

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 N₂, H₂, CH₄, O₂, and CO₂ 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).

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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 misleading 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

$$RE = \frac{P_r}{P_v} \times 100\% \quad (1)$$

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 O₂ 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 CO₂, 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 CO₂ are disrupted or perhaps reversed by the electric current. This interaction most likely results from the quadrupole moment and the free electrons of CO₂. As a result, adsorbed CO₂ 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 CO₂ from CH₄. 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 CO₂ 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 CO₂ 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(NO₃)₃·9H₂O (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

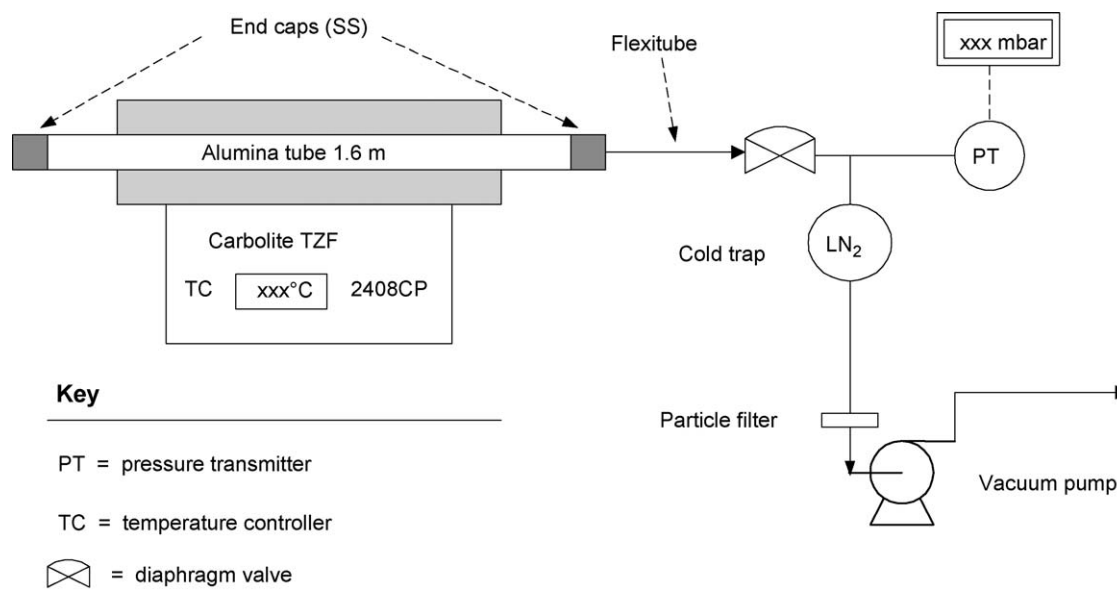


Fig. 1. Constructed set-up for carbonization (SS = stainless steel, LN₂ = liquid N₂ trap).

and after 4 days finally dried in a vacuum oven at 105 °C for about 18 h.

2.3. Carbonization procedure

Films were carbonized under mild vacuum (0.5 mbar) in a tubular furnace (Carbolite® TZF 12/100/900), using a working tube of alumina and a stainless steel grid as support for the films, see Fig. 1.

The basic protocol had a final temperature of 550 °C, kept for 2 h, a heating rate of 1 °C/min and several dwells. The protocol is pictured in Fig. 2, and is based on the protocol developed by Soffer et al. [2] for a cellulosic precursor. Their protocol was optimized with respect to mechanical properties of the carbon and its separation properties. The first two dwells are important in order to remove traces of water and solvent in the

