MINUTES

FCH JU Projects Workshop

Degradation of PEM Fuel Cells
- experience exchange and discussions

April 3rd + 4th 2013 at SINTEF, Oslo, Norway

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Objective

As part of the FCH JU funded projects related to PEMFC degradation, STAYERS, KEEPEMALIVE, PREMIUMACT and EURECA, a workshop on degradation of PEM fuel cells was organized by SINTEF. The workshop aimed at gathering the partners within these projects to exchange experience and discuss PEM degradation issues, potentially focussing on:

- ➢ *experience/results from the relevant FCH JU projects*
- ➢ *MEA sensitivity to gas impurities*
- ➢ *components and cell lifetime prediction methods/models*

The workshop focus was thus to provide for enhanced insight into PEM fuel cell degradation issues and how to counteract these to ensure longer lifetime and more reliable fuel cell operation.

Scope

Degradation and cost are still seen as the main barriers to large scale market introduction of PEM fuel cell systems. FCH JU has funded several projects on this topic since the programme started in 2008, four of them are STAYERS, KEEPEMALIVE, PREMIUMACT and EURECA. During the FCH JU Review Days in November 2012, the external reviewers recommended to have an inter-project exchange of experience. Since this also was planned as an activity within the STAYERS project, this event will now be arranged before some of the projects are coming to an end.

Program PEMFC Degradation workshop, SINTEF OSLO room 4+5

Wednesday April 3rd

12:00-13:00	Lunch (in the SINTEF canteen, reception will show you the way)
13:00-13:10	Coffee and welcome
13:10-13:45	Tour de table and short intro (2 slides) on the relevant projects (STAYERS, PREMIUMACT, KEEPEMALIVE and EURECA)

13:45-16:30 Topic 1 "Contaminants – H2 and air quality" (15 min pres + 10 min disc)

13:45-14:10	Thomas Martin, SolviCore:
	Comparison lab test - field test, reversible - retrievable - irreversible decay, contaminants investigation.
14:10-14:35	Jorg Coolegem, Nedstack:
	30,000 h operation of a 70 kW stationary PEM fuel cell system using hydrogen from a chlorine factory, effect of contaminants on FC performance
14:35-14:50	Coffee break
14:50-15:15	Jari Ihonen, VTT:
	Enrichment of impurities and inert gas in anode recirculation loop – experience from HyQ project and Finnish national projects.
15:15-15:40	Robert Alink, Fraunhofer ISE:
	STAMPEM - degradation issues regarding mobile fuel cells
15:40-16:30	Discussions (+ refill coffee)

16:45-19:00 Topic 2 "Degradation mechanisms" (15 min pres + 10 min disc)

16:45-17:10	Sylvie Escribano, CEA:
	Premium Act results on the degradation of PEMFC operated with reformate fuel (in-situ, ex-situ, single cells, stacks and post mortem)
17:10-17:35	Andrea Casalegno, POLIMI
	Experimental and modelling analysis of DMFC degradation
17:35-18:00	Nadine Jacobs, Next Energy
	PEM degradation at Next Energy
18:00-18:15	Coffee break
18:15-19:00	Discussions

Thursday April 4th

09:00-13:00 Topic 3 "Diagnostics and AST protocols" (15 min pres + 10 min disc)

09:00-09:25 Kaushik Jayasayee, SINTEF:
AST protocol vs. real life operation and CO contamination

09:25-09:50 Laila Grahl-Madsen, IRD
Real-life experience obtained in during field test with hydrogen fuelled LT PEM µCHPs

09:50-10:10 Coffee break

10:10-10:35 Astrid Stadlhofer/Martin Geymayer, TU Graz
Results from KEEPEMALIVE

10:35-11:00 Luis Colmenares, SINTEF
Catalyst ex-situ degradation experiments/KEEPEMALIVE results

11:00-12:00 Discussions, intro lifetime prediction, George Tsotridis, JRC

12:00-13:00 Open discussions with lunch served, summary questionnaires

13:00 End

Summary of the presentations

Topic 1 "Contaminants – H2 and air quality"

