

Development and comparative study of different nanofiltration membranes for recovery of highly charged large ions

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Abstract

The development of membranes for polyoxometalate (POM) recycling based on charge or size effects is described. POM recycling via nanofiltration with surface charge membranes is a new approach. From the properties of solute–membrane interaction three different kinds of nanofiltration membranes have been selected to find out most suitable one for recycling process. A new generation surfactant templated inorganic silica film has been prepared and characterised. This type of material could be promising for future NF membrane applications.

Keywords: Nanofiltration; Inorganic membrane; Gamma alumina membrane; Nafion; Hybrid membrane; Polyoxometalate

1. Introduction

Nanofiltration (NF) membranes can be used to separate solvents from multivalent ions and small organic molecules. The separation of these membranes is thought to be controlled by a combination of size and charge effects. NF membranes can be divided into two groups i.e., porous membranes and dense membranes with a swollen

network. The first category comprises mainly inorganic membranes while the second category consists mainly of polymeric materials. Both types can be either charged or uncharged, although no uncharged porous inorganic membranes with NF properties are known.

Sandwich-type ceramic composite membranes with NF characteristics became available. These membranes are reported to have pore sizes in the range of 0.5–2 nm [1]. These show high retentions for organics with a molecular weight

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larger than 500 D, high retentions for bivalent ions and moderate retention for monovalent ions. The surface charge of the pores depends upon pH and can be either positive or negative, depending upon the pH relative to the iso-electric point (IEP) of the oxide surface. Under moderate process conditions the pore size and structure of ceramic membranes are fixed. On the other hand, polymeric membranes tend to swell, the level of which depends upon electrolyte strength and the nature of the solvent. As a variation on swollen network membranes, a large number of organo-mineral membrane systems are also available for filtration processes [2]. These membranes can be efficiently used for large ion recovery. Promising membrane materials for separation of highly charged large molecules are Nafion, Nafion/silica hybrid membranes, supported γ -alumina membranes and mesostructured silica layers supported on porous α -alumina. The target of the work presented here is to explore the transport and retention properties of potentially suitable membranes for recovery of highly charged large (~2–3 nm) POM catalyst molecules [3] from aqueous solutions.

We studied the NF characteristics of three different kinds of membranes, namely mesoporous γ -alumina, Nafion and Nafion/silica hybrid membranes. Home-made γ -alumina membranes have an IEP of ~8–9. Nafion 117 is a commercially available perfluorosulfonic membrane. It consists of a polytetrafluoroethylene backbone and regularly spaced long perfluorovinyl ether pendent side chains terminated by a sulfonate ionic group. These membranes show excellent ion conductivity and ion selectivity [4], which can be utilized in NF experiments. Nafion has an IEP of ~6 [5]. The surface charge characteristics of Nafion can be modified through *in situ* hydrolysis of inorganic alkoxide precursors, e.g. tetraethylorthosilicate (TEOS). This will yield Nafion membranes with surface charge properties resembling those of an oxide. These three types of membranes are assumed to be

representative examples of organic, inorganic and organic-inorganic hybrid NF membranes. Preliminary results on the preparation and characterization of mesostructured silica, a promising new type of NF membrane with regular pore structure, are also reported. The latter type of membrane requires the use of advanced sol-gel methods.

2. Experimental

2.1. Preparation of supported mesoporous γ -alumina

The α -alumina supports were made by colloidal filtration of well-dispersed 0.4 μm α -alumina particles (AKP-30, Sumitomo Chemical Company Ltd, Tokyo, Japan). The dispersion was stabilized by peptising with nitric acid. After drying at room temperature, the filter compact was sintered at 1100°C. Flat disks of \varnothing 39 mm and 2 mm thickness were obtained after machining and polishing. The final porosity of these supports is ~30%. Mesoporous γ -alumina membranes of ~1 mm thickness and with pore sizes of 2.5 nm were prepared by dip coating the above-mentioned porous α -alumina supports in a boehmite sol, followed by drying and calcining at 600°C. The pore size of the layer was controlled by the calcination temperature. For more details the reader is referred to Benes et al. [6].

