Besides this, the data in
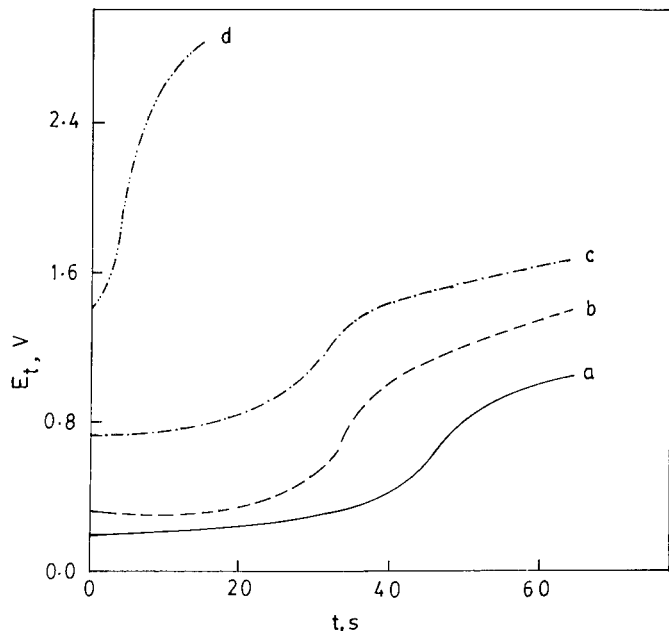
FIG. 4. Potential vs time characteristics of the lead-deposited cation-exchange membranes in 10 mM NaCl at $I = 0.8$ mA cm^{-2}; (a) plain (b) $\frac{1}{2}$-h, (c) 1-h, and (d) 2-h.

Fig. 4 and in Table 1 revealed that the height of the inflection (ΔE) at τ is less susceptible to the deposited metal indicating the formation of identical diffusion layers at the interfacial zones of all plain and metal-deposited membranes in a given electrolyte.

Equation [2] relating $I\tau^{1/2}$ and C_0 will not apply to these modified membrane surfaces because the total number of surface ionic charges on the membrane establishing equilibrium conditions with Na$^+$ ions in solution decreases. Although Na$^+$ ion concentration C_0 remained constant in the bulk, the concentration of this ion establishing equilibrium in the membrane solution interface was reduced. It is possible to explain the behavior of such modified membranes by

$$I\tau^{1/2} = \frac{z_c F(\pi D_s)^{1/2}}{2(1 - t_+) P} (C_0 - \Delta C_{div}) \qquad [3]$$

where ΔC_{div} measures the number of ion conductive sites masked by the deposited material in molar concentration with respect to [Na$^+$] in the bulk.

The $I\tau^{1/2}$ data obtained in 1 mM 10 mM NaCl solutions with copper- and lead-deposited membranes are summarized in Table 2. These values, in both cases of metal deposited membranes, are less than 0.54 in 1 mM NaCl and 5.52 in 10 mM NaCl observed with the plain membrane. It is apparent that for a given metal-deposited membrane in a given NaCl concentration, the $I\tau^{1/2}$ value decreases with a corresponding increase in the degree of metal deposition. This shows that the deposited metal conceals some of the conductive ionic sites on the membrane surface. However, the plots $I\tau^{1/2}$ vs I and $I\tau^{1/2}$ vs [NaCl] (Figs. 3A(b–d) and 3B(b–d)) shown for copper-deposited membranes suggest that the modified membranes possess all of the transport phenomenal functions of a plain membrane. But the parameters P and $\bar{t}_+$ evaluated by substituting the observed $I\tau^{1/2}$ values in Eq. [1] are found to be more than those of a plain membrane. The approximate percentages of metal coverage % M$_c$ and the values of ΔC_{div} for each copper- and lead-deposited membrane may be defined as in Eqs. [4] and [5], and they are calculated by substituting inserting values.

$$M_c = \frac{\Delta(I\tau^{1/2})}{(I\tau^{1/2})_P} 100 \qquad [4]$$

$$\Delta C_{div} = \Delta(I\tau^{1/2}) \frac{2(1 - t_+) P}{Z_c F(\pi D_S)^{1/2}} \qquad [5]$$

where $(I\tau^{1/2})_M$ and $(I\tau^{1/2})_P$ corresponding to the deposited and plain membranes, respectively; $\Delta(I\tau^{1/2}) = (I\tau^{1/2})_M - (I\tau^{1/2})_P$. According to this data, the deposited copper covers about 3.7 to 7.6% in 30 min, 9.8 to 11.1% in 1-h, 21 to 35.2% in 2-h, 74 to 75% in 5-h, and above of the 7-h deposit of the metal's effective membrane surface area. These values are well in congruence with the quantity of metal deposition per cm^2 (Table 2) estimated by the voltammetric method. This amounts to masking the number of total conductive ionic sites on the membrane surface, varying in terms of molar concentration between 0.04 to 1 mM with respect to 1 mM NaCl and 0.8 to 10 mM with respect to 10 mM NaCl. In the case of lead-deposited membranes, the metal covers about 1.9 to 17.2% surface in 30 min, 18.5 to 19.6% in 1-h, and nearly 100% in 2-h. The ionic sites covered by deposited lead vary in terms of

