INNOMEM

First Workshop

November 17-18, 2022
Hilton Sorrento Palace Hotel & Conference Center
Sorrento NA, Italy

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Program and abstracts

Institute on Membrane Technology
National Research Council of Italy

tecnalia
MEMBER OF BASQUE RESEARCH & TECHNOLOGY ALLIANCE

Summary

Program

November 16th – afternoon

Time		Duration (min)	
18:30	19:30	60	Welcome Drink & Registration

November 17th – morning

Time		Duration (min)	Title/Speaker	Affiliation
08:30	09:00	30	Registration	
09:00	11:00	120	Session I – Chair: *Adele BRUNETTI*	
09:00	09:10	10	Welcome Coordinator / Host organization *Jon ZUNIGA/Adele BRUNETTI*	TECNALIA/CNR
09:10	09:50	40	DeltaH, a new facility for the validation of H_2-related materials and components *Raffaele AGOSTINO*	University of Calabria
09:50	10:20	30	INNOMEM OPEN CALLS AND CATALOGUE *Filipa TOMÈ*	PNO
10:20	10:40	20	Palladium-based membrane plating system *Alba ARRATIBEL*	TECNALIA
10:40	11:00	20	Integrated membranes reactors for hydrogen separation *Jon MELÉNDEZ*	H2SITE
11:00	11:20	20	**Coffee break**	
11:20	13:00	100	Session II – Chair: Anita BUEKENHOUDT	
11:20	11:40	20	Development of new nanostructured hollow fiber membranes by surface modification for wastewater treatment *Céline CASETTA/Jeanne CASETTA*	IEM
11:40	12:00	20	Pilot line - Zeolite membrane fabrication *Hannes RICHTER*	FRAUNHOFER-IKTS
12:00	12:20	20	Showcase – Evaluation of zeolite and polymeric membranes in natural gas treatment *Andreas OSSMAN*	DBI
12:20	12:40	20	Pilot line - Flexible flat sheet polymeric membranes *Juliana CLODT*	HEREON
12:40	13:00	20	Pilot Line - Dual layer mixed matrix HF manufacturing system *Miren ETXEBERRIA-BENAVIDES*	TECNALIA
13:00	14:30	90	**Lunch**	

November 17th - afternoon

Time		Duration (min)	Title/Speaker	Affiliation
14:30	16:50	140	Session III – Chair: *Céline POCHAT-BOHATIER*	
14:30	15:10	40	Membrane technologies for new sustainable and resilient solutions in the wastewater sector *Anna Laura EUSEBI*	Università Politecnica delle Marche
15:10	15:30	20	Pilot Line for Fabricating Micro-Tubular Ceramic Membranes *Mahesan SUBRAMANIAM*	IC/AU
15:30	15:50	20	In-line modification of nano-coatings on hollow fiber membranes via E-beam irradiation *Kyra VAN DIJK*	UTWENTE
15:50	16:10	20	Showcase - Functionalized polymeric HF membranes for aqueous applications *Dennis REURINK*	NXFILTRATION
16:10	16:30	20	Oriented GO and ALD modified separation membranes *Nikolaos KANELLOPOULOS*	DEMOKRITOS
16:30	16:50	20	Possible uses of membrane technology in the context of the circular economy *Stefano BINOTTI*	CURSA
16:50	18:30		**Coffee break & Poster Session**	
20:00			**Dinner**	all

November 18th - morning

Time		Duration (min)	Title/Speaker	Affiliation
09:00	11:00	120	Session IV – Chair: Joaquin CORONAS	
09:00	09:40	40	Membrane and catalytic processes: their role in the energy transition *Girolamo GIORDANO*	University of Calabria
09:40	10:00	20	VIRTUAL LAB - TESTING AND CHARACTERIZATION *Giuseppe BARBIERI*	CNR
10:00	10:20	20	VIRTUAL LAB - MODELLING *Zançat SAHIN*	TUE
10:20	10:40	20	Pilot Line - Roll-to-Roll Coating of Advanced Nanophase-Segregated Ion-Exchange Polymer Membranes+Showcase – Anion-Conducting Membranes for Energy Applications *Lukas FISCHER*	UDE
10:40	11:00	20	Pilot line - Grafting of Ceramic Membranes *Anita BUEKENHOUDT*	VITO
11:00	11:30	30	**Coffee break**	
11:30	12:50	90	Session V – Chair: Giuseppe BARBIERI	
11:30	11:50	20	Modifications of hollow fibers by microfluidics *Joaquin CORONAS*	UNIZAR
11:50	12:10	20	Hollow fiber membrane spinning with improved geometric features *Maria RESTREPO*	RWTH
12:10	12:30	20	Showcase – Polymeric HF membranes with for ultra- and microfiltration *Daniel KNAUT*	RWTH/FILATECH
12:30	12:50	20	Methods of manufacturing hollow fiber modules *Krzysztof TRZASKUŚ*	MESEP
12:50	13:00	10	Remarks, conclusions, and final greetings	TECNALIA/CNR
13:00	14:00	60	**Lunch**	

