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Preparation and Characterization of Bilayer Carbon/Polymer Membranes.

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Abstract

The objective of the present research work was to develop a membrane with a high H₂O/alcohol selectivity for pervaporation and for applications like DMFC for which reduced fuel cross-over is important. Sulphonated poly(ether ether ketone) (SPEEK) was coated with a continuous and thin carbon molecular sieve (CMS) layer. The obtained membranes having 180 and 400 nm thick CMS layer led to a clear reduction of the alcohols cross-over, while keeping high water permeability. The molecular sieving effect was clearly demonstrated, when membranes were tested for their pervaporation properties using water-alcohols mixtures. The H₂O/alcohol separation factor increased with the size of the alcohols molecule in the row methanol - ethanol - n-propanol - iso-propanol.

1. Introduction

Carbon Molecular Sieves (CMS) are characterized by a very narrow pore size (3.0 to 10Å) distribution, with dimension of small molecules, which can therefore be separated according to their size. They can be produced from distinct raw materials by a variety of methods such as:

- Carbonization, control activation and thermal treatment of carboneous materials;
- Pyrolysis of polymers;
- Modification of coals by mixing with tars and resins and subsequent carbonization;
- Carbon deposition (by CVD) onto the activated carbon;

The concept of carbon molecular sieve has been known for at least last 30 years, but it is only during the last 10 years that these were successfully used as membranes for gas separation. Excellent separation properties have been reported for gas mixtures. The most important applications are the production of high purity nitrogen from the air and recovery of hydrogen from gas streams.

Carbon molecular sieve membranes are basically prepared in four different configurations like flat sheet, tubes, capillary and hollow fibres [1,2].

In the recent years the incorporation of carbon molecular sieves flakes into polymeric membranes has been reported [2,3] as a very effective strategy to increase the gas selectivity, leading to membranes which are far above the Robeson curve. The membranes are in all the cases prepared as mixed matrix membranes. CMS-filled poly (vinyl alcohol) membranes have been reported for pervaporation of benzene/cyclohexane mixture [4]. CMS filled silicone membranes have been described for the pervaporation of acetic acid /water mixture [5].

Here in this paper a very thin but continuous layer of carbon molecular sieve (CMS) is prepared as a coating for a very hydrophilic membrane based on sulphonated poly (ether ether ketone).

The initial motivation of this work was to develop membranes with reduced alcohol permeabilities to be used in direct methanol fuel cell (DMFC). Sulphonated poly (ether ether ketone) (SPEEK) is under investigation by several groups [7-10] as an alternative for Nafion[®] as proton conductive membrane. However like Nafion[®], the problem of excessive swelling and high methanol cross-over hinders its application for DMFC. Many attempts have been reported in the literature [11-15] to modify SPEEK, many of them based on inorganic modifications with incorporation of silica, layered silicates and polysilsesquioxanes. However in most of the cases, the alcohol permeability is well coupled to the water (and proton) permeability. When the methanol is effectively reduced, in most of the cases the water permeability is also reduced as well and at the same time considerable reduction of proton conductivity is also observed.

The idea to use a carbon molecular sieve as a coating for SPEEK membranes was to find a way to block the alcohol transport across the membranes without reducing water and proton conductivity.

The same membrane would be useful for pervaporation of alcohol/water mixtures. Hydrophilic membranes with preferential permeation of water have been widely used for the removal of water from organic solvents with great advantages for azeotropic mixture. Usually the selective layer is a very hydrophilic material like poly(vinyl alcohol) (PVA) and the separation is predominantly based on solubility. More recent developments for pervaporation are based on inorganic membranes with a selective layer of zeolite. In this case also a molecular sieve effect is important for separation. Here in this paper the molecular sieve effect is added to a membrane, which otherwise mainly works with high water permeability due to high water.

The focus of this work is on the membrane preparation and its characterization as far as the molecular sieve properties are concerned. A further investigation on the performance of these membranes for DMFC is going on.

2. Experimental:

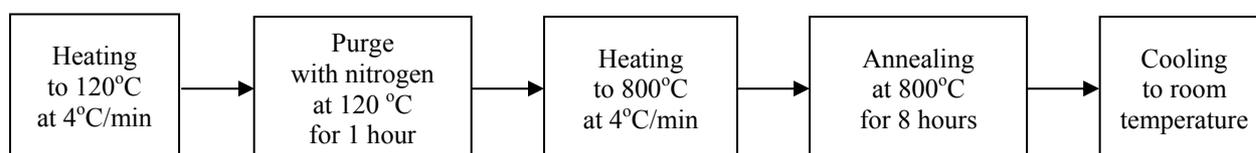
2.1 Materials

The polyimide precursor used for synthesis of carbon molecular sieve (CMS) in this research was Matrimid[®] 5218 (polyimide of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and diamino-phenylindane) bought from Ciba Geigy (Switzerland). The polymer was used as received since the TGA investigation showed no volatile residue. Before dissolution in chloroform, the precursor was heated in an oven at 120 °C for 24 h to remove any water residual. Quartz plates purchased from GE Quartz Europe GmbH were cut according to the size of the furnace tube for pyrolysis of thin Matrimid[®] films. Chloroform (99.0 – 99.4 %) from Merck was used as purchased. Poly (ether ether ketone) (PEEK), purchased from Victrex, was sulphonated according to the procedure described in ref. [12]. For preparation of (7 wt %) SPEEK solution, dimethyl sulphoxide (DMSO) solvent of 99.9% purity was purchased from Merck and was used as such.

2.2 Preparation of Carbon Molecular Sieves (CMS)

The preparation of the CMS was conducted based on the procedure published by W. J. Koros [2,3]. To prepare CMS flakes, Matrimid[®] solutions of two different concentrations (1 and 2 wt %) were prepared using chloroform as solvent. The solutions were stirred for about 3 to 4 h to ensure complete dissolution of the polyimide in the solvent, filtered through a fine cotton filter and cast on quartz plates at room temperature. The solution was protected from dust contamination and allowed to evaporate for 12 h. Quartz plates with the thin polymer layer were treated in vacuum oven at 110°C for at least 12 h to remove any residual solvent.