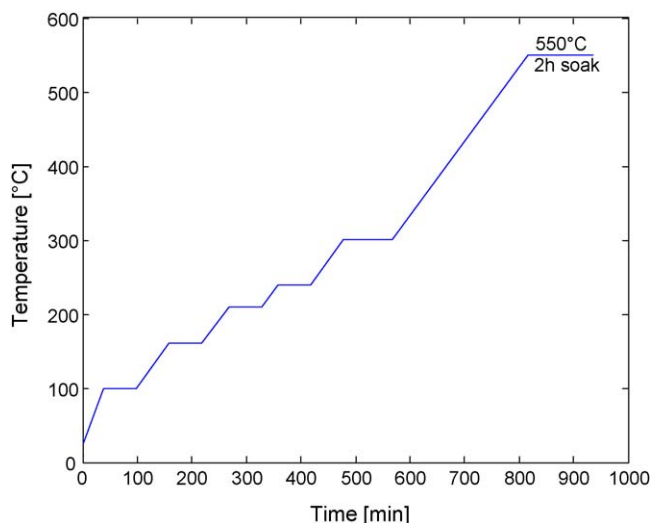
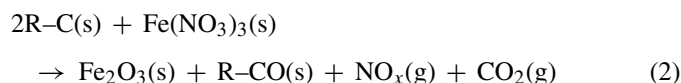


Fig. 2. Basic carbonization protocol (based on [2]).

precursor. The other dwells are important in order to allow the carbon matrix to rearrange and form micropores in between turbostratically arranged layers of graphene sheets. In addition, different final temperatures in the range 500–850 °C (no soak) were tested, in order to optimize the protocol for pure carbon. After the final temperature was reached the system was allowed to cool naturally to a temperature less than 50 °C, before the furnace was purged with ambient air and the films removed.

Thermogravimetric analysis (Q500, TA Instruments, New Castle, DE, USA) was performed on selected samples, with 100 ml N₂ (99.999%) per min and the samples in an open platinum pan. Each sample was dried in vacuum at 105 °C for 18 h prior to analysis.

Metal oxides are known to be stable at high temperatures, whereas, metal nitrates probably decompose to MeO and NO_x. For example, copper nitrate seems to form CuO with evaporation of the remaining nitrate groups, according to Silverstein et al. [13]. The following reaction may take place during carbonization of iron nitrate in a carbon matrix (R-C):



The release of gases should make the iron nitrate-containing membranes more open-structured and permeable than membranes without additives. The released gases may to a large extent contribute to the formation of micropores and rearrangement of the cellulosic carbon. Thus the nitrates may be regarded as porogens.

2.4. Permeation tests

The circular carbon films were masked using an impermeable aluminum tape, leaving open a defined permeation area. Epoxy was then applied along the interface of the tape and the carbon. A sintered metal disc covered with a filter paper was used as sup-

port for the film in the test cell. Single gases were tested at 30 °C and a feed pressure of 2 bar (permeate side evacuated) in a standard pressure-rise setup (MKS Baratron® pressure transducer, 0–100 mbar range) with LabView® data logging. The experimental method and setup is described elsewhere [14,15]. The order of testing was always N₂, H₂, CH₄, O₂, CO₂, SF₆, and finally N₂ again to measure any degree of aging (productivity loss). This test order prevents the strongly adsorbing gases from disturbing the performance of the more ideal or non-interacting gases in carbon. The tests were run for several hours or days, to ensure that the transient phase of diffusion was passed and steady state obtained (linear pressure versus time correlation). For CH₄ and SF₆ 1 or 2 days of permeation were typically needed, while for H₂ a linear regression curve was obtained after a couple of hours. The permeation system was evacuated overnight in between each gas test. In this paper, selectivity is defined as the ratio of the single gas permeabilities. Permeability is often expressed in Barrer, which is converted to SI-units (kmol m⁻² s⁻¹ kPa⁻¹) by dividing by 2.99 × 10¹⁵.

2.5. Regeneration procedure

Electrothermal regeneration was used. First, soldering was tested as a way of attaching single-core cables to the membrane. A soldering paste was used to increase the wettability of the tin solder on carbon, but poor adhesion remained a problem. Hence, a two-component conductive epoxy (ITW Chemtronics® CW2400) was used. An increasing current was applied on a test membrane (not masked), and at about 100 mA current the carbon started to burn. Initial tests showed that when burning occurs, the electric circuit is disrupted or the carbon membrane is cracked. The amount of current used in this work was therefore set well below this failure limit. A carbon membrane was then masked. After the ordinary epoxy had dried, and the membrane was found to function, the single-core cables were connected with conductive glue at opposite regions at the membrane feed side and then cured at 65–70 °C for 10 min.

