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The preparation of SPEEK/phosphate salts membranes and application for CO_2/CH_4 separation

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ABSTRACT: SPEEK/phosphate salts membranes were prepared and utilized for CO_2/CH_4 separation. SPEEK with abundant $–SO_3H$ groups and EO groups on polymer chains would be beneficial for CO_2 transport. The doped phosphate salts (NaH_2PO_4, Na_2HPO_4 and Na_3PO_4) with different acid-base properties increased the water content in the membrane, and water was expected to increase both the solubility and diffusivity of CO_2 in the membrane. All membranes were characterized by FTIR, TGA, and XRD. The CO_2 permeability and CO_2/CH_4 selectivity of SPEEK/Na_3PO_4 membranes were higher than that of SPEEK/NaH_2PO_4 and SPEEK/Na_2HPO_4 membranes. Compared to the pure SPEEK membrane, the CO_2 permeability and CO_2/CH_4 selectivity of SPEEK/Na_3PO_4−10 membrane were increased by 144% and 65%, respectively. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43399.

KEYWORDS: hydrophilic polymers; membranes; separation techniques

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INTRODUCTION

Efficient CO_2 capture has attracted worldwide attention, such as the purification of synthesis gas, greenhouse gas sequestration, natural gas sweetening, etc.[1–3] Polymer-based membrane gas separation has been proved to be an effective technology for CO_2 capture due to its advantages of cost-effective, easy operation, energy-effective and environmental sustainability.[4] The commonly used membrane materials for CO_2 separation could be divided into two categories: glassy polymers and rubbery polymers. The properties of high separation factor as well as good mechanical and thermal stability made glassy polymers desirable materials for CO_2 capture.[5–14]

Sulfonated polyether ether ketone (SPEEK) was a glassy polymer and widely utilized as proton conducting membranes in fuel cells.[15] Recently, SPEEK have been studied as a potential membrane material for CO_2 separation among many other polyelectrolyte materials ascribed to the hydrophilic -SO_3H groups and carbon dioxide-philic ethylene oxide (EO) groups on polymer chains. Khan and co-workers prepared SPEEK membranes and found that the gas permeability and selectivity simultaneously increase when the sulfonation degree and the valent of counterions of membranes increased.[16] In addition, SPEEK/Matrimid blend membranes[17] and SPEEK/inorganic hybrid membranes,[18–21] such as $–SO_3$ functionalized mesoporous MCM-41, amine-functionalized metal organic frameworks, TiO_2 and amino acid-functionalized graphene oxide, were studied and used for separation CO_2 from gas mixture. The results suggested that the increase of fractional free volume facilitated the transport of CO_2 by modified SPEEK with nanoinorganic particles.

In addition, water is important in facilitated transport of CO_2 by means of the reaction of CO_2 with water forming the bicarbonate anion and water-induced membrane swelling, for instance water-swollen polymeric membranes (includes polymer electrolyte membranes) and fixed carrier membranes.[22] The accommodation of water in the membrane was achieved by using hydrophilic groups, salt hydrate and nanohydrogels, etc.[16,23–26] The incorporation of salt hydrate in polymer membrane has been showed good water uptake capacity and water retention performance. To increase CO2 transport properties, phosphate salts such as sodium dihydrogen phosphate, sodium hydrogen phosphate and sodium phosphate can be used. Compared with hydrophilic sulfonic acid ($–SO_3H$), the binding energy of phosphonic acid with water molecule (47.3 KJ mol^{-1}) is higher than that of sulfonic acid with water molecule (44.4 KJ mol^{-1}),[27] which indicated that phosphonic acid has easier capacity to bind with water molecule and retained more water. Furthermore, phosphate salts has different acid-base properties, the acid−base interaction between salts and CO_2 could increase the solubility of CO_2.

In this study, we select three phosphate salts such as sodium dihydrogen phosphate ($NaH_2PO_4·2H_2O$), sodium hydrogen

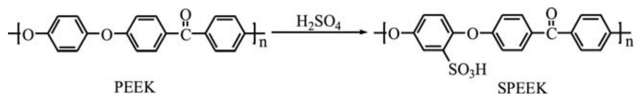

Figure 1. Chemical synthesis of SPEEK from PEEK.

phosphate ($Na_2HPO_4 \cdot 12H_2O$) and sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) with weak acid, weak alkali, strong alkaline to tailor water uptake in SPEEK membrane for enhancing CO_2 separation performance. The effect of salt type, salt content, feed pressure, and operating temperature on CO_2 separation properties were systematically investigated.

