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Ultra-selective defect-free interfacially polymerized molecular sieve thin-film composite membranes for H2 purification — Source link

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Published on: 01 Jan 2018 - Journal of Materials Chemistry (The Royal Society of Chemistry)

Topics: Membrane, Thin-film composite membrane, Permeance, Synthetic membrane and Hydrogen purifier

Journal of
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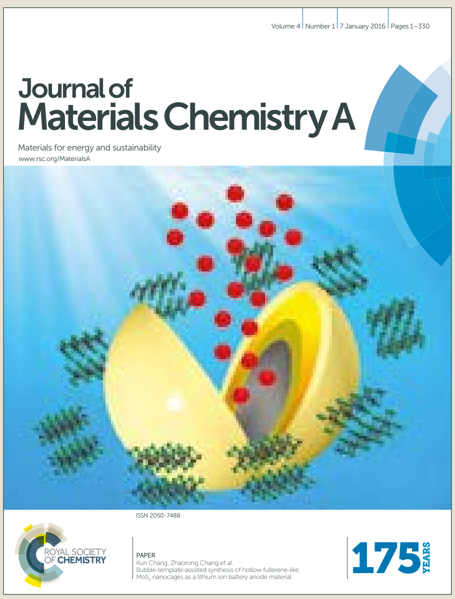

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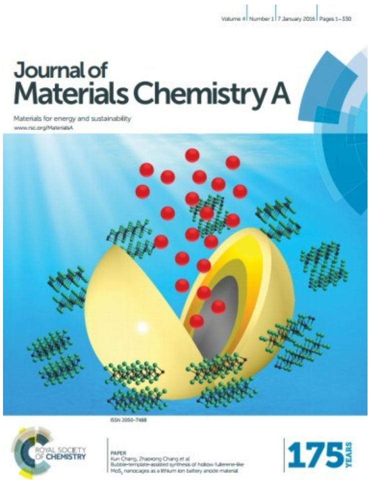

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Ultra-selective defect-free interfacially polymerized molecular sieve thin-film composite membranes for H_2 purification

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Purification is a major bottleneck towards generating low-cost commercial hydrogen. In this work, inexpensive high-performance H_2 separating membranes were fabricated by modifying the commercially successful interfacial polymerization production method for reverse osmosis membranes. Defect-free thin-film composite membranes were formed demonstrating unprecedented *mixed-gas* H_2/CO_2 selectivity of ≈ 50 at 140 °C with H_2 permeance of 350 GPU, surpassing the permeance/selectivity upper bound of all known polymer membranes by a wide margin. The combination of exceptional separation performance and low manufacturing cost makes them excellent candidates for cost-effective hydrogen purification from steam cracking and similar processes.

Introduction

The transport sector consumes between 30-50% of global energy with demands continuing to increase annually.[1] Coupled with established correlations between anthropogenic greenhouse gas emissions and global climate change, the need for energy efficient, environmentally friendly fuels is greater than ever.[2] Hydrogen offers huge potential as an alternative fuel of the future due to its high energy storage capacity (119 MJ/kg) and zero-emissions combustion (produces only water).[3–5] Approximately 8.5 x 10^{11} m^3 of hydrogen – carrying 6 x 10^{12} MJ of energy – are produced annually, with over 90% obtained from fossil fuels (mainly natural gas and coal) and biomass or its derivatives.[6] A much smaller fraction (~ 8%) is produced using water electrolysis.[6]

During steam cracking of natural gas to produce hydrogen (steam-methane reforming, SMR), methane and water are reformed to CO and H_2 at ∼ 800 °C. The H_2/CO mixture is then converted at about 350 °C into H_2 and CO_2. Composition of output streams can vary depending on the specific method employed. A typical SMR plant produces a H_2/CO_2 ratio of ~75/20 with 5% methane and <1% of other impurities.[6] Integrated Gasification Combined Cycle (IGCC) plants using biomass or coal feedstock can produce H_2/CO_2 ratios of ~60/40.[7] Currently about half of globally synthesized hydrogen is used for the production of ammonia employed as fertilizer by the Haber process, while most of the remaining half is utilized in hydrocracking *i.e.* breaking large hydrocarbons into smaller ones for use as fuel.[8] Smaller quantities are used for production of methanol, plastics, pharmaceuticals, hydrogenation of oils, desulfurization of fuels, etc.[8] Hydrogen production is currently growing at 10% annually, but it is estimated that availability of lower-cost hydrogen could immediately boost its use by 5- to 10-fold.[9]