Polymer coated quartz plates were placed into the furnace for the pyrolysis under nitrogen atmosphere. The procedure of the pyrolysis can be seen from the block-scheme below:



After cooling to room temperature the CMS coated quartz plates were removed from the furnace. The quality of the CMS coating was controlled visually: only uniformly black samples without visible cracks were used for further experiments.

2.3 Preparation of SPEEK solution

Dried SPEEK (DS 56%) was dissolved in dimethyl sulphoxide (7 wt %). The solution was stirred for 24 hours at 70°C to ensure complete dissolution and uniform mixing.

2.4 Preparation of bilayer membranes

CMS coated quartz plates were placed on a levelled table at 80 °C and the SPEEK solution (7 wt %) was cast on the surface of the CMS layer and allowed to dry at this temperature for about 24 h. Quartz plates were then placed into the vacuum oven at 110 °C for about 24 h more to remove all the residual solvent. After the polymer layer formation bi-layered membranes were easily removed from the quartz surface without damages of the CMS.

2.5 Morphology of the bilayer membrane

The morphology of the CMS layer before coating with SPEEK was studied using the tapping mode of the VEECO NANOSCOPE 4 Surface Probe Microscope.

The surface and cross-section morphology of CMS coated SPEEK membrane was studied by scanning electron microscopy (SEM) (LEO 1550 VP). Samples for the SEM study were prepared by fracturing the membrane in liquid nitrogen. Samples were vacuum sputtered with a thin layer of Au/Pd prior to analysis.

2.6 Pervaporation measurements

Pervaporation experiments were performed according to the procedure described elsewhere [6] using solutions of different concentrations at 55 °C, pressure of 1 bar on the feed side, vacuum (10^{-2} mbar) on the permeate side. The effective membrane area was 12.5 cm². The used pervaporation set up is described in Fig.1 After the steady state was achieved, the permeate was collected for 1 hour in cold traps immersed in liquid nitrogen. The compositions of feed and permeate were determined using gas chromatograph Hewlett Packard 5890 equipped with SUPELCOWAXTM-10 capillary column (30m x 0.53 mm x 1.0 um film thickness) with oven temperature of 280°C and flame ionization detector 280°C. Prior to the pervaporation experiments, the membranes were kept in the corresponding solutions over night.

The permeabilities (P) were calculated according to the equation:

$$P = \frac{m \cdot d}{A \cdot t}$$

where: m is the mass of permeate (Kg); d is the thickness of membranes (m); A is the effective area of membrane in contact with the feed (m²); t is the permeation time (s).

3. Results and Discussion

3.1 Surface Probe Microscopy (SPM) of the CMS surface

Topographic (height) and phase contrast images of both surfaces of the CMS layer, exposed to the atmosphere during the pyrolysis (top) and facing quartz (bottom) are similar, indicating that the membrane is isotropic. The SPM image of the top surface of CMS is presented on Fig. 2.

In order to evaluate the size distribution of the structures seen in the Fig.3, a diagonal starting from the upper left to the lower right angle of the phase contrast image was traced and the position of every observed peak was marked. Interpeak distances were calculated and the histogram of the interpeak distance occurrence was plotted in Fig 4. The histogram has a monomodal nature with the most frequent Interpeak distance being 6 ± 1 nm. The interpeak distance reflects the periodic structure in the CMS, which is indeed larger than the actual pore size. The pores responsible for the molecular sieve characteristics of the membrane are probably located in the bottom of the “valleys” between peaks.

3.2 Scanning electron microscopy of the bilayer membranes

The SEM micrographs (Fig. 4) of the surface cross-section of CMS coated SPEEK membrane show good adhesion between the CMS layer and SPEEK and absence of crack on the surface of the CMS. The SEM also allowed to determine the thickness of the CMS layer, which depends on the concentration of the Matrimid[®] solution used as a precursor. A 1 wt % Matrimid[®] solution led to a CMS layer with the average thickness 180 nm and a 2 wt % solution 400 nm.

3.3 Effect of alcohol concentration and CMS layer thickness

Water and methanol permeabilities across the plain SPEEK polymeric membranes and CMS coated SPEEK membranes (thickness around 70- 76 μm) were measured by pervaporation at 55 °C. Methanol solutions of different concentration (5 wt %, 10 wt % and 20 wt %) were

circulated on the feed side and the permeate side was evacuated. The difference in permeabilities across the plain SPEEK and CMS coated membranes can be seen in Fig 5.

In pervaporation experiment with 5 wt % methanol solution, the methanol permeation is 36% and 62% reduced when the plain SPEEK membrane is coated with CMS thickness of 180 nm and 400 nm respectively. When the concentration of methanol is increased to 10 wt % and 20 wt % then again the same level of reduction of methanol cross over is observed for CMS coated SPEEK as compared to plain SPEEK polymeric membrane. This reduction of methanol permeation occurs mainly because the CMS contains a proportion of nano pores, which are even smaller than a methanol molecule (0.38 nm). In the case of 20 wt % methanol pervaporation, a much higher permeability was observed for plain SPEEK as compared to the CMS coated ones. The reason is the excessive swelling. The CMS coating gives mechanical strength to polymeric membrane and inhibits the excessive swelling. Further-more the CMS layer on the fuel side protects the SPEEK layer from the direct contact with concentrated methanol solution during the measurements.

3.4 Effect of alcohol molecular size

Beside methanol, other alcohols like ethanol, n-propanol and iso-propanol were used in pervaporation experiments. Results of the permeation experiment of 5 wt % aqueous solutions of alcohols (methanol, ethanol, n-propanol and iso-propanol) are presented in Fig.6. From Fig 6, it is clear that selectivity is dependent on the molecular shape and size of alcohols. The permeability is higher for methanol as compared to ethanol, while n-propanol and iso-propanol separate completely from the water during pervaporation through the CMS coated SPEEK.

Here one can conclude that the possible pore size of the CMS is equal or less than 0.47 nm. As the molecular size of alcohols increases, the permeability of the concerned n-propanol and iso – propanol decreases while their selectivity increases. For propanol with molecular size ca. 0.47 nm there is a drastic reduction of permeability with the CMS coatings.

