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Preparation, characterization and study of nanofiltration composite membrane: Electrochemical and optical properties

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ABSTRACT

The polystyrene based molybdate composite membranes were prepared by the sol–gel method by applying different pressures. XRD data shows that formation of nanocomposite and exhibit no other impurity phase. The membrane potential is found to be effected by both pressure and ion concentration. The effective charge density of these membranes was determined by TMS method and reveal dependence of membrane potential on physicochemical properties. The change in membrane capacitance and resistance values with the change in electrolyte concentration and applied frequency had been interpreted in terms of the charges produced in the electrical double layer at the membrane solution interface.

Introduction

The membrane filtration process had the two interesting features: a fractionation capacity for different organic components in aqueous solutions and potential of realizing the Donnan effect with respect to the anions of different valency. Many separation problems solved economically by membrane filtration alone or in combination with other separation processes. An alternative approached is to dope membranes with inorganic dopant [1–3]. This approached improved the mechanical properties and ion conductivity, and reduces the dependence of later on ambient humidity [4–6]. This primarily effect, the alteration of the walls of transport pores and channels by specific interactions at the organic–inorganic interface [7].

The selectivity of an ion exchange material depends considerably on the specific interaction of the counter ions with the exchanger. This interaction varies with the chemical composition of the exchanger that can be altered with greater ease and facility in inorganic materials than in the organic ones. Of the various inorganic ion exchangers studied earlier, the cobalt is probably the least well investigated. Cobalt molybdate ($CoMoO_4$) belongs to an interesting group of compounds because of its structure, electronic and catalytic properties [8–10]. At atmospheric pressure, two phases [11], usually designated α and β are known for $CoMoO_4$. The phase transition of the low temperature phase α-$CoMoO_4$ to high temperature β-$CoMoO_4$ has been studied using many physical methods [12]. $CoMoO_4$ is an important component of industrial catalysts used for many organic reaction processes [13,14]. However, a detailed and systematic study on the ion exchange properties of cobalt (III) molybdate is lacking. Bishop and co-workers [15,16] synthesized it only when they investigated the mixed oxides of groups III, IV and V as selective ion exchangers for incorporation into electrodialysis membranes. Therefore, organic–inorganic composite materials as new membrane materials have attracted more and more attentions [17,18]. They expanded considerable applications in optoelectronic [19], ion-conduction [20], biology [21], catalysis [22] and membranes [23]. Several organic–inorganic composite membranes have been prepared by casting either a bulk mixture of powder or colloidal state of inorganic material with polymer solutions [24]. Therefore membranes have been applied widely in industrial fields such as the food and pharmaceutical [25], textile reuse [26] and regeneration of pulp and paper waste water [27]. Some characteristics such as porosity, ionic conductivity, mechanical properties and chemical stability are important issues in membrane separators [28–30,27]. It is also of interest to study the properties of such membranes with polystyrene [31]; and successfully used it to manufacture inorganic composites with increased ion conductivity [32]. We have therefore synthesized and characterized cobalt (III) molybdate and studied its ion exchange properties, sorption behavior and electrochemical results.

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Nomenclature

C_1,C_2	concentration of electrolyte solution either side of the membrane (mol/l)
C_{1+}	cation concentration in membrane phase 1 (mol/l)
C_{2+}	cation concentration in membrane phase 2 (mol/l)
D	charge density in membrane (eq/l)
F	Faraday constant (C/mol)
K	distribution coefficient of ions
$K_{2\pm}$	distribution coefficient of ions (electrolyte solution C_2)
P	pressure (50–80 MPa)
q_1	charge effectiveness of membrane phase 1
q_2	charge effectiveness of membrane phase 2
R	gas constant (J/K/mol)
SCE	saturated calomel electrode
SEM	scanning electron microscopy
TMS	Teorell, Meyer and Sievers
XRD	powder X-ray diffraction
FTIR	Fourier transform infrared
CMM	cobalt molybdate
CMP	cobalt molybdate polystyrene
t_+	transport number of cation
t_-	transport number of anion
u	mobility of cations in the membrane phase (m^2/V/s)
U	$((u-v)/(u+v))$
v	mobility of anions in the membrane phase
V_k	valency of cation
V_x	valency of fixed charge group

