Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24323

161 (2019) 161–170
September

PPO/PVA hybrid membranes for application in bipolar membrane electrodialysis

Yonghui Wu*, Ke Gao, Lingfei Zou, Juan Yao

School of Chemistry and Environmental Engineering, Yancheng Teachers University, Yancheng, Jiangsu 224051, China, Tel. +86-515-88233188; emails: wuyonghui1000@126.com (Y.H. Wu), 2504589743@qq.com (K. Gao), Tel. +86-515-88233080; emails: 603411257@qq.com (L. Zou), 1076747411@qq.com (J. Yao)

Received 23 September 2018; Accepted 25 April 2019

ABSTRACT

The bipolar membrane electrodialysis (BMED) process requires three types of membranes: cation exchange, anion exchange and bipolar membranes. As commercial membranes are limited in performance, and have a relatively high cost, anion and cation exchange hybrid membranes were prepared in this study from poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), polyvinyl alcohol (PVA) and two kinds of alkoxysilanes. The anion and cation exchange layers, containing $–N^+(CH_3)_3OH^–$ and $–SO_3H$ groups, respectively, can be combined to prepare a bipolar membrane. These membranes were used in BMED process to regenerate CH_3COOH and NaOH from the CH_3COONa waste residue. The newly developed anion and cation exchange hybrid membranes are compact and homogeneous, having the water uptakes between 58.0% and 65.0%, an ion exchange capacity of 1.04–1.58 mmol $g^{–1}$ and an area resistance of 0.73–1.55 Ω cm^2. The anion and cation exchange layers were combined as a bipolar membrane. This increases the membrane stability and area resistance (6.47 Ω cm^2). The bipolar membrane is intact without layer separation after immersion in 65°C water or NaOH solution (1–2 mol $L^{–1}$). The PPO/PVA hybrid membranes can produce 0.25–0.43 mol $L^{–1}$ CH_3COOH/ NaOH during the BMED process. The energy consumption is 18.2–26.5 kWh $kg^{–1}$, and the current efficiency is 70%–72% after running 3 h at 20 mA $cm^{–2}$.

Keywords: PPO; PVA; Bipolar membrane; Electrodialysis; CH_3COONa waste residue

1. Introduction

The BMED process, driven by electric field, can combine the water dissociation of bipolar membrane with electrodialysis of common ion exchange membranes [1,2]. Hence, the process can transform salt (MX) into its corresponding acid (HX) and base (MOH) without introduction of any other agents [3,4]. The process is environmentally friendly, highly effective and can be easily operated. Hence, the BMED process is widely used to desalinate salt solutions to produce corresponding acids and bases [3–5]. For example, the BMED was used to dissociate the CH_3COONa waste residue to regenerate CH_3COOH and NaOH [6].

During BMED process, anion exchange membrane, cation exchange membrane and bipolar membrane are commonly separated by the silicone partition net to form different chambers such as feed, acid, base and electrode chambers [1]. Those membranes are the key factors to determine the running efficiency. Though there are many investigations on the BMED application, the categories of the membranes are restricted and several commercial membranes are generally utilized, such as AMV, CMV and BP-1 [6]. As the structures of commercial membranes cannot be optimized and the prices of commercial membranes are high, membranes with novel structure and low cost need to be developed. The developed membranes should show low voltage drop, high selectivity and high stability in BMED process [7].

The bipolar membrane contains multi layers, including anion exchange layer, intermediate layer and cation exchange layer [8], which can be fabricated by different methods.

---

* Corresponding author.

1944-3994/1944-3986

For example, one porous substrate may be grafted with two oppositely charged groups on both sides, or one ion exchange membrane can be functionalized with oppositely charged groups by grafting or plasma polymerization [9,10]. Another method is direct adhering of anion and cation exchange membranes through hot-pressure or adhesive paste [11,12]. Besides, bipolar membranes can also be prepared by continuous electrospinning of the layers, followed by the solvent evaporation and hot-pressing [8]. In addition, the casting method is more convenient and widely applied, namely, a cation (or an anion) exchange solution is cast onto the oppositely charged layer [7,13]. The casting method is suitable for various casting solutions and requires no special equipments and complex procedures.

However, there are three challenges for the casting method, including the introduction of intermediate layer, the combination strength between two layers, and the coordination of layer properties. First, bipolar membrane needs intermediate layer to reduce the voltage of water splitting [8,14]. The introduction of intermediate layer not only increases the difficulty of membrane preparation but also reduces the combination strength between anion and cation exchange layers. Second, high combination strength is required to avoid layer separation. As the casting method does not include the hot-pressure procedure, layer separation may occur if the two layers lack sufficient combining strength. Finally, the cation and anion exchange layers need to be coordinated in properties [15]. For example, similar hydrophilicity of the two layers is desired; otherwise, the formed bipolar membrane may be greatly curled and layer separated after being immersed in water. Hence, coordinated layers with high combining strength need to be searched for preparing the bipolar membrane.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a versatile starting polymer [16], which provides the possibility for the development of BMED membranes. The PPO could be sulfonated to form SPPO or quaternized to form QPPO. The SPPO and QPPO could be hybridized with alkoxysilanes and mixed with polyvinyl alcohol (PVA) to form casting solutions and then PPO/PVA hybrid membranes [17,18]. The QPPO contains $–N^+(CH_3)_3OH^-$ groups, which can be combined with PVA–OH groups through weak interactions such as hydrogen bonds. Thus, the compatibility beween QPPO and PVA phases is enhanced and the membrane stability is elevated [18]. However, the SPPO, containing $–SO_3Na$ groups (SPPO–Na), is seriously phase-separated with the PVA component. The SPPO–Na/PVA membranes are highly hydrophilic (244%–470%, [17]), which need to be restricted to develop more stable membranes. The stable cation exchange layer may be further combined with anion exchange layer to form bipolar membrane.

Hence in this work, more stable cation exchange membrane will be prepared from the SPPO containing $–SO_3H$ groups (SPPO–H) and PVA, which are cross-linked with two kinds of alkoxysilanes. The cation exchange layer will be combined with QPPO/PVA layer to form bipolar membrane. The bipolar membrane does not need to introduce another intermediate layer, for the PVA–OH groups may reduce the water splitting voltage. Besides, the $–SO_3H$ groups in cation exchange layer would be combined with $–N^+(CH_3)_3OH^-$ groups in anion exchange layer through acid–base ionic bonds, which may enhance the combining strength between the two layers. The PPO/PVA hybrid membranes are all used in BMED process to dissociate the CH_3COONa waste residue for regenerating CH_3COOH and NaOH. The target in the membrane performance is sufficient stability and suitable BMED performance when compared with those of commercial membranes.

2. Experimental

2.1. Materials

All reagents were supplied by companies of China. Monophenyl triethoxysilane (EPh) was purchased from Dalian Yuanyong Organosilicon Plant (Dalian). The other reagents, such as polyvinyl alcohol (PVA), tetraethoxysilane (TEOS), CH_3COOH, NaOH and Na_2SO_4 were purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd., (Shanghai). The PVA, with an average degree of polymerization 1,750 ± 50, was dissolved in water to form 5 wt.% aqueous solution [18]. Purified water supplied by Tidynet purified Water Company (Yancheng) was used throughout the experiments. The water conductivity was lower than 6 μS cm^{-1} at 25°C.

