



FLUIDCELL

ADVANCED M-CHP FUEL **CELL** SYSTEM BASED ON A NOVEL BIO-ETHANOL **FLUID**ISED BED
MEMBRANE REFORMER

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D7.1

State-of-the-art of PEM FCs for stationary applications

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 Date: 27/05/2015
 Page N°: 2 of 20

Content

1. EXECUTIVE SUMMARY (3 pages max. all points).....	3
1.1. Description of the deliverable content and purpose.....	3
1.2. Brief description of the state of the art and the innovation brought.....	3
2. Introduction	4
2.1. Fuel cells-based CHP systems	4
2.2. Typical operative conditions.....	5
3. Components	7
3.1. PEM membranes	7
3.2. Catalyst	9
3.3. Gas diffusion layer	10
3.4. Bipolar plates and stack assembly.....	10
3.5. Reactant supply.....	14
3.6. Cooling systems	14
4. Life-time and degradation mechanisms.....	15
5. ANNEXES.....	19

1. EXECUTIVE SUMMARY (3 pages max. all points)

1.1. Description of the deliverable content and purpose

The following sections summarize the state of the art of Polymeric Electrolyte Membrane (PEM) fuel cells, in particular low temperature type, when applied to cogeneration systems. Typical operating conditions, degradation phenomena, life-time issues and some components characteristics, namely Membrane Electrodes Assembly (MEA) and Bipolar Plates are described. The overview points out some characteristics of fuel cells stack into the FluidCELL contest. Some parameters of commercial fuel cells stacks are reported as benchmark in the final section. The document has a descriptive nature and highlights possible interaction of the stack with the m-CHP unit.

Most of the information is taken from books that illustrate the state of the art of PEM fuel cells ^{1 2} as well as from review papers dedicated to specific components or issues (cited in the relative sections). Pictures and manufacturer data, they have been taken from the web.

1.2. Brief description of the state of the art and the innovation brought

No innovative content. Review of the technology

¹ C. Harting and C. Roth, *Polymer electrolyte membrane and direct methanol fuel cell technology*. Woodhead publishing, 2012.

² F. Barbir, *PEM fuel cells*, 2nd ed. 2013.

2. Introduction

Micro-cogeneration of heat and electric power (m-CHP) is an interesting way to reduce primary energy consumption in domestic and tertiary sectors. Conventional internal combustion engines or Stirling engines are adopted, but at few kW scale, they have limited electric efficiency: around 20% and 10% respectively. Furthermore, internal combustion engines are noisy and polluting, which are undesired characteristics most of all for domestic use. An attractive technology is the adoption of fuel cells as electric generator, which has a much higher efficiency and low or negligible emissions. Among fuel cells, Polymer Electrolyte Membrane (PEM) type is the most interesting for m-CHP. The drawback is that PEM fuel cells require high purity hydrogen (at least without CO and sulphur compounds) as fuel. In m-CHP units, hydrogen is produced from a primary energy source like natural gas, light hydrocarbons (LPG) or alcohols (ethanol) in the fuel processors. Description and performances of conventional (reforming followed by purification steps) and innovative (membrane reactor) fuel processor technologies for ethanol fed systems are presented in D8.1 and D8.2 respectively.

2.1. Fuel cells-based CHP systems

Combined heat and power today is the largest market for fuel cells. Table 1 lists the commercial m-CHP devices available worldwide, including all types of fuel cells, with respective overall performances and prices.

Table 1. Fuel cells micro CHP products³.

Manufacturer (country of origin ^a)	Stack type	Electrical capacity (kWe)	Electrical efficiency (%)	Thermal output (kWth)	Auxiliary heater included	Cost	Commercial availability	Partners/ projects	Comments
Baxi (UK)	PEM	1	32	1.7	20 kWth	–	2015	Ballard/ Callux	Requires external heater
Toshiba (JPN)	PEM	0.7	35	1	–	\$20,000	Japan 2009 EU – 2015	EneFarm	80,000 operational hours expected
Viessmann (GER)	PEM	0.75	37	1.3	19 kWth	€ 35,000	Germany –2014 Europe – 2015	Panasonic	Uses Japanese stack
Elcore (GER)	PEM	0.3	33	0.6	–	€ 9,000	Enefield – 2013	Enefield	Low electrical/heat output means fuel cell runs continuously
Dantherm Power (DEN)	PEM	1.7, 2.5 and 5	–	–	–	–	Danish field trials	Ballard	Only short duration tests thus far
Panasonic (JPN)	PEM	0.7	40	0.9	Yes	€ 25,000	Japan – 2011 Europe – 2014	EneFarm	European R&D started in 2012
JX Eneos (JPN)	PEM	0.7	40	–	–	–	Japan – 2011	EneFarm	Now pursuing SOFC technology
Vaillant (GER)	PEM	5	–	25–50	–	–	–	PlugPower	Aimed at multi-family homes
Plug Power (USA)	HT-PEM	0.3–3	30	1.65	Yes (7–25 kW)	–	–	–	Operates on natural gas
CFCL (AUS)	SO	1.5	60	0.6–1	No	£20,000	Yes	E.On	Highest electrical efficiency on market
Hexis (SUI)	SO	1	30–35	1.8	20 kW	–	Callux – 2012	Viessmann/ Callux	Electrical efficiency similar to PEMFC
Ceres Power (UK)	SO	1	–	–	–	–	2016	British Gas/ KD Navien	External reformer
Vaillant (GER)	SO	1	30	1.7	–	–	2013	Staxera/ Callux	Unit focussed on reliability
Kyocera (JPN)	SO	0.7	46.5	0.65	–	–	Japan – 2012	Osaka Gas	Uses flat tubular cells
Aisin Seiki (JPN)	SO	0.7	46.5	–	Yes	£21,000	Japan – 2012 Europe – 2014	Osaka Gas/ Bosch	Highest Japanese SOFC product efficiency
JX Eneos (JPN)	SO	0.7	45	–	40 kWth	\$31,000	Japan – 2012	Kyocera	Robust unit
Topsoe (DEN)	SO	1	–	–	–	–	–	Wärtsilä/ Dantherm	Robust cells
Acumentrics (US)	SO	0.25–1.5	< 35	–	–	–	2013	–	Able to respond to thermal cycling
SOFC power (SUI)	SO	0.5/1	30–32	–	–	–	–	–	Poor electrical efficiency for SOFC
Acumentrics (USA)	SO	1/2.5 peak	30	–	Up to 24 kW	–	Not yet in general availability; qualified customers only	–	Operates on natural gas

^a UK=United Kingdom, JPN=Japan, GER=Germany, DEN=Denmark, AUS=Australia, SUI=Switzerland, USA=United States of America.