EXPERIMENTAL

Materials

Polyether ether ketone (PEEK) (Victrex®, Grade 450 PF), was purchased from Shanghai Huipu Chemical. Concentrated sulfuric acid (H_2SO_4) (95 − 98%) was obtained from Kelong Chemical Reagent Factory (Chengdu, China). *N, N*-Dimethyl acetamide (DMAc) was purchased from Tianjin Fuyu Fine Chemical. $NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$ and $Na_3PO_4 \cdot 12H_2O$ were supplied by Tianjin Shengao Chemical Reagent. All chemicals were of analytical grade and used without further purification. Deionized water was produced in our laboratory and used throughout the study.

Sulfonation of Polymers

PEEK was sulfonated by concentrated sulfuric acid (Figure 1) according to the methods reported in the literature.[28] First, a mount of PEEK powder was dried in an oven at 80 °C for 24 h. Then, 10 g of PEEK sample was gradually dissolved in 250 mL concentrated sulfuric acid under vigorous stirring for 7 h at 50 °C in a three neck flask. Afterward, the resulted solution was gradually precipitated into ice-cold water under mechanical agitation for 1 h further and let the suspension overnight. Finally, the polymer precipitate was filtered and washed several times with deionized water until the pH was neutral. After drying at room temperature for 24 h, the polymer was then dried in vacuum oven at 50 °C for another 24 h. The degree of sulfonation (DS) of the prepared SPEEK was measured by the acid−base titration method. The SPEEK with a DS of 65% was used in the follow research.

Membrane Preparation

SPEEK was dissolved in DMAc (15 wt %) under mechanical stirring at 60 °C for 6 h to obtain a homogeneous solution. After cooling the solution to room temperature, a certain amount of phosphate salts powder, such as $NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$ and $Na_3PO_4 \cdot 12H_2O$, was prepared as solution with distilled water as solvent, then added to the polymer solution for another 3 h stirring. The obtained solution was ultrasonic degassing and poured on a clean flat glass plate, dried at ambient temperature for 48 h and further annealed in vacuum oven at 40 °C for another 24 h to remove residual solvent. The pure SPEEK membrane was also fabricated without the dope of salt solution.

The as-prepared membranes are named as SPEEK/X-Y, where X represent the salts of $NaH_2PO_4 \cdot 2H_2O$, $Na_2HPO_4 \cdot 12H_2O$ and $Na_3PO_4 \cdot 12H_2O$, respectively, and Y is the weight percentage of the salt content (5, 10, 15, and 20%) relative to the weight of SPEEK (Table I). The membrane thickness is range from 40 to 70 μm.

Membrane Characterization

The surfaces and cross-sectional morphology of pure SPEEK and SPEEK/phosphate salts membranes were observed by scanning electron microscope (SEM, JSM-6490LV). Membrane samples were cryogenically fractured in liquid nitrogen and then sputtered with gold before SEM analysis.

Fourier transform infrared spectrometer (FTIR, Nicolet AVATAR 360) were recorded for pure SPEEK and SPEEK/phosphate salts membranes with the scan range of $400 - 4000$ cm^{-1}.

The thermal stability of the pure SPEEK and SPEEK/phosphate salts membranes were conducted by thermogravimetric analysis (TGA, NETZSCH STA 449 F3). The samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min in nitrogen atmosphere with a flow rate of 30 mL/min.

The crystalline structure of pure SPEEK and SPEEK/phosphate salts membranes were performed by X-ray diffraction (XRD) at wide angles ($10 - 90°$ in 2θ) using a Bruker D8 X-ray diffractometer with Cu Kairradiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA.

Mechanical property of pure SPEEK and SPEEK/phosphate salts membranes was studied using an Instron Mechanical Tester (STRUN 3366). Each sample was cut into 0.5 cm × 3.0 cm and examined with an elongation rate of 5 mm/min at room temperature.

Water Uptake

Water uptake of the pure SPEEK and SPEEK/phosphate salts membranes were measured according to the literature.[29] Each membrane was weighted to determine the "humidified" weight (W_h) after immersed in deionized water until no more weight gain at room temperature, and then dried in vacuum oven at 150 °C to determine its "dried" weight (W_d), thus the water uptake of the membrane was calculated as follows:

$$\text{Water uptake}(\%) = \frac{W_h - W_d}{W_d} \times 100 \quad (1)$$

Gas Permeation Experiments

Gas permeation performance of the flat-sheet membranes were performed at 25 °C based on the conventional constant pressure/variable volume method under humidified conditions (Figure 2). Mixed-gas CO_2-CH_4 (10/90 vol %) were used as feed gas

