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Carbon membranes from cellulose: Synthesis, performance and regeneration

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Abstract

Cellulose hydrolysis with trifluoroacetic acid (TFA), that is gentle enough to preserve the monosaccharides, provided an anticipative route to carbon membrane formation. Increasing the hydrolysis time, resulted in reduced weight loss during carbonization, and better separation performance for selected gas pairs. The permeability of N_2, H_2, CH_4, O_2, and CO_2 is reported for carbon membranes obtained from wood pulp hydrolyzed to different extents, as well as for carbon membranes obtained from different heating protocols (single gas tests at 30 °C and 2 bar).

A simple, energy effective and rapid regeneration method for membranes that are conductors or semi-conductors has been developed: when a low voltage, direct current was applied on an iron-doped carbon, enhanced permeation rates were immediately observed. The permeability increase depends on several factors, including gas critical temperature and current size. Electrothermal regeneration may also be applied on-stream, avoiding process interruption or an extra set of membranes. The method can be used for a continuous process, and not only for batchwise regeneration (e.g. activated carbon).

Keywords: Carbon; Cellulose; Trifluoroacetic acid; Metal additive; Electrothermal regeneration

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1. Introduction

Koresh and Soffer [1] produced molecular sieve carbon membranes for a continuous gas separation process by simple thermochemical treatment two decades ago. In 1995, Soffer et al. [2] had developed a protocol suitable for cellulose carbonization. It is well known that depolymerization to monosaccharides (mainly levoglucosan) occurs during carbonization, see e.g. Kawamoto et al. [3]. Monosaccharides then form condensed, aromatic structures, releasing gases containing non-carbon atoms (O, H). Cellulose treatment with an acid that is gentle enough to preserve the monosaccharides, will provide an anticipative route to carbon formation. Only a limited number of solvents exist for cellulose.

Trifluoroacetic acid (TFA) is an example of this kind of acid, and is widely used in fractionation of plant materials. Depolymerization to oligo- or monosaccharides is expected to occur. The 1,4-β-linkage in cellulose is hydrolyzed with subsequent decrease in molecular weight. Morrison and Stewart [4] evaluated the stability of oat straw in 99% TFA at 37 °C. Their findings did not indicate any major depolymerization of the cellulose molecules during the first 8 days, but after 12–16 days some depolymerization seemed to have occurred. Glucose was one of the major hydrolysis products. TFA is gentle towards monosaccharides compared to sulfuric acid. But extensive TFA treatment converts the monosaccharides to furan derivatives (caramel-like) through dehydration [5]. Hemicellulose is more susceptible to decomposition because of its more amorphous structure compared to cellulose. Carbonization of glucose produces more furans (five-membered rings), but less levoglucosan compared to carbonization of cellulose. The higher yield of furans is due to the kinetic preference to form five-membered rings over six-membered rings when both are possible (as here). In addition, furans are particularly thermally stable because of their aromatic nature. This was also documented by Sanders et al. [6]. Furans are more volatile than the six-membered rings, hence degradation will take place at a higher temperature—this is favorable for the formation of microporous carbon.

A carbon membrane may be modified by adding metals to the precursor solution. Adding metals to the carbon matrix has a three-sided motivation in the current work:

1. Increasing the micropore volume in the membrane (a spacer effect).

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2. Stimulating interactions with the preferred penetrant by stronger adsorption and possible selective surface flow (condensation on metal oxide clusters).
3. Increasing the electric conductivity of the matrix, for regeneration purposes.

Membrane performance is often evaluated by a type of Robeson plot [7]. In order to better evaluate membrane performance, a time dimension should be added to this kind of performance plot. A specified membrane permeability could be very misguiding if it changes rapidly over time. To achieve an attractive membrane lifetime, the membrane should have a long-time stable permeance (i.e. no significant aging). A stable permeance may be achieved by regeneration, and several techniques exist. The regeneration efficiency (RE) is often defined as

$$\mathrm{RE} = \frac{P_\mathrm{r}}{P_\mathrm{v}} \times 100\% \tag{1}$$

where P_r is the permeance of the regenerated carbon membrane and P_v is the permeance of the virgin carbon.

Traditionally, *thermal regeneration* has been applied to carbon membranes. The method usually has limited regeneration efficiency, see e.g. Menendez and Fuertes [8]. Thermal regeneration also suffers from other drawbacks such as the high temperature requirement (200–500 °C) with possible burnout of the carbon.