Abstracts

DeltaH, a new facility for the validation of H_2-related materials and components

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The target for European decarburization encourages the use of renewable energy sources and H2 is considered the link in the global energy system transformation. So, research studies are numerous, but only few facilities can test materials and components for H2 storage. This talk offers a brief review of H2 storage methods and presents the preliminary results obtained in the DeltaH new facility and it will show the lab capabilities to analyze and evaluate the H2 effects on materials and so on their storage capability, both with mechanical tests, on materials and components, and adsorbent materials, connecting these storage abilities with morphological, structural, and chemical properties of materials. Thank to these skills, the facility represents an interdisciplinary laboratory able to help the research and industrial sector to develop and validate materials and components for the new hydrogen economy.

Palladium-based membrane plating system

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The aim of the pilot-plant is to scale-up and up-grading the production of Pd-based membranes for hydrogen separation. The development of supported thin Palladium based membranes (< 5 µm) it is critical due to the high cost of materials present at the membrane and to increase the production capacity. Tecnalia has been working on the manufacturing cost reduction and scaling up the electroless process technique.
Up to now Tecnalia has had the production capacity up to 8 membranes per batch up to 50 cm long and outer diameter around 14 mm. The required steps prior to electroless plating are manually performed equal to the plating system, which is not automatic. Two weeks are required for the membrane manufacturing. There are key parameters on the plating process that need to be controlled/monitored in order to manufacture a suitable thin Pd-based membrane, such as temperature and plating solution composition.
In the pilot plant system developed in Innomem (Figure 1 left), the pre-processing and plating steps will be automated and integrated, allowing to increase the production capacity by a factor of 4. Full control of the process will be established to assure online quality control, where temperature apart from other parameters, are monitored.
A non-destructive characterization technique (membrane permeation properties, Figure 1 right) has been also integrated at the pilot-line. Allowing to study the relationship between process conditions and membrane performance.

Figure 1. Membrane manufacturing pilot plant (left) and non-destructive permeation properties setup (right).

The manufacturing parameters at the pilot line has been tuned to improve the membrane quality (low nitrogen permeation properties) during INNOMEM project. 20 membranes have been delivered for the Show Case where membrane will be tested for pure hydrogen production.

KEYWORDS: Palladium; hydrogen;

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ACKNOWLEDGEMENT

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Integrated Membrane Reactor for hydrogen separation

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On an industrial scale, hydrogen is currently mainly produced by reforming of natural gas, an endothermic reaction system carried out at high temperature (>850 °C) followed by high and low temperature water-gas-shift reactors and final hydrogen purification step(s) [1], wherethe large amount of CO_2 emissions is one of the major drawbacks. About 48% of the global production for H_2 is currently coming from natural gas via steam methane reforming [2].

Among different technologies related to production, separation, and purification of H_2, membrane-based technologies are considered ideal candidate for substituting conventional systems. The specific thermodynamic constrains limiting traditional reactors can be circumvented by using innovative integrated systems, such as the so-called membrane reactors (MRs), engineering systems in which both reaction and separation are carried out in the same device [3]. The integration of reaction and separation in one multifunctional reactor allows obtaining higher conversion degrees, smaller reactor volumes and higher efficiencies compared with conventional systems.

Palladium-based membranes have also received a growing interest for the production and purification of H_2 since they can be used in the described membrane reactors where reaction and separation are coupled. Comparing with other membrane gas separation technologies,Pd based membranes have advantages of high hydrogen flux and exclusive perm-selectivity for H_2 due to the unique permeation mechanism [3]. These characteristics make Pd based membranes the most suitable device to achieve high hydrogen purity at a reduced cost.

Within INNOMEM project, H2SITE is building an integrated membrane reactor (IMR) that is an actual system to be proven in operational environment for fuel cell purity hydrogen production (Figure 1).

Figure 1.- Membrane integrated reactor skid

H2SITE systems can be applied and adapted to different gas streams or liquid feedstocks such as methanol, ethanol and/or ammonia, in distributed applications. Onsite H_2 generation eliminates the cost of transportation, compression, and decompression associated to centralized generation, which can amount an average of 80% of the total H_2 cost for industry.