2.2. Typical operative conditions

Fuel cells operative conditions include temperature, pressure and reactants' flow rates and compositions.

The anodic feed stream can be either pure hydrogen or a reformat hydrogen-rich gas; in any case, the abatement of poisoning species like carbon monoxide, ammonia, nitrogen oxides and sulphur compounds must be included upstream the fuel cells stack. The effect of fuel gas composition, with H₂ fraction reduced from 85% to 72%, on the stack performances is shown in Figure 1 (voltage and power of a stack by Power Cell). The cathodic feed can be pure oxygen in niche applications (submarines, space) or air for the large part of applications (automotive, distributed and back-up power generation).

³ T. Elmer, M. Worall, S. Wu, and S. B. Riffat, "Fuel cell technology for domestic built environment applications: State-of-the-art review," *Renew. Sustain. Energy Rev.*, vol. 42, pp. 913–931, Feb. 2015.

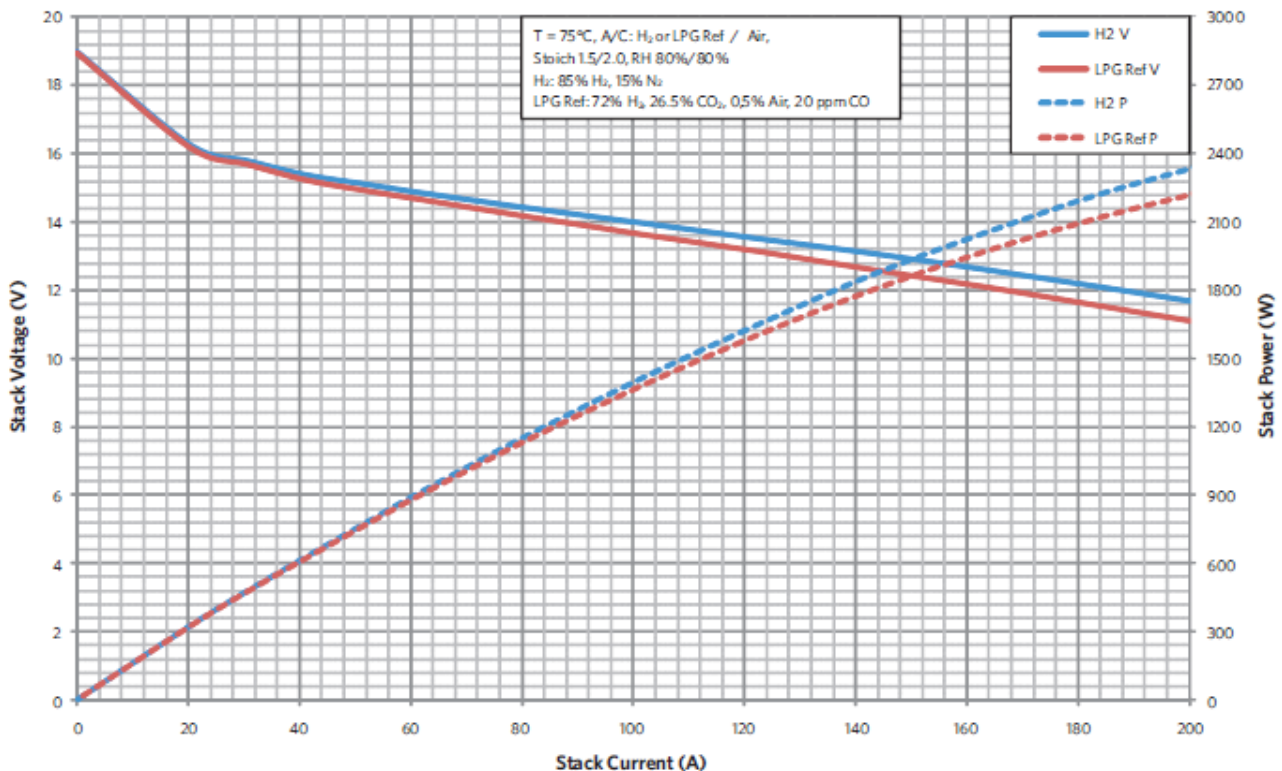


Figure 1. Polarization and power curves of S1-20 Stack by Power Cell under pure hydrogen (blue line) and reformat fuel (red line) operation.

Reactants are usually fed to fuel cells at slightly higher pressure than atmospheric; in order to overcome the pressure drops along the distribution channels. Increasing the operative pressure causes a gain in cell voltage (that means efficiency), in a logarithmic proportion to the pressure ratio. Pressurized operation can be convenient when hydrogen is already available in a pressurized form, e.g. from bottles, even though the cathodic air should be pressurized in loco. In this case hydrogen pressure regulation is easily accomplished by a pressure reduction valve downstream the bottle and one downstream the stack. In many cases, like CHP applications, hydrogen is produced in situ as a low-pressure and diluted (by inert species like CO_2 , CH_4 and N_2) stream, depending on the fuel processor technology. Its compression would be beneficial for the fuel cells voltage, but would require parasitic energy consumption overcoming the voltage benefits. The compression can be done upstream the fuel processor, on reactants streams, but the reduction of the volume of the reactors, rather than the fuel cell performances is usually the main target of this solution. Concerning the CHP system developed in FluidCELL project, hydrogen pressurization is not a viable option, since it is produced as pure stream through selective Pd-based membranes, which need as low as possible hydrogen partial pressure on the permeate side, obtained by sweep gas dilution (or even by vacuum pump action).

About operating temperatures, the common range for PEM fuel cells is 60-80°C. The lower bound is mainly set by the kinetics of cathodic reactions and liquid water formation (flooding), the upper by transition to a plastic behaviour of the polymers inside the electrolyte, as well as drying phenomena of the polymeric membrane, which become more stringent as the temperature and the excess of air sent to the fuel cells rise.

Fuel cells are commonly operated at single cell voltage between 0.6 and 0.8V; the higher voltage refers to pure hydrogen pressurized cells, the lower to ambient pressure cells fed by reformat. Decreasing the voltage means decreasing the efficiency. Anyway, operating the cells at higher potentials (maximum is

the Open Circuit Voltage) is detrimental because corrosion mechanisms of the electrode carbon support start on the cathode side leading to a short lifetime. In fact, the increased cell voltage translates in more energy available for electrochemical degradation mechanisms. Faster degradation occurs also when the fuel cell works at high current density, due to the impact of kinetics, ohmic and concentration losses.