To prove if the alcohol permeation causes any damage in the CMS layer, a simple pervaporation test was performed. First pervaporation of a 5 wt % iso-propanol solution was performed. After that another pervaporation test was performed with 10 wt % iso-propanol through the same plain SPEEK and CMS coated ones. Finally pervaporation of 5% iso-propanol solution was performed again. All the permeation data are represented in Fig 7.

From these experiments it was evident that the effect of swelling is at least partially irreversible indicating that some cracks are created during the permeation of alcohols solutions with high concentration. However the CMS coated SPEEK still provide better separation for alcohols from water as compared to plain SPEEK even when high concentration solutions are used. When butanol is used as feed, both the plain SPEEK and the CMS coated membranes are badly damaged due to even more swelling.

3.5 Separation factors

H₂O/alcohol separation factors were calculated according to the following equation.

$$\text{Separation Factor (H}_2\text{O / Alcohol)} = \frac{X / (1 - X)}{Y / (1 - Y)}$$

Where X and Y are the wt % fractions of alcohols in the feed and permeate respectively.

Fig 8a shows how the water/alcohols separation factor varies with the CMS thickness and with the size of the permeate molecules. Separation factors higher than 100 were measured using 5 wt % propanol solutions. The separation factor decreases to less than 1/10 when alcohols used were ethanol and methanol. This again confirms the molecular sieve effect.

When high alcohols concentration (10 wt %) are used, damages of the CMS layer due to excessive swelling of the SPEEK layer lead to a decrease of water/propanol separation factor while for methanol and ethanol not much change was observed.

In the case of propanol there is a large swelling of the SPEEK membrane during the experiment, what also promotes the water transport through the membrane. When bilayer membranes were tested, the CMS layer was placed to the feed side. During the pervaporation experiment due to the high water/propanol selectivity in the steady state the membrane was “protected” from the contact to alcohol and interacted partially only with water. This decreased the excessive swelling and the water permeability came to values similar to those measured using methanol or ethanol aqueous feed solutions.

4. Conclusions

The bilayer CMS coated SPEEK polymeric membranes separate alcohol/water mixture based on the particle size of the alcohols. The permeability decreases from methanol to propanol. The separation factor for water/alcohols increases as the size of alcohol molecules increases.

The coating with CMS layers leads to high performance membranes for separation of molecules with size near to 0.47 nm. Beside pervaporation, the membranes are interesting for application such as direct methanol fuel cell, for which low alcohol cross-over is important requirement.

Acknowledgment

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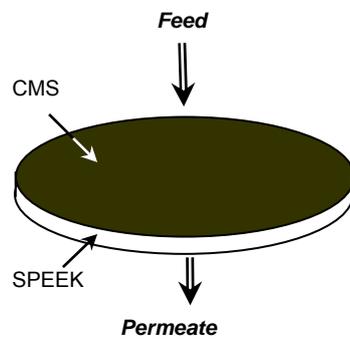
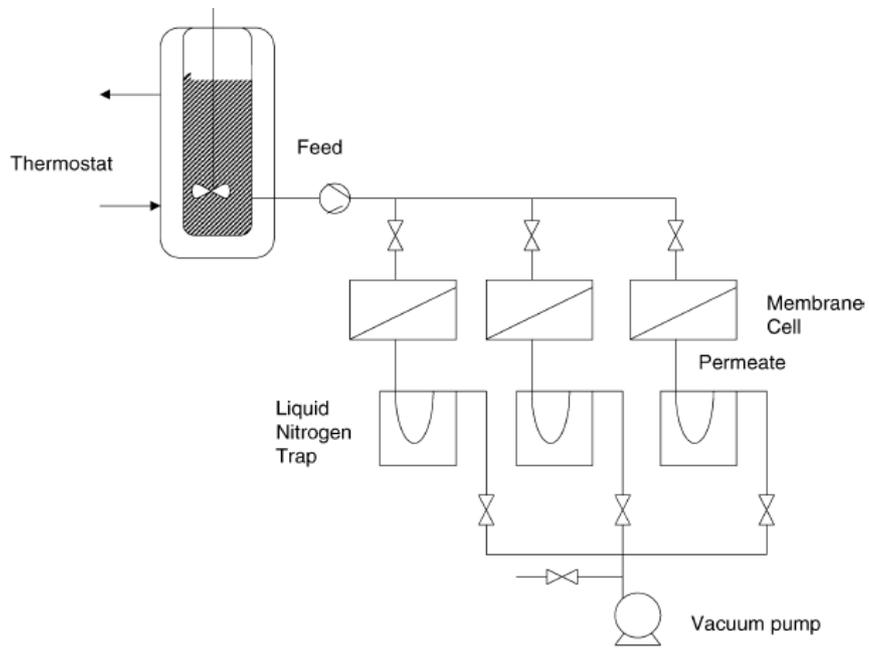