Table I. The Contents of Phosphate Salts in Membranes

Membrane	The content of phosphate salts (g)
SPEEK-65	0.00
SPEEK/NaH_2PO_4−5	0.15
SPEEK/Na_2HPO_4−5	0.15
SPEEK/Na_3PO_4−5	0.15
SPEEK/Na_3PO_4−10	0.30
SPEEK/Na_3PO_4−15	0.45
SPEEK/Na_3PO_4−20	0.60

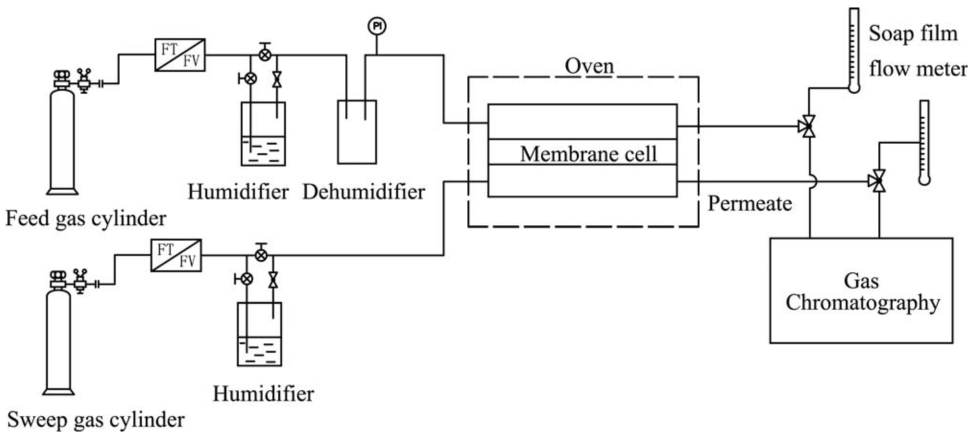

Figure 2. Schematic of gas permeation apparatus.

while H_2 was used as sweep gas. In a typical test, 2 bar of feed gas was firstly introduced into a humidifier with temperature of 40 °C to be saturated with water then passed through an empty pot to remove the condensate water. Meanwhile, the sweep gas was humidified at room temperature and atmosphere pressure. Both two types of gases were leaded into the membrane cell placed in an oven after humidified. The flow of feed and sweep gas were conducted by two mass flowmeters. The composition of feed and permeate gas were analyzed by gas chromatograph. The effective membrane area was 15.9 cm^2.

Gas permeability (P_i, barrer, 1 barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg) was defined as:

$$P_i = \frac{Q_i l}{\Delta P_i A} \tag{2}$$

where Q_i is the gas volumetric flow rate (cm^3/s) (STP), l is the thickness of the membrane (cm), $\Delta\ p_i$ is the trans-membrane pressure difference (cmHg), and A is the effective membrane area (cm^2).

The CO_2/CH_4 selectivity was calculated by

$$a_{ij} = \frac{P_i}{P_j} \tag{3}$$

RESULTS AND DISCUSSION

Membrane Characterization

SEM Images of SPEEK and SPEEK/Phosphate Salts Membranes. The surface and cross-section morphology of pure SPEEK and SPEEK/phosphate salts membranes with different salts were shown in Figure 3. The surface and cross-section of all membranes were dense and uniform. The results suggested that the phosphate salts have good compatibility with SPEEK matrix, and were homogeneously dispersed in SPEEK matrix.

FTIR Spectra of SPEEK and SPEEK/Phosphate Salts Membranes. FTIR spectra were utilized to confirm the chemical structure of the pure SPEEK and SPEEK/phosphate salts membranes. As shown in Figure 4, the pure SPEEK presented characteristic bands at 1080 cm^{-1} ascribed to the vibration of

