Nafion/PEG hybrid membrane for CO_2 separation: Effect of PEG on membrane micro-structure and performance

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ABSTRACT

In the present work, PEGDME with different molecular weight ($Mn \sim 250$ and $500 \, g/mol$) was added into Nafion-based membranes as CO_2-philic additive, aiming at improving their CO_2 capture performance. The physical, chemical and morphological characteristics of the hybrid membranes were thoroughly investigated using different techniques, including TGA, XRD, SEM and FTIR. The gas transport properties were studied by means of mixed gas permeation tests at different relative humidity conditions. CO_2 permeability is greatly enhanced upon the addition of the PEGDME. The addition of 40 wt% PEGDME 250 into the Nafion matrix shows a CO_2 permeability of 57.4 Barrer at the dry state, which is 36 folds higher than the pristine Nafion. The presence of water vapor in the gaseous streams further enhances the CO_2 permeability and CO_2/N_2 selectivity, reaching a value of 446 Barrer and 37, respectively, under fully saturated conditions. However, the further increase of the PEGDME content in the Nafion matrix leads to undesirable micro phase separation (defects were observed from the morphological analysis), causing serious loss of the selectivity. Finally, in order to improve the theoretical understanding of the transport mechanism, a modified Maxwell model was successfully applied to describe the separation performances of the resulted Nafion/PEGDME hybrid membrane. The model results suggest that an interconnected CO_2-philic structure is obtained upon the addition of PEGMDE and water to the ionomer matrix, forming preferential pathways for gas permeation able to enhance the membrane performance.

1. Introduction

Gas separation membranes have been applied in different industrial separation processes for many decades, such as H_2 purification, N_2 production, natural gas purification and vapor recovery [1]. In the recent decade, membranes have also been widely studied for CO_2 capture from flue gas [2,3]. Compared to conventional amine scrubbing process, membrane processes have many advantages such as process simplicity, low energy consumption, no moving parts, easy operation/retrofitting, linear scaled-up and small footprint [4]. However, membranes must have both high permeability and high selectivity to make the membrane separation competitive to the current amine absorption process [5].

The application of polymer-based hybrid materials is a promising approach in developing new membranes with high separation performance, as hybrid membranes can combine the superior separation properties of selected additives and the good processability of polymers. Recent studies have demonstrated remarkable separation properties of various types of hybrid membranes, exhibiting performance well beyond the intrinsic properties of the polymer matrix [6,7] and the additive materials. Numerous materials have been used as additives in the hybrid membranes, such as inorganic porous nanoparticles [7], carbon nanotubes [8], metal organic frameworks [9], and different liquid additives [10–13]. Among the liquid additives, the most commonly studied are ionic liquids (ILs) [14,15] and poly(ethylene glycol) (PEG) [16–18]. ILs have been employed as CO_2-philic additives in different membranes, including supported ionic liquid membranes (SILMs), poly(ionic liquid)–ionic liquid (PIL–IL) composite membranes, polymer-

ionic liquid composite membranes and ion-gel membranes [19,20]. However, ILs can suffer from drawbacks such as toxicity, complicated preparation and high price.

PEG is a physical solvent with many features of ILs, such as low vapor pressure and high CO_2 sorption capacity. PEG has been successfully used at industrial scale for acid gas removal (e.g., Selexol™) for many years, since the inherent affinity between ethylene oxide (EO) units and CO_2 molecules results in high CO_2 solubility [18]. Moreover, compared to ILs, PEG is a much cheaper absorbent with lower toxicity, better biocompatibility and more economical. When applied in membranes, PEG can act as artificial plasticizers and free volume regulators, which are beneficial to both the solubility and diffusivity of CO_2 in the hybrid membranes [18]. Therefore, liquid PEG has been widely used to fabricate hybrid membranes with different polymeric materials, including PEG based block copolymers (e.g., Pebax and Polyactive) [21], cross-linked PEG membranes [22], cellulose nitrate [23] and cellulose acetate [24], polyvinylchloride (PVC) [25] and polyimides [26]. Among these mentioned polymeric matrix, PEG based block copolymers are the most intensively investigated polymer matrix. Since Patel et al.'s pioneer study on Pebax/PEG hybrid membrane [27] and Car et al.'s consequent further investigation [21,28], PEG with different molecular weight and various end groups have been systematically studied. The end groups in PEG are found strongly affect the ultimate transport properties of the membrane. PEG with hydroxyl ending groups can form hydrogen bonds in the polymer matrix while the bulkier terminal groups create a more open structure and therefore easier pathways for gas molecules [10]. CO_2 exhibits high diffusivity and high solubility in the PEG dimethyl ether (PEGDME), thus the addition of PEGDME in membranes results in the highest CO_2 permeability and CO_2/H_2 selectivity among membranes of the PEG additives with various end groups. The increase of PEGDME molecular weight from 250 to 500 g/mol results in a slight increment in CO_2 permeability as well [10]. PEGDME has also been used in cross-linked PEG membranes as additives. Shao et al. [18] employed a thermally induced cross-linked PEG matrix to absorb free PEGDME. The resulted hybrid membrane exhibited around 4-time higher CO_2 permeability compared to the pristine membrane. The CO_2/H_2 selectivity increased with the free PEGDME content increasing, while the CO_2/N_2 selectivity only had a slight reduction [17]. In our previous report, by adding free PEGDME into a membrane of cross-linked PEG matrix, the CO_2 permeability increased over 50 times [29], and both CO_2/N_2 and CO_2/CH_4 selectivity significantly improved as well. In a more recent report from Shao et al. [18], PEGDME was added into a UV cross-linked PEG matrix, where the addition of PEGDME significantly reduced the density of the resulted membranes and increased the free volume, thus greatly improved the CO_2 permeability. A CO_2 permeability of up to 2980 Barrer was obtained at optimized condition, which is around 6 times of the pristine PEG membrane permeability value.

Nafion is a perfluoro-sulfonated ionomer (PSFI) developed in the late 1960s by Dupont. It has been intensively studied as membrane materials used in fuel cell applications [30]. Gas transport properties of Nafion has also been studied, but mainly focused on the fuel cell related gases such as O_2 and H_2. Starting from the 1980s, some work on Nafion membranes for CO_2 gas separation has been reported. However, the unacceptably low CO_2 permeability (~ 2 Barrer) and CO_2/N_2 selectivity (8 ~ 10) at the dry state have hindered its further application [31]. In Nafion membranes, it is widely accepted that the hydrophilic sulfonic acid ($-SO_3H$) moieties can aggregate and form ionic clusters with the size from *ca.* 1.5 to 5.0 nm. Absorbing water

into the Nafion matrix will gradually swell these nanoclusters. Similar to other hydrophilic polymers [32], the gas permeability in hydrated Nafion increases to a significant extent: a CO_2 permeability of 260 Barrer was obtained at 100% relative humidity (RH), 2 orders of magnitude higher compared to that in the dry state [33,34]. Giacinti Baschetti et al. have also tested the gas permeation properties of Nafion membrane at different RH values [35]. As the RH value increases from 50 to 75%, the CO_2 permeability values increase from 90 to up to 160 Barrer at 25 °C.

