INTERNATIONAL JOINT WORKSHOP

ON

PALLADIUM MEMBRANE TECHNOLOGY SCALE UP

12-14 November 2012 - Rome, ITALY

Venue : Visconti Palace Hotel
Via Federico Cesi 37. Rome, Italy

Workshop objectives, summary and outcomes

Thanks to its outstanding hydrogen selectivity, palladium membranes have attracted extensive R&D interest in the 21st century. It is envisaged as a potential breakthrough technology on hydrogen production, with promising applications for hydrogen power, refining and petrochemicals, hydrogen vehicles and many more.

CACHET-II, CARENA and CoMETHy are three research projects funded by the European Commission through FP7. Although the projects were originated from three different funding priorities, CACHET-II under the ENERGY, CARENA under the NMP and CoMETHy under the FCH JU priority, the three projects have found commonality and synergy in their research objectives related with the development of palladium membranes for hydrogen production.

Due to such technology synergy, the three projects have joined force to organize a workshop together, focusing on “palladium membrane scale-up challenges and solutions”.

The three-day workshop was organized in Rome on 12-14th November 2012, including two days of presentations and interactive discussions in Rome, and a site visit to Tecnimont KT membrane reforming pilot plant at Chieti.

The workshop brought together more than 70 participants from more than 45 different organizations worldwide, with a broad participation of industrial stakeholders besides representatives of research institutions and universities. In addition to the members of the three organizing projects, a good number of “external” participants and projects also presented and contributed to the interactive discussion. Therefore, the event proved to be a unique knowledge-sharing experience for the three projects and all participants, providing a clear picture of the status of palladium membrane technology in view of its commercialization. The workshop covered a good breadth of topics that are critical for palladium membrane technology scale-up: from the fundamentals of palladium membranes, support and seal manufacturing, mechanical design, to various concepts of membrane module design and system integration; from lab-scale long-term stability testing results to industrial pilot plant operational insights.

The closing discussion session sketches a picture of the general opinion on the status of the Pd-technology and an overview of the critical issues to be addressed in the near future.

Individual Scale-up Challenges

Scale-up of Pd/Pd-alloy deposition process

This session focused on different thin Pd-alloy film fabrication methods, and their challenges related to up-scaling. The electroless plating method, presented by ECN and Tecnalia, has low cost and can deposit Pd on any for the solution accessible surface, and is thus shape-independent. However, plating becomes increasingly more complex with the number of alloying elements. The sputtering method, introduced by HEF, enables production of complex alloys with controlled stoichiometry in an easily controlled manner, but the method is currently less developed for large-scale membrane production. Large sputtering equipment, though, that could be applied in a large-scale demonstration is available.

The preparation of thin membranes directly on porous supports puts strong demands on the support quality making the support a large cost contributor. To circumvent this, SINTEF developed a two-step manufacturing process based on magnetron sputtering. Here, a defect free Pd-alloy membrane is first prepared by sputtering deposition onto the 'perfect surface' of, e.g. a silicon wafer. In a second step the membrane is removed from the wafer and transferred to a porous stainless steel support. Currently, this method is being scaled-up.

To conclude, various Pd-alloy film fabrication methods thus exist for up-scaling, but the optimum way is at the current stage difficult to identify. This will not only depend on the methods themselves, but also on IP issues.

Scale-up of membrane support manufacturing

This session covered the use of porous ceramic and metallic tubes as Pd-membrane support. Presentations on the ceramic supports were given by St. Gobain and IKTS Fraunhofer. IKTS indicated clearly that there is already a lot of ceramic-based membrane area installed in industrial environment. In particular, the application of ceramic membranes in the nuclear industry exceeds millions of m2. For chemical industrial application it is in the order of 2000 m2. Ultra filtration

membranes seem feasible as supports for Pd-membranes but have to be qualified. The limitations in the scale-up of the ceramic supports depending on the manufacturing process were highlighted. The maximum length of 1- 2 m is limited by the sintering process. The tube diameter is in principle limited by the green forming technique, i.e. till 100 mm for extrusion, till 300 mm for tape rolling and compaction pressing. Further limitations to the scale-up of the dimensions of ceramic tubes are imposed by the mechanical strength requirements. It was also indicated that coating layers for defect free deposition of Pd can be made by dip coating and slurry coating in a wide range of pore sizes.
Presentations on the metallic supports were given by GKN and Plansee. GKN showed that the use of metallic supports has the benefit of high mechanical strength, stability of shape, thermal shock resistance and good seal-ability or connections by welding. The concept of the multi-layer design for the sintered metal supports by GKN opens up the possibility of a wide range of porosity and pore sizes plus the possibility of a gradient of pore sizes in the metallic support. In addition a diffusion bonding procedure can be applied to prepare a seamless bond between a dense and porous metal part, which might facilitate the sealing of Pd-membranes. The required diffusion barrier layer for Pd-deposition can be applied by wet powder spraying. A critical point in the application of the metallic support according to GKN is the reduction of surface defects and roughness. Plansee has demonstrated the feasibility of porous metal tubes as support for Pd-membranes by showing working metallic supported Pd-membranes.

