Journal of Materials Chemistry A

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Z. Ali, F. Pacheco, E. Litwiller, Y. Wang, Y. Han and I. Pinnau, *J. Mater. Chem. A*, 2017, DOI: 10.1039/C7TA07819F.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [author guidelines](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the ethical guidelines, outlined in our [author and reviewer resource centre](#), still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

Journal of Materials Chemistry A

Materials for Energy and Sustainability

Communication submission

Journal of Materials Chemistry A is a weekly journal in the materials field. The journal is interdisciplinary, publishing work of international significance on all aspects of materials chemistry related to energy and sustainability. Articles cover the fabrication, properties and applications of materials.

2016 Impact Factor of *Journal of Materials Chemistry A*: **8.867**
For more information go to www.rsc.org/materialsA

The following paper has been submitted to *Journal of Materials Chemistry A* for consideration as an urgent **Communication**.

The Editorial Board stress a **very high quality and novelty** standard is needed for acceptance.

Journal of Materials Chemistry A wishes to publish original research that demonstrates significant **novelty and advance**, either in the chemistry used to produce materials or in the properties/applications of the materials produced. Work submitted that is outside of these criteria will not usually be considered for publication. The materials should also be related to the theme of materials for energy and sustainability. Furthermore, Communications must demonstrate sufficient **quality and urgency** to warrant publication in that form.

We ask referees to examine manuscripts very carefully, and recommend rejection of articles which do not meet our high novelty, quality and impact expectations. Please note that **the rejection rate for JMCA is currently ~80%** of submitted manuscripts.

Routine or incremental work, however competently researched and reported, should not be recommended for publication if it does not meet our expectations with regard to novelty and impact.

It is the responsibility of authors to provide fully convincing evidence for the homogeneity and identity of all compounds they claim as new. Evidence of both purity and identity is required to establish that the properties and constants reported are those of the compound with the new structure claimed.

Thank you for your effort in reviewing this submission. It is only through the continued service of referees that we can maintain both the high quality of the publication and the rapid response times to authors. We would greatly appreciate if you could review this paper in **one week**. Please let us know if that will not be possible.

Once again, we appreciate your time in serving as a reviewer. To acknowledge this, the Royal Society of Chemistry offers a **25% discount** on its books: <http://www.rsc.org/Shop/books/discounts.asp>. Please also consider submitting your next manuscript to *Journal of Materials Chemistry A*.

Best wishes,

Annie Harvey
Executive Editor, *Journal of Materials Chemistry A*

Journal Name

COMMUNICATION

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

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

Z. Ali, F. Pacheco, E. Litwiller, Y. Wang, Y. Han and I. Pinnau*

DOI: 10.1039/x0xx00000x

www.rsc.org/

Purification is a major bottleneck towards generating low-cost commercial hydrogen. In this work, inexpensive high-performance H₂ 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 H₂/CO₂ selectivity of ≈ 50 at 140 °C with H₂ 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 8.5×10^{11} m³ of hydrogen – carrying 6×10^{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 ($\sim 8\%$) 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 H₂ at ~ 800 °C. The H₂/CO mixture is then converted at about 350 °C into H₂ and CO₂. Composition of output streams can vary depending on the specific method

employed. A typical SMR plant produces a H₂/CO₂ ratio of $\sim 75/20$ with 5% methane and $<1\%$ of other impurities.⁶ Integrated Gasification Combined Cycle (IGCC) plants using biomass or coal feedstock can produce H₂/CO₂ ratios of $\sim 60/40$.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 H₂ 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 H₂/CO₂ separation offers a potential path to reduce process costs and debottleneck H₂ 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 H₂/CO₂ separation have been discussed by Merkel *et. al.*, suggesting that H₂/CO₂ 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 H₂/CO₂ selectivity of approximately 11 with H₂ permeance of 500 GPU (1 GPU = 10^{-6} cm³ (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

