

Functional properties and electroanalytical selectivity of some anion exchange membranes

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Abstract. Heterogeneous membranes of Fe(III)–Zr(IV), Cr(III)–Zr(IV) mixed hydrous oxides and one doped with Sn(II) ion have been prepared using polystyrene as a binding material. Functional properties like water content, porosity, swelling, electrolyte absorption and conductance of these membranes have been determined in various anionic forms and correlated with their electroanalytical selectivity.

Keywords. Ion exchange membranes; analytical selectivity; hydrous oxide membranes.

1. Introduction

The first prerequisite for understanding the electrochemical performance of an ion exchange membrane, particularly the permselective one, is its complete physico-chemical characterization, but this particular aspect has received little attention as far as inorganic gel membranes are concerned.

In continuation of our work (Srivastava and Jain 1985, 1986) on pure and mixed hydrous oxides and their membranes, it was observed that the two mixed oxides iron–zirconium and chromium–zirconium (with iron or chromium as a major constituent) exhibit many-fold increase in their anion-uptake capacities as compared to pure iron, chromium or zirconium oxide. Mixed and Sn(II)-doped oxides exhibit even higher anion uptake as compared to the mixed one. The choice of dopant depends on relatively similar ionic size of metal ions used for preparing oxides. The polystyrene-based membranes of these products also possess promising anion selectivity as compared to the individual oxide membranes.

The functional properties *vis-a-vis* selectivity of the polystyrene supported membranes of these two products viz., iron–zirconium and chromium–zirconium oxides and one doped with Sn(II) are reported in this paper.

2. Experimental

2.1 Materials

Ferric chloride (BDH), chromium chloride (BDH) and zirconium oxychloride (AR)

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were used as such. All other chemicals used in these investigations were also of analytical grade.

2.2 Apparatus

Membrane potentials were measured with a Radiometer (PHM-64) millivoltmeter coupled to a servoscribe recorder. Ceramic junction calomel reference electrodes were used. The assembly used for potential measurements was the same as that reported earlier (Malik *et al* 1982).

2.3 Preparation of hydrous oxide gels and their membranes

Ferric chloride, chromium chloride and zirconium oxychloride were used as starting materials. The concentrations for the preparation of mixed and doped oxides were obtained after a good deal of preliminary investigations. These, however, represented the optimum conditions when the product is chemically and thermally stable and exhibits maximum sorption capacity. The following general procedures were used for the preparation of the mixed and doped hydrous oxides.

The salt solutions were mixed in the molar ratio of 8:1 (iron or chromium being the major constituent). The hydrous oxides were coprecipitated by adding 1.0 M ammonium hydroxide slowly under constant stirring. The precipitate was left to stand with the mother liquor for two days at room temperature, and then washed several times by decantation with distilled water, filtered and dried at 80°C for 24 h. Doped oxide was prepared by adding 0.075 g stannous chloride to a 450 ml mixed solution containing the respective metal salts in a molar ratio of 8:1 and was also precipitated with 1.0 M ammonium hydroxide.

Homogeneous membranes could not be prepared. Those obtained by pressing the material, even at very high pressure, were found to be fragile and dispersed when kept in contact with electrolyte solutions. Heterogeneous membranes, obtained by embedding polystyrene in respective oxide gel, were found to be quite satisfactory. These were prepared by mixing 1.275 g oxide with 0.225 g polystyrene and heating the homogeneous mass in a die kept in a metallurgical specimen mount press at 120°C under a pressure of 45–48 MPa. Membranes prepared in this way were quite stable and did not show any dispersion in different electrolyte solutions. These were also examined under an electron microscope for cracks and homogeneity of the surface and were finally tested for generating reproducible potentials.

2.4 Water content

The membrane was soaked for one day in a 0.1 M solution of NaCl solution. It was then washed several times with distilled water, and the adherent liquid removed with blotting paper. The soaked membrane was weighed and later dried to a constant weight in a vacuum desiccator at 60°C. The difference in the two weighings, divided by the weight of the wet membrane was taken as its water content.

2.5 Porosity

It was determined by the method followed by Mizutani and Nishimura (1970).

$$\text{Porosity} = \frac{\text{water content}}{A.L. Q_w}$$

where A is the area of membrane, L its thickness and Q_w is the density of water.

2.6 Swelling

The thickness of the dry membrane was accurately measured. It was then immersed in a solution of electrolyte for one day and the thickness measured after dabbing it with blotting paper. The difference between the thickness of the dry and the swollen membrane was taken as a measure of swelling.

