Joint Workshop on

Scale-up of Pd Membrane Technology

From Fundamental Understanding to Pilot Demonstration


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Scope & Objectives of the Workshop

Thanks to their outstanding hydrogen selectivity, palladium membranes have attracted extensive R&D interest in the 21st century with promising “breakthrough” applications for hydrogen power, refining and petrochemicals, hydrogen vehicles and many more. The workshop is the follow-up of the first “Pd-membrane Scale-Up” workshop (Roma, Italy, November 2012), a unique knowledge-sharing experience for both the EU-funded organizing projects and all participants. This experience has strengthened the belief that there is a need and a ground for a second workshop, where the whole Pd-membrane R&D spectrum “From Fundamental Understanding to Pilot Demonstration” will be further explored together by representatives of academia, research institutions and industrial stakeholders.

Organizing Committee

Frans van Berkel (ECN, Netherlands; CARENA), Chair
Laurence Bosch (EMH, Belgium; CARENA)
Gilbert Rios (EMH, Belgium; CARENA)
Alberto Giaconia (ENEA, Italy; CoMETHy)
Emma Palo (KT, Italy; CARENA, CoMETHy)
Adele Brunetti (UniCal, Italy; DEMCAMER)
Enrico Drioli (UniCal, Italy; DEMCAMER)
Thijs Peters (SINTEF, Norway; ReforCELL)
The supporting Projects

**The CARENA project** (Large collaborative project) aims to create technologies - **CA**talytic **R**eactors based on **N**ew **mA**terials - enabling an efficient conversion of light alkanes and CO₂ into higher value chemicals.

www.carenafp7.eu

CARENA aims for breakthroughs in catalytic membrane materials and processes by having materials sciences and engineering progress at all scales. Therefore an essential aspect of CARENA is the multi-scale approach from molecule to industrial plant, based on the following activities:

1. **CREATE** novel process schemes that turn novel materials and reactions concepts into innovative industrial processes with new opportunities, such as reduction of the number of process steps and elimination of energy intensive separations. CARENA targets 30% lower CAPEX and operating costs.

2. **DEVELOP** reactor concepts that match and control highly intensified rates of mass and heat transfer resulting from application of novel materials and architectures. Process intensification combining in-situ reaction and separation will be designed for equilibrium-limited reactions of strong industrial relevance.

3. **OPTIMIZE** membranes and catalysts through the development of novel nano-architected materials and their integration e.g. using nano-membrane coated catalysts and multi-layer membrane/catalyst interfaces to enable selective conversion of raw feedstocks such as light alkanes (C1, C3) and CO₂ by generating (in-situ) active species (O*, H⁺, H₂O₂, ...).

**19 Partners**

- Energy Research Centre of the Netherlands, The Netherlands (Coordinator)
- ARKEMA, France
- Akzo Nobel Industrial Chemicals B.V., The Netherlands
- Johnson Matthey PLC., United Kingdom
- Saint Gobain CREE, France
- Acktar Ltd., Israel
- CEA, Commissariat à l’Energie Atomique, France
- CNRS- Institut de Recherches sur la Catalyse et l’Environnement de Lyon, France
- CNRS- Institut Européen des Membranes de Montpellier, France
- Stiftelsen SINTEF, Norway
- KT - Kinetics Technology S.p.A., Italy
- Linde AG, Germany
- Process Design Center, The Netherlands
- TECHNION - Israel Institute of Technology, Israel
- University of Salerno, Italy
- University of Twente, The Netherlands
- Diamond Light Source Ltd., United Kingdom
- European Membrane House, Belgium
- Leibniz University of Hannover, Germany
The **DEMCAMER project** aims to develop innovative multifunctional Catalytic Membrane Reactors based on new nano-architected catalysts and selective membranes materials to improve their performance, cost effectiveness over 4 selected chemical processes for pure hydrogen, liquid hydrocarbons & ethylene production. It is conducted by 18 partners and coordinated by Tecnalia.