King Abdullah University of Science and Technology, Advanced Membranes and Porous Materials Center, Division of Physical Sciences and Engineering, Thuwal 23955-6900, Saudi Arabia. E-mail: ingo.pinnau@kaust.edu.sa

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

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 H₂/CO₂ 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 H₂/CO₂ 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 H₂/CO₂ 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)	<i>m</i>
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 H₂ 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

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

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, Weinkauff, Kim and Paul⁴⁰ 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 $^\circ\text{C}$ of only 0.026 and 0.1 Barrer, respectively (1 Barrer = $1 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$). 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 $^\circ\text{C}$. However, equally important requirements for membranes in H_2 purification from syngas are stability at high feed temperatures ($\sim 150\text{--}250$ $^\circ\text{C}$) 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 $^\circ\text{C}$, 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. Weinkauff 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 $^\circ\text{C}$ 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^{TM14}, ZIF-8/PBI¹⁵, PEBAX-coated SWC4 (PEBAX-SWC4)³².

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 $\sim 300^\circ\text{C}$ (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 $\$/\text{ft}^2$,⁴³ which would lower the membrane cost by 50–100-fold based on the DOE target value of 100 $\$/\text{ft}^2$. 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.

Notes and references

‡ Electronic Supplementary Information available at:

- 1 R. P. Lively and D. S. Sholl, *Nat. Mat.*, 2017, **16**, 276–279.
- 2 J. Hansen, R. Ruedy, M. Sato and K. Lo, *Rev. Geophys.*, 2010, **48**, RG4004.
- 3 D. Teichmann, W. Arlt and P. Wasserscheid, *Int. J. Hydrogen Energy*, 2012, **37**, 18118–18132.
- 4 United States Congress, *Energy Policy Act: Public Law 102-486*, Washington, 1992.
- 5 J. A. Turner, *Science*, 2004, **305**, 972–974.
- 6 N. W. Ockwig and T. M. Nenoff, *Chem. Rev.*, 2007, **107**, 4078–4110.
- 7 T. C. Merkel, M. Zhou and R. W. Baker, *J. Membr. Sci.*, 2012, **389**, 441–450.
- 8 P. Häussinger, R. Lohmüller and A. M. Watson, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2011.
- 9 Y. Bilge, C. Guenter, M. C. Petri and C. Forsberg, *Configuration and Technology Implications of Potential Nuclear Hydrogen System Applications prepared by Nuclear Engineering Division*, Chicago, 2005.
- 10 D. S. Sholl and R. P. Lively, *Nature*, 2016, **532**, 6–8.
- 11 Thomas L. Buchanan, Michael G. Klett and Ronald L. Schoff, *Capital and Operating Cost of Hydrogen Production from Coal Gasification*, Pittsburgh, 2003.
- 12 R. Spillman, in *Membrane Science and Technology. Volume 2*, eds. R. D. Noble and S. A. Stern, Elsevier B.V., 2nd edn., 1995, pp. 589–667.
- 13 United States Department of Energy, *Basic research needs for the hydrogen economy. Workshop on hydrogen production, storage and use*, Lemont, 2003.
- 14 United States Department of Energy, *Advanced Carbon Dioxide Capture R&D Program: Technology Update: Pre-combustion membranes*, Pittsburgh, 2013.
- 15 K. J. Bryden and J. Y. Ying, *J. Membr. Sci.*, 2002, **203**, 29–42.
- 16 Y. H. Ma, *Adv. Membr. Technol. Appl.*, 2008, 671–684.
- 17 D. R. Pesiri, B. Jorgensen and R. C. Dye, *J. Membr. Sci.*, 2003, **218**, 11–18.
- 18 K. A. Berchtold, R. P. Singh, J. S. Young and K. W. Dudeck, *J. Membr. Sci.*, 2012, **415–416**, 265–270.
- 19 T. Yang and T.-S. Chung, *Int. J. Hydrogen Energy*, 2013, **38**, 229–239.
- 20 S. S. Hosseini, N. Peng and T. S. Chung, *J. Membr. Sci.*, 2010, **349**, 156–166.
- 21 S. Japip, K. S. Liao and T. S. Chung, *Adv. Mater.*, 2017, **29**, 1–6.
- 22 P. Li, Z. Wang, Z. Qiao, Y. Liu, X. Cao, W. Li, J. Wang and S. Wang, *J. Membr. Sci.*, 2015, **495**, 130–168.
- 23 X. Li, R. P. Singh, K. W. Dudeck, K. A. Berchtold and B. C. Benicewicz, *J. Membr. Sci.*, 2014, **461**, 59–68.
- 24 S. C. Kumbharkar, Y. Liu and K. Li, *J. Membr. Sci.*, 2011, **375**,

