

Synthesis of composite ion-exchange membranes and their electrochemical properties for desalination applications†

Chalida Klayson,^a Roland Marschall,^a Lianzhou Wang,^{*ab} Bradley P. Ladewig^{ac} and G. Q. Max Lu^{*ab}

Received 2nd December 2009, Accepted 22nd March 2010

First published as an Advance Article on the web 26th April 2010

DOI: 10.1039/b925357b

A new type of composite ion-exchange membrane of sulfonated polyethersulfone (sPES) and sulfonated mesoporous silica (SS) was synthesized by dispersing inorganic SS nanoparticles as the fillers in the organic polymer matrix. Physical and electrochemical properties of the composite membranes were investigated in order to evaluate their key parameters as electromembrane candidates in their application in electrodialysis (ED) water purification. The results revealed that incorporating small amounts of SS enhanced the properties of the ion-exchange membranes with negligible influence on their thermal and mechanical properties. Membranes with 0.5 wt% SS were found to have the optimal properties, with good water uptake, ion-exchange capacity (IEC ~ 1.1 mequiv g^{-1}), transport properties and excellent permselectivity while maintaining excellent mechanical and thermal stability. These newly-developed membranes can be considered as excellent candidates suitable for water desalination by ED.

Introduction

Ion-exchange membranes have recently attracted great attention from both academic and industrial fields due to their versatile applications from desalination of salt-rich water to food production processes including waste water treatment to recover some valuable elements in chemical industry.^{1–5} Different applications usually require specific membrane properties. For desalination particularly electrodriven processes such as electrodialysis (ED), which is the scope of interest of this work, the ion-exchange membranes were expected to possess high permselectivity, excellent conductivity, and good chemical, thermal and mechanical stabilities. Most polymer based ion-exchange membranes are still insufficient for the desalination process as they have some common drawbacks including insufficient mechanical, chemical and thermal stabilities, and poor fouling resistance. Therefore, the concept in designing composite membranes by introducing inorganic materials to an organic matrix becomes a strategic tool for the development of new composite ion-exchange membranes. The hybrid membranes are expected to possess better strength from the inorganic materials and enhanced electrical conductivity with minimised effects on other properties such as ion-exchange capacity, and functionalities of the polymer matrix.

In this work, we focus on the development of composite ion-exchange membranes from sulfonated polyether sulfone (sPES) and SiO_2 nanoparticles. A commercial polymer, polyether sulfone, known as a high performance polymer possessing excellent chemical, thermal and mechanical properties at low cost,⁶ was selected as the polymer matrix of the ion-exchange membranes. Sulfonation reaction was introduced to functionalize the aromatic rings of the polymer chains to enhance the hydrophilicity and ion-exchange properties of the PES.

From the viewpoint of ion-exchangeable inorganic materials, mesoporous silica have been widely studied for more than a decade. It is one of the most versatile particles with high potential in many applications due to its wide varieties in shapes, porosities and functionalities. Recently, much research has been focusing on incorporating sulfonated mesoporous silica, $\text{SO}_3\text{H-SiO}_2$ (SS), into proton conductive membranes (PEM) for fuel cell applications.^{7–10} The studies revealed that not only the proton conductivity, but also the water uptake and mechanical stability of the membranes can be improved. However, there has been no research exploring the use of SS as an additive for ion-exchange membranes especially for water desalination applications. In this study, we report for the first time the development of a new type of composite membrane by incorporating SS into sPES membranes for desalination applications. It is known that a great challenge in development of nanocomposite materials is the distribution of inorganic nanoparticles in the organic matrix due to the aggregate tendency of the nanoparticles. Herein we will introduce our strategy on the functionalization of mesoporous SiO_2 using sulfonate groups in order to improve the distribution of the nanoparticles in the polymer matrix. Moreover, the addition of functionalized mesoporous nanoparticles will not only increase charged functional groups in the composites, but also enhance the ionic transport properties due to their high surface area and well-accessible mesopores. Systematic characterization of the composite sPES and sulfonated SiO_2 were