This technology can be only used not only on H_2 generation applications but can be also applied to separate hydrogen from gas blends with concentrations as low as 5%. It allows the use of existing network infrastructure to transport hydrogen across long distances. If hydrogen is to be a widely spread fuel, large amounts of hydrogen will have to be transported. Pipelines can be used to move hydrogen at relative low cost. While hydrogen dedicated infrastructures are built, existing infrastructures can be used for blended hydrogen. Bloomberg New Energy Finance suggest that renewable hydrogen will be produced between 1-2.3 EUR/kg by 2030. However, intercontinental transportation of hydrogen, even at massive scale, can double the cost of hydrogen for distances over 1000 km [4].

KEYWORDS: On site hydrogen production; Integrated membrane reactor.

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ACKNOWLEDGEMENTS

This project has received funding from the European Union´s Horizon 2020 research and innovation program under grant agreement No 862330 (INNOMEM project). https://www.innomem.eu/

Development of new nanostructured hollow fiber membranes by surface modification for wastewater treatment

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For water treatment, polysulfone (PSU) is one of the leading choice to prepare hollow fiber (HF) membranes because of its excellent chemical and thermal resistance during membrane washing, and its good mechanical properties suitable for long-term use. However, the main drawback of this polymer is its intrinsic hydrophobicity that affects especially antifouling performances [1]. Modifying the PSU HF membrane surface by coating or by inserting nanoparticles can improve the surface hydrophilicity. In this work, two modification methods are investigated: off-line modification by deposition of TiO_2 oxide on commercial PSU HF membrane (supplied by our industrial partner POLYMEM) using atomic layer deposition (ALD) and on-line direct modification by using co-extrusion spinning using a second collodion containing graphene oxide (GO) to produce composite HF.

ALD is a unique technology [2] which allows the deposition of inorganic coating layers such as oxides with high uniformity and precise sub nanometer thickness control. Few recent studies have shown that ALD is applicable to flexible and temperature-sensitive polymeric membranes and suggested that it would increase their hydrophilicity, can affect their pore size and allow to create low-fouling membrane surface [3]. GO is an atomic-layer thick nanosheet 2D material that has attracted interest [4] because of its exceptionally high crystal and electronic quality. Its noteworthy hydrophilicity due to its oxygen-rich functional groups [5-6] is attractive for water treatment application.

These two processing routes have been developed in parallel to produce surface modified HF membranes. The production of composite HF was realized on a pilot line allowing a spinning speed of 6-13 m min^{-1} with a capacity of 2 kg collodion. The TiO_2 deposition was achieved in ALD chamber with the capacity of 25 HF of 50 cm length each. The obtained HF membranes were evaluated in terms of permeability, mechanical and antifouling properties. Their characteristics were extensively studied by means of several techniques, such as Scanning Electron Microscopy (SEM), Raman, Energy Dispersive X-Ray Analysis (EDX), Water contact angles (WCA) and X-ray Photoelectron Spectroscopy (XPS).

KEYWORDS: Membrane, Atomic layer deposition, Graphene oxide

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Pilot line - Zeolite membrane fabrication

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Zeolite ZSM-5-membranes are ideal for separating organic solvents from water [1], branched and non-branched hydrocarbons [2] or higher hydrocarbons from natural gas [3]. Zeolite SAPO-34 membranes of great interest for CO_2/CH_4-separation. However, for industrial application the synthesis of zeolite membranes has to be scaled-up in terms of membrane geometry and manufacturing technology.
Zeolite membranes were prepared by slurry coating for seeding, hydrothermal crystallization and detemplating at 450°C on ceramic support tubes. For ZSM-5 membranes in first step ceramic supports with a length of 250 mm and an increasing number of channels (1, 4, 7, 19 channels) were used. The success of the synthesis was checked by PV-separation of ethanol from water (5 wt% ethanol) at 40°C. In a second step, 15 membranes with a length of 600 mm and 19-channel geometry were synthesized in a single batch. Two batches were run. The membranes were examined using permporometry. In case of SAPO-34 in first step the length of single channel tubes was increased step wise from 100 mm up to 500 mm. In a second step reproducibility and membrane quality was improved. All membranes were characterized by single and mixed gas permeation.
In PV tests with ZSM-5 membranes prepared on ceramic supports with different numbers of channels all membranes showed a clearly hydrophobic separation behavior and were able to prove their functionality. Two 600 mm long membranes in 19-channel geometry from each synthesis batch of 15 membranes were examined using permporometry. It was found that all membranes achieved a relative permeance, i.e. a flux through membrane defects, of <1%. With three membranes, the value was even 0.1%. Excellent CO_2/CH_4 selectivities of around 200 were found for SAPO-34 membranes on 105 mm long tubes in single and mixed gas permeation. However, simply increasing support tube length reduced selectivity down to 30. Synthesis optimization enabled membranes with CO_2/CH_4 selectivities of around 250 to be produced on both 250mm and 500 mm long support tubes with best selectivity of 1,250.
Excellent ZSM-5 and SAPO-34 membranes in increased geometry and batch size are available for separation tasks in the field of natural gas and biogas processing.

