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Zwitterionic multisilicon copolymer used for preparing PVA based hybrid membranes for alkali recovery

Chunhua Dai[a,b], Chuanyu Deng[b], Lei Zhang[b], Liang Wu[a], Tongwen Xu[a,*], Yonghui Wu[b,*]

[a]*CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, China, Tel. +86-551-3601587; email: twxu@ustc.edu.cn (T. Xu), Tel. +86-515-88233188; email: daichunhua2172@163.com (C. Dai), Tel. +86-551-3601587; email: liangwu8@ustc.edu.cn (L. Wu)*
[b]*School of Chemistry and Environmental Engineering, Yancheng Teachers University, Yancheng, Jiangsu 224051, China, Tel. +86-515-88233188; emails: wuyonghui1000@126.com (Y. Wu), 942409934@qq.com (C. Deng), 1160915706@qq.com (L. Zhang)*

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ABSTRACT

Zwitterionic multisilicon copolymer is prepared from the copolymerization of 2-acrylamide-2-methyl-1-propanesulfonic acid and γ-methacryloxy propyl trimethoxyl silane, which contain –NH–, $–SO_3H$ and $–Si(OCH_3)_3$ groups. The copolymer is then taken sol–gel reaction with polyvinyl alcohol to form hybrid membranes. The hybrid membranes are strong acidic and weak basic, which are used in diffusion dialysis (DD) process for alkali recovery. The hybrid membranes are generally homogeneous and compact. The initial decomposition temperature values are in the range of 204°C–210°C and the T_d values are in the range of 225°C–231°C. The highest value of tensile strength is 51.8 MPa and the elongation at break (E_b) is in the range of 72.1%–289.7%. The membranes have the water uptake (W_R) of 27.7%–88.3% and cation exchange capacity of 0.90–2.15 mmol g^{-1}. The DD process shows that the dialysis coefficient of NaOH (U_{OH}) is in the range of 0.0079–0.0151 m h^{-1} and the selectivity (S) can reach up to 32.7. The favorable performances are attributed to the combining effect of –OH, –NH– and $–SO_3H$ groups.

Keywords: Multisilicon copolymer; Zwitterionic hybrid membrane; Polyvinyl alcohol (PVA); Diffusion dialysis (DD); Alkali recovery

1. Introduction

Organic-inorganic hybrid membranes have been reported widely due to their combining advantages of both organic and inorganic materials [1]. The hybrid membranes can also show some new characteristics in different applications, such as optimal device and separation processes [2,3]. Zwitterionic hybrid membrane, as a new type of hybrid membranes, contains both anion and cation exchange groups [4]. The anion exchange groups may come from $–NR_3^+$, $–NH_2$ and –NH–, while the cation exchange group may come from $–SO_3H$ and –COOH. The zwitterionic hybrid membranes show the advantages of anti-pollution, chemical stability, high mechanical strength and especially high permeability for organic electrolyte [5]. Hence, the membranes can be used in ions sorption, heavy metal ions removal [6] and nanofiltration [7].

The zwitterionic hybrid membranes can be prepared by different methods. The inorganic component such as silica comes from sol–gel reaction of alkoxysilane or directly inorganic materials such as nano silica and mesoporous silica [8]. The anion and cation exchange groups come from the mixing of different polyelectrolyte or ring opening of a lactone reagent with tertiary amine groups. For example, a lactone reagent of 1,3-propanesultone is used to create the ionic groups ($–NR_2$, –COOH) through sol–gel process of hybrid precursor [1]. Another method is mixing anion and cation exchange solutions to form polyelectrolyte complexes membranes [9]. Such zwitterionic hybrid polymer and their derivatives exhibit higher performances than the

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* Corresponding author.

pure organic or inorganic materials, such as higher mechanical strength, thermal stability, permeability and selectivity [7,10]. However, these zwitterionic hybrids have some defects which may restrict their preparation and application. The strong acidic and basic groups are easily combined through electrostatic interaction, which may lead to the deposition of charged particles. Besides, the inorganic components may have some phase separation with the organic matrix.

Previous work had shown that the basic and acidic groups had different effects on membrane performances. For example, the $–NH_2$ groups could enhance the compatibility between polyvinyl alcohol (PVA) and γ-aminopropyl triethoxysilane through the formation of hydrogen bonds [11]. However, the $–NH_2$ groups reduced the membrane permeability in diffusion dialysis (DD) process. Other works prepared multisilicon copolymers, which contained different functional groups such as $–SO_3H$ and $–Si(OCH_3)_3$ [8]. The functional groups were combined to show some coordinate effect to elevate membrane permeability and selectivity. However, the combination of acidic and basic groups was rarely prepared and investigated.

Hence in this work, zwitterionic multisilicon copolymer will be prepared from 2-acrylamide-2-methyl-1-propanesulfonic acid (AMPS) and γ-methacryloxy propyl trimethoxyl silane (γ-MPS), which contain –NH–/$–SO_3H$ and $–Si(OCH_3)_3$ groups. The copolymer thus is weak basic and strong acidic. The $–Si(OCH_3)_3$ groups is then taken sol–gel reaction with PVA. Hence, membranes containing silica network and –NH–/$–SO_3H$ groups are formed. The membranes are expected to have favorable compatibility between organic and inorganic phases, and the elevated DD performances in separating $NaOH/Na_2WO_4$ solution.

