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Preparation of cation-exchange hybrid membranes with multi-functional groups and their performance on alkali recovery

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ABSTRACT

Cation-exchange hybrid membranes have been prepared via the blending of sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) with poly(vinyl alcohol) (PVA), which is cross-linked with multisilicon copolymer of poly(acrylic acid-co-γ-methacryloxypropyl trimethoxy silane) (poly(AA-co-γ-MPS)). The SPPO phase, PVA phase, and multisilicon copolymer can provide the membranes with functional groups of $–SO_3Na$, –OH and –COOH, respectively. Hence, multi-functional groups are formed within the hybrid membranes. The hybrid membranes have a short-term thermal stability of 234–260°C, tensile strength (TS) of 12–13 MPa, and elongation at break of 27–49%. Membrane stability in alkaline solution is much affected by the content of SPPO. The membranes are potentially applied in diffusion dialysis (DD) for alkali recovery ($NaOH/Na_2WO_4$). The dialysis coefficients of NaOH (U_{OH}) are in the range of 0.0075–0.032 m/h, which are higher than those of commercial membranes and reported membranes. The separation factor can reach up to 21.2 at 25°C for the membrane containing 10 wt% SPPO. Meanwhile, the membrane shows relative stability during long-term DD process. Hence, the multi-functional groups are effective for the diffusion dialysis process.

Keywords: SPPO; Cation-exchange membrane; Hybrid membrane; Diffusion dialysis; Alkali recovery

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1. Introduction

Alkaline waste solutions are produced largely from the soda production, pulp and paper industry, printing and dyeing factory, tanneries, refineries factory, tungsten, and aluminum ore-smelting industries. These alkaline waste solutions are tentative to be treated by various methods including concentration and burning, acids neutralization, biological treatment, as well as membrane separation processes, such as diffusion dialysis (DD) [1–7]. The DD process has some unique advantages which are irreplaceable during applications. Firstly, DD is driven by the gradient concentration, which is low-energy consumption. Secondly, DD is easy to operate, thus the installation and operating costs are low. Finally, the DD process is more environmental friendly [3,8,9]. These advantages urge us to investigate the DD process further for the treatment of alkali waste solutions. DD was first developed into an industrial membrane process in Japan before 1993, and there have been more than 50

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factories using this technology in Japan [3,10]. Up to now, the DD process is mainly concentrated on the recovery of acids and valuable metals [3–5]. Although alkali recovery by the DD process had been expected for a long time, it became true only after the invention of membrane TSD10-300 by Japan Tokuyama soda Co., which enabled the industrial separation between AlO_2^- and OH^- ions [3]. Inspired by the success of $NaOH/NaAlO_2$ system, some work has been done on the $NaOH/Na_2WO_4$ system. In tungsten metallurgy, alkali autoclave is adopted for the decomposition of tungsten ore which will lead to a great quantity of dissociative alkaline and sodium tungstate in the steeping solution [11]. Direct discharge of alkaline solution will not only cause serious environmental pollution, but also waste energy and some useful components. Hence, the alkaline solution needs to be separated and recovered through the DD process. Nevertheless, the recovery of alkaline waste solution through membrane process is seldom reported at present, which is mainly attributed to the lack of suitable cation-exchange membranes. The membranes need to be stable, and have acceptable permeability and selectivity. However, the permeability of commercial cation-exchange membrane, such as sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) is at a low level (0.00137 m/h [4]), when compared with commercial anion-exchange membrane, such as DF–120 for acid recovery (0.009 m/h [12]). The low permeability may be mainly attributed to the single functional group within membrane matrix. For example, commercial SPPO membrane contains only $–SO_3Na$ groups, which are able to transport Na^+ ions effectively but are reluctant to transport OH^- ions due to electrostatic repulsion. Hence, NaOH in the waste solution is restricted to be transported through the membranes, and novel membrane structures need to be designed, while organic–inorganic hybrid membranes show some specific advantages for DD application, such as good thermal and chemical resistance and improved mechanical stability [12]. In our previous work, cation-exchange hybrid membranes were prepared from poly(vinyl alcohol) (PVA) and multisilicon copolymers. The multisilicon copolymer has a long main chain and many branched chains, with plenty of functional groups including the ion-exchange groups ($–SO_3Na$ or –COOH) and $–Si(OCH_3)_3$ groups. The $–Si(OCH_3)_3$ groups are able to cross-link with polymer chains to enhance membrane stability, while the ion-exchange groups can enhance membrane permeability. Hence, hybrid membranes containing various functional groups are prepared, including –COOH with –OH groups [5,13–15], and $–SO_3Na$ with –OH groups [16,17]. The –COOH or $–SO_3Na$ groups can transport Na^+ ions, and the –OH groups are beneficial for the transport of OH^- ions. The membranes have the dialysis coefficient of NaOH (U_{OH}) in the range of 0.002–0.012 m/h at room temperature, with the separation factors (S) higher than our previous membranes [13–16]. However, there are still several limitations including: (1) the permeability of the membranes containing Si–OH (silica) and $–SO_3Na$ groups is insufficient [4]. (2) –COOH groups are weak acidic; and (3) multisilicon copolymer with –COOH and $–Si(OCH_3)_3$ groups are easily to be gelled during polymerization [5]. In our following work, hybrid membranes were prepared from PVA and ternary multisilicon copolymer. The multisilicon copolymer contains acid anhydride and $–SO_3Na$ groups, which can combine with PVA-OH groups to enhance membrane DD performance [18]. However, the anhydride groups are less hydrophilic, which reduce their compatibility with PVA. The excessive dosage of multisilicon copolymer would cause phase separation in the final membranes. Besides, the multisilicon copolymer, together with the monomers, is difficult to be purified, which reduces membrane stability. Finally, the ratio of anhydride and $–SO_3Na$ groups is fixed, which hinders the following investigations on the effects of different functional groups.

