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PVA–PSSS membranes for alkali recovery through diffusion dialysis: effect of alkoxysilanes

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ABSTRACT

Poly(sodium-p-styrene-sulfonate) (PSSS) is synthesized by the method of ARGET ATRP, then mixed with polyvinyl alcohol (PVA), and cross-linked with different alkoxysilanes, that is, tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APTS), or γ-glycidoxypropyltrimethoxysilane (GPTS). The obtained flexible cation-exchange membranes have water uptakes (W_R) of 46.8–120.7% and ion-exchange capacities (IEC) of 1.03–1.64 mmol/g. The category of the alkoxysilanes strongly influences the membrane properties. The membrane from GPTS has the highest thermal stability with T_d (temperature at 5% weight loss) of 267.4℃, the highest IEC, and the lowest swelling degree in 65℃ water, which is due to the dual cross-linking of Si–O–Si and C–O–C between GPTS and PVA. When applied for diffusion dialysis (DD) process of $NaOH/Na_2WO_4$ mixture, the membranes exhibit excellent alkali flux. The OH^- dialysis coefficients (U_{OH}) are in the range of 0.0072–0.0208 m/h, higher than PVA blank membrane (0.0077 m/h) or commercial poly(2,6-dimethyl-1,4-phenylene oxide)-based membrane (0.004 m/h) (Tianwei Membrane Co., Ltd., Shandong of China). The separation factors (S) are in the range of 16.8–25.7, higher than PVA–PSSS membrane cross-linked with formaldehyde ($S = 8.0$). Hence, the membranes can be potentially applied in DD process for alkali recovery.

Keywords: Polyvinyl alcohol (PVA); ARGET ATRP; Cation-exchange membrane; Diffusion dialysis (DD); Alkali recovery

1. Introduction

Diffusion dialysis (DD) has been developing quickly during the last decades because of its advantages of simple operation, low energy consumption, no pollution to the environment, low installation, and operating cost [1,2]. Hence, a series of ion-exchange membranes (IEMs) have been initiated and commercially manufactured for DD [3,4]. For instance, inorganic acids (such as HCl, HNO_3, H_2SO_4) and organic acids (such as carboxylic acid, propionic acid, and lactic acid) have been successfully recovered with the use of commercial IEMs based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), polysulfone (PSf), and

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polystyrene (PS) [5–7]. As a contrast, alkali (such as sodium hydroxide (NaOH) and KOH) treatment with DD lags behind. One crucial reason is the much lower diffusivity of OH^- ions as compared with H^+ ions [8]. Developing IEMs with high permeability to OH^- ions is a critical challenge for alkali DD process.

The nature of the membrane matrix needs to be carefully selected and designed to meet the above-mentioned challenge. The matrices of commercial PPO, PSf, and PS IEMs are of hydrophobic nature and hence are disadvantageous to the transport of hydrated ions. For instance, the dialysis coefficient of HCl (U_H) through PPO-based IEMs is at a low level (~0.006 m/h at 15˚C and 0.009 m/h at 25˚C) [9]. One DD device with 500 m^2 membrane can only treat 6 m^3 acidic solution a day during practical application [10]. The permeability of the PPO-based IEM for NaOH is even lower (U_{OH} = ~0.004 m/h) [11]. Hence, membranes based on hydrophilic polymers are desirable for enhancing alkali permeability.

Polyvinyl alcohol (PVA) is a common hydrophilic polymer and has recently been tried for DD. It can provide a membrane matrix friendly for the transport of hydrated ions, and furthermore, the –C–OH groups can accelerate the transport of H^+ and OH^- ions through hydrogen bonding [12]. However, the high hydrophilicity may induce excessive swelling behavior, and there are no ion-exchange groups in PVA chains, both of which hinder the application of PVA in practical DD process. Accordingly, the membrane swelling resistance and the variety/content of the ion-exchange groups need to be considered.