Thomas Martin, SolviCore: *Comparison lab test - field test, reversible - retrievable - irreversible decay, contaminants investigation.*

Components investigated in this work are membrane, MEA and catalyst/electrode. Differences were seen between real life operation and lab tests. PEMPowerPlant experiences high degradation rate and saw tooth effects, whereas test center operation showed lower degradation effects but also saw tooth behavior. 4 different ways on how to estimate degradation and lifetime were discussed. These might be validated based on historical data. Possible causes of degradation were discussed:

- Internal poisoning
- change in key physical/chemical properties
- temperature
- fuel starvation
- load cycling (operating protocol)

Contamination results: Effect of NO_2 is almost completely reversible, while effect of SO_2 in literature is reported to be not reversible. Catalyst poisoning by SO_2 can be cleaned by cycling up to 1.4 V. Results were shown for impurities with NO_2 (1+2 ppm) and SO_2 (0.5 ppm). Removal of SO_2 by water condensation has been attempted by cooling down the cell and waiting for 10 hours. Not complete recovery after one cycle, but the cleaning effect increases with number of cycles. Hence the effect of SO2 as tested is found to be largely reversible. When re-adding the poison to an already saturated catalyst, the voltage decay will be faster. The strategy to increase the impurity tolerance is to work on the catalyst type as well as catalyst layer properties and composition and positive results have been shown.

A question was raised whether or not the saw tooth behavior could be caused by (local) oxygen concentration, oxide formation on the catalyst.

It was remarked that since low amounts of air contaminants may always be present in it might be worthwhile to check the performance with synthetic air.

Jorg Coolegem, Nedstack: *30,000 h operation of a 70 kW stationary PEM fuel cell system using hydrogen from a chlorine factory, effect of contaminants on FC performance*

The ultimate goal of STAYERS is to achieve 40 000 hours of operation lifetime of stationary PEMFC. Improvements are mainly made on the components membrane, catalyst, bipolar plates, sealing and stack housing. At the workshop, results from MEA and BOP development were presented. A brief overview of the PEMPowerPlant was given, were 2 x 6 75-cell stacks are being operated in parallel. So far with more than 33 000 hours of operation to "grid". The best performing stack has had over 20 000 hours of operation, corresponding to a performance loss of ~2.5 µV / hrs. Analysis of both air and hydrogen quality has been performed, showing some NOx and SO2 in the air as well as CO and CH4 on the anode loop. A ranking of suspected degradation mechanisms was presented (similar to SolviCore):

1. Cathode loss of active surface area; irreversible
2. Anode loss of active surface area by poisoning; reversible
3. Cathode loss of active surface area by poisoning; reversible
4. Cathode increase of proton resistance; irreversible

During discussions it was stated that the membrane durability so far seems satisfactory now when it is reinforced, and that the catalyst loading can be varied to increase durability. However, not to increase the loading inevitably as thicker layers may cause cracks and induce failure in membrane.

Jari Ihonen, VTT: *Enrichment of impurities and inert gas in anode recirculation loop – experience from HyQ project and Finnish national projects.*

A 50 kW power plant based on Nedstack components is under construction in Finland. Concept and work from HyQ was presented, with focus on enrichment of impurities in anode recirculation loop and why this is important. Enrichment of certain species up to 100 times have been seen in re-circulation loops, while other species/components wash out in the same recirculation. Nitrogen enrichment comes from the cathode through the membrane, as shown by JARI Japan. Two relevant papers from VTT are recently published; One on CO tolerance on "flow-through" stacks and one on system experiments on hydrogen efficiency. The HyQ results of CO poisoning are similar to the results from SINTEF on CO, which shows CO is still left at the surface even after the performance of the cell has recovered.

Due to the contaminant build up in the recirculation loop, the highest fuel efficiency may not always lead to the highest system efficiency.

During discussions it was stated that a CO mass balance in the system is difficult. Oxygen diffusion through the membrane (internal air-bleed) oxidizes the adsorbed CO to CO2. In general, system related aspects complicate the effect of contaminants by enrichment and/or water solubility.