^aARC Centre of Excellence for Functional Nanomaterials, Australian Institute of Bioengineering and Nanotechnology, The University of Queensland, Qld, 4072, Australia. E-mail: l.wang@uq.edu.au; maxlu@uq.edu.au; Fax: +61 7 3365 4199; Tel: +61 7 3365 4218

^bSchool of Chemical Engineering, the University of Queensland, Qld, 4072, Australia

^cMonash University, Department of Chemical Engineering, Vic, 3800, Australia

† This paper is part of a *Journal of Materials Chemistry* themed issue on advanced materials in water treatments. Guest editors: Dongyuan Zhao, Benjamin S. Hsiao and Mietek Jaroniec.

conducted to better understand the relationships among synthesis conditions, structure and significantly enhanced properties of the composite membrane for ED applications.

Experimental

Materials

Polyether sulfone (RADEL A) provided by Solvay Advanced Polymers Co. was dried at 120 °C for 24 h before use. Other chemicals were obtained commercially and were used as received without further purification.

Sulfonation reaction of PES

PES was sulfonated with chlorosulfuric acid (Sigma). In a typical procedure, 20 g of PES was dissolved in 400 g of dichloromethane (Merk) under N₂ atmosphere with stirring at room temperature. Then, 20 cm³ of chlorosulfonic acid was gradually added to the solution. The reaction was allowed to proceed for 240 min and then was terminated by precipitating the solution into cold water. The products were filtered and washed multiple times with deionized (DI) water until the pH became approximately 5–6. Finally, the sulfonated PES product was dried at 120 °C under vacuum. This sPES polymer was used as a polymer matrix for the composite cation-exchange membranes.

Preparation of the sulfonated mesoporous SiO₂

SO₃H-functionalized mesoporous SiO₂ was prepared following the procedure described elsewhere.⁹ Specifically, a mixture of 96 cm³ of DI water, 0.7 cm³ of 2 mol dm⁻³ NaOH solution and 0.2 g of surfactant cetyltrimethylammonium bromide (CTAB, Aldrich) was heated to 80 °C under stirring. After a clear solution was obtained, 0.903 cm³ of tetraethylorthosilicate (TEOS, Fluka) and 0.09 cm³ mercaptopropyl trimethoxysilane (MPMS, Sigma) was added to the solution and was stirred for another 2 h. The synthesized powders were filtered and subsequently washed with DI water and ethanol. The template was removed by extraction in boiled acidified ethanol solution under reflux for 24 h. Then, 0.3 g of the as-synthesized powder was collected, dried and re-dispersed in a mixture of HNO₃ (70%, Ajax Finechem) and H₂O₂ (30%, Ajax Finechem) at room temperature for 48 h. The suspended powders were centrifuged and added into 30 cm³ of 1 mol dm⁻³ H₂SO₄ under stirring to ensure that protonated forms were obtained before the measurement of ion-exchange capacity by back titration.

Membrane preparation

Ion-exchange membranes were prepared by the solvent evaporation technique. Firstly, 25 wt% polymer solutions were prepared using dimethylformamide (Sigma) as the solvent. Then 0–2 wt% of SS were mixed with the polymer solutions at 60 °C for 4 h while stirring. Sonication was applied to the mixture solution before it was cast on glass substrates using the doctor blade method to control the thickness of the membranes. The resultant membranes were then dried in a vacuum oven at 60 °C for 24 h and at 80 °C for another 24 h. A series of membranes were named after the wt% of SS added in the polymer matrix. For instance,

0.2SS is the abbreviation of the composite membranes of sPES containing 0.2 wt% of SS. The prepared membranes were then treated in hot water for 2 h and then in 1 mol dm⁻³ HCl for 24 h. After that, the membranes were rinsed with DI water and kept in 1 mol dm⁻³ NaCl solution. All the membranes were equilibrated in working solution for at least 6 h before use.