For increasing the swelling resistance, PVA membranes are commonly cross-linked with aldehyde, acid, and etc., during which process the –OH groups of PVA chains (PVA–OH) undergo aldolization or esterification reaction [13,14]. The content of PVA–OH groups is decreased accordingly, which is disadvantageous for DD application. For introducing ion-exchange groups into the membrane, PVA can be mixed with polyelectrolyte such as poly(sodium-p-styrene-sulfonate) (PSSS) or poly(styrene sulfonic acid) (PSSH) [15,16]. Nevertheless, PSSS or PSSH is strongly water soluble due to the highly hydrophilic $–SO_3Na$ or $–SO_3H$ groups. Hence, the membrane is highly swelled in aqueous solution and cannot be directly used for water treatment. For suppressing the swelling behavior, aldehyde, acid, or dibromoethane cross-linking has to be conducted afterward [15–17], and the obtained membrane can be used as one layer for bipolar membranes, or as nanofiltration, fuel cell membranes. However, the PVA–OH groups are partly consumed during the cross-linking process. Accordingly, PVA–PSSS or PVA–PSSH membranes have not been applied in DD process.

The application of PVA-based membranes for DD has been initiated in our laboratory by the use of multisilicon copolymers as both cross-linking agents and ion-exchange component providers. For instance, poly (sodium styrene sulfonate (SSS)-co-γ-MPS) or poly(vinylbenzyl chloride (VBC)-co-γ-MPS) is synthesized from copolymerization of SSS or VBC with γ-methacryloxypropyl trimethoxy silane (γ-MPS) [18,19]. The $–Si(OR)_3$ groups from γ-MPS can self-cross-link to form Si–O–Si bonds and also partially cross-link with PVA to form Si–O–C bonds [20]. Meanwhile, the $–SO_3Na$ groups from SSS can provide cation-exchange properties, and the $–CH_2Cl$ groups from VBC provide anion-exchange properties after quaternization. However, the preparation of the multisilicon copolymers is through conventional radical polymerization technique, which lacks effective control over the polymer architectures, compositions, and functionalities [21]. Another problem with multisilicon copolymer is that they tend to become gel during preparation and preservation [12,22] due to the pre-hydrolysis and condensation of the $–Si(OR)_3$ groups, which is disadvantageous to practical applications.

PSSS is synthesized through activators regenerated by electron transfer atom transfer radical polymerization (ARGET ATRP) in this study. Subsequently, it is mixed with PVA, followed by cross-linking with different alkoxysilanes to yield IEMs for DD application. Compared with traditional anionic polymerization, ARGET ATRP does not require strict purification of monomers and solvents [23] and shows promising prospective in designing well-defined polymeric materials [24]. The obtained PSSS contains abundant $–SO_3Na$ groups and hence can increase membrane ion-exchange capacities (IEC). Cross-linking with alkoxysilane instead of aldehyde can be more environmental friendly. Though the PVA–OH groups can be partly consumed when cross-linking with alkoxysilanes, the self-cross-linking between –Si–OH groups is predominant because of the higher activity of –Si–OH groups. Accordingly, the consumption of PVA–OH is lower than that in formaldehyde cross-linking. Besides, the –Si–OH groups are also favorable for OH^- ions permeability. The physico-chemical properties of the membranes are characterized and correlated with the DD performances.

2. Experimental

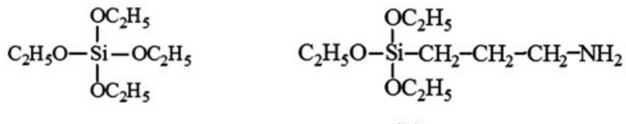
2.1. Materials

PVA, with average degree of polymerization 1,750 ± 50, was supplied by Shanghai Yuanli Chemical Co., Ltd. (China). Pre-weighed PVA was immersed in water at room temperature for 1 d, then heated to around ~102°C at the rate of 10°C/h, and kept at 102°C for around 4 h. The homogenous and transparent solution (5 wt%) was cooled to room temperature before use. SSS was purchased from Zibo Xingzhilian Chemistry Co., Ltd. It was purified by dissolving in a mixture of water/ethanol (90/10 v/v) and then recrystallizing under vacuum. Copper (II) bromide ($CuBr_2$, AR), 2-bromoisobutyrate (EBiB, 98%), ascorbic acid (AsAc, AR), and N,N,N´,N´,N´´-pentamethyldiethylenetriamine (PMDETA, 99%) were supplied by domestic chemical reagents companies. Three different alkoxysilanes, tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APTES), and γ-glycidoxypropyltrimethoxysilane (GPTS), were used, and their structures were illustrated in Fig. 1. Distilled water was used throughout the experiments.