Robert Alink, Fraunhofer ISE: *STAMPEM - degradation issues regarding mobile fuel cells*

Fraunhofer ISE is partner in the FCH JU projects EURECA (degradation) and STAMPEM (BPP development). Equipment for spatially resolved measurement of performance and degradation cell, in-plane and through-plane conductivity measurements were described. More detailed understanding of degradation is sought, as the main parameters e.g T, rH, cell voltage, gas concentration also varying over the cell area. In a German state funded project the effect of air contaminants has been investigated at different locations, at roof of the Fraunhofer ISE research building, city environment, near a heavy traffic road and rural at a natural reserve. After 6000 hours of operation of cells the main components influencing performance were seen to be NO, NO_2 and CO.

During discussions it was mentioned that the effect of start-stop of these systems, recovery effect would be interesting to investigate further.

Topic 2 "Degradation mechanisms"

Sylvie Escribano, CEA: *Premium Act results on the degradation of PEMFC operated with reformate fuel (in-situ, ex-situ, single cells, stacks and post mortem)*

CEA is partner in the PEM degradation project PremiumAct, where the main objectives/expected achievements are to develop operating strategies enhancing lifetime and to design a lifetime prediction methodology. Cycling tests are performed with objective to identify accelerating parameters (e.g. fuel composition, operating parameters ….). With pure hydrogen membrane failure occurs and a large part of the degradation is reversible. With reformate fuel there were no signs of membrane failure. The same test protocol was performed with CO additions of 0, 10 and 50 ppm. CO leads to reversible losses, but only if in-between operated with pure H2 (with reformate an irreversible decay remains). CVs and EIS results were shown from these tests. Post mortem analysis showed little changes in catalyst layers. Some alternation in catalyst and increase of cathode particle size. TEM showed Ru on Pt core precipitate in the membrane. Mostly at the gas inlet, and in general there were different changes in properties over cell area. No membrane mechanical degradation was seen.

During discussions it was stated that membrane degradation is a minor problem as long as the operating conditions are not extreme. When optimizing operating strategies e.g. by air bleed and stop start strategy, it needs to be checked what effect these will have on degradation. For reformate fuel, about 50 ppm CO should be expected as input to the fuel cells. Normally the range is around 10 ppm, but higher might occur.

Andrea Casalegno, POLIMI *Experimental and modelling analysis of DMFC degradation*

Operating strategies to avoid (temporary/reversible?) degradation of DMFC has been investigated. This was done by ocv + air break protocol for fuel cell (full cell) and by OCV + 0A for half cell (anode). The temporary degradation at anode can be removed by going up to OCV for a period. Longer (300 sec) is better than short (60 sec). Cathode degradation had been analyzed and linked to crossover of methanol. Modeling analysis of DMFC with a physical model of anode EIS.

Nadine Jacobs, Next Energy *PEM degradation at Next Energy*

Next energy and the FCH JU PEM degradation project EURECA were presented. Main focus is development of µCHP systems PEM stacks. MEAs (from CEA), bipolar plates, gaskets, stack and systems are components that are being addressed. Development, characterization/degradation, stack and system test and verification are tasks within the project. FCTESQA protocols are applied for stack testing. MEA degradation and effect of compression had been investigated. OCV and performance decreases with increased compression, for both flow field structures (serpentine and interdigitated flow fields). µCT was used to investigate mechanical damages, and a video from µCT of cross section "post mortem" showed the MEA during compression.

During discussions reuse of catalyst was questioned. To assure long lifetime, high loading can be applied and later recycled. Losses and high cost during recovering prevents this from being a viable option. Use high loading of catalyst can also be used if Pt cost is not the most critical. But generally this is probably not adding much to lifetime or impurity tolerance.

Topic 3 "Diagnostics and AST protocols"

Kaushik Jayasayee, SINTEF: *AST protocol vs. real life operation and CO contamination*

In STAYERS, AST of cathode catalyst have been performed. The following protocols have been compared: 0.7 and 0.9 V cycling vs 0.7, 0.9 and 1.0 V. Similar degradation indicates that the 1.0 V step doesn't influence much. A protocol including a 1.2 V step (in addition to 0.7 and 0.9 V) showed very rapid degradation and was deemed not relevant for real operation/degradation. A brief comparison of STAYERS AST in-situ data with KEEPEMALIVE ex-situ RDE on catalyst was shown. The in-situ AST 0.7 and 0.9V protocol accelerates cathode catalyst degradation about 10 times compared with real life operation at Nedstack PEMPowerPlant.
Poisoning of the anode catalyst with different CO concentrations was performed. Different anode loadings show different decline in performance/behavior. After returning to pure hydrogen and high performance, CO stripping of the anode shows large amounts of CO still on the surface.