2. Experimental

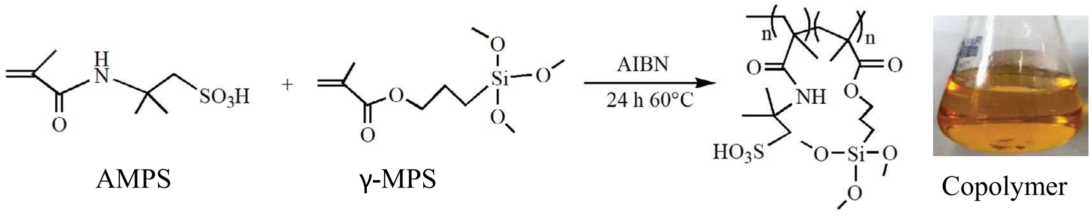
2.1. Materials

Polyvinyl alcohol, with the average degree of polymerization 1,750 ± 50, was supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd. (China). AMPS was purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai of China). γ-MPS was supplied by Saen Energy Chemical Co., Ltd. (Shanghai of China). Azobisisobutyronitrile and N,N-dimethyl formamide (DMF) were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai of China). All other reagents were of analytical grade and supplied by domestic chemical reagents companies in China. Deionized water was used throughout the experiments.

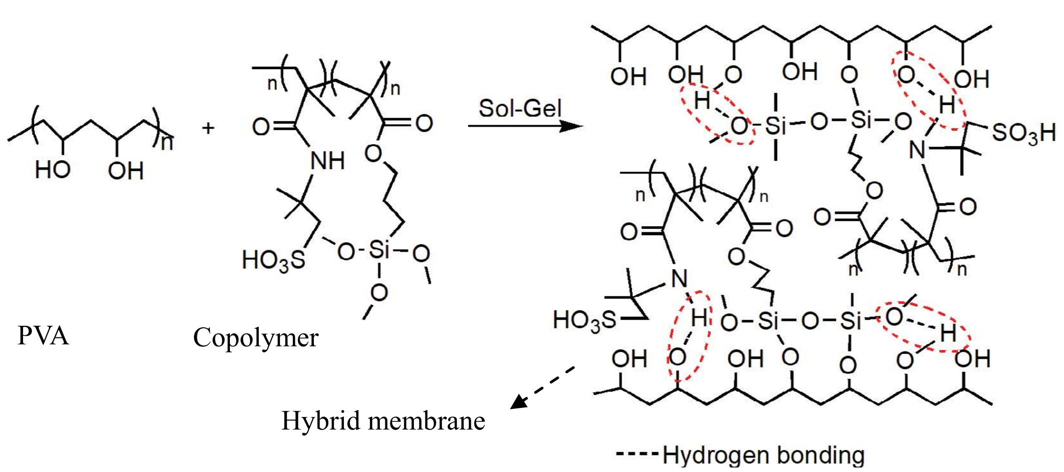
An aqueous 5 wt.% PVA solution was prepared by dissolving dry PVA in water at room temperature for a span of 12 h. The mixture was then heated at 102°C for 4 h under vigorous stirring, and then the obtained transparent solution was cooled to room temperature.

2.2. Preparation of the multisilicon copolymers

Copolymerization of γ-MPS and AMPS is depicted in Fig. 1. AMPS was dissolved in 100 mL DMF at 70°C under stirring, then the solution was added with γ-MPS and ethanol (10 mL) within 0.5 h. The mixture was heated at 70°C



(a) preparation of the multisilicon copolymer



(b) preparation of the hybrid membrane

Fig. 1. Preparation of (a) the multisilicon copolymer and (b) the hybrid membranes.

under stirring for 24 h to obtain a homogeneous solution. Afterwards, a part of solvents of DMF and ethanol (about 50–70 mL) was removed by rotary evaporation at 85°C to obtain a concentrated solution. The concentrated solution was viscous and homogeneous with the color of tan or orange. The whole process must avoid trace moisture into the copolymerization system, and use fresh monomers and solvent.

The molar ratio between AMPS and γ-MPS increased from 0.5, 1, 2–3, and thus four types of copolymers were obtained. The copolymers were designated as $A_{0.5}$, A, A_2 and A_3.

2.3. Preparation of the hybrid membranes

The hybrid membranes were prepared through the sol–gel process of the copolymer and PVA (Fig. 1). The concentrated copolymer solution was added into PVA solution (100 mL) at 60°C within 0.5–1 h. The solution was continued to stir at 60°C for 24 h, during which the solution was homogeneous with no precipitation. The homogeneous solution was cast onto a glass plate to form a film. The film was dried at room temperature for two days, and finally heated from 60°C to 130°C at the rate of 10°C h^{-1}, and kept at 130°C for 4 h for thermal cross-linking. The membrane thickness was in the range of 97–186 μm.

The dosage of copolymer decreased from 5, 2.5, 1.67 to 1.25 g, and thus the mass ratio of PVA to copolymer was increased from 1, 2, 3 to 4, as shown in Table 1. The membranes were designated as P_mA_n, where "*m*" refers to the mass ratio of PVA to the copolymer, and "*n*" refers to the molar ratio of AMPS to γ-MPS. Two series of membranes were prepared. Series P_mA fixed the copolymer A and increased the mass ratio of PVA to the copolymer. Series P_2A_n fixed the mass ratio of PVA to the copolymer, and increased the molar ratio of AMPS to γ-MPS.

2.4. Membrane characterizations

Fourier transform infrared spectroscopy (FTIR) of the copolymer and membrane samples was recorded using a Bruker Vector 22 spectrometer with a resolution of 2 cm^{-1} and a spectral range of 4,000–400 cm^{-1}. Thermo-gravimetric analysis (TGA) was conducted on a Shimadzu TGA-50H analyzer with a heating rate of 10°C min^{-1} under persistent nitrogen flow. Membrane morphology was observed by scanning electron microscope (SEM, FEI-Sirion 200). Besides, energy dispersive spectrometer (EDS) was employed to observe the membrane cross-sections. Before observation, the cross-sections of membrane samples were coated with gold. Mechanical property was analyzed by TA-Q800 dynamic mechanical analyzer under isothermal conditions. All measurements were performed with ramp force at an increasing rate of 0.5 N min^{-1} at 25°C.

