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Gas permeability properties of modified membranes based on exfoliated graphite

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ABSTRACT

This article presents the results of the gas permeability measurements of the graphite foil after gas-phase fluorination. Membranes based on exfoliated graphite were treated with undiluted F2 under variation of temperatures. Gas diffusion measurements were carried out using integral method. It was shown that modified graphite possesses incredibly high permeability in relation to H_2, CO_2, N_2 and O_2 in comparison with initial foil.

Keywords: Exfoliated graphite; Gas-phase fluorination; Gas diffusion measurements

1. Introduction

Inorganic porous membranes including carbon based materials have attracted significant interests in recent years due to its high thermal, chemical and mechanical stability [1]. They also demonstrate good permeability and reasonable selectivity in relation to gases. Thermoexpanded graphite (TEG) has been also considered as a promising membrane material because of its low cost, usability on its practical use. It has been applied widely in sealing, catalysis, environmental protection, etc. [2]. The morphology and pore structure of TEG can be modified by variation of preparation conditions. Some research on modification of graphite foil and composites with exfoliated graphite have been adopted to improve its permeability and chemical stability in order to use this material in fuel cells as gas-diffusion layers or bipolar plates [3,4].

This article presents the results of the influence of gas-phase fluorination on the properties of foils fabricated from exfoliated graphite. Since fluorination is one of the most effective chemical methods to modify and control physicochemical properties of materials, this process has become an important tool of great interest. The extreme reactivity of F_2 molecule constitute exceptional tool to modify the surface properties of materials without changing the bulk characteristics of the pristine material. Depending on the type of starting materials and employed techniques, the improved properties concerns gas-permeability, wettability, adhesion, chemical stability, etc. [5]. Graphite reacts with fluorine gas over a wide range of the fluorination conditions. Properties of products obtained by fluorination depend on temperature, reaction time, pressure, composition of the gaseous reactants [6]. Experimental data demonstrate that intercalated graphite with F (CF_x, $x < 0.1$), establishing C–F ionic bonds, possess extremely high electrical conductivity (close to that

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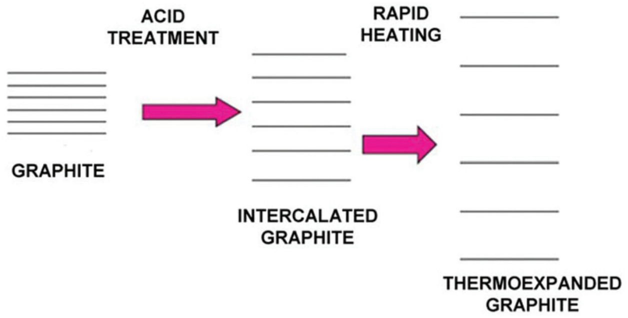

Fig. 1. A schematic illustration of the TEG formation.

observed for metals, e.g. 2 × 10^5 S cm^{-1}) [7]. This fact is extremely important for fuel cell applications.

There are two possible ways to apply the fluorination for carbon materials modification: an ordinary direct fluorination and oxyfluorination. Direct fluorination is a heterogeneous reaction of gaseous F_2 and its mixtures with a material surface. It is normally used to modify surface properties; bulk properties of the starting material remain unchanged.

2. Materials and methods

2.1. Materials and preparation

All experiments were carried out with graphite foil. TEG was prepared by treatment of natural flake graphite with nitric acid with subsequent heat-treatment. The schematic illustration of the preparation process of TEG is shown in Fig. 1. Treatment results in an increase of the volume of TEG by a factor of several tens to several hundred times compared to initial graphite. The expanded graphite keeps a layered structure similar to natural graphite flakes but with enlarged interlayer spacing. TEG has low density (about 2 g/L), mesoporous structure, large surface area and high surface activity. TEG can be pressed without any binding agent. Microphotograph of the expanded graphite is presented in Fig. 2. TEG has been widely used in gasketing, adsorption, electrochemical applications, supporting material, etc. However, the information about the TEG's use as a membrane material for gas separation is poor.

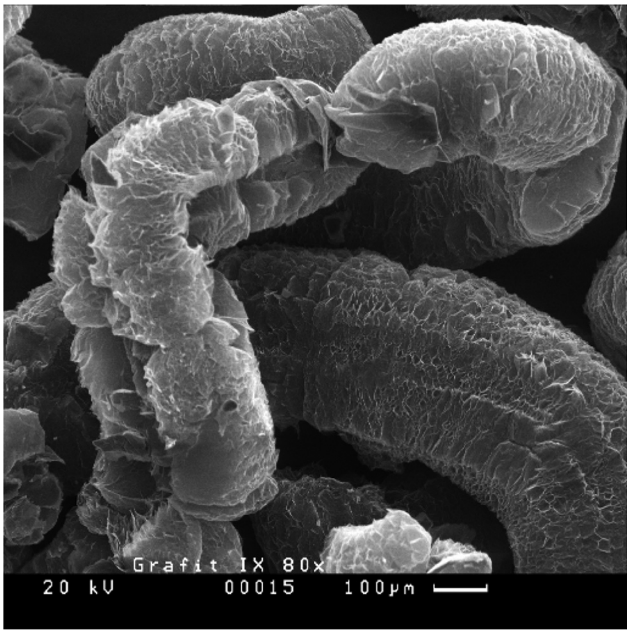

Fig. 2. TEG microstructure.