2.7 Electrolyte absorption

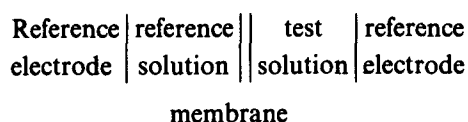
Excess electrolyte solution adhering to the membrane after attaining equilibrium was removed and the membrane dipped in 20 ml of distilled water. It was intermittently shaken and left as such for a few hours. The whole process was repeated three to four times and the entire solution was collected in the measuring flask. It was finally made up to the mark with distilled water and the strength was measured conductometrically.

2.8 Conductance

The method adopted by Lakshminarayanaiah and Subrahmanyam (1968) which makes use of a mercury pool on both sides of the membrane to minimize polarization at the membrane interface, was employed for conductance measurements at three different concentrations (0.1, 0.01, 0.001 M) of electrolyte solution. The membrane was cemented in between the two halves of a U-tube with the help of araldite and kept in contact with an electrolyte solution of desired concentration. Two platinum electrodes were dipped in two halves and connected to a bridge for conductivity measurements. The solution was then replaced by mercury previously equilibrated with electrolyte solution of the same concentration and the conductance was measured. The whole assembly was clamped in a thermostatic water bath to conduct all measurements at a constant temperature of $30 \pm 0.2^\circ\text{C}$.

2.9 Potential measurements

Membranes were equilibrated with NaCl solution (1 M) for 3–4 days, the solution being intermittently replaced. The equilibration time was determined following some preliminary investigations. The membranes were then washed with distilled water to remove excess electrolyte and used for potential measurements. 0.1 M NaCl was taken as reference solution and the concentration of test solution was changed up to 10^{-6} M. All measurements were made at $30 \pm 0.2^\circ\text{C}$. The cell set up for potential measurement is as follows.



3. Results and discussion

The results of water content, porosity, swelling, electrolyte absorption and conductance measurements of mixed and doped oxide membranes are given in tables 1 and 2.

When a dry membrane is immersed in water or electrolyte solution, swelling takes place and the solution penetrates into the membrane structure and occupies the interstices. These interstices are either already present on the membrane matrix or develop on immersion due to different swelling properties of membrane material and binder. The interstices act as a film and the diffusion of different electrolytes also becomes possible by film diffusion besides the normal diffusion through the membrane material. The magnitude of swelling thus depends on the gel structure as well as the amount of binder present in the membrane.

It is apparent from the water content data (table 1) that a lesser amount of water is incorporated into the Cr–Zr mixed oxide membrane in comparison with the Fe–Zr membrane. It is further observed that doped membranes have lower water contents as compared to undoped ones.

Porosity, as calculated from the water content data, is the volume of water incorporated in the cavities per unit membrane volume. The values show that a Fe–Zr mixed oxide membrane has higher porosity than a Sn(II) doped Fe–Zr mixed oxide membrane. Similar behaviour is also observed with the Cr–Zr system. This is further supported by the fact that doped membranes swell to a lesser extent in comparison with the undoped ones.

Both Fe–Zr and Cr–Zr mixed oxide membranes have lower values of porosity and swelling, thereby suggesting that diffusion through these membranes would depend on the exchange sites rather than porosity. Thus in a membrane having low values of porosity, water content and swelling, the number of interstices available are lesser than in one having relatively larger values of these parameters. The membranes under investigation should, therefore, respond selectively to a particular ion. It appears that an inverse relationship exists between the selectivity of a membrane and its swelling properties. The Cr–Zr [Sn(II)-doped] oxide membrane, being the least-swollen, should exhibit higher selectivity as compared to the Fe–Zr mixed oxide membrane.

Electrolyte absorption studies (table 1) reveal that the amount of electrolyte absorbed is lesser in the Cr–Zr as compared to the Fe–Zr system. This behaviour also finds support from water content, porosity and swelling data.

Gregor *et al* (1957) and George and Courant (1967) have measured the membrane conductance by indirect methods. They took the resistance of a membrane as the difference between the resistance of a conductivity cell containing solutions with and without the interposition of a membrane. With dilute solutions and highly conducting membranes the difference in the conductance values becomes negligible and so reliable data is not obtained. The method recommended by Lakshminarayanaiah and Subramanyam (1968) was therefore adopted to ensure reliable and meaningful data. All measurements have been made with membranes previously equilibrated with electrolyte solution so that well-identified counterions were the only conducting species in the membrane matrix.