To date, chemical separation processes account for 10-15% of global energy consumption.[10] The state-of-the-art technologies for H_2 purification, *i.e.* cryogenic distillation and pressure-swing adsorption, are extremely energy intensive, accounting for around 30% of total plant capital and operating cost.[11,12] Membrane-based H_2/CO_2 separation offers a potential path to reduce process costs and debottleneck H_2 purification.

Table S1 lists the United States Department of Energy (USDOE) membrane performance targets for hydrogen purification from syngas mixtures.[13,14] A number of materials are being considered for such separations, including inorganics such as carbon molecular sieves, zeolites, and metal membranes, as well as glassy polymers such as polybenzimidazole and polyimides with and without nanoparticles.[15–25] The economic and environmental benefits of using membranes for H_2/CO_2 separation have been discussed by Merkel et. al., suggesting that H_2/CO_2 selectivities greater than 10 can significantly reduce hydrogen production cost.[7,14,26] Proteus™ by Membrane Technology & Research Inc. is a proprietary commercial membrane offering H_2/CO_2 selectivity of approximately 11 with H_2 permeance of 500 GPU (1 GPU = 10^{-6} cm^3 (STP) cm^{-2} s^{-1} $cmHg^{-1}$) at 150 °C mixed-gas operation.[14]

Thin-film composite (TFC) reverse osmosis (RO) membranes constitute the most successful implementation of membrane technology in large-scale industrial separation processes due

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† Electronic Supplementary Information (ESI) available: Materials, methods, FTIR, XPS, XRD, TGA, FESEM, gas permeation data. See DOI: 10.1039/x0xx00000x

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DOI: 10.1039/C7TA07819F

to their unmatched combination of high water flux and salt rejection. Their high water flux results from the extremely thin selective polyamide layers made by interfacial polymerization (IP). Polymers made by this process have been applied widely for industrial use, including reverse osmosis and nanofiltration membranes as well as microcapsules.[27]

Fig. S3 shows the structure of the partially crosslinked fully aromatic polyamide layer fabricated by reacting *m*-phenylenediamine (MPD) and trimesoyl chloride (TMC) on polymeric supports, pioneered by Cadotte and commercially named FT-30.[28] This TFC is currently employed in more than 15,000 desalination plants, accounting for 90% of the global market.[29] In commercial settings, the FT-30-type RO membranes are produced by impregnating (*via* dipping or spraying) a highly porous support material (usually polysulfone) with MPD dissolved in water. Typically, excess solution is removed from the surface by using an air knife or a rubber roller. The diamine-soaked porous polysulfone support is then exposed to TMC dissolved in a hydrocarbon solvent (typically *n*-hexane or Isopar®) between 1 to 60 seconds.[28] Most commonly, solutions in the IP process are applied at room temperature (20-25 °C). The membrane is then immediately exposed to high temperatures (~80-100 °C) for drying and curing of the polyamide. *Commercial* RO membranes made by the IP process have been laboriously studied and reported in the literature with no usable gas separation properties. Gas permeation studies of dry FT-30-type RO membranes[30–33] demonstrated Knudsen diffusion transport, implying presence of mesoporous surface defects. Interestingly, Louie et al. demonstrated that plugging the surface defects by coating FT-30-type membranes with a rubbery polyether–polyamide block copolymer (PEBAX® 1657) showed some potential for H_2/CO_2 separations.[32]

In this work, the successful fabrication of highly crosslinked, *ultra-selective, defect-free* MPD-TMC polyamide thin-film composite molecular sieve membranes is reported for the first time for H_2/CO_2 separation. Pure- and mixed-gas permeation experiments were performed across a range of temperatures up to 140 °C. The TFCs were further characterized using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The performance of these inexpensive high-performance membranes exceeded the USDOE targets and the H_2/CO_2 permeance/selectivity upper bound for polymer membranes by a wide margin.