The permeation tests were run in the same manner as described in the previous section. When steady state was reached, the current was turned on and monitored by a 30 V power supply (Mascot 719) and a multimeter in series.

3. Results and discussion

3.1. Effect of hydrolysis time on performance of carbons from pulp without metal additives

Depolymerization and formation of furan and its derivatives (see Section 1) may explain the increased carbon yield when

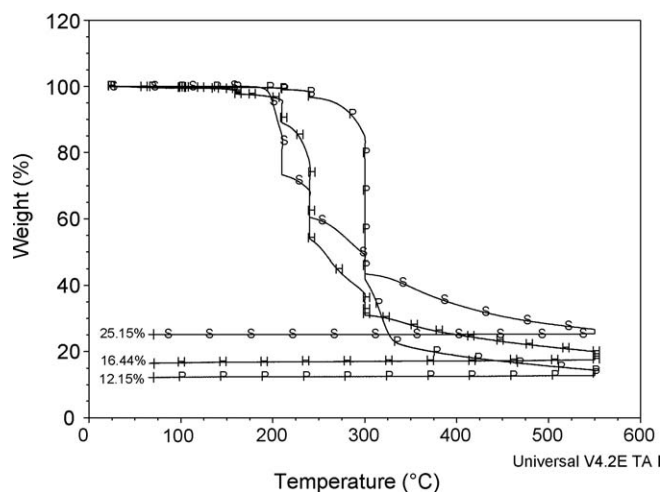


Fig. 3. Thermogravimetric analysis of kraft pulp (P), pulp hydrolyzed for 14 days (H) and sucrose (S) in N₂ atmosphere with the heating procedure identical to the membrane carbonization procedure (550 °C, 2 h soak).

increasing the TFA exposure time, Table 1. The weight loss is based on the amount of total material. According to Kawamoto et al. [3], the path to solid carbon formation from cellulosic materials includes a depolymerization step followed by ring-opening polymerization. Carbon films from 5 days exposed pulp were also made, but were too porous and brittle to test. Using a light table it was observed that those films had pinholes and were non-isotropic.

Fig. 3 shows an overlay of curves from thermogravimetric analysis of sucrose (a disaccharide), kraft pulp (polysaccharide) and hydrolyzed pulp (oligosaccharide). The heating procedure is identical to the membrane carbonization protocol, except for the atmosphere being pure nitrogen (vacuum was not possible with the TGA). From the figure it is clear that the hydrolyzed pulp has a track that resembles that of sucrose: the onset of thermal decomposition is found at a lower temperature and the carbon yield is increased compared to the original pulp. This supports the idea that the pulp is transformed to a saccharide with short chain fragments when exposed to TFA.

Permeation test results for several gases are given in Table 2 and Fig. 4 for CO₂/CH₄. The wide range of film thicknesses was due to thickness variations within each precursor film. One of the reasons for this is most likely the variation in surface tension between the Teflon™ dish and the different casting solutions. TFA exposure for only 6 days resulted in films showing non-selective diffusion. After 2 weeks a critical threshold in the hydrolysis process has been reached, and the CO₂/CH₄ separation performance seems to increase with time. All the films used

Table 1
Descriptions of carbons from pure pulp exposed to TFA for different times (carbonized at 550 °C, 2 h soak)

Sample ID	Exposure time (days)	Precursor appearance	Carbon appearance	Weight loss of carbon batch (%)	Diameter shrinkage (%)
C-6	6	Flexible, rough	Black/grey, dull, rough	84.4–84.5	42–46
C-14	14	Black, brittle, smooth	Black, shiny, smooth	80.6–81.2	–
C-74	74	Black, brittle, smooth	Black, shiny, smooth	71.9–72.6	31

Table 2

Results for carbons (550 °C, 2 h soak) from pure pulp exposed to TFA for 6, 14 and 74 days, respectively (single gases, 2 bar, 30 °C)