Membrane characterization

Membrane morphology. The morphology and structure of the membranes were observed on a JEOL 6300 electron microscope (SEM). To obtain sharp cross-sectional surface fractures, the samples were cut under liquid nitrogen, then the captured water was dried out in the oven overnight. Transmission electron microscopy (TEM) on a JEOL 1010 electron microscope was used to study the distribution of inorganic fillers in the polymer matrix. The TEM samples were cut using an ultramicrotome with diamond knives.

Thermal and mechanical stabilities of membranes

Thermal stability of the membranes was investigated using thermogravimetric analysis (TGA) (Mettler Toledo) under nitrogen flow using a heating rate of 10 °C min⁻¹ in the range of 25–800 °C.

The mechanical properties of membranes were measured by means of tensile tests in the wet state at room temperature using an Instron 5800 at a speed of 2 mm min⁻¹. Membranes were cut into a rectangular shape with dimensions of 50 mm × 5 mm and were equilibrated in DI water for 48 h. The gauge length of each specimen was 14 mm. At least five specimens from each sample were tested to obtain average values.

Ion-exchange capacity (IEC) and water uptake of membranes

Ion-exchange capacities were measured using a titration method.¹¹ The cation-exchange membrane was equilibrated in 1 mol dm⁻³ HCl. After that, the membrane was washed with DI water to remove excess HCl and then was immersed into 1 mol dm⁻³ NaCl solution for 6 h. The number of displaced protons from the membrane was determined by titration using standard 0.01 mol dm⁻³ NaOH solution, and phenolphthalein was used as the indicator. Then the ion-exchange membrane was soaked in DI water for 24 h or more. After that, the membrane was taken out and water on the surface was wiped off with tissue paper. The wet weight of the membrane was measured. Then the membrane was placed in an oven at 50 °C for 10 h or until the weight of the membrane did not change any more. The dry weight of the membrane was then measured. The IEC and water uptake of membranes were calculated using eqn (1) and (2),

$$\text{IEC} = \frac{ab}{W_{\text{dry}}} \quad (1)$$

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (2)$$

where *a* is the concentration of NaOH solution used (mol dm⁻³), *b* is the volume of NaOH solution used (dm³), *W*_{dry} is the dry

weight of the membrane and W_{wet} is the wet weight of the membrane.

Electrochemical properties of ion-exchange membranes

Membrane resistance. An ion-exchange membrane was equilibrated in 0.5 mol dm^{-3} NaCl before being placed in a 2-compartment cell between platinum electrodes with an effective area of 1 cm^2 . The resistance of membranes was measured at room temperature by impedance spectroscopy (IS) using a Solartron 225B in a frequency range from $1\text{--}10^7$ Hz with an oscillating voltage of 100 mV amplitude.¹² The resistance corresponding to the phase angle closest to zero in the Bode diagram was recorded. Then, membrane resistance (R_{mem}) was calculated by subtraction of the electrolyte resistance (R_{sol}) from membrane resistance equilibrated in electrolyte solution (R_{cell}), according to the equation $R_{mem} = R_{cell} - R_{sol}$. Based on the electrical resistance measurement, the conductivity of membranes (σ , S cm^{-1}) was calculated according to eqn (3),

$$\sigma = \frac{L}{R_{mem} A} \quad (3)$$

where R_{mem} is the resistance of the membrane, L is the thickness of the membrane (cm), and A is the effective area of the membrane (cm^2).

Membrane potential and transport number

Membrane potential was measured in a two compartment cell, in which a vertical membrane of 1.0 cm^2 effective area separated two solutions of $0.001 \text{ mol dm}^{-3}$ NaCl and $0.005 \text{ mol dm}^{-3}$ NaCl respectively. The dilute solutions of NaCl were used in order to render the negligible activity coefficient of the dilute electrolyte.¹³ The potential difference (E_m) across the membrane was measured at room temperature using a multimeter which was connected to an Ag/AgCl reference electrode. The transport number, \bar{t}_+ , was calculated using the following equation:⁴

$$E_m = \frac{RT}{F} (2\bar{t}_+ - 1) \ln \left(\frac{C_1}{C_2} \right) \quad (4)$$

where R is the gas constant; F is the Faraday constant; T is the absolute temperature; and C_1 and C_2 are the concentrations of electrolyte solutions in the testing cell.