In this work, multi-functional groups of $–SO_3Na$, –OH, and –COOH would be introduced into the hybrid membranes through the blending among SPPO, PVA, and multisilicon copolymer. The PVA-OH groups can not only enhance membrane hydrophilicity, but also are beneficial for the transport of OH^- ions. The content of SPPO–SO_3Na groups is variable to adjust membrane ion-exchange capacity. The –COOH groups of multisilicon copolymer are compatible with PVA during sol–gel and membrane-formation process. The multisilicon copolymer is prepared from copolymerization of acrylic acid (AA) and γ-methacryloxypropyl trimethoxy silane (γ-MPS) in the presence of SPPO to depress the gel formation. Despite its large solvent consumption, the preparation method has several advantages, such as low-temperature chemical process, well-controlled contents of sulfonated groups, and economical material precursors. The hybrid membranes are fully characterized for their physicochemical properties and DD performances. Besides, the influence of the multi-functional groups in the membrane for the transport of different ions is discussed.

2. Experimental

2.1. Materials

SPPO in Na^+ form was supplied by Tianwei Membrane Co. Ltd. Shandong of China. The molecular weight of SPPO, which can be evaluated from the molecular weight of PPO (90,000) and sulfonation degree, was about 117,000. PVA with an average degree of polymerization of 1,750 ± 50 was supplied by Shanghai Sinopharm Chemical Reagent Co. Ltd., China. The other reagents, including AA, γ-MPS, toluene, chloroform, and dimethyl formamide (DMF) were all of analytical grade and commercially obtained from domestic chemical reagent companies. Azobisisobutyronitrile (AIBN) was dissolved in ethanol (50℃), recrystallized in an ice bath, and then dried in a vacuum oven at room temperature. Deionized water was used throughout.

2.2. Preparation of poly(AA-co-γ-MPS) in the presence of SPPO

Certain amount of SPPO was dissolved in 100 mL DMF, then added with 30 mL chloroform and 40 mL toluene within 15 min, 2.3 mL (33 mmol) acrylic AA, and 7.9 mL (33 mmol) γ-MPS. The mixture was heated to 70℃, and then added with AIBN as an initiator every 12 h. The copolymerization was carried out at 70℃ for 24 h, and thus AIBN was added twice. The copolymer solution was concentrated by rotatory evaporation at 65℃ to remove chloroform and toluene, for the chloroform and toluene are incompatible with the following aqueous PVA solution. The mass ratios of SPPO with respect to AA and γ-MPS were varied from 10, 20, 30 to 40%. The dosage of AIBN was calculated by

$$m_{\mathrm{AIBN}} = (n_{\mathrm{AA}} + n_{\gamma-\mathrm{MPS}}) \times 0.6\% \times M_{\mathrm{AIBN}} + m_{\mathrm{SPPO}} \times 5\% \tag{1}$$

where n_{AA} is the molar quantity of AA, $n_{\gamma\text{-MPS}}$ is the molar quantity of γ-MPS, M_{AIBN} is the molar mass of AIBN, and m_{SPPO} is the weight of SPPO.

2.3. Preparation of the cation-exchange hybrid membranes

The concentrated solution containing poly(AA-co-γ-MPS) and SPPO produced form the last step was added into 80 mL 5% PVA solution at 60℃ within 0.5 h. The mixture solution was stirred at 60℃ for 24 h, then cast onto glass plates, and dried at room temperature under ventilated circumstance for two days. The formed film was peeled off from the glass plate, heated from 60 to 130℃ at the rate of 10℃/h, and kept at 130℃ for 4 h. The heat treatment can not only remove residual solvent, but also enhance the crosslinking between PVA and poly(AA-co-γ-MPS). Finally, transparent membrane was obtained. The mass ratio of poly(AA-co-γ-MPS) to PVA was fixed as 1:1, but the dosage of SPPO with respect to poly(AA-co-γ-MPS) was increased from 10, 20, 30 to 40%. Hence, the membranes can be designated as M10, M20, M30, and M40, respectively. Membranes M10–M40 have similar thicknesses of 102–110 μm. The membrane preparation process is shown in Fig. 1.