Film	Thickness (μm) ± 2S.D.	P_{N_2} (Barrer)	P_{H_2} (Barrer)	P_{CH_4} (Barrer)	P_{O_2} (Barrer)	P_{CO_2} (Barrer)	P_{SF_6} (Barrer)	Aging (% change in N_2 permeability)
C-6	86 ± 7	29 × 10 ³	55 × 10 ³	32 × 10 ³	17 × 10 ³	28 × 10 ³	21 × 10 ³	−18
C-14	40 ± 4	4.2	9.4 × 10 ²	4.6	54	1.9 × 10 ²	0.63	+14
C-74	46 ± 9	5.7	8.6 × 10 ²	1.3	48	1.5 × 10 ²	–	−24

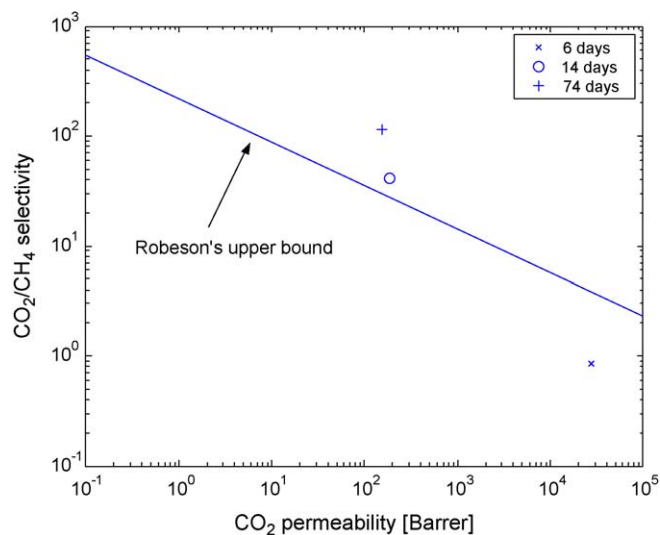
For conversion of Barrer to kmol m m^{−2} s^{−1} kPa^{−1}, divide by 2.99 × 10¹⁵.

Fig. 4. Separation performance for carbons (550 °C, 2 h soak) from different precursor exposure times in TFA (single gases at 30 °C, 2 bar). Robeson's upper bound was derived from measurements of polymers, mostly at 35 °C [7].

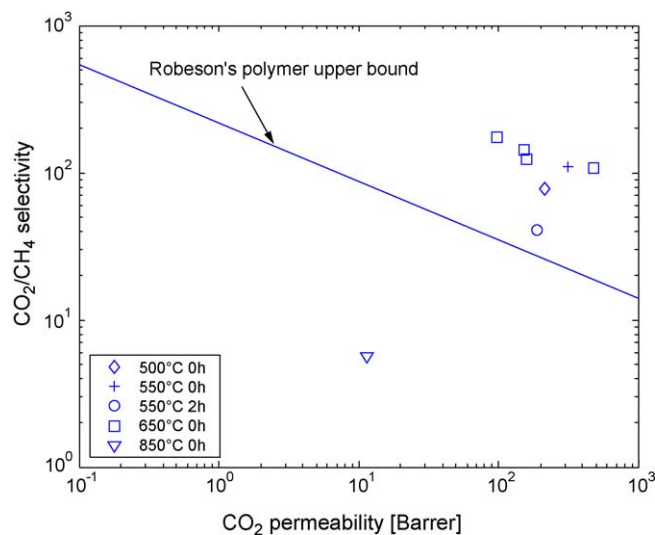
in the other experiments, i.e. for making carbons with metal additives and for testing different carbonization protocols, had a TFA exposure time of 2–5 weeks, for practical reasons. This variation in exposure time could influence the selectivity, but has minor influence on CO₂ permeability, according to Fig. 4. Increased exposure time probably causes a change in the carbon matrix, where the average pore width is shifted towards the sieving diameter of CO₂ (3.3 Å). This pore narrowing excludes methane to a larger extent.

As can be seen from Table 2, the permeabilities generally decrease with exposure time—this is according to what is to be expected. The value reported for nitrogen, however, after 14 days is most likely influenced by an experimental error (improper conditioning), and should be neglected.