Chronopotentiometry

Chronopotentiograms were recorded using the same two compartment cell mentioned above at room temperature. The chronopotentiogram was recorded in $0.025 \text{ mol dm}^{-3}$ NaCl with a constant applied current density of $250 \mu\text{A cm}^{-2}$. The cell was connected to a Solartron Multistat 1480 *via* two Pt electrodes and the corresponding potential between two reference electrodes (Ag/AgCl) was automatically recorded every 0.1 s for a period of 300 s .

Results and discussion

Properties of the composite ion-exchange membranes

In this work, nanosized mesoporous $\text{SO}_3\text{H-SiO}_2$ (SS) was prepared according to our previously reported procedure^{9,10} and used as an inorganic filler for sPES polymer. The SEM and TEM images in Fig. 1 indicate the uniformity of the obtained powders with particle sizes of $100\text{--}150 \text{ nm}$. The ion-exchange capacity of the SS was measured to be around $1.8 \text{ mequiv g}^{-1}$. The detail characterization of the sPES polymer matrix was described in our previous work.¹⁴ The composite ion-exchange membranes were prepared *via* the so-called solvent evaporation technique after direct mixing of the organic polymer and inorganic fillers in a solvent. Fig. 2 shows the cross-sectional area of the membranes, which were all dense without apparent large porosities. The mechanical properties of the membranes are shown in Fig. 3. When the amount of SS increased, the tensile strength of the membranes slightly decreased and so did the elongation of the membranes. On the other hand, the tensile modulus slightly rose from 1.2 GPa to 1.3 GPa , while the overall mechanical properties upon the addition of SS in the membranes did not change significantly.

Thermal stabilities of the pure sPES and composite membranes were investigated using TGA (Fig. 4). It was clear that the sPES is an excellent thermo-stable polymer, which starts to decompose at around $300 \text{ }^\circ\text{C}$. There are three steps of weight loss including the loss of absorbed water at around $100 \text{ }^\circ\text{C}$, the thermal decomposition of SO_3H groups at *ca.* $300 \text{ }^\circ\text{C}$ and the

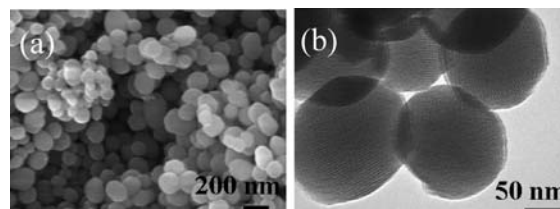


Fig. 1 SEM (a) and TEM (b) images of sulfonated mesoporous silica $\text{SO}_3\text{H-SiO}_2$.

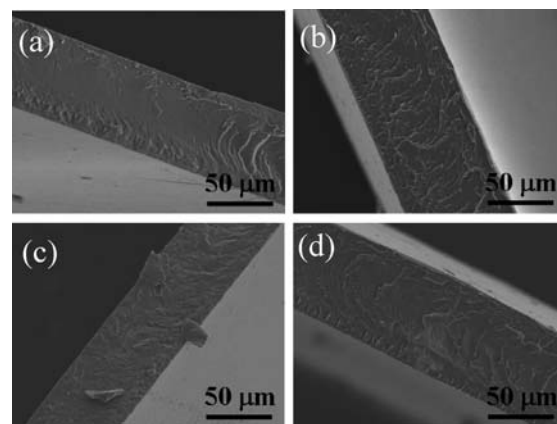


Fig. 2 SEM images of cross-sectional areas of (a) parent sPES membrane, (b) composite sPES-0.5 wt% of SS, (c) composite sPES-1.0 wt% of SS, and (d) composite sPES-2.0 wt% of SS.