http://www.demcamer.org

The aim of DEMCAMER is to develop innovative multifunctional Catalytic Membrane Reactors (MR) based on new nano-architected catalysts and selective membranes materials to improve their performance, durability, cost effectiveness and sustainability (lower environmental impact and use of new raw materials) over four selected chemical processes for pure hydrogen, liquid hydrocarbons and ethylene production:

- Autothermal Reforming (ATR)
- Fischer-Tropsch Synthesis (FTS)
- Water Gas Shift (WGS)
- Oxidative Coupling of Methane (OCM)

Moreover DEMCAMER will bring the proof of concept of these novel catalytic MRs by the set-up and validation of pilot prototypes relevant for each process.

**Scientific and Technical Objectives**

- New membrane materials with improved separation properties, long durability and reduced cost
- New nano-architected catalysts with better performance and at reduced cost
- Understanding of the fundamental physicochemical mechanisms and the relationship between structure/property/performance and manufacturing process in membranes and catalysts
- Design, model and build-up of novel more efficient MR configurations
- Validation of the new MR configurations, at semi-industrial prototype level, in four selected chemical process (ATR, FTS, WGS, and OCM) for pure hydrogen, liquid hydrocarbons and ethylene production
- Improving the cost efficiency of MRs by increasing their performance, decreasing the raw materials consumption and the associated energy losses
- Use of new raw materials (i.e. convert non-reactive raw materials)

Assessment of the health, safety and environmental impact of the four catalytic MR developed processes, a complete LCA of the developed technologies will be performed.

**Partnership Synergies**
The ReforCELL project aims at developing a high efficient PEM fuel cell micro combined heat and power cogeneration system based on a novel, more efficient and cheaper hydrogen reformer together to the new design of the subcomponent for the BoP. 11 partners are involved in this project and coordinated by Tecnalia.

http://www.reforcell.eu/

Advanced Multi-Fuel Reformer for Fuel CELL CHP Systems

ReforCELL aims at developing a high efficiency (above 42% electric and 90% total) PEM based micro-CHP system through:

1. Design, construction and testing of an advanced catalytic membrane reactor for pure hydrogen production from hydrocarbon reforming and
2. Design and optimization of all the components for the integration of the membrane reformer to the fuel cell stack.

The main idea of ReforCELL is to develop a novel more efficient and cheaper membrane reactor in order to intensify the process of hydrogen production through the integration of reforming and purification in one single unit. In order to achieve this objective, novel stable catalysts and high permeable and more stable membranes need to be developed. Afterwards, suitable reactor design will be realized and tested at laboratory scale for later scaling up to prototype scale (5 Nm³/h of pure hydrogen) and tested in a CHP system.

The connection of the novel fuel processor within the CHP will be optimized by designing heat exchangers and auxiliaries required in order to decrease the energy losses.
The CoMETHy project (Compact Multifuel-Energy To Hydrogen converter) is co-funded by the EU’s 7FP for the Fuel Cells and Hydrogen Joint Technology Initiative (grant agreement n. 279075). The project’s objective is developing a membrane reformer for hydrogen production adaptable to different heat sources. The project is implemented by 12 partners coordinated by ENEA (Italy).

http://www.comethy.enea.it

Objectives
CoMETHy aims at developing a compact and fuel-flexible steam reformer to convert reformable fuels (methane, biogas, bioethanol, etc.) to pure hydrogen, adaptable to several heat sources (solar, biomass derived fuels, fossil, etc.) depending on the locally available energy mix.

The following systems and components are developed:
- An advanced catalyst for the low-temperature (< 550°C) steam reforming processes
- A membrane reactor to separate hydrogen from the gas mixture
- The application of an intermediate low-cost and environmentally friendly liquid heat transfer fluid (molten nitrates) to supply process heat from a multi-fuel system.