Membrane seal technology development

Good sealing is a key issue in membrane technology, in particular a big problem is still represented by the sealing of ceramic tubes and their connection to the metal tubes. Two specific contributions were given on this topic during the workshop.
The activity performed at the Institute of Metal Research in the framework of CACHET-II project is relevant to the development of new brazing materials for ceramic supports. In particular, the direct metal-ceramic sealing technology foresees the introduction of metallic transition layer to improve the adhesion of Pd film to the glass sealer and gas-tightness of the seals. Long term stability tests also indicated satisfied H2 recovery and purity.
Graphite sealing was also studied by IDT SINYUAN Sealing Technology for both plate and tubular membranes, evidencing that the typical characteristics of graphite, such as high temperature resistance, chemical resistance to most media, no ageing, no embrittlement, make it an optimal choice for sealing manufacturing material.

Membrane module mechanical design

A huge number of parameters may influence and affect the design of a membrane module: choice of the module, selection of sweep gas configuration, integration of catalyst and membrane, heat management and so on. The aim of this session was to give first of all a general overview of all these main parameters, two actual examples of module design were given, one provided by ECN addressing the methanol synthesis from methane and developed in the framework of CARENA project, the other given by Technip France developed in the framework of CACHET-II project.
Core of the session was the discussion relevant to the two ways of integration of reaction unit with membrane separator, i.e the membrane integrated directly inside the reaction environment (in the so called “closed architecture”) or outside the reaction environment (in the so called “open

architecture”). The latter represents the configuration implemented in Tecnimont KT facility in Chieti Scalo.

<u>Membrane Implementation & Operation</u>

Simulation and modelling of membrane unit

Design criteria for the case of a methane steam reforming solar-heated reactor (COMETHY) and a propane dehydrogenation reactor (CARENA) have been presented. For the case of single reaction under isothermal conditions a preliminary modelling has been approached through the Pe number (reaction kinetics very fast). When considering secondary reactions, the contact time (catalyst density) should be optimized. The hydrogen permeation inhibition due to the presence of other gases (CO, CO2, methane) is very important but literature data are missing. Studies of the thermal design have been also presented: 1-D non-isothermal, Autothermal and 2-D non-isothermal.

Reactor design activities carried out in the CACHET-II project concerned a 2D axisymmetric model for tubular membrane reactors. Mass and energy balances have been described as well as the kinetics (related to the WGS reaction). For the hydrogen permeation through Pd a pressure correction factor has been used in the Sieverts’ law while for the support the dusty gas model has been proposed. Finally, results of the model validation through separation tests have been presented.

Process integration and techno-economics

Application of low temperature reforming (methane and ethanol) to concentrated solar plant (CSP) has been presented with description of process options (multi-stage membrane reformer, partial recirculation of retentate) and membrane reactor design. An analysis of the investment cost of the plant vs. the methane conversion for different kinds of membranes (composite and dense of different thickness) has been presented: 1) Pd-membrane introduction is always convenient when the cost of the membrane is limited below 6,000 €/m2 and permeance > 10 Nm3/h/m2/bar0.5, 2) when the membrane cost is within the range 2,000-6,000 €/m2 there may be an optimal conversion in the membrane reformer, depending on the CSP plant and membrane specific costs.

Another talk presented the results of CACHET-II on the integration of Pd-based H2-selective membranes in integrated gasifier combined cycles (IGCC). The selected gasification system is based on Shell technology. Two different dry feeding systems are investigated: the first is a state-of-the-art nitrogen-based lock hopper charger while the second uses CO2 as pressurization gas. The net electric efficiency of the two plants is evaluated as a function of the hydrogen recovery factor (HRF) and the membrane feed pressure in order to minimize the membrane surface area. 90% HRF and 54 bar feed pressure are the best operating parameters which correspond to a net electric efficiency of 39% both for N2 and CO2 feeding system. The cost of CO2 avoided is calculated as a function of a parameter named MI which represents the membrane development in terms of performances and costs. Results show that an improvement of membrane technology is necessary to match the state-of-the-art CO2 capture plant, even though membranes show good potentiality for cost abatement. At the state-of-the-art technology, Pd-membranes are too expensive for integration in a large power plant, where a high membrane area is required. Nevertheless, membranes present unique features which still make the technology an interesting option for medium term hydrogen and power co-production.

