Syntheses of Coordination Polymer Glass Membranes and Their Gas Separation Performance Research

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Abstract—Purity requirements for gas in daily life and industrial production have been increasing. Coordination polymer glass membranes can solve the problem of brittle and fragile inorganic membranes and retain some porosity. We obtained the novel CP material, to obtain self-supporting glass membranes by means of sheeting-melting-cooling, the selectivity of the \( \text{agCd-P-dmbIm} \) membrane in \( \text{H}_2/\text{CO}_2 \), \( \text{H}_2/\text{N}_2 \) and \( \text{H}_2/\text{CH}_4 \) are 68.8, 33.8 and 49.5 respectively. Its hydrogen permeance is 235 GPU, and its permeability is 7362 1 barrer. The results show that the diffusion coefficient of \( \text{H}_2 \) is much greater than that of \( \text{CO}_2 \). Relevant mechanism proved that the gas molecular size sieving properties of coordination polymers is the key factor to achieve efficient gas permeability and selectivity. \( \text{agM-P-dmbIm} \) is hydrogen purification membrane. Coordination polymer glass membranes have great potential in gas separation research.

1. Introduction

In the past two decades, Humans began to use gas separation methods based on physical and chemical force to separate and purify single-component gases. However, these traditional separation methods have disadvantages such as large energy consumption, large investment, and low recovery rate. As a kind of separation technology with high purification efficiency, membrane separation technology has the advantages of low energy consumption, easy operation, and small footprint, and is expected to be widely used in the future. Coordination polymer glass membranes can solve the problem of brittle and fragile inorganic membranes and retain some porosity, but the system has been less studied at present, the glass membranes aperture of 0.62 Å affects its screening of gases with smaller molecules.

For most materials, the melt usually forms crystal nuclei and grows into a crystalline substance near the freezing point temperature, but glassy materials will form a solid state with glass-like characteristics. The glassy state is isotropic and gradually softens when heated\(^{[1-3]}\). In 2012, Kitagawa\(^{[4]}\) combined into a new coordination polymer material \([\text{Zn(HPO}_4\text{-}(\text{H}_2\text{PO}_4)_2)](\text{ImH}_2)_2\) which improved the crystal specific surface area and ion conductivity at 160 °C. In 2013, the research team of Umeyama\(^{[5]}\) reported the crystal-glass transition behavior of a series of coordination polymers formed by metallic zinc ions, phosphoric acid and azole compounds. In 2016, Bennett\(^{[6]}\) report the glass behavior of the molten cold extraction of the metal-organic framework material of the scientific research team. Compared with the existing glass types (inorganic non-metal, organic non-metal and organic metal) at that time, the glass retains the connection mode of metal and ligand. And has good mechanical properties. In 2018, the research team of Bennett and Coudrt\(^{[7]}\) jointly discussed the thermal behavior of ZIF-4 material and discussed its liquid porous structure. ZIF-4 changed from a crystalline structure to an amorphous structure during the melting behavior. ZIF-8 has explored and found that its
$T_m$ is higher than ZIF-4, which is caused by its coordination bond strength and viscosity. In 2020, Li, Pan, and Jiang\cite{8} studied an important work. They developed the ZIF-62 coordination polymer glass membrane and used its gas separation characteristics to test the gas sieving ability. H$_2$/CH$_4$, CO$_2$/N$_2$, CO$_2$/CH$_4$ are 50.7, 34.5, and 36.6.

Aiming at the problems of high processing temperature, low selectivity, and less research. In this work, coordination polymer glass membrane with high flux and high gas selectivity was designed through a reasonable material structure, and its processability and gas separation performance were solved at the same time.

2. Methods and Materials

It is designed to synthesize coordination polymer materials by replacing the metal connecting unit and the type of imidazole or replacing the phosphoric acid with a longer chain organic phosphine. M-P-dmbIm (metal-ligand-ligand): M(OAc)$_2$∙2H$_2$O (1 mmol), 5,6-dimethylbenzimidazole (292.3 mg, 2 mmol), phosphoric acid (210 μL, 3 mmol) and ethanol (500 μL) were manually pulverized in a mortar for 30 min to obtain a white powder. The obtained powder is thoroughly washed with dichloromethane three times, and each time it is stirred for 3 h. Finally, it was dried in an oven at 70 $^\circ$C for 10 h to obtain the final coordination polymer product. (25~30 $^\circ$C, 30~40 RH%)

M-P-dmbIm powder into a powder in a mortar, take 100 mg of the powder and put it into the tablet press abrasive tool to fully flatten it. The continuous force is less than 30 s under 1.5 MPa. The diameter of the compressed tablet is 2 cm, thickness 200~300 μm, calcined in a tube furnace for 0.5 h under vacuum conditions, after cooling to room temperature, a self-supporting glassy polymer membranes $\alpha_M$-H-dmbIm (the abbreviation of glass material after glass state conversion) is automatically formed.

