Journal of Membrane Science 469 (2014) 284–291

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Pressed graphite crystals as gas separation membrane for steam reforming of ethanol

A. Schulz, F. Steinbach, J. Caro*

Institute of Physical Chemistry and Electrochemistry, Leibniz University Hannover, Callinstr. 3A, D-30167, Germany

ARTICLE INFO

Article history:
Received 15 April 2014
Received in revised form
19 June 2014
Accepted 23 June 2014
Available online 30 June 2014

Keywords:
Graphite membrane
Gas separation
Hydrogen separation
Membrane supported ethanol
steam reforming

ABSTRACT

Pressed graphite was evaluated as a potential membrane for steam reforming of ethanol in membrane reactors. In ethanol steam reforming, hydrogen has to be in situ removed selectively from a mixture with ethanol, CO_2, and H_2O. Commercial graphite flakes (single crystals) have been pressed into disc membranes of different thicknesses. Both single gas permeation and $H_2/CO_2/H_2O$ mixed gas permeation were studied. From single gas permeation, a relatively high ideal separation factor of 35,…,60 for the H_2/CO_2 mixture could be predicted. However, the study of the real separation factor of this mixture by gas-chromatographic analysis gave real mixture separation factors around 5. This experimental finding is explained by a Knudsen-type mechanism with permeation paths along the grain boundaries of the pressed graphite flakes. At temperatures between 100 and 250 °C, the pressed graphite membrane is indeed hydrogen-selective. Hydrogen is separated from a $H_2/CO_2/H_2O$ mixture with a separation factor of 5 relative to CO_2 and 12 relative to H_2O, but only 2.4 relative to ethanol. Pressing of the graphite crystals results in a self-orientation (brick layer structure) of the individual graphite crystals. Hydrogen permeation parallel to the aligned flake-shaped crystals is by the factor 25 faster than perpendicular to them. The hydrogen permeabilities through the pressed graphite membranes are about one to two orders of magnitude higher than those through molecular sieve membranes such as supported zeolite or MOF membranes.

1. Introduction

Using bioethanol as fuel, hydrogen can be produced by steam reforming according to $C_2H_5OH + 3\,H_2O \leftrightarrows 2\,CO_2 + 6\,H_2$. However, the reaction suffers from poor selectivity since other undesired products such as CH_4 and CO are formed during steam reforming and by ethanol decomposition [1–4]. There are also numerous other competing reactions like the *water-gas shift* (WGS) reaction and methanation [5,6]. In the past few years, the low temperature ($T < 600$ °C) ethanol steam reforming have become increasingly attractive but here also the wide range of undesired products and low hydrogen selectivity are the main hurdles [7–11]. Most of these problems can be solved if a hydrogen-selective membrane is applied for the in situ removal of hydrogen from the products at reaction temperatures < 400 °C.

However, the removal of H_2 in the presence of CO_2 and H_2O is a challenging task. Pd alloy membranes show severe degradation problems in the presence of hydrocarbons. Simple molecular sieve membranes will not work since hydrogen as the molecule to be removed has a larger kinetic diameter than water and is only slightly smaller than carbon dioxide (H_2: 2.9 Å, H_2O: 2.6 Å, CO_2: 3.3 Å).

The application of graphite is very diverse and ranges from its use as grease till the protection of plasma-facing components in thermonuclear fusion devices or for rechargeable battery techniques. There are only a few papers on the use of graphite as hydrogen-permeable membrane [12–14], on the application of graphite materials for hydrogen isotope separation [15,16], and on the molecular understanding of hydrogen transport in graphite [17–19]. However, most of these papers study hydrogen permeation under extreme conditions such as very low hydrogen partial pressures and very high temperatures. Except for the study of Kiyoshi et al. [20], the membranes were cut from bulk graphite materials instead of pressing graphite flakes as done in this work. Since graphite can adsorb carbon dioxide with a capacity of several mmol/g in the area of 3–12 bar, graphite has also been proposed as a cheap material for CO_2 storage [21]. A few attempts have been made to evaluate graphene as a novel carbon-based membrane material. Since the C_6 rings of the graphene carpet are impermeable for any gas, graphene oxide has been chosen as the material of choice [22–27].

The aim of this work is to investigate the separation behavior of pressed graphite discs as membranes for the ternary system $H_2/CO_2/H_2O$ as the key molecules of ethanol steam reforming with the aim to separate in situ hydrogen. Taking as a rough estimate, that the membrane selectivity can be approximated as diffusion selectivity multiplied by adsorption selectivity, it will be interesting to see which effect influences the permeation behavior: H_2 has the higher

* Corresponding author.
E-mail address: juergen.caro@pci.uni-hannover.de (J. Caro).

http://dx.doi.org/10.1016/j.memsci.2014.06.047
0376-7388/

Table 1
Sizes of the 4 charges of the commercial flake-shaped graphite crystals purchased from GK Kropfmühl and pressed into membranes.

Sample	Crystal length (μm)	Crystal width (μm)	Crystal height (μm)
1	400	250	13.0
2	290	190	9.4
3	28/36[a]	21/26	0.0/1.2
4	5	2.8	0.2

[a] Bimodal distribution.

diffusivity compared with CO_2, but CO_2 is better adsorbed than H_2. On the other hand, H_2 as the molecule to be separated through the membrane has a slightly larger kinetic diameter than H_2O which is expected to remain in the retentate. To identify the separation mechanism, single and mixed gas separation under variation of the partial pressure differences over the membrane and using different permeation methods such as flow measurement by soap bubble counter or permeate analysis using gas chromatography have been performed.