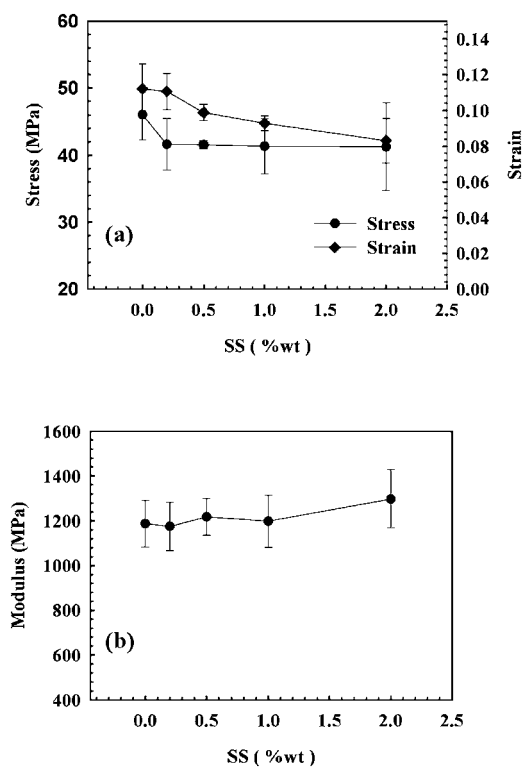


Fig. 3 Mechanical properties of the composite membranes: (a) stress and strain curve and (b) Young's modulus.

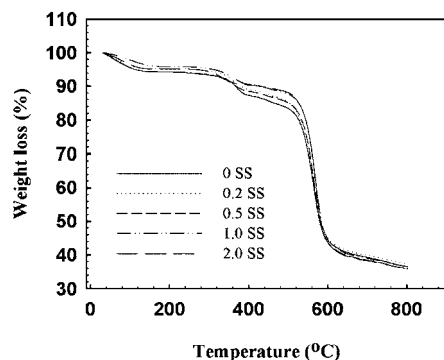


Fig. 4 TGA curves of the composite membranes.

degradation of polymer chains close to 500 °C.⁶ It was obvious that incorporation of SS nanoparticles in the composites did not significantly interfere with the thermal stability of the membrane materials. It thus can be concluded that the composite

membranes exhibited very good mechanical stability and reasonable thermal stability which should be sufficient for ED applications.

The ion-exchange capacity (IEC) provides information on the charge density in the membranes, which is an important factor related to the conductivity and transport properties of the membranes. The water uptake, ion-exchange capacity, conductivity, and transport number of the membranes are summarized in Table 1. It was encouraging to see that the incorporation of SS nanoparticles with high surface areas improved the IEC of the membranes. This in turn enhanced the conductivities and the transport properties of the membranes due to the increase of negatively charged functional groups, attracting cationic species while repelling anionic species.

The IEC and water uptake were increased with the increase of SS concentration in the range of 0.2–0.5 wt%. Further increase of the SS concentration did not further improve the properties of the membranes. This may be attributed to the interaction among the inorganic particles because they tend to aggregate to form inorganic particle clusters, resulting in poorer performance. Additionally, too much inorganic filler may interrupt the functional groups of the polymer matrix and thus decrease the IEC, conductivity and transport properties of the membranes. TEM images as shown in Fig. 5e and f give an evidence of aggregation of nanoparticles in the organic polymer. The term of fixed charge density was used as the ratio of the charged functional groups (IEC) and the absorbed water. Likewise, the fixed charge density and conductivity of the membranes were also increased with the increase of SS concentration, which then experienced an apparent decrease at 2 wt% SS, possibly due to the serious aggregation of nanoparticles in the polymer matrix. Because the porosity of our membranes was increased by adding inorganic fillers, the fixed charge density can also be easily altered by the parameters such as increased pores/voids or free space volume of the membranes, in addition to the sulfonic functional groups. It was apparent that 1.0SS membranes had good IEC, high fixed charge density and also considerable porosity, that might render these membranes possessing the optimal conductivity compared to other membranes in the same series. Thus the synergetic effect of the functional group concentration and porosity might play an important role in affecting the overall membrane properties.