CH_3COONa waste reside, provided by a domestic agrochemical Co., Ltd., was produced during the manufacturing process of dithianon [6]. The composition of the waste residue was complex, including most CH_3COONa (~76.6 wt.%) and other impurities such as naphthalene, anthraquinone and pigment. The waste residue was dissolved in water through mechanical stirring to form the feed solution of BMED [6].

Brominated poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO) and sulfonated poly (2,6-dimethyl-1,4-phenylene oxide) (SPPO) were kindly supplied by Tianwei Membrane Co. Ltd., Shandong of China. The BPPO, with bromination degree of 53.1% [19], was quaternized by trimethylamine to form quaternized poly (2,6-dimethyl-1,4-phenylene oxide) (QPPO) solution [18].

2.2. Preparation of PPO/PVA hybrid membranes

Anion and cation exchange membranes, together with bipolar membranes, were all prepared from PPO, PVA, TEOS and EPh, as shown in Fig. 1.

Cation exchange membrane *S* was prepared from SPPO–H. The SPPO–H was obtained by immersion of SPPO–Na (30 g) in 1 mol L^{-1} (M) HCl solution for 2 d, during which period the HCl solution (1,000 mL) was refreshed for once. The SPPO–H was washed in water for 4–6 times within 2 d, and then dried at room temperature under ventilated circumstance. The SPPO–H (16 g) was dissolved in 70 mL dimethyl formamide to form a homogeneous solution. Then 3.42 mL TEOS and 3.22 mL EPh were added dropwise into the solution within 0.5 h, and the mixture was taken sol-gel reaction at 65°C for 6 h. The mixture solution was added dropwise into 65°C PVA solution (192 mL) within 1 h, and then was continued to stir for 12 h to obtain the cation exchange casting solution. A part of the casting solution was cast onto a glass plate, and dried under adequate aeration to form a film. The film was peeled off from the glass plate and heated from 60°C to 130°C at the rate of 10°C h^{-1}, and kept at 130°C for 4 h.

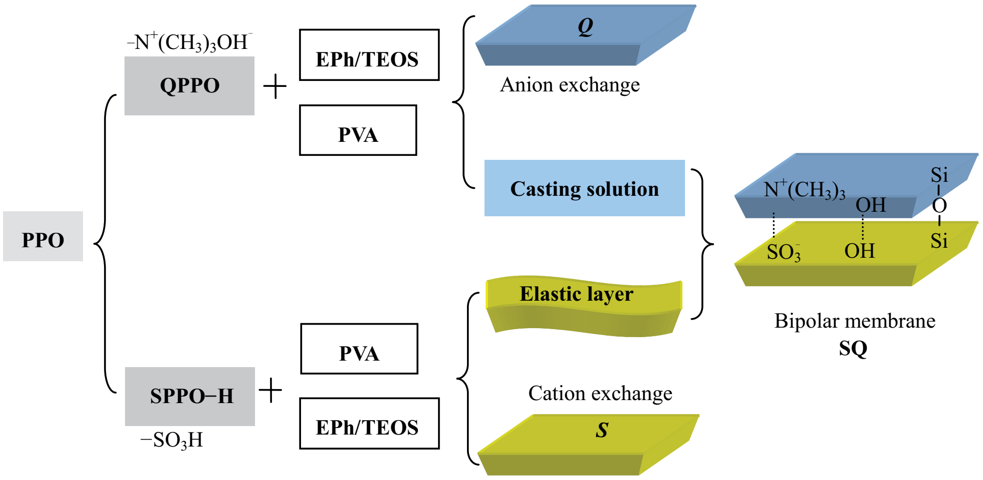

Fig. 1. Preparation of PPO/PVA hybrid membranes from PPO, PVA and two kinds of alkoxysilanes (TEOS and EPh).

Anion exchange membrane *Q* was prepared according to previous method [18]. QPPO solution (16 g) was mixed with 1.86 mL TEOS and 2.02 mL EPh, and then stirred at 65°C for 11 h to form a homogeneous solution. The solution was cast onto a glass plate and dried under adequate aeration to form a film. The film was immersed into 1 M NaOH solution for 2 h, then taken out and washed by water for six times within 3 h. The film was dissolved in 104 mL dimethyl formamide, and then added dropwise into 65°C PVA solution (192 mL) within 1 h. The mixture was stirred at 65°C for 6 h to obtain anion exchange casting solution. A part of the casting solution was cast and dried as the procedures of membrane *S*.

Bipolar membrane SQ was prepared from the anion and cation exchange casting solutions. Cation exchange casting solution (10.5 g) was first cast onto a glass plate. The casting solution was volatilized in a natural condition. The volatilized time was controlled to remove about 75% solvent, after which an elastic film was formed. The film was not totally dried, so that the surface was elastic but not viscous. Then the anion exchange casting solution (10.5 g) was cast onto the elastic film, and volatilized in the natural condition to form combining layer. The two layers were fully dried to form bipolar membrane, and then peeled off from the glass plate. The bipolar membrane was heated from 60°C to 130°C at the rate of 10°C h^{-1}, and kept at 130°C for 4 h.

2.3. Membrane characterizations

Fourier transform infrared spectroscopy (FTIR) was recorded using FTIR spectrometer (Nicolet 67, Thermo Nicolet) with a resolution of 0.09 cm^{-1} and a spectral range of 4,000-400 cm^{-1}. Membrane morphology was observed by scanning electron microscopy (SEM) and digital photos. The SEM was carried out using a microscopy of SU8000 (Hitachi of Japan). Before SEM observation, the membrane cross-section was coated with gold. The digital photos were taken by iPhone 5.

Cation exchange capacity (IEC) was determined through the back titration method. The sample was first equilibrated in 1.0 M HCl solution for 2 d. Then the sample was washed by water totally, and finally immersed in 0.05 M NaOH for 2 d. IEC was determined from the decrease of NaOH through titration with 0.05 M HCl [17].

Water uptake (W_R) and linear expansion ratio (LER) were measured to investigate the membrane hydrophilicity. Dry membrane sample was cut into 3 × 1 cm^2 and weighed, and then the sample was immersed in water for 2 d at room temperature. The wet sample was taken out, and wiped with filter paper to remove its surface water. The wet sample was weighed and measured the length again. W_R was calculated as the relative weight gain per gram of the dry membrane sample [17]. LER was calculated as LER = $(L_2–L_1)/L_1$ × 100%, where L_2 and L_1 are the lengths of wet and dry samples correspondingly [18].

Water swelling resistance was measured by their swelling behaviors in 65°C water. Pre-weighed membrane sample was immersed in 65°C water, and then taken out after 6, 24, 48, 96, and 192 h. The sample surface was quickly wiped dry with filter paper and the wet sample was weighed. The swelling degree was recorded as the weight gain per gram of dry membrane sample. Finally, the wet sample was dried at 65°C till constant weight. The weight loss percentage was calculated as the relative weight loss per gram of the dry membrane sample.

