Trapping bound water within polymer electrolyte membrane by calcium phosphotungstate for efficient CO$_2$ capture

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Experimental

Materials and chemicals: Pebax(R) MH 1657 was purchased from Arkema (French). Phosphotungstic acid was purchased from Aladdin Reagent Co., Ltd. (China). CaCl₂, Ca(NO₃)₂·4H₂O and ethanol were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). All chemicals were of reagent grade or higher, and were used without further purification.

Synthesis of Ca₁.₅PW: Ca₁.₅PW was synthesized via a double-replacement reaction:

\[ \text{H}_3\text{PW} + 1.5\text{Ca(NO}_3)_2 \rightarrow \text{Ca}_1.₅\text{PW} + 3\text{HNO}_3. \]

A certain amount of Ca(NO₃)₂ solution (3 M) was added into 1M phosphotungstic acid solution drop by drop. By heating the mixture of reactants in a 95 °C oven for 6 h, the by-product, HNO₃, was thermally decomposed and the synthesis reaction was allowed to be completed. A high yield about 96% was achieved by regarding H₃PW as the benchmark reactant.

Measurement of Ca₁.₅PW solubility: Excessive amount of Ca₁.₅PW was added into water to form saturated solution at different temperature. Each solution was further dried and the derived crystal grains were completely dehydrated at 150 °C under vacuum for over 24 h, and the weight of the anhydrous salt was measured and then the solubility of Ca₁.₅PW was calculated.

Membrane preparation: Pebax was dissolved in ethanol/water (70/30 wt%) under mild mechanical stirring (with reflux) at 80 °C for 3 h to obtain 5 wt% homogeneous solution. After cooling the solution to ambient temperature, a certain amount of Ca₁.₅PW was dissolved into the solution followed by 2 h stirring. The molar ratio of Ca²⁺ to ethylene oxide (EO) unit was controlled at 0, 1:240, 1:120, 1:60 and 1:30, respectively (Further increase of salt content will result in failure of membrane formation). After removing bubbles, the homogeneous solutions were cast onto Teflon petri dishes and then dried under ambient conditions for 24 h. The membranes were further annealed in a vacuum oven at 45 °C for three days to remove the residual solvent. The resultant membranes were designated as Pebax, where salt was absent, or Pebax–Ca₁.₅PW (X), where X means the molar ratio of Ca²⁺ to ethylene oxide (EO) unit. The thickness of all membranes was controlled within the range of 80–90 μm.

Measurement of total water, free water and bound water: Water uptake and water state were determined following the reported procedure. Each membrane was weighed to determine the “humidified” weight (m₁, mg) after gas permeation, and then heated at 100 °C in a vacuum oven
for 6 h to remove free water. The membranes were reweighed \((m_2, \text{mg})\) and further dried under vacuum at 150 °C for another 6 h. The completely dried membranes were weighed again to determine their “dried” weight \((m_0, \text{mg})\). In this way, the content of total water \((W_t, \%)\), free water \((W_f, \%)\) and bound water \((W_b, \%)\) were calculated based on the following equations:

\[
W_t = \frac{(m_1 - m_0)}{m_0} \times 100\% \\
W_f = \frac{(m_1 - m_2)}{m_0} \times 100\% \\
W_b = \frac{(m_2 - m_0)}{m_0} \times 100\%
\]

**Measurement and prediction of membrane density:** Experimental values of membrane density were determined at 25 °C by the buoyancy method using an electronic balance (OHAUS® CP224C) equipped with density determination kit. Silicon oil with known density \((\rho_0=0.972 \text{ g/cm}^3)\) was selected as the auxiliary liquid. Experimental values of density \((\rho_B)\) were calculated by the following equation:

\[
\rho_B = \frac{M_A}{M_A - M_L} \rho_0
\]

where \(M_A\) and \(M_L\) are the membrane weight in the air and in the liquid, respectively. Membrane density was also predicted by additive model. Notably, the density of humidified membrane was predicted by assuming that Ca\(_{1.5}\)PW was completely or partially dissolved by the adsorbed water, depending on the solubility and content of Ca\(_{1.5}\)PW. If Ca\(_{1.5}\)PW was completely dissolved, membrane density was calculated by assuming unsaturated Ca\(_{1.5}\)PW solution as the additive. If Ca\(_{1.5}\)PW was partially dissolved, membrane density was calculated by assuming saturated Ca\(_{1.5}\)PW solution and the residual Ca\(_{1.5}\)PW crystal as the two additives. The density of Ca\(_{1.5}\)PW solution was obtained by measuring the weight and volume of a certain amount of Ca\(_{1.5}\)PW solution, of which the Ca\(_{1.5}\)PW concentration was determined on the basis of the assumed Ca\(_{1.5}\)PW solution within membrane. In this way, the calculated density of humidified membrane could be calibrated by considering the effect of binary interactions between Ca\(_{1.5}\)PW and water.

