Synthesis, characterization and electrochemical properties of cation selective ion exchange composite membranes

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Particle size; Sol-gel method; SEM; XRD; Electrochemical properties; pH

Abstract In this work polystyrene based strontium phosphate membranes (SPMs) were prepared by applying different pressures. The membrane potential is measured with uni-univalent electrolytes (KCl, NaCl, and LiCl) solutions using saturated calomel electrodes (SCEs). The effective fixed charge density of these membranes is determined by the Torell, Meyer and Sievers method and it showed the dependence of membrane potential on the porosity, the charge on the membrane matrix, charge and size of permeating ions. The membranes are characterized by X-ray diffraction, scanning electron microscopy and IR spectroscopy. The order of surface charge density for electrolytes is KCl > NaCl > LiCl. Other parameters such as transport number, distribution coefficient, charge effectiveness and related parameters are calculated. The membrane was found to be mechanically stable, and can be operated over a wide pH range.

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1. Introduction

Over the past decade, organic–inorganic composite ionic membranes have gained tremendous attention for use in medium temperature fuel cells. The production of composite membrane materials by bridging organic and inorganic chemistry at a molecular level is an extensive and fascinating field of investigation. A major benefit of such hybrid research activities is linked to synergetic effects of organic and inorganic matrix with desired and improved properties in comparison with own unique properties of each component (organic or inorganic). It was found that an increase of NaCl concentration or a presence of divalent cations increased membrane fouling (Hong and Elimelech, 1997). The behavior of membrane systems has widely been investigated by studying the transport properties of artificial membrane (Lakshminarayanaiah and Siddiqui, 1971; Kobatake and Kamo, 1972). The addition of a functional or non-functional inorganic material into the organic material is a usual practice in proton exchange membranes to improve their thermal stability and performance. The inorganic precipitated membranes have acquired particular significance in last two decades e.g. their ability to bear very high temperatures and ionizing radiations without
A precipitated membrane was a system consisting of a thin inorganic precipitate such that when in contact with salt solutions containing precipitated generating ions, two oppositely charged layers at each membrane solutions interface are formed. These layers are due to the absorbed ions on the precipitated membrane which can easily be joined or removed from the membrane. The electrochemical properties of these membranes can dramatically change due to the absorption, deposition or diffusion of ions. A variety of transport phenomena arise across a membrane when subjected to different driving forces (Lakshminarayaniah, 1965; Lakshminaranyaniah, 1969) such as ion migration, electro osmosis, self diffusion, salt migration and membrane potential occurring across the ionic membrane described by Spiegler (1958) applying the principles of thermodynamics non-equilibrium.

In this paper, the preparation of strontium phosphate membranes using an appropriate concentration of polystyrene (25% Jabeen and Rafiuddin, 2007) as a binder prepared by applying different pressures has been described. An effort has been made to examine the validity of the method given by Torell, Meyer, and Siever (TMS) (Torell, 1935; Meyer and Siever, 1936). The charge density of membrane which was an important parameter controlling the membrane phenomenon had been used to determine membrane potential at different electrolyte concentrations using extended TMS theory to test the applicability of these equations for membrane potential for the system under investigation.

2. Experimental

2.1. Synthesis of membranes

The membranes were prepared by the sol–gel method (Jabeen and Rafiuddin, 2007; Beg et al., 1979). Strontium phosphate was prepared by adding an aqueous solution of 0.2 M sodium phosphate gradually into 0.2 M strontium chloride solution with continuous stirring. The pH of mixture was adjusted at 7 by adding 1 M HNO₃ and NH₃ solutions. The mixing ratio of the reactants was 1:1 (v/v). The strontium phosphate gel thus obtained was washed 2–3 times with deionized water to remove free electrolyte and dried at 100 °C. The dried precipitate was ground by pestle mortar and then sieved through 200 mesh (granule size ≤75 μm). Pure polystyrene granules (Otto Kemi, India, Analytical reagent) used as a binder were also ground and sieved (200 mesh). Those membranes containing a large amount of binder (>25%) did not give reproducible results while those containing lesser amounts (<25%) were quite unstable and then the mixture was kept into cast die having diameter 2.45 cm then die was placed into a pressure device (SL-89, UK) and different pressures were applied. For the evaluation of membrane fixed charge density, membrane potential measurements were carried out by constructing a concentration cell.