KEYWORDS: zeolite membranes, gas separation, natural gas treatment, membrane manufacturing

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Showcase – Evaluation of zeolite and polymeric membranes in natural gas treatment

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Flat sheet polymeric membranes from pilot line #5 (Helmholtz Zentrum Hereon) and zeolite membranes manufactured from pilot line #6 (Fraunhofer IKTS) were tested under almost realistic conditions. The separation of CO_2 from natural gas streams was investigated with TFCM and CHA membranes. A further task of lab testing was separation of n-butane from natural gas. POMS und ZSM-5 membranes were employed for this separation. In the relevant pressure, temperature and flow velocity range membrane samples were tested. In addition, the influence of typical impurities like water and hydrogen sulfide on membrane performance was investigated.

KEYWORDS: Natural gas processing, carbon dioxide, n-butane

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Pilot line - Flexible flat sheet polymeric membranes

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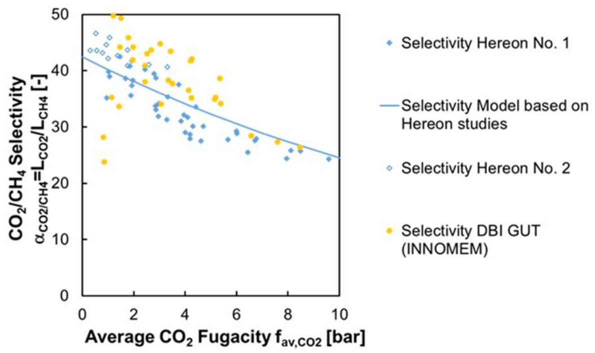
Hereon's Institute of Membrane Research is developing innovative membranes and membrane processes. This includes developing new materials, processing these materials into membranes as well as designing modules and pilot plants in which these systems are made ready for implementation. All steps are accompanied by comprehensive computer simulations. The core of Hereon's activities in INNOMEM is the improvement and operation of a pilot line for the production of thin film composite membranes for the separation of CO_2 and supplying the membranes installed in advanced membrane modules to project partners.

In PL #5 the production of membranes for CO_2/CH_4 separation using a specifically synthesized polymer were scaled up to 8 m^2, physical ageing was tested and the production of membrane envelopes to equip a module is in progress. The membranes were characterized using the single gas pressure increase (variable pressure, fixed volume) method at Hereon and with a mixed gas set-up at DBI (Showcase 2). The experimental results fit well into to those previously conducted at Hereon, using CO_2/CH_4 mixed gas (20 to 47 mol-% CO_2) at feed pressures between 5 and 50 bar, specifically with respect to the membrane selectivity.



Upgrading of the pilot line during the M30 period of INNOMEM included environmental and health aspects like an improved enclosure and suction of the coating device for the thin film composite membrane production. Additionally, a drawer for the applicator roller and the coating solution basin was implemented to the pilot line to minimize health risks and accelerate cleaning and exchange of the applicator roller. Old motors of the coating machine were exchanged, and electricity meters of to all machinery correlating to membrane production were implemented in order to monitor the energy consumption. Furthermore, the documentation of process data and quality parameters was improved to some extend with an automatic batch number registration.

Pilot line - Dual layer mixed matrix HF manufacturing system

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Large-scale separation applications demand highly productive membranes. Therefore, commercial separation membranes are processed into a highly elaborated structure: an extremely thin dense top layer (100 – 200 nm) supported by a porous layer. Preferentially, this structure is processed in the form of a hollow fiber (HF) because fibers can be densely packed into separation modules (over 10000 m^2/ m^3 membrane area per module volume) and increase furthermore the productivity. The introduction of well-defined nanostructured porous fillers with pores close to the kinetic diameter of the gas molecule into polymer matrix potentially combine the advantages in separation performances of filler particles with the processability of polymers [1]. The concept of dual layer HF membranes applied for MMMs aims to create a mixed matrix selective top layer and at the same time minimize the quantity of filler by adding this component only in the outer polymer solution while the inner polymer solution is filler free.

Fabrication of asymmetric HF membranes is done by dry followed by wet phase inversion method and the top layer and the support are formed simultaneously. There are multiple parameters that influence this process. Small fluctuations in each parameter can have a strong effect over final fiber gas permeation properties. Therefore, process parameter precise control is essential when experimental campaigns are conducted for the elaboration of a new spinning recipe. Also, in line monitoring and registration of all spinning parameters with the objective to automatically correlate fabrication parameter with membrane separation properties in a sequent step via a customized software will allow easy and in deep data analysis and interpretation of the results.