Table 3

Permeation results from pure pulp carbonization (single gases, 2 bar, 30 °C)

Protocol	Thickness (μm) ± 2S.D.	P_{N_2} (Barrer)	P_{H_2} (Barrer)	P_{CH_4} (Barrer)	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	P_{SF_6} (Barrer)	Aging (% N_2 permeability change)
500 °C, no soak	23 ± 6	6.6	4.6 × 10 ²	2.8	2.2 × 10 ²	49	0.050	−0.76
550 °C, no soak	52 ± 7	8.6	11 × 10 ²	2.8	3.1 × 10 ²	90	0.23	−1.0
550 °C, 2 h soak	40 ± 4	4.2	9.4 × 10 ²	4.6	1.9 × 10 ²	54	0.63	+14
650 °C, no soak	66 ± 5	15	13 × 10 ²	4.4	4.8 × 10 ²	1.3 × 10 ²	0.61	−6.1
850 °C, no soak	33 ± 7	3.7	55	2.0	11	5.8	–	−48

For conversion of Barrer to kmol m m^{−2} s^{−1} kPa^{−1}, divide by 2.99 × 10¹⁵.Fig. 5. CO₂/CH₄ separation performance of pure carbon films from different protocols (same heating rate), single gases at 30 °C and 2 bar. The samples were exposed to TFA for 2–5 weeks. Robeson's upper bound was derived from measurements of polymers, mostly at 35 °C [7].

The results indicate that furans are a key intermediate in forming microporosity with high separation performance. It is probably favorable that this intermediate also is formed *prior to* carbonization (through TFA treatment), and not only during the carbonization process.

3.2. Effect of final carbonization temperature and soak

In order to optimize the carbonization protocol, different final temperatures were tested, Table 3. From the carbon batch made at 650 °C, four films were tested, but only the results from the first tested film is given in the table. Results for all four films are shown in Figs. 5 and 6.

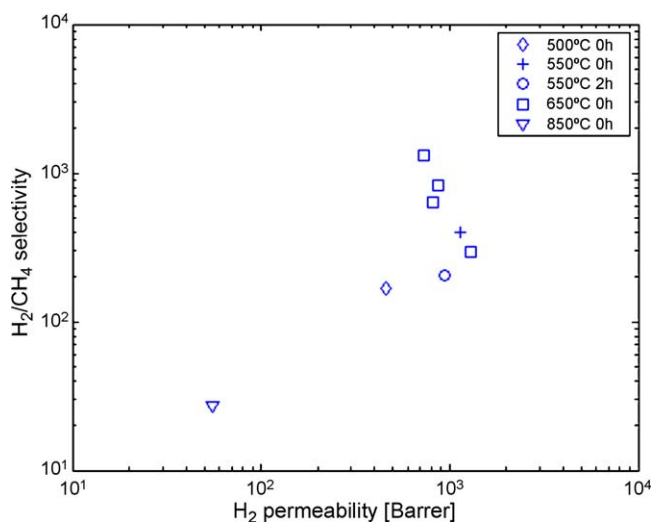


Fig. 6. H_2/CH_4 separation performance of pure carbon films from different protocols (same heating rate), single gases at 30°C and 2 bar. The samples were exposed to TFA for 2–5 weeks.

The performance for CO_2/CH_4 separation as a function of carbonization temperature (Table 3) is plotted in Fig. 5. The increase in permeability as the final carbonization temperature is brought up to 650°C is in agreement with a gradual pore opening. At 850°C , the permeability of all gases is reduced, in accordance with a sintering of the carbon matrix. At 850°C , the volumetric loss (film diameter and thickness change) was found to be larger than the weight loss, whereas, at 650°C , the losses were equal. Below 650°C , the weight loss was slightly larger than the volumetric loss. The low selectivity of the carbon made at 850°C is somewhat unexpected. However, the H_2/N_2 selectivity is higher than at 650°C and the strong aging (Table 3) suggests that large penetrants (N_2 and CH_4) are still sorbed in some of the pore network and hinder O_2 and CO_2 permeation.