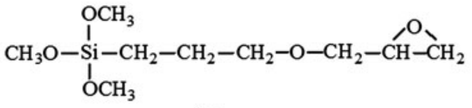
2.2. Preparation of PSSS via ARGET ATRP

SSS (2.0 g) was dissolved completely in water/methanol (50/50 v/v, 30 mL) at 60°C in a dried 100 mL conical flask. $CuBr_2$ (0.0034 g), PMDETA (0.156 mL), and EBiB (0.43 mL) were then added and completely dissolved. The mixture was degassed by N_2 bubbling for an hour. The mixture, together with 0.013 g AsAc, was added into a sealed tube quickly. Three freeze–pump–thaw cycles were performed to remove oxygen. After the tube was flame-sealed under vacuum, it was stirred in 80°C oil bath for 24 h. The polymerization reaction was stopped by cooling and exposure to air. Then the mixture was added to tetrahydrofuran for precipitation. Subsequently, it was centrifuged, washed, and dried at 60°C until constant weight.

Gel permeation chromatography (GPC) analysis of the water soluble PSSS was performed on a P230 (Elite, Dalian) system. SEC-AQ-150 (XIYU Tech, Shanghai) columns (guard, 104 and 103 Å) were used, and a 0.2 PBS aqueous solution was used as the eluent. The columns were operated at 40°C with a flow rate of 0.6 mL/min.



(a) TEOS (b) APTS



(c) GPTS

Fig. 1. The chemical structure of the three alkoxysilanes.

2.3. Preparation of the cation-exchange membranes

PSSS (0.5 g) was dropped into 5% PVA solution (20 mL) within 20 min. The mixture was transparent and homogeneous with no precipitation. Afterward, 4.8×10^{-3} mol TEOS, APTES, or GPTS was added, and then the mixture was stirred at 60°C for 6 h, 2 h, or 20 min, respectively, for cross-linking. The casting solution was then coated on a polytetrafluoroethylene plate. After drying at room temperature for 2 d, the film was peeled off from the plate and heated from 60 to 130°C at the rate of 10°C/h, and kept at 130°C for 4 h to get the membrane. The cross-linking time was shortened for APTES or GPTS, because the solution viscosity was increased and might become gel after long-time reaction. In particular, for GPTS, the tendency to become gel was more serious and the reaction time was controlled as 20 min. The membranes from TEOS, APTES, and GPTS were noted as PVA–PSSS–T, PVA–PSSS–A, and PVA–PSSS–G, respectively. The thickness of the PVA–PSSS–G membrane was ~0.252 mm, higher than PVA–PSSS–T (~0.106 mm), PVA–PSSS–A (~0.093 mm) membranes because of the higher viscosity of the casting solution.

Formaldehyde cross-linking was also tried as comparison. PVA and PSSS mixture was cast, and then dried at room temperature for 2 d. The obtained film was immersed in a solution containing formaldehyde (12.98 mL), sulfuric acid (7.07 mL), and water (47.0 g) for 2 h at 60°C. Afterward, the membrane was washed with distilled water for three times, and then dried at room temperature overnight. The membrane with thickness of ~0.103 mm was noted as PVA–PSSS–F.

2.4. Membrane characterizations and DD

Fourier transform infrared (FTIR) spectroscopy of the membrane samples was recorded using FTIR spectrometer (Vector 22, Bruker) with a resolution of 2 cm^{-1} and a spectral range of 4,000–400 cm^{-1}.

Thermogravimetry analysis (TGA) was conducted on a STA449F3 analyzer under air flow, with a heating rate of 10°C/min.

Water uptake (W_R) was measured to investigate the membrane hydrophilicity. The membrane samples were dried and weighed. Then they were immersed in water at 25°C for 2 d and weighed after removal of the surface water with filter paper. W_R was calculated according to the following equation:

$$W_R = \frac{W_w - W_d}{W_d} \times 100\% \qquad (1)$$

where W_w was the weight of the wet membrane samples after immersion in water at room temperature, and W_d was the weight of the dry membrane samples.

IEC was measured to investigate the content of $-SO_3Na$ groups. The dry membrane sample was accurately weighed and converted to H^+ form in 1.0 mol/L HCl for 1 d. Excessive HCl was washed off with water for 4–6 times within a day. Then the sample was immersed in 0.05 mol/L NaOH for 2 d. Cation-exchange capacities per dry membrane samples were obtained by determining the decrease of NaOH through titration with 0.05 mol/L HCl.