2.4. Characterizations

2.4.1. FTIR spectra, TGA analysis, mechanical property, and morphology

FTIR spectra of the membrane samples were recorded using an FTIR spectrometer (Vector 22, Bruker) with a resolution of 2 cm^{-1} and a spectral range of 4,000–400 cm^{-1}. TGA was conducted on a Shimadzu TGA-50H analyzer under air flow, with a heating rate of 10℃/min. The tensile properties were measured using Dynamic Thermal Mechanical Analyzer (DMA Q800) at room temperature with strip-shape specimens. The ramp force is 0.5000 N/min and the maximum force can reach 18 N. TS and elongation at break (E_b) were recorded. The membrane morphology was observed through scanning electron microscopy (XT30 ESEM-TMP PHILIP). Before observation, the membranes were fractured in liquid nitrogen and then coated with gold.

2.4.2. Water uptake and contact angle

Water uptake (WU*)* was measured to investigate the membrane hydrophilicity. The membrane sample was dried and weighed. Then it was immersed in water at room temperature for two days, and weighed after quick removal of surface water. The value of WU was calculated as the relative weight gain per gram of the dry sample.

Contact angle (CA) was measured based on dynamic sessile drop at room temperature, using a static and dynamic optical contact Angle Goniometers (SL 200B, KINO, USA). For the sessile-drop method, 2 mL of DI water was dropped onto a dry membrane surface using a microsyringe, and the CA was measured. A minimum of at least 10 contact angles were averaged to ensure that a reliable value was obtained for this method.

2.4.3. Ion-exchange capacity and proton conductivity

Ion-exchange capacities (IECs) were measured to investigate the contents of –COOH and $–SO_3Na$

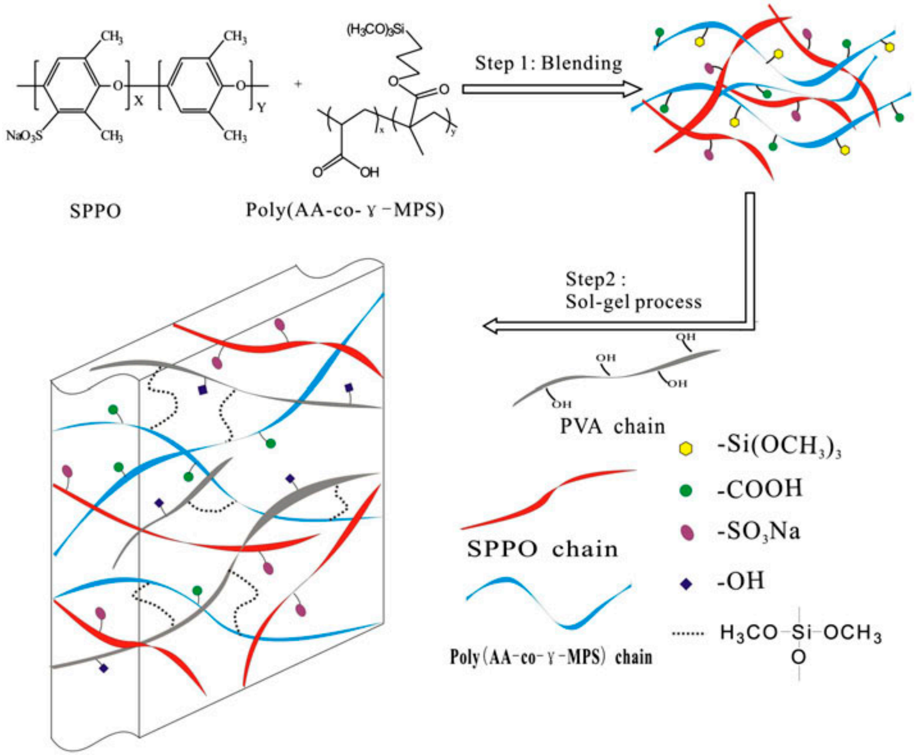

Fig. 1. Illustration for the preparation of the cation-exchange hybrid membranes containing multi-functional groups.

groups. Dry membrane sample was accurately weighed and converted to H^+ form in 1.0 mol/L HCl for 48 h. Excessive HCl was washed off with water, and then the sample was immersed in 0.04 mol/L NaOH for 48 h. Cation exchange capacity was obtained by determining the decrease of NaOH concentration through titration with 0.04 mol/L HCl.

Proton conductivity was measured using a standard four-electrode AC impedance technique on a PGSTAT302 N Autolab (Metrohm China Ltd.) at 30°C in water. The impedance was determined using galvanostatic mode with AC current amplitude of 0.1 mA over a frequency range from 10 W Hz to 1,000 Hz. Using a Bode-type plot, the frequency region over which the impedance had a constant value was checked, and the corresponding resistance (R) was obtained from a Nyquist plot. The in-plane conductivity (σ) was calculated according to the following equation:

$$\sigma = \frac{L}{RWd} \tag{2}$$

where L was the distance between the potential-sensing electrodes, W and d were the width and thickness of the membrane under test conditions, respectively.

