



Preparation, characterization, biological activity, and transport study of polystyrene based calcium–barium phosphate composite membrane

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ARTICLE INFO

Article history:

Received 9 June 2012

Received in revised form 19 May 2013

Accepted 15 June 2013

Available online 21 June 2013

Keywords:

Composite membrane

Membrane potential

Transport number

Mobility ratio

Fixed charge density

ABSTRACT

Calcium–barium phosphate (CBP) composite membrane with 25% polystyrene was prepared by co-precipitation method. Scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transformed infrared (FTIR), and Thermogravimetric analysis (TGA) were used to characterize the membrane. The membrane was found to be crystalline in nature with consistent arrangement of particles and no indication of visible cracks. The electrical potentials measured across the composite membrane in contact with univalent electrolytes (KCl, NaCl and LiCl), have been found to increase with decrease in concentrations. Thus the membrane was found to be cation-selective. Transport properties of developed membranes may be utilized for the efficient desalination of saline water and more importantly demineralization process. The antibacterial study of this composite membrane shows good results for killing the disease causing bacteria along with waste water treatment.

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1. Introduction

The technological development of inorganic precipitated membrane is projecting new dimensions to replace biological cell membranes. The combined efforts of chemists, biologists, physicists and chemical engineers have achieved considerable success not only in the particular area of artificial kidney, liver, skin, and desalination of sea water economically but also in the areas of employing various membrane processes for hemodialysis, hemofiltration, and gas separation [1].

Purification of water is more effective, lower cost and robust method, to improve the disinfection and decontamination of water, as well as efforts to increase water supplies through the safe re-use of wastewater and efficient desalination of sea and brackish water [2].

The proton exchange membranes require water to maintain their proton conductivity. However, this technique enhances the mass and complexity of the fuel cell system, and makes unsuitable for portable applications. Recently, the researchers have developed self-humidifying membranes mainly focusing on the several directions viz. Incorporating Pt or Pt/C catalysts in the membrane to combine the permeable oxygen and hydrogen to produce water and humidify the membrane and incorporating hygroscopic metal oxides, such as SiO₂, or TiO₂ to adsorb water and accordingly improve the proton conductivity [3].

The synthesis of novel organic–inorganic composite membrane has received a great deal of attention because it provided new material with good mechanical, chemical, electrochemical and optical as well as magnetic properties and find large scale application in antibiotic purification, separation of radioactive isotopes, water treatment and pollution control [4].

The polystyrene based calcium–barium (CBP) phosphate composite membrane can be considered as a novel composite material that show extremely different properties from their original components (polystyrene and inorganic materials), mainly in the case of molecular stage composites. Thus, organic–inorganic composites are likely to offer many possibilities as new composite materials [5].

Moreover, in this work, the composite membrane synthesized is expected to give remarkably better results than those reported. These findings of superior application of the novel composite can be observed based on the characterization and other experimental parameters, which are excellent and fruitful than the other composite membranes known to our knowledge [6].

Hence, the polystyrene based CBP composite membrane prepared here can be used in separation of heavy toxic metal ions, separation of foods, desalination of saline water, more importantly demineralization process and other industrial applications giving excellent results.

Various thermodynamics parameters namely distribution coefficient, transport numbers, mobility ratio, charge effectiveness, etc. of the membrane–electrolyte system have been determined at different pressures in order to understand the mechanism of ion transport through the membrane. The surface charge density (\bar{D}) is the most effective parameter that controls the membrane phenomena. The TMS method has been utilized for charge density calculations [7–10].

$$\Delta\bar{V}_m = 59.2 \left(\log \frac{C_2 \sqrt{4C_1^2 + \bar{D}^2} + \bar{D}}{C_1 \sqrt{4C_2^2 + \bar{D}^2} + \bar{D}} + \bar{U} \log \frac{\sqrt{4C_2^2 + \bar{D}^2} + \bar{D}\bar{U}}{\sqrt{4C_1^2 + \bar{D}^2} + \bar{D}\bar{U}} \right) \quad (1)$$

$$\bar{U} = (\bar{u} - \bar{v}) / (\bar{u} + \bar{v})$$

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Nomenclature

AR	Analytical reagent
C_1, C_2	Concentrations of electrolyte solution on either side of the membrane (mol/l)
\bar{C}_{1+}	Cation concentration in membrane phase 1 (mol/l)
\bar{C}_{2+}	Cation concentration in membrane phase 2 (mol/l)
C_i	i th ion concentration of external solution (mol/l)
\bar{C}_i	i th ion concentration in membrane phase (mol/l)
\bar{D}	Charge density in membrane (eq/l)
F	Faraday constant (C/mol)
100–160	Pressure (MPa)
q	Charge effectiveness of the membrane
R	Gas constant (J/K/mol)
SCE	Saturated calomel electrode
SEM	Scanning electron microscopy
TMS	Teorell, Meyer and Sievers
t+	Transport number of cation
t–	Transport number of anion
\bar{u}	Mobility of cations in the membrane phase ($\text{m}^2 \text{v}^{-1} \text{s}^{-1}$)
\bar{v}	Mobility of anions in the membrane phase ($\text{m}^2 \text{v}^{-1} \text{s}^{-1}$)
V_k	Valency of cation
V_x	Valency of fixed-charge group
\bar{U}	$\bar{U} = (\bar{u} - \bar{v}) / (\bar{u} + \bar{v})$
CBP	Calcium–barium phosphate
TGA	Thermogravimetric analysis
XRD	X-ray diffraction

