# Gas permeability through graphite foil: The influence of physical density, membrane orientation and temperature

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ABSTRACT

Gas permeability parameters of microporous foils based on exfoliated graphite prepared by controlled pressing as membrane material for gas separation are reported. Permeability of $H_2$, $N_2$, $CH_4$, $CO_2$ and $C_1$-$C_4$ lower hydrocarbons for pressed graphite foil (GF) samples with various densities (240–1500 kg/$m^3$) within the temperature range 20–90 °C was studied. It was found that GF samples with density around 1000 kg/$m^3$ demonstrate high $H_2$/$CO_2$ ideal selectivity ($\alpha$ = 14–22) which significantly exceeds Knudsen selectivity. The influence of anisotropy structure features of GF membranes, physical foil density, transport pore distribution and gas flow direction on gas transport and separation properties was investigated as well. The evaluation of the surface flow contribution to the overall gas flow was carried out by approximation method using temperature dependences of gas permeance. It is concluded that the presence of noticeable surface flow can lead as to a decrease of gas permeance in comparison with Knudsen flow (for example, for $CO_2$) as to an increase of gas permeance (for example, for lower hydrocarbons). Development of separation process for particular gas mixture compositions needs to take into account obtained tendency. Future potential applications of GF membranes are discussed as well.

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## 1. Introduction

One of the promising directions of membrane materials development for gas separation applications is design of microporous inorganic materials, for example, zeolites [1–4], carbon based molecular sieves [1,5–8], glassy membranes [9–11] and others. Such materials can be effectively used as for separation processes where preferable permeability of light molecules, such as hydrogen, helium, nitrogen is required and can be provided due to sieving effect [1–6] as for processes where preferable permeability of the strongly adsorptive molecules (e.g., lower hydrocarbons) is required and can be provided due to strong surface flow contribution as in adsorption selective membranes [11,12]. Besides high selectivity level and high permeance, such materials demonstrate good chemical and thermal stability. Combination of these properties makes the microporous inorganic materials more desirable comparing to traditional industrially produced membranes based on nonporous polymeric materials. However, main disadvantages of such porous materials are brittleness and difficulty in scaling up for large area membranes production. From this point of view, industrially produced inorganic matrices, such as foils based on exfoliated graphite, could extend the area of application of micro porous inorganic materials, particularly for gas separation. Graphite foils (GF) are mainly known as sealing materials. Celzard and others [13–16] have shown that exfoliated graphite-based materials demonstrate wide range of gas diffusion mechanisms depending on such pore structure parameters as pore diameter, open and closed porosity relation, and anisotropy of structure [13,16]. Foil based on exfoliated graphite is one of such materials that currently produced at industrial scale as sealing material and potentially could be applied as microporous inorganic membranes for gas separation. Authors of the present paper have previously investigated membranes based on exfoliated graphite with optimal density produced by INUMIT Ltd. (Russian Federation) and showed that the GF can provide high ideal $H_2$/$CO_2$ and (lower hydrocarbons)/$CO_2$ selectivity [17,18].

This paper is aimed to understanding of GF gas selective properties and presents the set of new permeation data for exfoliated GF in relation to $H_2$, $N_2$, $CH_4$, $CO_2$ and n-$C_4H_{10}$. This paper presents the set of new permeation data for exfoliated GF in relation to $H_2$, $N_2$, $CH_4$, $CO_2$ and n-$C_4H_{10}$. The estimation of the surface flow contribution to the overall gas flow in GF is carried out for the first time by using of temperature dependences of gas permeance. The gas permeability anisotropy of GF matrix is shown as well. The influence of foil density, transport pore distribution and aniso-

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tropy of gas flow direction on transport properties and diffusivity mechanism of gases in the graphite foils studied are considered. Future potential applications of GF membranes are discussed as well.

## 2. Experimental

### 2.1. Materials

The samples of GF studied were prepared from exfoliated graphite particles based on graphite nitrate produced by the previously reported method [19,20]: natural graphite was first treated by 98% nitric acid at mass ratio 1:0.8, and then intercalated graphite was treated by hydrolysis followed by thermo-expansion at 900 °C. Obtained exfoliated graphite was pressed to foil with required specified thickness and density. The thickness of GF samples was varied within the range of 0.2–1.0 mm, density was varied within the range of 260–1500 kg/m$^3$. The samples were stable in air up to 550 °C.

### 2.2. Pore structure investigation

Microstructure of samples was investigated by scanning electron microscopy (SEM). Transport pore size distribution was investigated by nanopermporometer TNF-WH3 (Seika Corporation) with hexane as a filler of porous matrix and nitrogen as a gas-carrier.