Membrane stability was also investigated in 65°C NaOH solutions. Dry sample was immersed in NaOH solutions (1–2 M) for 60 h. Then the sample was taken out and washed by water for four times within 12 h. The wet sample was weighed after removing its surface water, and finally was dried till constant weight.

$$\text{Swelling degree} = \frac{m_2 - m_3}{m_3} \times 100\% \tag{1}$$

$$\text{Weight loss percent} = \frac{m_1 - m_3}{m_1} \times 100\% \tag{2}$$

Here m_1, m_2 and m_3 represent the initial sample weight, wet weight and final dried weight, respectively.

Membrane area resistance (R_m) was measured by using a specific measuring cell provided by Hefei Chemjoy Polymer Materials Co. Ltd. The membrane sample was immersed in 0.5 M NaCl solution for about 12 h. The electrode chamber was filled with 0.3 M Na_2SO_4 solution, and the inner chamber was filled with 0.5 M NaCl solution. The sample was inserted into the slot (effective area 7.065 cm^2), and the constant current was 0.05 A [20]. The area resistance R_m (Ω cm^2) is calculated by the following equation:

$$R_m = \frac{U - U_0}{I} \times S \tag{3}$$

where U_0 (V) is the gap voltage without membrane, U (V) is the membrane voltage, I (A) is the applied current and S (cm^2) is the effective membrane area.

2.4. BMED for CH_3COONa waste residue

The membrane configuration was adopted as BP–A–C–BP, which contained three compartments, as shown in Fig. 2. CH_3COO^- and Na^+ ions in the feed compartment were passed through the anion and cation exchange membranes, to combine with the H^+ and OH^- ions produced from the bipolar membrane, respectively. Hence CH_3COOH and NaOH were formed in the recovery compartments correspondingly.

The BMED setup was composed of: (1) a direct current power supply (DC power supply WYJ-0-60V/2A×2), purchased from Shanghai Querli electronic equipment Co. Ltd.; (2) two peristaltic pumps (BT300-2J), purchased from Baoding Longer precision Pump Co. Ltd.; (3) the membrane stack, which used titanium-coated ruthenium as anode and cathode. The membrane stack contained several Plexiglass partitions (thickness of 10 mm), one piece of anion exchange membrane, one piece of cation exchange membrane and two pieces of bipolar membranes. The effective area of each piece membrane was 20 cm^2; and (4) four beakers to store electrode rinsing solution, feed solution, acid and base recovery solutions, which contained 0.3 M Na_2SO_4, 1.5 M CH_3COONa, 0.1 M CH_3COOH and 0.1 M NaOH (250 mL), respectively.

The visible bubbles in each compartment were eliminated through circulating the solutions. Then the BMED proceeded with the current density of 20 or 50 mA cm^{-2}. The NaOH and CH_3COOH solutions were sampled every 0.5 h, and their concentrations were determined by acid–base titration.

The BMED performance was evaluated by the recovered acid/base concentrations, voltage drop, energy consumption E (kWh kg^{-1}) and current density η (%). The E and η were calculated according to Eqs. (4) and (5).

$$E = \int_0^t \frac{U \times I \times dt}{\left(C_t - C_0\right) \times V \times \underline{M}} \tag{4}$$

Here U is the voltage drop across the whole membrane stack (V); I is the current across the stack (A); t is the running time (s); C_t and C_0 are the concentration of recovered NaOH or CH_3COOH at time t and 0, respectively; V is the volume of recovered NaOH or CH_3COOH solution (L); M is the NaOH or CH_3COOH molar mass.

$$\eta = \frac{n \times \left(C_t - C_0\right) \times V \times F}{N \times I \times t} \tag{5}$$

Here n is the absolute valence of the ion (n = 1); F is the Faraday constant (96,500 C mol^{-1}); N is the repeating unit of the stack.

3. Results and discussion

3.1. Preparation of the bipolar membrane

Though commercial polymers of BPPO and SPPO are directly used here, the polymers can be modified according to the requirements. For example, the bromination degree of BPPO can be elevated to 95%, and the BPPO can also be quaternized by triethylamine [21]. Besides, the sulfonation degree of SPPO can be adjusted under different bromination or sulfonation processes [22].

The SQ membrane is prepared without the addition of intermediate layer or the hot-press procedure, which are often used in the preparation of other bipolar membranes [7,15]. The hot-press procedure is avoided due to the present casting method and the acid–base ionic bonds. On one hand,

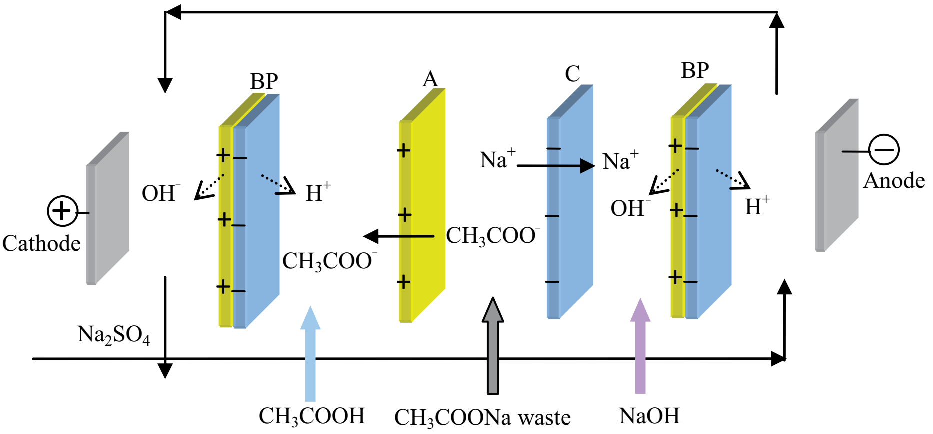

Fig. 2. Schematic of the BMED configurations, in which "BP", "A" and "C" represent bipolar, anion and cation exchange membranes, respectively.

the cation exchange casting solution is volatilized to remove about 75% solvent and to form an elastic film, which can be directly combined with the anion exchange casting solution so that the combining strength between the two layers is enhanced. On the other hand, the $–SO_3H$ groups in cation exchange layer is able to be combined with $–N^+(CH_3)_3OH^–$ groups in anion exchange layer through acid–base ionic bonds, which may enhance the combining strength between the two layers further.

The addition of intermediate layer is also avoided due to the incorporation of PVA in both anion and cation exchange layers. The PVA component is essential due to its three main functions. First, the high density of PVA–OH groups may reduce the voltage drop during BMED process, for the groups can accelerate the transport of H^+ or $OH^–$ ions through weak interactions such as hydrogen bonds [17,18]. Second, the PVA–OH groups may also combine with the ion exchange groups ($–SO_3H$ and $–N^+(CH_3)_3OH^–$) through weak interactions, which elevate membrane stability such as swelling and alkaline resistances [18]. Finally, the PVA component can enhance the membrane flexibility due to its high mechanical strength [23].

Materials containing –OH or $–NH_2$ groups are also used as the intermediate layer in previous reports, such as polyethylene glycol, $Fe(OH)_3$ and $Fe–MIL–101–NH_2$ [8,13,14]. Hence, other polymers such as cellulose derivative and chitosan may also be added in the bipolar membrane to reduce the voltage drop.