Current densities are in 200-800 mA/cm² range, depending on the desired power density and efficiency. Power density for pure hydrogen atmospheric fuel cells is around 0.5W/cm², up to 1W/cm² for pressurized systems, while net electric efficiency, is over 40% on hydrogen LHV basis, up to 60%.

3. Components

Single components are assembled as a sandwich to form the modular unit, and then the unit is repeated to form the stack. Hereafter the key components are described moving from the core of the cell to the entire assembly.

3.1. PEM membranes

Many types of polymeric membranes are employed in PEM fuel cells. Their characteristics strongly affect the cells performance and the operative range. Membranes based on perfluorosulfonic acid (PFSA) polymeric materials, like for instance Nafion® (Figure 2), 3MTM PFSA, Acquivion®, need water to transport protons from the acid site to the other. Water content inside the membrane is quantified in terms of number of water molecules per sulfonic acid group. The water content also depends on the physical state of water, e.g. Nafion membrane can contain up to 25 water molecules per sulfonate group if water is liquid, around 14 if vapor. As the water content inside the membrane decreases also the proton conductivity of the membrane drops, for instance from 0.2 S/cm at 80-100% relative humidity, to 0.01-0.001 at 20% relative humidity. A research line to obtain high conductivity is to create shorter chains and insert more sulfonic acid groups on each monomer. Anyway, the voltage drop due to protonic resistance (30-80 mV, depending on current density) is several times less than activation losses due to oxygen reduction reactions (350-400 mV). Typical value of membranes thickness is <40 µm, compared to >150 µm of ten years ago. Thinner membranes (<20 µm) with increased resistance to mechanical stress (induced by water content variation or pressure difference on anode and cathode side) are obtained adding a fiber nano-structure to support the membrane (reinforced membrane).

PFSA polymers have a glass transition temperature around 100-120°C. Below the glass transition temperature they are stiff, above becomes too malleable and not suitable to resist typical stress condition of PEM fuel cells.

Lower operative temperatures are not interesting for cogeneration purposes because, beyond the kinetics drawbacks, also the quality of the heat recovered by the stack would not be useful neither for domestic use. This is definitely true when cogeneration is connected to conventional heating systems working at 60-80°C. The operating temperature can be reduced still providing useful heat if radiant systems around 40°C are taken into account (e.g. with floor heating). Finally, the size of a potential thermal storage system can be reduced when storage temperature are higher than the heating system ones.

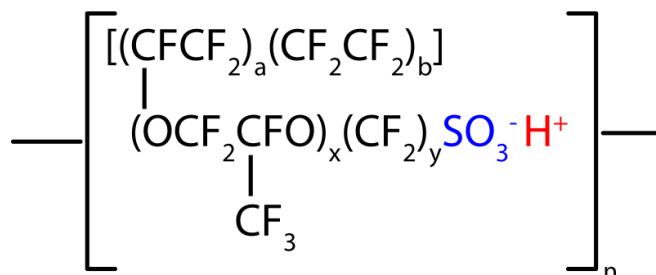


Figure 2. Nafion monomer structure: carbon-fluorinated main chain, pendant CF₃ chain and sulfonic acid activated site for proton transfer.

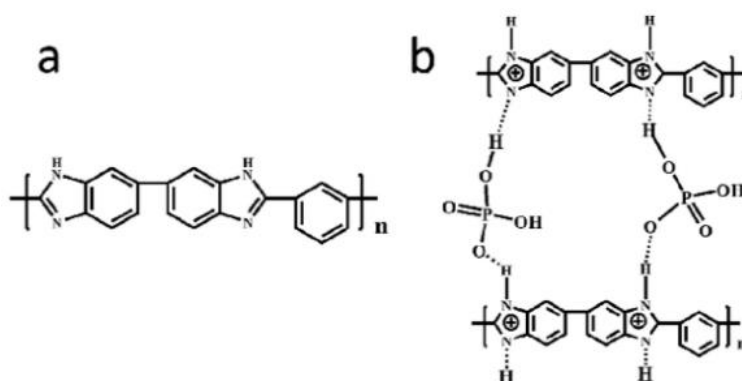


Figure 3. (a) PBI aromatic structure; (b) mechanism of proton transfer.

It is possible to increase the operative temperature over 100°C adopting a different class of membranes. They are based on non-perfluorinated polyaromatics, e.g. PBI polymers, still with sulfonic acid or with phosphoric acid functionalized groups. In polyaromatic membranes, the function of proton solvent is accomplished by acids, which guarantee membrane humidity even at higher temperature, instead of water. Structure and proton transfer mechanisms in polyaromatic membranes are depicted in Figure 3. The benefits of higher temperatures are faster kinetics, lower catalyst charge on electrodes, with lower content of noble metals and, most of all, increased CO poisoning resistance, which is one of the most critical aspects of PEM FC. New HT PEM FC tolerates up to 2% CO in the anode feed stream, opposite to 5-20 ppm of conventional LT PEM FC. Increase CO tolerance is fundamental for PEM fed by reformat in CHP systems based on conventional fuel processor, because the reformat purification is less critical. Figure 4 shows the tolerance to CO contamination of HT PEM MEA Celtec® P1100W developed by BASF. The possibility to run HTPEM FC without humidification further simplifies the system. Also, the heat recovered from HT PEM FC stacks has a higher thermodynamic value. Against these advantages, the voltage of HT PEMFC is lower than LT PEMFC, penalized by a lower reversible voltage predicted by Nernst equation.

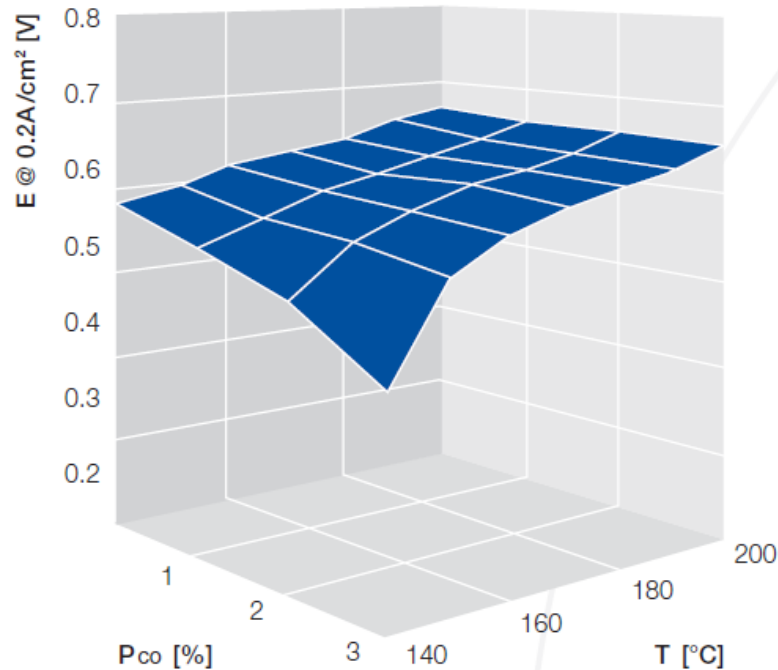


Figure 4. CO tolerance of high temperature MEA Celtec® by BASF.