DD running was conducted at room temperature following previous reported procedures [11]. One two-compartment cell was filled with 100 mL water and 100 mL mixture of NaOH (1.0 mol/L) and Na_2WO_4 (0.1 mol/L) on either side. The membrane sample (~6 cm^2) was fastened in between, and the diffusion process was allowed for 1 h. The previous research has shown that the DD performances are generally stable with the time [25], and hence, the diffusion time was allowed relatively short (1 h) here, mainly for convenience of the experiments. The solutions were then removed from both sides of the cell to measure NaOH and Na_2WO_4 concentrations.

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:

$$U = \frac{M}{At\Delta c} \tag{2}$$

M in Eq. (2) is the amount of the component transported in moles, A is the effective area in square meters, t is the time in hours. Δc is expressed as follows [26,27]:

$$\Delta c = \frac{c_f^0 - (c_f - c_d)}{\ln \frac{c_f^0}{c_f - c_d}} \tag{3}$$

where c_f^0 and c_f are the feed concentrations at time 0 and t, respectively, and c_d the diffusate concentration at time t.

3. Results and discussion

3.1. PSSS and membrane formation process

PSSS is synthesized by ARGET ATRP, with EBiB as the initiator, $CuBr_2$ as the catalyst, PMDETA as the ligand, and AsAc as the reducing agent. The merit of ARGET ATRP as compared with the normal ATRP is that it can be successfully carried out with lower dosage of catalyst and in the presence of trace air. Besides, the catalysts are high state transition metal compounds, and the reducing agent is easily available and of low toxic. Therefore, the processes of production, post-treatment, storage, and transportation are simpler and easier [23,28].

GPC analysis shows that PSSS has the number average molecular weight (M_n) of 3,500, with the weight average molecular weight (M_w)/M_n of 1.55. For reference, the multisilicon copolymer poly(VBC-co-γ-MPS) obtained through conventional radical polymerization technique is separated into two products after purification, one is liquid with M_n of 733, the other is viscous with M_n of 3,565 [19]. When used for cross-linking with PVA, these two poly(VBC-co-γ-MPS) products with the different M_n values yield membranes with different properties and DD performances. Therefore, PSSS obtained by ARGET ATRP has more regular molecular weight distribution, which is advantageous to prepare cation-exchange membranes.

PSSS contains abundant $-SO_3Na$ groups but no $-Si(OR)_3$ groups. Hence, it is stable and may not become gel during preparation and preservation processes. Only in preparation of membranes, gel appears when alkoxysilane is added for long-time cross-linking. The gel can be effectively avoided if reaction time is shortened, so that homogeneous and stable membranes can be obtained. As comparison, the multisilicon copolymer such as poly (SSS-co-γ-MPS) can easily become gel in preparation and preservation, which increases the difficulty for practical applications. PSSS is also compatible with water and can be homogeneously mixed with PVA to get homogeneous casting solution. The hydrogen bonding between $-SO_3^-$ and –OH can enhance the solution homogeneity further. For suppressing the membrane swelling, three different alkoxysilanes are used for cross-linking. TEOS is the most commonly used alkoxysilane and contains four –Si–OR groups to undergo hydrolysis and condensation. Silica network and partial cross-linking with PVA chains through Si–O–C bonding can be formed in the membrane matrix. Aside from the –Si–OR groups, APTES contains $-NH_2$ groups which can form hydrogen bonding with –C–OH and $-SO_3^-$ groups. GPTS, on the other hand, has epoxy groups and may cross-link with PVA through –C–O–C– bonding to strengthen the membrane structure further. The membrane structures are illustrated in Fig. 2. APTES and especially GPTS can have strong interactions with PVA and PSSS chains, which can be proved by the increasing viscosity of casting solution during membrane preparation.

3.2. FTIR spectra and TGA analysis

FTIR spectra of the cation-exchange membranes are shown in Fig. 3. All the spectra show a strong and broad band in the range of 3,200–3,600 cm^{-1}, which is mainly due to the stretching vibration of PVA–OH groups. The bands at 1,722 and 1,198 cm^{-1} are attributed to the skeleton vibration of the aromatic ring and the stretching vibration of the sulfonate groups respectively [29]. Bands at 1,050–1,150 cm^{-1}, which are characteristic of C–O–C and Si–O–Si stretching, illustrate formation of the silica network.