2.2. Nafion and Nafion/silica hybrid membranes

Nafion 117 membranes (thickness 0.183 mm) were directly purchased from DuPont. As it is well known that the retention behaviour of Nafion depends on the pre-treatment, Nafion membranes were immersed in a 1:1 ethanol/water solution for 2 h prior to mounting it in the NF cell.

For the preparation of Nafion/silica hybrid membranes, the membrane matrix used in this work is also Nafion 117. To ensure protonation

of the sulfonate groups the membrane was immersed in 1.0 N HCl for 24 h at room temperature. The membranes were then removed from the solution, surface-blotted and soaked in stirred deionised water for 24 h at 40°C to leach out any excess HCl. During this period the deionised water bath was refreshed every 8 h to ensure full free acid extraction. The membranes were subsequently dried in air for 5 h and in vacuum for 24 h. The membranes were then pre-swollen in a 2:1 (vol/vol) methanol/water solution for 5 h at 22°C. The pre-swollen membranes were then dipped into a tetra-ethyl-orthosilicate TEOS (Merck) solution. The water/TEOS ratio was kept constant at 4:1 (mol/mol). The *in situ* hydrolysis of TEOS was promoted by the presence of membrane-bound acidic sites. The membranes were removed from the solution after 10 min and surface blotted and dried in a vacuum oven at 45°C for 5 h [7].

2.3. Preparation of thin mesoporous silica film on dense glass support

The thin film of surfactant templated mesoporous silica was synthesized using cationic surfactant cetyl-trimethyl-ammoniumbromide (CTAB) (Aldrich) and TEOS derived sols. The required amount of TEOS was mixed with 1-propanol and stirred for 5 min. The TEOS was then hydrolysed by addition of a solution of HCl in water. The solution was stirred for 1 h; 2-butanol was added to the hydrolysed sol and stirring continued for another 30 min. The surfactant solution was prepared separately and slowly added to the sol under stirring conditions.

The typical sol formulation was (8):

- TEOS: 1 propanol: 2 butanol: H₂O: HCl(N) = 8 mL: 17.47 mL: 8.75 mL: 6.63 mL: 0.33 mL
- TEOS: CTAB = 7.62:1

Spin coating was used to deposit thin silica films on glass substrates.

After spin coating, the coated glass substrate

was dried at room temperature and heated to 400°C in air with heating and cooling rates of 0.5°C/min to remove any residual surfactant and solvent molecules.

2.4. Characterization of the membranes and films

The γ -alumina membrane was characterized by permoporometry [6]. The Nafion/silica hybrid membranes were characterized by scanning electron microscopy (JEOL-SEM). The mesoporous silica film structure was characterized by small angle X-ray diffraction (SAXD) using CuK α radiation ($\lambda = 1.542 \text{ \AA}$) (Phillips SR5056) and the silica film thickness was determined with a Philips CM30 transmission electron microscope (TEM).

2.5. Nanofiltration experiments

The steady-state water flux was measured for γ -alumina, pure Nafion and Nafion/silica hybrid membranes. NF measurements were performed with the water-soluble polyoxometalate catalyst H₃[PMo₁₂O₄₀] \cdot 3H₂O (kindly provided by Prof. R. Neumann, Weizmann Institute of Science, Israel) at a concentration of 1 wt% in water. Retention studies were carried out in a dead-end NF cell. The volume of the cell is 700 ml and the operating pressure range was kept in the range of 2–10 bar. The retention of a given membrane is characterised by the retention coefficient which is defined by $R_{\text{obs}} = 1 - C_p/C_b$, with C_p the solute concentration in the permeate and C_b the solute concentration in the bulk. The concentration of the catalyst was measured using an ionic conductivity bridge for both the permeate and retentate.