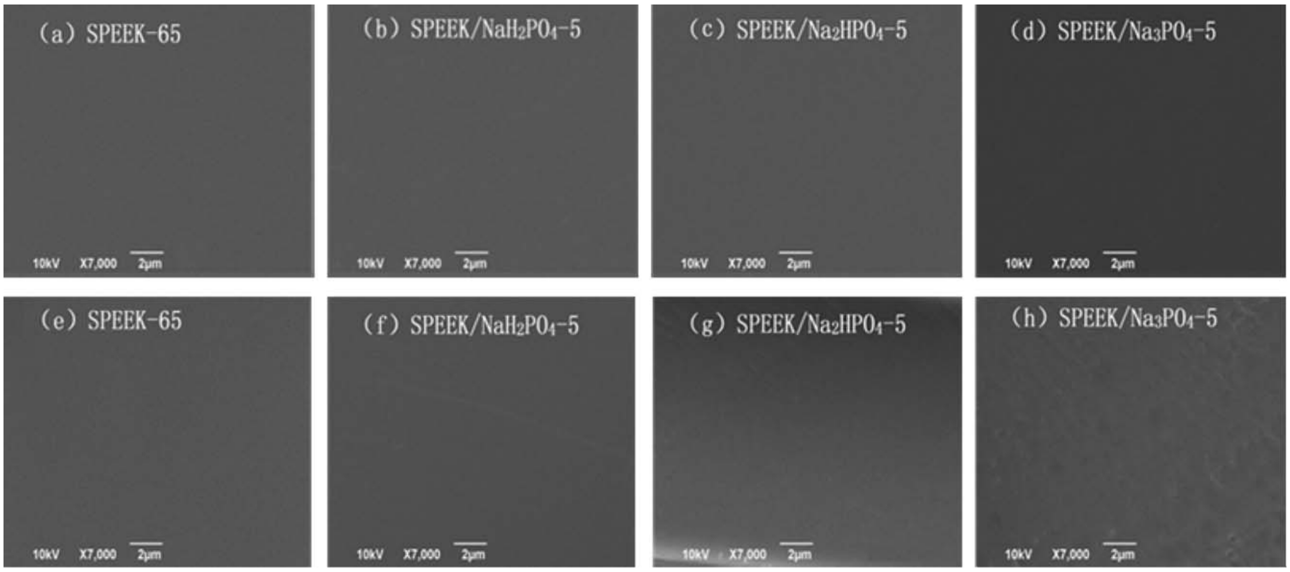

Figure 3. SEM images of the surface of (a) SPEEK-65, (b) SPEEK/NaH_2PO_4−5, (c) SPEEK/Na_2HPO_4−5, (d) SPEEK/Na_3PO_4−5 membranes; cross-section of (e) SPEEK-65, (f) SPEEK/NaH_2PO_4−5, (g) SPEEK/Na_2HPO_4−5, (h) SPEEK/Na_3PO_4−5 membranes.

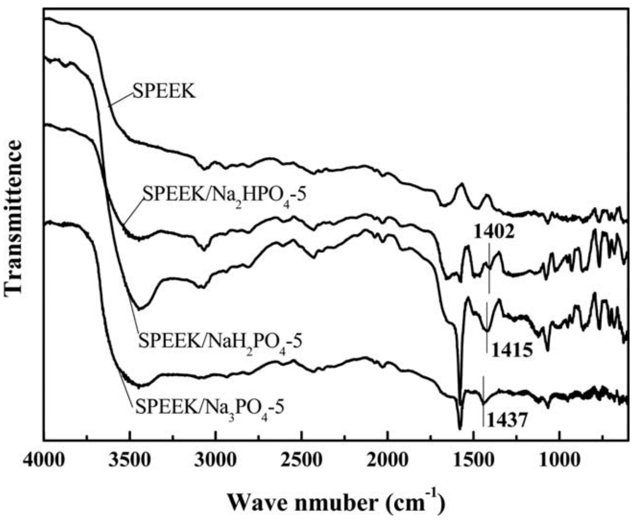

Figure 4. FTIR spectra of pure SPEEK and SPEEK/phosphate salts membranes.

O=S=O groups, corresponding to the chemical structure of SPEEK. SPEEK/phosphate salts membranes showed similar characteristic spectra to the pure SPEEK membrane without distinct variation. The membranes doped with NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 showed the stretching vibration peaks of P=O at 1415, 1402, and 1437 cm^{-1}, these characteristic bands suggested that the phosphate salts were successfully introduced into the polymer matrix. All membranes showed the representative peaks of –OH at the position of 3445 cm^{-1}, phosphate salts were presented in SPEEK membranes, the corresponding peak intensity increased, which indicating the enhance hydrophilic of membranes.

TGA of SPEEK and SPEEK/Phosphate Salts Membranes. The thermal stability of the as-prepared membranes was investigated by TGA. As shown in Figure 5, all samples displayed three stages of weight loss. The first weight loss before 240 °C was attributed to the evaporation of water and residual solvent in the membrane. The second weight loss ranged from 240 − 370 °C was ascribed to the degradation of $–SO_3H$ groups, and the weight loss starting from about 400 °C was related to the decomposition of the polymer main chains. The pure SPEEK membrane started to decompose around 160 °C, while the SPEEK/phosphate salts membranes started to decompose at a higher temperature, indicating the doping of phosphate salts into the membrane improved the thermal stability of the membrane. Moreover, the second degradation step of SPEEK/Na_3PO_4 membrane was not obvious gradually with increasing the content of Na_3PO_4 in the SPEEK membrane, which suggested the membrane thermal stability also improved.