Water uptake (W_R) was measured to evaluate the membrane hydrophilicity. The membrane sample was dried and weighed (W_{dry}). Then the sample was immersed in water at room temperature (25°C) for 48 h and weighed again (W_{wet}) after getting rid of surface water with a filter paper. The value of W_R was calculated according to Eq. (1) [12].

$$W_R = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \tag{1}$$

Membrane dimensional stability was monitored by linear expansion ratio (LER) in 25°C water. The membrane sample was cut into 3 × 1 cm and immersed in water for 48 h. The lengths of wet and dry membrane samples were measured as L_{wet} and L_{dry} respectively. The value of LER was calculated according to Eq. (2).

$$\text{LER} = \frac{\left(L_{\text{wet}} - L_{\text{dry}}\right)}{L_{\text{dry}}} \times 100\% \tag{2}$$

Ion-exchange capacity (IEC) was determined through the classical back titration method. The membrane sample was equilibrated in 1.0 mol L^{-1} (M) HCl solution for 48 h. Then the sample was washed with water for four times to remove the trace amount of HCl, and immersed in 80 mL 0.05 M NaOH for 48 h. The amount of H^+ ions released was determined from the decrease of NaOH through titration with 0.05 M HCl using phenolphthalein as an indicator. The IEC value was calculated according to Eq. (3), in which C_{NaOH}, V_{NaOH}, C_{HCl}, V_{HCl} and *m* represent the concentration and volume of NaOH solution, the concentration and volume of HCl consumed in titration, and the dry membrane weight, respectively.

$$\text{IEC} = \frac{C_{\text{NaOH}} V_{\text{NaOH}} - C_{\text{HCl}} V_{\text{HCl}}}{m} \tag{3}$$

The alkali resistance was estimated by swelling degree and weight loss percent in NaOH solution. The pre-weighed membrane sample (m_0) was immersed in 25°C 2 M NaOH for 60 h. Then the sample was taken out and washed with water for four times. The wet sample was wiped with filter paper to

Table 1
Composition, thickness and ion exchange capacity of the P_mA_n hybrid membranes (Note: P_2A can also be designated as P_2A_1)

Series	P_mA				P_2A_n		
Membrane	P_1A	P_2A	P_3A	P_4A	$P_2A_{0.5}$	P_2A_2	P_2A_3
molar ratio of AMPS to γ-MPS	1:1	1:1	1:1	1:1	0.5:1	2:1	3:1
poly(AMPS-co-γ-MPS)/g	5	2.5	1.67	1.25	2.5	2.5	2.5
PVA/g	5	5	5	5	5	5	5
Thickness/μm	186	165	153	126	173	143	97
IEC/mmol g^{-1}	1.53	1.97	1.48	0.90	1.83	2.15	2.01

remove surface water and weighed as m_1. Finally, the sample was dried at 60°C till constant weight (m_2). The swelling degree and weight loss percent were calculated according to Eqs. (4) and (5).

$$\text{Swelling degree} = \frac{\left(m_1 - m_2\right)}{m_2} \times 100\% \tag{4}$$

$$\text{Weight loss percent} = \frac{\left(m_0 - m_2\right)}{m_0} \times 100\% \tag{5}$$

2.5. DD of NaOH/Na_2WO_4 solution

The membrane sample was immersed in the feed solution for 1 h, and then was equipped in a two-compartment cell. One compartment was used as dialysate side and filled with the feed solution (100 mL). The feed solution was the mixture of NaOH (1.0 M) and Na_2WO_4 (0.1 M), which simulated the base solution formed from tungsten metallurgical processes. The other compartment was filled with 100 mL water as diffusate side. Both compartments were stirred continuously to minimize the concentration polarization. The DD was running for 1 h at room temperature (~8°C), and then both dialysate and diffusate solutions were taken out. The OH^- concentration was determined through titration with 0.1 M HCl solution, while WO_4^{2-} concentration was detected by ultraviolet spectrophotometry method.

The separation factor (S) is calculated as the ratio of dialysis coefficients (U) of the two species existing in the solution. U can be expressed by Eq. (6) [8]:

$$U = \frac{M'}{At\Delta c} \tag{6}$$

where M' is the quantity of component transported in molars, A is the effective membrane area, t is the time, and Δc is calculated as Eq. (7) [8].

$$\Delta c = \frac{c_f^0 - \left(c_f - c_d\right)}{\ln \dfrac{c_f^0}{c_f - c_d}} \tag{7}$$

where c_f^0 and c_f are the feed concentration at time 0 and t correspondingly, and c_d is the dialysate concentration at time t.

3. Results and discussion

3.1. FT-IR spectra

The FT-IR spectra of the multisilicon copolymer A is shown in Fig. 2(a). The peak around 1,719 cm^{-1} is attributed to the stretching vibration of C=O group, and the sharp peak at 1,207 cm^{-1} is due to the stretching vibration of C(=O)–O–C group, which confirms the ester group existing in the copolymer. The band around 1,651 cm^{-1} is mainly attributed to the C=O stretching vibration of amido group [13]. The band around ~1,470 cm^{-1} is indicative of C–N stretching vibration [14]. The absorption bands around ~1,100 cm^{-1} and ~1,380 cm^{-1} are ascribed to symmetric and asymmetric stretching of the $-SO_3H$ group respectively, which confirms the presence of sulfonate groups in the copolymer [15,16].