3.2. Morphology of membrane *S*

The SEM graphs of previous membrane SPPO–Na/PVA and present membrane *S* are compared in Fig. 3. Previous SPPO–Na/PVA membranes have serious phase separation [17]. The SPPO–Na phase is similar to "islands" distributed in the PVA matrix. The serious phase separation is attributed to the low compatibility between SPPO–Na and PVA phases, and the low membrane cross-linking degree. The previous membranes are prepared from SPPO–Na, PVA and tetraethoxysilane (TEOS) [17]. The SPPO–Na and PVA have different polarities, which may be difficult to be cross-linked with only one kind of alkoxysilane (TEOS) [18]. Hence, the membrane is highly hydrophilic, as revealed by the high W_R in the range of 244%–470% and the high swelling degrees in the range of 335%–878% in 65°C water. The membranes have been utilized in diffusion dialysis (DD) application but cannot be used in ED process.

The SEM graphs show that membrane *S* is generally homogeneous without significant phase separation (Fig. 3). The digital photo in Fig. 4 also shows that the membrane is smooth and homogeneous. The favorable homogeneity should be attributed to the improved compatibility among SPPO–H, PVA and two kinds of alkoxysilanes. First, the $–SO_3H$ group of SPPO can be combined with PVA–OH groups through hydrogen bonds. Second, the alkoxysilanes including TEOS and EPh may be cross-linked with PVA and SPPO-H correspondingly owing to their different polarities [18]. Finally, the acidic $–SO_3H$ groups may act as an acidic catalyst [24], which would accelerate the sol-gel reaction among $–Si(OC_2H_5)$ and –OH groups and thus elevate the cross-linking degree of silica network. The $–SO_3H$ group, as an acidic catalyst, is superior to the HCl during membrane preparation. The HCl would induce the loss of PVA–OH groups and the emergence of unsaturated bonds during heat treatment, and thus membrane coloration occurs after the heat treatment [25].

The improved compatibility and cross-linking can elevate membrane stability. Membrane *S* has the W_R of 65.0% and LER of 13.9%, as shown in Table 1, which are much lower than the previous values (W_R of 244%–470% [17]). The IEC value is proper (1.58 mmol $g^{–1}$) and the area resistance is low (1.55 Ω cm^2). Hence, the membrane may be suitable to be used in ED process.

3.3. Morphology of membrane SQ

The digital photo of membrane SQ, as shown in Fig. 4, is homogenous and compact. The membrane is a little

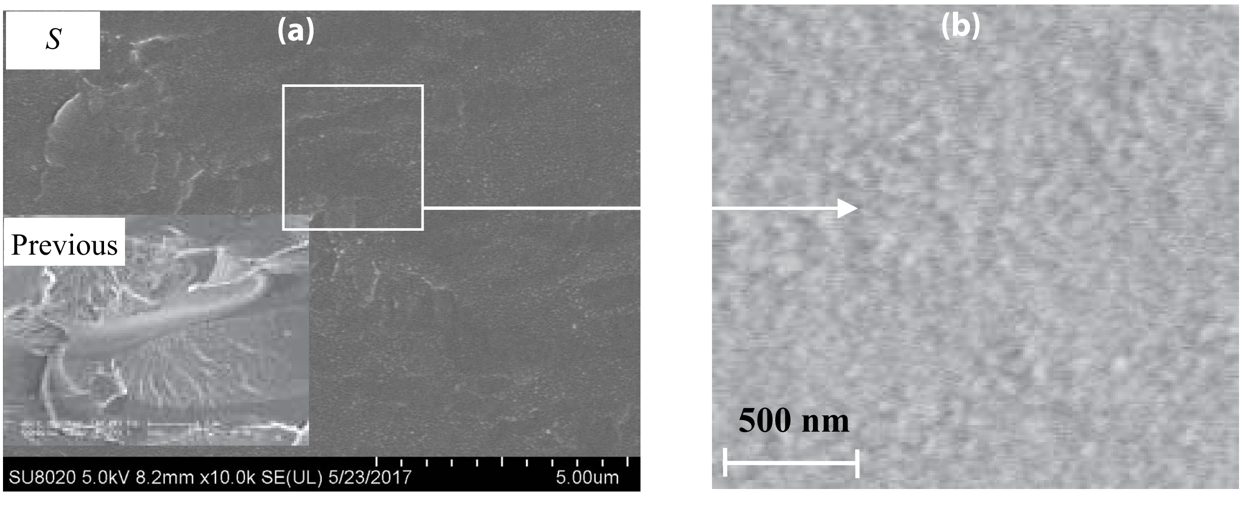

Fig. 3. SEM graphs of previous and present membranes with the magnifications of 10,000× (a) and 55,000× (b). The previous membrane has serious phase separation due to its usage of SPPO–Na, while the present membrane *S* is generally homogeneous due to its usage of SPPO–H.

