Progress and Prospect in Membrane CO_2 Separation

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ABSTRACT

Carbon dioxide emissions seriously harm the environment, causing the attention of all countries. Carbon capture and sequestration is the most direct way to control carbon dioxide emissions in the world. However, CO_2 separation has attracted significant interest due to its high energy efficiency, low operation cost, low investment, and easy maintenance and operation. This article reviews the current main CO_2 separation membrane technologies and summarizes the advantages and disadvantages of various technologies. Sorted by their structures, composite membranes include inorganic membranes, polymeric membranes, Mixed matrix membrane (MMMs) and Metal-Organic frameworks membrane (MOFs). Pure inorganic and organic membranes cannot have both thermal stability and low cost, but MMMs can have both advantages. The problems affecting the development of MMMs are: poor compatibility between filler and polymer, resulting in non-selective defects. According to their advantages and disadvantages, the key issues restricting the development of composite membranes were analyzed and discussed.

Keywords: *Carbon dioxide, membrane technology, separation*

1. INTRODUCTION

CO_2 is one of the most important greenhouse gases and the raw material for chemical products such as urea, soda ash and dry ice. Therefore, the separation and recycling of CO_2 have good environmental and economic benefits. The membrane material is selective transmission, so membrane separation technology can be different particle size, shape of the mixture using pressure difference, electric potential, concentration difference, chemical potential difference and other methods, to achieve selective separation. And Membrane separation is also can use in gas separation method, according to different gas components through the membrane rate to achieve the separation of mixed gas. Compared with other CO_2 capture technologies, membrane separation has been widely used for its advantages of low cost, small footprint, low energy consumption, easy amplification, easy operation and no environmental pollution.[1] However, due to the poor separation performance and stability of membrane materials, the application is limited. New membrane materials and modified methods need to be discovered urgently. This review will describe the mechanisms of six popular membranes, analyze and compare their advantages and disadvantages, and evaluate various types of membranes. The review is aimed to provide some reference value for industrial application. According to their materials, this discussion will introduce six separation membranes, which are porous membrane, dense membrane, gas membrane, Vapor-Liquid contact membrane, mixed matrix membrane (MMM) and metal-organic framework membrane (MOF) respectively.

2. MEMBRANE FOR CO_2 SEPARATION

2.1 Inorganic membrane

Inorganic membranes are semi-permeable membranes made of inorganic compounds such as metals, ceramics, metal oxides, glass, and carbon. According to the materials used, they can be divided into ceramic, metal, and carbon molecular sieve membranes. Depending on whether the material contains a pore structure or not, it can be divided into the dense membrane, porous membrane.[2]

Generally speaking, Inorganic membrane materials have unique physical and chemical properties, greater heat stability, acid and alkali corrosion resistance. This allows it to maintain its performance under high temperature working environment or and corrosive gases it still provides a strong stability.

2.1.1 Porous membrane

Porous membranes refer to separation membranes containing 10 to 100 million pores per square centimeter, with 70-80% of the overall pores, and pore sizes ranging from 0.02 μm to 20 μm.[3] The porous membrane contains nano-pore structure, which is very suitable for the separation of CO_2 gas, and gas as molecules can be diffused through both the pores in lamellar and the channels between lamellar.[4] It contains porous Ni Membranes, porous Ag Membrane, porous Pd Membrane and so on.[3] There are lots of mechanism of porous membrane diffusion, one of the more effective ways is the molecular sieve effect, which separates gases by the size of the molecules being separated. The molecular sieve has very good separation performance and good flux, but it can be constrained by the conditions of membrane preparation.[5]

2.1.2 Dense membrane

The pore size is 0.5~1nm, porosity is less than 10%, thickness is 0.1~1.25μm inorganic membrane. It consists of dense structures, and the pore size is not observable under an electron microscope.[6] They have a higher selectivity, but the permeation rate of the components through the dense membrane is too low. The mechanism of gas passage through the dense membrane is firstly, gas adsorption and dissolution on the upstream surface of the membrane, then diffusion under the concentration difference of gas, and finally gas dissolution on the downstream surface of the membrane. Its selectivity is relatively more enhanced, and it is a good choice for some gas separations that require high selectivity permeability. However, because of its small pore size, the flux problem will be its major drawback.[5]