Fig 1

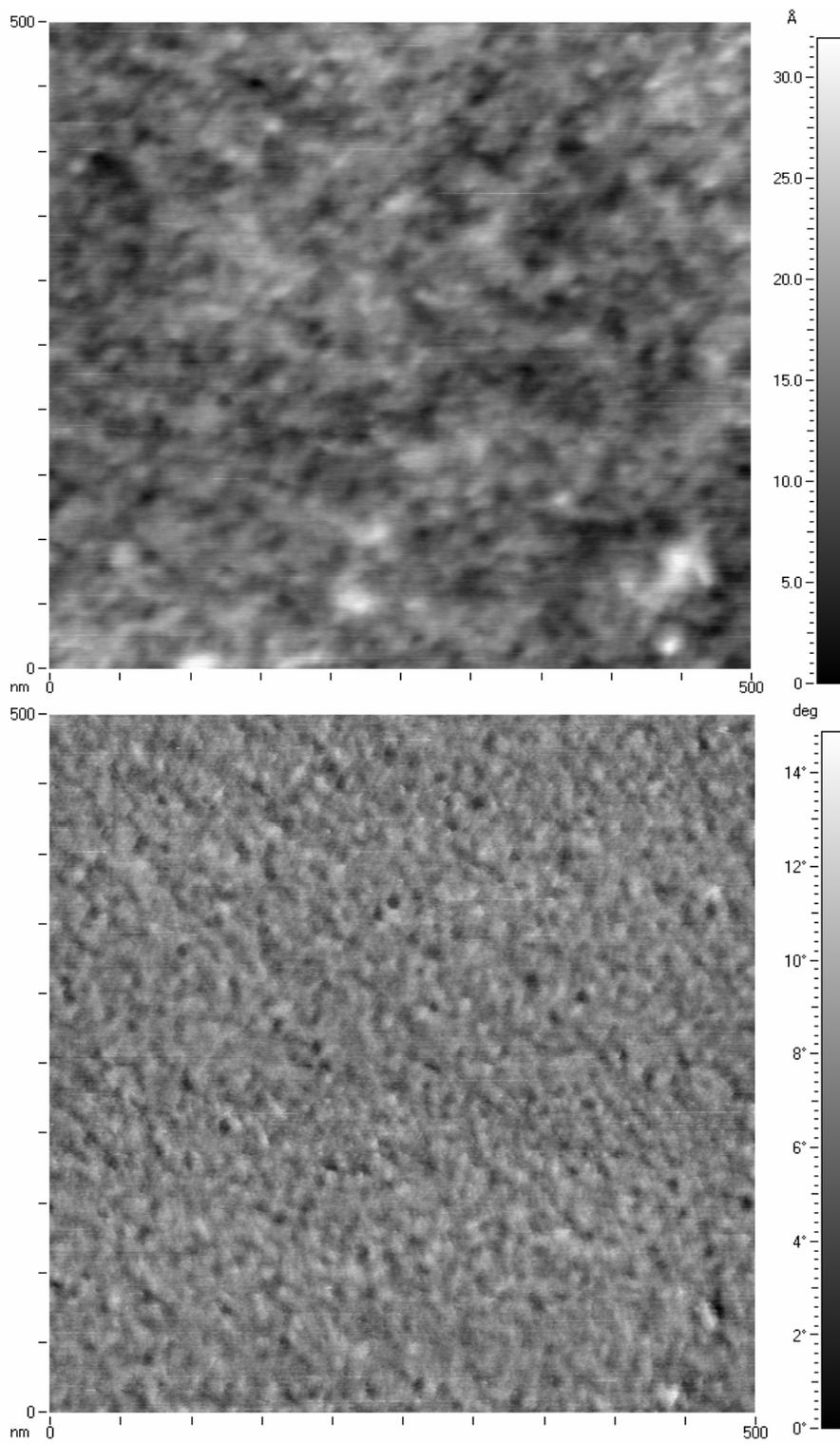


Fig 2

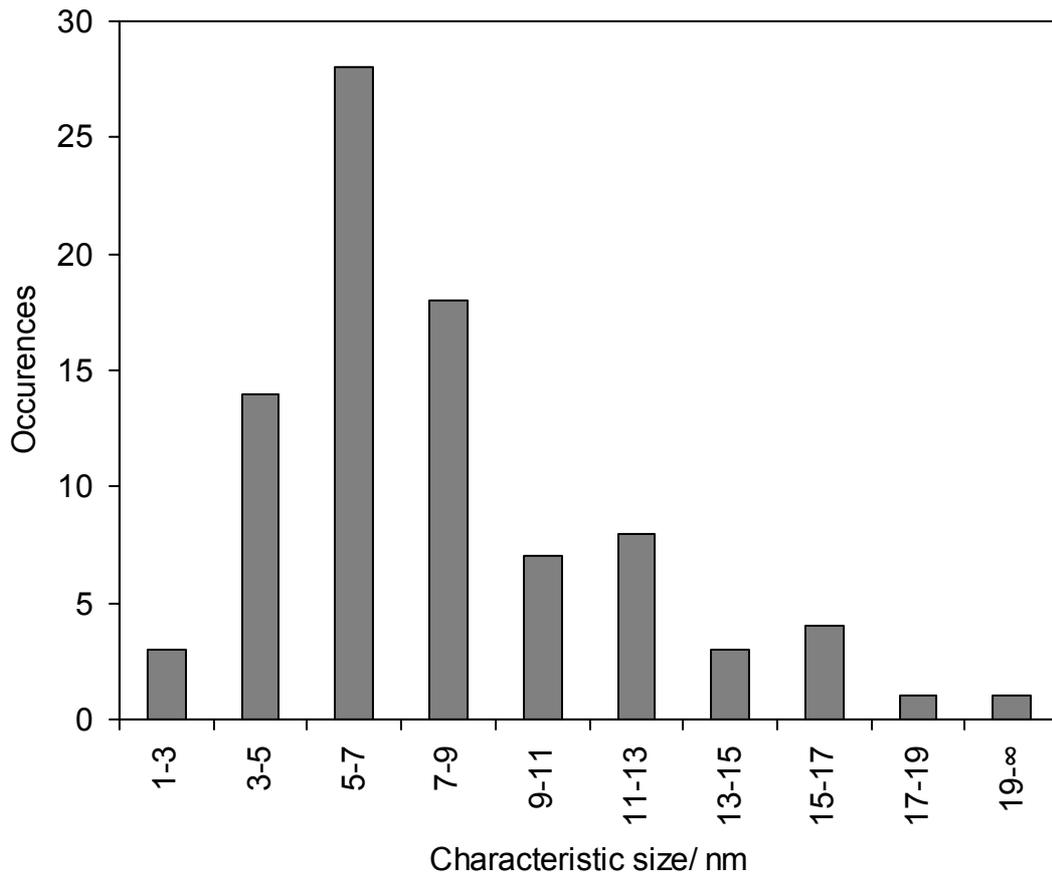