Transport number is the fraction of total current carried by counter ions passing through the membrane.¹⁵ The transport number can be measured by means of potential differences which develop across the membrane when the membrane separates unequal electrolyte concentrations. Then the ion selectivity of ion-exchange membranes was quantitatively expressed in terms of membrane permselectivity, which measures how easy the

Table 1 Properties of the composite membranes

Properties	0 SS	0.2SS	0.5SS	1.0SS	2.0SS
Water uptake (%)	12.37	14.30	11.41	11.32	9.75
IEC/mequiv g ⁻¹	0.99	1.10	1.09	1.01	0.74
Fixed charge density/mequiv dm ⁻³	7.12	8.06	9.06	11.7	6.68
Conductivity/mScm ⁻¹	0.114	0.128	0.142	0.238	0.068
Transport number	0.92	0.97	1.00	0.98	0.80
Permselectivity (%)	86.78	95.04	100	96.69	66.94

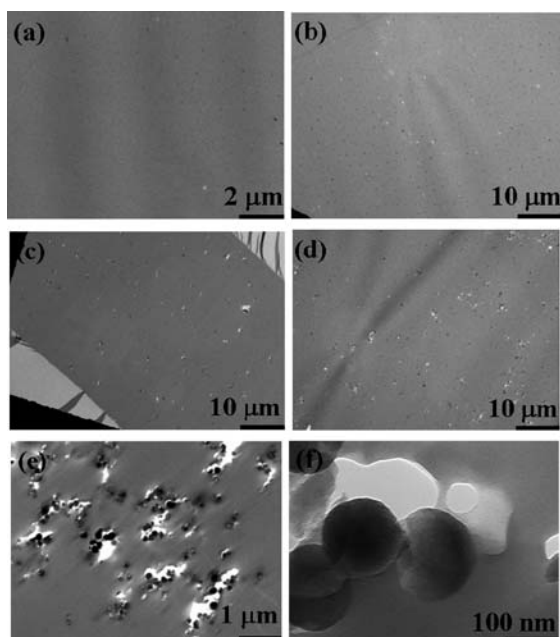


Fig. 5 TEM images of (a) parent sPES membrane, (b) composite sPES–0.2 wt% of SS, (c) composite sPES–0.5 wt% of SS, and (d)–(f) composite sPES–1.0 wt% of SS at different magnifications.

counter-ion migration occurs through an ion-exchange membrane,¹⁶ as defined by eqn (5),

$$P_s = \frac{\bar{t}_i - t_i}{1 - t_i} \quad (5)$$

where P_s is the permselectivity of ion-exchange membrane, \bar{t}_i is the transport number of the counter-ion in the membrane and t_i is that of the same ion in free solution at the same concentration. The transport number and permselectivity had a tendency to increase for the membranes up to 1 wt% SS since these properties are highly dependent upon the characteristic charge of the membranes.¹⁷

Porosity of ion-exchange membranes has also been reported to affect the transport and ion selectivities of the membranes.^{18,19} While membranes with bigger porosities will lose the ion selectivity, pores smaller than ionic species will behave like the inaccessible pathways as non-conducting regions for ionic species.^{18,19} Therefore, the control of optimal pore sizes suitable for sieving ionic species is of crucial importance. In this work, it was encouraging that the transport number of most composite membranes reached above 0.97, and the 0.5 wt% SS membrane demonstrated the ideal ion-selective property of 1.00.

Chronopotentiograms of the composite ion-exchange membranes

Chronopotentiometry is a useful technique for studying concentration polarization and the transport phenomena of ionic species close to the interface of ion-exchange membranes. The potential response differs with time while constant current density applied across ion-exchange membranes provides crucial important information such as polarization concentration, electrical conductance, limiting current density, ionic transport properties, and also the surface homogeneity of the