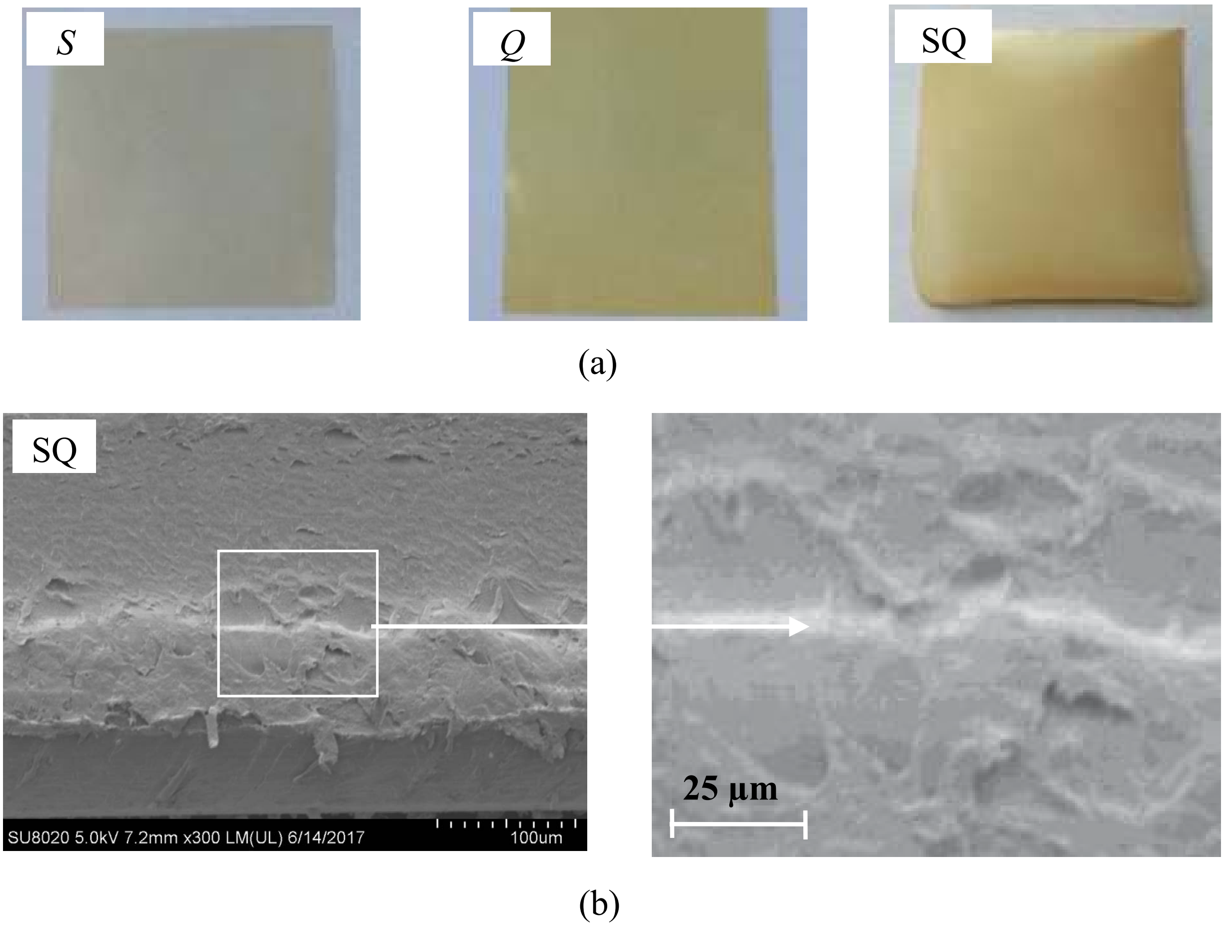

Fig. 4. (a) Digital photos and (b) SEM graphs of PPO/PVA hybrid membranes.

Table 1
Fundamental properties of PPO/PVA hybrid membranes

Membrane	S	Q	SQ
Thickness/mm	0.16–0.18	0.12–0.14	0.22–0.26
Composition	SPPO–H, SiO_2 and PVA	QPPO, SiO_2 and PVA	SPPO–H, QPPO, SiO_2 and PVA
Ion exchange property	Cation exchange	Anion exchange	Bipolar
IEC/mmol g^{-1}	1.58	1.04[a]	–
Area resistance/Ω cm^2	1.55	0.73	6.47
W_R/%	65.0	58.0	77.0
LER/%	13.9	16.3	14.2

[a] Value is cited from the study by Wu et al. [18].

curled, which happens during the combination of anion and cation exchange layers, for the two layers have different volatilizing and contraction rates during the aeration and following heat treatment. The curled degree increases as the membrane area increases. Besides, the membrane is also curled in water due to the different hydrophilicity of the two layers. Fortunately, here anion and cation exchange layers are coordinated in structure and property. The two layers are both prepared from PPO, PVA and alkoxysilanes, and they have similar hydrophilicity (58%–65%). The coordination can reduce membrane curly degree and thus elevate membrane smoothness. The smooth membrane is more suitable to be equipped in the BMED stack.

The SEM graph with low magnification (Fig. 4) can show the whole membrane cross section. The two layers are combined tightly without significant pores or interstices. The tight combination should be attributed to the casting method and the compatibility between two layers. The anion exchange casting solution was cast onto the elastic cation exchange layer, which still contains ~25% solvent to enhance their combining strength. Besides, the two layers should be compatible due to their coordinated structures, which may further elevate their combining strength.

3.4. Membrane FTIR spectra

The FTIR spectra of PPO/PVA hybrid membranes are shown in Fig. 5. The broad band of 3,100–3,600 cm^{-1} is attributed to the stretching vibration of −OH groups from $-SO_3H$, PVA and Si–OH [24,26]. The peak at 1,600 cm^{-1} corresponds to the vibrations of C=C groups of benzene. The peak at 1,465 cm^{-1} is due to the stretching of CH_3–, $-CH_2-$ and –CH– groups (δ), and the intensity is stronger for membrane *Q* due to its $-N^+(CH_3)_3$ groups. Another two peaks at 1,095 and 1,035 cm^{-1} are due to the Si–O–Si and Si–O–C vibrations [27], indicating the formation of silica network. Besides, a significant peak at 1,065 cm^{-1} appears for membrane *S*, which is due to the S=O bonds of $-SO_3H$ groups [28].

3.5. Membrane area resistance

Membranes *S* and *Q* have the area resistances of 0.73–1.55 Ω cm^2 (Table 1), which are lower than those of commercial membranes AMV and CMV (1.5–3.0 Ω cm^2 [6]). The lower area resistance can be analyzed from the membrane structures, including silica network and functional groups. The silica network provides some interfaces between organic and inorganic phases [29] and thus may reduce the area resistance. The functional groups, including ion exchange and –OH groups, can elevate membrane hydrophilicity and thus reduce the area resistance.

However, bipolar membrane SQ has much higher area resistance (6.47 Ω cm^2) than previous commercial bipolar membrane FBM (< 3 Ω cm^2 [6]). The value is also much higher than the total value of membranes *S* and *Q*. The high area resistance indicates that the ion exchange groups, including $-SO_3H$ and $-N^+(CH_3)_3OH^-$ have been combined in the interface between anion and cation exchange layers. The ion exchange groups should form ionic bonds through the acid–base reaction, which reduce their conductivity and elevate the interface resistance.

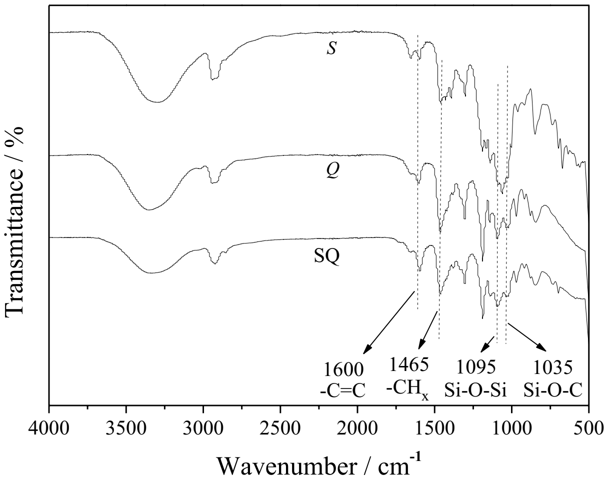

Fig. 5. FTIR spectra of the PPO/PVA hybrid membranes including *S*, *Q* and SQ.

3.6. Stability in 65°C water

Membrane stability is first investigated in 65°C water. The swelling degrees, as shown in Fig. 6, are in the range of 108%–118%, 346%–412% and 230%–264% for membranes *S*, *Q* and SQ, respectively, which are much higher than the W_R values (58.0%–77.0%). The high swelling degrees indicate that some weak interactions, such as hydrogen bonds and electrostatic interaction within PPO/PVA hybrid membranes, are damaged in hot water. The weight loss percentages are in the range of 19.0%–25.6%, as shown in Table 2. The values increase with the membrane swelling degree.

The swelling degrees of membrane *S* are stable in the range of 108%–118% within 192 h, which are much lower than previous SPPO–Na/PVA membranes (335%–878%) [17]. The stable and lower values are attributed to the enhanced cross-linking degree and the favorable compatibility between SPPO–H and PVA phases. The stability of membrane *S* means that the cation exchange layer is also stable within the bipolar membrane. Hence, the swelling degrees of membrane SQ are lower than those of anion exchange membrane *Q*.