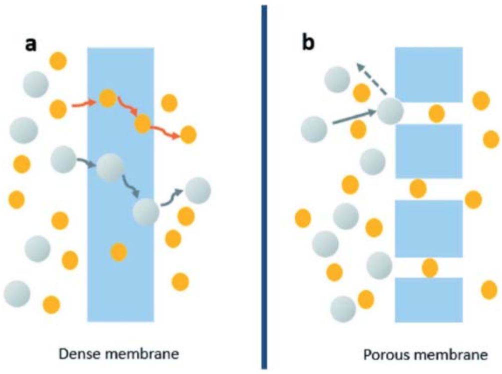

Figure 1: The mechanism of Dense membrane and Porous membrane [19]

2.2 Polymeric membrane

Polymer separation membrane is a kind of semi-permeable membrane with selective permeability made of polymer material that is rich in content and has an extremely wide range of applications. About film-making materials, common examples are cellulose acetate (CA), polyacrylonitrile (PAN), polycarbonate (PC).[7] It can be observed that polymer membranes have good gas permeability, which can be used to separate gases well, and per unit volume has a large filtration area, easy assembly, small volume of filtration equipment, and a relatively high investment Low. So, it is widely used in industry. However, its chemical resistance and heat resistance is poor, and it is easy to decompose under high temperature and poor chemical environmental conditions.[8]

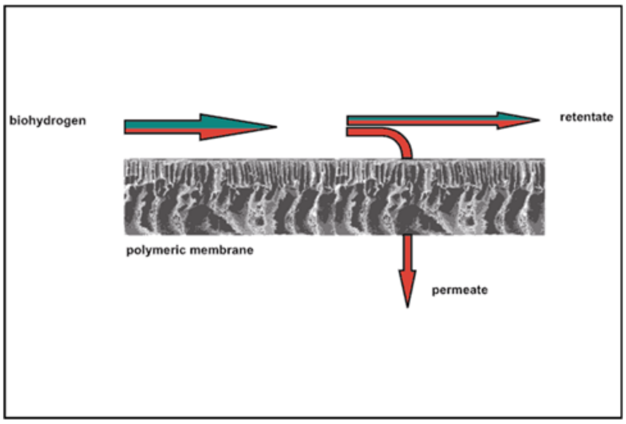

Figure 2: Selective permeability of polymeric membranes[9]

2.2.1 Gas membrane

Different polymer membranes have different permeability and selectivity for different types of gases and other molecules. A gas separation membrane is a membrane that separates various substances in a gas mixture by using the difference in permeation rates of the gas mixture in the gas separation membrane under pressure difference. It has the advantages of energy saving, high efficiency and simple operation, but the current material variety is relatively lacking, so it has not been promoted to more fields.[10]

2.3 Mixed matrix membrane (MMMs)

A mixed matrix membrane is a complex of polymers in a continuous phase, mixed with a dispersed phase. In its preparation, the materials of continuous and dispersed phases are usually mixed and made into a film by solvent evaporation, etc. Because inorganic membrane materials have poor film property, fragile and other shortcomings, and flexible polymer materials can overcome these. In addition, inorganic materials can be introduced into the polymer matrix to optimize the polymer chain arrangement, so as to optimize the membrane separation performance.[13] This membrane has the advantages of both inorganic and polymer membranes. The transfer mechanism of gas molecules in a mixed matrix membrane is the diffusion of the high-pressure side to permeation side brought about by the pressure difference between the two sides of the membrane. Therefore, adding suitable filler to the membrane can help reduce the mass transfer resistance of the membrane and thus improve the permeability of the membrane.[12]

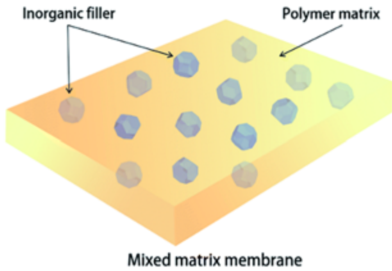

Figure 3: Approximate microstructure of the Mixed matrix membrane [14]

Therefore, in the preparation of a mixed matrix membrane, appropriate polymer and filler can ensure that the membrane has good separation performance. Due to the different properties of the filler, their interaction may also have negative effects on the separation performance. Therefore, the structural characteristics and interaction between filler and polymer and the selection of an appropriate filler in the manufacture of mixed matrix membrane are very important. [15] Its effect on CO_2 permeability and selectivity is shown in the following figure.

