

Novel Anion-Exchange Organic-Inorganic Hybrid Membranes Prepared Through Sol-Gel Reaction and UV/Thermal Curing

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Received 1 April 2007; accepted 22 August 2007

DOI 10.1002/app.27304

Published online 25 October 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Anion-exchange organic-inorganic hybrid membranes were prepared through sol-gel reaction and UV/thermal curing of positively charged alkoxy silane and the alkoxy silane containing acrylate or epoxy groups. Properties of prepared hybrid membranes were varied by control of the molar ratio of the precursors. It was shown that the thermal degradation temperatures (T_d) of the membranes were in the range of 212–226°C, water uptakes

in the range of 9.6–14.6% and IEC values in the range of 0.9–1.6 mmol g⁻¹. The hybrid membranes show high permeability to anions, as reflected by the high static transport number (t_-) of the anion (Cl⁻). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1865–1871, 2008

Key words: organic-inorganic hybrid membranes; anion exchange membranes; sol-gel; UV curing

INTRODUCTION

Ion-exchange membranes are now widely used for membrane electrolysis, solid polymer electrolytes, and fuel cell storage batteries as well as electrochemical separation, which includes diffusion dialysis, electrodialysis, electro-deionization, etc.^{1–4} For these processes, thermally and mechanically stable ion-exchange materials should be developed. Hence, the exploration of new organic polymeric ion-exchange materials or modification of the commercial examples continues to be a hot topic.^{5,6} In recent years, a new kind of material, the organic-inorganic hybrid has been extensively investigated because of the ability to combine the best properties of both organic and inorganic components.^{7–9} In the hybrid materials, ion-exchange groups are grafted to the organic components,^{10,11} in some cases, organic or inorganic ion-exchangers may be directly incorporated into the hybrid matrices.^{12,13} Up till now, the proton-exchange or cation-exchange hybrid materials/membranes have been widely reported.^{10,12,13} Investigations of anion-exchange membranes are less com-

mon, mainly because the commercial applications of anion exchange membranes are not as wide as cation exchange materials.⁴ However, as the applications of ion-exchange membranes increase, anion exchange membranes are finding an increasingly wider range of applications. For applications such as the separation of species with positive charge (e.g., biomacromolecules) below their isoelectric points, and recovery of cathode electrophoresis lacquers, anion-exchange membranes are required.^{14,15} In some electroanalytical processes, such as electrochemical sensors and electrocatalysis, anion-exchange organic-inorganic membranes are highly desirable.^{11,16,17}

In our laboratory, a series of supported cation- and anion-exchange organic-inorganic hybrid membranes have been prepared.^{18–21} Porous alumina plates were used as the substrates so that composite membranes with asymmetrical structure (top active hybrid layer and porous intermediate and bottom layers) could be synthesized. These membranes are targeted at liquid separation processes (microfiltration, nanofiltration, etc.). For application in other fields (e.g., membrane electrolysis, solid polymer electrolytes, and electrochemical separation), the development of free-standing anion-exchange hybrid membranes is essential.⁵ The present work continues a series of work investigating the preparation of free-standing anion-exchange hybrid membranes. Different alkoxy silanes were used as the precursors for the sol-gel process in this study. Precursors containing acrylate/epoxy groups or quaternary amino groups were used. The quaternary ammonium

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Contract grant sponsor: Natural Science Foundation of China; contract grant numbers: 20576130, 20604027.

Contract grant sponsor: Key Program of Natural Science Foundation of China; contract grant number: 20636050.

Contract grant sponsor: China Postdoctoral Science Foundation; contract grant number: 2005038481.

Journal of Applied Polymer Science, Vol. 107, 1865–1871 (2008)
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groups yield anion-exchange functionality, while the acrylate/epoxy groups allow formation of organic polymeric network via UV/thermal curing. Research by other groups developing proton exchange hybrid membranes suggests that such UV and/or thermal curing procedure is simple and effective.²² Variation of the feed ratio of the different precursors allows hybrid membranes with different hydrophilicity, electrical properties, and thermal/chemical stabilities to be prepared. The physicochemical properties of these hybrid membranes were investigated.