Within INNOMEM project, Tecnalia´s spinning line has been up-graded in terms of production capacity and improved control over process parameters. The up-grade will be demonstrated with a dual layer mixed matrix hollo fiber membrane.

Figure 1. Up-graded dual layer mixed matrix membrane spinning line at Tecnalia

KEYWORDS: hollow fiber spinning; mixed matrix membrane

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Membrane technologies for new sustainable and resilient solutions in the wastewater sector

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To date, advanced and resilient water and wastewater treatments are increasingly aimed to remove emerging pollutants, to recover flows and materials and to possibly reuse water also with synergic approach between productive activities and water sector. The presentation will highlight the applications, also in innovative contexts of European or international projects, of membrane technological solutions, for the improvement of the qualitative aspects and for the valorization of the urban and industrial water and wastewater flows.

Pilot-Line for Fabricating Micro-Tubular Ceramic Membranes

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This pilot line is for fabricating inorganic micro-tubular-membranes with unique bi-modal pore structures, and of various macro-structures (single-layer, multi-layer, and multi-channel etc.) for advanced membrane separation and catalysis processes. The membranes fabricated would be used for developing compact and high throughput membrane units (microfiltration & ultrafiltration), compact reactors enabling high conversion and selectivity, together with significant reduction of catalyst needed. Current preparation of such membranes is limited to laboratory research, which offers good flexibility of investigating membrane materials and membrane structures. However, the capacity of current fabrication system is limited to preparing 20-30 m of single-channel membrane per day, or 5-10 m of multi-channel membranes per day, which needs to be significantly increased for high TRL applications.

This project aims to upscale/upgrade the current system for continuous production of high quality nanostructured inorganic micro-tubular-membranes of a wider variety of macro- and micro-structures, with accurate, robust, and systematic control of all fabrication parameters for processing a wider range of inorganic materials. Production extrapolation to 10 times the capacity of current membrane fabrication system, more robust control of fabrication parameters, greater handling of more viscous suspension, with membrane straightening, cutting, and picking-up integrated and systematically monitored for greater consistency in macro- and micro-structures, reducing 30-40% of fabrication time.

The upscale/upgrade targets include 400-500 m of single-channel membrane or 50-100 m of multi-channel membrane per day, at a rate of 1.5-2.0 and 0.5-1.0 m per min, respectively. Meanwhile, the pilot line will incorporate in-line control of key membrane fabrication parameters via programmable logic control (PLC) system and a haul-off cutting system.

KEYWORDS: micro-tubular inorganic membranes; membrane separation; membrane reactor.

ACKNOWLEDGEMENTS

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In-line modification of nano-coatings on hollow fiber membranes via E-beam irradiation

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In the industry hollow fiber (HF) membranes are produced using a continuous spinning process. Often a surface modification on nanoscale is done to enhance their performance. This is mostly done off-line and batch-wise, in one or even several post-treatment steps (layer-by-layer). All these off-line treatments are accompanied with a lot of handling of the membranes, which are sensitive for damaging or defects. Within the scope of the INNOMEM project, University of Twente/EMI Twente upgraded their hollow fiber pilot spinning line with an integrated, in-line, surface modification technology by means of electro-beam. Treatmentby e-beam can improve the stability of the membranes and potentially enhance the selectivityof the separation layer(s). The penetration depth of the e-beam allows for modifications within the porous structure or at the inner side of the hollow fibers instead of only at the visible surface (as in the case with UV).

The pilot line is equipped with a winder to allow fabrication of larger bundles of hollow fiber membranes with sufficient length to allow making full scale modules. With the in-line dope preparation (mixing, filtering and degassing), precise control of the area around the air gap/chimney and well controlled, heated coagulation and rinsing baths, we can guaranteethe product of fibers with consistent performance. It is possible to do multiple passes throughthe e-beam so an evenly e-beamed fiber will be collected on the winder at the end.

Specifications E-beam:

High voltage range: 80-200 kV
Beam current range: 0 – 29 mA
Beam power; max 4.000 W Beam width 27cm

KEYWORDS: surface modification, e-beam irradiation, nanofiltration, hollow fiber membranes, crosslinking

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Oriented GO and ALD modified separation membranes