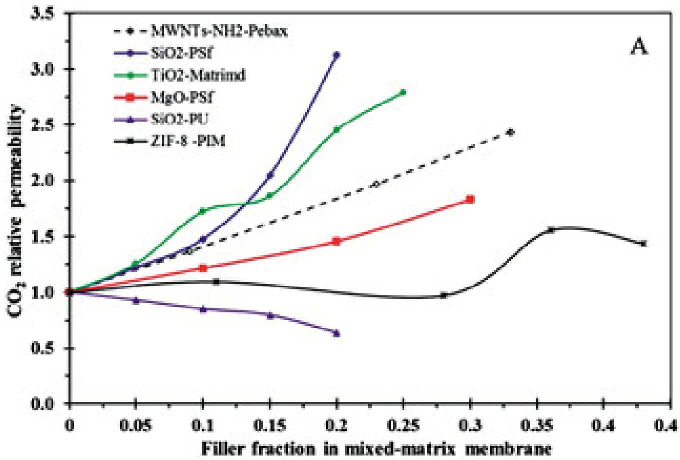

Figure 4. Effect of filler loading in mixed matrix membrane on CO_2 permeability [16]

2.3.1 Metal-Organic frameworks membrane (MOFs)

Metal–organic frameworks (MOFs) are a class of compounds consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures, with the special feature that they are often porous[17], which are constructed from metal 'nodes' and organic molecules known as 'linkers'.[18] MOFs are a promising potential material as an adsorbent to capture CO_2, because of their small, tunable pore sizes and high void fractions.[17] And due to its high specific surface area and large pore volume, MOF materials have a higher saturated adsorption capacity for carbon dioxide.[19]

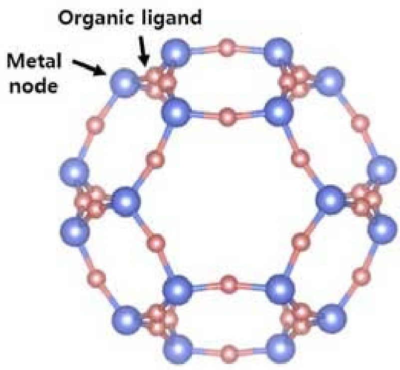

Figure 5: Schematic illustration of a metal-organic framework [20]

By making the MOF from different metal atoms and organic linkers, the materials that selectively absorb specific gases into tailor-made pockets within the structure. MOFs therefore can select capture of specific gases.

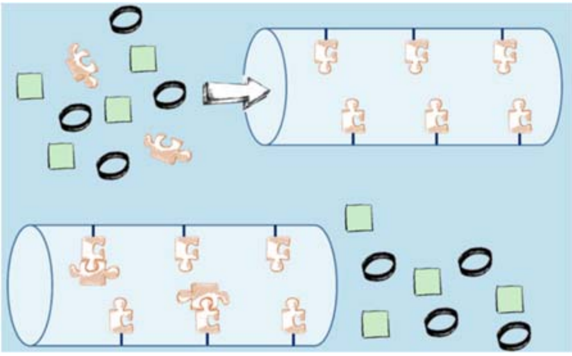

Figure 6: Schematic illustration of a metal-organic framework[21]

Nowadays relatively mature and common MOFs materials are ZIF series, UiO series and so on. The material ZIF is topologically isomorphic with zeolites, composed of tetrahedrally-coordinated transition metal ions connected by imidazolate linkers[22] Due to their robust porosity, it possesses resistance to thermal changes and chemical stability;[23] The material Uio-66 is a kind of metal-organic framework material, chemical formula is C48H28O32Zr6. It is made of organic framework of terephthalic acid link zirconium node.[25] Resulted from their strong Zr-O bond and high coordination number of Zr (IV), it has ultrahigh thermal stability and chemical stability. More important, it is easy graft modification to meet the desired specific function. It can also combine functional groups to improve permeability, which is also one of the research hotspots;[26] In addition to the two membranes mentioned above, more and more membranes have been developed and applied, and they have good selectivity and permeability. New material membranes are also the research focus of MOFs at present.