EXPERIMENTAL

Materials

Glycidylmethacrylate (GMA) was purchased from ACROS Organics (USA), while triethoxysilylpropylamine (TESPA), γ -methacryloxypropyltrimethoxysilane (γ -MPS), γ -glycidoxypropyltrimethoxysilane (GPTMS), and tetraethoxysilane (TEOS) were purchased from Nanjing Crompton Shuguang Organosilicon Specialties Co (China). Photoinitiator (Darocur 1173) was kindly provided by Jingjiang Hongtai Chemical Engineering Co. Ltd (Jiangsu, China). All the reagents were of analytical grade and used as received. Deionized water was used throughout.

Preparation of the charged sol-gel precursor: Alkylated triethoxysilylpropylamine [TESPA (+)]

TESPA was added dropwise into methyl iodide (CH_3I) at room temperature (TESPA: CH_3I molar ratio = 1:6). The temperature was then raised to 58°C and the mixture was stirred for a further 12 h. At the end of the reaction, excess methyl iodide was recovered by distillation.

Synthesis of the hybrid organic-inorganic membranes

Into a ethanol solution of GPTMS, γ -MPS, TESPA(+), TEOS, and GMA (ethanol: Si(molar ratio) = 4), a quantitative amount of water (H_2O :Si (molar ratio) = 1.5 : 1) was added and the mixture was stirred at room temperature for 2 days. The molar ratio of the different precursors was varied to yield six sol-gel samples (A–F) (see Table I). The solution was then blended with 0.25% photoinitiator which had been diluted by ethanol (ethanol: Darocur 1173 mass ratio = 20) and further stirred for 6 h. Subsequently, the mixture was cast onto Teflon plate. The film produced on solvent evaporation at room temperature was cured by exposure to a medium pressure Hg lamp (300 W in^{-1} , Fusion UV Systems, USA) for 1 min followed by treatment from 60 to 110°C at a rate of 5°C h^{-1} and holding at 110°C for

TABLE I
Feed Ratio of the Different Precursors for the Preparation of the Hybrid Membranes A–F

Hybrid membrane	γ -MPS ^a	TESPA(+)	TEOS	GMA
A	1	1	2/13	
B	1	1	4/13	
C	1	1.6	4/13	
D	1	1.6	4/13	0.5
E	1	1.2	4/13	
F	1	1.2	4/13	0.5

^a GPTMS is used and the molar ratio of GPTMS to γ -MPS is fixed as 1 : 1 for all the membranes.

2.5 h. The final hybrid membranes obtained are designated A–F in all following discussion.

Membrane characterization

FTIR spectra of the hybrid membranes were recorded using FTIR spectrometer (Vector 22, Bruker) with a resolution of 2 cm^{-1} and a spectral range of 4000–400 cm^{-1} . The morphology of the hybrid membrane cross sections were studied using scanning electron microscopy (XT30 ESEM-TMP PHILIP).

