

Electrochemical Studies on Zinc Containing Zirconium Phosphate Membrane

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Abstract: The present study deals with the formation and characterization of Zinc containing Zirconium Phosphate membranes. Impregnation has been done using Pyrex sinter. For the estimation of transmission characteristics of the formed membranes, membrane potential and membrane conductance measurements were carried out. The resulting membrane structure is endowed with cation selectivity and improved permselectivity. The membrane also exhibits enhanced resistance towards impairment in electrochemical activity.

IndexTerms–Zirconium Phosphate, Zinc, Membranes, Permselectivity, Transport number.

I. INTRODUCTION

Zirconium phosphate ($ZrPO_4$) is a prominent inorganic ion-exchange material endowed with cation selectivity [1-4]. Membranes based on this material have been extensively studied with the object of determination of their electrochemical characteristics in different electrolytic environment [5-7]. A priori considerations suggest that incorporation of zinc in zirconium phosphate network may result in alteration in its electrochemical characteristics. We have prepared zinc containing zirconium phosphate ($ZrZnPO_4$) membranes by impregnation using pyrex sinter. Characterization of this composite system has been attempted on the basis of membrane potential and membrane conductance measurements. Estimation of transmission characteristics of the membrane was carried out on the basis of TMS theory [8]. Membrane potential measurements were carried out using electrolyte solutions of unequal concentration on the two sides of the membrane in the usual manner [9-10].

II. EXPERIMENTAL PROCEDURE

Preparation of zirconium zinc phosphate membrane was carried out using impregnation method. A mixture of zirconyl chloride and zinc sulphate; and disodium hydrogen phosphate solution were kept in contact overnight through a pyrex sinter fixed in a glass cell. The solutions were interchanged and impregnation allowed for another about 24 hours. Thereafter, the membrane was kept soaked in distilled water which was renewed repeatedly to ensure removal of the sulphate ions. The membrane was then kept in 1M sodium chloride solutions overnight to transform it to sodium form. It was then equilibrated with sodium chloride solutions of desired concentrations.

Zirconium phosphate membrane was also formed by impregnation using equimolar solutions of disodium hydrogen phosphate and zirconium chloride.

The electrochemical set-up,

SCE || Solution | Membrane | Solution || SCE
(C₁) (C₂)

was employed for this purpose. || denotes KCl salt bridge and SCE, the saturated calomel electrode. The solutions were renewed before measurements. A digital multimeter (model HIL 2161) was used for potential measurements. For conductance measurements potential difference in steps across the membrane was applied using Hindustan Powertonic INC power supply. These potentials were measured using saturated calomel electrodes and Philips (PM 2518) digital multimeter. Corresponding currents were measured employing HIL digital multimeter and silver-silver chloride electrodes. Conductance values were delivered from current vs potential plots.

III. RESULTS AND DISCUSSION

Membrane potential data obtained using the Zirconium zinc phosphate when sodium chloride solutions of different concentrations having a fixed concentration ratio of ten, are presented in Table 1. The membrane exhibits cations selectivity as inferred on the basis of transport number values derived using the relationship [11]

$$(\Delta\phi)_{I=0} = (2t_+ - 1) \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

t_+ denotes transport number of the cation in the membrane phase. C_1 and C_2 denote concentrations of sodium chloride separated by the membrane. The transport number values are also included in the Table 1 along with permselectivity, P_s values estimated using the relationships[12].

$$P_s = \frac{t_+ - T_+}{1 - T_+}$$

T_+ represent the transport number of the counter ions in solution.

Table 1: Membrane potential, transport number, permselectivity and membrane conductance values. Sodium chloride solutions having $C_1/C_2 = 10$ were used. Membrane- $(ZrZn)PO_4$ deposited in the pyrex sinter using mixture of 0.1M $ZrOCl_2$ and 0.1M $ZnSO_4$; and 0.1M Na_2HPO_4 .

Concentration (M)		$[\Delta\phi]_{I=0}$ (mV)	t_+	P_s	$[I/\Delta\phi]$ (Ω^{-1})
C_1	C_2				
0.01	0.10	46.4	0.8867	0.8151	1.6×10^{-3}
0.02	0.20	40.3	0.8359	0.7331	2.93×10^{-3}
0.03	0.30	37.0	0.8083	0.6892	3.06×10^{-3}
0.04	0.40	36.5	0.8042	0.6834	4.9×10^{-3}
0.05	0.50	35.0	0.7917	0.6639	5.95×10^{-3}

Membrane selectivity ordinarily changes because of:

- de-swelling of the membrane matrix upon increasing concentration of the electrolyte.
- Reduction in co-ion exclusion and
- Altered adsorbability of counter-ions on to the membrane matrix.