Reducing reforming temperatures below 550°C by itself will significantly reduce material costs. The process involves heat collection from several energy sources and its storage as sensible heat of a molten salts mixture at 550°C. This molten salt stream provides the process heat to the steam reformer, steam generator, and other units.

The choice of molten salts as heat transfer fluid allows improved compactness of the reformer, rapid and frequent start-up operations with minor material ageing concerns, enhanced heat recovery from different external sources, and coupling with intermittent renewable sources like concentrating solar power plants with heat storage systems to provide the renewable heat when required.

Methane, either from desulfurized natural gas or biogas, and ethanol are considered as a reference feed material to be converted to hydrogen. The project involves RTD activities on the single components, followed by proof-of-concept of the integrated system at the laboratory and pilot scale (2 Nm³/h of hydrogen) and cost-benefit analysis.

12 Partners
- ENEA, Agenzia per le Nuove Tecnologie, l’Energia e lo Sviluppo Economico Sostenibile, Italy
- Processi Innovativi Srl., Italy
- Acktar Ltd., Israel
- Technion - Israel Institute of Technology, Israel
- Fraunhofer - Gesellschaft Zur Foerderung Der Angewandten Forschung E.V - Institute for Ceramic Technologies and Systems, Germany
- University of Salerno, Italy
- Centre for Research and Technology Hellas, CPERI/CERTH, Greece
- Aristotle University of Thessaloniki, Greece
- University of Rome - La Sapienza, Italy
- Energy Research Centre of the Netherlands, ECN, The Netherlands
- GKN Sinter Metals Engineering GmbH, Germany
- University of Rome - Campus Bio Medico, Italy
Programme

Thursday 20th November 2014

8:30-9:00 – Registration

9:00-10:00 – Opening & Welcome
9:00-9:15 – Opening speech
9:15-10:00 – Project introduction of workshop partners

- Introduction to CoMETHy: Compact multi-fuel-energy to hydrogen converter (Alberto Giaconia, ENEA, Italy)
- Introduction to ReforCELL: Advanced multi-fuel reformer for fuel CELL CHP systems (José Luis Viviente)
- Introduction to DEMCAMER: Design and manufacturing of catalytic membrane reactors by developing new nano-architectured catalytic and selective membrane materials (José Luis Viviente)
- Introduction to CARENA: Pd-membrane based reactors for C1 to C4 conversion (Arend de Groot)

10:00-10:20 – Coffee Break

Session 1: Fundamental Aspects of Membrane Technology

1a- H₂-Transport mechanism/modelling

- 10:20-10:40 – Wim Haije (ECN), Hydrogenography and hydrogen transport phenomena
- 10:40-11:00 – Hilde Johnsen Venvik (Norwegian University of Science and Technology), Investigation of fundamental phenomena affecting the performance of thin Pd-Ag membranes
- 11:00-11:20 – Alessio Caravella (UniCal, ITM-CNR), Concentration polarization and inhibition by CO in supported Pd-based membranes

1b- Membrane robustness/impact of contaminants

- 11:20-11:40 – José-Maria Sánchez-Hervás (CIEMAT), Impact of syngas components - CO₂, H₂O, and CO - on hydrogen permeance behaviour over relevant testing times
- 11:40-12:00 – Thijs Peters (SINTEF), The performance of Pd-Ag alloy membrane films under exposure of trace amount of H₂S

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**12:00-13:00 – Lunch (Incl. Poster session)**

**1c- Membrane stability/degradation mechanisms**

- 13:00-13:20 – **Andreas Goldbach (DICP)**, Stability of Pd-membranes under practical operation conditions
- 13:20-13:40 – **Frans van Berkel (ECN)**, Long term testing of Pd-membranes under methane steam reforming conditions
- 13:40-14:00 – **Amanda Lewis (Pall)**, presenting on behalf of **Doug Way (CSM)**, High temperature stability of Pd alloy composite membranes and their application to membrane reactors