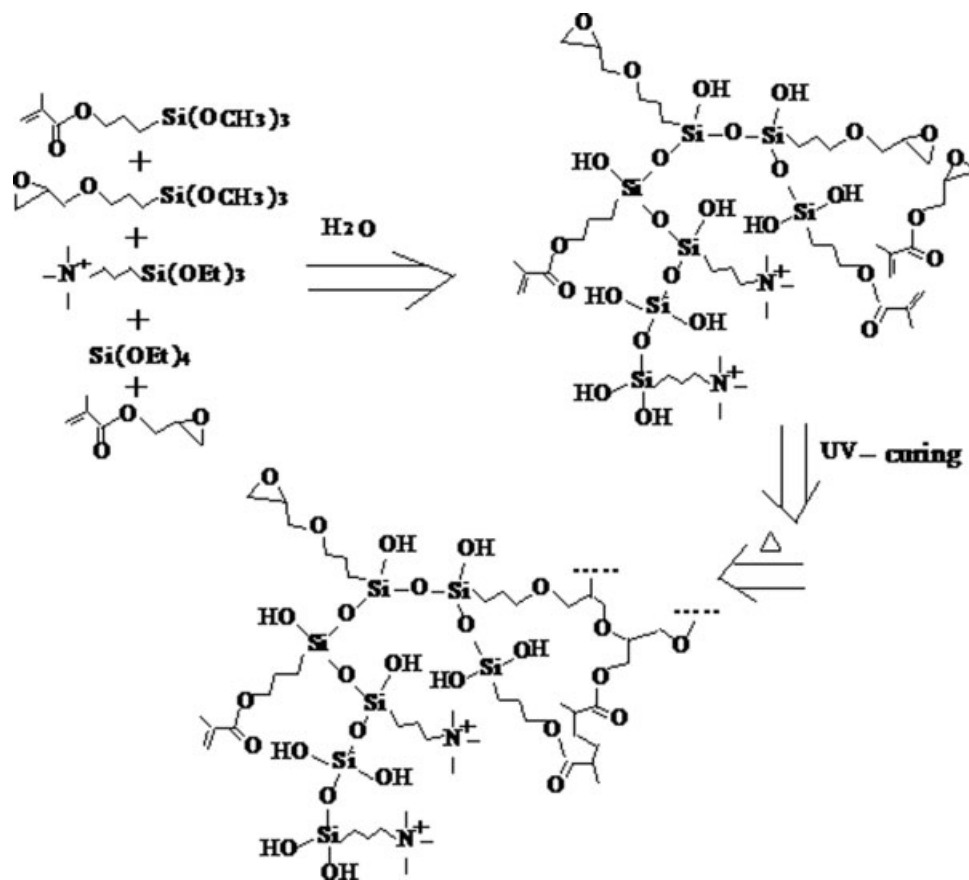
To explore hydrophilicity of the hybrid membranes, the gravimetric water uptakes (W_R) were measured as following: The dried membranes were weighed and immersed in water at $\sim 25^\circ\text{C}$ for one and a half days. Surfaces of the wet membranes were then carefully dried and the membranes weighed again. W_R was calculated as the relative weight gain per gram of the dry membrane samples:

$$W_R = (W_W - W_D)/W_D \times 100\%$$

where W_W or W_D is the weight of the wet or dry membrane respectively.

Ion exchange capacities (IECs) of the membranes (Cl^- form) were determined using the Mohr method as described in a previous article²³. Accurately weighed dry membranes A–G were converted to Cl^- ionic form through immersion in 1 mol dm^{-3} NaCl for 2 days. Excess NaCl were washed off and then the membranes were immersed in 200 cm^3 0.5 mol dm^{-3} Na_2SO_4 . The amount of Cl^- was determined using titration with AgNO_3 ; anion exchange values were obtained and expressed as mmol g^{-1} of dry membrane (in Cl^- form).

To evaluate the chemical stability of the membranes under basic conditions, the IECs of the membranes in the OH^- form were monitored with time after immersion in 0.2 mol dm^{-3} NaOH solution, with subsequent water washing and soaking to remove any remaining NaOH. Then, the samples were immersed in 0.02 mol dm^{-3} HCl for 24 h,



Scheme 1 The preparation of the anion-exchange hybrid membranes.

back-titrated by 0.02 mol dm⁻³ NaOH. The immersion time in 0.2 mol dm⁻³ NaOH for membrane D was 2, 4, 8, 12, 24, or 36 h. For the other membranes, the immersion time was simply 12 h.

The thermal behavior of the hybrid membranes was determined with a Shimadzu TGA-50H analyzer under airflow, with a heating rate of 10°C/min.

The membrane potentials (E_m) were determined using the procedure reported previously.²³ The hybrid membrane was placed between two half cells which were fitted with a specially designed double junction saturation calomel electrodes (S.C.E.).²⁴ The unit was designed to permit continuous flows of aqueous KCl (0.1 mol dm⁻³) and KCl (0.2 mol dm⁻³) on each side of the membrane surface. Membrane potential (E_m), i.e., the potential difference between the two sides of the membranes, was determined using a digital multimeter (model: GDM-8145, Goodwill Instrument Co., Taiwan). From E_m , the static transport number of the anion (t_-) in the membrane is calculated using:

$$t_- = \frac{E_m + E_0}{2E_0} \quad \text{with} \quad E_0 = -\frac{RT}{F} \ln \frac{C_2}{C_1}$$

where E_0 is the standard solution potential; R is gas constant, $T = 298.15$ K, F Faraday constant, and C_1

and C_2 the concentrations of the aqueous solutions in the two sides of the cell.