Experimental

Ultra-selective, defect-free MPD-TMC polyamide TFC membranes were fabricated varying three parameters: (i) reaction time, (ii) TMC concentration and (iii) organic phase temperature. Materials and methods are given in the Electronic Supplementary Information (ESI). Porous polysulfone support layers (11.5 x 15.5 cm) were immersed in tap water for 24 hours followed by immersion in 2 wt/vol% of MPD dissolved in distilled water for 5 minutes. The support was then passed through a rubber roller to remove any excess droplets on the surface and fixed in a sealed Teflon frame. Isopar® was heated to the desired temperature and TMC was dissolved in a specific concentration. The TMC solution was then poured on the polysulfone surface, initiating the reaction. After the specified reaction time, excess solution was poured off. The membrane was immediately washed in the frame three times consecutively with 30 ml Isopar® and isopropanol. Finally, it was dried at room temperature for 48 hours and stored in a desiccator prior to testing. Table 1 lists the TFC membranes prepared in this study. The membrane designation is defined by: (i) reaction time between organic TMC and aqueous diamine phases (10-300 s); (ii) TMC concentration (0.1-10 wt/vol%); (iii) organic phase temperature (20-100 °C). Data for at least three duplicate samples are reported for each permeation test.

Table 1. Membrane formation variables and sample information. Concentration = TMC concentration; temperature = organic phase temperature; *m* = crosslinking degree (details in ESI Section 8). (N.M. = not measured).

Membrane	Reaction time (s)	Concentration (wt/vol%)	Temperature (°C)	*m*
FT-30 variant RO4		Proprietary		
10s-0.1TMC-20C	10	0.1	20	N.M.
60s-0.1TMC-20C	60	0.1	20	N.M.
300s-0.1TMC-20C	300	0.1	20	0.62
600s-0.1TMC-20C	600	0.1	20	N.M.
300s-0.1TMC-60C	300	0.1	60	0.66
300s-1TMC-60C	300	1	60	0.55
300s-10TMC-60C	300	10	60	0.39
300s-0.1TMC-100C	300	0.1	100	0.89

Results and discussion

Commercially produced dry FT-30 membranes are known to contain micropores larger than the dimensions of gas molecules, as Knudsen selectivity has been measured in a variety of FT-30-type products.[32,33] Although specific production information is proprietary, it is widely known that these membranes are made with IP reaction times under one minute. Figs. 1 (a) and (b) show how defect-free polyamide layer characteristics, as indicated by significantly increased selectivity, start to emerge at longer reaction times. Permeance for H_2 and He decreased 10-fold, whereas an average decrease of at least 100-fold was observed for larger gases as reaction time was increased from 10 to 300 s. Longer reaction times presumably allow more MPD to penetrate into the reaction zone forming additional polyamide and thus closing any defects in the ultrathin-film by a diffusion-driven self-healing process, as schematically shown in Fig. S4. During this process, the mode of transport shifted from Knudsen flow to solution/diffusion, and gas pair selectivity increased at 60 s while reaching an optimum at a reaction time of 300 s. Numerical performance data are summarised in Table S2 and S3. The 10s-0.1TMC-20C membrane demonstrated identical gas permeation properties to a commercial FT-30-type (Sepro