TABLE 2
Amount of Metal Deposited, Approximate Percentage of Metal Coverage (%M$_c$) and the Number of Ionic Sites Masked by the Deposited Metal in Terms of Counterion Concentration (ΔC_{dv}) on the Metal-Deposited Membrane Surface in 10 mM NaCl

Membrane	Amount of metal deposition (mg/cm^2)	$I\tau^{1/2}$	%M_c	ΔC_{div} (mM)
		Cu-deposited		
$\frac{1}{2}$ h	0.547	5.10	7.6	0.8
1 h	1.640	4.98	9.8	1.0
2 h	5.171	4.36	21.0	2.1
5 h	11.082	1.38	75.0	7.5
7 h	11.0818	–	>75.0	>7.5
		Pb-deposited		
$\frac{1}{2}$ h	0.725	4.57	17.2	1.7
1 h	1.270	4.44	19.6	2.0
2 h	1.296	–	>19.6	>2.0

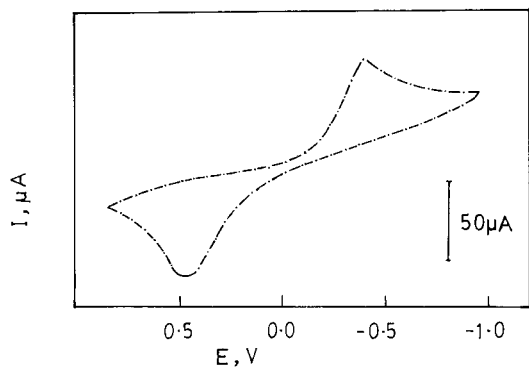**FIG. 5.** Cyclic voltammetric responses of one-hour copper-deposited cation-exchange membrane at pH 2.8 in 0.2 M CH_3COONa–H_2SO_4 solution.

molar concentration between 0.02 and 1 mM with respect to 1 mM NaCl and 1.5 to 10 mM with respect to 10 mM NaCl.

Cyclic Voltammetry

A piece (1 cm $\times$ 3 cm) of 1-h (copper or lead) deposited membrane was firmly mounted on a single-sided platinum surface both of equal dimensions. The edges of both platinum and lead membrane were wrapped with a Teflon tape ensuring that the deposited membrane surface had good electrical contact with the platinum surface. The metal composite membrane supported on platinum was taken as the working electrode by dipping one end (about 0.5 cm) in the electrolyte solution while extending the other end by a platinum wire. The electrical responses of such composite membrane electrodes were investigated in the potential range between 0.8 to -1.0 V in 0.2 M CH_3COONa and H_2SO_4 mixtures at pH 2.8 or 4.5.

The copper-deposited membrane exhibited (Fig. 5) a pair of ill-defined anodic peaks at $+0.420$ V at pH 2.8 and $+0.410$ V at pH 4.5, and a cathodic peak juxtaposing the solution to Cu(II), whereas the cathodic couple at -0.384 V at pH 2.8 and -0.435 V at pH 4.5 was assignable to Cu(0)/Cu(II) (19, 20).

The lead-deposited membrane, on the other hand, peaked at -0.342 V during an anodic scan and -0.515 V in the reverse scan. These responses, which shift to cathodic potentials (-0.347 V and -0.435 V) with the change in pH to 4.5 are attributed to the Pb(0)/Pb(II) couple. The membrane exhibited additional responses corresponding to the Pb(II)/Pb(IV) couple's peak at -0.197 V and -0.357 V at pH 2.5 and a single anodic response at -0.113 V at pH 4.5.

The present study revealed that the ion-exchange capability of cation-exchange membranes is gradually masked with increasing thickness of the film due to metal deposition on the surface. The surface coverage by the metal in a given duration of deposition time under identical conditions depends also on the nature of the metal. From the measured values of $I\tau^{1/2}$ for the plain and deposited membranes, the percentage of surface covered by the metal is determined. The data further confirmed that the metal-deposited membranes are porous and useful as electron- as well ion-conductive materials. These findings throw light on the conditions of metal deposition for obtaining modified membranes in applications involving electroorganic syntheses and chemical sensors employing electroanalytical techniques.

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