AMPEA workshop:

"Materials for membranes in energy applications: gas separation membranes, electrolysers and fuel cells"

Organized by:

SINTEF

Oslo (Norway); February 7-8th, 2017

METALLICA

GREEN

The Research Council of Norway

This document reports briefly on the agenda of the workshop, and summarizes the discussion following the lectures given on four thematic areas:

- High temperature electrolysers and fuel cells
- Ceramic membranes
- Metal based membranes and electrodes
- PEM fuel cells and electrolysers

EERA European Energy Research Alliance

AMPEA Advanced Materials and Processes for Energy Applications

TOPIC

Tuesday, February 7th-8th 2017: ***Workshop on "Materials for membranes in energy applications: gas separation membranes, electrolysers and fuel cells"***

Focus: The transformation to sustainable power generation to mitigate greenhouse gas effects is one of the key challenges to mankind and its implementation will impose significant societal changes. There is a strong need for new energy technology with very low greenhouse gas emissions. Membrane separation and electrochemical conversion are examples of key processes that enter into many highly efficient technologies related to clean energy. Membrane separation may, for example, be integrated into technology used for sustainable power generation and hydrogen production with CO_2 capture from fossil fuels, while fuel cells and electrolysers are technologies for smaller scale energy efficient production of electricity and hydrogen. These technologies are expected to have significant impact in future energy systems and thus give large commercial opportunities to the technology vendors. The present workshop aims at addressing recent progress and current challenges on materials, cells and stack development of relevance for dense ion conducting membranes for gas separation, electrolysers and fuel cells operating at low, intermediate or high temperature.

The workshop is sponsored by the following projects:

The Research Council of Norway

AMPEA: EERA Joint Programme for Advanced Materials and Processes for Energy Applications (AMPEA)

Grant agreement: 257728/E20

METALLICA

METALLICA: Metal supported proton conducting electrolyser cell for renewable hydrogen production

Grant agreement 221819/E20

GREEN

GREEN CC: Graded membranes for energy efficient new generation carbon capture process

Grant Agreement Number: 608524

Agenda

Tuesday, February 7th 2017: ***Workshop on "Materials for membranes in energy applications: gas separation membranes, electrolysers and fuel cells"***

- **10:45-11:15**: Coffee and registration
- **11:15-11:30**: Welcome to the workshop
- **11:30-12:30**:
  - Plenary lecture 1: Truls Norby, *Fundamentals of materials for high temperature fuel cells, electrolysers, and gas separation membranes*
  - Plenary lecture 2: Magnus Thomassen, *Material challenges for PEM fuel cells and electrolysers; Degradation mitigation and cost reduction*

- ***12:30-13:30****: Lunch break*
- **13:30-15:00**: Second session of workshop: High temperature electrolysers and fuel cells; **Session sponsored by METALLICA**

Chair: Yngve Larring

  - Marit Stange: *Fabrication of metal supported proton ceramic electrolyser cells (PCEC)*
  - Ragnar Strandbakke: *Proton Ceramic Electrolysers; operation, challenges and development*
  - Remi Costa (invited lecture): *Metal Supported Solid Oxide Cells: performances and limitations*
  - Jose Serra: *Novel electrodes for Solid Oxide Electrochemical Cells*

- ***15:00-15:30****: Coffee break*
- **15:30-17:00**: Third session of workshop: Ceramic membranes; **Session sponsored by Green CC project.**

Chair: Marie-Laure Fontaine

  - Kjell Wiik: *The concept of self-healing membranes: Basic ideas and observations from diffusion couples and membrane testing*
  - E. Rebollo: $BaCe_{0.65}Zr_{0.20}Y_{0.15}O_{3-\delta}$ *doped ceria ceramic composites for hydrogen separation*
  - Stefan Baumann: *Oxygen Transport Membrane Modules for Oxyfuel Applications developed in GREEN-CC*
  - Wolff-Ragnar Kiebach: *Long-Term Stability of Oxygen Transport Membranes in simulated Flue Gas Environments – Lesson learned in the GREEN-CC Project*

- **17:05-17:25:** Flash presentation for each poster with max 3 slides: 2 min
- **17:25-18:00:** Discussion about H2020

- **18:00-20:00:** Buffet with poster session

Wednesday, February 8th 2017:

- **08:30-09:00**: Coffee and welcome
- **09:00-10:30**: Fourth session: Metal-based membranes and electrodes

Chair: Marit Stange

- S. Fasolin: *HiPIMS deposition of dense Silver-Palladium films for hydrogen separation*
- M. Marono: *Development of novel Pd-alloy Membranes based on improved supports*
- Thijs Peters: *Palladium (Pd) membranes as key enabling technology for pre-combustion CO_2 capture and hydrogen production - from lab-scale to demonstration*
- Anja Bieberle-Hütter: *High Ion Flux Plasma Nanostructures for Electrochemical Applications*