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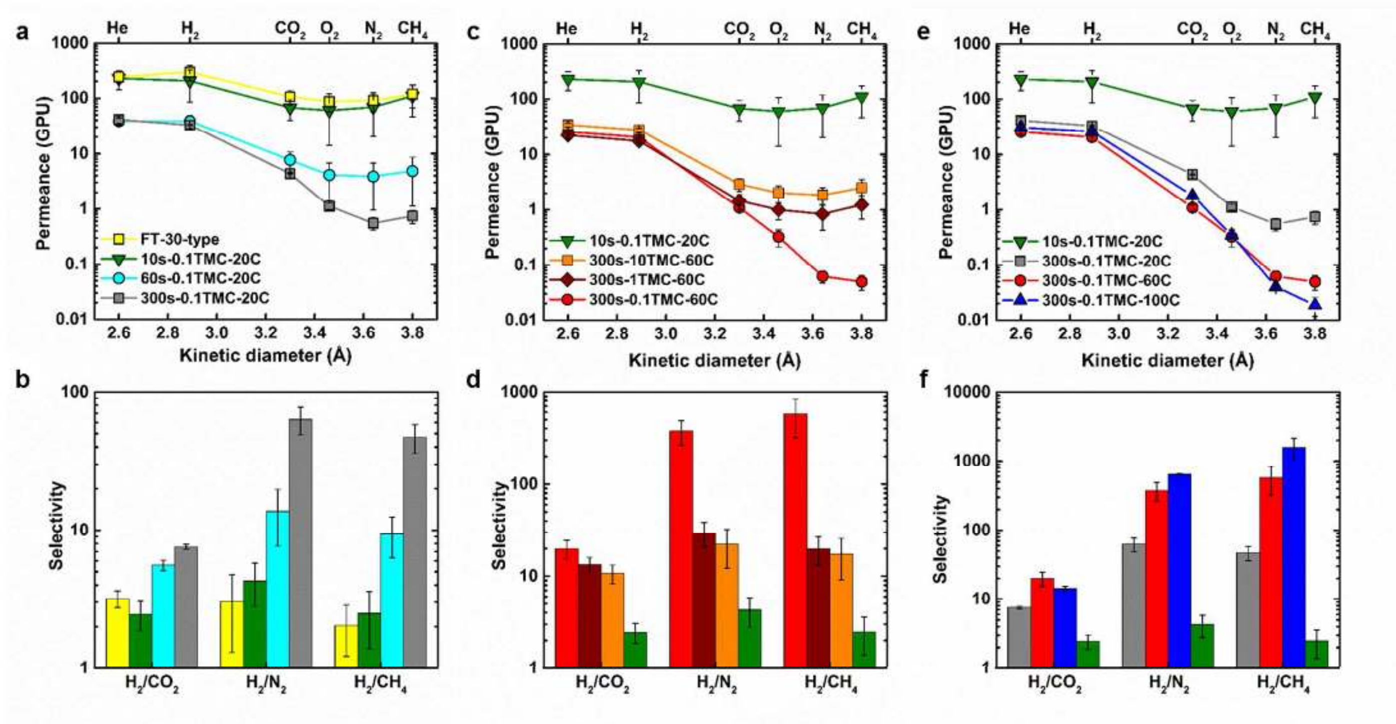

Fig. 1 Pure-gas separation performance of polyamide thin-film composite membranes. Effect of: a) and b) reaction time; c) and d) TMC concentration; e) and f) organic phase temperature on permeance and selectivity, respectively.

RO4) and was used as the reference for comparing the performance of other TFCs in this work.

Figs. 1 (c) and (e) show the effects of varying TMC concentration and organic phase temperature on gas permeance properties of the TFCs. No significant variation in permeance was observed for helium (kinetic diameter (k_d) = 2.60 Å) and hydrogen (k_d = 2.89 Å) but a clear trend of decreasing permeance started to emerge for gases with k_d values larger than 3 Å (O_2, CO_2, N_2, CH_4).[34] FTIR spectra (Fig. S5) demonstrated no visible difference in polyamide chemistry for different fabricated samples compared to the 10s-0.1TMC-20C reference membrane. However, as TMC concentration decreased, the ratio of amine to acyl chloride functional groups increased as demonstrated by XPS analysis, indicating an increase in the degree of crosslinking (Table 1). This resulted in tightening of the polyamide network, consequently hindering transport for larger gas molecules while no significant effect was observed for smaller gases (He and H_2), which resulted in significant boost in selectivity. Similarly, increasing organic-phase temperature also increased the degree of crosslinking, which lowered the permeance of gases larger than H_2 thereby significantly enhancing selectivity. Presumably, increase in reaction-zone temperature increased the overall reaction rate as well as solubility and diffusivity of MPD in the organic phase (reaction-zone), resulting in increased formation of amide linkages and, hence, increased crosslinking.[35]