The E_m experiments were repeated at least three times under identical conditions; the experimental error of E_m and t_- was calculated from the variation between each measurement.

RESULTS AND DISCUSSION

Chemical structure and morphology

Six different membranes (Table I) were prepared from different molar ratio of the precursors. In samples D and F, the organic monomer GMA was also added. This was to show how the organic monomer influences the properties of the membranes. In the sol-gel process, hydrolysis and condensation processes of the alkoxy silane groups ($-\text{Si}(\text{OR})_3$) take place, leaving most of the epoxy and the acrylate groups unaffected. During the subsequent UV- and thermally-curing steps, the epoxy and the acrylate groups undergo a crosslinking reaction forming an organic polymeric network. The reaction steps are schematically shown in Scheme 1.

FITR spectra of the hybrid membranes were recorded to investigate the chemical structure (Fig. 1). The ~ 1720 cm⁻¹ and ~ 1200 cm⁻¹ bands are due

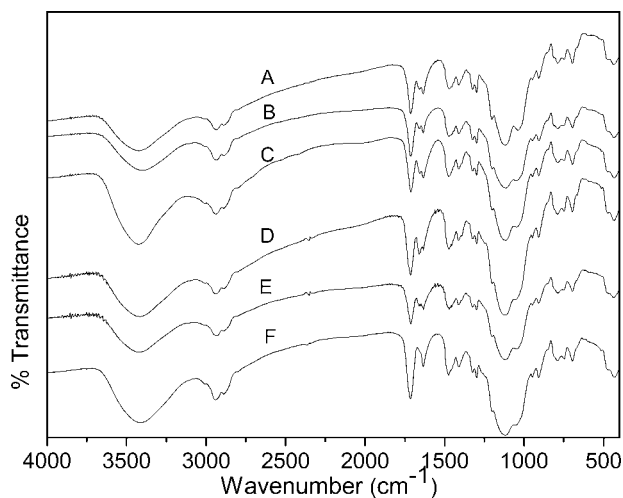


Figure 1 The FTIR spectra of hybrid membranes A–F.

to the $\nu_{\text{C=O}}$ or $\nu_{\text{C-O}}$ modes of the ester groups respectively, while the $\sim 1635 \text{ cm}^{-1}$ band is due to the $\nu_{\text{C=C}}$ mode of the remaining CH=CH groups.

The $\sim 1120 \text{ cm}^{-1}$ and $\sim 1040 \text{ cm}^{-1}$ bands are due to the C-O-C and Si-O-Si bonds. The strong absorption band at $\sim 3420 \text{ cm}^{-1}$ indicates that $-\text{OH}$ groups are present in the hybrid membranes due to uncondensed $-\text{SiOH}$ groups and the product of the reaction between water and the epoxy groups.

Morphologies of the hybrid membranes were probed using SEM. The SEM micrographs of membranes A–F are similar, therefore, only four images of membranes A, C, E, and F are presented in Figure 2. The membrane cross sections were very smooth and dense with no obvious separated silica particles. Therefore, a good compatibility between the inorganic and organic component is indicated.