Fig 3

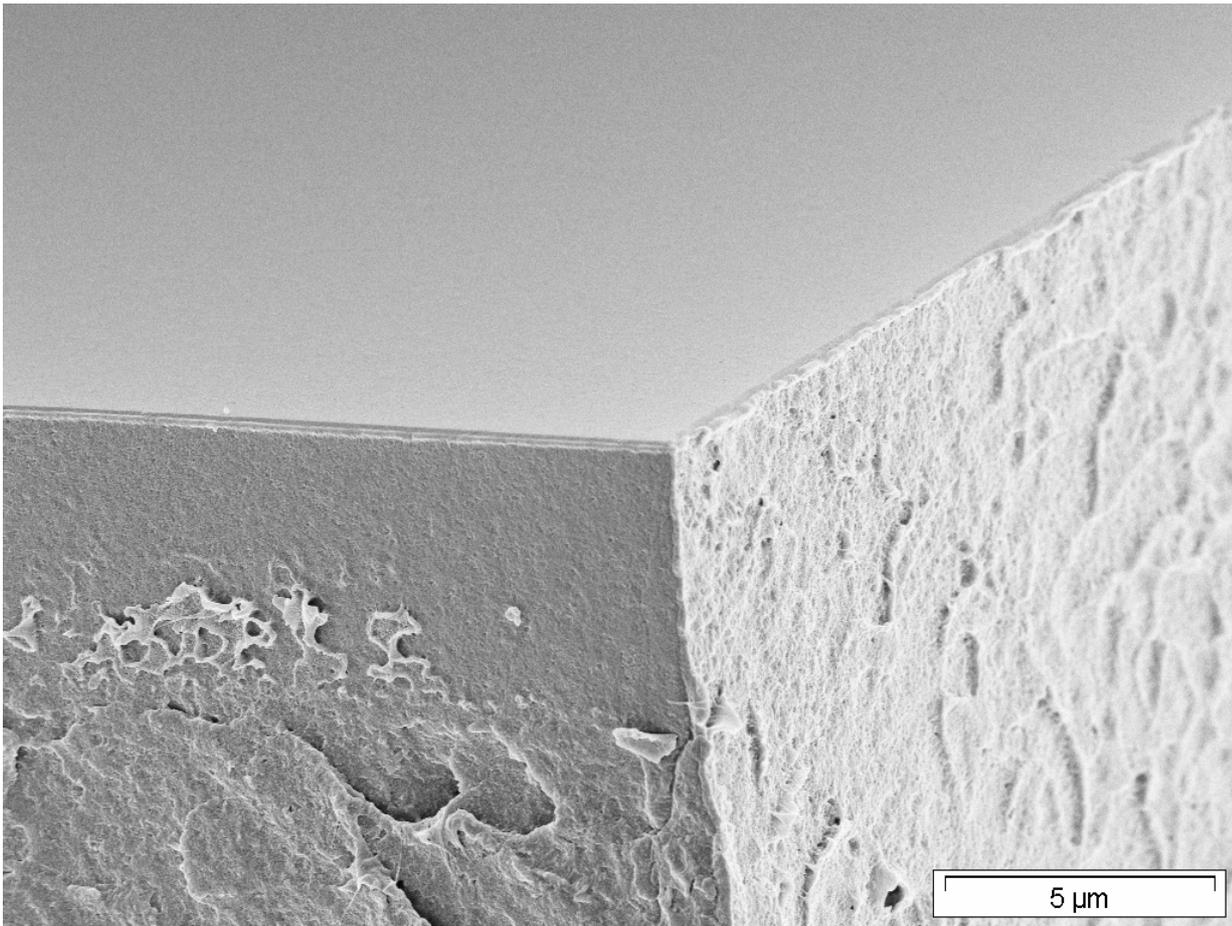


Fig 4

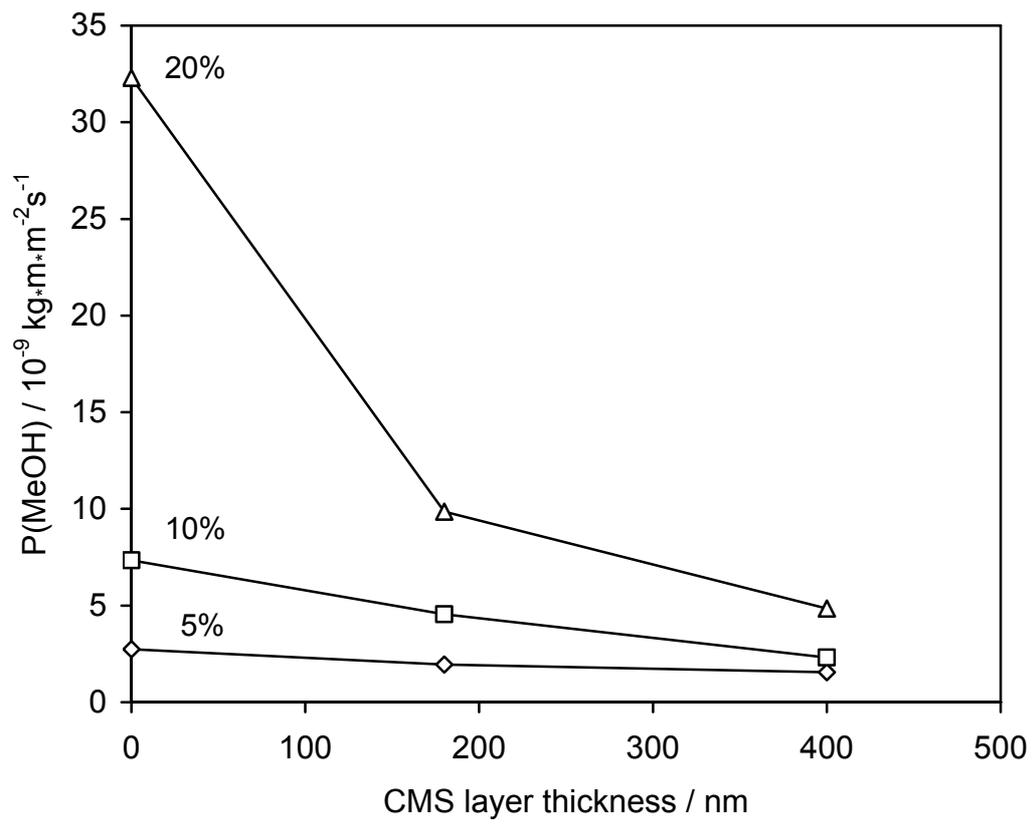