This behavior has been related to the formation of water-like channels in the hydrate matrix [36–41], where the gaseous penetrants can permeate to a faster rate due to the increase of the diffusion coefficient. A number of model has been presented to describe and predict the mass transport of gases in hydrated PSFI [42–44]. Recently, Olivieri et al. [45] showed that Maxwell-Wagner-Sillar [46], a simple extension of Maxwell model for composite materials, is able to describe consistently the gas permeation in hydrated Aquivion, on the basis of a single parameter describing the shape of water inclusion in the matrix. The interest of PSFI membrane in gas separation application is obviously high due to their high chemical resistance, which make them suitable for a range of different applications. However, to achieve a higher competitiveness in the CO_2 capture market, both CO_2 permeability and selectivity must be improved, possibly reducing the influence of water vapor on the achievement of suitable separation performance. Indeed, the need of large amount of water vapor could be a limitation in retrofitting gas separation units in existing processes where a steam cycle is not present.

In the present study, PEGDME of two different molecular weight (i.e. 250 and 500) are selected to prepare hybrid membranes with Nafion for CO_2 separation, as combining CO_2-philic PEGDME with Nafion matrix should further promote the CO_2 transport toward a higher value and reduce its dependence on RH. To the best of our knowledge, PEGDME has never been used to fabricate hybrid membranes with Nafion for gas separation applications. In this membrane, the linear PEG chains are expected to act as CO_2-philic moiety, artificial plasticizers and free volume regulator, which should be able to increase both the solubility and diffusivity of CO_2 in the Nafion/PEG hybrid membranes. Membranes containing different amounts of PEGDME 250 (up to 60 wt%) and PEGDME 500 (up to 40 wt%) were prepared and characterized in terms of physiochemical and transport properties. Mixed-gas permeability tests of CO_2/N_2 in Nafion/PEGDME membranes at 35 °C and various RH conditions were performed, and the effects of different types/amounts of PEG as well as the role of water vapor on the morphology and permeation properties of these hybrid membranes were discussed. Finally, the experimental data were interpreted by using a modified Maxwell model, pursuing the achievement of a more fundamental understanding on the effect of PEGMDE addition on the polymer structure and on the permeation mechanisms.

2. Experimental

2.1. Materials

Alcohol-based Nafion solutions (5 wt%, D520, total acid capacity of 1.03–1.12 meq/g, equivalent weight = 1100 g_{pol}/mol_{SO3}) were obtained from Ion Power (Munich, Germany), whereas PEGDME, *M*n 250 and *M*n 500 were purchased from Sigma-Aldrich (Buchs, Switzerland) and used without further purification (Nafion and PEGDME are shown in Fig. 1). The gases examined in the gas permeation tests included a CO_2/N_2 mixture and CH_4 were purchased from AGA (Oslo, Norway) and used as-received. The purity of the CH_4 was 99.999%.
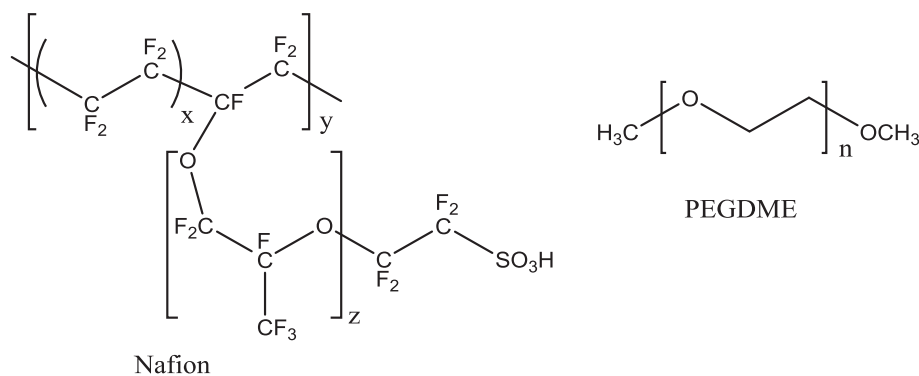
Fig. 1. Chemical structure of Nafion and PEGDME.

2.2. Membrane preparation

A calculated amount of PEGDME was added into the Nafion solution and stirred for at least 30 min. Afterwards, the Nafion/PEGDME solution was poured into a glass Petri dish, and a second glass Petri dish was covered on the Nafion/PEGDME solution to reduce the solvent evaporation. The Petri dish with Nafion solution was then put on a IKA® C-MAG HS digital IKAMAG™ hot plate magnetic stirrer and heated to 80 °C for 100–120 min to generate uniform and un-cracked membranes [47]. The liquid content (ω_{PEG}, wt%) in each hybrid membrane was calculated from Eq. (1):

$$\omega_{PEG} = \frac{w_{PEG}}{w_{PEG} + w_{Nafion}} \times 100 \tag{1}$$

where w_L and are the weights of PEGDME and Nafion, respectively.

Membrane thicknesses were measured with a Digimatic ID-H thickness gauge (Mituyoto, Aurora, IL). The final data were the average of at least 10 measurements. The membranes were dried in vacuum oven at 40 °C for at least 6 h before any test.

2.3. Membrane characterization

A thermo-microbalance from Netzsch (TG 209F1 Libra) was employed to investigate the thermal stability of the Nafion/PEGDME hybrid membranes. Samples were heated from ambient temperature to 700 °C at a heating rate of 10 °C/min under N_2 protection.

X-ray diffraction measurements were conducted on a Bruker D8 A25 DaVinci X-ray Diffractometer with Cu Kα radiation of characteristic wavelength λ = 1.54 Å. The scans were taken in the 2θ range with a step size 0.045° from 5° to 75°.

A scanning electron microscope (SEM, TM3030 tabletop microscope, Hitachi High Technologies America, Inc.) was used to study the membrane morphology. The cross-section specimens were prepared by breaking the samples in liquid N_2. All samples were sputter coated for 2 min with a gold nanoparticle layer to ensure good electrical conductivity.

The pure and hybrid membranes were characterized for intermolecular interactions and presence of PEGDME within the polymer matrix using FT-IR spectra. A Nicolet iS-50 FTIR spectrometer equipped with a Specac ATR unit (Golden Gate high performance single reflection monolithic diamond ATR) in the range of 650–4000 cm^{-1} under ambient conditions was used.

The mixed-gas permeation test were performed at 35 °C using a custom-designed mixed-gas permeation system as described elsewhere [48]. In the current study, the active membrane permeating area was fixed to 19.6 cm^2. A gas mixture contained 10 vol% CO_2, 90 vol% N_2 was used as the feed gas, whereas pure CH_4 was used as sweep gas. The pressure of the feed gas was kept constant at 2.0 bar while the sweep side pressure was set as 1.05 bar. The permeation test was carried out until a steady state was reached. CH_4 was used as sweep gas instead of

an inert gas (e.g., Helium) since Helium was used as the carrier gas in the gas chromatograph (GC).