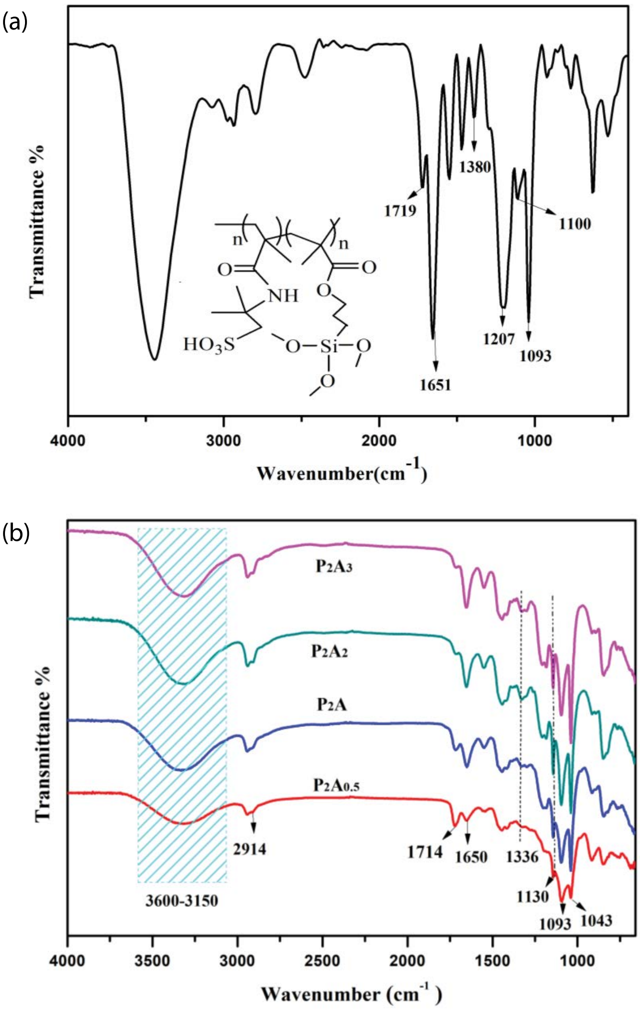


Fig. 2. (a) FT-IR spectra of the multisilicon copolymer A (molar ratio of AMPS to γ-MPS = 1:1), (b) FT-IR spectra of membranes P_2A_n (n = 0.5, 1, 2 or 3).

The FT-IR spectroscopy of membranes P_2A_n is selected as the representative cases as shown in Fig. 2(b). The broad strong band in the range of 3,150–3,600 cm^{-1} is attributed to the stretching vibration of −OH and N–H groups [12]. Sharp multi-headed peaks from 2,914 to 2,943 cm^{-1} are due to the stretching of $-CH_3$ and $-CH_2$ groups. The band around 1,093 cm^{-1} indicates the formation of Si–O–Si, while peak at 1,043 cm^{-1} is characteristic of Si–O–C bonds [17,18]. Hence, the condensation reaction occurred among Si–OH groups from hydrolyzed $Si(OCH_3)_3$ groups and C–OH groups from PVA. The organic and inorganic phases are cross-linked through Si–O–C bonds, which may elevate their compatibility and thus membrane homogeneity.

3.2. SEM and EDS graphs

Morphologies of membrane cross-sections are observed through SEM, as shown in Fig. 3. Most membranes are homogeneous and compact without any pores. The uniform

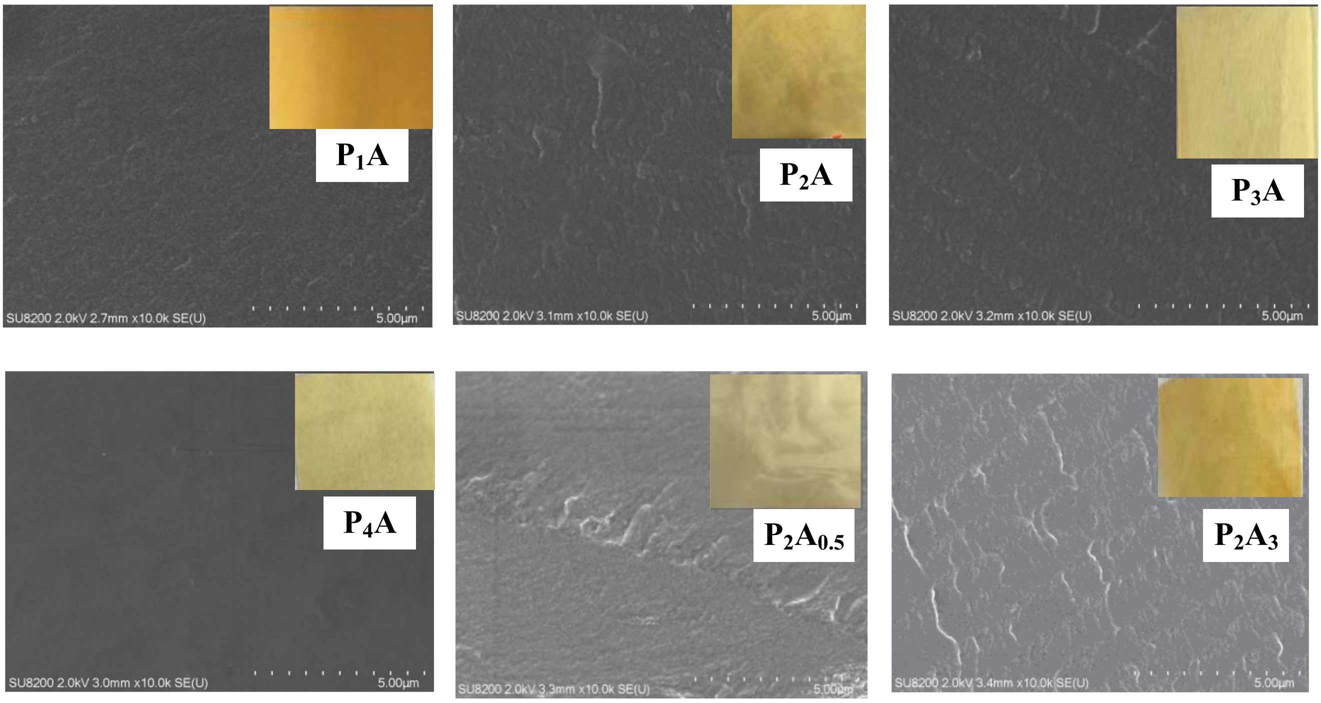


Fig. 3. SEM images and digital photos (in the right upper corner) of the hybrid membranes.

morphology indicates the favorable compatibility between PVA and multisilicon copolymer. The copolymer contains $-Si(OCH_3)_3$, –NH– and $-SO_3H$ groups. The $-Si(OCH_3)_3$ group can take sol–gel reaction with –OH groups to form covalent bonds; the –NH– group can form hydrogen bonds with –OH groups [19], and the $-SO_3H$ group has high polarity and thus also enhances the compatibility between PVA and the copolymer. Hence, the casting solution is transparent, and its corresponding membrane is homogeneous. Membrane P_2A_3 contains a few aggregations, which means that excessive dosage of AMPS would reduce membrane homogeneity. However, the particles are less and smaller than those in our previously reported PVA–SiO_2 hybrid membranes (0.2–2 μm) [20].