**Membrane characterizations:** Thermal properties of samples were measured under nitrogen atmosphere by Differential Scanning Calorimetry (DSC) module (DSC 200F3, NETZSCH), with the temperature rising from -70 to 250 °C at a heating rate of 10 °C/min. The chemical structure of membrane was characterized by Nicolet-560 Fourier transform infrared spectrometer (FT-IR) with scan range of 4000–400 cm\(^{-1}\). The crystalline structures of membranes were determined using
wide-angle X-ray diffraction (WAXD) in the range of 10–50° at the speed of 10°/min (Rigaku D/max 2500 v/pc, CuKα 40 kV, 200 mA, λ=1.5406 Å). Fractional free volume (FFV) was calculated based on the density data following the previous method.\(^1\)

**Gas permeation experiments:** Single CO\(_2\), CH\(_4\), N\(_2\) and binary CO\(_2\)–CH\(_4\) (30vol\%:70vol\%), CO\(_2\)–N\(_2\) (10vol\%:90vol\%) gas permeation experiments were conducted based on the conventional constant pressure/variable volume technique. The details of the apparatus can be found in our previous work.\(^1\) N\(_2\) was selected as sweep gas when no N\(_2\) existed in feed gas, while CH\(_4\) was utilized as sweep gas to determine the permeability of N\(_2\). In a typical measurement, 3 bar of feed gas was firstly introduced into a water bottle to be saturated with water vapor, and then passed through an empty bottle to remove the residual water. The humidification temperature for feed gas was set 10 °C higher than that of the membrane cell. Meanwhile, the sweep gas was humidified at the same temperature of membrane cell. The flow rate and composition of sweep gas were recorded every 5 minutes until they no longer varied with time. For comparison, dry-state gas permeation experiments were also conducted, in which case the feed gas and sweep gas were directly introduced into the membrane cell. The compositions of the feed, retentate, and permeate were measured using gas chromatography. The permeability \((P_i, \text{ Barrer, } 1 \text{ Barrer}=10^{-10} \text{ cm}^3/\text{cm}^2 \text{ s cmHg})\) of either gas was obtained from the average value of at least 3 tests by the following equation:

\[
P_i = \frac{Q_i l}{\Delta p_i A}
\]

where \(Q_i\) is the volumetric flow rate of gas ‘i’ (cm\(^3\)/s) at standard temperature and pressure (STP), \(l\) is the membrane thickness (cm), \(\Delta p_i\) is the transmembrane partial pressure difference of gas ‘i’ (cmHg), and \(A\) is the effective membrane area (12.56 cm\(^2\)). The ideal selectivity \((\alpha_{ij})\) was calculated by equation (2):

\[
\alpha_{ij} = \frac{P_i}{P_j}
\]

Since the permeate side is maintained at ambient pressure, the mixed-gas separation factor could be also calculated by this equation.
**Fig. S1** WAXD spectra of the synthesized Ca$_{1.5}$PW powder

**Fig. S1** shows the Keggin-type characteristic peaks for PW$^{3-}$ at 2$\theta$ = 7–10 $^\circ$, 16–23 $^\circ$, 25–30 $^\circ$ and 31–38 $^\circ$, respectively, indicating the successful synthesis of Ca$_{1.5}$PW.$^2$
As shown in Fig. S2, the characteristic bands assigned to PW\(^{3-}\) are observed at 1078 cm\(^{-1}\), 978 cm\(^{-1}\), 895 cm\(^{-1}\), and 811 cm\(^{-1}\), respectively.\(^{3-5}\) With the addition of Ca\(_{1.5}\)PW content, the absolute intensity of these bands firstly increases and then decreases. However, compared to the bands for Pebax (amide-I at 1637 cm\(^{-1}\), amide-II at 1542 cm\(^{-1}\) and ether bond vibration at 1101 cm\(^{-1}\)), the relative intensity of the characteristic bands for PW\(^{3-}\) actually increases with the addition of Ca\(_{1.5}\)PW. The sharp decrease of absolute band intensity for Pebax at high Ca\(_{1.5}\)PW content lies in the fact that the actual content of Ca\(_{1.5}\)PW in membrane is already 39.5 wt% and 57.6 wt%. The synchronous decrease of the absolute band intensity for PW\(^{3-}\) can be interpreted by the delocalization of the electron cloud of W–O bonds towards the C–O bonds.
Fig. S3 WAXD spectra of Pebax–Ca$_{1.5}$PW membranes