For the separation of CO_2 from CH_4 a soak at 550°C has a negative impact on performance. The increase in CH_4 permeability when adding a soak is difficult to explain, and could be caused by measurement errors. From the 650°C batch, four different films were tested to check the scattering in performance data of the films produced. From Fig. 5, a significant scattering can be seen. However, the repeats seem to line up on a line parallel to the trade-off line. Hence, it is possible to distinguish at least the results at 550°C with soak and those at 850°C , from the results at 650°C . Still the exact optimum carbon formation temperature is difficult to tell.

Table 4
Results from carbonization (550°C , 2 h soak) of metal nitrate containing wood pulp (single gases, 2 bar at feed side, 30°C)

Film	Weight-loss (%) \pm 2S.D.	Thickness (μm) \pm 2S.D.	P_{H_2} (Barrer)	P_{CH_4} (Barrer)	P_{CO_2} (Barrer)	P_{O_2} (Barrer)	P_{N_2} (Barrer)
C-FeN 1.8	69.0 ± 0.8	75 ± 8	10×10^2	2.1	3.1×10^2	86	8.2
C-FeN 4.4	83.14 ± 0.04	41 ± 9	3.3×10^2	5.5	30	14	6.0

For conversion of Barrer to $\text{kmol m}^{-2} \text{s}^{-1} \text{kPa}^{-1}$, divide by 2.99×10^{15} .

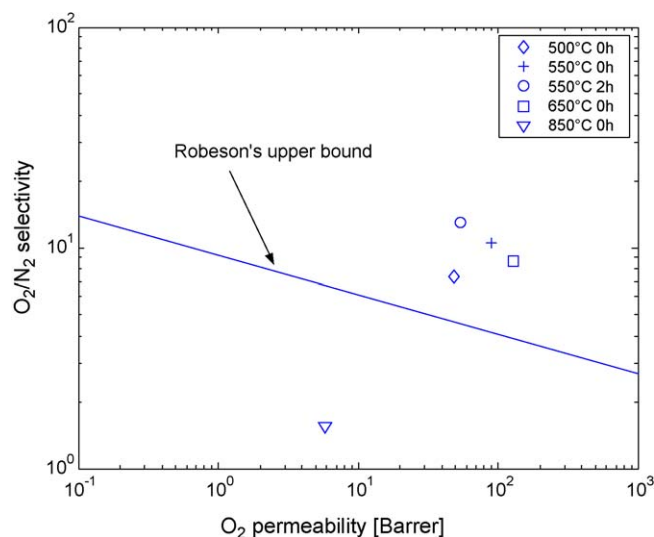


Fig. 7. O_2/N_2 separation performance of pure carbon films from different protocols (same heating rate), single gases at 30°C and 2 bar. The samples were exposed to TFA for 2–5 weeks. Robeson's upper bound was derived from measurements of polymers, mostly at 35°C [7].

The repeated tests for the gas pair H_2/CH_4 are shown in Fig. 6. Again the repeats at 650°C are lined up, and it is possible to distinguish them from 500 and 850°C .

For the gas pair O_2/N_2 , Fig. 7 (from data in Table 3), the situation is different. The soak is not a drawback, and can easily be explained by a sintering mechanism.

From the permeation results presented, it is clear that other final temperatures need to be tested to identify the exact optimum for carbonization, as well as repeats to measure the repeatability. Most of the presented carbons have however a better separation performance than the upper bound [7] for polymers.

3.3. Electrothermal regeneration

To make the carbons more conductive, iron nitrate (FeN) was added to the precursor solution. On the other hand, too high metal loading resulted in carbons that were too brittle to test. Hence, a trade-off between mechanical properties and electric conductivity exists. The metal nitrate content of the precursor (crystal water subtracted) was 1.8 wt.% for one batch and 4.4 wt.% for another batch. Membranes were carbonized at 550°C , with a 2 h soak. Membrane data and single gas permeabilities are given in Table 4.