The permeability coefficient (P_i) of the ith penetrant species can be calculated based on Eq. (2):

$$P_i = \frac{N_{perm}(1 - y_{H_2O}) y_i l}{A(\langle p_{i,feed}, p_{i,ret} \rangle - p_{i,perm})} \tag{2}$$

where N_{perm} is the total permeate flow, y_{H_2O} is the molar fraction of water in the permeate flow (calculated according to the RH value and the vapor pressure at the given temperature), y_i is the molar fraction of the species of interest in the dry permeate, and $p_{i,feed}$, $p_{i,ret}$ and $p_{i,perm}$ identify the partial pressures of the ith species in the feed, retentate and permeate, respectively. A and l represents the active membrane area and membrane thickness, respectively. The mixed gas CO_2/N_2 separation factor can be obtained from Eq. (3):

$$\alpha_{i/j} = \frac{y_i/x_i}{y_j/x_j} \tag{3}$$

3. Model development

In the attempt of better elucidating the influence of PEGMDE addition to Nafion on the gas permeability under different humidity conditions, the Maxwell-Wagner-Sillar model has been used to describe permeation behavior of the different materials investigated in present work.

The model is a modification of the well-known Maxwell model, frequently used to describe permeation behavior of composite materials where both the matrix (continuous phase) and the filler (dispersed phase) are endowed with a known permeability. In particular, the MWS model tries to improve Maxwell description by allowing the dispersed phase to have different shape, specifically oblate or prolate spheroids with different aspect ratio, by introducing the parameter n.

To be more precise the permeability of the composite materials can be described as Eq. (4):

$$P_i = P_i^C \left[\frac{nP_i^D + (1-n)P_i^C - (1-n)\phi_D(P_i^C - P_i^D)}{nP_i^D + (1-n)P_i^C + n\phi_D(P_i^C - P_i^D)} \right] \tag{4}$$

where and and are, $respectively$, $the permeability of the$ are, respectively, the permeability of the i-th gas in the continuous phase and in the dispersed phase; $is the dispersed phase volume fraction$, $and the parameter$ is the dispersed phase volume fraction, and the parameter n. As mentioned, n is a geometrical parameter which describes the shape of the dispersed domains, going from a in series ($n = 1$) to a in parallel phases configuration ($n = 0$), as shown in Scheme 1. This shape parameter can be can be calculated according to the Eq. (4), where a is the length along the major axis and b is the length along the minor axis of the prolate (major axis along the flow direction) spheroids Eq. (5) [49].
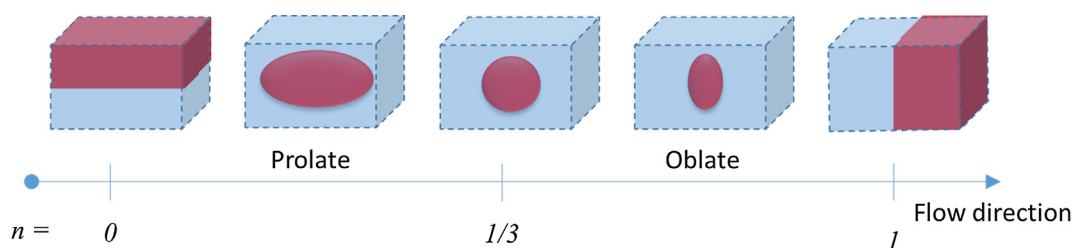
Scheme 1. Configuration of the dispersed phase as a function of the *n* parameter.

$$n = \frac{-1}{(a/b)^2 - 1} + \frac{a/b}{[(a/b)^2 - 1]^{1.5}} \ln\{(a/b) + [(a/b)^2 - 1]^{1/2}\} \quad (5)$$

The model has been chosen as it proved to correctly describe the permeability of different gases in PFSI materials under humid conditions. The model considers the membrane as formed by a continuous phase with the characteristics of the dry polymer and a dispersed hydrophilic phase behaving as a pure water. In this condition, when the water volume fraction is known from independent sorption experiments, the only adjustable parameter in the model is represented by *n*, which takes values ranging from 1/3 to almost 0 at increasing RH consistently with the formation of more interconnected water channels in the matrix [45].

4. Results and discussion

4.1. Thermal properties

Fig. 2 shows the TGA results of the PEGDME, Nafion and hybrid membranes prepared in the study. A small mass loss was observed for pure Nafion between 50 and 250 °C, indicating the evaporation of water, trapped in the membrane matrix even after drying under vacuum for more than 6 h. It is well accepted that it is difficult to fabricate anhydrous Nafion membrane without destroying the sample [30,50]. Besides the water removal, by coupling TGA an FT-IR spectrometer, Wilkie et al. [51] have also observed SO_2 and CO_2 as products of the first mass loss stage (in the temperature of 35–280 °C). The second stage weight loss is apparent from 290 to 420 °C and the third stage weight loss ranging from 400 to 530 °C. These two stage weight losses are attributed to de-sulfonation and side-chain and/or backbone decomposition, respectively. In the second stage, the SO_2, CO_2, SiF_4, CO, H_2O and substituted carbonyl fluorides are affected, while the last step of mass loss involves the formation of HF, SiF_4 and substituted carbonyl fluorides. The overall mechanism proposed in Ref. [51] shows the initial breakage of the C−S bond, forming a fluorocarbon radical and a •SOH_3 radical, which cleaves to produce SO_2 and an •OH radical. Compared to Nafion, the pure PEGDME curve is relatively simple: there is only one single stage weight loss, which is attributed to the thermal decomposition of PEGDME typically observed at 170 °C and 320 °C for PEGDME 250 and PEGDME 500, respectively. The degradation mechanism involves a radical decomposition [52]. The low molecular weight esters are the main product from PEG thermal degradation [52].

Concerning the Nafion/PEGDME hybrid membranes, three steps of mass loss could be observed. The first decomposition stage for the hybrid membrane prepared with PEGDME 250 is in the range 120–150 °C, which is related to the decomposition of PEGDME 250. Surprisingly, in the case of PEGDME 500, the hybrid membranes showed a significant weight loss at a relatively lower temperature (120–150 °C), even though both Nafion and PEGDME are reported to be relatively stable within this temperature range. A possible explanation could be the presence of the radicals produced in the first step of the Nafion decomposition (i.e., fluorocarbon, •SOH_3 and •OH) which can accelerate the PEG decomposition in the hybrid membranes, resulting in an overall lower thermal
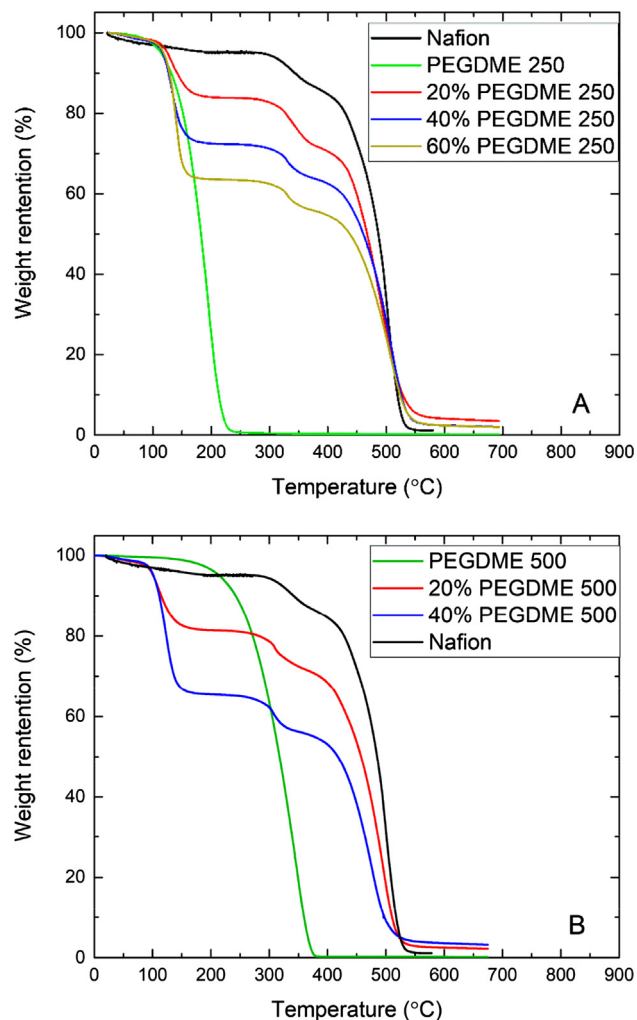