- ***10:30-10:45**:Coffee break*

- **10:45-12:30**: Fifth session: PEM fuel cells and electrolysers

Chair**:** Magnus Thomassen

- M.N. Tsampas: *Towards visible light activated porous photoanodes in conjunction with polymeric electrolyte photoelectrochemical cell with gaseous reactants*
- Feina Xu: *Investigation of Electro-osmotic Drag Coefficients in Nafion Membrane by Electrophoresis NMR*
- *Frederic Chandezon: Advanced ionomer membranes for PEMFC: design and studies*
- Paul Inge Dahl: *Supported catalyst particles for PEM fuel cells by one-step flame synthesis*

- ***12:30-13:30**: Lunch and departure*

General discussion for each session

Session 2: High temperature electrolysers and fuel cells: key messages from general discussion

Materials and components:

- Good to excellent performance of composite electrodes were reported. The electrodes are produced by infiltration of secondary phase(s) in an oxide based porous backbone. This electrode design enables to embed all desired conduction pathways and catalytic activity which can't be achieved in a single phase material. This route is to be developed further and several aspects should be focused:
  - Process control of the infiltration step should be developed. In current work, it is hard to determine the quantity of material infiltrated in backbone of button cells, and this will be more problematic for larger samples. Automated infiltration would be desirable. In-situ exsolution of nanoparticles from host matrix could provide an interesting and simple way.
  - Long-term stability of the nano-particles infiltrated in the backbone is questioned: will there be grain growth/rearrangement and/or loss of percolation during ageing?

Manufacturing of cells:

- Need to improve cell's quality (reduction of pinholes, etc.): in particular, it is emphasized that the quality of the supporting layers (cermet or alloy) is of utmost importance to achieve leak tight membranes and reducing the need for coating thick layers
- Need to rationalize the processing routes: many protocols investigated to produce a complete single cell require several casting, coating and firing/sintering steps. This has strong impact on the roll-to-roll yield of the manufacturing, and is also contributing to increase the production cost.

Cells/stack performance:

- Industries want to see long term testing of stacks before engaging themselves in commercial deployment: activity on long term testing (> 5000 hours) should be prioritized in new projects to demonstrate the robustness and efficiency of the technology;
- Degradation of cells/stacks may only start after several khours of operation, *e.g.*, as observed with metal supported cells. This also points out for the need for performing R&D projects with activity on long term testing at an early stage of the projects to be able to initiate and study degradation rate and mechanisms underpinning the degradation. Stress test ageing protocols should be defined also for this purpose.
- Degradation mechanisms are dependent on materials, architectures and manufacturing routes selected for each cell / stack. Changing one process parameters (*e.g.* dopant, sintering temperature, layer thickness, etc.) may induce other degradation mechanisms and it is therefore recommended to address relevant mechanisms for the specific cells/stacks investigated.

Session 3: Ceramic membranes: key messages from general discussion

Self-healing:

A new approach to develop self-healing of ceramic membranes was presented during the workshop. This brought discussion about the nature of defects appearing in membranes and when/how they form, *e.g.*, during manufacturing and/or operation. Degradation mechanisms during membrane operation may involve many phenomena associated with cations diffusion, thermomechanical stress, etc. The exact nature or roles of defects/cracks potentially yielding failure of membranes during operation is therefore unclear. This makes it difficult to propose a self-healing approach for preventing formation of these defects/cracks during operation. On the other hand, defects such as pinholes or small cracks formed because of manufacturing process can be more easily detected and possibly remedied by clever nano-engineering and designing of the membranes. Provided that self-healing of defects is efficient, this would enable to:

- Alleviate the requirements for manufacturing defect-free layers as the defects, and therefore, use cheaper methods/environment (no need of clean room).
- Increase roll-to-roll yield

Scaling up:

Mass production of ceramic membranes is challenging as integration of membranes in industrial plants typically requires large surface area achieved by millions of tubes/plates. There are limited work in Europe on demonstration of oxygen transport membranes in large scale production, and even less on hydrogen transport membranes, although the latter may benefit from the same production route. This may be due to:

- Efficiencies of OTM/HTM technologies integrated in various processes (IGCC, oxy-fuels, etc.) have been reported by several groups and diverge significantly, depending on the integration schemes. This is however, an information which is critical in order to raise industrial interest, and in particular, convince ceramic producers to invest efforts in these technologies. Further work on optimizing integration schemes and selecting appropriate industrial sector is required. It is emphasized that membranes technology offers the advantages of being down-scalable and can therefore be competitive with cryogenic distillation (State-of-the-art production of pure oxygen at large scale) for lower scale application. Furthermore, they can also be integrated in catalytic reactors for chemical production, which is an area that should be investigated more intensively.
- Achieving high yield of production is critical to ensure sustainable business. Per today, the membranes are produced as thin dense layers coated on porous supports. Thin membranes are required to achieve sufficient flux. Tolerable leakage rate (and therefore defects) is highly dependent on the flux of the membranes and the required oxygen purity for the process. While high flux membranes can tolerate few pinholes (typically less than 1 ml/min.cm^2), they mostly suffer from long term degradation. The more stable membranes have lower flux, around 1-2 ml/min.cm^2 in operation. Hence, the requirements for achieving (almost)-defect free membranes are stronger.