Higher percentage of Fe in carbon results in lower carbon yield probably due to catalytic oxidation (Fe as the catalytic metal and nitrate as the oxidiser). The carbon with 4.4 wt.%

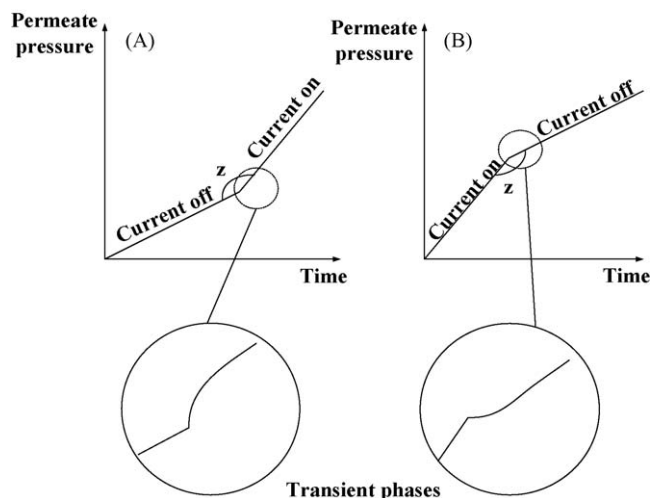


Fig. 8. Procedure for permeation test, and shapes of the transient phases.

FeN was chosen for regeneration experiments, because of its higher conductivity. Hence, the chance of detecting any effect of electric current should increase.

When a low voltage direct current (17.5 V, 10 mA) is applied to the metal-doped carbon during a permeation test, the permeability increases instantaneously and remains stable, see Fig. 8.

The relative permeability increase depends among other factors on the gas type and on the amount of current applied. Oxygen permeation tests showed that the effect (or the knee angle z) was the same, whether the current was applied during the first half of the experiment (Fig. 8B), or during the second half (Fig. 8A). The *absolute* permeabilities had a small change between the experiments, indicating history dependence (amount of preadsorbed gas in the carbon, etc.), while the *relative* permeabilities (the angles) seem to depend on the physics of the process. Fig. 9 shows the relative permeabilities for gases tested according to Fig. 8A. In this work, relative permeability is defined as the ratio

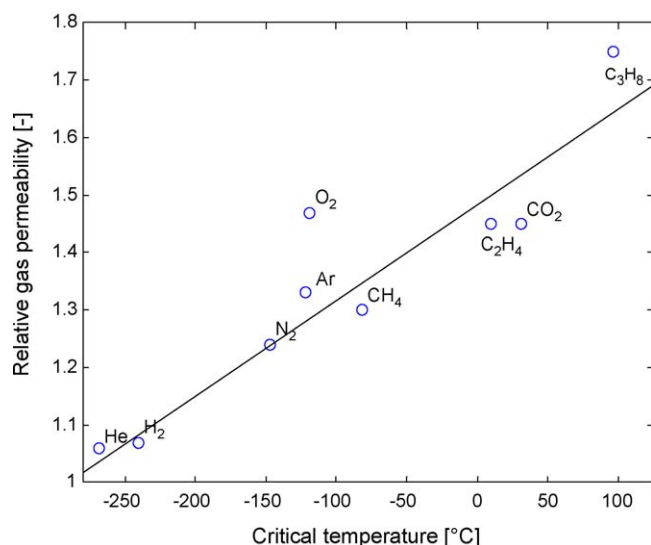


Fig. 9. Relative gas permeability as a function of gas critical temperature (10 mA, 30 °C, 2 bar feed).

of the permeability with current applied and the permeability without any current.

Several factors may cause enhanced permeability when a direct current is applied: traditionally, carbon is used as resistors, and ohmic heating of the carbon may increase the desorption rate of the gas through the membrane. If desorption is the rate-limiting step for gas transport, the effect of heating should be pronounced. Since the heat is generated in the inner parts of the carbon, and not by an external fluid (i.e. the direction of heat and mass transfer are the same), this kind of regeneration will be very energy efficient. The shapes of the transient phases during permeation (Fig. 8) and the correlation between gas critical temperature and relative permeability (Fig. 9) also indicate that desorption enhancement is involved. Secondly, the magnetic field generated by the electric current may cause orientation of the diffusing polar molecules, and hence less degree of rotation. This entropy reduction *prior to* entering the pores thus increases the chance of overcoming the pore entrance barrier.