In the case of inorganic ion-exchange membranes factor (i) normally does not make a significant contribution. Adsorption of counter sodium ions in this case is somewhat unlikely. Observed variation in selectivity therefore principally arises on account of reduction in co-ion exclusion with increase in concentration. It may also be noticed that permselectivity of the membrane does not decline substantially with increase in concentration. Membrane conductance values vary with concentration and this variation is depicted in Fig. 1. Membrane conductance values were obtained on the basis of current voltage studies. Relevant data are plotted in Fig. 2. Observed increase in conductance with concentration is consistent with lowered co-ion exclusion inferred above on the basis of membrane potential studies.

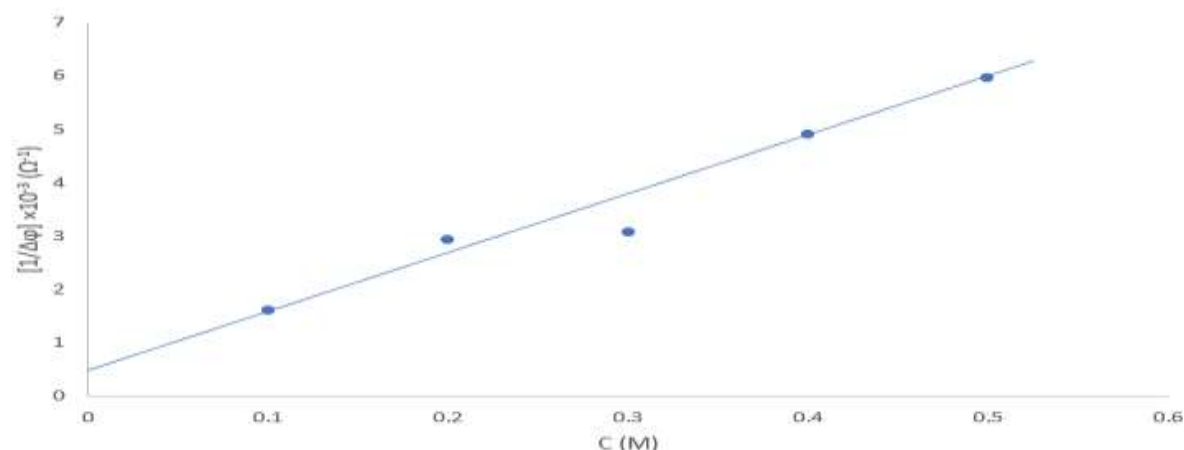


Figure 1: Dependence of membrane conductance on concentration of sodium chloride solutions.

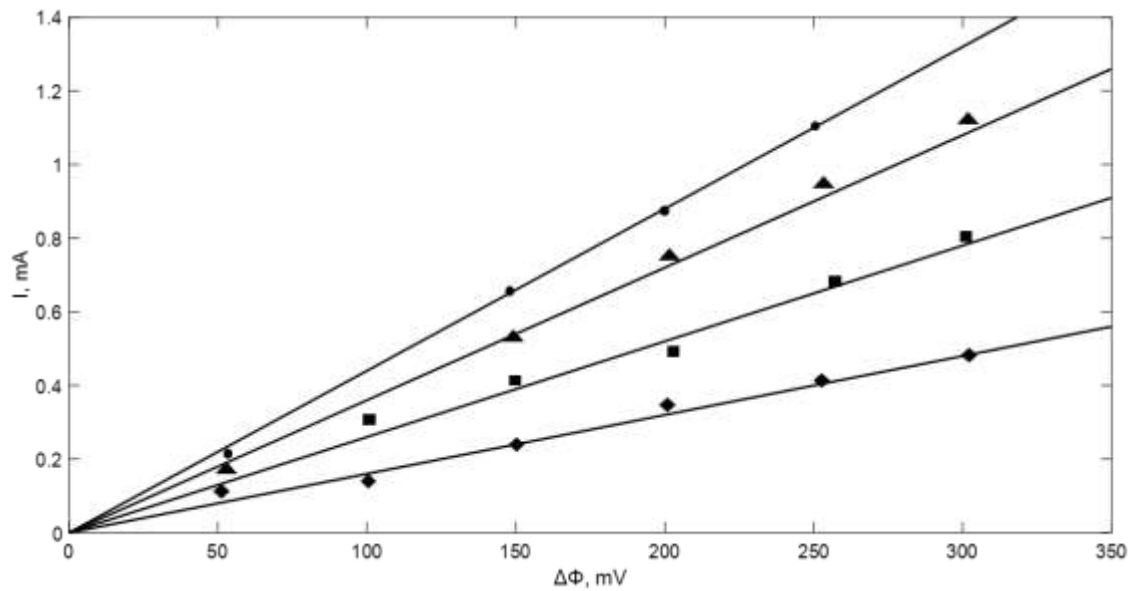


Figure 2: Determination of membrane conductance on the basis of current-voltage studies
 [-•- = 0.055 M NaCl; -▲- = 0.11 M NaCl; -■- = 0.22 M NaCl; -◆- = 0.275 M NaCl]