2.4.4. Alkaline resistance in 65°C NaOH solution

Dry membrane sample was firstly weighed as m_1 and immersed in 65°C 2 mol/L NaOH solution for 60 h. Then the sample was taken out and immersed in water for one day, during which the water was refreshed 3–4 times. The wet sample was quickly wiped with filter paper to remove its surface water, and then weighed as m_2. Swelling degree was calculated from the following equation:

$$\text{Swelling Degree} = \frac{m_2 - m_1}{m_1} \times 100\% \tag{3}$$

2.4.5. Diffusion dialysis performance

DD running was carried out using our previous method [4,5,14–16] to investigate the dialysis coefficient of NaOH (U_{OH}) and S at different temperatures. The predominant counter-ions existing in tungsten deposit, such as Fe^{2+} and Mn^{2+} had been precipitated under alkaline condition. The waste solution, therefore, was mainly composed of NaOH and Na_2WO_4 and the simulated solution was in tally with the actual situation. The membrane sample was clipped in a two-compartment cell with the effective area of 6 cm^2.

One compartment was used as the dialysate side, and was filled with the mixture solution of NaOH (1.0 mol/L) and Na_2WO_4 (0.10 mol/L). The other compartment was used as the diffusate side, and was filled with water. During the diffusion test, both compartments were maintained by a water bath at different temperatures (25, 35, 45, and 55℃) and stirred at an identical rate to minimize concentration polarization effects. Diffusion was allowed for 1 h and then the dialysate and diffusion solutions were removed from both sides of the cell. OH^- concentration in the solution was determined by titration with HCl solution, while WO_4^{2-} concentration was determined by thiocyanate spectrophotometric method [19].

The separation factor (*S*) with respect to one species over another is given as the ratio of dialysis coefficients (*U*) of the two species present in the solution. *U* can be calculated by the following formula:

$$U = \frac{M}{At\Delta C} \tag{4}$$

where *M* is the amount of component transported in moles, *A* is the effective area in square meters, *t* is the time in hours, and Δ*C* is the logarithm average concentration between the two chambers in moles per cubic meter and defined as below:

$$\Delta C = \frac{C_f^0 - (C_f - C_d)}{\ln[C_f^0/(C_f - C_d)]} \tag{5}$$

where C_f^0 and C_f are the feed concentrations at time 0 and *t*, correspondingly, and C_d the dialysate concentration at time *t*.

3. Results and discussion

3.1. FTIR spectra

The FTIR spectra of the hybrid membranes are shown in Fig. 2. A characteristic strong and broad band appears in the range of 3,450–3,650 cm^{-1} corresponding to –OH stretching vibrations, including C–OH, Si–OH, C(=O)–OH, and $–SO_3H$ groups [15]. The band at ~1,730 cm^{-1} is attributed to the carbonyl stretching vibration (νC=O) from the ester groups and carboxylic acid groups, while absorptions in the range of 1,000–1,200 cm^{-1} should be attributed to the stretching of dialkyl ether, diphenyl ether, sulfonate groups [20,21], and siloxane bands [22]. The band at 1,637 cm^{-1} is attributed to the stretching vibration of aromatic C=C groups. The band becomes strong from membranes M10 to M40, indicating an increase in the content of SPPO.

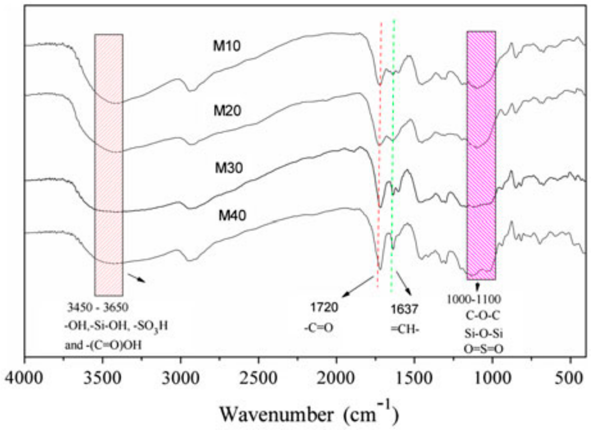

Fig. 2. FTIR spectra of membranes M10–M40.

3.2. Thermal stability (TGA analysis)

The short-term thermal stability was investigated by TGA, as shown in Fig. 3. The membranes generally have three weight-loss steps as the temperature increases. The first step is the weight loss before 130℃. Since the membranes have been heated at 130℃ for 4 h during the preparation process, the first weight loss should be mainly attributed to the evaporation of absorbed water, which is supposed to be bounded with the functional groups via hydrogen bonds [20]. The first weight loss is neglected for the determination of thermal degradation temperature (T_d, defined as the temperature at 5% weight loss), as shown in Table 1. The second step is the weight loss between 240 and 320℃, which should be mainly attributed to the decomposition of $–SO_3Na$ groups [4,20,23,24] together with their polymer chain of SPPO, since $–SO_3Na$ group is less stable than –COOH group

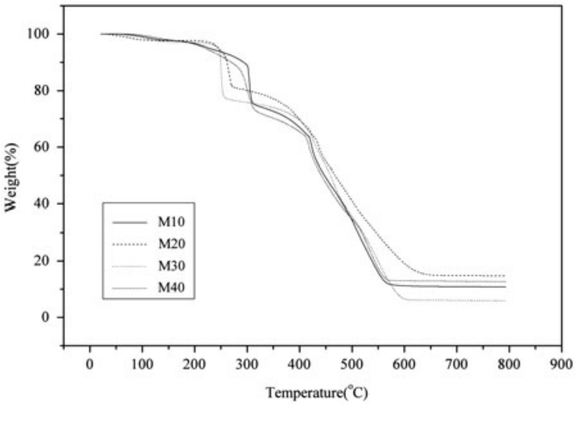

Fig. 3. TGA diagrams of membranes M10–M40.

in some cases [25]. The last step is the degradation of poly(AA-co-γ-MPS) near 400℃.