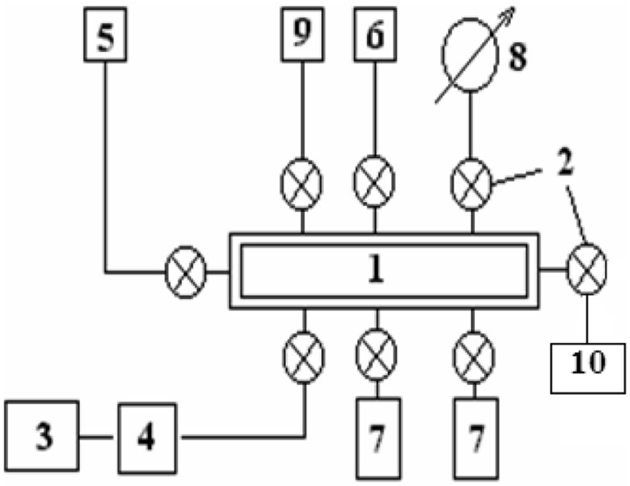

Fig. 3. Fluorination facility (1-control block, 2-gas valves, 3-vacuum pump, 4-trap to remove F2 and HF from exhaust gases, 5-tank for mixture preparation, 6-cylinder with gaseous fluorine, 7-cylinders for various gases, 8-vacuummeter, 9-thermocouple to measure the pressure of residual gases, 10-fluorination chamber.

TEG was rolled to prepare the graphite foil. Graphite foil has special ''sandwich'' structure with two dense surface layers and porous layer in between. The density of the initial foil was equal to 1.7 g/sm^3.

Both boundary layers were removed mechanically in order to increase the permeability and examine the influence of boundary properties on gas permeability and selectivity. Gas permeability coefficients were obtained for the initial foil, the foil without boundary layers and the fluorinated foil.

2.2. Fluorination of carbon-based materials

An overview of the laboratory facilities is shown in Figs. 3 and 4. Direct fluorination was performed to modify surface properties of the samples with the thickness about 400 μm. Before treatment the sample sides were carefully covered with epoxy resin to

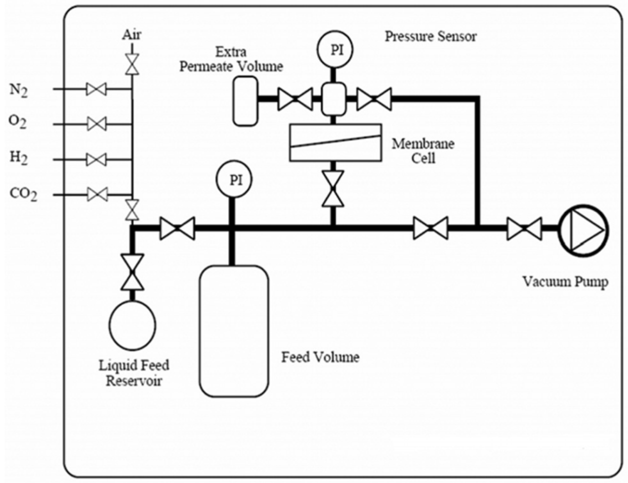

Fig. 4. Gas permeability test facility.

prevent bulk modification. The samples were placed inside the vacuum chamber and evacuated. The scheme of the facility is shown in Fig. 3. Treatment with undiluted F_2 has been carried out at various temperatures (147°C, 190°C, 225°C). The treatment has been performed in static conditions; duration did not exceed 6 h. At the end of the experiment gaseous F_2 was eliminated from the reaction chamber.

2.3. Gas permeability measurements

For gas permeability measurements integral permeability method was used. This technique offers the opportunity to assess experiment, the gas permeability coefficient as well as the gas diffusion coefficient quickly and reliably during a single experiment. All measurements were carried out using GKSS membrane test facility at ambient temperature and pressure difference 0.5 bar. The scheme of the experimental setup is presented in Fig. 4. A disc shape sample was inserted inside the stainless steel permeation cell. Both compartments of the cell were connected to a vacuum pump and controlled by manometers (permeate compartment pressure was monitored with a 0.1 mBar sensitivity). Feed side was fed by a permanent gas (H_2, CO_2, N_2, O_2) from a reservoir after evacuation of the cell. The controlled pressure difference across the membrane (i.e. between feed and permeate sides of the membrane) was created. Both feed and permeate pressure were measured during the experiment. Gas permeability coefficients were calculated using ''Time Lag program'' produced by GKSS.

The permeability parameters of following single gases were determined: H_2, CO_2, N_2, O_2. All the permeability values were obtained under the same operating conditions.

3. Results and discussion

The results of the gas permeability measurements of individual gases for initial graphite foil, foil without dense boundary layers and for fluorinated foil are presented in Figs. 5 and 6.