XRD of SPEEK and SPEEK/Phosphate Salts Membranes. Figure 6 showed the XRD curve of pure SPEEK membrane and SPEEK/phosphate salts membranes. As can be seen, the pure SPEEK membrane existed a crystalline peak at the 2θ of 19°. The SPEEK/phosphate salts membranes presented the crystalline peaks at the same position and no characteristic peaks of phosphate salts were observed, indicating that the phosphate salts dispersed at the molecular level in the polymer matrix. Meanwhile, SPEEK/phosphate membranes were amorphous in nature, which endowed the easy mobility of polymer chains and improved the gas permeability through the membranes.

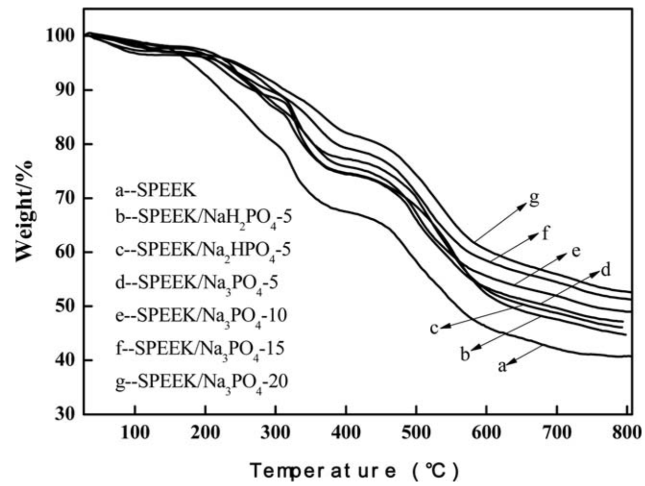

Figure 5. TGA curves of pure SPEEK and SPEEK/phosphate salts membranes.

Mechanical Properties of SPEEK and SPEEK/Phosphate Salts Membranes. The mechanical properties of pure SPEEK and SPEEK/phosphate salts membranes were evaluated by tensile tests. As shown in Table II, the tensile strength and Young's modulus of SPEEK/Na_3PO_4−10 membrane was higher than that of pure SPEEK. The elongation at break of SPEEK/Na_3PO_4−10 membrane showed the highest value among all membranes. The increased tensile strength and Young's modulus indicated that there existed the strong interactions between salts and polymer matrix. The high elongation at break of membranes demonstrated that the increase of membrane plasticity.

Membrane Separation Performance

Effect of Salt Type on Gas Separation Performance. SPEEK was a hydrophilic polymer with large amount of $–SO_3H$ groups and EO groups, which possess high CO_2 selectivity. However,

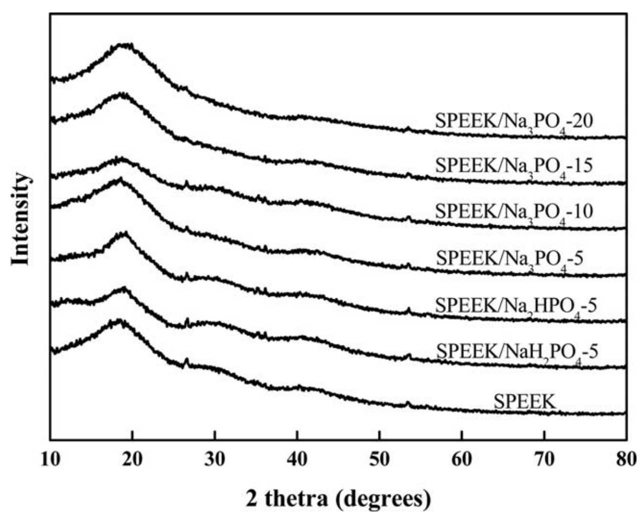

Figure 6. XRD patterns of pure SPEEK and SPEEK/phosphate salts membranes.

Table II. Mechanical Properties of Pure SPEEK and SPEEK/Phosphate Salts Membranes

Membrane	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (GPa)
SPEEK-65	46.94	6.67	0.70
SPEEK/NaH_2PO_4−5	59.61	3.33	0.97
SPEEK/Na_2HPO_4−5	33.83	36.67	0.60
SPEEK/Na_3PO_4−5	33.44	33.33	0.65
SPEEK/Na_3PO_4−10	54.46	53.33	0.84
SPEEK/Na_3PO_4−15	59.52	20.00	0.91
SPEEK/Na_3PO_4−20	77.63	16.67	1.11

high sulfonation degree of SPEEK matrix was not favorable for fabricating the membrane with high mechanical and thermal stability, thus a suitable sulfonation degree of 65% was used in this study.