The conductance of membranes in different anionic forms at different concentrations were measured. A constant value of membrane conductance is observed in all the measurements. These results point to negligible polarization on the mercury membrane interface.

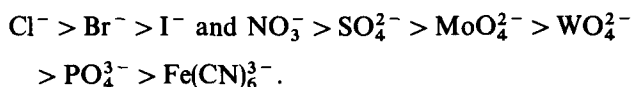
Table 1. Water content, porosity, swelling and electrolyte absorption of Fe-Zr mixed and Sn(II) doped hydrous oxide membranes. Corresponding values for Cr-Zr mixed and Sn(II)-doped hydrous oxide membranes are given in parentheses.

State	Mixed oxide membrane				Mixed and doped oxide membrane			
	Water content	Porosity	Swelling	Electrolyte absorbed/g of wet membrane (mol) × 10 ⁵	Water content	Porosity	Swelling	Electrolyte absorbed/g of wet membrane (mol) × 10 ⁵
Cl ⁻	0.2014 (0.1908)	0.2053 (0.1944)	0.008 (0.008)	48.8 (38.2)	0.1812 (0.1702)	0.1847 (0.1734)	0.008 (0.007)	42.0 (34.2)
Br ⁻	0.2368 (0.2242)	0.2413 (0.2285)	0.010 (0.009)	64.7 (53.7)	0.2173 (0.2040)	0.2215 (0.2079)	0.010 (0.008)	62.3 (51.2)
I ⁻	0.2341 (0.2237)	0.2386 (0.2280)	0.010 (0.010)	61.3 (52.2)	0.2137 (0.2031)	0.2178 (0.2070)	0.010 (0.009)	60.0 (50.7)
NO ₃ ⁻	0.2304 (0.2207)	0.2351 (0.2249)	0.010 (0.010)	65.6 (54.3)	0.2082 (0.2008)	0.2122 (0.2046)	0.010 (0.009)	63.2 (52.7)
SO ₄ ²⁻	0.2028 (0.1922)	0.2067 (0.1959)	0.009 (0.009)	62.4 (52.3)	0.1832 (0.1733)	0.1867 (0.1766)	0.009 (0.008)	60.1 (50.7)
WO ₄ ²⁻	0.2026 (0.1920)	0.2065 (0.1957)	0.009 (0.009)	61.2 (52.1)	0.1817 (0.1731)	0.1852 (0.1764)	0.009 (0.008)	59.8 (49.8)
MoO ₄ ²⁻	0.2022 (0.1912)	0.2061 (0.1949)	0.009 (0.009)	60.8 (50.9)	0.1811 (0.1713)	0.1846 (0.1746)	0.009 (0.008)	58.9 (49.1)
PO ₄ ³⁻	0.1888 (0.1846)	0.1924 (0.1881)	0.008 (0.008)	57.3 (49.2)	0.1682 (0.1652)	0.1714 (0.1683)	0.008 (0.007)	56.4 (47.8)
Fe(CN) ₆ ³⁻	0.1882 (0.1828)	0.1918 (0.1863)	0.008 (0.008)	57.1 (48.1)	0.1678 (0.1618)	0.1710 (0.1649)	0.008 (0.007)	56.1 (46.3)

Table 2. Specific conductance ($\text{mhos cm}^{-1} \times 10^4$) of Fe-Zr mixed and Sn(II)-doped oxide membranes. Corresponding values for Cl-Zr mixed and Sn(II)-doped hydrous oxide membranes are given in parentheses.