Fig. 4 displays TGA graphs. Since the membranes have been heated at 130˚C for 4 h during the preparation process, the weight loss before 130˚C, which should be mainly due to the evaporation of absorbed water, is neglected for determining the initial decomposition temperature (IDT) and thermal degradation temperature (T_d, defined as the temperature at 5% weight loss).The IDT and T_d data as shown in Table 1 illustrate that PVA–PSSS–G membrane has the highest thermal stability ($T_d = 267.4$˚C), which should be due to the dual cross-linkings of Si–O–Si and C–O–C between GPTS and PVA. The PVA–PSSS–A membrane demonstrates the lowest thermal stability since the $–NH_2$ groups are less stable under high temperature.

3.3. IEC and W_R

The IEC and W_R are shown in Fig. 5. IEC values are in the range of 1.03–1.64 mmol/g, which are higher than those of previous PVA-based hybrid membranes. Previous membranes from multisilicon copolymer poly(SSS-co-γ-MPS) and PVA have IEC of 0.72–1.05 mmol/g, though the dosage of poly(SSS-co-γ-MPS) is much higher (4.8 g poly(SSS-co-γ-MPS) (30–35 wt%) for 4 g PVA (5 wt%)) [18]. The higher IEC of the present membranes should be attributed to the use of PSSS with abundant $–SO_3Na$ groups [30]. The PVA–PSSS–A membrane has the lowest IEC, probably because of the formation of acid–base interaction between the $–NH_2$ and $–SO_3H$ groups after the membranes are transformed to H^+ form for IEC measurement. The previous studies have also revealed that the formation of acid–base interaction can consume partial $–SO_3^-$ groups, leading to lower IEC [31].

The W_R values are in the range of 46.8–120.7%. Membrane hydrophilicity is highly related to the IEC value, since the $–SO_3Na$ groups are highly hydrophilic. The –Si–OH groups and –Si–O–Si–, Si–O–C and other cross-linking interactions can also play important role. The PVA–PSSS–T hybrid membrane has the highest W_R, because of the highest content of –Si–OR groups which can be hydrolyzed into –SiOH groups. PVA–PSSS–A membrane, on the other hand, has the lowest W_R since the membrane has the lowest IEC. The PVA–PSSS–G membrane has the highest IEC, yet the W_R value is much lower than PVA–PSSS–T hybrid

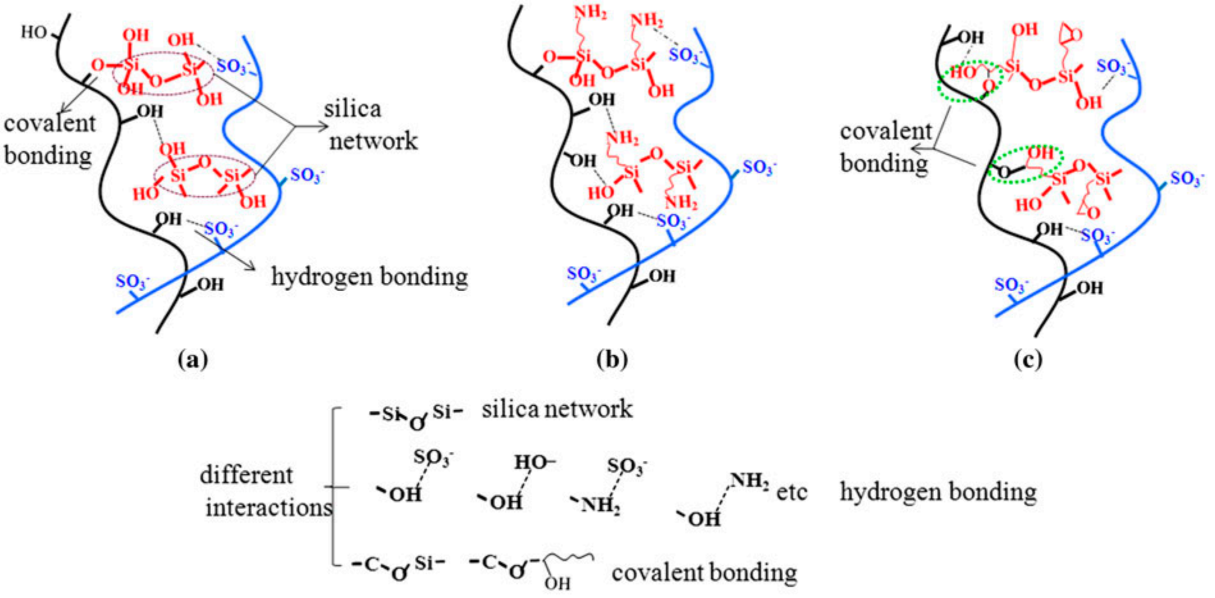


Fig. 2. Illustration of the membrane structures including (a) PVA–PSSS–T, (b) PVA–PSSS–A A, and (c) PVA–PSSS–G.