Thermal stability (TGA analysis)

The weight-loss behaviors of the hybrid materials were studied using TGA at a heating rate of $10^\circ\text{C min}^{-1}$ in flowing air atmosphere. Thermal degradation temperatures (T_{d5} ; defined as the temperature at 5% mass loss) were determined from TGA thermo-

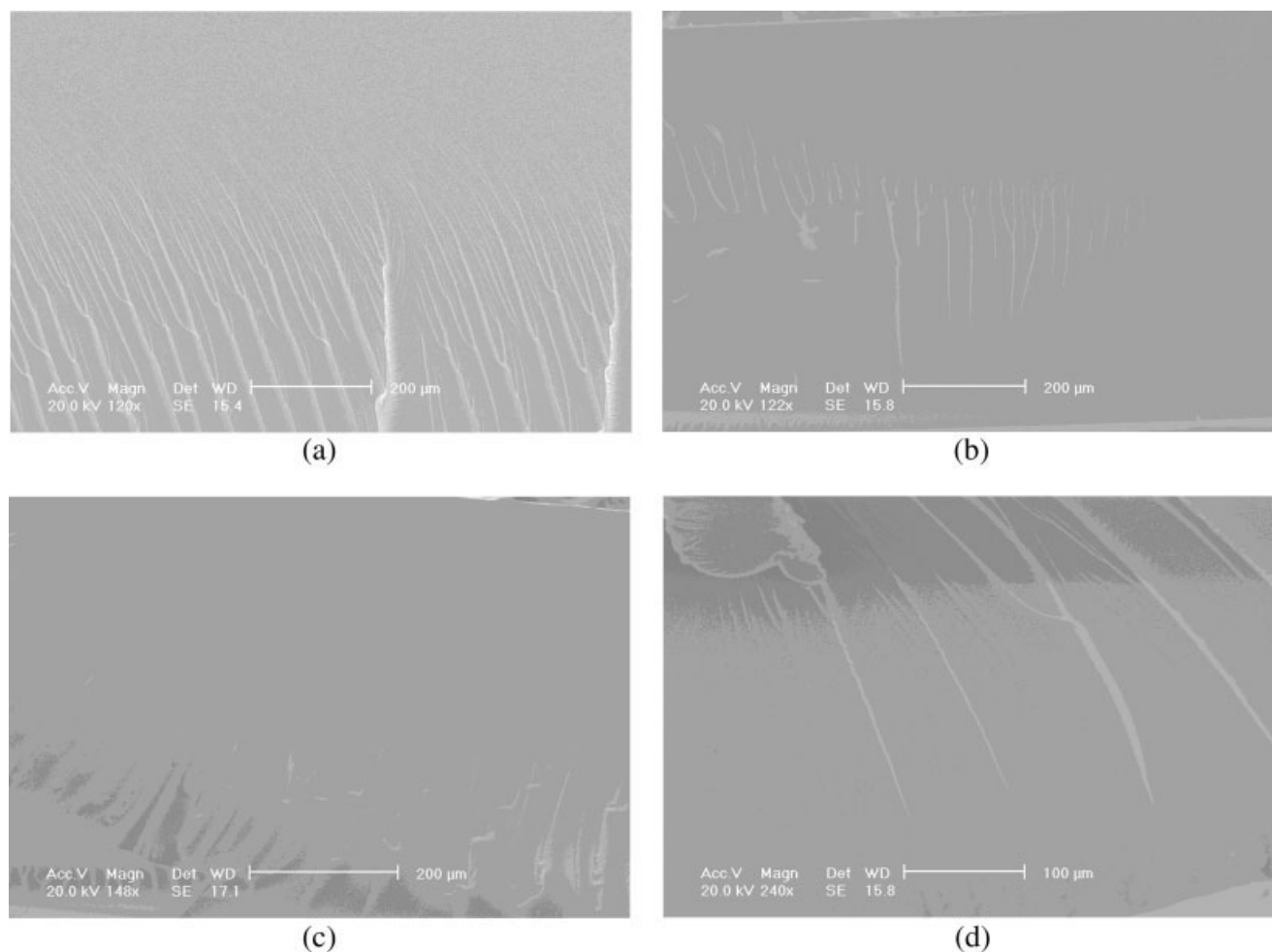


Figure 2 The SEM micrographs of (a) membrane A; (b) membrane C; (c) membrane E; (d) membrane F.