3. Test Results and Discussions

3.1. Basic structure characterization of coordination polymers

XRD is no peak from metal salt and ligand in the diffraction peak, which is a new diffraction peak, which proves the synthesis of a new coordination polymer. in Fig.1a. Between 2500-3150 cm$^{-1}$, the N-H stretching vibration broadband of dmbIm almost disappears, indicating that dmbIm has been deprotonated. The P-O stretching peak of phosphoric acid at 1011 cm$^{-1}$ has a significant shift from the original 1018 cm$^{-1}$. This is due to the deprotonation of H$_3$PO$_4$. These features indicate that H$_3$PO$_4$ and dmbIm should be involved in the coordination. in Fig.1b.

(a) XRD(b) FTIR-ATR

Fig.1 XRD and FTIR-ATR for M-P-dmbIm
TGA and DSC measurements were performed under nitrogen as a protective atmosphere to study its melting behavior. In the TG test, the three samples all showed weight loss behavior at about 200 °C. In Fig.2a. Combined with the DSC test results, the weight loss temperature corresponds to an absorption/exothermic peak, which is the decomposition temperature (Td) of the sample. in Fig.2b. All three samples exhibited endothermic characteristics before thermal decomposition, which corresponds to their melting temperature (Tm), representing their transition from solid to liquid. It is worth noting that the Tm values of the three samples are in the range of 162~172 °C, which is much lower than the ZIF glass transition temperature (>400 °C), proving that they can be melt-processed at a lower temperature. After the melting temperature was obtained in the first round of the DSC test cycle, the second round of the DSC test scan was performed immediately to obtain the glass transition temperature (Tg). Cd–P–dmbIm exhibited an endothermic behavior during the second scan, which corresponds to its Tg. In the same way, the Tg of Cu-P-dmbIm and Mn-P-dmbIm can be obtained. The ratio of the obtained Tg to Tm is the glass formation ability (GFA) of the material. GFA generally defines the difficulty of glass recrystallization. The larger the value, the more difficult it is to recrystallize the material in the glass state. These three materials all have ultra-high GFA, which may be due to the large steric hindrance of the ligand hindering the recrystallization process of the coordination polymer in the liquid state.

3.2. Basic structure characterization of coordination polymers glass

It can be seen that the coordination polymer glass has no diffraction peak after the glass state transition in XRD, which proves that the material has changed from a crystalline ordered structure to a disordered structure, in Fig.3a. Similar to the results obtained from crystalline materials, it proves that the ligand still retains coordination in the glass structure in FTIR-ATR, in Fig.3b. Both M-P-dmbIm and aM-P-dmbIm have characteristic peaks at 1.5 ppm in the 31PNMR spectra, in Fig.1c. Due to the single coordination H2PO4–, the peak positions of the crystalline state and the glass state can be preliminarily judged that they have similar coordination. Way. The obtained glass materials were subjected to elemental analysis and ICP characterization, and the element compositions and ratios of the obtained three glasses were basically similar to the element contents of the previously obtained crystalline materials.
Through the tableting-melting-cooling method, a complete and defect-free glass membranes material can be obtained. The microscopic morphology of coordination polymers and glassy coordination polymers can be studied by SEM. Due to the crystal characteristics of inorganic materials, the plane SEM image of the M-P-dmbIm tablet shows the discrete distribution of crystal grains with large gaps, and the particle size is in the order of micrometers in diameter. On the contrary, the glass membranes material has no obvious cracks to prove that it is defect-free, and a₈M-P-dmbIm has the characteristics of uniformity and compactness, indicating that a₈M-P-dmbIm has successfully transformed from a crystal to a glass state. In addition, the cross-sectional SEM image 3.6 shows that a₈M-P-dmbIm exhibits uniform thickness, and the a₈Cd-P-dmbIm membranes, a₈Cu-P-dmbIm membranes, and a₈Mn-P-dmbIm membranes have thicknesses of 313, 425, and 297 μm. in Fig.4.
Next, test the gas separation performance of the glass membrane at a constant inlet pressure of 1 bar. First, the single air permeability of the glass membrane is tested, and there is an obvious cut-off effect. The illustration shows the selective comparison and found the actual choice, in Fig.5a. The performance is close to the ideal and the selectivity is far greater than the Knudsen diffusion selectivity, which proves to be a good gas separation membrane material. In addition, the two-component mixed gas (1/1, v/v) membrane separation test was performed on the three materials. All three glasses showed gas separation performance similar to the ideal selectivity, \( a_g \text{Cd–P–dmbIm} \) selectivity for \( \text{H}_2/\text{CO}_2 \), \( \text{H}_2/\text{N}_2 \) and \( \text{H}_2/\text{CH}_4 \) is the highest, respectively, 64.1, 34.4 and 54.4, in Fig.5b. The hydrogen flow rate is as high as 74950 barrer, which proves that these three glass materials are ideal hydrogen separation membrane materials.