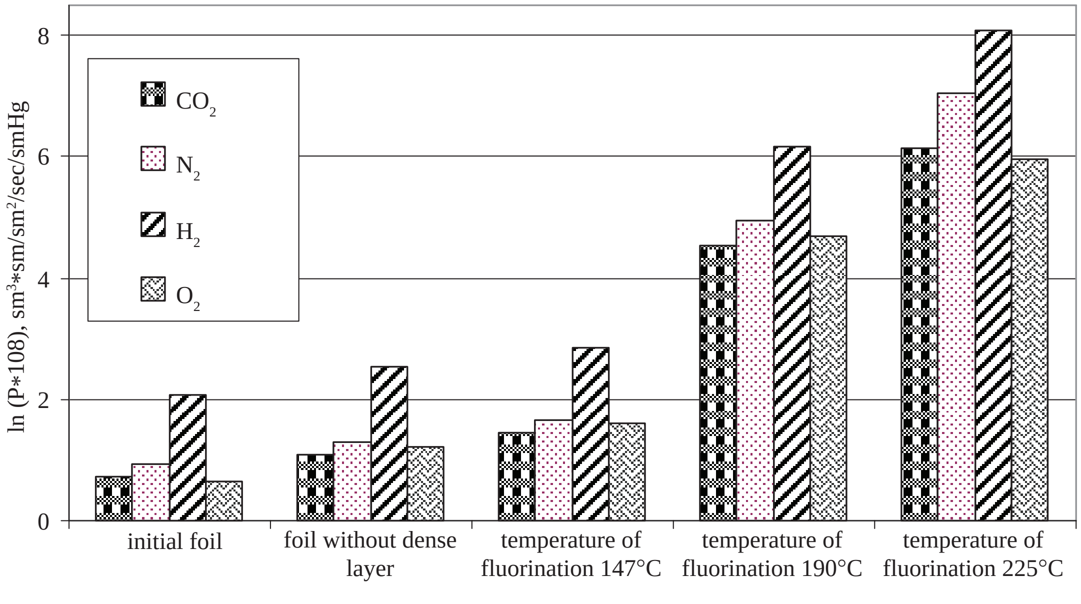

Fig. 5. Gas permeability coefficients for initial graphite foil, foil without dense boundary layers and for foil after fluorination treatment.

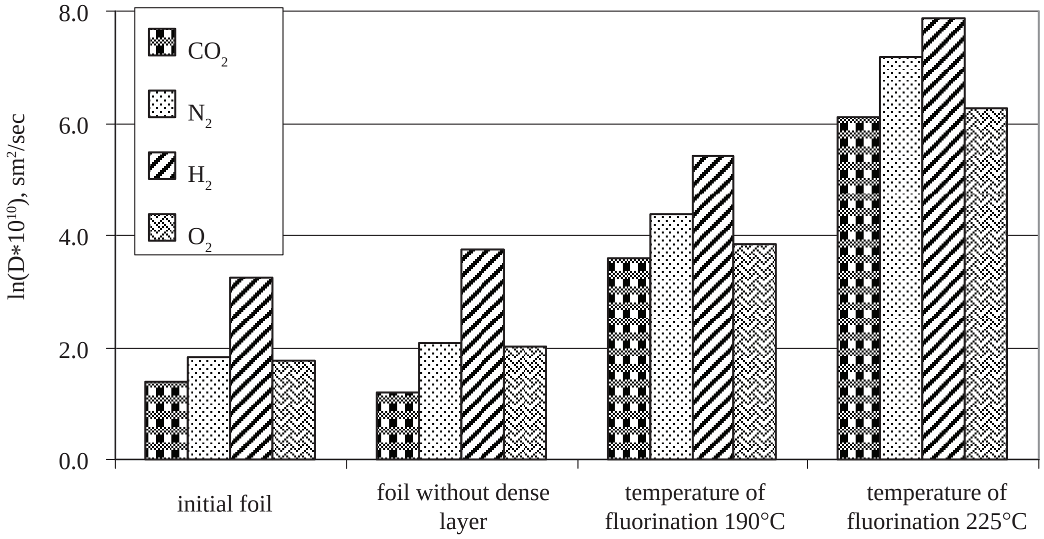

Fig. 6. Gas diffusion coefficients for initial graphite foil, foil without dense boundary layers and for foil after fluorination treatment.

Initial foil demonstrates comparatively low ideal permeability in relation to all examined gases and high H_2/CO_2 selectivity. In order to increase the permeability and examine the influence of boundary layers on gas permeability and selectivity both boundary layers were removed. It was shown that selectivity of the foil is determined by central high-porous layer. Permeability slightly increases after such modification, but selectivity remains constant.

It can be seen that after gas phase fluorination at high temperatures permeability significantly increases. H_2/CO_2 selectivity remains constant after fluorination under all conditions.

4. Conclusions

A new method of graphite foil modification by gas-phase fluorination was suggested. It was shown that modified graphite possesses incredibly high permeability in relation to all gases in comparison with initial samples. The results obtained can be used for further development of new carbon membranes for gas separation, and for gas-diffusion layers in fuel cells.

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