At present, the research of MOF membrane in CO_2 separation is still in the early stage, and it is not realistic to apply it to industrial scale production

3. OUTLOOK

By comparing two types of Inorganic membranes, it can be found that the porous membrane has a large flux, but low selectivity. On the opposite, dense membranes have better selective permeability, but are less capable in terms of flux size. Thus, under the present research, it can be considered very important to solve the problem of selective permeability and flux in terms of inorganic membranes.

Through the above explanation of the properties of polymer membranes, it is clear that all the polymer membranes have a disadvantage, which is that they cannot maintain their chemical workings in a poorer chemical environment or higher temperatures. Therefore, the next research direction should be to make the polymer film have better chemical and heat resistance properties so that it can work in more aggressive environments. In addition, it reduces the cost of manufacturing polymer films and enables the application of polymer films in specialized fields. Furthermore, it reduces the cost of manufacturing polymer membranes and enables the use of polymer membranes in specialized applications, e.g., in the food or chemical fields, in medicine, etc. It is also a very good research direction.

Combining the advantages of single materials can make up for the defects of membrane materials， MMMs have the advantages of easy processing and low cost of organic membrane and high mechanical properties and thermal stability of inorganic membrane. In mixed matrix membrane, suitable filler can reduce the mass transfer resistance and provide faster gas molecular transport channel, thus improving the permeability.[27]

MOFs particles tend to agglomerate in organic membranes, resulting in membrane defects. And The synthesis process is complicated and time-consuming, which is difficult to produce on a large scale. In view of the above problems, the future research should focus on the modification of MOFs' materials by adding some functional groups (e.g. -OH, $-NH_2$). By enhancing the compatibility between materials and membrane molecules, the group appearance can be reduced, and the overall quality of MOF membrane can be continuously improved. The development of cheaper and more readily available MOFs materials is also conducive to industrial production.

And since membranes for gas separation are still in the laboratory stage, it can also be considered as a very important research direction to reduce the cost of membrane production, enhance the application scenario of inorganic membranes, and put them into industry as soon as possible.

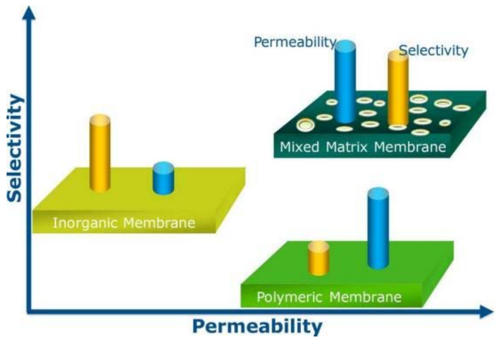

Figure 7: Selectivity and permeability of three kinds membrane[28]

4. CONCLUSION

This review summarizes and compares six CO_2 separation membrane. In conclusion, compared with pure inorganic membrane and polymer membrane, combining the advantages of single materials to prepare composite membrane can make up for some defects of membrane materials. The characteristics of high specific surface area, large porosity, functional pore structure and can overcome the shortcomings of organic polymer membrane and inorganic membrane, and is the most promising CO_2 gas separation membrane. At present, carbon dioxide separation membrane is still in the primary stage, although some progress has been made, due to the particularity and complexity of membrane materials, there is still some distance to realize industrialization. Simplifying the preparation process of membrane materials, reducing the cost of membrane materials and the operation cost of membrane separation process is the important premise to promote the large-scale development of carbon dioxide membrane, and also the main direction of the development of composite membrane. The solution to these problems can make membrane separation technology more widely used in industry. It is believed that through further scientific research, membrane separation technology will play a greater role in the field of CO_2 separation and contribute to the mitigation of global warming.

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