3.2. Catalyst

In LT PEM FC, Platinum catalyst is required to promote hydrogen oxidation at anode and oxygen reduction at cathode. For a large diffusion of FC based systems, in CHP or automotive sectors, it is fundamental reduce the amount of precious catalyst. At present, total loadings are in the range 0.6-0.8 mg_{Pt}/cm². More than 60% of catalyst is on the cathode side, due to slow kinetics of the oxygen reduction reaction. A significant reduction of Pt content on the electrodes is possible: for instance Panasonic, one of the major actors in Japanese ENEFIELD project, claims a 50% reduction of Platinum load in its fuel cells from 2011 to 2013.

Platinum is employed in alloys with other metals like ruthenium, molybdenum, iron and nickel. The poisoning of the noble metal and the corrosion of the non-noble metal are the major problems of the catalyst that influence long-term stability and lifetime of the stack.

Platinum is the most active metal to promote the oxidation reaction of oxygen, via the so-called “4 electrons transfer step” reaction. The adoption of less active metals, e.g. Au and Hg, promote the oxidation via the “2 electrons transfer step” with formation of highly reactive H₂O₂ as intermediate product. H₂O₂ is responsible for fast chemical degradation of the MEA.

Pt is also the best current catalyst for the anode side. The Pt loading can be particularly reduced when operating with pure hydrogen. However, in the particular case of LT-PEM operating under reformat fuel, better tolerance to CO needs to maintain higher Pt loadings and most often not only pure Pt is used. Better state-of-art catalyst is Pt-Ru, thanks to the double function of ruthenium, which decreases the CO adsorption and promotes the CO oxidation into CO₂ at lower potential than pure Pt. Major problem of this state-of-art catalyst is related to the dissolution of Ru which occurs even at low potential. One operating solution consists in using some air (air bleeding, 1-5% of air) in the fuel stream to promote CO oxidation and reduce the voltage losses due to anode catalyst poisoning.

Air bleeding can be adopted as a normal operative condition of the stack to prevent CO poisoning, as well as ex-post or temporary solution to regenerate already poisoned catalyst and recover performances of the fuel cells⁴. Anode air bleeding is the most effective method since it is simple, efficient, and inexpensive. Although the benefits of air bleeding for the performance of CO-poisoned PEM are well known, the effects on long-term durability and recovery are still investigated.

In order to reduce the price of the stack, research has followed two ways to reduce Platinum content: de-alloyed nanoparticles and Pt-free catalyst.

De-alloyed nanoparticles are obtained via electrochemical procedures on Pt-Cu materials. The result is a structure with a Pt-poor core and a Pt-rich surface, both in a compressed lattice stain. Strain compression that characterize the so-called “core & shell” structure, results in activity even higher than pure Pt catalysts.

Pt-free catalysts are in early stages of development and are mainly affected by two problems: resistance to corrosion in acidic environment and low activity.

3.3. Gas diffusion layer

The gas diffusion layer has to fulfil several properties/tasks: high electronic conductivity, gas permeability, provide mechanical support to MEA, promote uniform feed gas diffusion from flow field channels to MEA and remove water. Usually the porous structure is made of carbon fiber paper or carbon clothes. These are hydrophilic materials, treated with PTFE in order to obtain hydrophobic pores to prevent flooding. GDL are characterized by porosity and tortuosity, which determine the effective gas permeability across the structure. The thickness of GDL is in the range 0.1-0.5 mm. Carbon or graphite fiber are very costly and offer limited design flexibility. They could also cause the fiber penetration through the polymer electrolyte membrane. To solve these problems, significant efforts are being made by researchers to find the best alternative materials. Progress to reduce mass transfer limitation leads to the development of dual-layer GDL: a carbon fiber macroporous layer treated with PTFE is set on the bipolar plate side, a PTFE-bounded carbon powder microporous layer is set on the electrode side.

An alternative to carbon-based materials are metal-based GDL, such as metal mesh, metal foam, and micro-machined metal substrate, suitable for PEM due to good mechanical strength and high stability over a wide potential range.

Many studies focuses on the GDL materials and structures, with particular attention to two-phase flow inside the GDL^{5 6}. Flooding of GDL is more critical on cathode side, but if the cell is operated at high fuel utilization factor and high fuel humidity can occur also on anode side, cause local starvation and start corrosion mechanisms of catalyst and electrode support. Compression on the GDL affects the contact resistance, the GDL porosity, and the fraction of the pores occupied by liquid water and ultimately the performance of PEMFC.

3.4. Bipolar plates and stack assembly

Bipolar plates, with inside flow field channels, give the major contribution to the stack weight and volume, thus are a key-component to obtain high power density. Thickness of current bipolar plates, with integrated cooling circuits, is <5 mm. Bipolar plates have to accomplish many functions in the fuel cell

⁴ L.-Y. Sung, B.-J. Hwang, K.-L. Hsueh, and F.-H. Tsau, “Effects of anode air bleeding on the performance of CO-poisoned proton-exchange membrane fuel cells,” *J. Power Sources*, vol. 195, no. 6, pp. 1630–1639, Mar. 2010

⁵ L. Cindrella, a. M. Kannan, J. F. Lin, K. Saminathan, Y. Ho, C. W. Lin, and J. Wertz, “Gas diffusion layer for proton exchange membrane fuel cells—A review,” *J. Power Sources*, vol. 194, no. 1, pp. 146–160, Oct. 2009.

⁶ S. Park, J.-W. Lee, and B. N. Popov, “A review of gas diffusion layer in PEM fuel cells: Materials and designs,” *Int. J. Hydrogen Energy*, vol. 37, no. 7, pp. 5850–5865, Apr. 2012.

stack: uniform distribution of the gases by flow field channels, conduct current (electrons) from in series cells, heat removal through coolant channels, prevent gas and liquid coolant leakages.