CO_2 permeability and CO_2/CH_4 selectivity of SPEEK and SPEEK/phosphate salts membrane were presented in Figure 7. As can be seen, SPEEK/phosphate salts membranes exhibited better CO_2 separation performance than pure SPEEK membrane. SPEEK/Na_3PO_4 membrane showed the best CO_2 separation performance compared with SPEEK/NaH_2PO_4 and SPEEK/Na_2HPO_4 membranes at the same salt loading of 5 wt %. In addition, the water content in SPEEK/phosphate salts membranes was measured and presented in Figure 8. The water uptake of SPEEK/phosphate salts membranes was higher than that of pure SPEEK membrane. Furthermore, the water uptake of SPEEK/Na_3PO_4−5 membranes was highest than SPEEK/NaH_2PO_4−5 and SPEEK/Na_2HPO_4−5 membranes. The increase of water uptake could swell the polymer matrix and decrease the crystallization of SPEEK/phosphate salts membrane, which could increase CO_2 permeability.[16] In addition, NaH_2PO_4, Na_2HPO_4 and Na_3PO_4 aqueous solution was weak acid, weak alkaline and strong alkaline respectively. The addition of these salts increased water uptake and basicity of membranes, improving CO_2 dissolution. Hence, among three types of SPEEK/phosphate salt membranes, SPEEK/Na_3PO_4−5 membrane has the highest water uptake and presents the highest CO_2 permeability of 57 barrer and CO_2/CH_4 selectivity of 53.9.

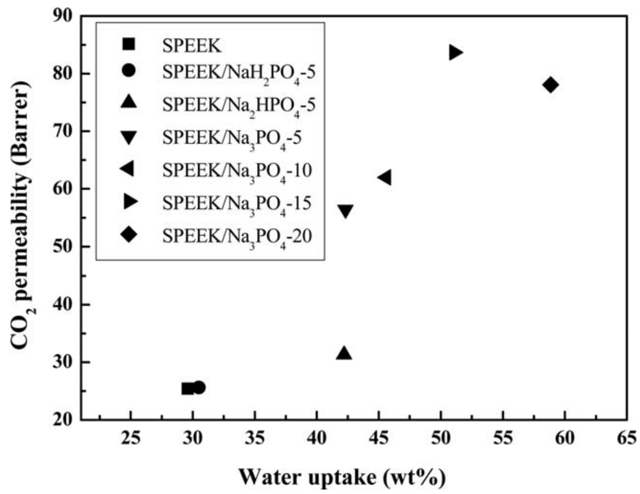

Figure 8. Correlations between CO_2 permeability and water uptake of membrane.

Effect of Salt Content on Gas Separation Performance. The SPEEK/Na_3PO_4 membranes were chosen as representation samples to elucidate the effect of Na_3PO_4 content in SPEEK membrane on CO_2 separation performance as plotted in Figure 9. The CO_2 permeability increased with the increase of Na_3PO_4 content in the membrane. The CO_2/CH_4 selectivity increased first, and then decreased with increasing Na_3PO_4 content in the membranes. The highest CO_2/CH_4 selectivity of 61.0 was obtained when 10% Na_3PO_4 was doped in membrane.

The increase in CO_2 permeability was attributed to the increase of water uptake (see Figure 9) and basicity in the membrane with increasing Na_3PO_4 content. However, the increased water in the membranes lead to the swell of SPEEK matrix when the salt content further increased more than 10 wt %, which

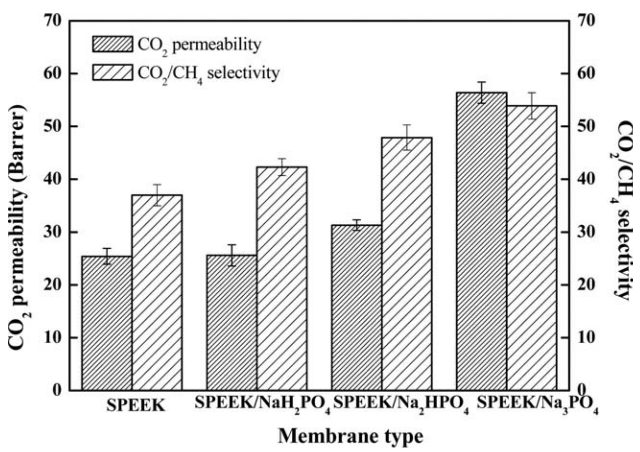

Figure 7. Effect of the different salt types in membranes on CO_2 permeability and CO_2/CH_4 selectivity (Permeation tests were performed at 25 °C and 2 bar under humidified state).