Fig. 2. TGA results from Nafion, PEGDME and Nafion/PEGDME hybrid membranes. (A) PEGDME 250, (B) PEGDME 500.

stability. Nevertheless, the hybrid membrane exhibits a thermal stability higher than 120 °C, making them suitable for post combustion CO_2 capture requirements.

4.2. FTIR analysis

The FTIR spectra of Nafion, PEGDME and Nafion/PEGDME hybrid membranes are displayed in Fig. 3. Table 1 also listed the FTIR peak assignments for Nafion, PEGDME and Nafion/PEGDME hybrid membranes in detail.

As can be clearly observed from Fig. 3, peak intensities change with the blend compositions in the hybrid membranes. For instance, peaks at position 982 cm^{-1}, 1056 cm^{-1}, 1144 cm^{-1} and 1200 cm^{-1} are typical
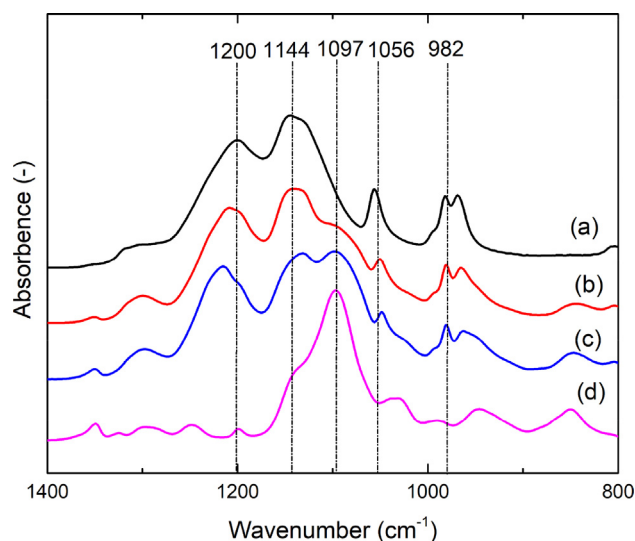
Fig. 3. FTIR spectra of Nafion, PEGDME and Nafion/PEGDME hybrid membranes. (a) Nafion, (b) 20%PEGDME 500, (c) 40%PEGDME 500 and (d) PEGDME 500.

Nafion peaks. The intensities of these peaks reduce as the PEGDME content increases in the membrane. On the other hand, the intensity of the peak at $1097\,cm^{-1}$, which represents the C–O stretching from the PEG molecule, increases as the PEGDME content increases in the hybrid membrane. Overall, no new spectral features can be identified upon the addition of PEGDME in the Nafion matrix, indicating that no chemical reactions occurred between Nafion and PEGDME at room temperature. PEGDME 250 and PEGDME 500 have similar FTIR spectrums thus only Nafion/PEGDME 500 results are presented in Fig. 3.

4.3. XRD analysis

Fig. 4 presents the XRD pattern of Nafion and Nafion/PEGDME hybrid membrane in the 2θ range of 5–75°. The XRD of Nafion showed three main peaks located at 6.3°, 17.1° and 39.5° (2θ), respectively, which are in good agreement with the literature values [57,58]. For both cases, adding PEGDME into Nafion did not shift the two characteristic peaks (corresponding to d-spacings of 5.0 and 2.2 Å) [59]. The sharp peak at 17.5° is related to the crystalline scattering of the

Table 1
FTIR peak assignments [53–56].

|	Wavenumber (cm^{-1})	Peak assignment
Nafion	969	C–O–C stretching
	982	symmetric S–O stretching
	1056	symmetric S–O stretching
	1144	symmetric C–F stretching
	1200	asymmetric C–F stretching
	1716	bending vibrations of H_2O and H_3O+
	3430	stretching vibrations of H_2O and H_3O^+
PEGDME	850	CH_2 rock, C–O stretching
	946	CH_2 rock, C–C stretching
	1031	O–CH_3 stretching
	1038	O–CH_3 stretching
	1097	C–O stretching
	1199	CH_3 rocking
	1248	CH_2 twisting
	1297	CH_2 twisting
	1325	CH_2 waging
	1349	CH_2 waging
	1418	CH_2 waging
	1454	CH_2 scissor, CH_3 deformation
	2744	Combination vibration
	2866	Combination vibration
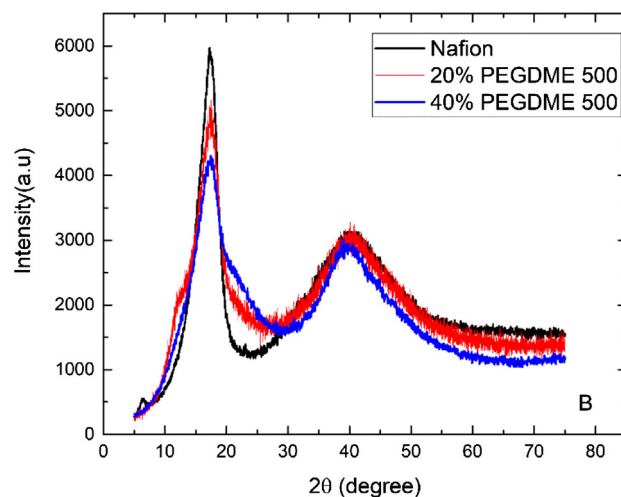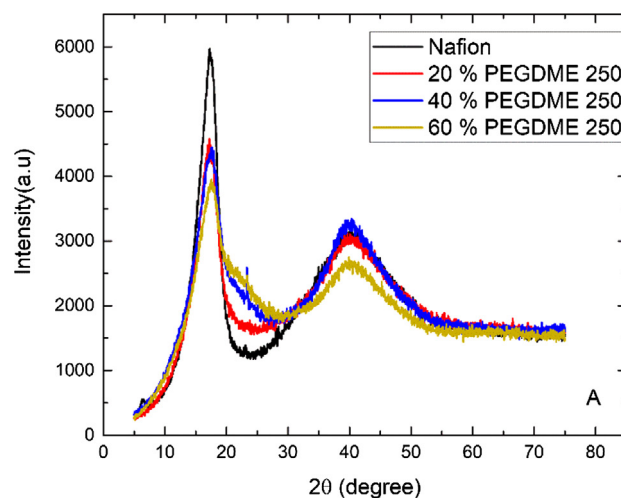
Fig. 4. X-ray diffraction pattern of the Nafion/PEGDME membranes with different PEGDME content, (A) PEGDME 250, (B) PEGDME 500.