Zirconium zinc phosphate membrane was also prepared using a mixture of 0.05M ZnSO₄ and 0.1M ZrOCl₂; and 0.15M Na₂HPO₄ for impregnation. Electrochemical behavior of the membrane thus formed was investigated on the basis of membrane potential studies. In this case counter-ion transport number and permselectivity did not exhibit any variation with change in concentration of sodium chloride solutions (Table 2). Likewise in all cases membrane conductance values derived on the basis of current-voltage measurements (Fig. 3.) were found to be invariant at $1.1 \times 10^{-3} \text{ ohm}^{-1}$.

Table 2: Membrane potential, transport number and permselectivity and values when Sodium chloride solutions were used. Membrane- (ZrZn)PO₄ deposited in the pyrex sinter using mixture of 0.1M ZrOCl₂, 0.05M ZnSO₄; and 0.15M Na₂HPO₄.

Concentration (M)		[Δφ] _{t=0} (mV)	t ₊	P _s
C ₁	C ₂			
0.01	0.1	46.5	0.8875	0.8164
0.02	0.2	45.5	0.8792	0.8035
0.03	0.3	46.5	0.8875	0.8176
0.04	0.4	45.3	0.8775	0.8019
0.05	0.5	45.2	0.8767	0.8011

These findings are somewhat intriguing and defy explanation on the basis of usual considerations. The same membrane when tested using potassium chloride solutions exhibited electrochemical behavior expected of an inorganic ion-exchange membrane. The relevant information is summarized in Table 3.

Table 3: Membrane potential, transport number, permselectivity and membrane conductance values when Potassium chloride solutions were used. Membrane- (ZrZn)PO₄ deposited in the pyrex sinter using mixture of 0.1M ZrOCl₂, 0.05M ZnSO₄; and 0.15M Na₂HPO₄.

Concentration (M)		[Δφ] _{t=0} (mV)	t ₊	P _s	[I/Δφ] (Ω ⁻¹)
C ₁	C ₂				
0.01	0.1	41.0	0.8417	0.7416	0.6×10^{-3}
	0.2	38.0	0.8167	0.7019	1.2×10^{-3}

0.02					
0.03	0.3	33.8	0.7817	0.6461	1.6×10^{-3}
0.04	0.4	31.5	0.7625	0.6159	2.0×10^{-3}
0.05	0.5	29.6	0.7467	0.5913	2.5×10^{-3}