3. Characterization of membrane

3.1. Water content (% total wet weight)

The physicochemical properties of prepared membranes are summarized in Table 1. The water content of all prepared membranes decreases with applied pressure. The water content (total wet weight) is calculated as,

\[ \text{% Total wet weight} = \frac{W_{\text{Wet}} - W_{\text{Dry}}}{W_{\text{Wet}}} \times 100 \]

where \( W_{\text{Wet}} \) is the weight of soaked/wet membrane and \( W_{\text{Dry}} \) is the weight of dry membrane.

3.2. Scanning electron microscopy (SEM)

The characterization, composite pore structure, micro/macro porosity, homogeneity, cracks and surface morphology of
membranes have been well studied by scanning electron microscope (SEM) micrographs Huang et al., 2000; Izutsu et al., 1997 Fig. 1. In the SEM, different interactions gave images based on topography, elemental composition or density of the sample.

3.3. FTIR studies

The FTIR spectrum of polystyrene (A), composite of strontium phosphate and polystyrene (B), and pure strontium phosphate (C), dried at 40 °C, were taken by the KBr disc method at room temperature (see Fig. 2).

3.4. XRD analysis

The XRD pattern was obtained in an aluminum sample holder for composite using PW, 1148/89-based diffractometer with Cu Kα radiations shown in Fig. 3.

3.5. Measurement of membrane potential

A charged membrane was placed in the center of two collared shaped glass containers. Both containers were filled with electrolyte solutions of different concentrations and membrane potential was determined with the help of SCEs. The Electrochemical cell of type used to measure electrical potentials arising across the membrane by maintaining a tenfold difference in concentration ($C_2/C_1 = 10$) at 25 °C ($±0.1$ °C). The various salt solutions (chloride of Li⁺, Na⁺ and K⁺) were prepared from analytical-grade reagents (BDH) with deionizer water.

<table>
<thead>
<tr>
<th>Pressure applied (MPa)</th>
<th>Thickness of membrane (cm)</th>
<th>Water content as the % weight of wet membrane</th>
<th>Porosity</th>
<th>Swelling of % weight of wet membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.090</td>
<td>0.080</td>
<td>0.0940</td>
<td>No swelling</td>
</tr>
<tr>
<td>60</td>
<td>0.085</td>
<td>0.005</td>
<td>0.0745</td>
<td>No swelling</td>
</tr>
<tr>
<td>70</td>
<td>0.080</td>
<td>0.040</td>
<td>0.0330</td>
<td>No swelling</td>
</tr>
<tr>
<td>80</td>
<td>0.075</td>
<td>0.020</td>
<td>0.0280</td>
<td>No swelling</td>
</tr>
</tbody>
</table>

Figure 1  SEM images of polystyrene-based SPMs (a), (b), (c) and (d) prepared at different applied pressures (50, 60, 70 and 80 MPa) respectively.

Table 1  Characterization parameters of SPMs at different pressures.
3.6. Effect of pH

A series of solutions of varying pH in the range of 2–11 were prepared, keeping concentration of the relevant ion constant \((1 \times 10^{-2} \text{ mol L}^{-1})\). The value of electrode potential at each pH was recorded, and plot of electrode potential versus pH was plotted.

4. Result and discussion

Scanning electron microscopy (SEM) has been studied by a number of investigators for the characterization of membrane morphology (Santos et al., 1997). From SEM images (Fig. 1) composite pore structure, micro/macroporosity, surface texture homogeneity, and crack free membranes have been widely studied (Resina et al., 2007) and SEM surface and cross sectional images (Arfin and Rafiuddin, 2009) of SPMs were taken and given in Fig. 1. SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a membrane and can provide information about the uniform distribution of polystyrene and strontium phosphate in the sample membrane. The SEM images are composed of intense and loose aggregation of small particles and pores with non-linear channels. The FTIR spectra were performed to a certain composition and the possible addition sites of the SPM and pure polystyrene. The spectra contained weak to strong intensity peaks assigned to various functional groups in the material synthesized. The observed peak ranges from 696–874 cm\(^{-1}\), shows presence of the aromatic ring in composite material (Nakamoto, 1986). The peaks 2852 and 2927 cm\(^{-1}\) support the C-H bond frequency due to stirring moiety in the material. The characterization peaks of phosphate groups are present in the spectra exhibiting the presence of a phosphate group in composite material (see Fig. 2). The polymeric nature of the composite has also been supported by other studies (Vide Supra). And the XRD pattern of composite cation exchange material recorded in a powdered sample exhibited some sharp peaks in the spectrum Fig. 3. It was clear from the figure that the nature of composite material is semi-crystalline. And different physicochemical characterization parameters of composite membranes are given in Table 1.