The materials suitable for bipolar plates are graphite, metal sheets and graphite polymers composites. The selection of the best material takes into account electrical and thermal conductivity, thermal expansion coefficient, gas permeability and resistance to corrosion in acid environment, as a fuel cell is. Beyond the physical properties, also the fabrication process must be considered, in view of a massive production of plates. Molded composite bipolar plates and stamped stainless steel plates are the two major types used in current fuel cell systems. Carbon-based plates offer high corrosion resistance and low electric contact resistance, but are brittle and permeable to gases, with poor cost effectiveness for high volume manufacturing. Metal plates instead offer mechanical resistance, better durability to shocks and vibration, no permeability, and much superior manufacturability. On the other side, they suffer corrosion that leads to membrane contamination by metal ions. Corrosion resistant metals develop a passivating oxide layer on the surface that protects the bulk metal from progression of corrosion, but also cause an undesirable effect of a high surface contact resistance.

Two examples have been selected for comparison below. Nedstack developed a two-component molding process: plates are made of a highly conductive compound in the active area, and non-conductive injection molding grade polymer in the border area⁷. For comparison, properties of graphite polymers by Nedstack and metallic sheets adopted by Nuvera are reported in Table 2.

Table 2. Properties of graphite polymers and metallic bipolar plates

Properties	Nedstack composite materials	Nuvera stainless steel sheets
Thickness [mm]	3 (flow field, cooling channels included)	0.16
Maximum operative temperature [°C]	100-225	-
Electrical resistance [Ω m]	46-60 10^{-6}	73 10^{-8}
Thermal conductivity [W/(m K)]	28-40	16
Coefficient of thermal expansion [1/K]	12-28 10^{-6}	18 10^{-6}
Density [kg/m ³]	1600-2000	8000
H ₂ diffusivity [m ² /s]	50-80 10^{-12}	<10 ⁻¹²
Mechanical resistance [MPa]	Flexural strength: 40-45	Modulus of elasticity: 193 10^3
Corrosion current [mA/cm ²]	<0.01	<0.1
Cost	14 €/kg (2003; flow field, cooling channels, gaskets included)	7 \$/kg (2005)

In the MEA assembling phase, sealing structure and plates should align well and be clamped by a sufficient force to obtain good contact between the parts. With poor contacts, the electrical resistance increase, decreasing stack performance⁸ and gas leakage can occur. Sealing solutions can be different depending on the relative size of the PEM membrane and GDL areas⁹.

⁷ E. Middelmann, W. Kout, B. Vogelaar, J. Lenssen, and E. de Waal, "Bipolar plates for PEM fuel cells," *J. Power Sources*, vol. 118, no. 1-2, pp. 44-46, May 2003.

⁸ S.-D. Yim, B.-J. Kim, Y.-J. Sohn, Y.-G. Yoon, G.-G. Park, W.-Y. Lee, C.-S. Kim, and Y. C. Kim, "The influence of stack clamping pressure on the performance of PEM fuel cell stack," *Curr. Appl. Phys.*, vol. 10, no. 2, pp. S59-S61, Mar. 2010.

⁹ D. Ye and Z. Zhan, "A review on the sealing structures of membrane electrode assembly of proton exchange membrane fuel cells," *J. Power Sources*, vol. 231, pp. 285-292, Jun. 2013.

In parallel to these two main types of plates, some innovative routes are considered.

An example of innovative stack assembly is the adhesive bonded stack technology proposed by Protonex: removing the need for a compression gasket the adhesive bonded design eliminates exterior leakage paths making the stack highly durable (Figure 5).

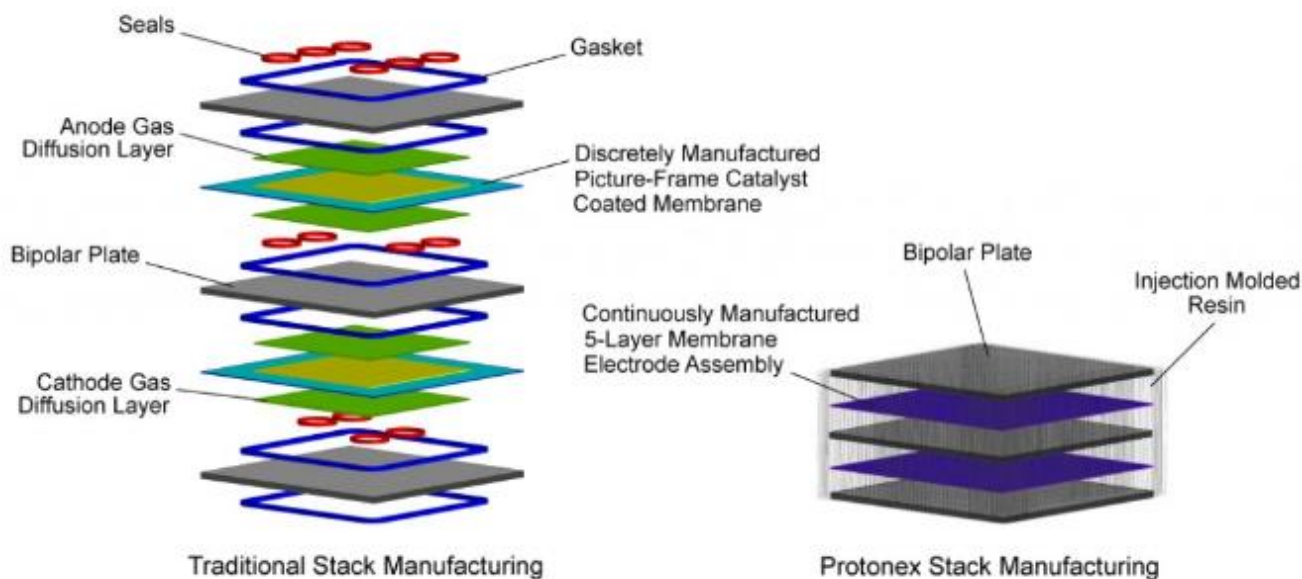


Figure 5. Protonex stack assembly reduces the number of components compared to traditional technology.

Nuvera has developed H₂e™, a 5.5 kW stack to replace batteries in forklifts, and then the Orion series. Cell layout is depicted in Figure 6. Main features are: direct water injection cooling, metal bipolar plates, dead-end anode with passive hydrogen recycle system. Water is recovered from the cathode exhausts and re-injected through reticulated Ni-alloy metal foam between the bipolar plate and the electrodes. Nuvera stack uses uncoated stainless steel bipolar plates in the stack, to fulfil resistance to shock and vibration in industrial settings. Metallic components have the additional advantages of high-volume manufacturability, and can be replaced without risk of damage. The purge cycle (pressure profile depicted in Figure 7) on the anode side is set every single minute; hydrogen is vented to the cathode air exhaust every 10 purge cycles. This operation results in very high fuel utilization (>99.5%) and high efficiency.