An analysis concerning the NGCC cycle studied in CACHETII has been presented. Among the process cases considered, the oxy-burner without expander presents maximum net efficiency and smaller membrane area. Other parameters have been optimized: the ATR temperature and the S/C ratio. The techno-economic analysis verified that the Pd-membrane based concept with oxy combustion is the optimum choice for the CO2 stream purification (i.e. increased energy efficiency than MDEA pre-combustion CO2 capture technology and reduced cost of CO2 avoided, given that the membrane cost does not exceed the threshold of about 4.5 k€/m2).

Membrane stability and robustness under long-term operation in industrial environment

The section's attention was focused on the membrane characteristics regarding stability and robustness on industrial case since excellent resistance to long term operation and poisoning are key parameters in the commercialization of membrane technology.
Results coming from different membranes testing applied to Steam Reforming Reaction (Shell and Processi Innovativi/Tecnimont KT) and Water Gas Shift Reaction (Dalian Institute of Chemical Physics) were reported.

All data confirmed the membrane stability of Pd based membranes over significant reaction time and under real reaction environment.

Start-up/shut-down/maintenance requirements

The session represents a sort of collection of the main experimental results on semi-industrial scale in terms of membrane operation, such as start-up and shut-down phases gained by Tecnimont KT and Tokyo Gas in their membrane steam reforming plants of capacity of 20 and 40 Nm3/h respectively. The two plants are different regarding the type of membrane integration: open architecture for the former, closed architecture for the latter but for both plants the durability of the membrane module and the reliability of the system have been demonstrated.

<u>Alternatives</u>

Alternative applications of palladium membrane, i.e. beyond hydrogen production

The session discussed alternative applications where Pd Membranes are applicable and included two presentations. In the first session presentation, Prof. Fausto Gallucci from the Eindhoven University of Technology presented the basic concept of the REforCELL Project, which aims at developing a high efficiency CHP system based on the design, construction and testing of an advanced reformer for pure hydrogen production with optimization of all the components of the reformer and the design and optimization of all the components for the connection of the membrane reformer to a fuel cell stack. The main idea of REforCELL is to develop a novel more efficient and cheaper multi-fuel membrane reformer for pure hydrogen production in order to intensify the process of hydrogen production through the integration of reforming and purification in one single unit. In the second presentation by Dr. Kyriakos Panopoulos from the National Technical University of Athens potential applications of Pd membranes in thermochemical biorefinery operations were examined. The potential for chemicals production derived from biomass has been investigated concerning the type of membrane catalyst, maturity of technology, conversion selectivity readiness etc and it was shown that the implementation of Pd membranes on chemicals production (methanol, H2O2, dehydration etc) has a better distribution of reactants & thermal management.

Alternative configurations of palladium membrane, i.e. not palladium deposited on a tubular support

The session included one presentation from Dr. Silvano Tosti from ENEA, concerning the development and applications of Pd-Ag dense permeator tube. It was shown that selectivity and durability of composite Pd-membranes are strictly related to the hydrogen uploading into Pd-Ag. Self-supported Pd-Ag tubes produced at ENEA by cold-rolling and diffusion welding have been characterized in long term permeation tests demonstrating complete permselectivity and durability, whereas reaction tests have been also carried out by verifying high hydrogen yields.

Closing discussions

The closing discussion session of the workshop was moderated by:
- Dr. Rune Bredesen, a research director at SINTEF Materials and Chemistry in Norway;
- Dr. Gaetano Iaquaniello, Vice President Technology at Technip KTI in Italy;
- Prof. Gilbert Rios, chair of the European Membrane House in France.

A summary of the discussion session per representative is given in the following.