membranes.^{4,13,18,20,21} In this work, chronopotentiometry was used to investigate the polarization phenomena and to estimate the degree of heterogeneity of the composite ion-exchange membranes. Fig. 6 shows the chronopotentiogram of the composite membranes measured at low electrolyte concentration. Typical potential response was observed and there were three stages of potential changes. The first slow growth of potential is due to the decrease in the concentration in depleting solution near one side of the membrane surface. When the ionic concentration of depleting solution was dropped to zero, the potential significantly increased and finally reached a steady state. The starting potential (E_o) and maximum potential (E_{max}) for the composite of 2 wt% SS was much higher in comparison with those for other membranes due to the higher resistance of this membrane system. This result is in good agreement with the previous discussion that too high amount of SS interrupted the polymer matrix and its properties. The important characteristic from the chronopotentiogram is the transition time, τ , which is determined by the intersection of the tangents of the first and second states. The transition time can be expressed as a function of concentration and the diffusion coefficient of an electrolyte which is known as the Sand equation:

$$\tau = \frac{(C_0 z_i F)^2 \pi D}{4i^2 (\bar{t}_i - t_i)^2} \quad (6)$$

where i is the current density, C_0 is the concentration of electrolyte, and z_i is the valence of the i^{th} ion. However this equation was derived based on the assumption of the entire conductive membrane area. In the heterogeneous membranes, ion-exchange membranes consist of conducting and non-conducting phases. In this work, the fraction of conducting region, ϵ , was calculated using the derived Sand equation which was proposed by Choi *et al.*^{4,13,18} as shown below:

$$\epsilon = \frac{2i\tau^{1/2} (\bar{t}_i - t_i)}{C_0 z_i F (\pi D)^{1/2}} \quad (7)$$

The characteristic values from the chronopotentiograms are summarized in Table 2. The transition time increased with the increment of SS as a result of the increase of conducting regions. As the conducting regions increased, the better distribution of current line on the membrane surface was obtained. Thus, the local current density was lower and the interfacial concentration

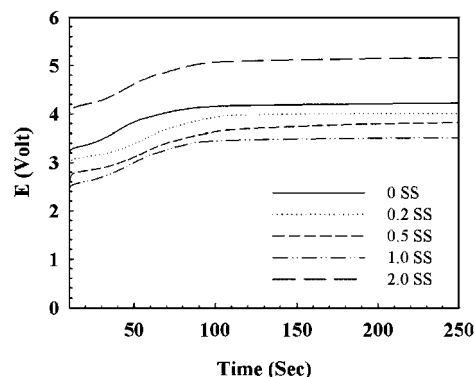


Fig. 6 Chronopotentiograms of the composite membranes.

Table 2 Characteristic values from chronopotentiogram of the composite ion-exchange membranes

Properties	0SS	0.2SS	0.5SS	1.0SS	2.0SS
Transport number	0.92	0.97	1.00	0.98	0.80
Transition time/s	34.5	48.5	50.0	40.3	36.0
E_0/V	3.21	2.97	2.60	2.46	4.00
E_{max}/V	4.22	4.01	3.86	3.53	5.17
$\Delta E/V$	1.01	1.05	1.27	1.07	1.17
ε	0.09	0.12	0.12	0.11	0.07

close to the conducting surface decreased gradually. As a consequence, the potential drop which depends on the interfacial concentration at the steady state became lower. It is clear from Table 2 that the optimal conditions were acquired from the membrane containing 0.5 wt% SS. Too much SS in the polymer matrix led to poorer conducting region and permselectivity of the membranes due to the aggregation of inorganic particles and enlarged pore sizes.

Conclusions

Incorporating small amounts of sulfonated mesoporous SiO₂ in sPES was proved to be an innovative strategy to improve the properties of ion-exchange sPES membranes. While IEC, conductivity, permselectivity of the membranes were enhanced, the composites still maintained excellent mechanical stability and sufficient thermal stability. Porosity of the membranes was improved through the particle cluster formation when SS was added into the organic polymers. Porosity and pore sizes were proved to play important roles as effective channels for ionic species to pass through which in turn affect the properties of the ion-exchange membranes especially the transport phenomena and the permeability of the membranes. Therefore the control of pore sizes and pore distribution in the membranes is of crucial importance and is highly recommended to further improve the IEC, conductivity and transport phenomena of the composite ion-exchange membranes. In order to better understand the effect of inorganic fillers on organic polymers and their membrane properties and also the correlation among them, further detailed characterization of the composite membranes such as porosity, the volume fraction of inorganic particles in the polymer matrix, and the interface interaction among them will be performed and presented in a future publication. This study provides evidences that small amounts of SS (0.2–1 wt% SS) could lead to drastically enhanced overall properties. This type of newly-developed composite sPES–SS membrane may be

promising candidates for use as ion-exchange membranes in electro dialysis water purification.