### 2.3. Gas permeability measurements

GF permeance was measured by a differential method with gas chromatography analysis [21] within the temperature range of 20–90 °C for the following gases: H$_2$, O$_2$, N$_2$, CH$_4$ (purity 99.5 vol.%), CO$_2$ (purity 98.9 vol.%), n-C$_4$H$_{10}$ (purity 97 vol.%). Helium (purity 99.5 vol.%) was used as a gas-carrier, the partial pressure drop across membrane was approximately 1 bar.

The scheme of experimental set-up for gas permeability measurement is presented in Fig. 1. The set-up consists of gas cylinders with gas-carrier and penetrant, pressure and gas flow regulators,

gas flow switch, membrane cell, membrane cell thermostat, gas flow meters, gas chromatograph, analog-to-digital converter and signal recording and treatment hardware-software complex «ECOCHROM».

Experimental measurement of gas permeability is carried out as follows: the membrane hermetically fixed in the membrane cell is placed in a thermostat oven. The studied membrane divides the cell volume into two cavities: the reservoir and receiver. At the beginning of the experiment carrier gas (He or Ar) was supplied to the reservoir and receiver to measure background signal. For measuring of permeability the carrier gas flow in reservoir is switched to the flow of penetrant gas. After reaching of steady state conditions the gas mixture (gas-carrier and penetrant) flow from receiver is analyzed by gas chromatograph.

Gas-carrier counter diffusion occurs and it can be especially significant in case of porous membrane. Both penetrant and carrier gas flows pass through the cell (not dead end, not circulation). Flow rates of studied gas and carrier gas had been adjusted to obtain low concentration of gas-carrier over membrane and low concentration of penetrant under membrane. For all experiments low stage cut conditions were provided. Our experimental set-up provides possibility of using as gas-carrier as vacuum on permeate side of membrane. To be fully confident in obtained results we checked gas permeability for some GF samples using vacuum and obtained similar results as in experiments with application of gas-carrier therefore.

Membrane permeance Q of single gas was calculated as:

$$Q_i = \frac{J_i}{A \cdot \Delta p_i}, \tag{1}$$

where $J_i = c_i \cdot J$ is penetrant flow rate through membrane; $c$ is the penetrant mole fraction in gas-carrier flow from receiver, $A$ is the area of a membrane, m$^2$; $\Delta p_i$ is the partial pressure drop of penetrant across the membrane, Pa; $J$ is the gas-carrier flow rate, m$^3$/s.

The ideal selectivity for a pair of gases $i, j$ was defined as:
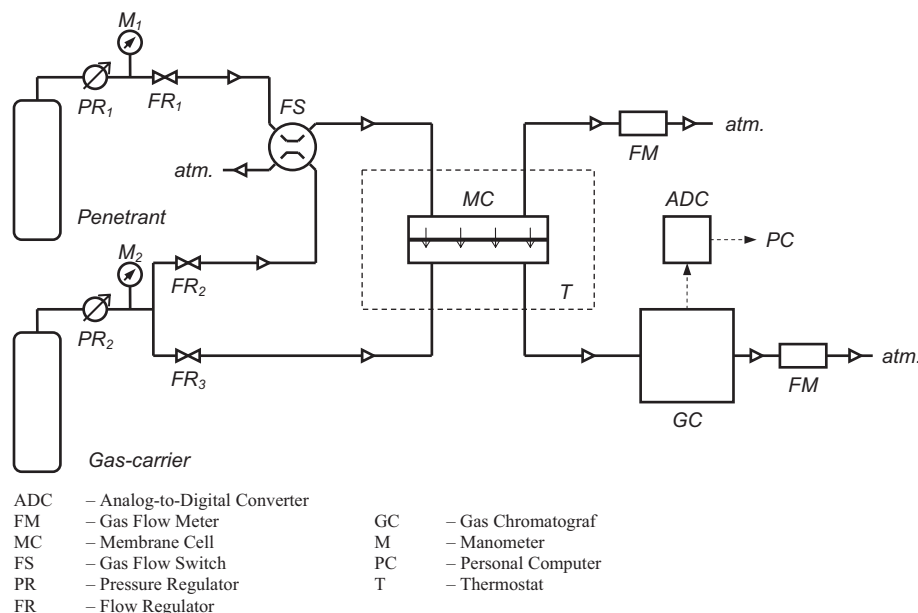
$$\alpha_{ij} = \frac{Q_i}{Q_j}, \tag{2}$$



| ADC | – Analog-to-Digital Converter | | |
| FM | – Gas Flow Meter | GC | – Gas Chromatograf |
| MC | – Membrane Cell | M | – Manometer |
| FS | – Gas Flow Switch | PC | – Personal Computer |
| PR | – Pressure Regulator | T | – Thermostat |
| FR | – Flow Regulator | | |

**Fig. 1.** Scheme of gas permeability set-up.