Rune Bredesen (SINTEF)

In his introduction, co-Chairman Dr. Bredesen pointed out that at present Pd-alloy membranes represent the best combination of flux and selectivity of known high temperature inorganic membranes. The remarkable hydrogen flux for the 2 μm thick Pd-23% Ag SINTEF membranes on macro porous stainless steel support mentioned in several presentations illustrates the potential. For affordable scale-up of the Pd-alloy membrane technology 4 points were raised for discussion by Dr. Bredesen as critical for success:

- ✓ Long term stability and robustness
- ✓ High flux and selectivity
- ✓ Cheap manufacturing technology
- ✓ Cost effective process integration

During the Workshop evidence of long term membrane stability had been given both from Tokyo Gas and Shell in the reforming of natural gas at 450-550ºC and 10-35 bar pressure. Both companies reported a stable operation that produced hydrogen with purity from 98-99.99%, and that temperature cycling was possible. A reasonable conclusion from the Workshop is that (for sulfur free) operation in natural gas appears possible. Concerning the flux it was pointed out that membrane reactor modeling shows that concentration polarization effects are important and that

the support may contribute significantly to the resistance. It was concluded that further development of the support is important to combine high permeability and mechanical strength. Also new module design can contribute to the reduction of concentration polarization effects.
The development of very thin Pd-alloy composite membranes has shifted the main cost of the membrane part from the Pd-alloy film to the support. Further research to development of cheaper support manufacturing processes is therefore recommended. Also the sealing and module design must be further developed to reduce the cost. Finally the importance of defining the right processes for Pd-alloy membranes and their smart integration was underlined in the discussion.

Gaetano Iaquaniello (TKT)

Iaquaniello's speech was related on how to move ahead with membranes into the next step: commercialization.
Dr. Iaquaniello particularly focused on two key aspects.
The first is the quest for a process where the insertion of the membrane module into the so-called membrane reactor architecture will greatly improve the competitiveness of the process itself. He indicated alkanes-to-alkenes dehydrogenation and low-temperature steam reforming as the more promising ones. In the former, the lowering of temperature may eliminate the coking formation where today the existing processes need to work in batch sequences or rely on continuous catalyst regeneration. In the latter, the steam reforming reaction duty may be reduced and the supply of heat may be provided by the exhaust flue gases from a gas turbine (for hydrogen and power production) greatly enhancing the overall energy efficiency. The quest is not however finished, conversely we need to have more resources to investigate in this direction.
The second point was related to the cost of membranes. In any process on which we are going to envisage advantages, such advantages are related to the final costs of membranes, which in turn depend on their geometry and the Membrane Manufacturing Strategy (MMS). Such MMS will need to adopt a geometry able to sustain a cost reduction based on the economy of scale, once a cumulative volume of production high enough will be reached. A precondition for such behavior is the emerging of one or two technologies which can support such MMS: 3-6 meter long cylindrical membranes, with a 1-3 micron Pd/Ag layer, supported on porous SS structure, with an internal diameter of 1-2", where the Pd/Ag layer is applied through Physical Vacuum Deposition (PVD), have been indicated and supported by other colleagues as the most promising ways to reach such industrial productions.

These two points are going to be conjugated, the first is going to indicate a way and will create the economical support to develop the second.

Gilbert Rios (EMH)

Gilbert Rios reminded participants that after the time of scientific results, there must be also a time for decision and for proposals in order to be able to preserve what has already been done, and to continue (if your action was prompted by a vision and not simply conceived as an entertainment supported through public funding...). A lot of good achievements have been obtained in the field of H_2 production with Pd membranes: efficient membranes (ECN), nice pilot-plant (Chieti), a lot of excellent scientific, technical and demonstration results, partnerships set-up... It would be necessary now from his point of view:

- To preserve and reinforce if possible the groups of actors directly concerned with the topic: a good base is the staff assembled for this workshop!
- To communicate about this Workshop and to open debates (when appropriate) with other groups working on similar topics: during next ECCE9 in the Hague? during ICCMR11 in Porto? .... Could this communication be insured starting from a kind of platform as suggested by Arend? or another form of organization?...
- To work as soon as now so to try to integrate such large project as SPIRE and others of the same kind...

Follow-up workshop

In accordance with the comments of Dr. Gilbert Rios, it was decided to form a committee who will take care of a follow-up of the current workshop. It is envisaged that a follow-up workshop will be organized approximately two years from now, which coincidently marks the final phase of both CARENA and CoMETHy EU-projects.

The following committee members have been suggested:

- Dr. Alberto Giaconia (ENEA, Italy)
- Dr. Sadika Guedidi (EMH, France)
- Dr. Thijs Peters (SINTEF, Norway)
- Dr. Frans van Berkel (ECN, Netherlands)