3. Results and discussion

3.1. Nafion/silica hybrid membranes

Figs. 1 and 2 show SEM images of as-formed and mechanical pressure-treated samples,

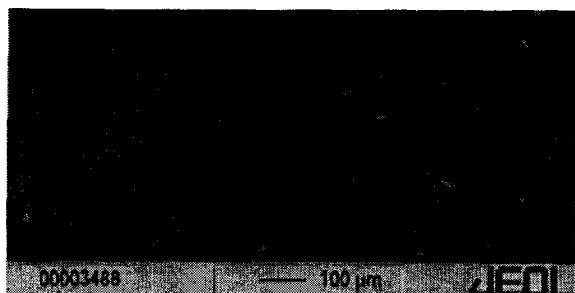


Fig. 1. SEM image of an as formed Nafion/silica hybrid membrane.

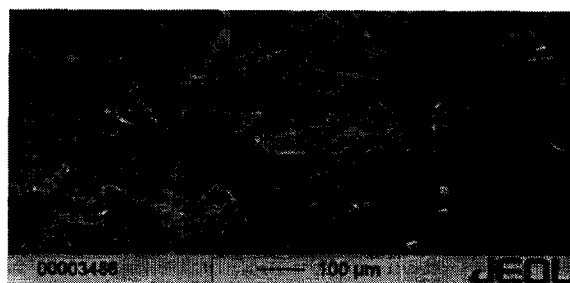


Fig. 2. SEM image of Nafion/silica hybrid membrane after mechanical pressure.

respectively. It is clear that a visually homogeneous silica layer has been formed on top of the Nafion surface that undergoes brittle fracture upon application of mechanical pressure. The presence of the silica layer formed on the Nafion surface may indicate an extra resistance for the diffusion of TEOS into the Nafion matrix. Ideally, this layer is removed if the membrane is to be used for separation. As reported elsewhere [7], the weight difference of the membranes before and after treatment with TEOS is not always a good measure of the silica uptake inside the Nafion matrix. Elemental analysis in combination with depth profiling is a better way to answer the question to what extent TEOS diffuses into the membrane.

3.2 Nanofiltration experiments

The water flux through γ -alumina, the unmodified Nafion membrane and Nafion/silica hybrid membranes were measured under the same process conditions and are compared in Fig. 4. It was found that the steady-state water flux through unmodified Nafion is quite poor in the low-pressure range, but with increasing pressure the water flux increases more strongly than that of its γ -alumina counterpart. The initial water flux through the Nafion/silica hybrid membrane is rather low in the lower pressure

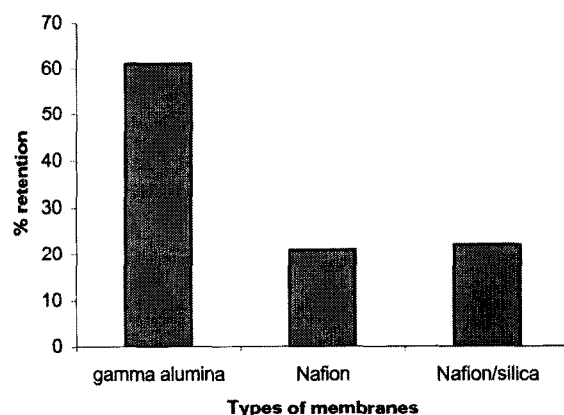


Fig. 3. Comparison of POM retention in water solution using different membranes.

range, but it reaches that of Nafion at ~ 10 bar. It appears that the Nafion/silica hybrid membrane has a higher water flux than pure Nafion in the low-pressure region. This can possibly be explained by an increased hydrophilicity of the Nafion matrix due to the presence of silica clusters [9].