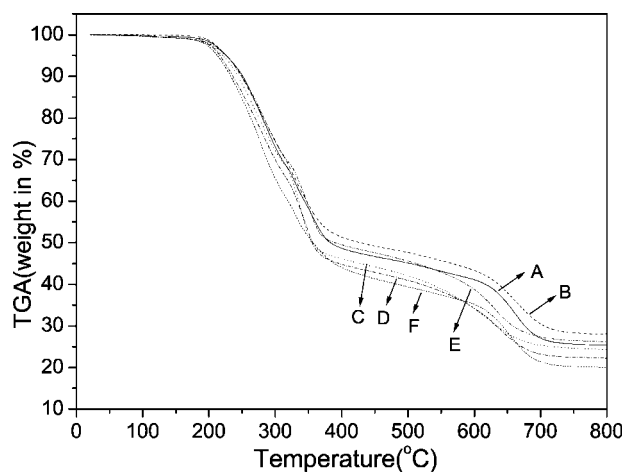


Figure 3 TGA results for hybrid membranes A–F.

grams in Figure 3, with the main results summarized in Figure 4.

The T_d values of the hybrid membranes were in the range of 212–226°C. Changes in the T_d with the content of TESPA(+) or TEOS was not observed (similar content of inorganic silica component is introduced by both of the precursors). However, addition of organic monomer GMA led to a slight decrease in T_d values (membrane D compared with membrane C or membrane F compared with E), indicating that an increase in the organic component may possibly lead to a decrease of the thermal stability of the hybrid membranes.

Water uptake (W_R) and ion-exchange capacity (IEC)

The result from water uptake (W_R) and ion-exchange capacity (IEC) measurement of the hybrid membranes are shown in Figure 5. It can be seen that the W_R of the membranes are in the range of 9.6–14.6%, while the IEC in the range of 0.91.6 mmol g⁻¹. The influence of the content of TESPA(+) on the hydrophilicity of the membranes is obvious when comparing membranes D and F or membranes B, E, and C. For the preparation of these membranes, the molar ratio of the other precursors (KH-570, GPTMS, TEOS, and/or GMA) are fixed. The content of TESPA(+) increases from membranes F to D or from membranes B, E to C and the W_R and IEC value generally increases accordingly.

Comparison of the values for membrane A and B indicates that on increasing the TEOS content, the IEC value decreases, while W_R increases. The decrease of IEC corresponds to the decrease in ionic content of the membrane. A decrease in IEC of organic polymeric membranes is anticipated to lead to a decrease in W_R ²³ (ion-exchange groups have a strong hydration effect). However, the silica compo-

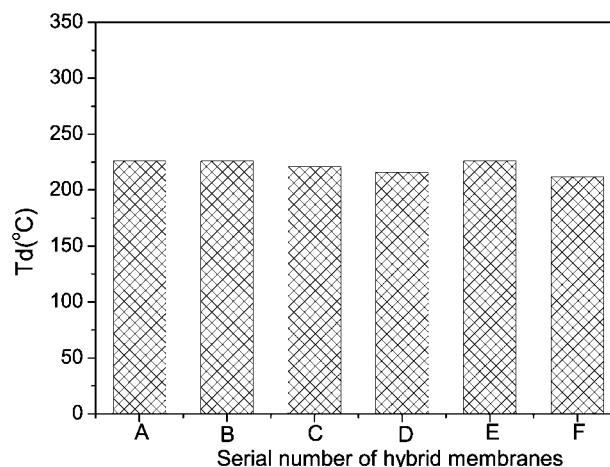


Figure 4 The thermal degradation temperatures (T_d), defined as the temperature relating to 5% weight loss, for hybrid membranes A–F.

nent contains hydrophilic Si—OH groups and so the W_R value increases as the TEOS content increases. These two factors balance with each other and it is clear that the latter is predominant.

Comparison of membrane D with C, or membrane F with E demonstrates that the addition of GMA decreases W_R values. Two factors may be responsible for such change: (1) the decrease of the IEC value and (2) the increase in the organic polymer network crosslinkage.