fluorocarbon backbone in the Nafion structure, which overlaps the X-ray scattering from the amorphous region of the membrane at lower Bragg angles ($2\theta = 16°$) [60]. The addition of PEGDME to the Nafion matrix enlarged the width of this peak and reduced its intensity, indicating that the crystallinity is slightly reduced. Furthermore, the presence of the PEGDME led to a reduction of order in the ionic clusters resulting in the disappearance of the broad peak located at 6.3° which is attributed to the ionic domains [58]. Finally, the peak at 39.5° is reported as one of the characteristic amorphous peaks for Nafion [58]. It is worth to mention that similar to water, adding PEGDME into the Nafion matrix may also lead to an increase in the X-ray absorption in the sample and a consequent loss in peak intensity [58]. Similar trend can be observed from Nafion/PEGDME 500 hybrid membranes as shown in Fig. 4B.

4.4. Membrane morphology study

The morphology of pristine Nafion membrane and Nafion/PEGDME hybrid membranes were investigated by SEM analysis and the corresponding images are shown in Fig. 5.

Based on Fig. 5, it can be seen that the pristine Nafion membrane owns a neat and smooth surface (Fig. 5A). The addition of 20 wt% of low molecular weight PEGDME (250) did not affect the membrane morphology in a notable manner (Fig. 5D). However, for the hybrid membrane containing 20 wt% PEGDME 500, a significant increase of the roughness could be observed from the surface image (Fig. 5B).
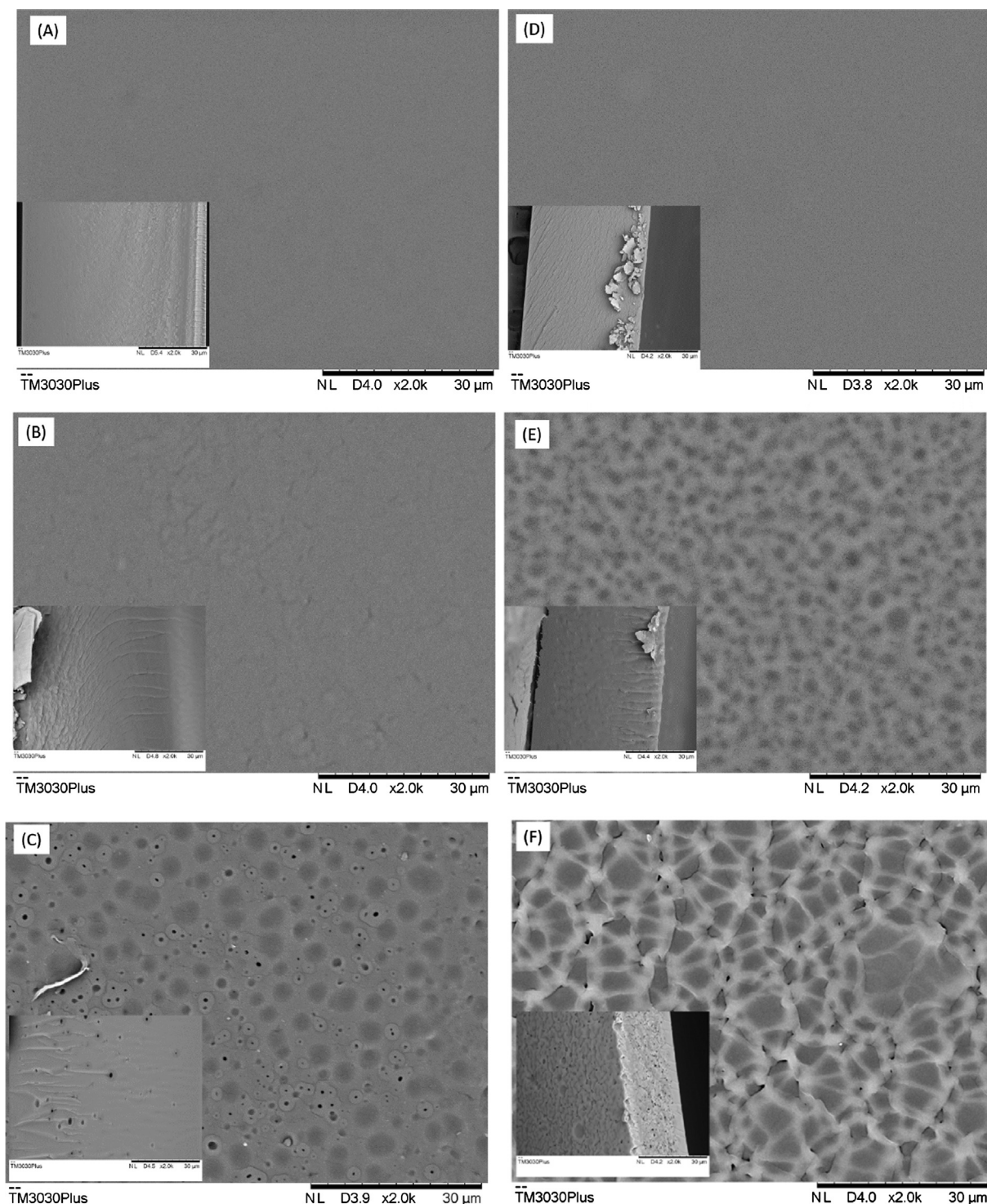
Fig. 5. Cross section (insets) and surface morphology of the Nafion/PEGDME hybrid membranes. (A) Pure Nafion, (B) 20% PEGDME 500, (C) 40% PEGDME 500, (D) 20% PEGDME 250, (E) 40% PEGDME 250, (F) 60% PEGDME 250.

Further increase of the PEGDME content to 40 wt% led clearly to microphase separation in the membrane matrix (Fig. 5C and E), with the formation of spherical domains up to 6 μm (PEGDME 250) or 10 μm (PEGDME 500) in size. Surprisingly, small pores (diameter ~ 2 μm) can be found in the membrane containing 40 wt% PEGDME 500 (Fig. 5C). Pores with similar size are visible also in the membrane cross section, indicating that these pores are formed not only on the membrane surface, but in the entire membrane structure. Possibly, the longer hydrophilic PEG chain is easier to induce phase separation with the