Thirdly, when a magnetic field is applied to a ferromagnetic solid like iron oxide, the iron oxide clusters are oriented parallel to the magnetic field, causing a mechanical change in the carbon matrix. This phenomenon is called magnetostriction, and may cause a reduction in tortuosity. However, application of current to a metal-free carbon and a copper-containing carbon also showed permeability increase. Hence, magnetostriction is not a significant factor. Another possibility is that application of current may displace or further carbonize the structure. However, this should result in permanent changes in permeability, which is not observed.

By focusing on the first two explanations a simple pore model, like that given in Fig. 10, may be useful to illustrate the observed phenomenon. Spherical molecules, e.g. Ar, are also affected by the current, though less than a linear molecule like O₂, having about the same critical temperature. Hence, ohmic heating stands as a general explanation to the phenomenon. By electroheating the effective pore entrance is increased due to gas desorption from low energy sites of the pore entrance, and thus higher permeability is achieved. This may also be viewed as an increase in the gas hopping rate along the pore walls in the direction of diffusion.

When it comes to terminology, *permeability* is a material property and is not a quite correct expression in this case. The system (membrane + electrical field) property *flux* is a better

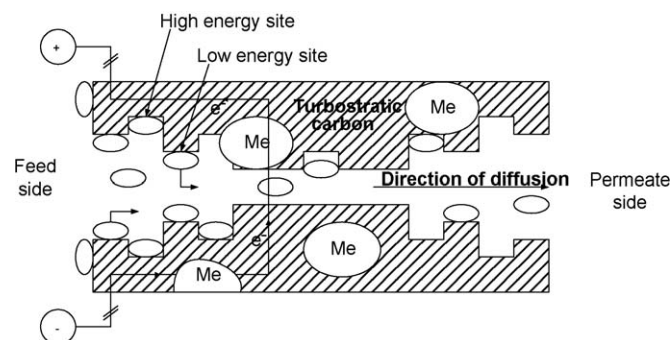


Fig. 10. Simplified pore model in a wired carbon membrane (Me = metal, e = electron).

term, but since the gas fluxes are obtained with a standard permeability measurement setup and normalized by trans-membrane pressure and thickness, yet the term permeability is used in this work.

When it comes to the long-term effect of electrothermal regeneration, the same carbon film was used for hydrogen and methane permeation tests (30–50 °C and 0.5–2.0 bar) for 2 weeks. Current (5–15 mA) was applied for 2 h in average each day. After the test series, the hydrogen permeability (with the current off) was increased by 14%, i.e. a regeneration efficiency of 114% (Eq. (1)). The overall increase in methane permeability was 7%, which gives an overall increase in H₂/CH₄ selectivity of 7%.

Electric current can be used not only as a periodic regeneration method, but also in a continuous way, facilitating the transport of some gases, but blocking others. In this way, both permeability and selectivity may be increased. The benefit of this approach depends on the power consumption (regeneration costs).

Deconvolution of any field effects and heating effects on permeation is a challenging task. Mixed gas tests will probably provide more insight to this problem and the mechanisms that are active, and have the highest priority in the further research, together with electrothermal treatment of other metal containing carbon membranes. Extended long-term tests with two membranes in parallel, one wired and one non-wired, should also be performed to obtain the actual benefit of the regeneration method.

4. Conclusions

An alternative path to carbons from cellulosic materials by hydrolysis of the cellulose prior to carbonization has been tested out in the current work. Increasing the hydrolysis time, resulted in reduced weight loss during carbonization, and better separation performance for the gas pair CO₂/CH₄.

The effect of changing the final carbonization temperature was evaluated for H₂, CO₂, CH₄, O₂ and N₂. Most of the presented carbons possess a better separation performance than the upper bound [7] for polymers.

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 is applied on an iron-doped carbon, enhanced permeation rates are achieved. This probably results from enhanced desorption rate and hopping rate of the gases in the carbon due to ohmic heating. The relative increase depends a.o. on gas critical temperature and current size. Electrothermal regeneration may be applied on-stream, hence avoiding process interruption or an extra set of

membranes. The method is able to fully restore the initial permeability of the carbon membrane. The method can also be used in a continuous way, and not only for batchwise regeneration.

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