2. Experimental

2.1. Graphite material and pressing of membranes

Four different charges of graphite flakes were purchased (Table 1). The graphite membranes were prepared by pressing (using 392 MPa) a certain amount of graphite flakes (RFL 99.5, Co. GK Kropfmühl: www.gk-graphite.com) as obtained (Fig. 1a) to 0.5/1.0 mm thick discs with a diameter of 18 mm. For the study of permeation anisotropy, a 25 mm high cylinder with the same diameter was pressed from sample 2 (see Table 1), drilled with a core drill and sliced and polished to a thickness of 1.0 mm (Fig. 6b).

2.2. Characterization

Scanning electron microscopy (SEM) pictures were taken with the Jeol JSM 6700F with a cold field emission gun using 2 kV excitation voltage. The transmission electron microscopy (TEM) pictures were measured with the Jeol JEM-2100F UHR with an acceleration voltage of 200 kV using a Schottky field-emitter (ZrO/W(100)) with a lattice resolution in STEM of 0.2 nm. For Small Area Electron Diffraction (SAED), a Gatan Imaging Filter (GIF 2001) using a 1k-CCD camera was used. The X-ray powder diffraction (XRPD) measurements were carried out on a Bruker D8 Advance diffractometer (Bruker AXS GmbH) with a Bragg–Brentano geometry using Cu ($K\alpha_{1,2}$) radiation, secondary Ni-filter and a 1-dimensional LynxEye detector (silicon strip). The XRD measurements of graphite membranes in Fig. 6 were performed between 10° and 85° (2θ), step size of 0.01°, time per step of 0.02 s for Fig. 6c and 0.6 s for Fig. 6d, a total number of 7133 steps, without rotation at room temperature. The shown XRD patterns are Cu ($K\alpha_2$) and background corrected. The indexing of reflexes related to graphite based on pattern data base (00-056-0159) with the space group of P $6_3/mmc$ (No. 194). The shown patterns are normalized to the intensity of the 002 reflex.

2.3. Evaluation of single gas permeation and mixture gas separation

For permeation studies the graphite membranes were stabilized by a porous α–Al_2O_3 support additionally.[1] The membranes were sealed in a permeation module using black O-rings (Vi370-FKM: www.cog.com) with an inner diameter of 14 mm and a cord diameter of 2 mm. For temperature-dependent measurements up to 250 °C, O-rings (Perlast G75B-FFKM) with a higher thermal

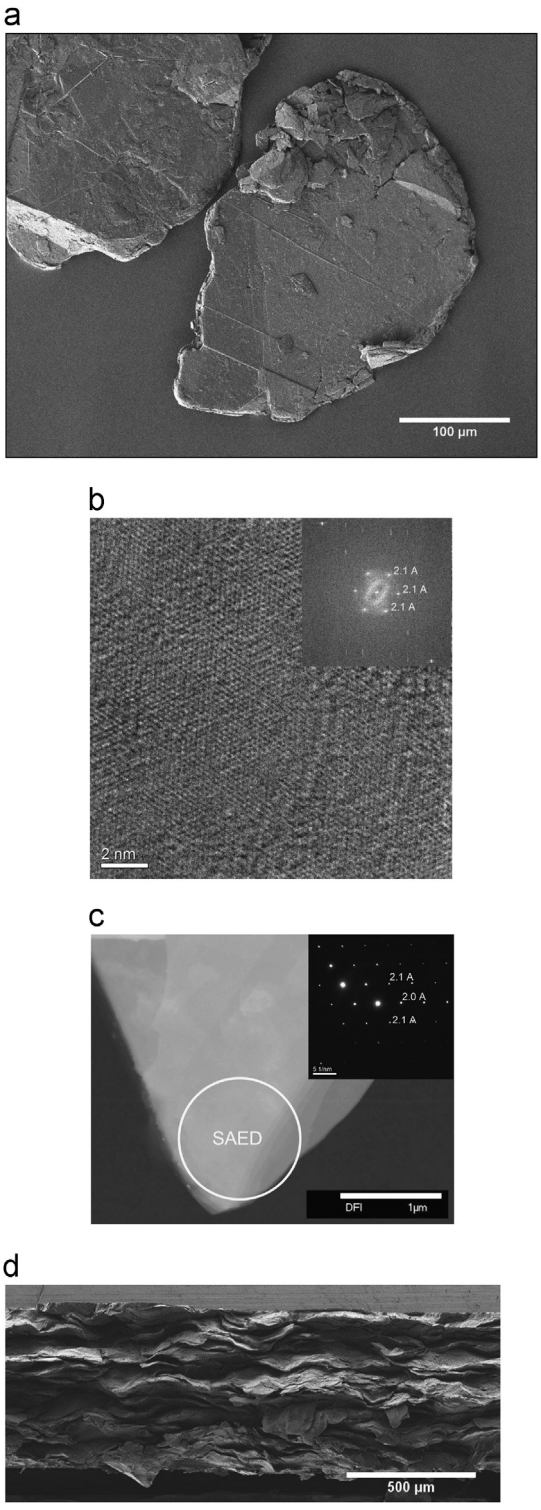

Fig. 1. (a) Graphite flakes as purchased from GK Kropfmühl before pressing into membrane discs (sample 1 of Table 1). (b) High-resolution TEM of a graphite flake. The inset shows Fast Fourier Transformation (FFT) of the shown area. (c) TEM of a graphite flake. The Small Area Electron Diffraction (SAED) shows the characteristic pattern of graphite (inset). (d) Cross section of the rough broken graphite membrane with self-arranged graphite crystals perpendicular to the direction of uniaxial pressing at ≈390 MPa (sample 1 of Table 1, see Fig. 1a).

[1] Up to 2 bar difference pressure, the pressed graphite membranes turned out to be mechanically stable without support. To measure at 4 bar pressure difference over the membrane (5 bar feed pressure, 1 bar permeate pressure), this stabilization of the pressed graphite was necessary.