When membranes are immersed in sodium chloride solution they show a negligibly small swelling. And the porosity of membranes was determined by,

\[
e = \frac{W_{\text{Wet}} - W_{\text{Dry}}}{AL \rho}
\]

where \(L\) and \(A\) are the thickness and area of the membrane respectively, \(W_{\text{Dry}}\) is the weight of dried membrane and \(W_{\text{Wet}}\) is the weight of wet membrane, and \(\rho\) the density of water. Like swelling, the membrane also has low porosity. The chemical resistance of membrane was tested in strongly oxidant, acidic and alkaline media. However, in strong acidic media (HNO\(_3\)) the composite membrane became fragile in 36 h and broken after 48 h, losing mechanical strength. In general membranes having the same chemical composition were found to absorb the same amount of water, where the densities of ionisable groups are same throughout the membrane (Koter et al., 1999). As it was already signaled in the introduction, ions are charged so they interact with the solution attracting and repelling each other with coulomb forces. These interactions influence ion behavior and do not allow to treat every ion in solution independently.

When membrane separated two-electrolyte solutions of different concentrations, the mobile species penetrate the membrane and various transport phenomena like diffusion potential, electro osmosis, are induced in the system. The electro neutrality was maintained by increasing the speed of slow moving ion and decreasing that of faster ion. The magnitude and sign of potential depend on characteristics of the membrane and permeating species. If the membrane carries no fixed charges or sites the electric potential across membrane would be same as the liquid junction potential. On the other hand, if membrane carries some charges the magnitude of potential is usually determined by the concentration of electrolyte solution surrounding the membrane and its sign by the nature of the fixed charge.
The charges fixed in the lattice are determined by Teorell, Meyer and Sievers (Teorell, 1935, 1951, 1953a,b) theory. In the TMS method there was an equilibrium process at each solution membrane interface which has a formal analogy with the Donnan equilibrium. According to TMS theory, the membrane potential in 8Ψm mV (applicable to a well idealized system) is given by the Eq. (1) at 25 °C.

\[
8Ψ_m = 59.2 \left( \log \frac{C_2 \sqrt{4C_1^2 + D^2 + D}}{C_1 \sqrt{4C_2^2 + D^2 + D}} + U \log \frac{\sqrt{4C_1^2 + D^2 + UD}}{\sqrt{4C_2^2 + D^2 + UD}} \right)
\]

; \( U = \frac{w}{(v+1)} \), \( u \) and \( v \) are the mobilities of cation and anion (m²/v/s) respectively, in the membrane phase. \( C_1 \) and \( C_2 \) are concentrations of electrolyte solution on either side of the membrane and \( D \) is the fixed charge on membrane expressed in an eq / l. To evaluate this parameter for the simple case of a 1:1 electrolyte and a membrane carrying a net negative charge of unity \((D = 1)\) as well as \((D < 1)\), theoretical concentration potentials across the membrane were calculated as a function of \(-\log C_2\), ratio \(C_2/C_1\) being kept at a constant value of 10 for different mobility ratios \(u/v\) and plotted as in a graph by smooth curves (Fig. 4). The experimental 8Ψm values for SPMs with KCl electrolyte were plotted in the same graph as function of \(-\log C_2\) (Fig. 4). Plots of membrane potential vs. \(-\log C_2\) for SPMs were prepared at different pressures 50, 60, 70 and 80 MPa. Smooth curves are the theoretical concentration potentials for \(D = 1\) at different mobility ratios. Broken lines are the experimental values \(\Delta 8Ψ_m\) for different concentrations of KCl solution. For various electrolyte solutions the observed membrane potential of SPM at 25 ± 1 °C is given in Table 2. The magnitude of the membrane potential is affected by several factors, like the ratio of counter ion to cation, mobility, concentration of salt solution and the exchange characteristics of membrane material for various cations. The values of membrane potential reveal the following order \(Li^+ > Na^+ > K^+\). The higher membrane potential observed with \(Li^+\) was due to the fact that \(Li^+\) was not thermodynamically favored in the membrane phase.