State	Mixed oxide membrane			Mixed and doped oxide membrane		
	0.1 M	0.01 M	0.001 M	0.1 M	0.01 M	0.001 M
Cl ⁻	30.41 (12.23)	13.26 (8.25)	5.62 (3.72)	32.68 (14.61)	14.51 (10.21)	7.02 (4.92)
Br ⁻	24.57 (10.79)	10.79 (4.62)	4.32 (2.92)	25.42 (11.81)	11.82 (5.42)	5.62 (3.51)
I ⁻	18.49 (9.40)	9.55 (4.32)	3.54 (2.62)	21.02 (10.01)	10.62 (5.01)	4.24 (3.02)
NO ₃ ⁻	30.05 (0.72)	11.87 (7.86)	5.24 (3.39)	30.95 (18.81)	12.52 (8.72)	6.12 (4.08)
SO ₄ ²⁻	29.28 (16.95)	12.02 (7.86)	5.24 (3.39)	29.62 (17.92)	13.01 (8.72)	6.16 (4.21)
WO ₄ ²⁻	26.20 (12.33)	11.25 (4.78)	5.09 (2.62)	27.04 (13.02)	11.95 (4.54)	5.97 (3.21)
MoO ₄ ²⁻	28.05 (15.41)	12.09 (5.70)	5.24 (3.24)	28.92 (16.37)	12.92 (6.60)	5.99 (4.03)
PO ₄ ³⁻	25.12 (12.17)	10.63 (4.62)	4.32 (2.47)	26.24 (13.12)	11.41 (5.35)	5.01 (2.90)
Fe(CN) ₆ ³⁻	24.35 (11.09)	9.86 (4.62)	4.01 (2.31)	25.32 (11.99)	10.52 (5.20)	4.96 (2.80)

Specific conductivity data (table 2) show the following sequence for the various anions,



Conductance decreases with increasing ionic radii in the case of halide ions while no such correlation, either on the basis of ionic size or hydration, is observed in the case of polyvalent anions. Further it is observed that doped membranes have higher conductance values as compared to the respective undoped membranes.

Membrane conductance increases with increasing external solution concentration. This may be attributed to the fact that Donnan exclusion becomes less effective at higher concentrations thereby leading to a higher value of membrane conductance.

Potentials generated by various membranes in contact with sodium chloride solution of different concentrations (reference solution 0.1 M) have also been observed and the same for chromium-zirconium mixed and doped oxide membranes is shown in figure 1. The extended form of the Debye-Huckel equation

$$\log f = -0.51Z^2\mu^{1/2}/(1 + \mu^{1/2}) \text{ where } \mu = \frac{1}{2}\Sigma CZ^2$$

where C and Z are the concentration and charge on the ion, has been used for activity calculations. The response time is almost a minute and the potentials are quite reproducible, remain stable for almost twenty minutes, and then show a slow drift.

Potential vs. concentration plots are linear in the range 0.1 to 10^{-4} M in the case of mixed oxide membrane (figure 1a), while for doped membrane linearity is observed in the range 0.1 to 5×10^{-5} M (figure 1b). The slope of the plot (doped membrane 29 mV per decade of concentration) is non-Nernstian. The non-Nernstian behaviour of the membrane under investigation is no deterrent to its use as an electrode. Perfect

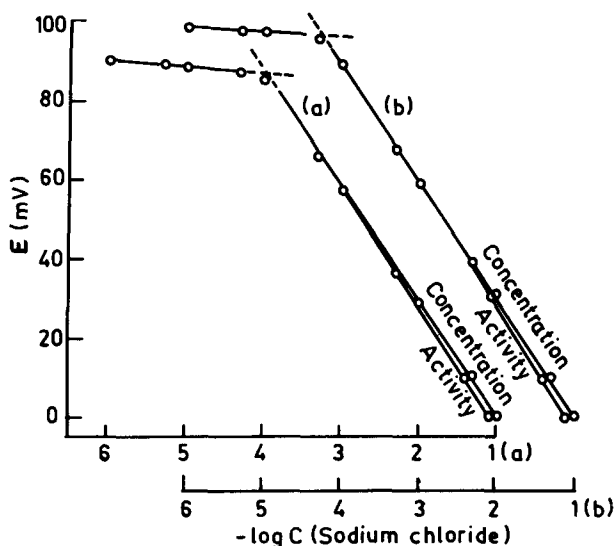


Figure 1. Plots of potential vs. $-\log$ concentration (or activity) of sodium chloride (a) for mixed oxide membrane, (b) for doped oxide membrane.

linearity of potential vs. concentration or activity plots suggests its utility as an ion sensor in the specified concentration range. Low permselectivity and transport of water across the membrane are some of the factors responsible for its non-Nernstian behaviour. It is worth mentioning that most of the commercial electrodes available in the market show non-Nernstian slopes. Potentials stay constant between pH 4 and 8 and beyond this range hydrogen or hydroxyl ions do interfere. Potentials also stay constant at concentrations $<10^{-4}$ or 5×10^{-5} M. The hydroxyl ions present in solution compete with the primary ions at lower concentrations and the membrane probably becomes more sensitive and accessible to them in comparison to chloride ions.