COMMUNICATION

Journal Name

- 231–240.
- 25 S. C. Kumbharkar and K. Li, *J. Membr. Sci.*, 2012, **415**–**416**, 793–800.
- 26 United States Department of Energy, *Cost and performance baseline for fossil energy plants: Report Number DOE/NETL-2007/1281*, Pittsburgh, 2007, vol. 4.
- 27 M. J. T. Raaijmakers and N. E. Benes, *Progr. Polym. Sci.*, 2016, **63**, 86–142.
- 28 J. E. Cadotte, *US patent 4,277,344*, 1981.
- 29 S. S. Shenvi, A. M. Isloor and A. F. Ismail, *Desalination*, 2015, **368**, 10–26.
- 30 J. S. Louie, I. Pinnau and M. Reinhard, *J. Membr. Sci.*, 2011, **367**, 249–255.
- 31 J. Duan, PhD thesis, King Abdullah University of Science and Technology, 2014.
- 32 J. S. Louie, I. Pinnau and M. Reinhard, *J. Membr. Sci.*, 2008, **325**, 793–800.
- 33 J. Albo, J. Wang and T. Tsuru, *J. Membr. Sci.*, 2014, **449**, 109–118.
- 34 N. Mehio, S. Dai and D. E. Jiang, *J. Phys. Chem. A*, 2014, **118**, 1150–1154.
- 35 A. K. Ghosh, B. H. Jeong, X. Huang and E. M. V Hoek, *J. Membr. Sci.*, 2008, **311**, 34–45.
- 36 F. Pacheco, R. Sougrat, M. Reinhard, J. O. Leckie and I. Pinnau, *J. Membr. Sci.*, 2016, **501**, 33–44.
- 37 L. Lin, C. Feng, R. Lopez and O. Coronell, *J. Membr. Sci.*, 2016, **498**, 167–179.
- 38 F. A. Pacheco, I. Pinnau, M. Reinhard and J. O. Leckie, *J. Membr. Sci.*, 2010, **358**, 51–59.
- 39 S. Karan, Z. Jiang and A. G. Livingston, *Science*, 2015, **348**, 1347–1351.
- 40 D. H. Weinkauf, H. D. Kim and D. R. Paul, *Macromolecules*, 1992, **25**, 788–796.
- 41 H. H. Hoehn and J. W. Richter, *US patent 3,899,309*, 1975.
- 42 L. M. Robeson, *J. Membr. Sci.*, 2008, **320**, 390–400.
- 43 X. Chen, Z. Zhang, L. Liu, R. Cheng, L. Shi and X. Zheng, *Desalination*, 2016, **397**, 185–193.
- 44 C.-W. Tsai, C. Tsai, R.-C. Ruaan, C.-C. Hu and K.-R. Lee, *ACS Appl. Mater. Interfaces*, 2013, **5**, 5563–5568.

Table of Contents use only

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

Zain Ali, Federico Pacheco, Eric Litwiller, Yingge Wang, Yu Han and Ingo Pinnau*

Ultrathin, defect-free thin-film polyamide composite membranes developed for H₂/CO₂ separation exhibit mixed-gas performance far exceeding all state-of-the-art polymeric membranes.