**Session 2: Manufacturing and Scale-up Challenges**

**2a- Membrane manufacturing**

- 14:00-14:20 – **Annarita Salladini (PI)**, Optimization of porous metal support for Pd-deposition
- 14:20-14:40 – **Alfredo Pacheco Tanaka (Tecnalia)**, Development of Pd-based supported membranes
- 14:40-15:00 – **Luigi Toro (Ecorecycling)**, Pd-recycling and LCA

**15:00-15:20 – Coffee Break**

**2b- Membrane module design and construction**

- 15:20-15:40 – **Giuseppe Barbieri (ITM CNR, UniCal)**, Membrane reactors innovating H$_2$ steam upgrading
- 15:40-16:00 – **Moshe Sheintuch (Technion)**, Reactor modelling, simulation and operating parameters optimization
- 16:00-16:20 – **Fausto Gallucci (TU/E)**, Fluidized bed membrane reactors for hydrogen production and CO$_2$ capture

**16:20-17:00 – Interactive Discussions Day 1:**

**Theme:** “Research as usual and die or recognize fundamental shortcomings and live?!”

**Day 1:** This session addresses selected critical hurdles in the Pd-membrane development and the required (fundamental) input in order to solve the following topics: membrane robustness and membrane manufacturing.

**17:00-18:00 – Poster Session (Incl. Drinks/Networking) + Possibility for ECN Lab Tour**

**20:00 – Workshop dinner & Networking**
Friday – 21st November 2014

9:00 – Workshop Opening

Session 3: Towards Industrial Applications

3a- Membrane development at the industry

- 9:00-9:20 – Annarita Salladini (PI), Solar assisted reforming and CCS in novel process schemes for H₂ production-techno economic assessment
- 9:20-9:40 – Markus Haydn (Plansee SE), Metal-supported Pd-membrane for hydrogen production
- 9:40-10:00 – Andy Tsai (T3 Scientific LLC), The road to robust Pd-membrane
- 10:00-10:20 – Scott Hopkins (Pall corporation), Pd-membrane development at Pall

10:20-10:40 – Coffee Break

- 10:40-11:00 – Xavier Quek (Johnson Matthey), Pd-membrane activities at Johnson Matthey
- 11:00-11:20 – Tony Boyd (MRT), Summary of fluidized bed reactor and membrane experience at Membrane Reactor Technologies

3b- Process integration and techno-economics

- 11:20-11:40 – Adele Brunetti (ITM-CNR, UniCal), How can membrane reactors can affect H₂ production cycles
- 11:40-12:00 – Leonardo Roses (HyGear), Simulation, integration and assembly of pilot-scale fluidized bed membrane reactors
- 12:00-12:20 – Giampaolo Manzolini (Polytecnico de Milano), Techno-economic optimization of Pd-based membrane reactors in PEM micro-CHP systems
- 12:20-12:40 – Spyros Voutetakis (CERTH), Integrated membrane reactor testing and modeling

12:40-13:40 – Lunch (incl. Poster session)
Session 4: Alternative Applications - Dehydrogenation Reactions Gas to Liquids

- 13:40-14:00 – Roland Ditmeyer (KIT), Overview on Pd-membrane reactors
- 14:00-14:20 – Thijs Peters (SINTEF), Investigation of Pd-based membranes in propane dehydrogenation (PDH) processes
- 14:20-14:40 – Emma Palo (KT), Novel process scheme for selective propane dehydrogenation
- 14:40-15:00 – Emma Palo (KT), Novel process scheme for syngas production for gas to liquid processes

15:00-15:20 – Coffee Break

15:20-16:00 – Interactive Discussions Day 2:

Theme: “Research as usual and die or recognize fundamental shortcomings and live?!”

Day 2: This session addresses selected critical hurdles in the Pd-membrane applications and the required (fundamental) input in order to solve the following topics: membrane economics, cost and implementation and membrane application in chemical processes.

16:00-16:15 – Closing Speech

16:15-17:15 – Possibility for ECN Lab Tour