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In SC #7 (PL11), ultrafiltration commercial PAN membranes are being modified by Layer by Layer (LbL) deposition of oriented PEI (polyethyleneimine) -functionalized Graphene Oxides (GOs)[1] to produce NF membranes with tailored bivalent-monovalent ion rejections. In addition, cost-effective and eco-friendly electrochemical graphite exfoliation was deployed to produce better quality GOs and Holey Graphene Oxides (HGOs)[2] to replace Hummer's method. The initial pilot unit was upscaled from a unit treating 5 membranes with a specific surface area of 0.001 m^2 to a module with a total membrane surface area of 0.72 m^2. Finally, an additional up-scale was also carried out, with a total membrane surface area of 0.9 m^2 tested in different operation conditions, by applying pressure or vacuum to optimize the GO layer nanostructure. The membranes exhibited a $MgCl_2$ rejection of 93.5% and a NaCl rejection of 63.8% with the flux of 10.5LMH. The low water permeance is due to the small nanopore size of the UF substrate. The same LbL methodology will be applied on hydrophobic ultrafiltration membranes (with 200nm instead of 20nm) to fabricate high-permeance Membrane Distillation (MD) membranes. The produced NF and MD GO membranes will be integrated to develop a membrane-lithium recovery showcase[3] to replace the conventional solar evaporation lithium recovery systems. The fractionation of monovalent ions from bivalent ions can be deployed to recover Li from the leach liquor of spent lithium-ion batteries.
In SC #10 (PL12), the TEOS/ozone methodology has been applied to tailor the nanopore size by depositing SiO_2[4,5]. An in-line probe-molecule permeation system was used to monitor the evolution of the nanopore size during the CVD or ALD processes. To this end, an in-situ Helium gas relative permeability and differential permeability will be deployed to evaluate the evolution of the nanostructure. The H_2O/H_2 selectivities obtained are of the order of 8. Based on these results, a membrane-intensified showcase for dehydrating methanol to DME is being developed. In addition, the upscaled 0.8 meter and the original CVD systems, these have been upgraded and automated to allow the cost-effective modification of nanoporous membranes by Atomic Layer Deposition. Several Ni, Pd and Al precursors will be used on nanoporous membranes to produce dehydration and dehydrogenation ALD modified nanoporous ceramic membranes and a second dehydrogenation membrane-intensified showcase will be developed.

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Membrane and catalytic processes: their role in the energy transition

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The trouble in the energy market, especially in this last year, and the need to reduce greenhouse gas emissions (CO_2, but also CH_4) push scientific research towards new processes for renewable energy production and new technologies with a reduced CO_2 footprint.
In this field both membrane and catalytic processes play an important role. Membrane catalytic reactors are able to increase the conversion in equilibrium reactions by the selective separation and an example of this positive impact is showed in MeOH to DME reaction when using a zeolitic membrane as catalyst.
A second example of an industrial application of the membrane in energy transition is the purification of bio-methane from municipal wastes by anaerobic digestion. Starting from raw bio-gas, the final step of the process is the separation of CH_4 from CO_2 carried out, in the more innovative plants, by ceramic membranes, in order to obtain a bio-methane with a purity of 99.99%.
Finally, an overview of the key minerals for energy transition (Co, Li and rare earth) will be presented and integrated with the new worldwide perspective of hydrogen production, storage and utilization.

Pilot line - Grafting of Ceramic Membranes

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About a decade ago VITO, in cooperation with University of Antwerp, developed a novel post-synthesis modification method for ceramic membranes using Grignard chemistry [1]. The method allows to graft a wide variety of organic groups onto the total pore surface of different porous metal oxide membranes. This introduces specific surface functionalities /affinities which can significantly enhance the performance in liquid filtrations. In contrast to other methods such as organosilanation, Grignard grafting creates a highly stable, unique metal-carbon bond and a relative simple surface chemistry, as no polymerization occurs. The flexibility offered is great: different metal oxides with a variety of pore sizes were successfully grafted, and also modification of powders or 3D structures proved feasible.

Grignard grafting of ceramic membranes proved advantageous in three fields: 1. Enhanced performance of nanoporous membranes in a variety of organic solvents (OSN) [2], 2. Unparalleled low fouling behaviour in a variety of difficult waste waters [3], 3. Affinity-based separations allowing to separate molecules with similar size but different functionalities.

Development started grafting small-scale tubular membranes in stirred glass wear, but soon evolved to grafting in filtration mode in a glove box. This was successfully scaled up to commercial size multichannel membranes (1,2 m long 19 to 163 channel membranes). Next, a closed-loop pilot system was build, able to graft up to 5 membranes simultaneously in one week. This Atex set-up allowed to graft membranes for different piloting campaigns. Moreover, the system is not limited to Grignard grafting alone. Within INNOMEM, VITO further upgraded/upscaled this pilot for increased production volumes (simultaneous grafting of 10 instead of 5 membranes) and improved production time (24h instead of one week). Moreover, a new pre-treatment was developed avoiding the high vacuum used previously. Together with membrane supplier LiqTech, VITO will demonstrate the beneficial use of grafted membranes for the purification of a specific waste water (Show Case #1).

KEYWORDS: ceramic membranes; grafting; anti-fouling; OSN.