![Fig.4 SEM for M-P-dmbIm and \( a_g \text{M-P-dmbIm} \)](image)

(a) Single gas test results of \( a_g \text{M-P-dmbIm} \) (b) Mixed gas test results of \( a_g \text{M-P-dmbIm} \)

![Fig.5 Gas test results](image)
The glass material shows good gas selectivity much higher than its corresponding Knudsen diffusion coefficient. Putting the glass material into the Robeson upper limit graph, it can be seen that the separation performance of the three gas pairs far exceeds the corresponding upper limit, breaking the gas permeability-selectivity game effect, and further judgement may be gas molecular sieving. in Fig.6.

The gas transport mechanism of the aM-P-dmbIm membranes is further studied. In the dissolution diffusion model, both the diffusion coefficient (D) and the solubility (S) have a crucial effect on the permeability (P). In terms of the mechanism of dissolution and diffusion, the diffusion coefficient of a gas is related to its permeability and solubility. The permeability is obtained through testing. The graph shows the adsorption curve of hydrogen and carbon dioxide gas on the glass membrane. The adsorption capacity of the material can be understood through the adsorption curve, and the solubility of the gas can be calculated. By calculation, the hydrogen diffusion coefficients of the three glass membranes are 547, 2650, and 622, which are much larger than the diffusion coefficients of carbon dioxide. Proved that hydrogen is easier to diffuse in the material than carbon dioxide. The gas solubility is calculated from the saturated adsorption capacity at 298 K. Through the ratio of permeability to solubility, the diffusion coefficient of the material to different gases can be calculated. The results are listed in Table 3.6. The hydrogen permeability of aCd-P-dmbIm, aCu-P-dmbIm, and aMn-P-dmbIm are 74.939, 100.70, and 41.985 (× 10−9 cm² cmHg⁻¹), respectively, and aCd-P-dmbIm, aCu-P-dmbIm, and aMn-P-dmbIm are 1.17, 2.03, and 1.03, respectively (× 10−9 cm² cmHg⁻¹). From the results, it can be concluded that the H₂ diffusion coefficient of the three glasses is much higher than that of CO₂, which proves that H₂ is easier to diffuse in the material. in Fig.7.

4. Conclusion
Based on the results and discussions presented above, the conclusions are obtained as below:
(1) In view of the selection of coordination polymer materials, new materials were synthesized by changing the metal connection unit and ligand types. Through XRD pattern, FTIR-ATR spectrum and
melting point test M-P-dmbIm, confirm that it has been coordinated and connected and combined with thermogravimetric and DSC test results to analyze its melting point between 162-172 °C.

(2) Three kinds of glass membranes were successfully prepared by pressing and cooling at a high temperature. The material changed from a crystalline structure to an amorphous structure before and after the glass state, and the proportion of the element group remained unchanged. The gas selectivity test was carried out by the Wicke-Kallenbach method, and the results showed that the three glass membranes all showed good separation performance, which exceeded the Robeson upper limit.

(3) The gas separation mechanism of a₈M-P-dmbIm was studied. The adsorption capacity of carbon dioxide and hydrogen was tested at 298 K, and the diffusion coefficients of the two materials in the glass material were calculated. The diffusion coefficients of hydrogen were both far greater than the diffusion of carbon dioxide. As a result of the coefficient, it is believed that this is the reason why the a₈M-P-dmbIm membrane material has good hydrogen gas selectivity.

In order to better study the performance of a₈M-P-dmbIm film and meet the needs of practical applications, future research is looking forward to two aspects: (1) Exploring the self-healing properties of the material; (2) Effectively controlling the thickness by adding support materials to meet the requirements of industrialization.

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