The polyoxometalate catalyst solution (1% wt in water) has a pH of 1.9. At this pH γ -alumina and Nafion membranes are positively charged whereas the Nafion/silica hybrid membrane is supposed to have a surface charge close to zero. Under these conditions effective retention can only be achieved by size exclusion effects, as the

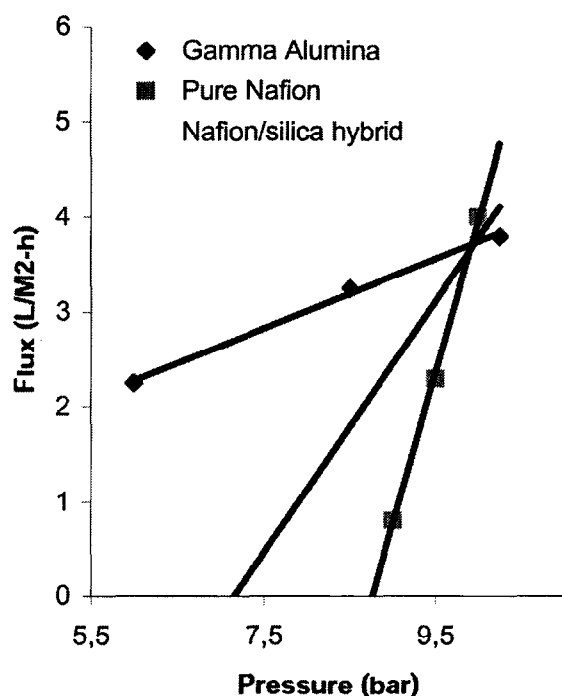


Fig. 4. Comparison of water flux through membranes.

effective charge of the POM anions is highly negative.

We found that at a pressure of 9 bar and a stirred speed of 100 rpm γ -alumina is more effective for the retention of water-soluble POMs than Nafion-derived membrane systems are. The retention behaviour of these membranes is shown in Fig. 3. The level of retention of the Nafion derivative is almost same as for pure Nafion. The probable explanation for this could be that the silica clusters make the Nafion matrix denser for the permeating molecules, though the extent of this effect is not much visible.

3.3. Mesoporous silica film

Fig. 5 shows a TEM image of a cross section of the spin-coated silica film after calcination. The film is ~ 100 nm thick. We found it formed a dense, crack-free and homogeneous film on the



Fig. 5. TEM image of thin silica film cross section on dense glass support.

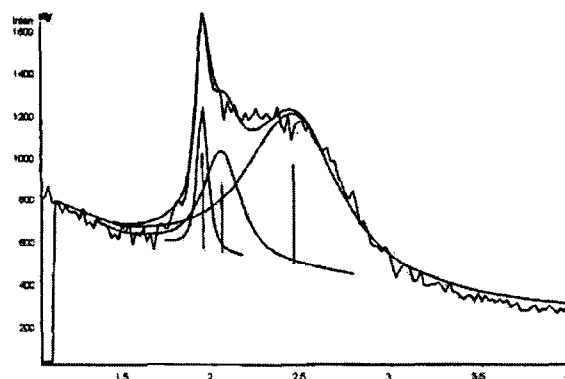


Fig. 6. SAXD spectrum of mesoporous silica layer.

Table 1
Indexation of XRD peaks of the MCM-48 like phase

$2\theta, ^\circ$	hkl	$d, \text{\AA}$
1.96	111	45.176
2.26	200	39.01
2.62	210	33.642

glass substrate. Fig. 6 shows a small angle X-ray diffraction pattern of the calcined film. There is a sharp peak at around 2θ 1.94° . The X-ray pattern is similar to the pattern of an ordered mesoporous MCM-48-like phase with cubic symmetry [10]. Table 1 lists the observed diffraction angles and the corresponding Miller indices under the assumption of cubic symmetry.

This implies a cell constant of about 75–78 Å. For these types of materials monodisperse pore sizes of about 3.7–3.8 nm have been reported [10] The cubic MCM-48 structure is supposed to have a low tortuosity and be (almost) devoid of dead end porosity. Hence, it is a promising type of pore geometry for NF-type applications.

4. Conclusions

The preparation and characterization of three different types of membranes for large ion recovery from water by investigating the retention of polyoxometalate type anions $[\text{PMo}_{12}\text{O}_{40}]^{3-}$. It has been shown that in the pressure range of 2–10 bar, γ -alumina membrane shows a high water flux and higher POM retentions than its organic counter parts Nafion and Nafion/silica hybrid. A new generation of surfactant-templated inorganic silica film has been prepared and characterised. This type of material could be promising for future NF applications.

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