Chemical stability

The hybrid membranes contain acrylate groups which will be sensitive to basic conditions. To probe this, the IEC values of the membranes in OH⁻ form were measured for evaluation of the chemical stabil-

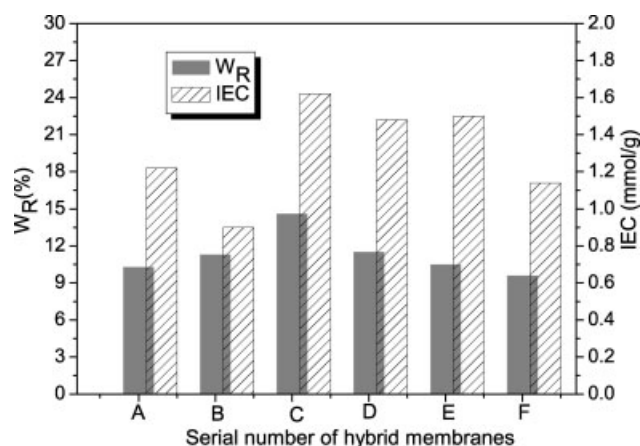


Figure 5 Water uptake (W_R) and ion-exchange capacity (IEC) (Cl⁻ form) for hybrid membranes A–F.

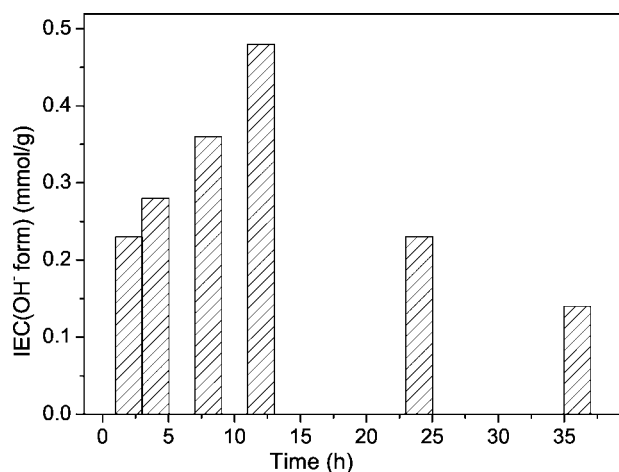


Figure 6 The change of the measured ion exchange capacity (IEC) (OH⁻ form) of the hybrid membrane D with the immersion time in 0.2 mol dm⁻³ NaOH solution.

ity of the membranes with time when immersed in NaOH (0.2 mol dm⁻³).

Firstly, membrane D was immersed in NaOH solution (0.2 mol dm⁻³) for different period of time. The IEC values in OH⁻ form obtained are shown in Figure 6. On increasing immersion times in NaOH, the IEC value instantly increases, then decreases. The highest IEC value (0.48 mmol g⁻¹) is at the immersion time of 12 h. Initially, the anion (I⁻) of the hybrid membranes will be gradually transformed to OH⁻ groups. However, as the immersion continues, the hybrid membrane degrades since the acrylate groups are hydrolyzed in the basic solution.

On the basis of the results above, the other membranes were immersed in 0.2 mol dm⁻³ NaOH for 12 h for similar measurements (Fig. 7). The IEC values for the OH⁻ forms are lower than for the Cl⁻ forms for all membranes. Therefore, degradation of

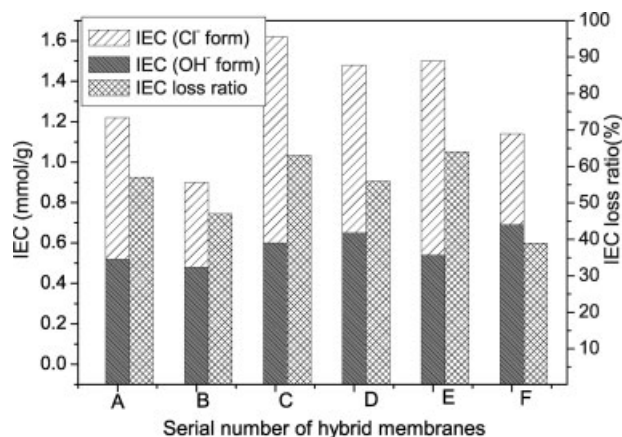


Figure 7 Ion exchange capacity (IEC) in Cl⁻ or OH⁻ form and IEC loss ratio for hybrid membranes A–F (For the IEC in OH⁻ form measurement, immersion time of the membranes in 0.2 mol dm⁻³ NaOH was all fixed at 12 h).