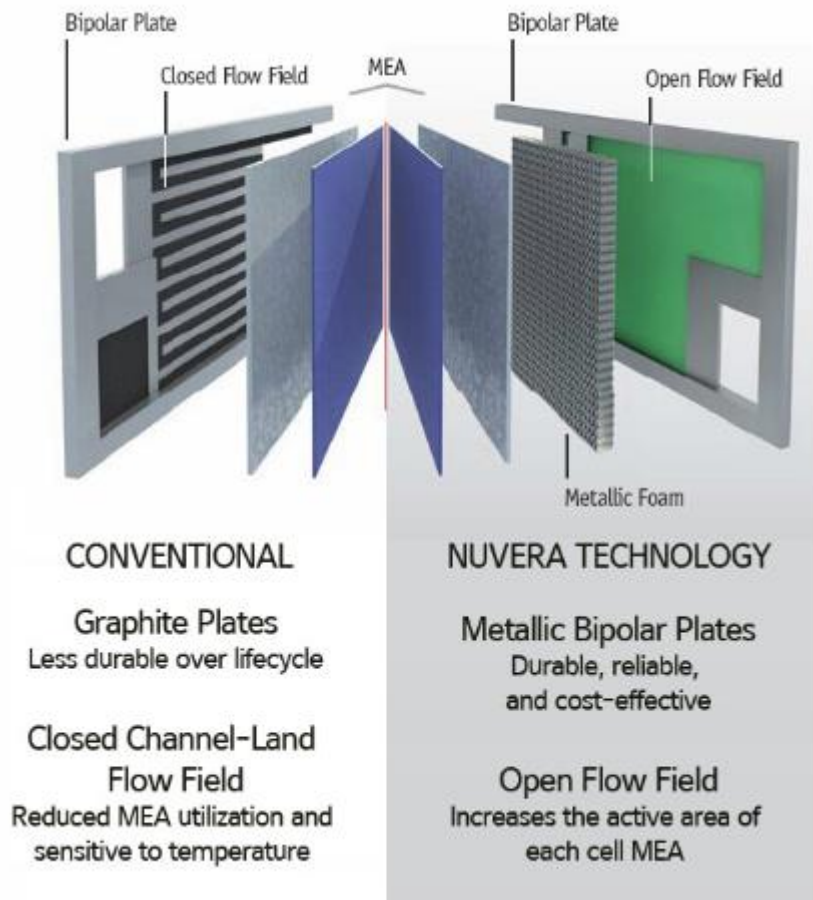


Figure 6. Nuvera stack assembly: metallic GDL and bipolar plates and open flow field.

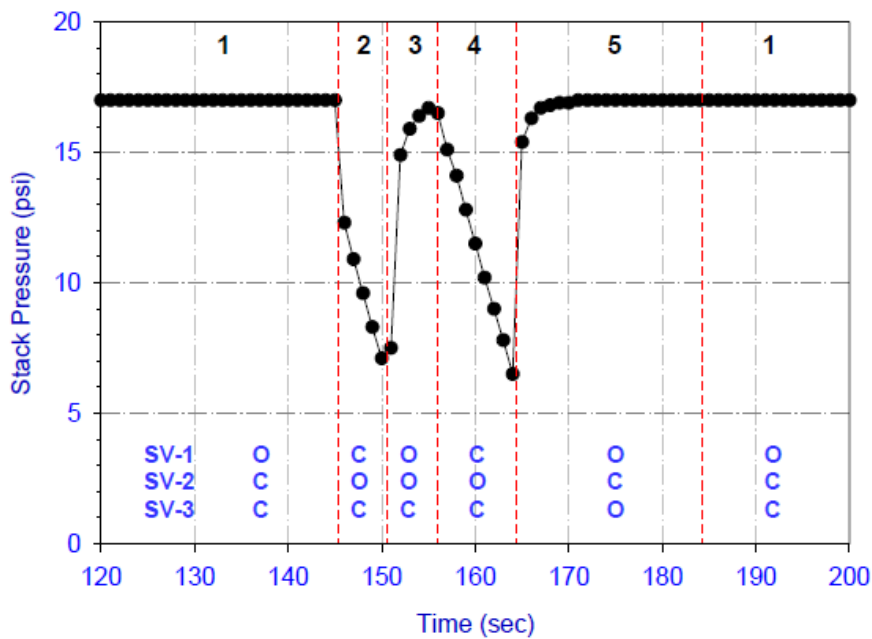


Figure 7. Pressure (gauge) during purging cycle in Nuvera stack.

3.5. Reactant supply

Pure hydrogen can be virtually fed to dead-end anode type fuel cells in a stoichiometric quantity. A periodic purge is anyway necessary to discharge the small amount of impurities, inert gases and water accumulated, with a small loss of hydrogen too. Anode open-end layout, with recirculation is another option for pure hydrogen fed stacks, so excess than stoichiometric hydrogen enters the fuel cell. Hydrogen can be recirculated by a blower or an ejector. The higher the excess, the lower the fuel utilization factor and the risk of water condensation and local fuel starvation, with consequent damages to the MEA. Typical values of hydrogen utilization factor are 90-70%. In case of stacks fuelled by reformat gas, open-end operation is mandatory. Due to hydrogen dilution lower fuel utilization factor are adopted (60-80%) to prevent fuel starvation, without the possibility of recirculation. The unconverted hydrogen is usually burnt to sustain endothermic reforming process.

In the case of FluidCELL system, recirculation coupled with anode purges could be an option as far as pure hydrogen is fed to fuel cells stack, but a little CO could be present, due to leakages in the membrane reactor.

Insufficient fuel flow is particularly damaging for fuel cells. Local and global fuel starvation has different effects. Local fuel starvation (when hydrogen is substituted by other species, like oxygen) causes cathode corrosion (typically in start-up transients). General fuel starvation (concerning many cells but not all) makes the anodic potential rise over 1.5V (even higher than cathode voltage), water electrolysis and carbon oxidation (corrosion of the electrode) occurs on anode side. The power to drive the starved cells in revers potential is provided by other cells in the stack.