Figs. 1 (d) and (f) show the membrane performance results expressed in terms of selectivity. High selectivity for H_2/CO_2 and negligible selectivity for He/H_2 implies a primary molecular-sieve-like cut-off around 3 Å. This is clearly displayed in the XRD spectrum for the MPD-TMC powder in Fig. S6, showing a main amorphous peak with average chain d-spacing centered around 3.5 Å. As *m* increased from 0.39 to 0.66, selectivity of hydrogen over CO_2, O_2, N_2 and CH_4 increased, implying increased ultramicroporosity. As degree of crosslinking increased further from 0.66 to 0.89, N_2 and CH_4 permeance decreased (k_d for N_2 and CH_4 are 3.64 Å and 3.80 Å, respectively) but CO_2 and O_2 permeances remained unaffected. As a direct consequence, O_2/N_2, CO_2/N_2 and CO_2/CH_4 selectivities increased (Fig. S7). These are all significant industrial gas separation applications for implementation of membrane technology.

SEM images, Figs. S8 (a-l) and S9 (a-d), illustrate TFCs of this study have typical average visual polyamide ridge-and-valley-based film thickness of approximately 100-300 nm.[36] However, it has been suggested that there is an appreciable difference between observed average cross-sectional thickness and *actual effective* thickness of the selective layer. The apparent visual thickness has been conventionally considered the true thickness of the polyamide barrier layer[35,37]; however, more recent research has indicated that the effective thickness of the separation layer lies around the order of only 10-20 nm.[36,38,39] The cross-sections of the defective FT-30-type reference membrane (10s-0.1TMC-20C) and the defect-free, highly gas-selective polyamide TFC of this work (300s-0.1TMC-100C) are shown in Fig. 2. Although it is difficult to clearly assign a thickness to the ultrathin selective polyamide barrier layer of both membrane types, it is clear that the PA layer is thicker and more tightly packed in the membrane made with

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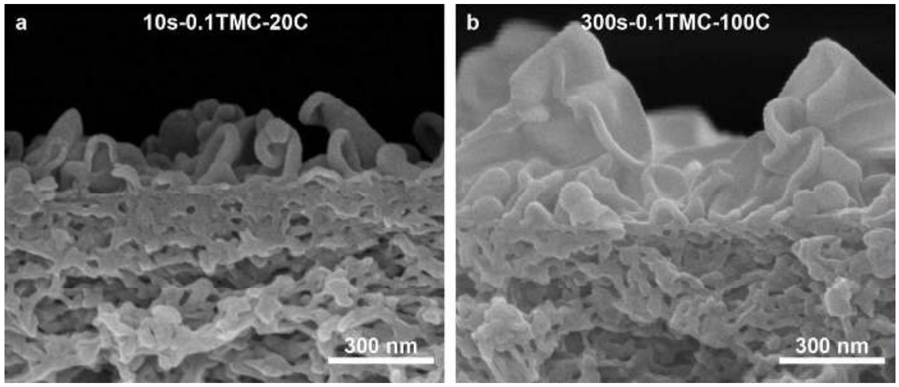

Fig. 2 SEM cross-section for: a) 10s-0.1TMC-20 and b) 300-0.1TMC-100C highlighting variation of morphology for lowest and highest performing samples, respectively.

both longer reaction time and higher reaction temperature (Fig. 2b).

Gas permeation data for an aromatic network polyamide based on MPD and TMC are not available because isotropic films cannot be produced due to the inherent insolubility of the crosslinked polymer. However, Weinkauf, Kim and Paul[40] reported the gas permeation properties of thick films of a related linear, amorphous aromatic polyamide made from phenylenediamine isomers and terephthaloyl chloride. The isotropic poly(phenylene terephthalamide) films used in their study were ~25-100 µm thick and demonstrated *gas barrier* behavior with O_2 and CO_2 permeabilities at 35 °C of only 0.026 and 0.1 Barrer, respectively (1 Barrer = 1 x 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$). Because of their extremely low gas permeabilities aromatic polyamides have been rarely considered for membrane-based gas separation processes.[41] However, as demonstrated here, this disadvantage can be overcome by fabricating ultra-thin films allowing the exploitation of highly selective barrier materials with industrially useable performance characteristics.