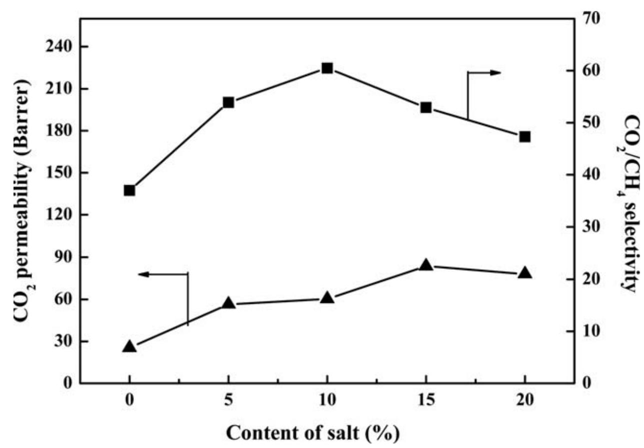

Figure 9. Effect of salt content on CO_2 permeability and CO_2/CH_4 selectivity (Permeation tests were performed at 25 °C and 2 bar under humidified state).

simultaneously increased CH_4 diffusion, thus resulted in the decrease of CO_2/CH_4 selectivity.

Effect of Feed Gas Pressure on Gas Separation Performance. The influence of feed gas pressure on CO_2/CH_4 mixed gas separation performance was plotted in Figure 10 by using SPEEK/Na_3PO_4−10 and pure SPEEK membranes. Both CO_2 permeability and CO_2/CH_4 selectivity decreased as the feed pressure increased from 2 to 6 bar. With increasing pressure, the gas permeability decreased due to the decrease in CO_2 solubility coefficients as a typical characteristic of glassy polymer. Also, there existed competitive adsorption between CH_4 and CO_2 molecules. Consequently, a reduction in CO_2/CH_4 selectivity was observed.

Effect of Operating Temperature on Gas Separation Performance. Figure 11 presented the effect of temperature on CO_2 separation performance for SPEEK/Na_3PO_4−10 and pure SPEEK membranes in the range of 25 − 65 °C. CO_2 permeability and CO_2/CH_4 selectivity simultaneously decreased with increasing temperature. The CO_2 permeability was ascribed to the comprehensive effect of reduced water retention in the membrane, increased gas diffusivity and decreased gas solubility as temperature increased. Meanwhile, the decreased CO_2/CH_4 selectivity was mainly attributed to the faster diffusion of CH_4 than that of CO_2, thus lead to the decreased CO_2/CH_4 diffusivity selectivity with increasing temperature.

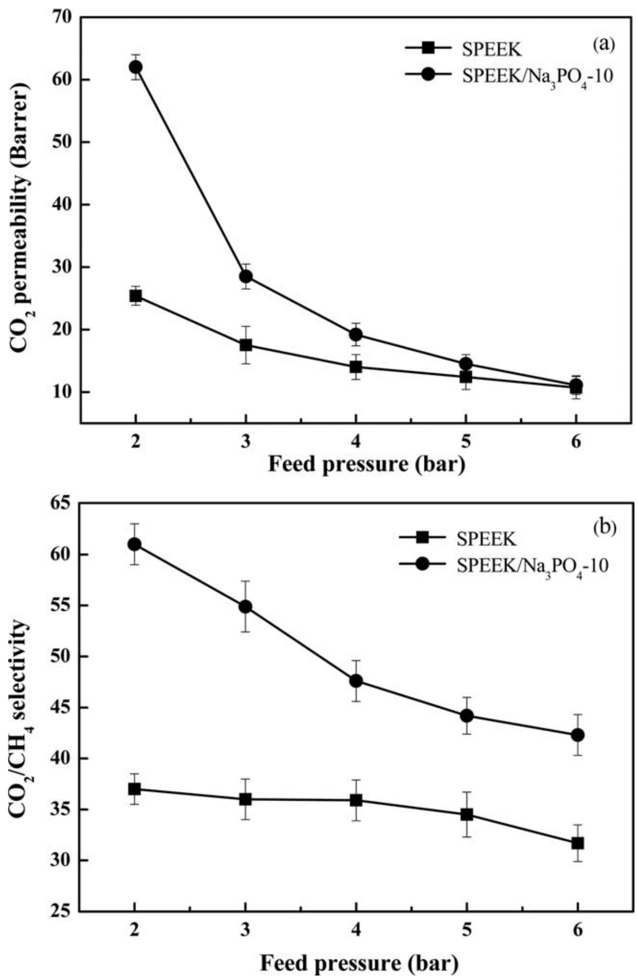

Figure 10. Effect of feed pressure on (a) CO_2 permeability and (b) CO_2/CH_4 selectivity (Permeation tests were performed at 25 °C under humidified state).

