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Electrochemical characterization and assessment of performance of zirconium phosphate and zinc modified zirconium phosphate membranes in aqueous sodium chloride solutions

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ABSTRACT

Prepared membranes, zinc-zirconium phosphate (M-1 and M-2) and zirconium phosphate (M-3) were electrochemically characterized by membrane potential and membrane conductance measurements using aqueous sodium chloride solution of varying compositions. The data have been used for the estimation of transport number of ions and solvent in the membrane phase in addition to permselectivity and membrane fixed charge density. Membrane conductance data were used to estimate the ionic permeability and verify diffusion controlled criteria endowed with the membrane phase. Solute and co-ion permeabilities were compared and found that their values were comparable. Solute rejection of membranes was examined for limiting and intermediate cases of solute–solvent interaction in the membrane phase along with positional solute rejection. Zirconium phosphate membrane showed considerable polarization index deviation from unity indicates its minor perspective than zinc-zirconium phosphate membrane. Results show that zinc modified zirconium phosphate membranes reflected modified elastic properties than zirconium phosphate membrane. The well-known Teorell–Meyer–Sievers (TMS) theory, which describes the membrane potential for charged membranes, was considered as a frame work.

1. Introduction

The first use of the insoluble salt of a hydrous oxide as a high capacity inorganic ion exchanger was reported in 1943, when zirconium phosphate was used to separate uranium and plutonium from fission products. Subsequently, this material and number of other insoluble salts of hydrous oxides such as phosphates, arsenates, tungstates, vandates, antimonates, chromates, oxalates, carbonates primarily of zirconium, thorium and titanium have been described in the literature as ion exchangers [1,2]. Incorporation of the acid salts in the cation exchange membranes, primarily for use in fuel cells, has been reported in open literature, only for zirconium phosphate. There is considerable utility of inorganic ion exchangers based primarily on inorganic materials than organic ion exchange membranes. Because of limited stability, poor resistance to elevated temperatures and aggressive environments [3–8]. A prior consideration suggests that incorporation of zinc in zirconium phosphate may result in improvement in its electrochemical characteristics. Zirconium phosphate has recently been demonstrated as an excellent sorbent for heavy metals due to its high selectivity, high thermal stability and absolute insolubility in water, but it has poor mechanical strength. Therefore, polymer supported zirconium phosphate membranes prepared, studied and recognized its potential applications. These composite membranes show controllable physical properties [9]. Zirconium phosphate has also identified as inorganic proton conductor and decreases the chemical potential of water inside the membrane. It provides H-bonding sites for water and increase in hydration of the membrane and decrease in water transport and evaporation [10,11]. In present study, M-1 and M-2 were identified as zinc modified membranes and M-3 as zirconium phosphate membrane. M-3 membrane showed deterioration in its performance while increasing the electrolyte concentrations. To abate deterioration, limitations and endow long range stability and improved performance of zirconium phosphate membrane was the aim of this study. Electrochemical characterization of the composite systems was carried out on the basis of membrane potential and membrane conductance measurements. The membrane potential

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List of symbols

a, b; a_i, b_i; A, B, C and D	adjustable parameters
A^{**}, B^{**}	adjustable parameters
$A^{*} = (A^{**} + t_i^0)$	
a_S	activity of salt (M)
C_1, C_2	external electrolyte solutions of different concentrations; also denote cation and anion concentration in the membrane phase (M)
C_1^0, C_2^0	cation and anion concentration in the solution phase (M)
C_E	current efficiency of the membrane
$(C1)_F$	total molar of salt in the free volume region in the membrane phase (M)
C_p	concentration of the permeating species in the membrane phase (M)
C_{surface}	solute concentration retained at the membrane surface (M)
C_e	mean electrolyte concentration of external solutions (M)
C_{em}	electrolyte concentration in the membrane phase (M)
C_T	the total equilibrium concentration of cation inside the membrane
$D_\varphi = (\partial\theta/\partial\Delta\mu)$	rate of change of the fraction of coverage on the membrane with respect to difference in chemical potential (mol/J)
D_s^m	solute diffusion coefficient in the membrane phase (m^2/s)
D_1^m	diffusion coefficient of counter-ion in the membrane phase (m^2/s)
D_s	solute diffusion coefficient in the solution phase (m^2/s)
E	adsorption energy (J/mol)
E_m	membrane potential (mV)
$f_\pm^m$	mean activity coefficient of salt in the membrane phase
f_{ssi}	fraction of the intrinsic salt separation
f_{sso}	fraction of observed salt separation
f_{ss}^N	ratio of f_{sso} to f_{ssi}
f_{sso}^{jv}	control coefficient
f_i	solvent effect on the ion conductance ($i = 1, 2$)
f_s	interaction parameter for solute and solvent in the membrane phase
F	Faraday number (C/mol)
g	normalized cation flux
g_1^o and g_2^o	diffusional conductance of cation and anion in the membrane phase respectively (m^2/s)
g_{i3}^o	diffusional conductance of hydrated ith ion in the membrane phase
$\lvert g \rvert$	modulus of membrane conductance elements (S^2/cm^4)
G_m	membrane conductance (S/cm^2)
g_1	cation conductance in the membrane phase (S/cm^2)
h	normalized anion flux
I	ionic strength of the solution
I^*	polarization index
J_s and J_w	solute and solvent flux in the membrane phase ($mol\ cm^{-2}\ s^{-1}$)
Ķ	correction factor
K	partition coefficient
K_d^s and K_d^f	equilibrium constant for ion-pair formation between cation and anion; and cation and membrane fixed charge density respectively (M)
K_d^{sf}	difference between K_d^s and K_d^f (M)
K_A	association constant (M^{-1})
L	membrane thickness (m)
M_E	membrane effectivity
n	ratio of membrane phase anion concentration to mean concentration
P_2^o	co-ion permeability in the membrane phase (cm/s)
p	ratio of membrane phase cation concentration to mean concentration
P_s	membrane permselectivity
K_d^s	membrane permeability in the membrane phase at zero electric current (cm/s)
P_1^m	membrane permeability to counter ion (cm/s)
P_1^{mo}	membrane permeability to counter ion under controlled diffusion (cm/s)
$P_p(y)$	proportion to ion
Q	ratio of effective fixed charge density of membrane to mean concentration
$\bar{q}_w$	membrane surface charge density (C/cm^2)
q	coupling coefficient for solute and solvent in the membrane phase
q_{ik}	coupling coefficient for ith and kth species
Q_W	membrane water content; hydrophilic parameter
R	gas constant ($J\ K^{-1}\ mol^{-1}$)
T	absolute temperature (K)
t_m^W	transport number of water in the membrane phase
t_1 and t_2	transport number of cation and anion in the membrane phase respectively
t_1^0 and t_2^0	transport number of cation and anion in the solution phase respectively
U_+^m and U_+^o	mobility of cation in the membrane phase and bulk phase respectively

Greek symbols

α	Peclet number
δ	diffusion layer thickness (m)
Δ^*	function of (K, D_φ, and φ) (M)
$\in_m$	dielectric constant of membrane/solution system
λ and ζ	membrane constants
μ_s and μ_w	chemical potential of salt and water respectively (J/mol)
V_s	stoichiometric coefficient of salt
ξ	electrokinetic potential (mV)
ρ	relative water coverage
ρ_m	membrane density (g/cm^3)
Γ_w	surface excess concentration (mol/cm^2)
φ	fraction of uncondensed counter-ion
χ	correction factor of the electro kinetic potential