During discussions it was recommended to check whether or not CO still is present at the surface after one extra day of pure hydrogen operation. I.e. do stripping and FTIR after one day instead of directly after switch from CO to H_2.

Laila Grahl-Madsen, IRD *Real-life experience obtained in during field test with hydrogen fuelled LT PEM µCHPs*

Presented about real life experience from operation of µCHP systems in Denmark. The Danish µCHP project started in 2006, and is now in the phase (3) of installing hundred systems (32 hydrogen fuelled µCHPs, the rest is NG fuelled). In Denmark it is not allowed to shut down wind power, so when too much power is produced this has to be exported. => hydrogen buffer will be needed. The IRD stack consists of 47 cell LTPEM and gives 1.5 kW electrical and the same heat, overall 47 % electrical efficiency (H_2 -> P_{AC}, LVH). The cell current is limited by inverter technology, but now they have initiated their own in-house development so that can increase the cell current to 0.55 A/cm^2. Of failures during test in phase 2, stack only caused 2%. BOP was mainly causing problems. A system design error was also found during the field testing. After shut down, the cells could go in reversal. Cell voltages were not monitored when the system was in idle-mode, so it took some time to figure out this. Operation for around 4-6000 hours with different protocols. Average degradation rates were high in the beginning (~100 µV/h) but decreasing down to 3.5 µV/h after more than 3000 hours. Extrapolation of this gives about 17 000 hours lifetime. By comparison of non-reinforced and reinforced MEAs, the non-reinforced experienced 20% failure and degradation of 10µV/h, while no failure with reinforced had 7µV/h degradation. The IRD MEA includes a PtRu anode, which means that CO perhaps is not a problem. The system operation also includes a daily (frequent) start and stop, which will remove CO. There is no nitrogen purge at shut down, but the system includes protective measures.

Martin Geymayer, TU Graz *Results from KEEPEMALIVE*

TU Graz had performed a fuel starvation protocol within the KEEPEMALIVE project. Operating conditions were varied, low and high settings of temperature, current density and humidity. High temperature, low rH and high current resulted in H_2 crossover increase to tenfold of original BoL after only 100 cycles. Segmented cell shows most impact early in the cell, near inlet. High temperature, high rH and high current: Not too much changes. CO and CO_2 were measured during operation, and values of CO_2 up to about 2000 ppm were seen. High temperature, low rH and low current: Increase in membrane resistance and lower ECSA. High temperature, high rH and low current: Not too much changes, increase in membrane resistance. Low temperature (65C), high rH and high current: Not too much changes, increase in membrane resistance. Low temperature (65C), high rH and low current: Not too much changes, increase in membrane resistance. Summarized: High temperature and high humidity leads to the highest degradation by starvation. Is there a relation between pinhole formation and starvation? Probably not, but it's related to operating conditions like high temperature and low rH.

During discussions, the test cell concept and design was evaluated. How was the current measured, check for variation of compression, take care that the gas inlet temp is not too high and also no condensation before gases enters the cell. Generally, MoL (Mid of Life (/test) characterization is avoided for not to alter the fuel cell/catalyst.