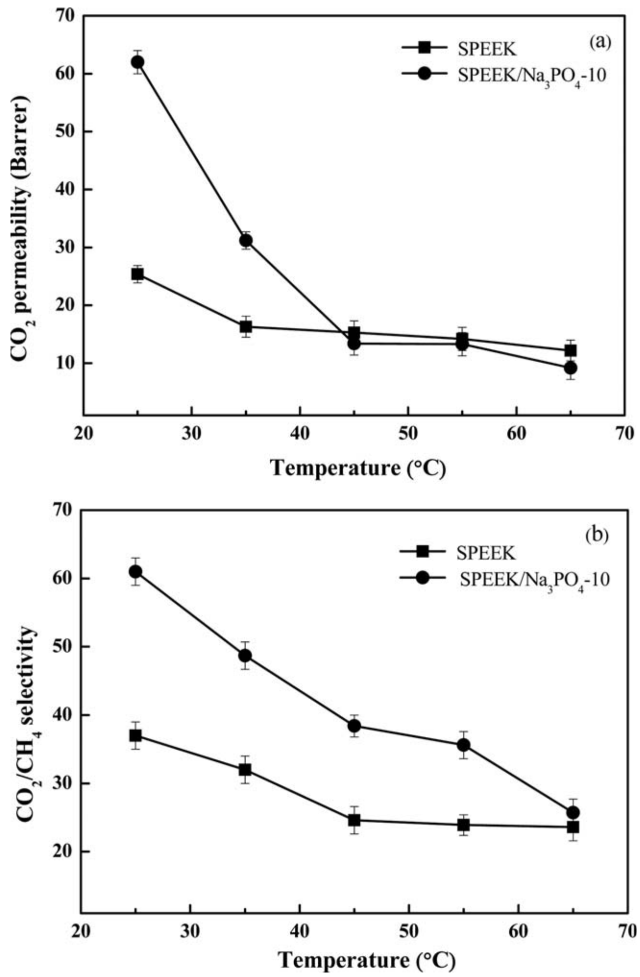

Figure 11. Effect of operating temperature on (a) CO_2 permeability and (b) CO_2/CH_4 selectivity (Permeation tests were performed at 2 bar under humidified state).

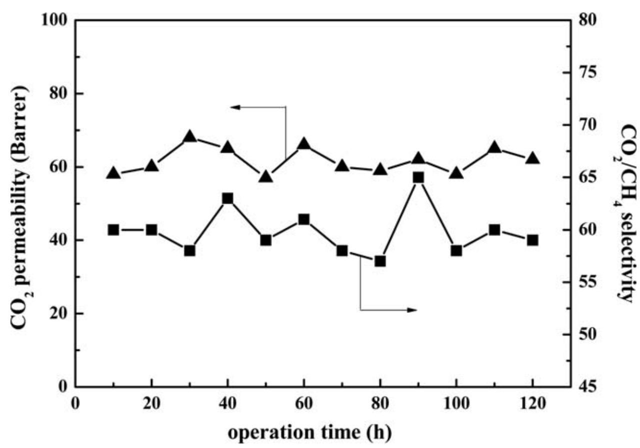

Figure 12. The long-time stability of SPEEK/Na_3PO_4−10 membrane for CO_2/CH_4 mixed gas. (Permeation tests were performed at 25 °C and 2 bar under humidified state).

The Long-Time Stability of the Membranes. The long-time stability of SPEEK/Na_3PO_4−10 membrane was measured during a continuous 120 h test at 25 °C and 2 bar under humidified state. As shown in Figure 12, the CO_2 permeability and CO_2/CH_4 selectivity remained stable values during the whole test period, demonstrating that the addition of phosphate salts within the membrane did not affect the structure and mechanical stability of the membrane.

CONCLUSIONS

SPEEK/phosphate salts membranes were prepared and used for CO_2/CH_4 separation. The doped phosphate salts increased the water content in the membrane and made a contribution to the improvement of CO_2 separation performance. Meanwhile, the increased basicity of phosphate salt was beneficial for CO_2 separation. However, with the increasing of feed pressure and operating temperature, both CO_2 permeability and CO_2/CH_4 selectivity simultaneously decreased. As a result, the SPEEK/Na_3PO_4−10 membrane showed the best CO_2/CH_4 separation performance with CO_2 permeability of 62.0 Barrer, and CO_2/CH_4 selectivity of 61.0. The present research may provide an approach for further applied on CO_2 capture in bio fermentation gas.

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