Table 1 shows that as the SPPO content increases, the T_d values decrease from 260 to 234℃. The values are higher than those of other cation exchange membranes (150–250℃ [23,24]), which are mainly attributed to the introduction of inorganic silica network from poly(AA-co-γ-MPS) and the stable –COOH groups [4,5,26]. The reduced thermal stability from membranes M10 to M40 may be partly attributed to the relatively reduced inorganic silica content. Besides, the SPPO component may also have “impediment effect” for the cross-linking between PVA and poly (AA-co-γ-MPS) [17].

3.3. Mechanical properties

Membrane mechanical properties, including TS and elongation at E_b, are shown in Fig. 4. The TS values are in the range of 12.5–13.3 MPa, with the E_b values of 28–49%. Compared with the epoxy polymer mesocomposites containing 12% (w/w) silica doping (3.41 Pa, 33.8% [27]), the mechanical properties of the hybrid membranes are favorable.

M30 has the highest TS (13.3 MPa) and E_b values (49%), indicating that proper dosage of SPPO is beneficial to membrane mechanical properties. The SPPO phase has favorable mechanical properties [28] and is compatible with PVA phase [17], which may enhance membrane strength and flexibility. However, excessive dosage of SPPO may cause phase separation and, thus, deduced flexibility [17].

3.4. Membrane morphologies

Morphologies of membrane cross sections have been observed through SEM. Membranes M10 and M30 are taken as examples and shown in Fig. 5. No obvious particles and phase separation can be observed, indicating the favorable compatibility among SPPO, PVA, and poly(AA-co-γ-MPS). The favorable compatibility may be attributed to the high polarity and strong/weak interactions among multifunctional groups. The –COOH and –Si$(OCH_3)_3$ groups from multisilicon copolymer can cross-link with PVA through chemical bonds or weak bonds, while the SPPO component can reduce the congregation of silica within PVA matrix.

Table 1
Thermal degradation temperature (T_d) of hybrid membranes M10–M40

Membrane	M10	M20	M30	M40
T_d (℃)	260	256	248	234

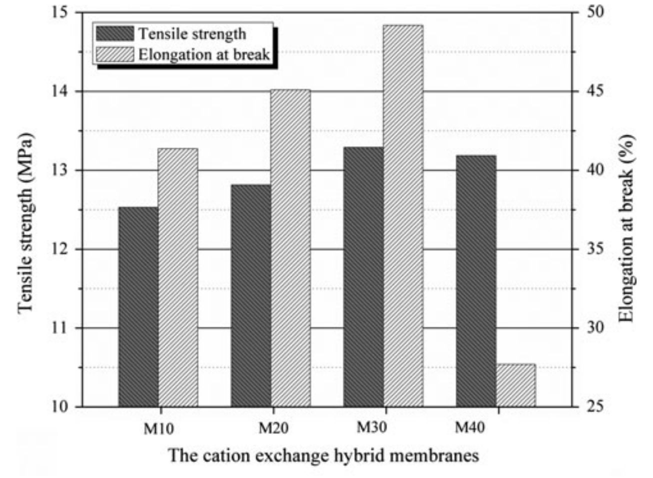

Fig. 4. TS and elongation at E_b of membranes M10–M40.

3.5. Water uptake and contact angle

Both the WU and CA values are shown in Table 2. WU values increase from 33 to 61% as the SPPO content increases. The enhanced hydrophilicity is mainly attributed to the increased –SO_3Na groups, reduced silica content, and the cross-linking degree, for the SPPO component may be disadvantageous to the cross-linking between PVA and poly(AA-co-γ-MPS). The CA values decrease from 80° to 66° as the content of SPPO increases. The decreasing CA values also indicate that the membrane hydrophilicity decreases due to the incorporation of SPPO, which is in accordance with the water uptake.

3.6. Ion-exchange capacity and proton conductivity

The Ion-exchange capacity (IEC) and proton conductivity are shown in Fig. 6. The IEC values increase from 1.22 to 1.43 mmol/g as the SPPO content increases. The IEC values are higher than those of our previous membranes without SPPO (0.76–0.90 mmol/g) [5], since –SO_3H groups are more acidic than previous pure –COOH groups and have no consumption in the whole sol–gel process.