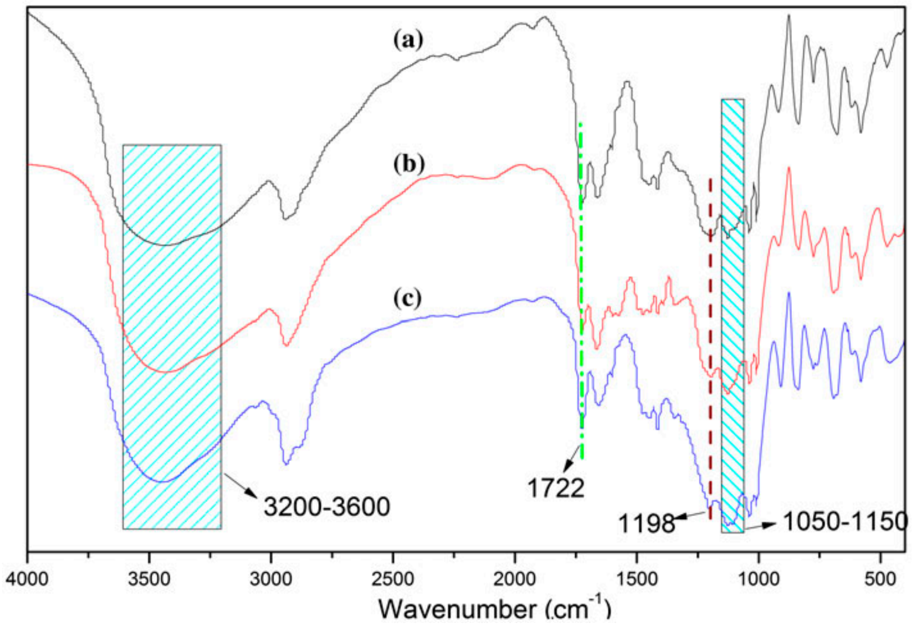


Fig. 3. The FTIR spectra of (a) PVA–PSSS–T, (b) PVA–PSSS–A, and (c) PVA–PSSS–G membranes.

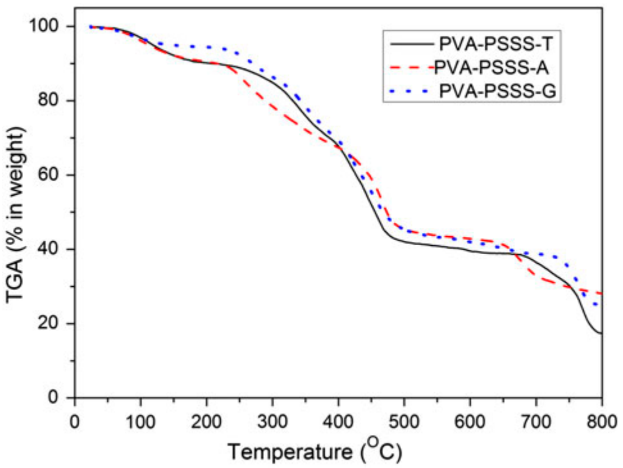


Fig. 4. TGA diagrams of the different cation-exchange membranes.