Pure- and mixed-gas temperature dependence

The membranes fabricated in this study showed excellent potential for syngas separations at 22 °C. However, equally important requirements for membranes in H_2 purification from syngas are stability at high feed temperatures (~ 150-250 °C) and high pressures (> 7 bar).

Fig. 3 (a) shows the performance of the 300s-0.1TMC-100C membrane as a function of temperature using pure-gas H_2 and CO_2 measurements. Permeance for both gases showed excellent Arrhenius regression with temperature (ESI section 11). H_2 experienced a larger increase in permeance compared to CO_2 presumably due to reduced sorption of CO_2 at higher temperatures. At 140 °C, H_2 permeance increased to 275 ± 4 GPU with H_2/CO_2 selectivity of 95.5 ± 5, the highest reported pure-gas selectivity to date of any polymer membrane. Activation energies for H_2 and CO_2 were calculated as 8.50 and 1.20 kJ mol^{-1}, respectively. The surprisingly lower activation energy of permeation for CO_2 than H_2 was previously observed by Li et al. for a series of polybenzimidazoles.[23] It was suggested that the smaller relative increase in CO_2 permeability with temperature resulted from strong CO_2-polymer interactions. Weinkauf et al. observed a similar trend for aromatic polyamides and evidenced strong polymer/CO_2 interactions by large negative CO_2 heat of sorption values.[40]

Mixed-gas separation was conducted using a 1:1 H_2/CO_2 feed at 140 °C to provide more realistic performance data in industrial systems. Fig. 3 (b) shows pure- and mixed-gas data for the 300s-0.1TMC-100C membrane compared to state-of-

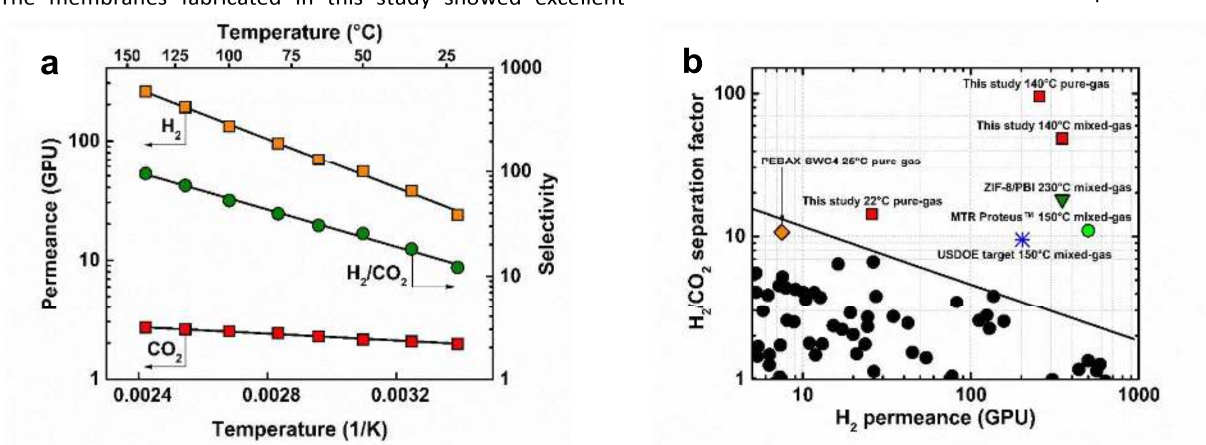

Fig. 3 a) TFC membrane (300s-0.1TMC-100C) pure-gas temperature dependence for H_2 and CO_2, and b) Robeson plot for performance comparison of TFC membrane studied here (300s-0.1TMC-100C) with other membrane types. Permeance/selectivity upper bound adapted from Robeson (2008) assuming 1 µm-thick films.[42] USDOE target membrane requirements for H_2/CO_2 separation[13,14] and performance data for MTR Proteus™[14], ZIF-8/PBI[19], PEBAX-coated SWC4 (PEBAX-SWC4)[32].