hydrophobic polytetrafluoroethylene ($-CF_2-CF_2-$) backbone from Nafion. Due to the porous structure of the 40 wt% PEGDME 500 hybrid membranes, the PEGDME content is not further increased. Since no pore formation was observed in the case of 40 wt% PEGDME, the content of the liquid phase was increased to 60 wt% and the morphology is shown in Fig. 5F. Clearly, by increasing the PEGDME content, the phase separation became more severe, leasing to the formation of larger domains and of elongated pores, visible on both the membrane surface and cross-section. According to the SEM results, the molecular
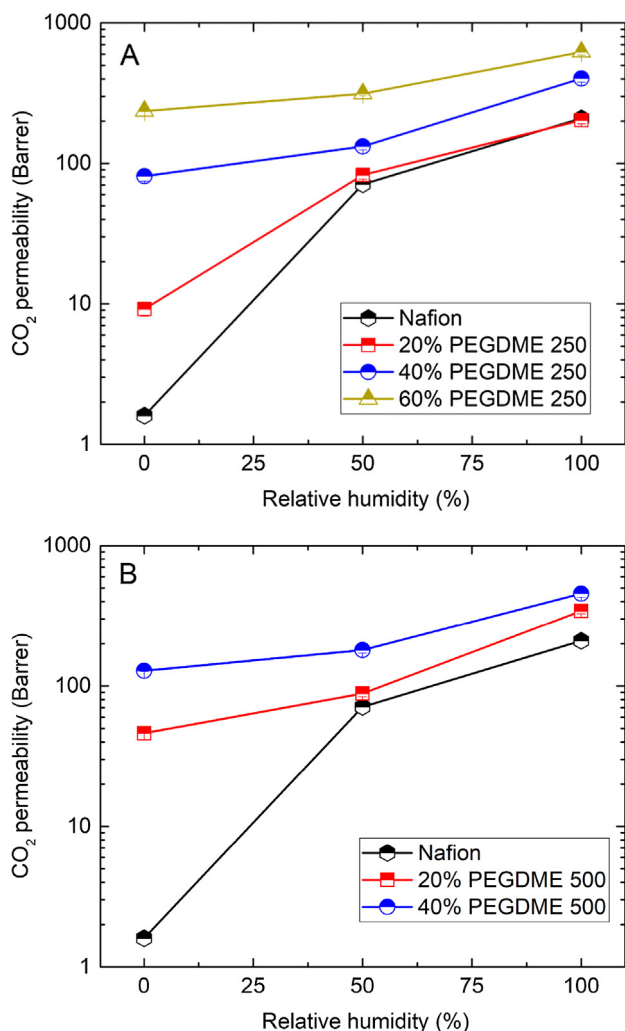
Fig. 6. CO$_2$ permeability of Nafion/PEGDME membranes varying in composition as function of RH at 35 °C and 2.0 bar, (A) PEGDME 250, (B) PEGDME 500.

Table 2
Enhancement factor of water vapor at different PEGDME 250 content.

RH (%)	Enhancement factor (P_{humid}/P_{dry})			
	Nafion	20% PEGDME 250	40% PEGDME 250	60% PEGDME 250
0	1	1	1	1
50	44.4	9.7	2.3	1.3
100	130.8	22.9	7.8	3.0

weight of PEGDME has large impact on the final hybrid membrane morphology. Apparently, a higher molecular weight PEGDME is more apt to induce phase separation in Nafion membranes.

4.5. Mixed-gas permeation studies

The permeation properties of Nafion/PEGDME hybrid membranes have been studied using a CO$_2$/N$_2$ mixture as feed at various RH levels, investigating the effect of the water vapor on the mass transport. The gas permeation results are presented in Fig. 6. As shown in Fig. 6A, dry Nafion is quite impermeable and owns a CO$_2$ permeability of 1.6 Barrer, which is in the same range with the literature value (2.4 Barrer) [31]. Adding PEGDME 250 into Nafion greatly improved the CO$_2$ permeability at dry state: as the PEGDME 250 content increases from 20 to 60 wt%, the CO$_2$ permeability increased from 9.2 Barrer to 235.9 Barrer, with an overall enhancement of more than 140 times compared to pristine Nafion. It is well accepted that the ionic clusters formed by sulfonic acid moieties behave as impermeable obstacles for gas diffusion at dry state. Possibly, the PEGDME chains surrounds the hydrophilic −SO$_3$H moieties, reducing the electrostatic interactions within the ionic domains and leading to a much higher CO$_2$ permeability (interconnected clusters serve as fast CO$_2$ transport channel). Gas separation performances of PEGDME 500 based membranes are also investigated and presented in Fig. 6B. Similar to PEGDME 250, the presence of PEGDME 500 can greatly change the gas transport properties

of Nafion. Adding 20 wt% PEGDME 500 in the hybrid membrane increases the CO$_2$ permeability from 1.6 Barrer to 46.2 Barrer at dry state, which is much higher than the PEGDME 250 with the same content. Increasing PEGDME 500 content to 40 wt% results in a further increase of CO$_2$ permeability to 128.0 Barrer, which is also much higher than that of the hybrid membrane with the same content of PEGDME 250 (81.2 Barrer). Unfortunately, the PEGDME 500 could induce serious phase separation at a higher content, leading to the formation of pores and consequently much lower CO$_2$/N$_2$ selectivity.

It has been reported by many researchers that the presence of water can greatly enhance the gas transport in Nafion membranes [33,35,61,62]. In the present study, the CO$_2$ separation performances of the hybrid membranes were also investigated under different RH values. With the RH value increasing to 50% and 100%, the CO$_2$ permeability of pure Nafion increased to 71 and 209 Barrer, respectively. These values are comparable with literature values, which are 66 and 260 Barrer [33]. The presence of water vapor could further improve the CO$_2$ permeability of the Nafion/PEGDME hybrid membranes, reaching higher performance compared to the pristine Nafion membrane. However, increasing the PEGDME content in membranes seemed to have reduced the effectiveness of water vapor. The enhancement factor associated to water vapor (defined as the permeability at different humidity values scaled over the dry permeability) decreases with the increase of the PEGDME content (as shown in Table 2).

At 20 wt% PEGDME 250 content, the enhancement factor showed a value of 22.9, but it decreased to 3.0 when the PEGDME 250 content increased to 60 wt%. As previously discussed, PEGDME 250 could enlarge the ionic cluster in the membrane, thus the water vapor becomes less effective in increasing the size of the clusters (gas permeation channels). Similar trend can be found in PEGDME 500 hybrid membranes. Water vapor is less effective in promoting CO$_2$ permeability at higher PEGDME 500 content. It is worth mentioning that the membrane containing 20 wt% PEGDME 500 shows better results at humid state: a CO$_2$ permeability of 343.5 Barrer was obtained at 100% RH, which is much higher than the corresponding PEGDME 250 membrane (205.4 Barrer).

The CO$_2$/N$_2$ selectivity measure in the mixed gas permeation setup for the various hybrid membranes is displayed in Fig. 7. Generally, the PEG-based membranes normally presents a CO$_2$/N$_2$ selectivity of around 45 ~ 60 [17,18], adding PEGDME 250 into Nafion membrane slightly improved the CO$_2$/N$_2$ selectivity at dry state (Fig. 7A). CO$_2$/N$_2$ selectivities of 16.32 and 11.47 were obtained for membranes containing 20 wt% and 40 wt% of PEGDME, respectively. The CO$_2$/N$_2$ selectivity for membrane containing 60 wt% PEGDME 250 was much lower, as expected due to the micro-phase separation at high PEGDME250 content and the formation of pin-holes (as shown in Fig. 5).