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Modifications of hollow fibers by microfluidics

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Microfluidics (MF) was first originated in separation applications. This was followed by the development of microfluidic based reaction technologies. In fact, preparation of hollow fiber membranes (HFMs) by MF simultaneously implies a chemical reaction (e.g. that corresponding to the crystallization of a MOF [1] or to the synthesis of a polymer [2]) on the inside of a very small in inner diameter pipe (ca. below 1 mm). In microfluidics the thicknesses of the mass and heat boundary layers (those in which the viscosity affects the layer fluid in the immediate vicinity of the corresponding bonding surface) are closer to the characteristic dimensions than in conventional systems[3]. In general, MF supplies suitable approaches for the synthesis of nanoparticles, hierarchical structures and continuous layers which may act as membranes. These advantages of MOF are the following[3].i) The simple and versatile synthesis of nano and microparticles. ii) The use of small reagent volumes, that leads to small carbon footprints and lower production costs than other synthesis methods. This is intimately related to the lower energy consumption per unit temperature, because of the efficient heat transfer during the reaction. iii) Reaction selectivity enhancement due to the precise control over local conditions. iv) Precise control of the synthesis in terms of particle size and layer thickness in membranes. v) Up-scaling potential by parallelization for both powders and membranes. vi) In membranes synthesis, the porous hollow fiber runs both as a reactor and a support for the MOFs or zeolites. vii) Versatility in step-sequencing synthesis, overall when the synthesis of composite membranes with several structures can be combined, or when carrying out post-functionalization processes.

More specifically regarding the synthesis of MOF based HFMs, besides the preparation of efficient separation membranes, MF allows the control of the selective membrane thickness,[4] the incorporation of MOF nanoparticles during the interfacial polymerization of polyamide membranes[5] and also the sequential functionalization of the MOF selective layer to enhance its separation properties[6] .Finally, the achieved membranes by this technique may find application in both liquid phase (e.g. nanofiltration) and gas phase separation (e.g. the separation of CO_2 and/or H_2 containing mixtures).

KEYWORDs: Microfluidics; Hollow fiber membrane; Molecular separation.

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Hollow fiber membrane spinning with improved geometric features

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Reengineering membrane geometries drives the improvement of sustainable and efficient membranes. The development of better membrane materials with enhanced permeability causes unfavorable concentration polarization in operation, resulting in mass transfer limitations. Thus, an improvement beyond the material is vital for efficient membrane processes. In flat sheet and tubular membrane modules, state-of-the-art strategies to counteract these performance-reducing effects focus on inducing local turbulence promotion. However, hollow fiber membranes lack the incorporation of genuine turbulence promoting features. This is because of their fragile nature, small size, limited spatial accessibility and tedious additional assembly or modification effort for thousands of single fibers per module. We overcome said prevailing limitations by developing a robust and scalable spinning methodology that integrally incorporates turbulence promoting microstructures inside hollow fiber membranes in a single production step.

Turbulence promoting structures intend to deflect the fluid flow and induce secondary flow patterns. Such structures include surface patterning and static mixer inserts. However, reported hollow fiber membrane geometry modifications are restricted to straight structures, which limits their capability to promote turbulence. Hence, twisting the microstructures during fabrication advances its functionality to manipulate hydrodynamics. Therefore, we propose a membrane spinning methodology that builds on our novel home-engineered rotating spinneret platform technology "Rotation-in-a-Spinneret". We combine this technology with established wet spinning techniques utilizing phase inversion. Moreover, interchangeable and customized microstructured 3D printed spinnerets allow the creation of various hollow fiber membrane geometries. Our methodology intrinsically fuses hollow fiber membrane fabrication with implementing turbulence promoting microstructures into the lumen of the hollow fiber.

KEYWORDS: Static-Mixer-Membranes, Rotation-in-a-Spinneret, Customized microstructured spinnerets, Turbulence propoters, 3D printing.

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Methods of manufacturing hollow fiber modules

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Depending on the diameter of the fiber, two module manufacturing techniques are commonly practiced: centrifugal potting and stationary potting. In stationary potting, the module is positioned vertically and the resin is injected into the bottom potting form where it hardens. Gel time of the resins used in this manufacturing technique is relatively long to guarantee proper infiltration of the adhesive between the fibers. Due to the presence of voids between the fibers, the capillary rising of the resin in stationary potted modules occurs, reducing the active length of the membrane fibers. The severeness of the capillary rising drastically increases for fibers with small diameter (e.g. dialysis, gas separation). To counteract the capillary rising effect, the centrifugal potting process was implemented. Here module is positioned vertically or horizontally in a centrifuge and is rotated during the potting process. After injection of the resin into the ends of the module, centrifugal force enforces flow of the resin between the fibers securing complete infiltration of the voids between the fibers. The centrifugal force can be adjusted with rotation speed and module length; thus, penetration of the glue is possible even for very small capillaries. Moreover, centrifugal force with opposite vector to the capillary force limits the severeness of the capillary rising. An application of the centrifugal force and quick potting process allows precise definition of the potting line and active length of the fibers.