3.7. Stability in 65°C NaOH solutions

The membranes are also immersed in 65°C NaOH solution to investigate their alkaline resistance. The swelling degrees are in the range of 210%–382% after immersion in 1 M NaOH solution, as shown in Fig. 7. The value of membrane *S* (210.2%) is higher than its swelling degree in 65°C water, indicating the erosion effect of alkaline solution.

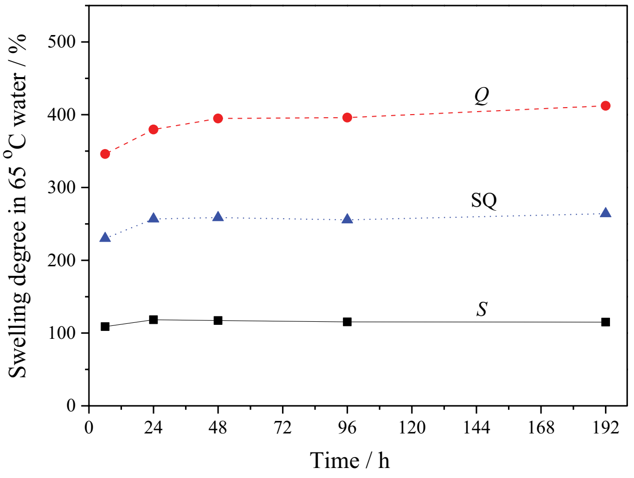

Fig. 6. Swelling degrees in 65°C water for 192 h.

Table 2
Weight loss percentages in 65°C water or NaOH solutions for PPO/PVA hybrid membranes

Membrane	*S*	*Q*	SQ
Water for 192 h/%	19.0	25.6	20.5
1 M NaOH for 60 h/%	31.4	30.7	24.7
2 M NaOH for 60 h/%	26.0	25.7	24.1

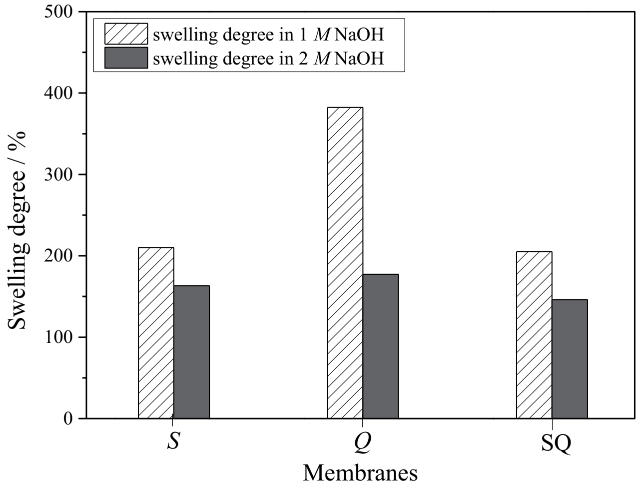

Fig. 7. Swelling degrees in 65°C NaOH solutions (1 M and 2 M) after 60 h.

The alkaline solution can not only swell the membrane but also erode membrane structure. The weight loss percentage (31.4%) is also higher than that in 65°C water due to the erosion.

As the NaOH concentration increases to 2 M, the swelling degrees and weight loss percentages decrease to 146%–177% and 24.1%–26.0% correspondingly. The results indicate that though the alkaline solution can erode the membrane structure, the erosion degree does not increase with the solution concentration. The decreased swelling degree may be attributed to the combination of PVA–OH groups and OH^- ions in the solution [30], which decreases the combining chances of PVA–OH groups to water.

The swelling degree and weight loss percentage of bipolar membrane SQ are lower than those of membranes *S* and *Q*, indicating the bipolar membrane has higher stability. The higher stability should be mainly attributed to the strong combination between anion and cation exchange layers. Anion exchange casting solution is cast onto the elastic cation exchange layer, which can enhance their combining strength. The two layers are combined through weak interactions, covalent bonds and ionic bonds (Fig. 1). The weak interactions include hydrogen bonds and electrostatic interaction, the covalent bonds include Si–O–Si and Si–O–C formed by sol-gel reaction, and the ionic bonds come from the reaction between $-SO_3H$ and $-N^+(CH_3)_3OH^-$ groups. Hence, the bipolar membrane can still be intact without layer separation after the high swelling in water and NaOH solutions, which is essential for the BMED application.

The ionic bonds, in the form of $-N^+(CH_3)_3\ -SO_3^-$ (Fig. 1), should be stronger than the previous combination between $-SO_3Na$ and $-N(CH_3)_3Cl$ groups [31] and thus can increase the membrane stability. The SQ membrane is still intact without layer separation after the swelling and erosion, though the membrane has much higher hydrophilicity (W_R of 77.0%) than commercial membrane BP-1 (23%–26% [1]). However, the ionic bonds would reduce the activity of $-SO_3H$ and $-N^+(CH_3)_3OH^-$ groups and thus increase the membrane area resistance. Fortunately, only a part of the groups are combined in the layer interface, and the membrane BMED performance is still comparable with that of commercial membrane, which will be discussed in the following section.

3.8. BMED for CH_3COONa waste residue

The produced CH_3COOH and NaOH concentrations increase with the time, as shown in Fig. 8. The recovered concentration is 0.25 M after running 3 h at 20 mA cm^{-2}, while the values increase to 0.42–0.43 M at 50 mA cm^{-2}. The results indicate that though membrane SQ employs no catalyst layer, it can also generate acid and base due to the PVA–OH groups. The groups, which can form weak interactions with H^+ or OH^- ions [17,18], are likely to catalyze water splitting reaction for acid and base generation.

The voltage drops are in the range of 21–61 V, as shown in Fig. 9, which are similar to previous values (21–58 V, [6]). The similar voltage drops can be analyzed from the membrane area resistances. Membranes *S* and *Q* have lower area resistances, while bipolar membrane SQ has higher area resistance than previous commercial membranes. Hence, the total resistance may be balanced between present and previous membrane stacks. Fig. 9 also shows that the voltage drops decrease with the time, which is attributed to the increasing concentrations in the acid and base compartments. The voltage drop at 20 mA cm^{-2} is much lower than that at 50 mA cm^{-2} before running 2.5 h, but the value increases after running for 3 h. The increased value is a little strange, which may be attributed to the membrane contamination. The membrane may be contaminated after running for 3 h due to many other impurities in the CH_3COONa waste residue [6].

The energy consumption is high in the initial time, especially for the NaOH at 20 mA cm^{-2}, as shown in Fig. 10. The high energy consumption should be attributed to the high voltage drop and the acid/base leakage during the initial time. The acid and base solutions are circulated to eliminate the visible bubbles before the BMED process, during which some of the acid or base may be leaked under the concentration gradient.

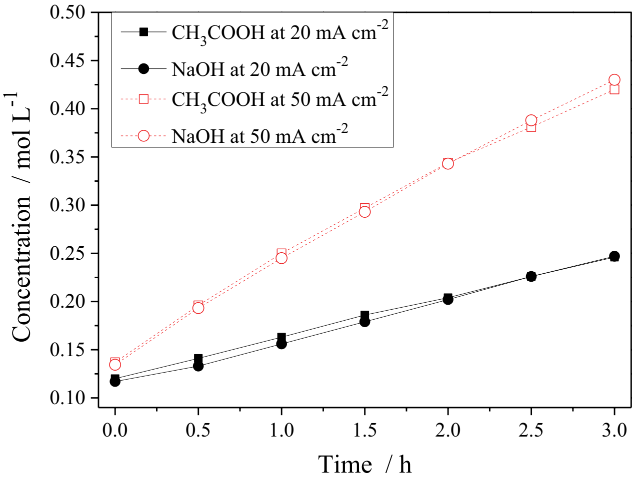

Fig. 8. Recovered CH_3COOH and NaOH concentrations during BMED process.