Fig 5

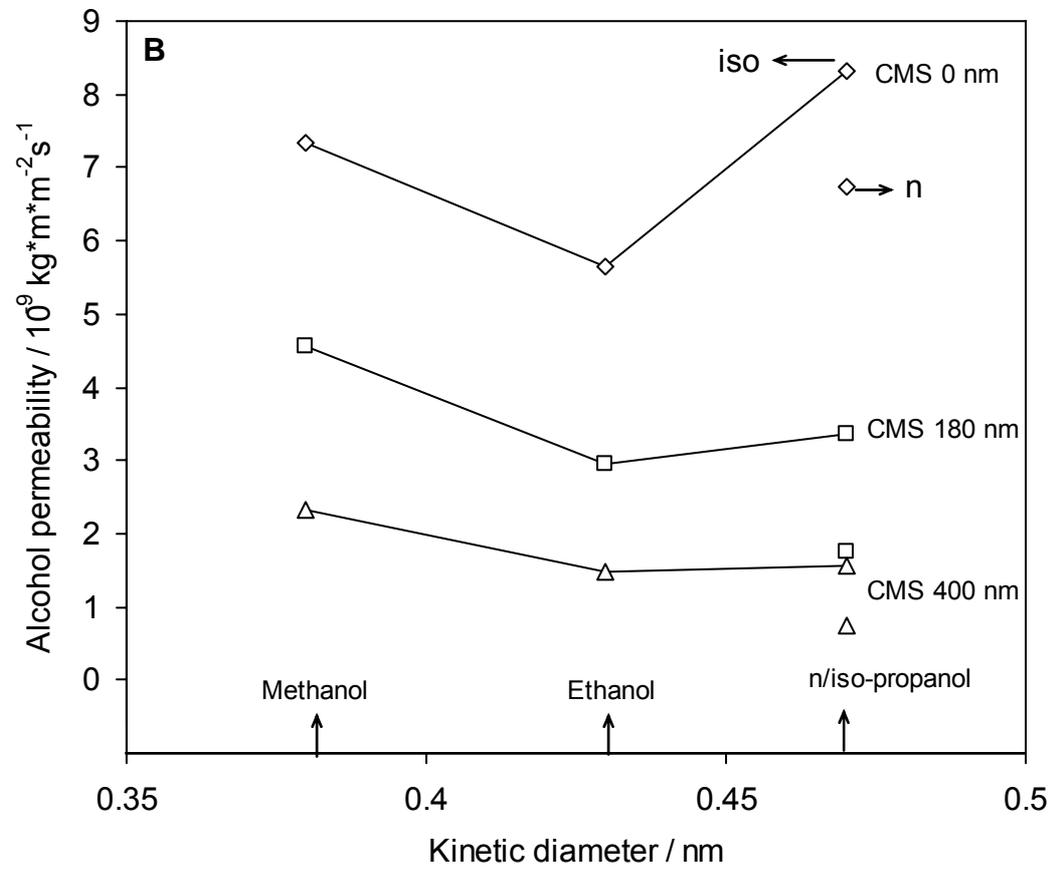
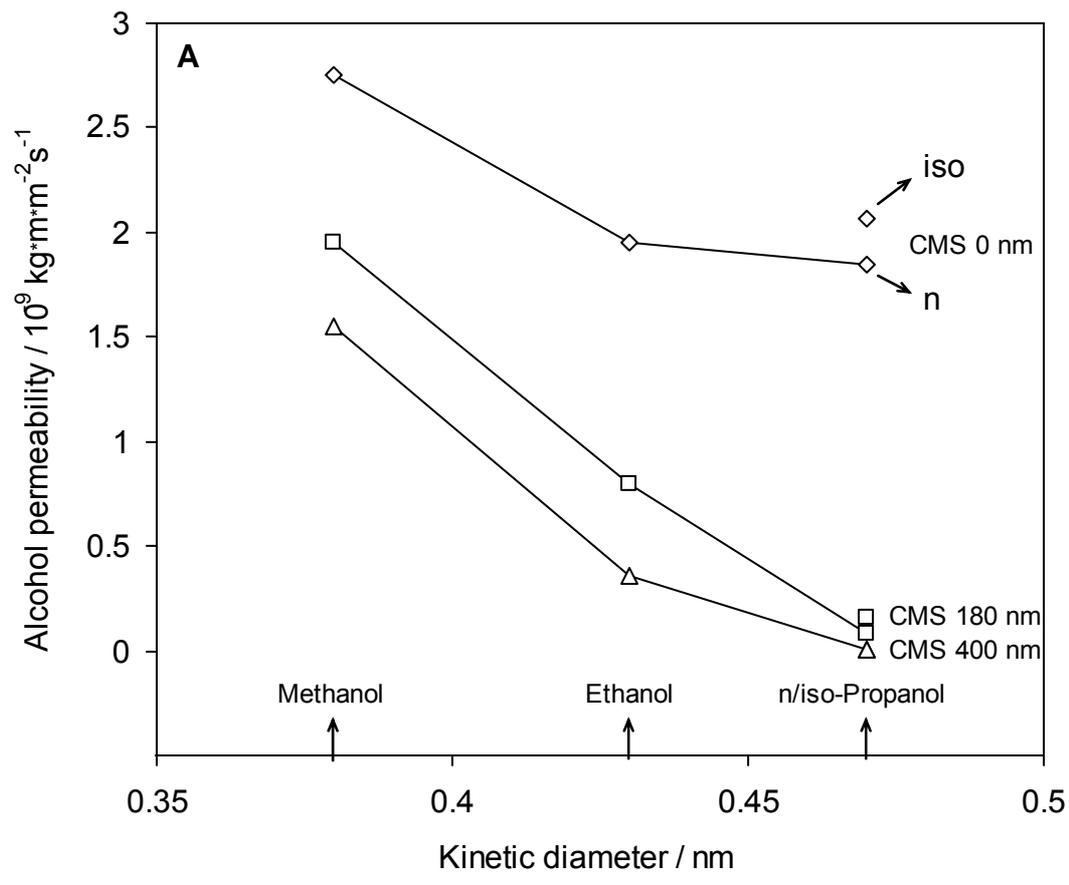