The absence of the characteristic sharp peaks for PW$^{3-}$ (see Fig. S1) in Fig. S3 illustrates that Ca$_{1.5}$PW does not form crystal within membrane. Instead, it complexes with Pebax and achieves a molecular level dispersion. A notable new peak is observed within the $2\theta$ range of 5–7 $^\circ$, indicating the formation of a hybrid semi-crystalline phase rich in Ca$_{1.5}$PW. With the increase of Ca$_{1.5}$PW content, the $2\theta$ value of the peak increases, and the peak becomes sharpened, from which we infer that the membrane becomes denser by ionic crosslinking. Besides, with the increase of salt content, there is a remarkable decrease of the intensity of the typical wide peak for PA6 phase within the $2\theta$ range of 10–30 $^\circ$, which is reasonably attributed to the disruption of PA6 semi-crystalline phase by Ca$_{1.5}$PW.
Fig. S4 DSC curves of Pebax and Pebax–Ca$_{1.5}$PW membranes: (a) high temperature zone; (b) low temperature zone

Fig. S4a represents the effects of Ca$_{1.5}$PW on the respective crystalline phase regions of the PEO and PA6 segments of Pebax. Obviously, the crystalline phase regions of PEO segment (characterized by the left peak) and PA6 segment (characterized by the right peak) become completely damaged when Ca$^{2+}$:EO increases up to 1:120 and 1:60, respectively. These results show that Ca$_{1.5}$PW can significantly complex with both PEO segment and PA6 segment, and the interactions between Ca$_{1.5}$PW and PEO appears to be relatively stronger. When Ca$^{2+}$:EO is higher
than 1:120, an exothermic heat flow is observed. Considering that any heat flow ascribed to phase change displays endothermic characteristics, the exothermic heat flow can be only interpreted by the degradation of Pebax catalyzed by Ca$_{1.5}$PW. With the increase of Ca$^{2+}$:EO from 1:120 to 1:30, the endothermic peak becomes more intense, and the valley temperature becomes lower, which can support the hypothesis that Ca$_{1.5}$PW lowers the thermally degradation temperature and accelerates the degradation process. Since the endothermic peak lies above 120 °C, the membrane is still expected to maintain thermal stability below 100 °C, which is adequate for common operation.

**Fig. S4b** reflects the effects of Ca$_{1.5}$PW on the chain rigidity of PEO segment. The glass transition temperature ($T_g$) remarkably increases with the increment of Ca$^{2+}$:EO, and the $T_g$ value for Pebax–Ca$_{1.5}$PW(1:60) membrane is already up to -6.1 °C (much higher than that of Pebax–CaCl$_2$(1:60)$^1$), demonstrating the strong complexation between PW$_3^-$ and PEO. Such strong interactions can be also understood by the fact that phosphotungstic acid is often purified by using diethyl ether as extraction solvent. For Pebax–Ca$_{1.5}$PW(1:30) membrane, the $T_g$ cannot detected, which may be interpreted by the highly crosslinked membrane structure.
Fig. S5 Correlations between pure-gas permeability and total water content of the membrane based on the previously reported plot from Ref. S1.
Fig. S6 Correlations between pure-gas CO$_2$/CH$_4$, CO$_2$/N$_2$ selectivity and bound water content of the membrane based on the previously reported plot from Ref. S1.
Fig. S7 Effect of operating temperature on CO₂ capture properties of Pebax–Ca₁.₅PW(1:60) : (a) CO₂/CH₄ separation; (b) CO₂/N₂ separation
Fig. S8 Effect of feed pressure on CO$_2$ capture properties of Pebax–Ca$_{1.5}$PW(1:60) at 25 °C: (a) CO$_2$/CH$_4$ separation; (b) CO$_2$/N$_2$ separation
Fig. S9 The long-time mixed-gas separation test of the Pebax–Ca$_{1.5}$PW(1:30) membrane at 85°C and 3 bar.
Table S1 Experimental and predicted densities of the dry membranes and humidified membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>ρ_B</th>
<th>ρ_M</th>
<th>ρ_B−ρ_M</th>
<th>ρ_B</th>
<th>ρ_M</th>
<th>ρ_B−ρ_M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pebax</td>
<td>1.140±0.005</td>
<td>1.140</td>
<td>0±0.005</td>
<td>1.108±0.004</td>
<td>1.133±0.005</td>
<td>-0.025±0.005</td>
</tr>
<tr>
<td>Pebax–Ca_{1.5}PW(1:240)</td>
<td>1.279±0.006</td>
<td>1.277</td>
<td>0.001±0.006</td>
<td>1.247±0.009</td>
<td>1.269±0.013</td>
<td>-0.022±0.014</td>
</tr>
<tr>
<td>Pebax–Ca_{1.5}PW(1:120)</td>
<td>1.413±0.007</td>
<td>1.405</td>
<td>0.008±0.007</td>
<td>1.367±0.007</td>
<td>1.406±0.012</td>
<td>-0.038±0.011</td>
</tr>
<tr>
<td>Pebax–Ca_{1.5}PW(1:60)</td>
<td>1.659±0.004</td>
<td>1.635</td>
<td>0.023±0.004</td>
<td>1.546±0.013</td>
<td>1.642±0.014</td>
<td>-0.096±0.014</td>
</tr>
<tr>
<td>Pebax–Ca_{1.5}PW(1:30)</td>
<td>2.055±0.005</td>
<td>2.014</td>
<td>0.041±0.005</td>
<td>1.933±0.006</td>
<td>2.014±0.013</td>
<td>-0.081±0.010</td>
</tr>
</tbody>
</table>