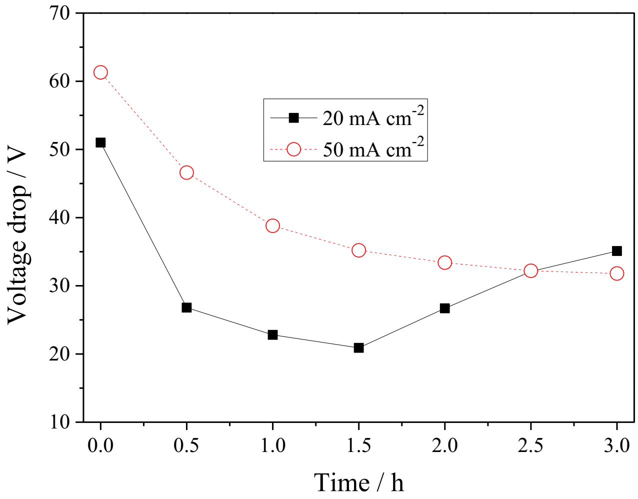

Fig. 9. Voltage drop at 20–50 mA cm^{-2}.

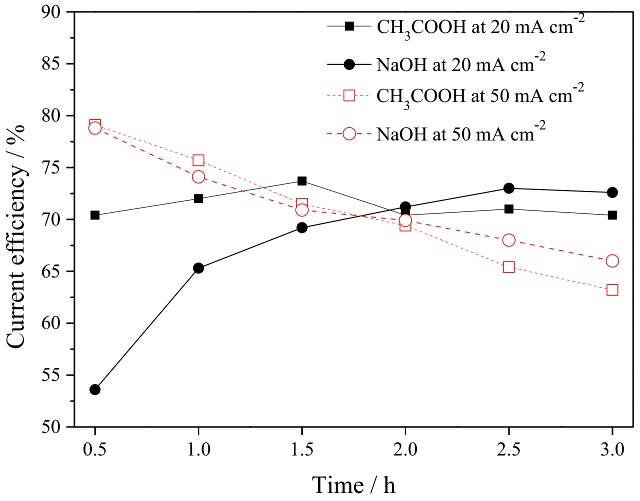

Fig. 11. Current efficiency at 20–50 mA cm^{-2}.

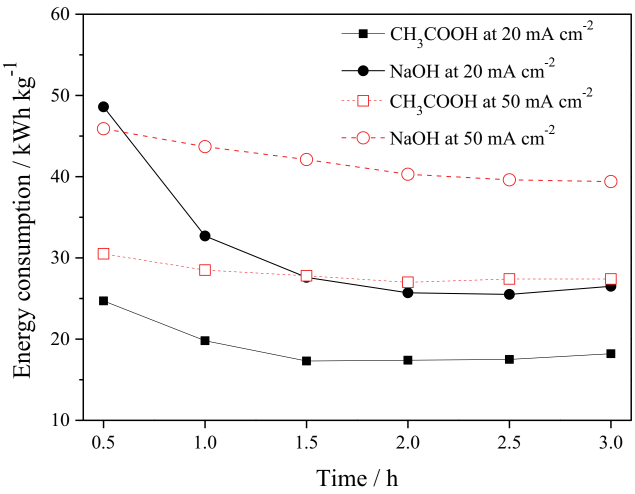

Fig. 10. Energy consumption at 20–50 mA cm^{-2}.

The energy consumption decreases with the time, which is 18.2 kWh kg^{-1} for CH_3COOH and 26.5 kWh kg^{-1} for NaOH at 20 mA cm^{-2}. The values are a little higher than the previous values (15 kWh kg^{-1} for CH_3COOH and 20 kWh kg^{-1} for NaOH [6]). However, the previous acid compartment was added with a strong acid 001*7 type of cation-exchange resin to decrease the voltage drop; otherwise the energy consumption would be much increased [6]. Here the BMED process can be proceeded without any resin.

The current efficiency is generally stable within 70.4%–73.7% for CH_3COOH at 20 mA cm^{-2}, while the value increases to 72.6% after 3 h for NaOH, as shown in Fig. 11. The values are lower than previous values (higher than 85%), which should be attributed to the acid/base leakage by the PPO/PVA hybrid membranes. The membranes contain plenty of –OH groups, which can transport H^+ or OH^- ions through hydrogen bonds [17,18]. Hence, the CH_3COOH or NaOH leakage would be more significant than that of previous commercial membranes [6]. The leakage may become more serious at high current density due to high recovered concentrations, which can be reflected by the decreasing current efficiency at 50 mA cm^{-2}.

4. Conclusions

Three types of hybrid membranes, including anion exchange, cation exchange and bipolar membranes, were prepared from PPO, PVA and alkoxysilanes. The cation exchange membrane contains –OH and $–SO_3H$ groups, which can form weak interactions such as hydrogen bonds to enhance membrane homogeneity and stability. The anion exchange membrane contains $–N(CH_3)_3OH^-$ groups, which is combined with the elastic cation exchange layer to form bipolar membrane.

The PPO/PVA hybrid membranes are compact and homogenous, with the W_R of 58%–77% and IEC of 1.04–1.58 mmol g^{-1}. The swelling degrees are in the range of 115%–412% in 65°C water and 146%–382% in 65°C NaOH solution (1–2 mol L^{-1}). The bipolar membrane is still intact without layer separation after the swelling. The anion and cation exchange membranes have the area resistance of 0.73–1.55 Ω cm^2, but the bipolar membrane has high area resistance of 6.47 Ω cm^2 due to the combination of $–SO_3H$ and $–N(CH_3)_3OH$ groups. The PPO/PVA membranes are used in BMED process to regenerate acid and base from CH_3COONa waste residue. The energy consumption is 18.2–26.5 kWh kg^{-1}, and the current efficiency is 70%–72% after running 3 h at 20 mA cm^{-2}. Further research may be focused on reducing the area resistance and leakage of the PPO/PVA hybrid membranes.

Acknowledgment

This project was supported in part by the Natural Science Foundation of China (Nos. 21376204 and 21476056).

References

[1] Y.M. Zhou, H.Y. Yan, X.L. Wang, Y.M. Wang, T.W. Xu, A closed loop production of water insoluble organic acid using bipolar

membranes electrodialysis (BMED), J. Membr. Sci., 520 (2016) 345–353.

[2] A.M. Rajesh, T. Chakrabarty, S. Prakash, V.K. Shahi, Effects of metal alkoxides on electro-assisted water dissociation across bipolar Membranes, Electrochim. Acta, 66 (2012) 325–331.

[3] Y. Yang, X.L. Gao, A.Y. Fan, L.L. Fu, C.J. Gao, An innovative beneficial reuse of seawater concentrate using bipolar membrane electrodialysis, J. Membr. Sci., 449 (2014) 119–126.