As the SPPO content increases, the proton conductivity increases from 17.3 to 36.9 mS cm^{-1} at 30℃ in water. The increasing proton conductivity should be

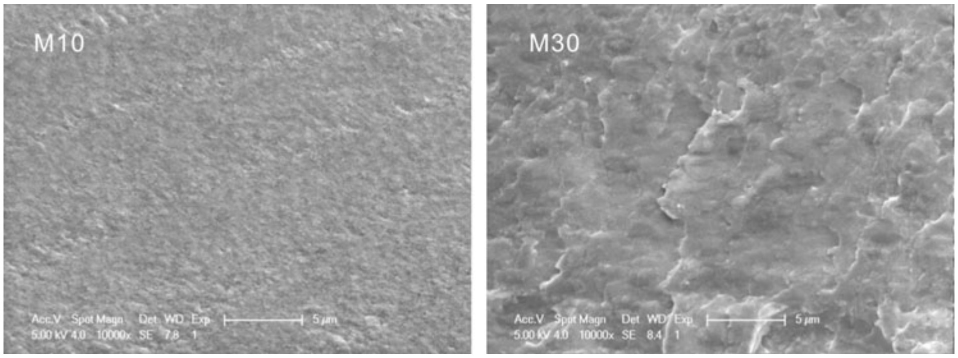

Fig. 5. The SEM image of the membrane cross-sections.

Table 2
WU and CA of membranes M10–M40

Membrane	M10	M20	M30	M40
WU (%)	33	39	45	61
CA (°)	80	75	72	66

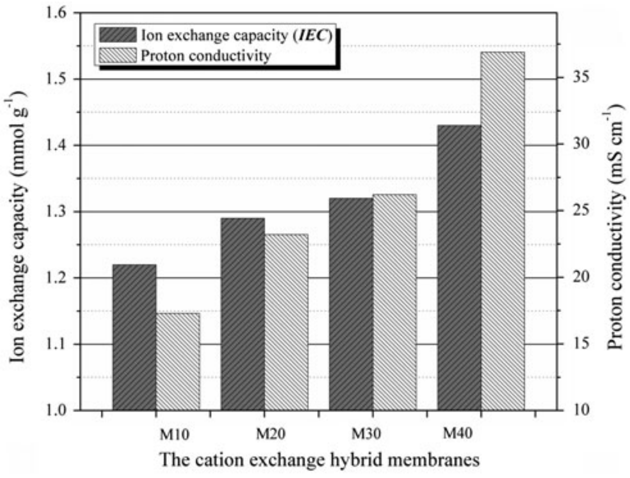

Fig. 6. IEC and proton conductivity of membranes M10–M40.

attributed to the enhanced IECs and WU, both of which are beneficial for the transport of H^+ ions.

3.7. Swelling degree in 65°C NaOH solution

Since the hybrid membranes are intended for the DD process at different temperatures and that PVA can be readily swelled or even dissolved in hot water, the membrane stability in alkaline solution at elevated temperature will be a major concern. For evaluating the membrane stability, the membranes are immersed in 2 mol/L of NaOH solution at 65°C for 60 h, and the swelling degrees (SD) are shown in Table 3.

The swelling degrees are in the range of 92–181%, which are comparable with those of membranes immersed in 65°C water (110–165% for 60 h [18]). Nevertheless, the present NaOH solution is much more corrosive than previous pure water, indicating that the swelling resistance of our present membranes is acceptable. Besides, as the PVA is dissolvable in hot water, the membrane swelling has been restrained through the cross-linking of multisilicon copolymer poly(acrylic acid-co-γ-methacryloxypropyl trimethoxy silane) (poly(AA-co-γ-MPS)). However, the conventional cross-linking of aldehyde treatment may be infeasible due to the great reduction of permeability in our previous report [17].

3.8. Diffusion dialysis performance

3.8.1. Dialysis coefficient of NaOH (U_{OH})

The membranes have taken the DD process to separate $NaOH/Na_2WO_4$ solution at 25–55°C. The dialysis coefficient of NaOH is shown in Fig. 7.

As the temperature increases from 25 to 55°C, the U_{OH} values increase from 0.0075–0.0189 to 0.0114–0.0319 m/h. The enhanced U_{OH} values can be explained by the swelled membrane structure and enhanced ion mobility [4,5,26]. The U_{OH} values of membrane M40 seems less affected by the temperature, which may be partly attributed to the lower swelling degrees in NaOH solution (91% in section 3.7).

Table 3
Membrane SD in 65°C 2 mol/L NaOH for 60 h

Membrane	M10	M20	M30	M40
SD (%)	115	116	181	92

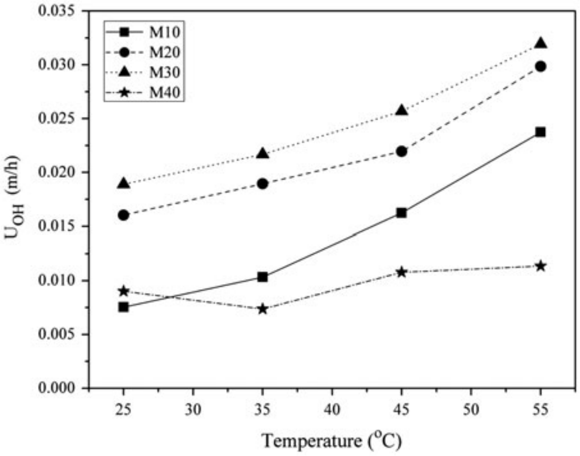

Fig. 7. Dialysis coefficients of NaOH (U_{OH}) with respect to the temperature.