For various membrane electrolyte systems the values of \(D\) are given in Table 3. The surface charge density \((D)\) of SPMs was found to depend also on applied pressure. The increased values of \(D\) with higher applied pressure may be due to an increase of charge per unit volume of the membrane and the order for electrolyte used was KCl > NaCl > LiCl. The membrane potential values are decreased with an increase of external electrolyte concentration. This shows membrane was negatively charged (cation selective) Jabeen and Rafiuddin, 2009; Arfin and Rafiuddin, 2009 and selectivity of the cation increases with dilution. The high degree of cation selectivity exhibited by the membranes makes it potentially useful for monitoring low concentration level of cation in industrial waste water samples. With \((1:1), (1:2), (1:3)\) selectivity character of ion exchange membrane had also been reported earlier (Singh et al., 1985; Singh and Tiwari, 2004) and researcher found similar trends (influence of electrolytes) in the clouding of amphiphilic drugs (Kumar et al., 2006; Sayem Alam et al., 2006).

In addition to Eq. (1), Teorell, Meyer and Sievers further extended their theory and derived another equation by considering total potential, as Donnan potential 8ΨDon, between the membrane surfaces and external solutions, and the diffusion potential 8ΨDiff within the membrane (Matsumoto et al., 1998; Chou and Tanioka, 1999a).

\[
8Ψ_m = 8Ψ_{Don} + 8Ψ_{Diff}
\]
Table 3 Derived values of membrane charge density 
$D \pm 0.1 \times 10^{-3}$ eq/l for various SPM electrolyte systems using TMS equation.

<table>
<thead>
<tr>
<th>Applied pressure (MPa)</th>
<th>Electrolyte</th>
<th>KCl $D \times 10^{-3}$</th>
<th>NaCl $D \times 10^{-3}$</th>
<th>LiCl $D \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.20</td>
<td>1.10</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1.25</td>
<td>1.19</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>1.33</td>
<td>1.25</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>1.39</td>
<td>1.34</td>
<td>1.26</td>
<td></td>
</tr>
</tbody>
</table>

Bold values are pressures applied during preparation of membrane.

where,

$$\Psi_{Don} = -\frac{RT}{V_i T} \ln \left( \frac{\gamma_i C_1 C_{i+}}{\gamma_i C_1 C_{i+}} \right) \quad (3)$$

$R$, $F$ and $T$ have their usual significance, $\gamma_i$ and $\gamma_i^0$ are mean ionic activity coefficient $C_{i+}$ and $C_{i-}$ are cation concentration on the two sides of the charged membrane,

$$C_+ = \sqrt{\left( \frac{V_i D}{2V_i} \right)^2 + \left( \frac{\gamma_i^0 C_i}{q} \right)^2 - \frac{V_i D}{2V_i}}$$  \quad (4)

where $V_i$ and $V_q$ are the valency of cation and fixed charge group on membrane matrix, $q$ is the charge effectiveness of the membrane and defined as,

$$q = \frac{\gamma_i^0}{K_k}$$  \quad (5)

where $K_k$ is the distribution coefficients for different cations determined as

$$K_k = C_i$; \quad C_i = C_j - D$$  \quad (6)

where $C_j$ is the $j$th ion concentration in the membrane phase and $C_i$ is the $i$th ion concentration of external solution. The diffusion potential, $\Psi_{Diff}$ was expressed as

$$\Psi_{Diff} = -\frac{RT_m - 1}{V_i F \sigma^2} + \frac{1}{V_i F \sigma^2} \ln \left( \frac{(\sigma + 1) C_{i+} + (V_i/V_k) D}{(\sigma + 1) C_{i+} + (V_i/V_k) D} \right)$$  \quad (7)

Here $\sigma = \nu/r$ is the mobility ratio of the cation to anion in the membrane phase. The total membrane $\Psi_{m.e}$ potential was, thus, obtained by simple addition of Eqs. (3) and (7).