The K-Shell of EDX graphs and element contents of series P_2A_n membranes are shown in Fig. 4 and Table 2. Series P_2A membranes are selected to investigate the element distribution through the membrane cross sections. The content of element *S* generally increases with the content of AMPS due to its $-SO_3H$ group. However, the *S* content of P_2A_3 membrane is lower than that of P_2A_2 membrane, which may be due to the inhomogeneous structure of membrane P_2A_3.

3.3. Thermogravimetric analysis

The TGA graphs in nitrogen atmosphere are shown in Fig. 5(a). The weight loss before 130°C is neglected for determining the initial decomposition temperature (IDT) and T_d (defined as the temperature at 5% weight loss), as because the membranes were heated at 130°C for 4 h during the preparation process. The values are represented in Table 3.

The IDT values are in the range of 204°C–210°C, and the T_d values are in the range of 225°C–231°C. The values are close to each other, indicating that the hybrid membranes have similar thermal stability. The values are lower than those of other PVA-based ion exchange membranes (IDT of 205°C–269°C [21] or 227°C–243°C [22], and T_d of 246°C–272°C [21] or 238°C–265°C [22]), which may be attributed to the effect of –NH– groups. The –NH– groups can combine with PVA–OH groups and thus may hinder the sol–gel reaction between PVA–OH and $-Si(OCH_3)_3$ groups, which leads to the lower cross-linking degree.

The derivative thermogravimetric curves of representative P_2A membrane is shown in Fig. 5(b). The initial weight loss in the range of 100°C–150°C is attributed to the removal of bound and hydrated water from the polymer chains and functional groups [23]. A weak stage at 220°C–240°C may be due to the degradation of N–H amide group. The sharp stage around the range of 250°C–320°C is attributed to the degradation of the sulfonic groups [20]. For example, TGA graphs show that membrane P_2A_3 has the highest weight loss in this stage due to its high content of AMPS (Fig. 5(a)), while membrane P_1A has the lowest weight loss. The final stage around 380°C–470°C is due to the degradation of the polymer main chains. The residual content after 700°C is in the range of 12.5%–26.3% (Table 3), which is mainly determined by the silica content and thus the dosage of the copolymer.

3.4. Mechanical properties

Mechanical properties are reflected as tensile strength (TS) and elongation at break (E_b), which are listed in Table 4. The highest TS value is 51.8 MPa, which is about two times higher than the value of Nafion-117 and those of other reported PVA-based hybrid membranes (14.2–28.3 MPa) [22]. The E_b values are in the range of 72.1%–289.7%, which are higher than the carboxylic acid type PVA based hybrid membranes (18.8%–67.3%) [22]. All E_b values are also higher than