- Search for materials exhibiting both high flux and long-term stability is still required, as per today, this solution is not proven at significant TRL (TRL>5).

Materials:

Several presentations highlighted promising results on composite membranes (OTM and HTM). This strategy may overcome limitations of single phase materials and further efforts should be dedicated to study long term operation of these composites.

Session 4: Metal-based membranes and electrodes: key messages from general discussion

Pd-based membranes:

There has been significant progress in the development and scaling-up of Pd-based membrane technologies up to industrial scale demonstration. It is emphasized that the cost of the thin Pd membrane layer in itself does not constitute the major part of the cost of an installed membrane area. The porous metallic or ceramic supports, on which the thin Pd layer is deposited or coated, contribute roughly to a similar cost than the Pd layer. This is explained by the simple and recyclable techniques used for making the membranes (*e.g.* sputtering) and the need for a smooth support with low and homogeneous surface porosity. This is usually achieved by addition of inorganic coating (using e.g. simple methods such as dip-coating or calcination) and/or polishing of the support. In addition, the high pressure membrane module involves a substantial cost.

To reach high hydrogen flux, the Pd based membrane should be thin (below 2-5 microns) and this puts strong requirements on the topography of the supports. Further efforts should be focused on developing processes for increasing surface quality, ensuring high gas flow through the support and decreasing production cost. In addition, an industrial scale membrane manufacturing should be set-up.

As for the other membranes, long term testing of the membranes should be carried out in order to determine process relevant operation efficiencies and degradation rates.

Novel route for highly porous metallic layers:

A new manufacturing route making use of He plasma to nano/micro engineer porous metallic layers has been presented. It offers new possibilities for designing highly catalytic layers for various applications, including fuel cells and electrolysers (electrodes); membranes (catalytic surface exchange layers), PEM, PEC, etc. As emphasized in the other sessions, manufacturing high surface area layer is critical for improving performance of many electrochemical devices. Further work on investigating the possibilities for using this method to nano/micro-engineer oxide layers is therefore highly desired.

Session 5: PEM fuel cells and electrolysers: key messages from general discussion

This session clearly highlighted synergies between technologies and cross-fertilization of ideas emerging from various disciplines and attendants background:

- Alternative OER electrodes of PEMFC are investigated as SnO_2 oxides coated with Pt nano-particles finely dispersed in the porous layers synthesized through a one-step flame spray pyrolysis methods and the possibility to scale-up the production of such materials. Their performances as a catalyst for the ORR reaction shows promising results although presently below performances of the state-of-the-art Pt/C catalyst.
- A novel concept combining PEMFC and photoelectrochemical cells technologies, called PEM-PEC has been presented. The philosophy is to benefit from the accumulated expertise on materials, characterization methods and devices to develop new materials, concepts and methods for photoelectrochemical cells. New porous photoanodes were developed showing promising results in terms of performances of the cells. Whereas the solar fuels community benefited from the expertise from thin films solar cells and dye-sensitized solar cells, there is an interest to foster synergies between PEMFC and solar fuels communities.
- Multiscale characterization of PEFMCs and the extraction of relevant parameters from the molecular scale to the device scale as well as simulation methods were also presented: this includes a NMR-based technique to extract electro-osmotic drag coefficients in Nafion membranes; a coupled AFM-Raman technique for imaging of membranes; electron tomography to image Nafion coating in membrane electrode assemblies of PEFMCs; X-ray and neutron scattering techniques for time and spatially resolved multi-scale studies of materials and processes in PEFMCs from the molecular to the device scale, with a special focus on *in situ* and *operando* methods; molecular dynamics based studies to study the formation of Nafion films on substrates or to understand the dynamics of water confined in membranes. for fuel cells
- Finally, a sol-Gel strategy to convert commercial membranes into high performing membranes in terms of ageing and durability was also presented.

This session highlighted that although PEM fuel cells approach a large deployment on the market there are still many challenges to be tackled in terms of developing new cost effective catalyst layers and polymer membranes, in terms of polymer membranes (ageing) and in terms of methods to study ongoing processes (*e.g.* ageing and corrosion). This showed the relevancy of *in situ*/*operando* methods based on large scale instruments (neutrons, synchrotron radiation). Last, the photoelectrochemical cells community from the expertise of the PEMFC community to develop new materials and concepts.