On cathode side air is used as oxidant. In order to limit polarization concentration losses a large excess of oxygen is used, that brings to air utilization factor <60%. Oxidant starvation itself has not strong direct effect on the stack lifetime. The consequence of low air utilization factor is a large airflow in cathode channels, and a relatively high pressure drop compared to anode. The risk of drying out the membrane and the increasing power consumption of the air blower limit the excess of air to the cathode. The air supply system includes a filter to remove dust and/or poisoning particles (depending on the location of the installation), a blower and finally a humidifier. Air humidification is essential to prevent the membrane running dry in the inlet zone of the air channels, where the water production cannot compensate the water uptake by air. Water for air humidification can be recovered from the cathode exhaust via a semipermeable membrane.

3.6. Cooling systems

Cooling technology is a key element in PEM fuel cells stack, especially for the automotive sector, where high power density and lightweight are mandatory. Cooling for CHP application is less critical than in automotive. Different methods and media are used to remove heat from the stack: airflow cooling, heat spreaders (edge cooling), liquid cooling and phase-change cooling¹⁰.

Air-cooling is suitable for small, low power density systems. Cooling channels can be made in bipolar plates or in dedicated cooling plates between the bipolar plates. Demonstration of air cooled stacks with optimized air flow channels shows parasitic energy consumption around 2-3% of the stack power. One of the major drawbacks of air cooling is non uniform temperature distribution between the cells.

Edge cooling (or passive cooling) relies on heat conduction in the in-plane direction of plates to remove heat from the central region of the stack, then rejected to heat-spreaders. To be effective, it requires high

¹⁰ G. Zhang and S. G. Kandlikar, "A critical review of cooling techniques in proton exchange membrane fuel cell stacks," *Int. J. Hydrogen Energy*, vol. 37, no. 3, pp. 2412–2429, Feb. 2012.

thermal conductivity plates (graphite based materials). Passive cooling can improve the overall system reliability and reduce the components, thus interesting in space applications.

Liquid cooling is more effective for stacks in the order of 5kW or more. It is of interest for both automotive and CHP applications. The refrigerant is deionized water with addition of antifreeze substances (glycols) for operation in freezing conditions. To maintain coolant electric conductivity $<10 \mu\text{S}/\text{cm}^2$, ion exchange resins are used to trap ions from the liquid, or new-developed antioxidant additives are added. In CHP systems, in order to limit the amount of resins or additives, a secondary loop is adopted for the heat removed from the stack by the demineralized water or water-glycol circuit.

Cooling channels integrated in bipolar plates have serpentine flow fields similar to gas distribution channels, in order to ensure temperature uniformity on the cell surface and across the stack. Increasing the number of cells between the cooling layers creates temperature gradients and reduces the performance of the stack. Complex 3D flow field geometries (chaotic channels for laminar flow) have been proposed for a more effective cooling ¹¹, but manufacturing costs and plate thickness increase too.

The last option is evaporative/boiling cooling, which exploit the latent heat of phase change instead of sensible heat. Liquid demineralized water is directly injected in the cathode channels or passes through bipolar plates with wicking material inside. These solutions can reduce the number of components, but require a higher level of integration in the heat recovery loop.

4. Life-time and degradation mechanisms

PEM fuel cells suffer performance degradation in time, in addition to sudden failure generally caused by incorrect operation or fabrication. The end of life is conventionally set when the voltage reduces 10% from the initial value.

Depending on applications, the targets are very different: 4000-5000h for automotive (20000h for buses), 40000-80000h for stationary power generation.

Panasonic has improved the durability of the CHP system from 40000h of the 2009 model to 70000h of 2015 model, improving the durability of the polymeric membrane.

Degradation rate results from many factor like operative conditions, thermal and voltage cycles, number of cold starts, which cause different mechanisms of degradation ^{12 13 14}.

The fact that lifetime for stationary applications is ten times that for automotive is partially compensate by the fact that thermal and voltage cycles of these systems are much less in number and dynamics. For CHP systems based on PEM fuel cells, the start-up time or the time of response of the fuel cells is adequate to follow the electric load fluctuations. FC stack itself can achieve the rated power in less than 30s at ambient temperature. The start-up time instead is set by the fuel processor that works at high temperatures (500-800°C) and needs tens of minutes to reach nominal conditions. Cogeneration systems based on PEM FC can tolerate hundreds of starts and stops per year, being the major thermal

¹¹ Y. Lasbet, B. Auvity, C. Castelain, and H. Peerhossaini, "Thermal and Hydrodynamic Performances of Chaotic Mini-Channel: Application to the Fuel Cell Cooling," *Heat Transf. Eng.*, vol. 28, no. 8–9, pp. 795–803, Aug. 2007.

¹² N. Zamel and X. Li, "Effect of contaminants on polymer electrolyte membrane fuel cells," *Prog. Energy Combust. Sci.*, vol. 37, no. 3, pp. 292–329, Jun. 2011

¹³ J. Wu, X. Z. Yuan, J. J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, and W. Merida, "A review of PEM fuel cell durability: Degradation mechanisms and mitigation strategies," *J. Power Sources*, vol. 184, no. 1, pp. 104–119, Sep. 2008.

¹⁴ W. Schmittinger and A. Vahidi, "A review of the main parameters influencing long-term performance and durability of PEM fuel cells," *J. Power Sources*, vol. 180, no. 1, pp. 1–14, May 2008.

inertia related to the fuel processor, while for a SOFC-based cogenerative system no more than 10 thermal cycles per year are suggested¹⁵.

To study degradation phenomena and measure effective lifetime requires long and expensive experimental campaigns, so in addition to long test at steady state on fuel cells stacks different accelerated stress tests (AST) are performed to characterize long-term behavior of the cells. Tests in steady state conditions indicate voltage decay of 2-10 $\mu\text{V}/\text{h}$, $>100 \mu\text{V}/\text{h}$ in ASTs. Similar figures are reported in Figure 8, which depicts voltage decay for a GORE MEA (in steady state tests) developed for stationary applications at different current densities.