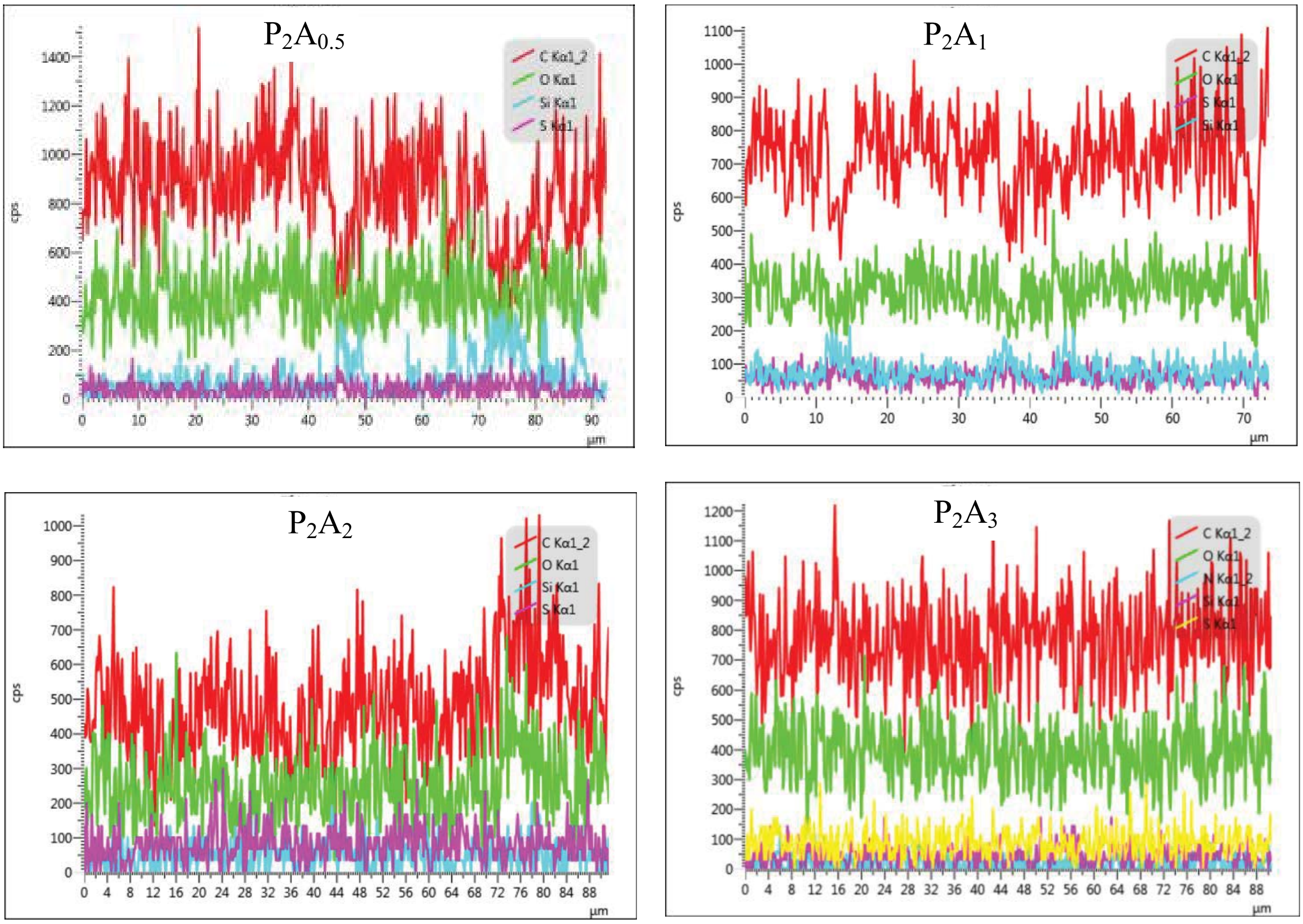


Fig. 4. EDX graphs of series P_2A_n membranes (n = 0.5, 1, 2 or 3).

that of the Nafion-117 (12.2%). The favorable mechanical properties indicate the superiority of the zwitterionic hybrid membranes. The membranes contain both –NH– and $–SO_3H$ groups, which can enhance the compatibility between silica network and organic matrix. Hence, the zwitterionic membranes show higher mechanical properties than the PVA/SiO_2 membranes containing only $–SO_3H$ group [24].

Membrane P_2A shows higher TS value than the other membranes, indicating that proper ratios among different functional groups can enhance membrane strength. Membranes with higher content of PVA–OH groups have higher E_b values, indicating the PVA component can elevate the membrane flexibility. Besides, the increasing content of AMPS also enhances membrane flexibility, which may be attributed to the low cross-linking degree with the decreasing content of $–Si(OCH_3)_3$ groups.

Table 2
Element contents of series P_2A_n membranes (n = 0.5, 1, 2 or 3)

Membranes	O/wt%	Si/wt%	S/wt%
$P_2A_{0.5}$	37.12	2.65	1.53
P_2A_1	32.88	2.85	3.08
P_2A_2	32.73	2.02	5.59
P_2A_3	35.37	1.21	4.33

3.5. Water uptake (W_R) and linear expansion ratio

Membrane hydrophilicity can be reflected by W_R and LER, whose values are shown in Fig. 6. The W_R values are in the range of 27.7%–88.3%, most of which are higher than those of commercial membrane DF-120 (42%). PVA based membranes with high content of –OH groups, always have high hydrophilicity (62%–464%) [25]. However, the membranes can still keep integrity under the high swelling extent.

The W_R values of series P_mA membranes increase from 52.3% to 83.1% and LER values increase from 17.2% to 24.1% as the dosage of PVA increases. The PVA-based membranes contain plenty of hydrophilic –OH groups, which elevate the membrane hydrophilicity. The multisilicon copolymer contains –NH–, $–SO_3H$ and $–Si(OCH_3)_3$ groups. Though the –NH– and $–SO_3H$ groups are also hydrophilic [26], the $–Si(OCH_3)_3$ groups are cross-linked with PVA through Si–O–Si and Si–O–C bonds, which restricts the membrane swelling. For example, the W_R values of series P_2A_n membranes increase from 27.7% to 88.3% and the LER values increase from 6.9% to 25.4% as the dosage of AMPS increases, which indicates the strong hydrophilicity of the $–SO_3H$ and –NH– groups.

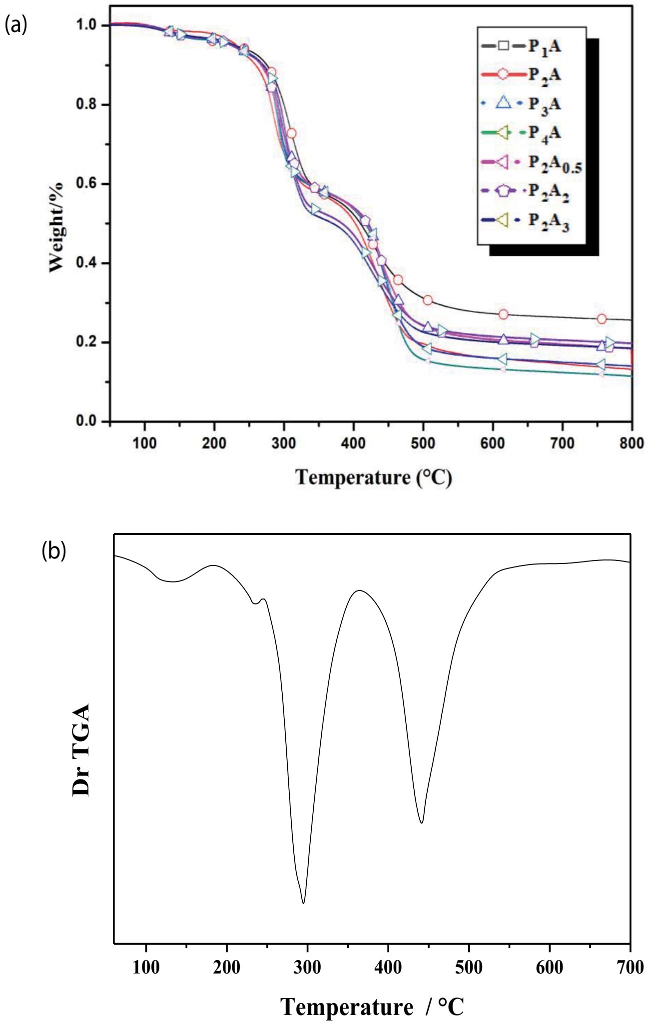


Fig. 5. (a) TGA curves from 60 to 700°C in N_2 atmosphere, (b) Dr TGA curve of membrane P_2A from 60 to 700°C in N_2 atmosphere.

