

PERSPECTIVE MEMBRANES BASED ON EXPANDED GRAPHITE

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Introduction

Search for novel membrane materials provides gas-separation technology development. Traditional membrane materials are polymers, zeolite- or cermet-based materials, carbon molecular nanosieves etc. [1-3]. There are two possible mechanisms of gas separation: the molecular-sieve and adsorption ones.

The advantages of carbon membranes (CM) are good mechanical properties and stability up different pressure:

- effective for gas separation of mixtures: O₂/N₂, CO₂/CH₄ and CO₂/N₂;
- structure stability provide for constant permeability under gas pressure loss;
- penetrability does not depend on time, CM durability is more than organic membranes;
- CM can be used in hostile environment (acids, solvent, organic vapor);
- CM have higher temperature stability than polymers;
- CM can be used at high temperature division (500–900°C).

Among the disadvantages the following should be noted: the fragility and complication to make CM with a high surface area.

Graphite foil (GF) produced from exfoliated graphite is a perspective material for gas- and steam-separation. In contrast to carbon molecular sieves, graphite foil possesses the regular layered structure and developed pore structure [4-5]. Moreover, as all the other materials made of exfoliated graphite, graphite foil is thermally stable up to 450°C in air and 3000°C in vacuum or inert atmosphere, chemically stable in aggressive mediums and environmentally friendly.

Experimental

Graphite foils with densities of 0.3-1.5 g/cm³ made of nitrate exfoliated graphite containing micro-, meso- and macro-pores were studied in present work. Graphite foil was prepared through several steps, including graphite intercalation with nitric acid followed by hydrolysis, thermal treatment and rolling without a binder. Exfoliation, multi-stepped compacting and rolling are realized through one technological cycle resulted in formation of graphite foil with a width of 150 mm [6].

Graphite foil and exfoliated graphite were studied by means of SEM, Raman spectroscopy, XRD, low temperature nitrogen adsorption etc. Slot-like macro-pores with a length of

2 μm and a width of 0.4 μm, meso-pores with an average diameter of 4nm and small amount of micro-pores were found out in the graphite foil.

Gas permeability Q(nl/m²·h·atm) of the porous graphite foil was measured by means of differential technique with a gas chromatography detector at temperature of 20-90 °C. Partial pressure overfall on a membrane was of 1 atm.

Results and Discussion

Graphite intercalation compounds and products of their hydrolysis are able to expand during thermal shock and form low-density carbon material exfoliated graphite. Expansion is accompanied with evolving of large amount of gaseous phase creating interlayer pressure of hundreds atmospheres that is the driving force of exfoliation. EG main characteristic is a bulk density that is about 1-10 g/l. According to XRD data, exfoliated graphite is a layered material with an interlayer distance of 3.35-3.36 Å. From the chemical composition point, EG is carbon with slight admixtures content less than 0.1%.

The presence of different pores in exfoliated graphite determines the graphite foil properties. Meso-pores are responsible for oil sorption ability, macro-pores makes EG enabled to be pressed without a binder. Strength properties of graphite foil are only due to the intermolecular surface interaction between EG particles. Properties of graphite foil are laid during intercalation and thermal treatment. The dirigible variation of graphite intercalation degree and using different intercalates allow changing of properties and morphology of thermally expanded graphite particles.

It is known, the membrane gas separation flows according diffusive solubility mechanism when permeability coefficient $P=D \times S$ is determined by gas solubility in S matrix and diffusion migration rate in membrane medium D. Separation selectivity is determined by magnitude ratio, for example, for binary mixtures $P_i/P_j=D_i/D_j=S_i/S_j$, i.e. ratio of diffusion selectivity and molecules solubility. The basic parameters of selective gas transfer are formed by gas properties and polymer medium characteristics. There are several requirements to membranes for gas separation: high permeability, high selectivity and availability.

The investigated gas permeability decreases simultaneously with graphite foil densification. Macro-pores at the sample surface do not influence the gas flow transferred through membrane. The transport stream is realized due to the pores with a diameter of 1-50 nm. The stream in graphite foil with a density of 0.3 g/cm³ is mostly realized due to the pores with diameter of 1-13nm and in graphite foil with a density of 1.5 g/cm³ – due to the pores with diameters of 1.5-2.5 and 4.5-6 nm. Gas permeability for the porous graphite foil is 492, 115, 112 and 22 nl/m²·h·atm for hydrogen, oxygen, nitrogen and carbon dioxide correspondingly.

The low individual gases selectivity for the low-dense samples is probably due to the predominance of viscous flow in meso-pores. The maximum H₂/CO₂ selectivity occurred for the sample with a density of 1.1 g/cm³ and is

equal to 22 that significantly exceeds selectivity of the most known polymer membranes (Table 1).

Table 1. The different membrane selectivity.

Membrane	H ₂ /N ₂	O ₂ /N ₂	H ₂ /CO ₂	CO ₂ /O ₂
Poly(vinyl-3-methyl-silane)	6.7	3.5	1.3	0.7
PVTMS				
Polysulfone	59.6	8.1	1.5	0.2
PSF				
Graphite foil (1,1 g/cm ³)	4.4	1.0	22.4	5.2
Theoretical selectivity for Knudsen gas flow regime	3,74	0,94	4,69	0,85

Thus, separation of such gas pairs as H₂/N₂ and O₂/H₂ is realized due to the difference in molecular weight. Good relation of selectivity coefficients, both experimental and calculated by Knudsen equation, is observed for H₂/N₂ and O₂/N₂ in contrast to mixtures containing CO₂. The obtained results allow assuming that in case of graphite foil the difference in kinetic diameters of gas molecules in CO₂ containing mixtures is not a determinative factor in contrast to the case of carbon molecular sieves.

Carbon dioxide adsorption isotherm under pressure overfall on the graphite membrane of 1.5 atm is similar to the Langmuir isotherm. The GF sorption capacity *q* is of 0.01 mol/kg (CO₂) and 0.005 mol/kg (N₂).

The hydrogen permeability through graphite foil with a density of 1 g/cm³ is close to that of other membranes whereas CO₂ permeability is anomaly low. Probably, CO₂ molecules strongly interact with GF surface and self-holding of CO₂ transport occurs.

Conclusions

Transport characteristics of the porous graphite foil were investigated. The obtained data could be applied for development of novel inorganic gas-separation carbon membranes for separation CO₂ containing mixtures.

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