For the neat hybrid membrane containing up to 40 wt% PEGDME250, the CO$_2$/N$_2$ selectivity increased along with the RH value at which the test was performed, indicating that the presence of water vapor is more effective in promoting the transport of CO$_2$ than N$_2$. Membranes containing 20 wt% and 40 wt% PEGDME 250 showed higher CO$_2$/N$_2$ selectivity compared to pristine Nafion, denoting a synergic effect of water vapor and PEGDME 250 in the enhancement of the CO$_2$ flux through the membrane. The two membranes exhibited selectivity value over 30 at high RH, which are larger than that of the
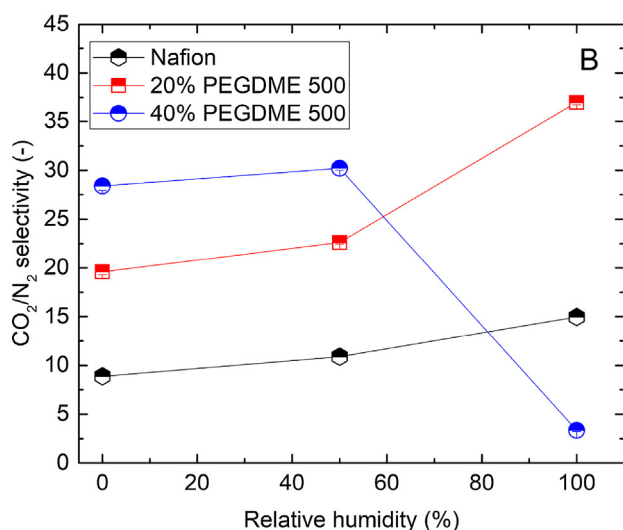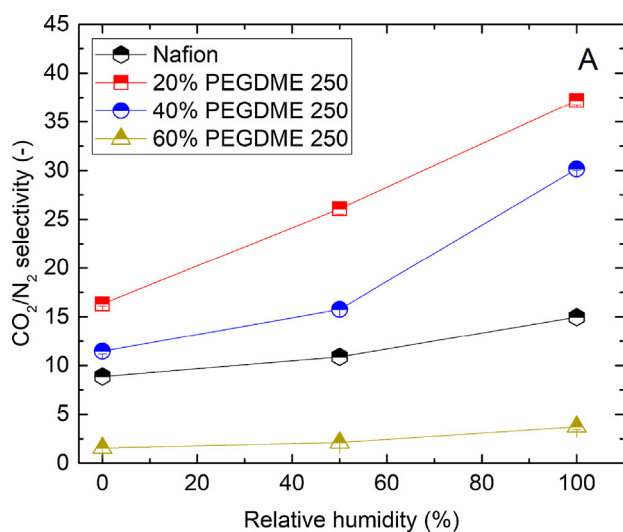
Fig. 7. CO_2/N_2 selectivity in Nafion/PEGDME hybrid membranes containing different PEGDME concentrations as a function of RH at 35 °C and 2.0 bar. (A) PEGDME 250, (B) PEGDME 500.

Fig. 8. Robeson plot for the Nafion/PEGDME hybrid membrane CO_2/N_2 separation performance.

The CO_2/N_2 separation performances of Nafion/PEGDME hybrid membranes were plotted together with the Robeson Upper Bound (Fig. 8) [63]. The trend in Fig. 8 indicates that adding PEGDME into Nafion matrix could be an effective way to increase CO_2 permeability and selectivity in the Nafion-based membrane. The membranes under humid condition show notably improved gas separation performances. Membrane with 40 wt% PEGDME 250 exhibits a CO_2 permeability of 446 Barrer with a CO_2/N_2 selectivity of 31, which is quite close to the 2008 Robeson Upper bound. Hybrid membranes with 20 wt% of PEGDME 500 has comparable performances with the 40 wt% PEGDME 250 membrane samples (see Fig. 9).

5. Modeling

In order to achieve a better understanding of the observed experimental behavior, the MWS model has been used to describe the permeability data of the different blends. In view of the results obtained from the SEM analysis, the Nafion/PEGDME system has been considered as a two-phase system: a continuous phase formed by the perfluorinated polymer chains and a discontinuous one with hydrophilic PEGDME interacting with the polar sulfonic group of Nafion. Following this idea, dry Nafion permeability was considered as the continuous phase permeability while pure PEGDME permeability was estimated to account for the transport in the discrete phase. In particular, the CO_2 permeability value for pure PEGDME was estimated assuming that the solution diffusion mechanism applies to describe the gas permeability through the low molecular weight system. Therefore, permeability is obtained as the product of the solubility coefficient S, calculated from literature data [64], and the diffusion coefficient D, estimated by a modified Stoke-Einstein equation [65]. Literature data for of CO_2 diffusivity in water [65] and PEGDME viscosity [66] were used. The final relationship was therefore the following.

$$P_{PEGDME}^{CO_2} = (S \cdot D)_{PEGDME}^{CO_2} = S_{PEGDME}^{CO_2} \cdot D_{H_2O}^{CO_2} \left(\frac{\mu_{H_2O}}{\mu_{PEGDME}} \right)^{0.8} \quad (6)$$

According to Eq. (6), the CO_2 permeability value through PEGDME is approximately 1620 Barrer at 35 °C. This value is in line with expectations and for example results very close to the one (~ 1800 Barrer) extrapolated from the permeability data of Pebax/PEGDME blends at different PEGDEM loadings [10]. Since nitrogen solubility data for the PEGDME were not found in literature, the latter study was used as a reference to estimate the nitrogen permeability through PEGDME, by extrapolating the CO_2/N_2 selectivity data for a membrane composition of 100% PEGDME. Using the CO_2 permeability found from Eq. (6), the value of the N_2 permeability in pure PEGDME is

pristine Nafion membrane (~15), suggesting that the gas selectivity in 20 wt% and 40 wt% PEGDME 250 hybrid membranes are mainly contributed by the PEGDME 250 inside the membrane matrix. It is worth mentioning that in the case of the membrane containing 60 wt% of PEGDME, the selectivity also increases with the RH increment. A CO_2/N_2 selectivity of 2.1 and 3.7 was obtained at RH value of 50% and 100%, respectively. The small pores created by the micro-phase separation at dry state might be partly clogged due to the swollen of the Nafion, resulting in a slight increase in the selectivity.