Luis Colmenares, SINTEF *Catalyst ex-situ degradation experiments/KEEPEMALIVE results*

Results from catalyst ex-situ degradation tests were presented. AST protocol performed on Pt/C as cathode, with RDE cycling 0.5 to 1.1 V. Particle size was correlated with ECSA after n number of cycles. Main changes in size were seen in the beginning of the tests. Extrapolation of results was performed to correlate with in-situ measures loss in ECSA. Values over 4-500 hours ex-situ cycling were in similar range as in in-situ testing. Dissolution is the main factor in the early phase of the cycling/operation – where more change in ECSA is seen. This effect may be recognized in the kinetic region of the polarization curves. It should be noted that differences observed in the region determined by mass transfer limitations may also originate (partially) from catalyst particle growth since this agglomeration of catalyst particles also results in increased mass transfer paths. In the KEEPEMALIVE project, these cycling protocols have been applied: constant load 0.6 and 0.9 V, start up 0.9 and 1.2 V, shut down 0.6 and 1.2 V. Constant load operation leads to less degradation, while shut down leads to most. Same extrapolation procedure was performed as earlier in the presentation. Again good correspondence with in-situ results is seen.

Conclusion from the workshop

General discussion

What is the preferred operation temperature stationary of PEMFC systems? Today's 65-70°C water is ok, but the heat would be much more worth at higher temperatures. Above 100°C is not needed, but 90-95°C would be better. However, this induces challenges with membrane and gas humidification, and may e.g. require other BOP. There was not much believe in this close to 100°C operation. Another disadvantage of higher temperature operation is the longer start-up time. PBI-based fuel cells are no solution today, 10 times more catalyst is required to get similar performance. The fuel cell system water temperature can also be boosted up to 90°C by some other means if necessary.

More focus on:

Summarized by the participants after the workshop, further focus should be on:

- Catalysts development
  - cathode ECSA loss and contaminants
  - anode contaminants
  - evaluation/test under real system conditions
- Systematic/statistical analysis of large amounts of data
- Lifetime prediction models

List of participants

	Name	Organization	Degradation Project
1	Jorg Coolegem	Nedstack	STAYERS (coord)
2	Hakan Yildrim	Nedstack	STAYERS
3	Stefan Andersch	SolviCore	STAYERS
4	Thomas Martin	SolviCore	STAYERS
5	Sylvie Escribano	CEA	PREMIUMACT (coord)
6	Andrea Casalegno	POLIMI	PREMIUMACT
7	Laila Grahl-Madsen	IRD	PREMIUMACT/KEEPEMALIVE
8	George Tsotridis	JRC	STAYERS/PREMIUMACT/KEEPEMALIVE
9	Robert Alink	Fraunhofer ISE	EURECA
10	Nadine Jacobs	Next Energy	EURECA (coord)
11	Astrid Stadlhofer	TU Graz	KEEPEMALIVE
12	Martin Geymayer	TU Graz	KEEPEMALIVE
13	Jari Ihonen	VTT	HyQ (gas quality)
14	Luis Colmenares	SINTEF	KEEPEMALIVE
15	Kaushik Jayasayee	SINTEF	STAYERS
16	Thor Anders Aarhaug	SINTEF	KEEPEMALIVE
17	Anders Ødegård	SINTEF	STAYERS
18	Steffen Møller-Holst	SINTEF	KEEPEMALIVE (coord)

List of invited projects and partners

STAYERS (http://www.fch-ju.eu/project/stayers-stationary-pem-fuel-cells-lifetimes-beyond-five-years):
Nedstack
SolviCore
Solvay Specialty Polymers
SINTEF
JRC

KEEPEMALIVE (http://www.fch-ju.eu/project/knowledge-enhance-endurance-pem-fuel-cells-accelerated-lifetime-verification-experiments):
SINTEF
FumaTech
IRD Fuel Cells A/S
CNRS
EIFER
JRC
TUG Graz University of Technology
SEAS-NVE Holding

PREMIUMACT (http://www.fch-ju.eu/project/predictive-modelling-innovative-unit-management-and-accelerated-testing-procedures-pefc):
CEA
IRD Fuel Cells A/S
DLR
Politecnico di Milano
JRC
Soprano
ICI Caldaie

EURECA (http://www.fch-ju.eu/project/efficient-use-resources-energy-converting-applications):
EWE - Forschungszentrum für Energietechnologie
Eisenhuth GmbH & Co. KG
Univerzitet u beogradu
CEA
Foundation for research and technology Hellas
inhouse engineering GmbH
Celaya a emparanza y galdos internacional, S.A.
Fundacion CIDETEC
Fraunhofer ISE