Table 3
Membrane thermal stabilities including initial decomposition temperature (IDT), thermal decomposition temperature (T_d) and the residual content after 700°C

Membrane	P_1A	P_2A	P_3A	P_4A	$P_2A_{0.5}$	P_2A_2	P_2A_3
IDT/°C	204	210	208	207	205	206	209
T_d/°C	228	231	228	229	226	225	229
Residual content/%	26.3	19.5	15.0	12.5	20.9	20.6	19.3

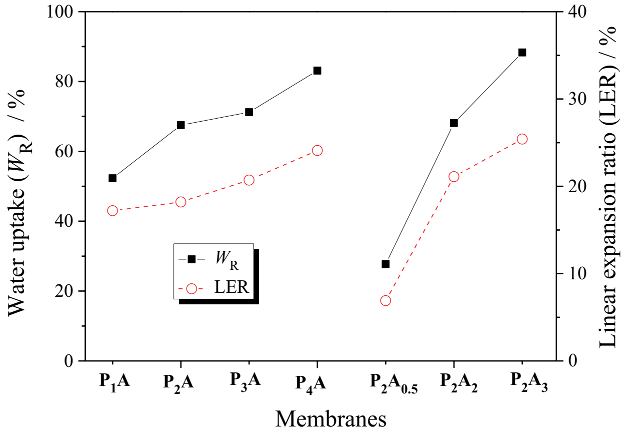


Fig. 6. Water uptake (W_R) and linear expansion ratio (LER) of the hybrid membranes.

3.6. Ion exchange capacity

The IEC values are in the range of 0.90–2.15 mmol g^{-1} (Table 1), which are higher than those of other reported PVA-based membranes containing –COOH groups (0.76–0.90 mmol g^{-1} [27]) or $-SO_3H$ groups (0.61–1.21 mmol g^{-1} [28]). The higher IEC values may be attributed to both the $-SO_3H$ and –NH– groups of the copolymer. The basic –NH– groups can sorb some HCl when the membrane immersed in the HCl solution during IEC measurement, which may also contribute to the IECs during the back titration.

The IEC values of series P_mA membranes increase from 0.90 to 1.97 mmol g^{-1} as the copolymer content increases, and the IEC values of series P_2A_n membranes increase from 1.83 to 2.15 mmol g^{-1} as the dosage of AMPS increases. However, the IEC values cannot increase further for membrane P_2A_3. Though membrane P_2A_3 contains excess AMPS, the SO_3H/–NH groups of excessive AMPS may be partly lost during IEC measurement, for the membrane has the highest hydrophilicity. The high hydrophilicity can be restricted by the γ-MPS. The γ-MPS, due to its functional group of $-Si(OCH_3)_3$, can restrict membrane swelling through the formation of the cross-linked silica network.

3.7. Alkali stability

The membranes need proper alkali resistance due to their application in alkaline solution. The alkali resistance is reflected from swelling degree and weight loss percent in 2.0 M NaOH solution at 25°C for 60 h. The swelling degrees are in the range of 108%–154%, and the weight loss percents are in the range of 11.0%–23.8%, as shown in Fig. 7 These values are close to previous values of PVA hybrid membranes containing $-SO_3H$ groups (swelling degrees

Table 4
Tensile strength (TS) and elongation at break (E_b) of the zwitterionic hybrid membranes and Nafion-117

	P_1A	P_2A	P_3A	P_4A	$P_2A_{0.5}$	P_2A_2	P_2A_3	Nafion-117
TS /MPa	14.3	51.8	7.1	8.4	20.2	11.1	7.8	23
E_b /%	26.9	73.7	97.4	150.0	72.1	126.8	289.7	12.2

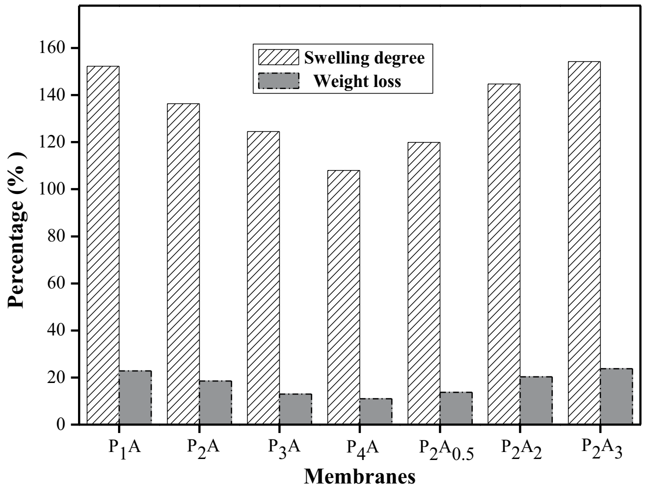


Fig. 7. Swelling degree and weight loss percent after immersed in 25°C 2.0 M NaOH for 60 h.

of 97%–157% [20]) or PVA cross-linked with other copolymers (weight loss percent of 18.4%–24.7% [29]). The present membranes remain intact after the erosion, indicating their acceptable alkali resistance.

The swelling degrees are higher than their corresponding W_R values, for the alkaline solution contains components of both water and NaOH. The water swells membrane and the alkaline component erodes membrane structure. The swelling degree and weight loss percent generally increase as the copolymer dosage increases, which may be attributed to the hydrolysis of C–O–C or Si–O–C bonds in strong alkaline solution. The weight loss should be due to the loss of residual monomers, the damage of silica network, and the dissolved PVA chains.

The swelling degree and weight loss percent increase as the molar ratio of AMPS increases in the copolymer, which may be attributed to the decreasing cross-linking degree due to the decreasing ratio of $-\text{Si(OCH}_3)_3$ groups. The decreasing cross-linking degree induces the possible inhomogeneity as discussed in the SEM graphs. Moreover, the membranes are less compact and stable as the cross-linking degree decreases.