Almost similar plots are observed for iron-zirconium mixed and Sn(II)-doped membranes (plots not shown here). In these membranes the linear relationship is only observed in solutions with concentration in the range 0.1 to 10^{-3} M NaCl. The response time and pH dependence is the same as that observed with chromium-zirconium membranes.

The performance of the membranes has been assessed in the presence of other ions and their selectivity for chloride ion over other anions has been determined by the fixed interference method (Guilbault 1979). In this method the selectivity coefficients ($K_{A,B}^{pot}$) for various interfering ions, are obtained by measuring the potentials in solutions containing a fixed quantity of the interfering ion and with varying activity of the primary ion for which the electrode is selective. The selectivity coefficient $K_{A,B}^{pot}$ has been calculated as equal to $a_A/(a_B)^{Z_A/Z_B}$ where a_A is the value corresponding to the intersection of that part of the calibration curve which corresponds to complete interference of ion B with the Nernstian part corresponding to the electrode function for the primary ion A, a_B is the fixed activity of the interfering ion and Z_A and Z_B are the charges on respective ions. The values are given in table 3.

It is apparent from the selectivity coefficient values that both the membranes exhibit

Table 3. Selectivity coefficient values $K_{Cl^-,B}^{pot}$ for mixed and doped hydrous oxide membranes at 10^{-3} M concentration of interfering ions [B].

Ion [B]	Mixed oxide membranes		Mixed and doped oxide membranes	
	Fe-Zr	Cr-Zr	Fe-Zr	Cr-Zr
Br ⁻	3.75×10^{-2}	1.75×10^{-2}	3.41×10^{-2}	1.34×10^{-2}
I ⁻	3.57×10^{-2}	1.64×10^{-2}	3.27×10^{-2}	1.29×10^{-2}
NO ₃ ⁻	2.14×10^{-2}	1.05×10^{-2}	1.82×10^{-2}	1.01×10^{-2}
ClO ₄ ⁻	1.31×10^{-2}	1.07×10^{-2}	1.01×10^{-2}	1.02×10^{-2}
SCN ⁻	1.43×10^{-2}	1.14×10^{-2}	1.12×10^{-2}	1.08×10^{-2}
CH ₃ COO ⁻	1.21×10^{-2}	1.08×10^{-2}	1.05×10^{-2}	1.02×10^{-2}
S ₂ O ₄ ²⁻	4.10×10^{-3}	1.29×10^{-3}	3.81×10^{-3}	1.12×10^{-3}
C ₂ O ₄ ²⁻	2.84×10^{-3}	6.44×10^{-4}	2.53×10^{-3}	6.23×10^{-4}
SO ₄ ²⁻	3.58×10^{-3}	8.50×10^{-4}	3.21×10^{-3}	8.25×10^{-4}
WO ₄ ²⁻	3.81×10^{-3}	1.13×10^{-3}	3.48×10^{-3}	1.02×10^{-3}
MoO ₄ ²⁻	3.89×10^{-3}	1.16×10^{-3}	3.57×10^{-3}	1.08×10^{-3}
PO ₄ ³⁻	1.25×10^{-3}	9.79×10^{-4}	1.01×10^{-3}	9.42×10^{-4}
AsO ₄ ³⁻	9.32×10^{-4}	4.36×10^{-4}	8.87×10^{-4}	4.12×10^{-4}
Fe(CN) ₆ ³⁻	1.16×10^{-3}	7.65×10^{-4}	9.12×10^{-4}	7.43×10^{-4}
Fe(CN) ₆ ⁴⁻	6.24×10^{-4}	3.36×10^{-4}	5.76×10^{-4}	3.18×10^{-4}

fairly good selectivity in their behaviour towards chloride ions over several other anions and that doped oxide membranes have better selectivity as compared to the one prepared without doping. This may be attributed to the low porosity of doped oxide membranes as compared to undoped one. It is also worth mentioning that Cr–Zr mixed and Sn(II)-doped oxide membranes exhibit a much better selectivity in comparison to Fe–Zr mixed and Sn(II)-doped oxide membranes. This is expected in view of the porosity, swelling, electrolyte absorption and conductance values of Cr–Zr mixed and doped [with Sn(II)] membranes.

4. Conclusion

Hydrous oxides have been used as adsorbents and ion exchangers. Mixed and doped oxides have better selectivity and adsorption potential. The membranes of Fe–Zr and Cr–Zr oxides and those doped with Sn(II) exhibit good selectivity for chloride ions and can be used for their estimation in the presence of other anions.

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