Greek symbols

γ_{\pm}	Mean ionic activity coefficients
$\bar{\omega}$	Mobility ratio
$\Delta\psi_m$	Observed membrane potential (mV)
$\Delta\bar{\Psi}_m$	Theoretical membrane potential (mV)
$\Delta\psi_{Don}$	Donnan potential (mV)
$\Delta\bar{\Psi}_{diff}$	Diffusion potential (mV)

where \bar{u} and \bar{v} are the ionic mobility's of cation and anion ($\text{m}^2 \text{v}^{-1} \text{s}^{-1}$), respectively, in the membrane phase, C_1 and C_2 are the concentrations of the membrane and \bar{D} is the charge on the membrane expressed in equivalent per liter. The assembly used in the investigation provides data for various membrane parameters, with reasonable accuracy.

2. Experimental

2.1. Preparation of composite material

CBP composite was prepared by mixing 0.2 M calcium (II) chloride (99.98% purity, E. Merck, Mumbai, India) and 0.2 M barium (II) chloride (99.98% purity, E. Merck, Mumbai, India) with 0.2 M tri-sodium phosphate (99.90% purity, E. Merck, Mumbai, India) in a 100 ml solution. The precipitate was washed well with deionized water (water purification system, 'Integrate, whose RO conductivity 0–200 $\mu\text{s}/\text{cm}$ and UP resistivity 1–18.3 M $\Omega\text{-cm}$ ') to remove free reactant and then dried and powdered. The precipitate was ground into fine powder and was sieved through 200 mesh BSS standard. Pure crystalline polystyrene (Otto Kemi, India, AR) was also ground and sieved through 200 mesh [6].

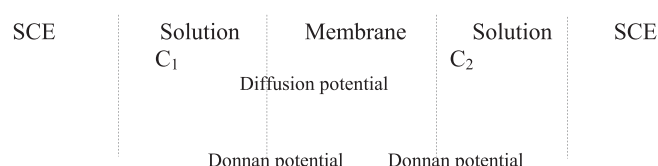
2.2. Preparation of composite membrane

The total amount of the mixture utilized for the preparation of the membrane contained 0.125 g polystyrene and 0.375 g composite material (CBP) was mixed thoroughly using mortar and pestle. The mixture was then kept into a cast die having a diameter of 2.45 cm and placed in an oven (Oven-Universal, Memmert Type) maintained at 200 °C for about an hour to equilibrate the reaction mixture. The membranes prepared by embedding 25% polystyrene were found to be mechanically most stable and give reproducible results. Those containing a larger amount (>25%) of polystyrene did not give reproducible results, while those containing a smaller amount (<25%) were found unstable [6,11–13].

The die containing the mixture was then transferred to a pressure device (SL-89, UK), and various pressures such as 100, 120, 140 and 160 MPa were applied during the fabrication of the membranes. Our effort has been to prepare the membrane of adequate chemical and mechanical stability. The membranes were subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface and only those which had smooth surface and generate reproducible potentials were considered.

2.3. Measurement of membrane potential

Membrane potential was measured by using a digital potentiometer (Electronics India model 118). The freshly prepared charged membrane was installed at the center of the measuring cell, which had two glass containers, on either side of the membrane. The various salt solutions (chlorides of K^+ , Na^+ , and Li^+) were prepared from B.D.H. (A.R.) grade chemicals using deionized water. Both collared glass containers had cavity for introducing the electrolyte solution and saturated calomel electrodes. The half-cell contained 25 ml of the electrolyte solution while the capacity of each of the half cells holding the membrane was about 35 ml. The electrochemical setup used for uni-ionic potential and membrane potential measurements may be depicted as:



2.4. Characterization of membrane

The pre-requisite criterion for understanding the performance of an ion-exchange membrane is its complete physico-chemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters include membrane water content, porosity, thickness, swelling, etc. These were determined in accordance with the method described by [14,15].

2.4.1. Water content (% total wet weight)

The conditional membrane was first soaked in water, blotted quickly with Whatmann filter paper to remove surface moisture and immediately weighed. These were further dried to a constant weight in a vacuum over P_2O_5 (dehydrating agent) for 24 h. The water content (total wet weight) was calculated as:

$$\% \text{Total (weight}_{\text{wet}}) = \frac{W_w - W_d}{W_w} \times 100$$

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