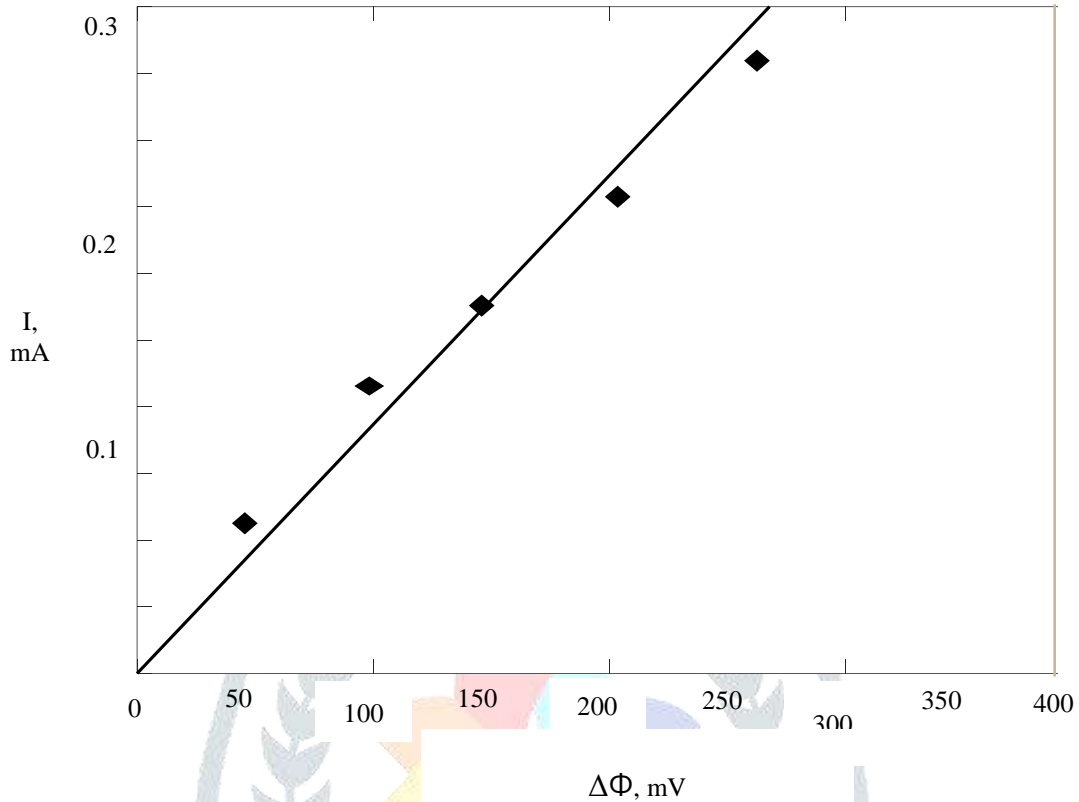


Figure 3: Determination of membrane conductance on the basis of current-voltage studies for NaCl solution.

For the purpose of comparison, membrane potential studies were also carried out using zirconium phosphate (Fig. 4.). Membrane potentials, transport number, permselectivity and membrane conductivity values are summarized in Table 4. It may be noted that in this case membrane permselectivity declines much more rapidly with concentration in comparison to the zirconium zinc phosphate membrane. It may, therefore, be inferred that zinc containing zirconium phosphate membranes are endowed with enhanced permselective behavior; and resist deterioration in permselectivity with increase in concentration in a substantial measure.

Table 4: Membrane potential, transport number, permselectivity and membrane conductance values obtained using Sodium chloride solutions. Membrane- ZrPO₄ deposited in the pyrex sinter using 0.1M ZrOCl₂ and 0.1M Na₂HPO₄.

Concentration (M)		$[\Delta\phi]_{I=0}$ (mV)	t_+	P_s	$[I/\Delta\phi]$ (Ω^{-1})
C_1	C_2				
0.01	0.1	43.9	0.8658	0.7809	1.9×10^{-3}
0.02	0.2	18.3	0.5607	0.2851	2.4×10^{-3}
0.03	0.3	15.8	0.5431	0.2573	2.8×10^{-3}
0.04	0.4	12.7	0.5367	0.2478	3.5×10^{-3}
0.05	0.5	9.6	0.5183	0.2193	4.1×10^{-3}

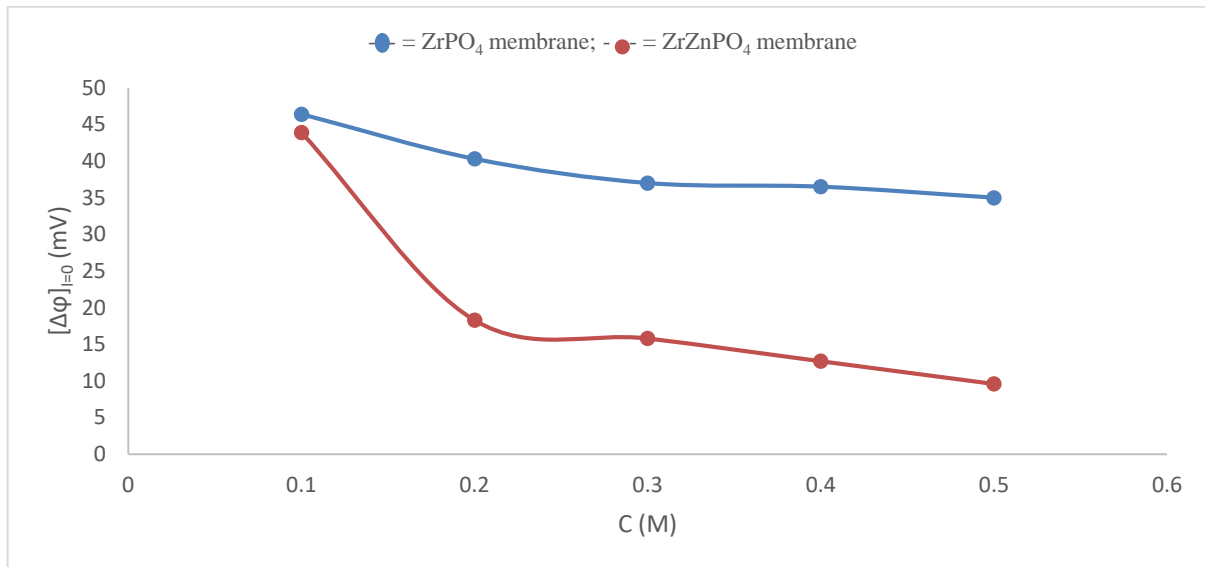


Figure 4: Variation of membrane potential with mean concentration of sodium chloride solutions

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