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the-art polymer membranes on the permeance/selectivity plot for H_2/CO_2 separation.[42] Average stabilized H_2 permeate concentration of 98% was achieved, translating to an unprecedented mixed-gas separation factor of 50 ± 4 with hydrogen permeance of 350 ± 15 GPU at 140 °C. Our mixed-gas permeation results clearly demonstrated unparalleled performance of the defect-free polyamide TFCs for H_2/CO_2 separation with properties far exceeding all state-of-the-art polymer membranes when tested under industrially relevant conditions. It is important to note that the aromatic polyamide is thermally stable up to ~ 300 °C (Fig. S10). However, the upper operational temperature of the TFC membranes reported here is limited by the thermal stability of the porous polysulfone support. Hence, future developments of TFC membranes for high-temperature H_2/CO_2 separation (~ 200-300 °C) must be directed towards the development of more thermally stable porous support.

Conclusions

The growing need for cleaner energy has dramatically increased interest in separations using membrane systems. Highly crosslinked, ultra-selective, defect-free MPD-TMC membranes were successfully fabricated in this study showing tremendous potential for H_2/CO_2 separation in syngas applications as well as a number of other challenging gas separations. These membranes exhibited unprecedented H_2/CO_2 selectivity combined with very high H_2 permeance at 140 °C, surpassing the performance of all other reported polymer membranes to date.

Fortuitously, these ultra-high-performance membranes can be produced by making only small changes to existing commercial membrane manufacturing processes by interfacial polymerization. Therefore, their fabrication cost should be similar to standard RO membranes of only ≈ 1-2 $/ft^2,[43] which would lower the membrane cost by *50-100-fold* based on the DOE target value of 100 $/ft^2. This study demonstrated that varying fabrication parameters can tune permselectivity to meet the needs of specific processes. A few simple modifications to a time-tested commercial membrane fabrication process can produce membranes that meet a key industrial need. With rapidly developing economic and environmental pressures to increase efficiencies for separation processes, such highly-selective, low-cost, commercial barrier materials fabricated as ultra-thin films show potential for a paradigm shift to streamline industrial use of membranes for hydrogen separations.

TFCs based on MPD and TMC also demonstrated remarkable selectivity for O_2/N_2, CO_2/CH_4, H_2/N_2 and CO_2/N_2 separations. However, the most promising TFC membrane for H_2/CO_2 separation (300s-0.1TMC-100C) exhibited very low CO_2 and O_2 permeances of only 1.8 and 0.4 GPU, respectively. Recent work by Tsai et al. demonstrated more promising results for O_2/N_2 separation for interfacially polymerized TFCs made by reaction of TMC with piperazine.[44]

Conflict of interest

There are no conflicts to declare.

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View Article Online
DOI: 10.1039/C7TA07819F

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Ultra-selective defect-free interfacially polymerized molecular sieve thin-film composite membranes for H_2 purification

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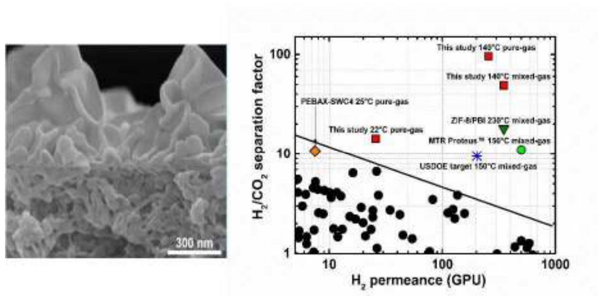

Ultrathin, defect-free thin-film polyamide composite membranes developed for H_2/CO_2 separation exhibit mixed-gas performance far exceeding all state-of-the-art polymeric membranes.