Fig 6

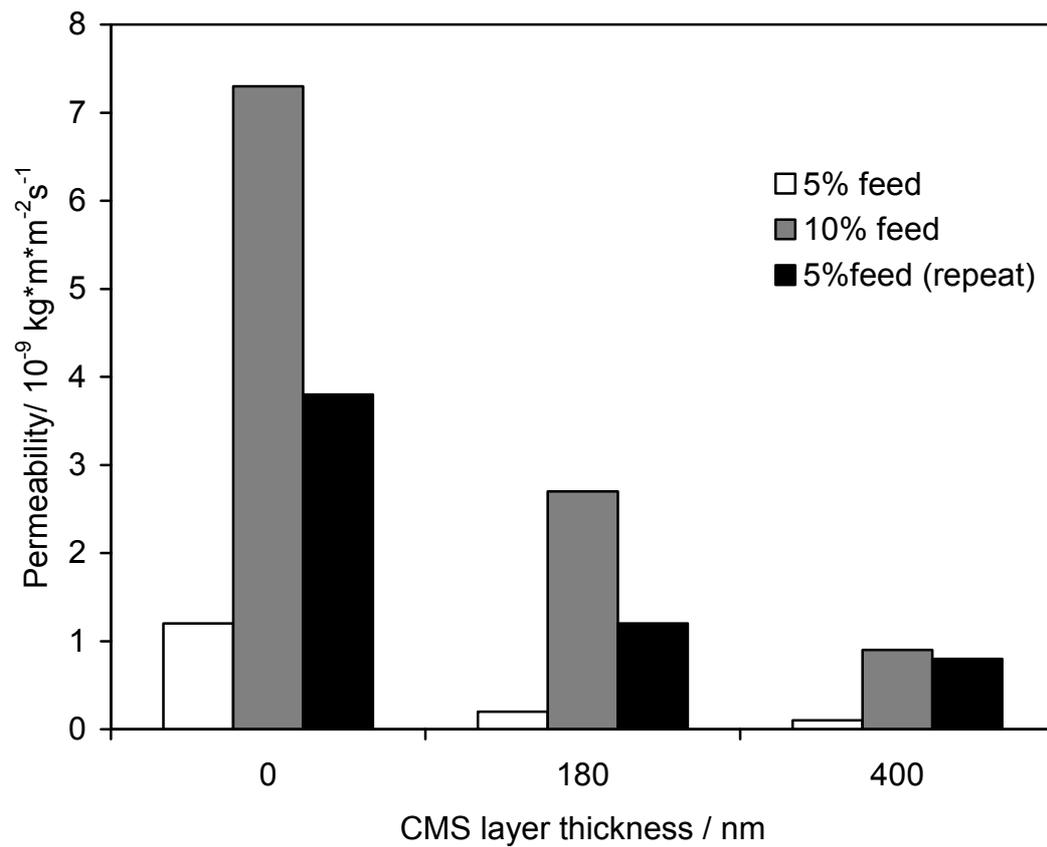


Fig 7

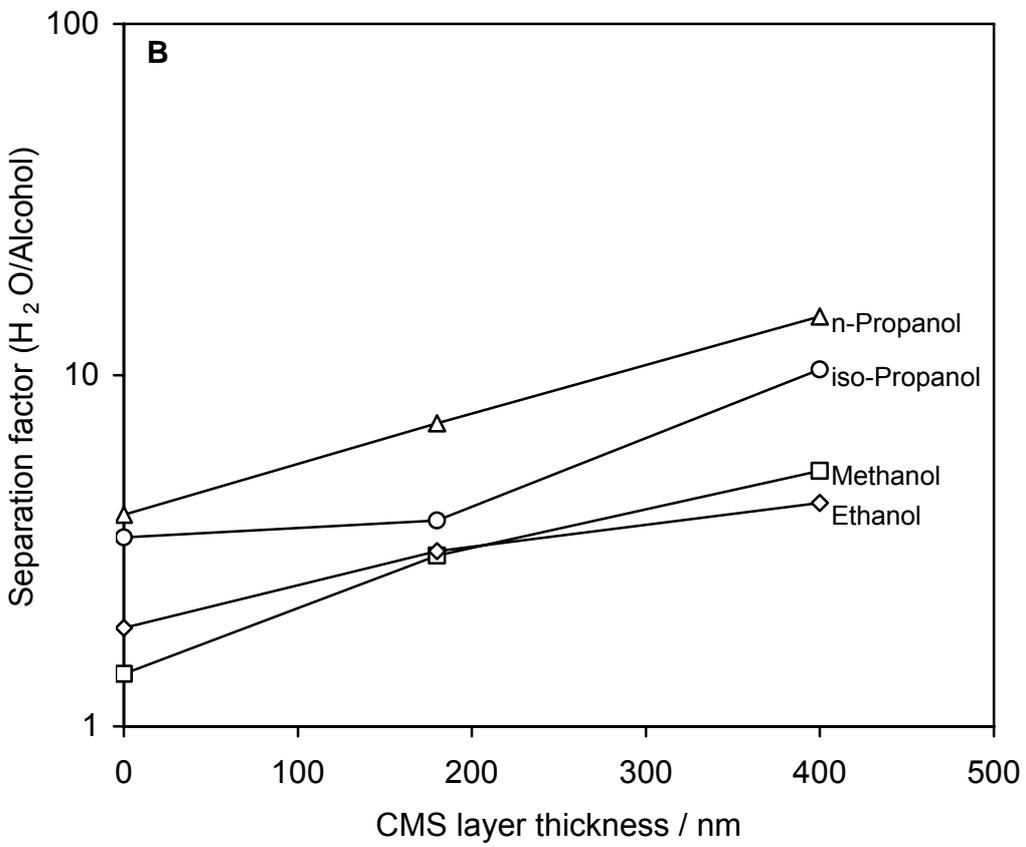