Chemical regeneration requires an additional chemical (if a regenerating gas/vapor is not part of the stream), followed by removal of that chemical. Jones and Koros [9] tested air feeds saturated with different organics on carbon membranes made from aromatic polyimides carbonized at 500 or 550 °C. They managed to completely remove sorbed hexane and isopropyl alcohol from carbon membranes by purging with pure propylene at about 10 bar. Membrane function was restored to varying degrees when exposed to some other organics. For example, the regeneration efficiency for O_2 permeance was about 65% after exposure to toluene.

Electrothermal regeneration of carbon membranes is especially suitable in non-oxidizing atmospheres. The continuous medium of graphene sheets makes the CMS membranes electrically conductive. The conductivity may be enhanced by adding metals to the carbon matrix. An adsorbed gas, such as CO_2, may be quickly and efficiently desorbed by the passage of a direct current (DC), thereby allowing for a low-energy, electric swing separation system with operational simplicity [10]. The van der Waals forces between the carbon skeleton and the CO_2 are disrupted or perhaps reversed by the electric current. This interaction most likely results from the quadrupole moment and the free electrons of CO_2. As a result, adsorbed CO_2 is released or repulsed from the micropore surface and desorption occurs. The same effect may apply to other adsorbed gases. Electrothermal desorption is a process where the heat is generated *inside* the adsorbent. Hence, the heat and mass flux directions are the same, i.e. from the solid to the fluid, as opposed to traditional thermal regeneration. Petkovska and Mitrovic [11] showed that electrothermal desorption is more energy efficient than conventional desorption because the fluid temperature can be substantially lower than the adsorbent temperature determining the adsorption equilibrium. They also showed that the same direction of heat and mass fluxes results in better desorption kinetics. Electrothermal regenerating of carbon membranes is especially suitable for separation in non-oxidizing atmospheres, like separation of CO_2 from CH_4. The risk of burning (oxidative degradation) is reduced. If the carbon burns, it will crack and render useless. The current can be applied when the membrane is in operation, without reducing the CO_2 flux. The method also has the possibility of high heating rates. Narbaitz and Cen [12] used electrothermal regeneration applying 50 mA for 5 h to desorb phenol from activated carbon. They reached a regeneration efficiency of 74–90%.

The aim for the reported research has been to make a suitable, cheap carbon membrane for CO_2 recovery from various gas mixtures, with special focus on upgrading biogas to fuel quality. In addition, a simple, online regeneration method was sought, since interruption of a process or having an extra set of membranes (regeneration in parallel with the process) would result in added cost.

2. Experimental

2.1. Materials

Wood pulp (also called kraft pulp) from a mixture of spruce and pine was supplied from Södra Cell Tofte, Norway. It is composed of cellulose and hemicellulose.

Trifluoroacetic acid (TFA, 99%) was supplied from Aldrich, Belgium. $Fe(NO_3)_3{\cdot}9H_2O$ (M_w 404.1) was delivered from Fluka, Switzerland. Gases for permeation tests were supplied from AGA, Norway, with a purity of 99.9% or higher.

2.2. Film formation

The pulp was dissolved in TFA to a concentration of about 1 wt.%. The TFA exposure time may have an effect on the separation performance. In this paper, the *hydrolysis time* is defined as the time from dissolving the cellulose in TFA until the film is dried in the vacuum oven. One pulp sample was exposed for 6 days, and another one for 74 days. For the rest of the films, the exposure time was 2–5 weeks for practical reasons (to limit time consumption).

Iron nitrate was added in various concentrations to some of the solutions to improve the separation performance of the resulting membranes and increase their ability to be regenerated. Other metal nitrates such as silver nitrate may also be used, but is more expensive. The solution was stirred overnight and then ultrasonicated with a VibraCell 130 (Sonics & Materials Inc., CT, USA) 6 mm rod for 2 min at amplitude 80 μm. Then a film was cast on a Teflon™ dish at room temperature. The film was covered to protect it from dust and to saturate the atmosphere above the film surface in order to slow down the evaporation rate, thereby increasing the homogeneity of the resulting film. Casting at room temperature was chosen, because 75 and 50 °C resulted in inhomogeneous films with bubble formations. The cast film precursor was left at room temperature