the membranes has taken place during the 12 h immersion in aqueous NaOH solution. The IEC loss ratio, defined below, can be used as an estimate of the chemical stability of the membranes under basic conditions:

$$\text{IEC loss ratio} = \frac{[\text{IEC}(\text{Cl}^- \text{ form}) - \text{IEC}(\text{OH}^- \text{ form})]}{\text{IEC}(\text{Cl}^- \text{ form})}$$

The IEC loss ratio decreases when the TEOS content increases (from membrane A to B—see Fig. 7). When the GMA content increases from membranes C to D or membranes E to F, the IEC loss ratio also decreases. When the TESP(+) content increases from membranes B, to E, C or from membranes F to D, the IEC loss ratio generally increases. Therefore, it was concluded that an increase in TEOS or GMA content increases the chemical stability of the membranes (due to the strengthening of the inorganic silica or organic polymeric network). On the other hand, when the TESP(+) content increases, the chemical stability decreases, partly due to the increase of the membrane hydrophilicity as discussed earlier.

Membrane potential E_m and static transport number (t_-)

E_m and t_- values of the hybrid membranes were measured and the results presented in Figure 8. The static transport number t_- of the anion (Cl⁻) in the membranes are calculated from E_m . Membrane potential were in the range of 14.8–18.8 mV and the t_- values were in the range of 0.92–1.03 (Some experimental errors for the E_m and t_- determination are shown in Figure 8, and therefore t_- in some case is greater than 1), indicating these membranes are positively charged and show excellent permselectivity to anions. Hence, the membranes can be used in

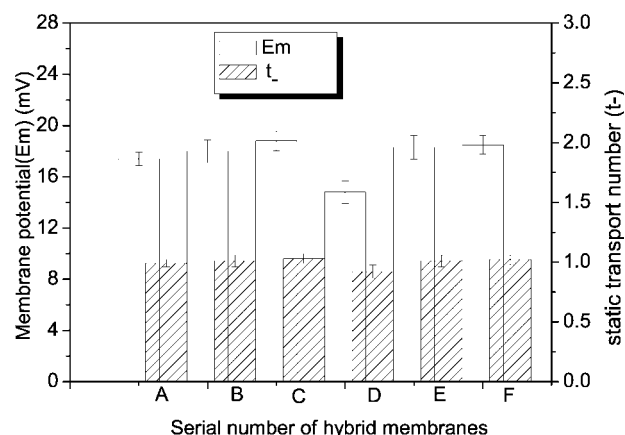


Figure 8 Membrane potential (E_m) and static transport number of the anion (Cl⁻) (t_-) for hybrid membranes A–F.

electrochemical separation processes. Among the hybrid membranes, membrane D shows relatively lower t_{-} value, though its IEC value is relatively high. The source of this is not currently known.

CONCLUSIONS

Free-standing positively charged organic-inorganic hybrid membranes were prepared through sol-gel and UV-/thermally- curing processes of different precursors: γ -methacryloxypropyltrimethoxysilane (γ -MPS), γ -glycidoxypropyltrimethoxysilane (GPTMS), alkylated triethoxysilylpropylamine (TESPA (+)), tetraethoxysilane (TEOS), and GMA.

By varying the molar ratio of the different precursors, hydrophilicity, thermal and chemical stability, and the electronic properties of the hybrid membranes can be changed. Increases in TEOS content increase water uptakes and chemical stabilities but decrease the ion-exchange capacities. The addition of GMA in the system decreases the hydrophilicity and IEC, but increases the chemical stability by strengthening of the organic polymeric network.

The chemical stability of the hybrid membranes forwards alkali show that all the membranes are sensitive to the basic conditions, largely because of the easily hydrolyzable acrylate groups. Other sol-gel precursors which contain styrene rather than acrylate groups are being explored to prepare related hybrid anion-exchange membranes and will be reported in due course.

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