[4] R. Ibáñez, A. Pérez-González, P. Gómez, A.M. Urtiaga, I. Ortiz, Acid and base recovery from softened reverse osmosis (RO) brines. Experimental assessment using model concentrates, Desalination, 309 (2013) 165–170.

[5] X.L. Wang, Y.M. Wang, X. Zhang, H.Y. Feng, T.W. Xu, In-situ combination of fermentation and electrodialysis with bipolar membranes for the production of lactic acid: continuous operation, Bioresour. Technol., 147 (2013) 442–448.

[6] S. Xue, C.M. Wu, Y.H. Wu, J. Chen, Z.X. Li, Bipolar membrane electrodialysis for treatment of sodium acetate waste residue, Sep. Purif. Technol., 154 (2015) 193–203.

[7] A.L. Wang, S.C. Peng, Y.H. Wu, C.H. Huang, T.W. Xu, A hybrid bipolar membrane, J. Membr. Sci., 365 (2010) 269–275.

[8] J.F. Pan, L.X. Hou, Q.Y. Wang, Y.B. He, L. Wu, A.N. Mondal, T.W. Xu, Preparation of bipolar membranes by electrospinning, Mater. Chem. Phys., 186 (2017) 484–491.

[9] C.-L. Hsueh, Y.-J. Peng, C.-C. Wang, C.-Y. Chen, Bipolar membrane prepared by grafting and plasma polymerization, J. Membr. Sci., 219 (2003) 1–13.

[10] G.W. Chen, T.W. Xu, J.S. Liu, Irradiation-induced grafting of polyacrylamide onto the sulphonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) films as well as its use as catalytical layer in a bipolar membrane, J. Appl. Polym. Sci., 109 (2008) 1447–1453.

[11] E. Lobyntseva, T. Kallio, K. Kontturi, Bipolar membranes in forward bias region for fuel cell reactors, Electrochim. Acta, 51 (2006) 1165–1171.

[12] T. Jeevananda, K.-H. Yeon, S.-H. Moon, Synthesis and characterization of bipolar membrane using pyridine functionalized anion exchange layer, J. Membr. Sci., 283 (2006) 201–208.

[13] Q.Y. Wang, B. Wu, C.X. Jiang, Y.M. Wang, T.W. Xu, Improving the water dissociation efficiency in a bipolar membrane with amino-functionalized MIL-101, J. Membr. Sci., 524 (2017) 370–376.

[14] J. Balster, S. Srinkantharajah, R. Sumbharaju, I. Pünt, R.G.H. Lammertink, D.F. Stamatialis, M. Wessling, Tailoring the interface layer of the bipolar membrane, J. Membr. Sci., 365 (2010) 389–398.

[15] K. Venugopal, S. Dharmalingam, Fundamental studies on a new series of SPSEBS-PVA-QPSEBS bipolar membrane: membrane preparation and characterization, J. Appl. Polym. Sci., 127 (2013) 4983–4990.

[16] T.W. Xu, D. Wu, L. Wu, Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)—A versatile starting polymer for proton conductive membranes (PCMs), Prog. Polym. Sci., 33 (2008) 894–915.

[17] Y.H. Wu, J.W. Hao, C.M. Wu, F.L. Mao, T.W. Xu, Cation exchange PVA/SPPO/SiO_2 membranes with double organic phases for alkali recovery, J. Membr. Sci., 423–424 (2012) 383–391.

[18] Y.H. Wu, M.M. Jiang, J. Cao, T.W. Xu, F.L. Mao, Combination of OH^- ions and –OH groups within QPPO/PVA hybrid membranes for acid recovery, Desal. Wat. Treat., 57 (2016) 21023–21033.

[19] J.Y. Luo, C.M. Wu, Y.H. Wu, T.W. Xu, Diffusion dialysis of hydrochloride acid at different temperatures using PPO–SiO_2 hybrid anion exchange membranes, J. Membr. Sci., 347 (2010) 240–249.

[20] G.S. Wang, C.Y. Zhang, M. J Sun, X. Zhang, C.M. Wu, Y.H. Wu, Separation of mixed amino acids by BMED process using porous SPES and SPSf cation exchange membranes, Sep. Purif. Technol., 188 (2017) 539–547.

[21] Y.H. Wu, C.M. Wu, J.R. Varcoe, S.D. Poynton, T.W. Xu, Y.X. Fu, Novel silica/poly(2,6-dimethyl-1,4-phenylene oxide) hybrid anion-exchange membranes for alkaline fuel cells: effect of silica content and the single cell performance, J. Power Sources, 195 (2010) 3069–3076.

[22] D. Wu, R.Q. Fu, T.W. Xu, L. Wu, W.H. Yang, A novel proton-conductive membrane with reduced methanol permeability prepared from bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO), J. Membr. Sci., 310 (2008) 522–530.

[23] M. Higa, M. Kobayashi, Y. Kakihana, A. Jikihara, N. Fujiwara, Charge mosaic membranes with semi-interpenetrating network structures prepared from a polymer blend of poly(vinyl alcohol) and polyelectrolytes, J. Membr. Sci., 428 (2013) 267–274.

[24] C.-E. Tsai, C.-W. Lin, B.-J. Hwang, A novel crosslinking strategy for preparing poly(vinyl alcohol)-based proton-conducting membranes with high sulfonation, J. Power Sources, 195 (2010) 2166–2173.

[25] B. Bolto, T. Tran, M. Hoang, Z. Xie, Crosslinked poly(vinyl alcohol) membranes, Prog. Polym. Sci., 34 (2009) 969–981.

[26] H.G. Zhang, D. Jiang, B.P. Zhang, J.G. Hong, Y.S. Chen, A Novel hybrid poly (vinyl alcohol) (PVA)/poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) membranes for reverse electrodialysis power system, Electrochim. Acta, 239 (2017) 65–73.

[27] L. Ge, L. Wu, B. Wu, G.H. Wang, T.W. Xu, Preparation of monovalent cation selective membranes through annealing treatment, J. Membr. Sci., 459 (2014) 217–222.

[28] P.R. Jothi, S. Dharmalingam, An efficient proton conducting electrolyte membrane for high temperature fuel cell in aqueous-free medium, J. Membr. Sci., 450 (2014) 389–396.

[29] C.-C. Yang, S.-J. Chiu, C.-T. Lin, Electrochemical performance of an air-breathing direct methanol fuel cell using poly(vinyl alcohol)/hydroxyapatite composite polymer membrane, J. Power Sources, 177 (2008) 40–49.

[30] A.N. Mondal, C.L. Zheng, C.L. Cheng, J.B. Miao, Md.M. Hossain, K. Emmanuel, M.I. Khan, N.U. Afsar, L. Ge, L. Wu, T.W. Xu, Novel silica-functionalized aminoisophthalic acid-based membranes for base recovery via diffusion dialysis, J. Membr. Sci., 507 (2016) 90–98.

[31] C. Wang, C.M. Wu, Y.H. Wu, J.J. Gu, T.W. Xu, Polyelectrolyte complex/PVA membranes for diffusion dialysis, J. Hazard Mater., 261 (2013) 114–122.