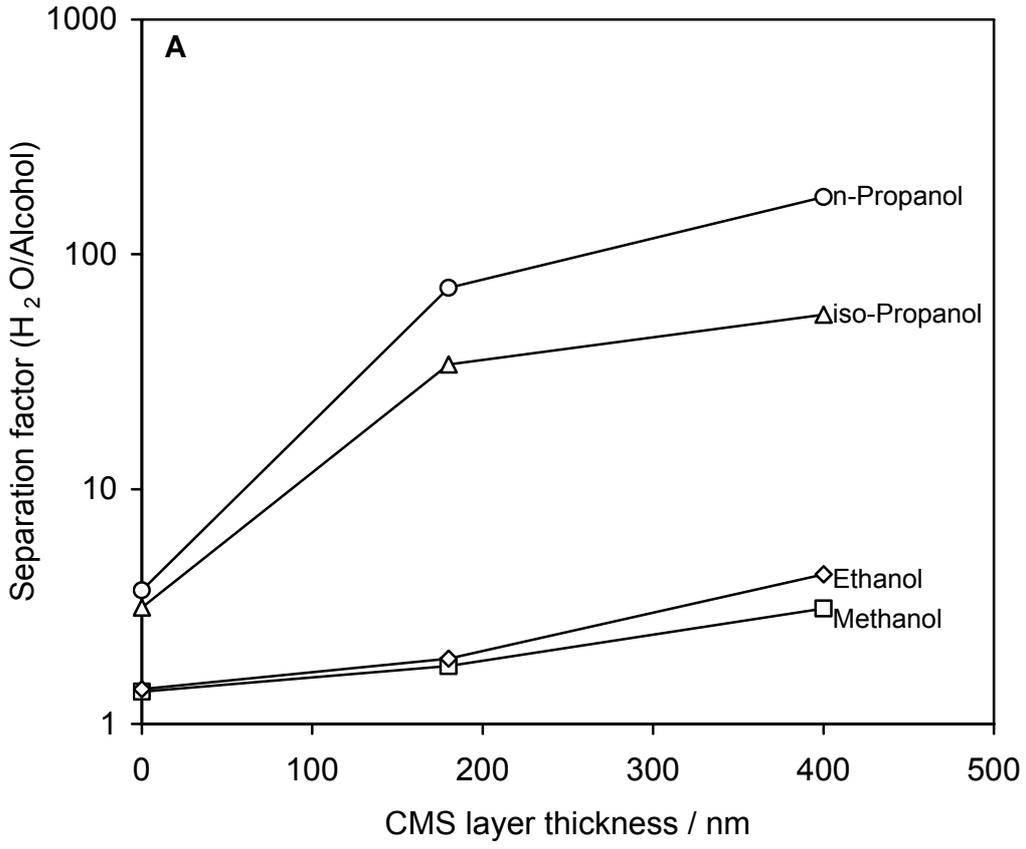


Fig 8

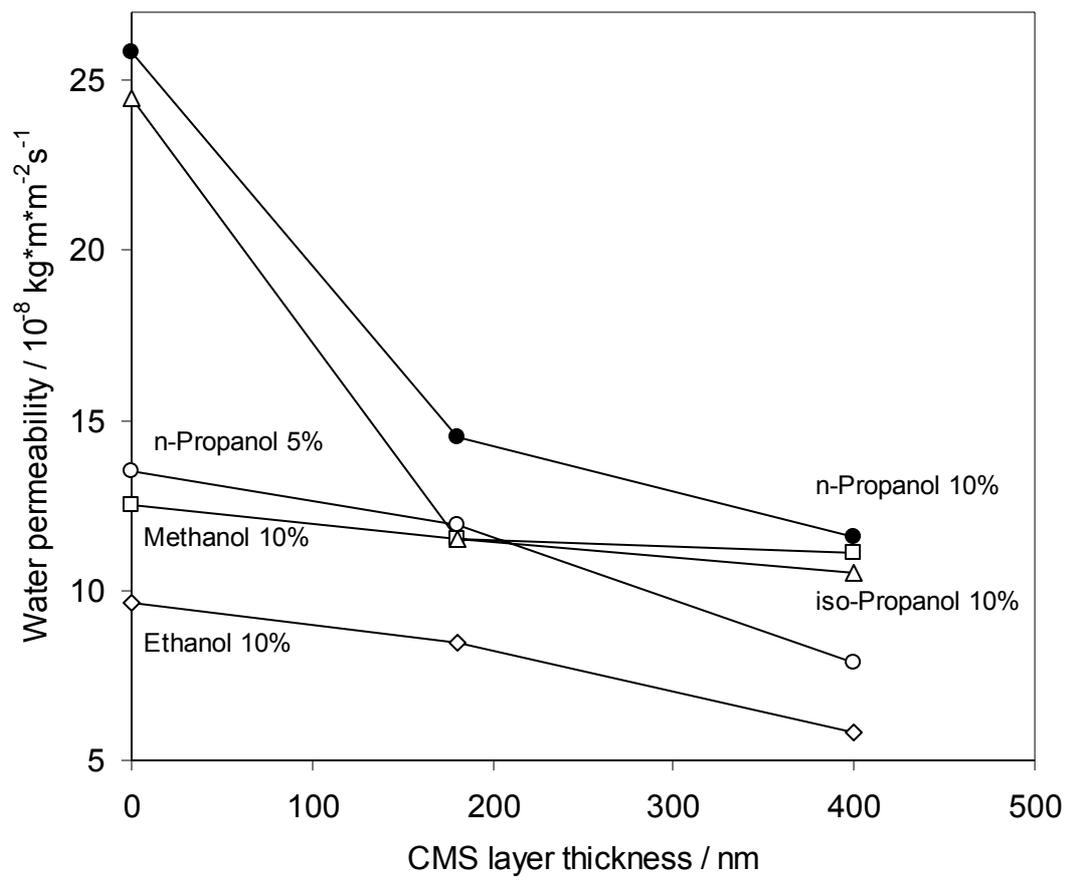


Fig 9