Table 1
IDT and T_d of the cation-exchange membranes

Membranes	PVA–PSSS–T	PVA–PSSS–A	PVA–PSSS–G
IDT (℃)	251	236	264
Td (℃)	250.0	238.5	267.4

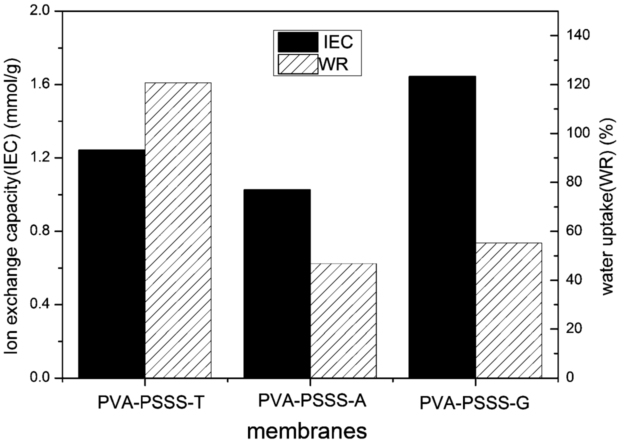


Fig. 5. The IEC and W_R of the different cation-exchange membranes.

membrane, which is quite desirable for the membrane application. The epoxy groups of GPTS can cross-link with the PVA chains through C–O–C bonding, and hence, dual network can be formed and the membrane swelling is significantly suppressed.

3.4. Swelling in 65℃ water

PVA membrane can be readily swelled and expanded or even partly dissolved in hot water. Hence, the stability in hot water is a major concern for PVA-based membranes, and the swelling behavior in 65℃ water has been measured, as shown in Fig. 6. The membrane swelling degrees increase rapidly during the first 6 h, indicating that water is adsorbed

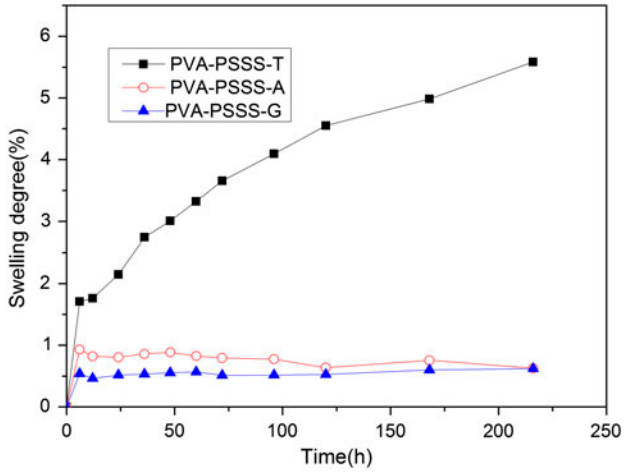


Fig. 6. The swelling degree in 65℃ water of the different cation-exchange membranes.

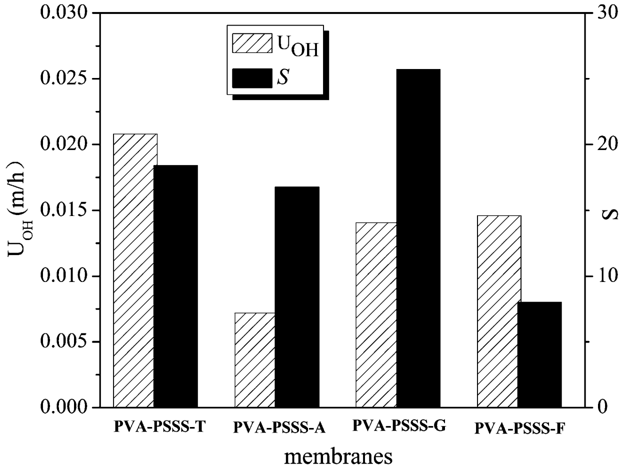


Fig. 7. Dialysis coefficients of NaOH (U_{OH}) and separation factors (S) of the different cation-exchange membranes. Note: PVA–SSS–F is cross-linked with formaldehyde and used as a reference membrane.

mainly in this period of time. As the time prolongs, PVA–PSSS–T membrane continues to be swelled whereas the swelling of PVA–PSSS–A and PVA–PSSS–G membranes becomes less obvious. The lower swelling degree of PVA–PSSS–A membrane as compared with PVA–PSSS–T should be due to the addition of $-NH_2$ groups, which can strengthen the membrane structure through hydrogen bonding with PVA and PSSS. PVA–PSSS–G membrane, on the other hand, has C–O–C cross-linking between GPTS and PVA as well as silica network through the membrane matrix. Hence the membrane is denser and can resist the swelling better. PSSS component, trapped in the dual cross-linking network, will show less swelling behavior. The swelling of PVA–PSSS–G membrane is lower than PVA–PSSS–A membrane despite its higher W_R value, which should be due to two main reasons: (1) the higher thickness of PVA–PSSS–G membrane; (2) the better swelling resistance from the C–O–C cross-linking.