Similar trend of CO_2/N_2 selectivity can also be found in Nafion/PEGDME 500 membranes, as shown in Fig. 7B. Blending PEGDME 500 into Nafion significantly changed the CO_2/N_2 selectivity at a lower PEGDME 500 content (e.g. 20 wt%). Increasing RH value could also enhance the membrane separation performances. At higher PEGDME 500 content (e.g., 40 wt%), phase separation during membrane formation was observed, which resulted in porous structure. A big decrease in CO_2/N_2 selectivity was observed over the RH range: at dry and 50% RH, CO_2/N_2 selectivity of 30 was obtained. However, increasing RH to 100% led to a sharp decrease of CO_2/N_2 to only 3.3. A possible explanation can be that at high RH conditions, the PEGDME 500 in the Nafion matrix is diluted by the absorbed water vapor. The consequent loss of the mechanical strength and sieving function of the PEGDME phase resulted in the decrease of the selectivity.
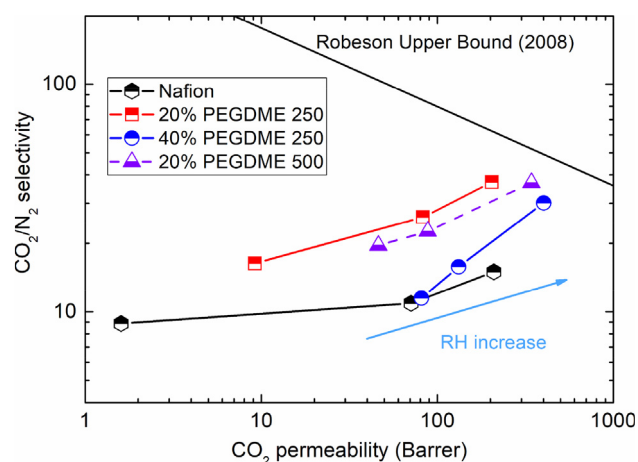
approximately 37 Barrer. With this information and by considering the volume fraction of the PEGDME in the system roughly equal to the weight fraction data for dry blends, the permeability behavior of the new materials could be described by using n as the only fitting parameter. Fig. 9 shows how the model is able to describe the CO_2 permeability under dry conditions for hybrid membranes containing different amount of PEGDME 250. The model is in good agreement with the experimental data within all the membrane composition. By looking at the n values used to fit the experimental data, a very steep decrease can be observed by passing from 20 to 40 wt%, suggesting that more interconnected domains are obtained at increasing the content of PEGDME.
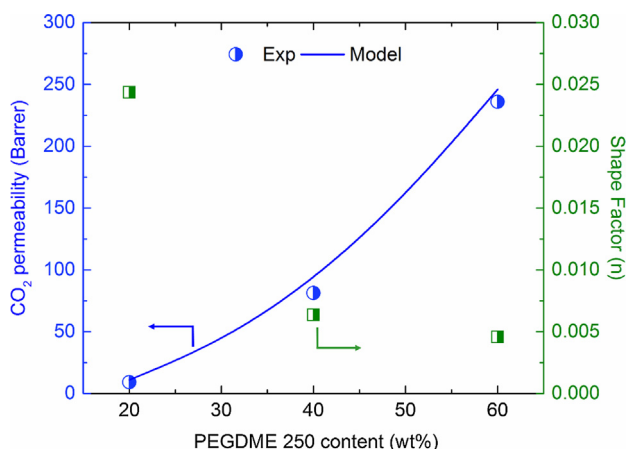

Fig. 9. Comparison between the experimental data and the results from the model for the hybrid membranes containing PEGDME 250 under dry conditions. In green, the values of the shape factor n are reported.

When water is added to the system, the same approach was considered, by assuming that water accumulates in the hydrophilic domains increasing their volumetric fraction while not changing the overall phase permeability. The latter assumption was made in view of the fact that liquid water present CO_2 and N_2 permeability values of 1727 Barrer and 47 Barrer, respectively, [45] that are extremely close to those previously estimated for PEGDME. Fig. 10 shows the comparison of the data measured experimentally and the results obtained from the model for all the investigated membranes and operating conditions. For each material, a single value of n was considered to describe both gas permeabilities, obtaining a good agreement in the description of CO_2 permeability. Worse prediction was obtained for N_2, since large errors have been obtained for the sample loaded with 60% PEGDME 250 and at 100% RH for the 40% PEGDME 500 membrane. However, in these cases severe phase separation was observed from morphology analysis, and the formation of micrometric defects could explain the large deviation of the experimental data from the predictions given by the considered modeling approach.

In general, the model appears to be able to properly describe the experimental behavior of the investigated materials and can be used to make additional consideration about the structure of the different materials considered. Indeed, by observing the value of n obtained from the different regression (Table 3), it can be noticed that apart from the sample with 20% PEG it is basically stable and does not substantially change while changing the amount of PEGDME in the membrane. The n values considered, being in the order of 10^{-3}, refers to very elongated prolate spheroids suggesting that PGDME 500 and PEGDME 250 above 20% loading, are able to create a sort of interconnected hydrophilic structure inside the matrix which can serve, also in dry condition, as preferential pathways to the permeating gases. In this case it is

worthwhile to notice that water only slightly decreases the value of n in agreement with the fact that, being the channel already present it does not cause major modification in the materials structure or permeation performance.
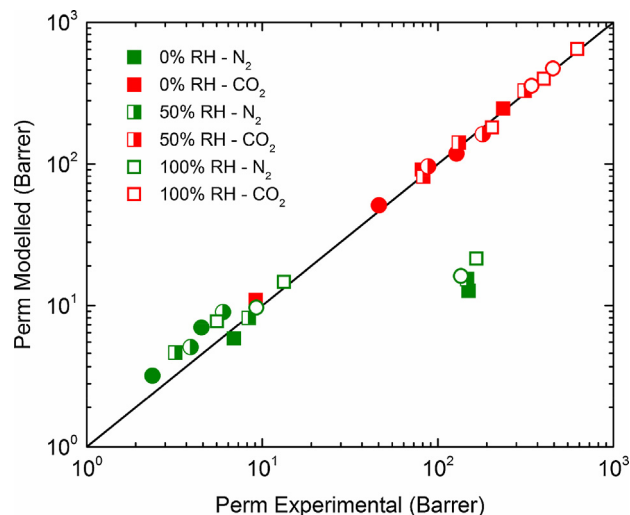

Fig. 10. Parity plot of the results from the model and the experimental data. The squares refer to the hybrid membranes prepared using PEGDME 250, the circles to the hybrid membranes prepared using PEGDME 500.

6. Conclusion

In the present study, Nafion/PEGDME hybrid membranes have been fabricated. The addition of PEGDME into Nafion matrix can significantly change the membrane morphology, but high additive content may lead to the formation of pin holes or pore structure in the hybrid membrane. The CO_2 permeability can be greatly improved by the addition of PEGDME into Nafion at dry state. Increasing RH value could further improve both CO_2 permeability and CO_2/N_2 selectivity. A CO_2 permeability of up to 446 Barrer with the CO_2/N_2 selectivity of 31 can be obtained for hybrid membrane with the addition of 40 wt% PEGDME 250. Hybrid membranes with the addition of 20 wt% PEGDME 500 show similar performance. A modeling approach based on a modified Maxwell model has been proposed in order to describe the experimental data. By using a single adjustable parameter (n) related to the shape of the dispersed domains, the model appeared able to describe the experimental observation with a good precision, in a wide range of operating conditions. The values of the parameter n confirmed that the addition of low molecular weight components in the Nafion matrix formed interconnected domains that contribute to the enhancement of the gas permeability to the largest extent.

These data presented in this paper can be a starting point of

Table 3
Value of parameter n used to fit the experimental data.

	n		
RH	0%	50%	100%
Content (wt%)	PEGDME 500		
20	0.0042	0.0025	0.0002
40	0.0046	0.0044	0.0011
Content (wt%)	PEGDME 250		
20	0.0243	0.0033	0.0014
40	0.0063	0.0048	0.0013
60	0.0046	0.0039	0.0014

developing Nafion/PEGDME hybrid membrane for CO_2/N_2 separation applications. The separation performance of the membrane could be further improved by the optimization of the types and amount of the additives and the morphology control in the fabrication of thin film composite membranes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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