Biomimetic material - poly(N-vinylimidazole)-zinc complex for CO₂ separation

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Experimental Details

1. Preparation of Poly(N-vinylimidazole)

Low molecular weight Poly(N-vinylimidazole): 10.0g N-vinylimidazole monomer (0.11 mol) and 0.2g azobisisobutyronitrile (0.0012mol) were dissolved in 46 ml toluene. Then the polymerization of PVI was carried out in a flask equipped with a stirrer at 70±2 °C for 4 h under nitrogen atmosphere. After polymerization, the deposit was filtered by Buchner funnel, and washed three times with acetone. At last, the product was dried in a vacuum oven at 60±2 °C for 48 h. The average molecular weight is about 3.0×10⁴, determined by viscosimeter.

High molecular weight Poly (N-vinylimidazole): 10.0g N-vinylimidazole monomer (0.11mol) and 0.034g azobisisobutyronitrile (0.207 mmol) were dissolved in 30 ml benzene. Then the polymerization of PVI was carried out in a flask equipped with a stirrer at 70±2 °C for 7 h under nitrogen atmosphere. After polymerization, the deposit was filtered by Buchner funnel, and washed three times with acetone. At last, the product was dried in a vacuum oven at 60 °C for 48 h. The average molecular weight is about 2.8×10⁶, determined by viscosimeter.

2. Preparation of PVI-Zn(II) complex

Various amount 1.0wt% zinc acetate aqueous solution and deionized water was dropped to 5.0wt% PVI aqueous solution slowly under stirring. Then the mixed
solution was stirred for half an hour in ambience for complexing. The details are showed in table 1. (I: mole ratio of PVI/Zn(II)=20; II: mole ratio of PVI/Zn(II)=10; III: mole ratio of PVI/Zn(II)=5)

Table 1 Details of preparation of PVI-Zn(II) complex materials

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<th>I</th>
<th>II</th>
<th>III</th>
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<tbody>
<tr>
<td>5.0wt% PVI</td>
<td>1.6g</td>
<td>1.6g</td>
<td>1.6g</td>
</tr>
<tr>
<td>1.0wt% zinc acetate</td>
<td>0.92g</td>
<td>1.85g</td>
<td>3.70g</td>
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<tr>
<td>Deionized water</td>
<td>2.81g</td>
<td>1.89g</td>
<td>0g</td>
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3. Permeation measurements

Separation measurements were performed with the coated membrane with the CO₂/N₂ (15/85 by volume) gas mixture at 25°C. The membrane was mounted in a circular stainless steel cell (effective membrane area = 19.26cm²). CO₂/N₂ mixed gas was fed through a humidifier, and the gas saturated with water vapor was admitted to the permeation cell. H₂ saturated with water vapor was used as sweep gas. The outlet sweep gas composition was analyzed by a gas chromatograph equipped with a thermal conductivity detector. Pᵢ is the partial pressure difference of component i between the upstream and downstream side of the membrane. Nᵢ is the flux of component i. The permeance Rᵢ and selectivity α are given by Rᵢ=Nᵢ/Pᵢ, α(CO₂/N₂)=RCO₂/RN₂. Gas permeance unit(GPU) used in this study is 10⁻⁶ cm³(STP)cm⁻²s⁻¹cmHg⁻¹.
Characterization

The characterization of the PVI-Zn(II) complex materials was accomplished by attenuated total reflectance infrared (ATR-FTIR) spectroscopy (FTS-6000, Bio-Rad of America), $^{13}$C-NMR (VARIAN INOVA 500MHz), scanning electron microscopies and UV-Vis absorption spectroscopy.

The cross-section morphologies and surface of the membranes were observed with scanning electron microscopies (SEM, Philips XL30 for surface observation and JEOL JSM-6700F for cross-section inspection). Membrane samples were prepared for cross-section observation by peeling away the polyester backing fabric, gently to ensure polysulfone and active layers remained together. Wet fabric free membrane samples were broken in the liquid nitrogen before being sputtered with gold. The active layer of
common membranes prepared by low molecular weight PVI-Zn(II) with 150 μm coating thickness is about 700nm, and the active layer of ultra-thin membranes prepared by high molecular weight PVI-Zn(II) with 50 μm coating thickness is about 120nm.

The pure PVI and PVI-Zn(II) complex were characterized by using $^{13}$C-NMR (VARIAN INOVA 500MHz).

![Diagram of the chemical structure of PVI and PVI-Zn(II) complex]

The spectrum of PVI contains characteristic signals from C1(136.3-137.1ppm), C2(128.6-129.4ppm), C3(116.8-117.2ppm), C4(50.9-53.7ppm), C5(39.8-40.5ppm).

In the spectrum of PVI-Zn(II), there are four new characteristic signals which are around 180ppm, 141ppm, 121ppm and 22ppm respectively. The peaks around 180ppm and 22ppm are contributed to C atoms of acetate. The peaks around 141ppm and 121ppm are due to the changing of chemical shift of C1 and C2 of imidazole rings which coordinate with Zn(II).

Because the No.3 N has lone pair electrons and Zn(II) has unoccupied orbital, when zinc ions are added into PVI, the No.3 N atoms of imidazole rings will coordinate with Zn(II). The lone pair electron of N atoms is attracted by Zn(II), leading the electron density of N atoms reducing. Meanwhile, the electron cloud of C atoms next to No.3 N is also influenced and moved to N atom. Thus, the shielding effect of C1 and
C2 become weak and their chemical shift increases, leading new peaks formed.

The NMR proves that the Zn(II) ions bind imidazole rings around themselves through coordination bond between Zn(II) and No.3 N atoms.

Fig. S2. SEM image of PVI-Zn(II) membrane surface
Fig. S3. SEM image of PVI-Zn(II) membrane cross-section: (A) common membrane, 150μm coating thickness (B) ultra-membrane, 50μm coating thickness
Fig. S4. $^{13}$C-NMR spectrums of PVI and PVI-Zn(II) (A: PVI, B: PVI-Zn(II))

- C1 (136.3-137.1 ppm)
- C2 (128.6-129.4 ppm)
- C3 (116.8-117.2 ppm)
- C4 (50.9-53.7 ppm)
- C5 (39.8-40.5 ppm)
Fig. S5. The UV absorption spectroscopy of PVI-Zn(II) complex solution
Fig. S6. The N$_2$ permeance of membranes prepared by complex materials and pure PVI (complex I: PVI/Zn(II)=20; complex II: PVI/Zn(II)=10; complex III: PVI/Zn(II)=5)

Fig. S7. The N$_2$ permeance of the ultra-thin membranes (PVI/Zn=10, 50μm, different pH of coating solution)
Fig. S8. Effects of temperature on the CO$_2$ permeance of membrane (PVI/Zn=10, 50μm, 0.11MPa feed pressure)

Fig. S9. Effects of temperature on the CO$_2$/N$_2$ selectivity of membrane (PVI/Zn=10, 50μm, 0.11MPa feed pressure)
Fig. S10. The test of thermal stability of membrane (PVI/Zn=10, 50μm, 0.11MPa feed pressure; A: CO₂ permeance, B: CO₂/N₂ selectivity)
Fig. S11. Separation performance stability of PVI/Zn(II) membrane (PVI/Zn=10, 50 μm, 0.2MPa feed pressure)