Acknowledgements

The financial support from Australian Research Council (through its ARC Centre of Excellence and Discovery programs), CSIRO Cluster Project, and Thai government (through Higher Educational Strategic Scholarship for Frontier Research Network) is gratefully acknowledged. Additional thanks are due to Robyn Webb for technical support on the ultramicrotomy and TEM.

Notes and references

- G. S. Gohil, R. K. Nagarale, V. V. Binsu and V. K. Shahi, *J. Colloid Interface Sci.*, 2006, **298**, 845–853.
- J. Balster, O. Krupenko, I. Punt, D. F. Stamatiadis and M. Wessling, *J. Membr. Sci.*, 2005, **263**, 137–145.
- R. Scherer, A. M. Bernardes, M. M. C. Forte, J. Z. Ferreira and C. A. Ferreira, *Mater. Chem. Phys.*, 2001, **71**, 131–136.
- M.-S. Kang, Y.-J. Choi, I.-J. Choi, T.-H. Yoon and S.-H. Moon, *J. Membr. Sci.*, 2003, **216**, 39–53.
- A. Elattar, A. Elmidaoui, N. Pismenskaia, C. Gavach and G. Pourcelly, *J. Membr. Sci.*, 1998, **143**, 249–261.
- D. Lu, H. Zou, R. Guan, H. Dai and L. Lu, *Polym. Bull.*, 2005, **54**, 21–28.
- D. Gomes, R. Marschall, S. P. Nunes and M. Wark, *J. Membr. Sci.*, 2008, **322**, 406–415.
- R. Marschall, I. Bannat, J. Caro and M. Wark, *Microporous Mesoporous Mater.*, 2007, **99**, 190–196.
- A. Elattar, I. Bannat, A. Feldhoff, L. Wang, G. Q. M. Lu and M. Wark, *Small*, 2009, **5**, 854–859.
- M. Wilhelm, M. Jeske, R. Marschall, W. L. Cavalcanti, P. Tolle, C. Kohler, D. Koch, T. Frauenheim, G. Grathwohl, J. Caro and M. Wark, *J. Membr. Sci.*, 2008, **316**, 164–175.
- T. Aritomi and M. Kawashima, U. S. Patent, US 6830671 B2, Tokuyama Corporation, Japan, 2004, pp. 1–14.
- R. K. Nagarale, G. S. Gohil and V. K. Shahi, *Adv. Colloid Interface Sci.*, 2006, **119**, 97–130.
- J.-H. Choi, S.-H. Kim and S.-H. Moon, *J. Colloid Interface Sci.*, 2001, **241**, 120–126.
- C. Klaysom, B. P. Ladewig, L. Wang and G. Q. M. Lu, *J. Membr. Sci.*, 2009, submitted.
- A. Noshay and L. M. Robeson, *J. Appl. Polym. Sci.*, 1976, **20**, 1885–1903.
- N. Lakshminarayanaiah, *Transport phenomena in membranes*, Academic Press, Inc., New York, 1969.
- G. S. Gohil, V. V. Binsu and V. K. Shahi, *J. Membr. Sci.*, 2006, **280**, 210–218.
- J.-H. Choi and S.-H. Moon, *J. Membr. Sci.*, 2001, **191**, 225–236.
- K. Sollner, *J. Dental Res.*, 1974, **53**, 267–279.
- S.-H. Choi, S.-Y. Park and Y. C. Nho, *Radiat. Phys. Chem.*, 2000, **57**, 179–186.
- E. Volodina, N. Pismenskaya, V. Vikonenko, C. Larchet and G. Pourcelly, *J. Colloid Interface Sci.*, 2005, **285**, 247–258.