The U_{OH} values (0.019 m/h at 25°C) are higher than those of previous SPPO/SiO_2 hybrid membranes (0.0022 m/h at 25°C [4]) and PVA/SiO_2 membranes [15], which should be mainly attributed to the effect of multi-functional groups. The functional groups are essential for the ion transport. Previous SPPO/SiO_2 membranes contain only –SO_3Na groups together with some Si–OH groups in some cases. Though the –SO_3Na groups are effective for the transport of Na^+ ions, the OH^- ions have less chances to transport through the membrane. Previous SPPO/PVA [17] membranes containing double functional groups of –OH and –SO_3Na have the higher U_{OH} values (0.007–0.013 m/h) than the commercial SPPO membrane [4]. Though the double functional groups can enhance membrane permeability significantly, the membrane structure may still need to be optimized. Our present membranes contain multi-functional groups including –SO_3Na, –COOH, and –OH. The multi-functional groups are beneficial for the transport of both Na^+ and OH^- ions.

The possible transport process of ions through the hybrid membrane is shown in Fig. 8. The –SO_3Na groups are strong and ion exchangeable with cations, and thus effective for the transport of Na^+ ions. The –OH groups can accelerate the transport of OH^- ions not only by enhancing the membrane hydrophilicity but also through weak interactions. The direct transport of OH^- ions through PVA-OH groups can be proved as following. (1) Theoretically, both –OH groups and OH^- ions can form hydrogen bonds with water molecules in aqueous solution [29,30], while the OH^- ions can be transported through the formation and cleavage of hydrogen bond with water molecules according to the possible dominant transport mechanisms for OH^- ions, such as Grotthuss mechanism, diffusion, migration, and convection mechanisms [31]. (2) Practically, though our present membranes have similar water uptake with SPPO/SiO_2 membranes (50%), the dialysis coefficients of NaOH (U_{OH}, 0.0075 m/h) are much higher than those of SPPO/SiO_2 membranes (0.002 m/h). Besides, though our membrane IECs (1.22–1.43 mmol g^{-1}) are lower than that of pure SPPO membrane (2.28 mmol g^{-1}), their U_{OH} values are 5–13 times higher than that of SPPO membrane (0.0014 m/h) [4]. The results show that except the IEC and membrane hydrophilicity, the assistant effect of –OH groups also plays an important role on the transport of OH^- ions.

Hence, the –OH groups can be regarded as "assistant functional groups." The –COOH groups are weak acidic, and thus weak ion exchangeable with cations. Besides, they may also interact with OH^- ions through weak interaction, such as hydrogen bonds. The –COOH groups, therefore, can be regarded as both ion-exchange groups and "assistant" groups, and may be effective for the transport of both Na^+ and OH^- ions.

3.8.2. Separation factors

Separation factors (S), defined as the ratio of U_{OH} to U_{WO4}, is shown in Fig. 9. The *S* values are in the range of 6.0–21.2. Though the S values are not very high, membrane M10 is still comparable with commercial anion-exchange DF–120 membrane in acid recovery (18.5 at 25°C) [26].

The S values decrease as the temperature increases except for membrane M40, which should be partly attributed to the different SD at different temperatures. Membrane SD increases as the temperature increases, which enhances the ion transport rates of both OH^- and WO_4^{2-} ions. As the OH^- ions have lower volume and valence state, proper swelling may be more favorable to the transport of OH^- ions, while excessive swelling would affect the transport of WO_4^{2-} ions more significantly. Hence, membranes M10–M30, due to their higher swelling degrees, have reduced S values as the temperature increases. Membrane M40, due to its lower swelling degrees, has higher S values at 35–45°C. Besides, membrane with lower swelling degrees may be more stable in alkaline solution, and thus its selectivity is more stable.

3.8.3. Long-term diffusion dialysis performance at 25°C

The fouling nature and membrane stability are investigated through long-term DD running. The DD

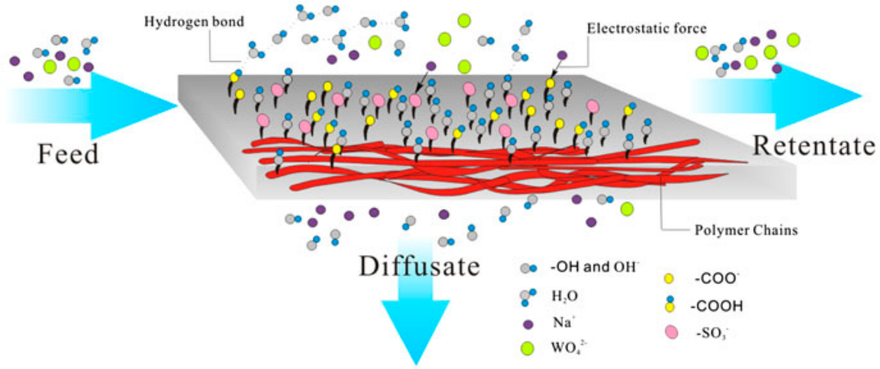

Fig. 8. Possible transport process of different ions through the hybrid membrane with multi-functional groups.