3.5. DD performance

Alkaline solution is produced largely in tungsten ore smelting industry, and the main ingredients are NaOH and salt (Na_2WO_4) [32]. Hence, the cation-exchange membranes are used in DD process to separate NaOH/Na_2WO_4 solution. The DD performances, including dialysis coefficient of NaOH (U_{OH}) and separation factor (S), are shown in Fig. 7.

The U_{OH} values are in the range of 0.0072–0.0208 m/h, higher than those of the PVA blank membrane (~0.0077 m/h) and commercial PPO-based membrane (~0.004) (Tianwei Membrane Co., Ltd. Shandong of China) [11]. The S values are in the range of 16.8–25.7, higher than the PVA blank membrane (~11) and PPO-based membrane (~8) [11]. Therefore, the alkali permeability and selectivity of the present membranes have been enhanced simultaneously. This can be ascribed to the hydrophilic nature of PVA matrix, the relatively high IEC, and the presence of abundant –C–OH, –Si–OH or $-NH_2$ groups. These functional groups can accelerate the transport of OH^- ions through hydrogen bonding. Transport of WO_4^{2-} ions cannot be enhanced by the different functional groups and hence both high alkali permeability and selectivity can be achieved.

Previous membranes from PVA and multisilicon copolymer poly(SSS-co-γ-MPS) have U_{OH} values of 0.0102–0.0111 m/h at 25℃, and S values of 16.9–18.5 [18]. The data are generally similar to those of the membranes cross-linked with alkoxysilanes. More careful observation shows that membrane PVA–PSSS–A has similar IEC value (1.03 mmol/g), but lower W_R value (46.9%) as compared with membrane C of Ref [18] (1.05 mmol/g and 54.8%). The S values of these two membranes are similar (16.8 and 17.3). Meanwhile, U_{OH} of membrane PVA–PSSS–A (0.0072 m/h) is lower than membrane C (0.103 m/h), which should be due to the lower hydrophilicity of PVA–PSSS–A. PVA–PSSS–F membrane, on the other hand, has U_{OH} of 0.0146 m/h and S of 8.03 as shown in Fig. 7. The much lower selectivity of PVA–PSSS–F membrane should be due to the consumption of the PVA–OH groups during formaldehyde cross-linking process. Therefore, alkoxysilane cross-linking is more advantageous for membrane DD application than conventional aldehyde cross-linking.

Among the different hybrid membranes, membrane PVA–PSSS–T has the highest U_{OH} value, because of the highest W_{R} and the highest content of –SiOH groups. The PVA–PSSS–G membrane shows the highest S value, which should be due to the denser membrane structure. Its U_{OH} is higher than PVA–PSSS–A membrane because of the higher IEC value. Overall, DD performances of the present membranes are acceptable for potential application in alkali recovery. The PVA–PSSS–G membrane can show both high permeability and selectivity and is the most desirable for DD application.

4. Conclusion

PSSS is synthesized by ARGET ATRP and then mixed with PVA, cross-linked with different alkoxysilanes to yield cation-exchange membranes. PSSS has more regular molecular weight distribution ($M_{\mathrm{n}} =$ 3,500 and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.55$) as compared with the multisilicon copolymer from conventional radical polymerization technique. The abundant –SO_3Na groups in PSSS lead to relatively high membrane IEC values (1.03–1.64 mmol/g). Meanwhile, the alkoxysilanes can induce silica network and form hydrogen or covalent bonding with PVA and PSSS. Hence the membrane structures are strengthened. In particular, for GPTS, the dual cross-linkings of Si–O–Si and C–O–C between GPTS and PVA lead to the highest membrane thermal stability ($T_{\mathrm{d}} = 267.4$℃) and the lowest swelling degree in 65℃ water.

The membranes show favorable DD performances because of the hydrophilic nature of PVA matrix, the relatively high IEC and the presence of different functional groups (PVA–OH, –SiOH or –NH_2). The U_{OH} values are in the range of 0.0072–0.0208 m/h, and the S values are 16.8–25.7. Both U_{OH} and S are higher than the PVA blank membrane or commercial PPO-based membrane. The S values are also higher than that of membrane cross-linked with formaldehyde ($S = 8.03$), demonstrating the advantage of alkoxysilane cross-linking as compared with conventional aldehyde cross-linking.

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