Greek symbols

$\gamma'_{\pm}$, $\gamma''_{\pm}$	mean ionic activity coefficient for electrolytes solution C_1 and C_2
ϖ	mobility ratio (TMS extension theory)
$\delta\psi_m$	membrane potential (mV)
$\delta\Psi_{m,e}$	membrane potential (mV) (TMS extension theory)
Ψ_{Don}	Donnan potential (mV)
$\delta\Psi_{Diff}$	diffusion potential (mV)

Experimental

Materials and membrane's preparation

Pure polystyrene (Otto Kemi, India) used as a binder was grounded and sieved through 200 meshes, 0.2 M trisodium molybdate solution (E. Merch. India with purity of 99.90%), 0.2 M Cobalt chloride ($CoCl_3$) solution (Otto Kemi, India, Analytical reagent) and different electrolytes solution (KCl, NaCl and LiCl) of different concentrations was also prepared.

Preparation of cobalt molybdate

Cobalt molybdate is prepared by a sol–gel process by taking 0.2 M aqueous solution of trisodium molybdate and slowly added 0.2 M cobalt chloride solution made by constant stirring at 90 °C at pH 7. The precipitate was washed with deionize water and dried for 2 h at 100 °C.

Synthesis of cobalt molybdate—Polystyrene composite membranes

The composite membranes were prepared by methods suggested by Rafiuddin and coworkers [33–35] and then transferred to a pressure device (SL-89, UK) where different pressures like 50, 60, 70 and 80 MPa were applied.

Structural characterization

The FT-IR spectra of the samples were recorded in 400-4000 cm^{-1} range at room temperature. The Scanning electron microscopy (SEM) was used to study the surface morphology, microstructures, distribution of particles and pore size of the dried membranes. X-ray Diffraction patterns and different parameters were collected with a Rigaku D/max2400 powder diffractometer using a Cu $K\alpha$ radiation. And the particle size was analyzed by using laser diffraction, for that sample had been mixed in water using ultrasonic waves. The suspended particles were measured by laser.

Water uptake and swelling

The water uptake of the composite membranes was determined by measuring the change in weight after hydration. The percentage of water uptake was calculated as,

$$\text{water uptake}(\%) = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) \times 100$$

weight of wet membrane (W_{wet}); weight of the dry membrane (W_{dry})

And the swelling ratio was calculated by the following equation:

$$\text{swelling}(\%) = \left(\frac{A_{wet} - A_{dry}}{A_{dry}}\right) \times 100$$

where A_{dry} and A_{wet} are the area of dry and wet samples, respectively.

Optical properties

To describe the photo absorption behavior of CM and composite material, a certain amount of the sample was uniformly dispersed in ethanol and UV–visible absorption spectra were recorded.

Determination of membrane potential

Membranes in their various cationic forms were obtained by dipping them in a 2 M solution of the particular electrolyte for 48 h to ensure complete exchange. After drying for 24 h these were placed among two collared glass tubes each having a hole for introducing the electrolyte solutions and stirred by magnetic stirrer. The membrane potentials were determined with the help of reference electrodes (SCE). All measurements were made at 25 °C.

Result and discussion

Characterizations

The results that derived from SEM about the membrane are external morphology (texture), chemical composition, well ordered precipitates, composite pore structure, micro/macro porosity, homogeneity, thickness and cracks free membranes [36,37] and orientation of materials making up the membrane. Areas of SEM images ranging from 1 cm to 5 μm in width (magnification ranging from 1000× to about 3500×, spatial resolution of 50 to 100 nm). The SEM micrograms are shown in Fig. 1(A–C).