Me-Sep, under umbrella of INNOMEM projects developed a pilot line for centrifugal potting of hollow fiber modules of the industrial size (8”x100 cm). INNOMEM (Open Innovation Test Bed for nano-enabled Membranes) aims at developing and organizing a sustainable Open Innovation Test Bed (OITB) on membranes for different applications. The OITB will offer a network of facilities and services through a Singl-Entry Point (SEP) to companies.

KEYWORDS: MEMBRANE module; Centrifuge; Pilot line.

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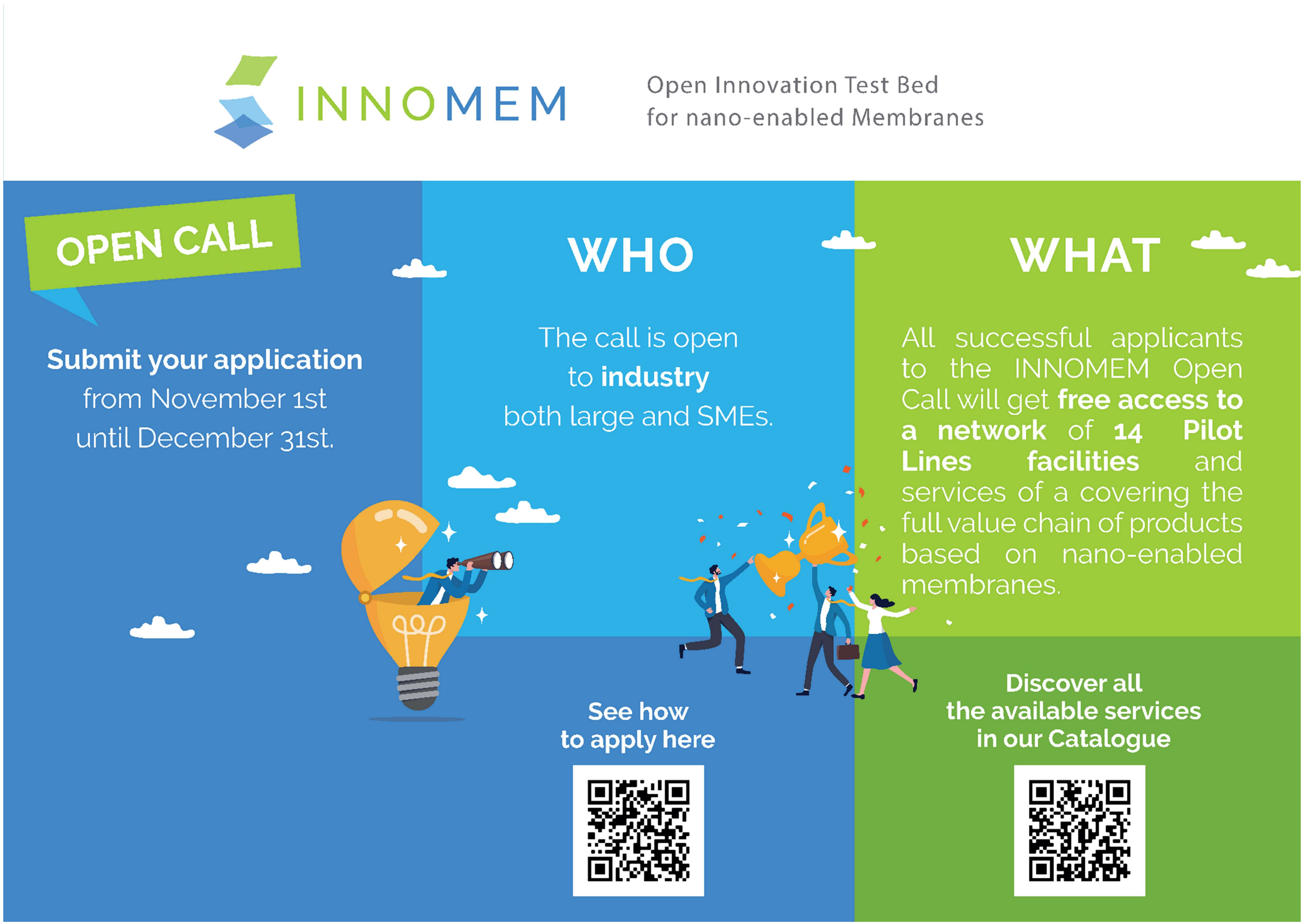
Open calls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