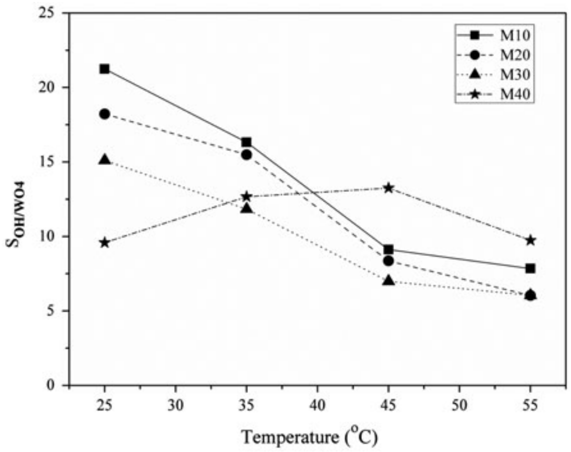

Fig. 9. S of membranes M10–M40 at 25–55˚C.

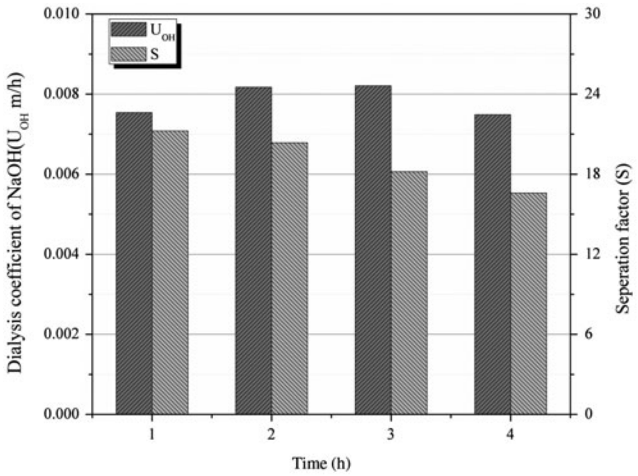

Fig. 10. DD performance of membrane M10 at 25˚C for 4 h.

running process is run for 4 h at 25˚C by M10, as shown in Fig. 10. The U_{OH} values are in the range of 0.0075–0.0082 m/h, indicating the relative stability during the DD process. The stability should be mainly attributed to the acceptable membrane stability and the anti-fouling DD process. DD is a process driven by concentration gradient with no significant pressure, which is unlike the processes of ultrafiltration and microfiltration. Hence theoretically, the membrane pollution during the DD process is less serious. Besides, DD running is done to separate NaOH/Na_2WO_4 solution, and the solution contains no large-size molecules like bovine serum albumin.

The S values decrease from 21.2 to 16.6 since the swelling effect of membrane in corrosive NaOH solution could lead to the loose structure of membrane and the leakage of Na_2WO_4. Meanwhile, when the operation time reached 4 h, the concentration gradient decreased and the DD process could be suppressed. These two factors resulted in the decreased selectivity of M10.

4. Conclusion

Cation-exchange hybrid membranes containing multi-functional groups are prepared from copolymerization of AA and γ-MPS in the presence of SPPO, followed by sol–gel reaction with PVA. The membranes have thermal degradation temperatures of 234–260˚C, water uptakes of 33–61%, IECs of 1.22–1.43 mmol/g, conductivities of 17.3–36.9 mS cm^{-1}, and swelling degrees of 92–181% after the erosion in 65˚C NaOH solution.

DD is taken for separating NaOH/$NaWO_4$ solution at 25–55˚C. The U_{OH} values are in the range of 0.0075–0.032 m/h, higher than the values of conventional cation-exchange membranes. After 4 h of DD operation at 25˚C, the membrane 10 still has a U_{OH} value of 0.0075 and the S value can reach up to 16.6. The multi-functional groups have a synergistic effect on the transport of NaOH. The $-SO_3Na$ groups are effective for the transport of Na^+ ions, the –OH groups are beneficial to the transport of OH^- ions, and the –COOH groups can act as both weak ion-exchange groups for Na^+ ions and as assistant functional groups for OH^- ions. Further investigations will be concentrated on the distribution of different functional groups, ion transport mechanisms, and, the practical DD applications.

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List of symbols

SPPO — sulfonated poly(2,6-dimethyl-1,4-phenylene oxide), which contains $-SO_3Na$ groups
PVA — polyvinyl alcohol
AA — acrylic acid
γ-MPS — γ-methacryloxypropyl trimethoxy silane
DD — diffusion dialysis
U_{OH} — dialysis coefficient of NaOH
S — separation factor
T_d — temperature at 5% weight loss in TGA
TS — tensile strength
E_b — elongation at break
IEC — ion-exchange capacity
WU — water uptake
CA — contact angle
SD — swelling degree

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