a. ρ_B and ρ_M mean the densities obtained by buoyancy method and additive model, respectively.

b. Error bar is added because the calculation involves the density of salt solution, which was measured experimentally.
### Table S2 Calculated FFV values of the dry membranes and humidified membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>FFV$_{dry}$</th>
<th>FFV$_{humidified}$</th>
<th>FFV$<em>{humidified}$–FFV$</em>{dry}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pebax</td>
<td>0.126±0.007</td>
<td>0.194±0.012</td>
<td>0.068</td>
</tr>
<tr>
<td>Pebax–Ca$_{1.5}$PW(1:240)</td>
<td>0.121±0.005</td>
<td>0.198±0.013</td>
<td>0.077</td>
</tr>
<tr>
<td>Pebax–Ca$_{1.5}$PW(1:120)</td>
<td>0.114±0.008</td>
<td>0.201±0.015</td>
<td>0.087</td>
</tr>
<tr>
<td>Pebax–Ca$_{1.5}$PW(1:60)</td>
<td>0.102±0.006</td>
<td>0.202±0.017</td>
<td>0.100</td>
</tr>
<tr>
<td>Pebax–Ca$_{1.5}$PW(1:30)</td>
<td>0.088±0.004</td>
<td>0.171±0.011</td>
<td>0.083</td>
</tr>
</tbody>
</table>
Table S3 Comparison of pure-gas permeation properties of the dry membranes and humidified membranes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dry membrane</th>
<th>Humidified membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{CO_2}$</td>
<td>$\alpha_{CO_2/CH4}$</td>
</tr>
<tr>
<td>Pebax</td>
<td>82±3.8</td>
<td>19±0.3</td>
</tr>
<tr>
<td>Pebax–Ca$_1$3PW(1:240)</td>
<td>59±2.2</td>
<td>22±1.7</td>
</tr>
<tr>
<td>Pebax–Ca$_1$3PW(1:120)</td>
<td>55±1.9</td>
<td>25±1.5</td>
</tr>
<tr>
<td>Pebax–Ca$_1$3PW(1:60)</td>
<td>49±2.1</td>
<td>28±0.7</td>
</tr>
<tr>
<td>Pebax–Ca$_1$3PW(1:30)</td>
<td>34±1.7</td>
<td>29±0.9</td>
</tr>
</tbody>
</table>

a. “—” means the data were not obtained, because the Pebax–Ca$_1$3PW (1:30) membrane at humidified state is not robust enough to afford the testing pressure difference (3 bar).
**The application prospects of Pebax-Ca$_{1.5}$PW membrane**

Pebax–Ca$_{1.5}$PW membrane exhibits a high CO$_2$ permeability of 2825 Barrer and a high CO$_2$/N$_2$ selectivity of 137 at 85 °C, and the data point is already well above the Robeson upper bound revisited in 2008. Considering the temperature of flue gas after recycling residual heat usually lies within 110–160 °C, high CO$_2$ capture performance at 80–100 °C not only eliminates the necessity of cooling down the feed gas to room temperature, but also provides proper temperature difference for condensing a thin water film onto membrane surface, where the possible defects are expected to be sealed. Pebax–Ca$_{1.5}$PW membrane also shows weak dependence of CO$_2$ capture properties on feed pressure (Fig. S8), which means that the membrane is also available at elevated pressure. Furthermore, the membrane maintains the separation performance during a 160 h-long mixed-gas separation experiment, and no evidence of membrane deterioration can be observed (Fig. S9).
References