3.8. Diffusion dialysis

The membranes are tentatively used in DD process to separate a model feed solution containing NaOH and Na_2WO_4 at room temperature (~8°C). The DD performances are evaluated by dialysis coefficient of NaOH (U_{OH}) and separation factor (S), as shown in Fig. 8. The U_{OH} values are in the range of 0.0079–0.0151 m h^{-1}, which are higher than the reported values at room temperature (0.0070–0.0130 m h^{-1} [30]). The higher U_{OH} values indicate the coupling effects among multi-functional groups, such as –OH and $-\text{SO}_3\text{H}$. The –OH groups linked on the PVA chains, are regarded as "assistant" functional groups [21]. The "assistant" functional groups can accelerate the transport of OH^- ions through weak interactions such as hydrogen bonds [27]. The $-\text{SO}_3^-$ groups, which graft on the multisilicon copolymer chain, are effective to transport Na^+ ions through ion exchange process [21].

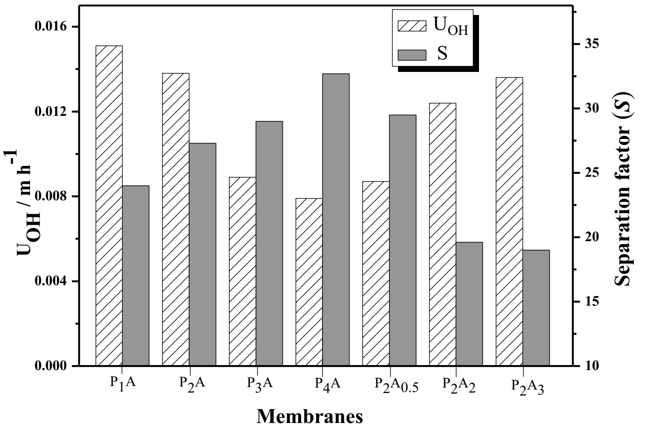


Fig. 8. Dialysis coefficient of OH^- ions (U_{OH}) and separation factors (S) for $\text{NaOH/Na}_2\text{WO}_4$ solution at about 8°C.

The U_{OH} values are also higher than other PVA based cation exchange membranes, which also contain the –OH and $-\text{SO}_3\text{H}$ groups. Hence, the –NH– groups in present membranes seem to have insignificant impediment to the transport of OH^- ions, or even accelerate the transport of OH^- ions. Previous work showed that the $-\text{NH}_2$ groups may hinder the transport of OH^- ions due to their basic property [11]. However, here the –NH– groups have lower alkalinity than the $-\text{NH}_2$ groups. Besides, the zwitterionic membranes also contain the acidic $-\text{SO}_3\text{H}$ groups, which should reduce the alkalinity of –NH– groups. Hence, the –NH– groups may accelerate the OH^- transport through the weak interactions such as hydrogen bonds. For example, the U_{OH} values increase from 0.0087 to 0.0136 m h^{-1} as the content of AMPS increases.

The separation factors are in the range of 19.1–32.7, which are comparable to previous values of PVA based cation exchange membranes (16.9–18.5 [24]) and commercial cation exchange material sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (36 [31]). The values increase as the PVA content increases, but decreases as the content of AMPS increases. The PVA component contains only the –OH groups, which can accelerate the transport of OH^- ions through hydrogen bonds, but should have less effect on the transport of WO_4^{2-} ions. Hence, membrane selectivity can be elevated as the PVA content increases. As the AMPS content increases, the dosage of γ-MPS and the content of $-\text{Si(OCH}_3)_3$ groups decrease, which reduces the membrane cross-linking degree and thus membrane selectivity.

4. Conclusions

Zwitterionic multisilicon copolymers have been prepared through the copolymerization of AMPS and γ-MPS, which contain functional groups of $-\text{NH}-/-\text{SO}_3\text{H}$ and $-\text{Si(OCH}_3)_3$ correspondingly. The copolymers are then taken sol–gel reaction with PVA to prepare zwitterionic hybrid membranes. The membranes are weak basic and strong acidic, which are tentatively used in DD process to separate NaOH/ Na_2WO_4 solution.

The membranes are generally homogeneous and compact. The IDT values are in the range of 204°C–210°C and the T_d values are in the range of 225°C–231°C. The highest TS reaches 51.8 MPa and the E_b is in the range of 72.1%–289.7%. The membranes have the water uptake of 27.7%–88.3% and the ion exchange capacities of 0.90–2.15 mmol g^{-1}. The DD process shows that the dialysis coefficients of OH^- ions (U_{OH}) are in the range of 0.0079–0.0151 m h^{-1}, which are higher than those of the previous membranes (0.0070–0.0130 m h^{-1}). The separation factors are in the range of 19.1–32.7, which are comparable with previous values. The data indicate that the –NH– groups can enhance membrane homogeneity, and have insignificant repulsion to the transport of OH^- ions with the existence of $–SO_3H$ groups. The $–Si(OCH_3)_3$ groups can enhance membrane cross-linking degree and thus enhance membrane stability and selectivity.

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Symbols

P_mA_n — the prepared hybrid membranes, where "*m*" refers to the mass ratio of PVA to the copolymer, and "*n*" refers to the molar ratio of AMPS to γ-MPS.
PVA — polyvinyl alcohol
AMPS — 2-acrylamide-2-methyl-1-propanesulfonic acid
γ-MPS — γ-methacryloxy propyl trimethoxyl silane
DD — diffusion dialysis
U_{OH} — dialysis coefficients of NaOH
S — separation factor for NaOH/Na_2WO_4 solution
M — mol L^{-1}
W_R — water uptake
LER — linear expansion ratio
IEC — ion-exchange capacity
IDT — initial decomposition temperature
T_d — the temperature at 5% weight loss
TS — tensile strength
E_b — elongation at break

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