$$\Psi_{m.e} = -\frac{RT}{V_i T} \ln \left( \frac{\gamma_i^0 C_1 C_{i+}}{\gamma_i^0 C_1 C_{i+}} \right)$$

$$-\frac{RT_m - 1}{V_i F \sigma^2} + \frac{1}{V_i F \sigma^2} \ln \left( \frac{(\sigma + 1) C_{i+} + (V_i/V_k) D}{(\sigma + 1) C_{i+} + (V_i/V_k) D} \right)$$

$$\Delta\psi = \frac{RT}{F} (t_+ + t_-) \ln C_2 \quad (9)$$

$$t_+ = \frac{\nu}{\nu}$$  \quad (10)

For the applicability of these theoretical equations for the system, Donnan potential and Diffusion potential were separately calculated from membrane potential measurement using a distinctive membrane prepared at 70 MPa pressure. Eqs. (9) and (10) were used to get the values of $t_+$ and $t_-$ from experimental membrane potential data and consequently, mobility ratio $\sigma = \nu/r$ within the membrane phase. At lower concentration of all electrolytes (KCl, NaCl, LiCl) $\sigma$ values in the membrane phase were found to be high. A further increase in concentration of electrolytes led to a sharp drop in the values of $\sigma$ as given in Fig. 5.

The higher mobilities were endorsed to the higher transport number of relatively free cation of electrolytes. The values of $t_+$ calculated from observing membrane potential are given in Table 4. Here, $t_+$ was not a true transport number since water permeation has not been taken into account, however, in dilute solutions values of $t_+$ approach closer to the true values. Fig. 6 shows that transport number decreases with an
increase in concentration of the salt solution. As the concentration of the electrolytes increased, values of distribution coefficients decreased, thereafter, a suitable drift was observed as shown in Fig. 7.

For different electrolyte concentrations Donnan potential was then calculated from the parameters, \( C_{2+}, m, q \), and \( K_+ \) by using Eqs. (3)–(7) and the values of parameters derived for the systems have been given in Table 4. The values of the charge effectiveness \( q \) estimated by fitting the experimental results to theoretical ones are shown in Table 4. Most of the \( q \) values do not equal unity. This means that we must consider not only the membrane inhomogeneity, but also electrostatic interaction between the fixed charge group and counter ion to explain the difference in effective charge density from experimentally obtained values of membrane potentials for the system have also been drawn in the same figure. Some deviations were observed which were prominent and simultaneously present in the membrane (Chou and Tanioka, 1999).

The pH response profile for membrane was tested by using \( (1 \times 10^{-2} \text{ mol L}^{-1}) \) electrolyte solution over the pH range 2.0–11.0. The pH was adjusted by introducing small drops of hydrochloric acid (0.1 M) or sodium hydroxide (0.1 M) into solutions. The influence of the pH response of the composite membrane is shown in Fig. 8. As it is seen, the potential remained constant from pH 2.0 to 7.0 beyond which some drifts in potentials were observed Fig. 8. The observed drift at higher pH values could be due to the formation of some Hydroxyl complexes of cations (K\(^+\), Cl\(^-\), Li\(^+\)) in the solution. The potentials increased, at the lower pH values indicating that membrane responded to protonium ions, as a result of some extent protonation of phosphorus atoms of the phosphate group. On the other hand, at lower pH values \( \text{H}_3\text{O}^+ \) ions start to contribute to the charge transport processes by the membrane, thereby causing interference.

**5. Conclusions**

The membrane potentials of SP composite membranes were measured with univalent electrolyte solutions using platinum electrodes. The polystyrene because its cross linked rigid framework provides an adequate adhesion to the strontium phosphate membranes, which accounts for the mechanical stability to the membrane. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various sizes and membrane material is crystalline in nature. Thus, in general the specific potential of ions across the membrane varies almost linearly with concentration in the lower concentration range (TMS). The values of specific membrane potential of the electrolytes follow the sequence for the cations, \( K^+ < Na^+ < Li^+ \). Membranes prepared at high pressure (80 MPa) carried higher charge density and have narrow surface openings and low porosity. And all the SP composite membranes work well in the pH range 2.0–7.0. The theoretical predictions of membrane potential are borne out quite satisfactorily by experimental results for all membranes.
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