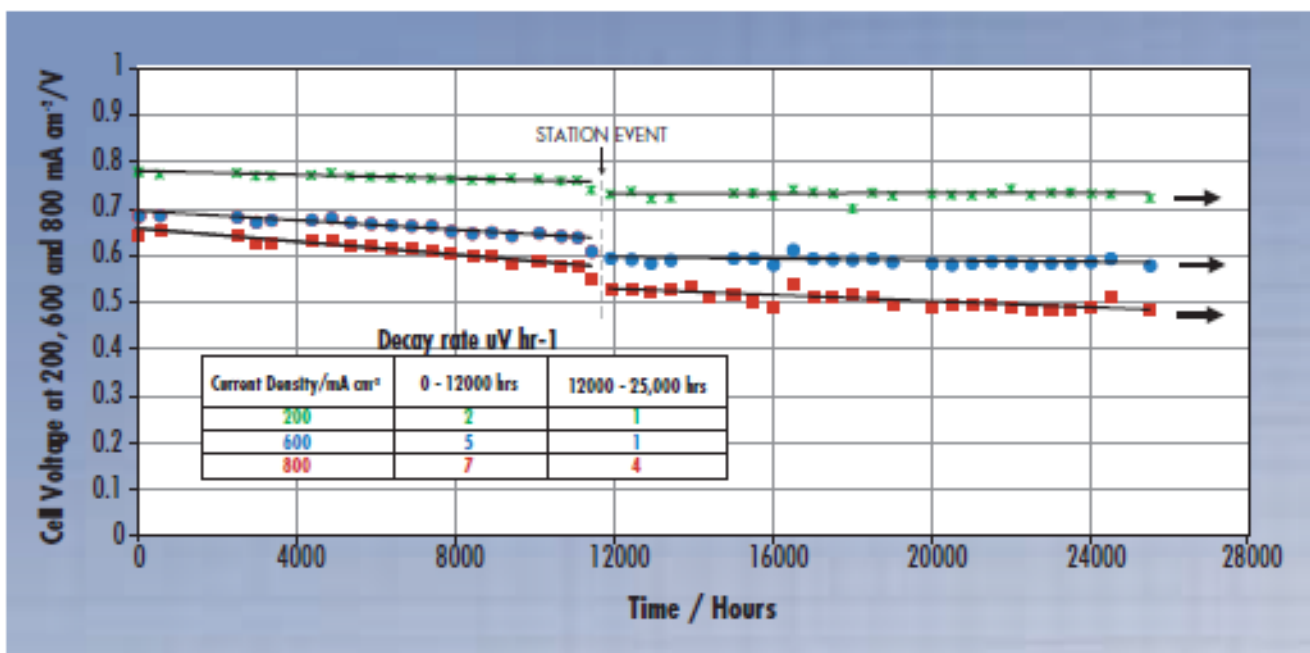


Figure 8. Ongoing life tests on GORE™PRIMEA® Series 57 MEA, exceeding 25,000 hours, demonstrate stable voltage over time.

Except during switch-on/off procedures, fuel cells stack in m-CHP systems usually works at nominal temperature and it has to withstand limited electrical power fluctuations since the cogenerator is usually grid connected or sometimes assisted by an electric battery. On the other hand, degradation tests are mainly based on electric (current or voltage) cycles. Indeed m-CHP systems usually work in thermal-driven mode, but the novel system developed in FluidCELL project should be able to operate in off-grid mode, hence facing significant electric load variations.

Several standard testing procedures are being developed in many countries worldwide, to provide methods for a fair comparison of m-CHP systems performances. They are gathered in the framework of Subtask B of Annex 54 of International Energy Agency. European countries procedures (Italy, Germany, UK) are based on thermal-led tests¹⁶, but on different load profiles. No special procedures for PEM-based system are mentioned.

¹⁵ "Solid Power Engen-2500." [Online]. Available: <http://www.solidpower.com/en/engen-2500/>.

¹⁶ G. Angrisani, E. Marrasso, C. Roselli, and M. Sasso, "A Review on Microgeneration National Testing Procedures," *Energy Procedia*, vol. 45, pp. 1372–1381, 2014.

Specific experimental campaigns to understand degradation on a short fuel cells stack under cyclic electric load to simulate a m-CHP operation are described in literature¹⁷.

Long term tests on a real m-CHP unit based on HT PEM fuel cells showed that over the time a considerable deviation in electric and thermal output, compared to nominal values, occurs due to degradation phenomena both in the reformer and fuel cells stack. Different management strategies lead to different electric and thermal energy output over the time, efficiency and primary energy saving¹⁸.

Many deterioration phenomena involve the MEA. They are classified in mechanical, thermal, chemical and electrochemical.

Mechanical failure of the membrane caused by fabrication defects or membrane-electrode assembling process appears in early life of the stack. Other sources of mechanical failure are wetting and drying cycles which cause swelling and shrinking of the membrane and tension and compression stress, respectively. Mechanical resistance is strongly improved by the adoption of reinforced membranes with fiber nano-structures, which stand higher stress conditions¹⁹ and even higher water content²⁰.

Local hot spots due to direct combustion of hydrogen and oxygen can cause pinholes. The direct combustion can occur into the membrane when fuel crossover occurs and can be accentuated if Pt particles are in the membrane after degradation of cathode catalyst. Hot spots are often located in the inlet region on anodic electrode-membrane interface due to air bleeding, where temperature can rise to 100°C.

The most critical chemical attack to the membrane comes from peroxide and hydrogen peroxide radicals. These radicals derive from H₂O₂ and cause thinning of the membrane and loss of mechanical strength. Polymer fragments and fluoride from the decomposition can be detected in the effluents from the fuel cell when chemical degradation is running.

Electrodes can deteriorate because of poisoning of the Pt or Pt-alloy catalyst by species present in supplied reactants. Furthermore, catalyst can lose activity through an oxidation/dissolution process due to the combination of high voltage and wet conditions. Part of Pt ions migrate to the membrane and are reduced by hydrogen and precipitate. Their presence into the membrane speeds-up pin-hole formation. The rest of Pt particles on the electrode surface tend to coalesce with other particles, leading to a particles growth and strongly diminishing the active surface area of the electrode (Ostwald ripening and sintering).

Temperature has a strong effect on degradation mechanisms: the higher the temperature the higher the kinetics of undesired reactions that cause the chemical degradation of the MEA. An exception is the CO poisoning: its adsorption on Pt surface is less prominent at higher temperatures. On the contrary, at lower temperatures, the presence of liquid water speeds up Pt dissolution and carbon support corrosion. When using fuel containing CO, a specific degradation issue is related to the poor stability of Ruthenium

¹⁷ R. Chattot and S. Escibano, "Ageing studies of a PEM Fuel Cell stack developed for reformat fuel operation in μ CHP units: Development of an accelerated degradation procedure," *Int. J. Hydrogen Energy*, vol. 40, no. 15, pp. 5367–5374, Apr. 2015.

¹⁸ Najafi, Mamaghani, Rinaldi and Casalegno, "Long-term performance analysis of an HT-PEM fuel cell based micro-CHP system: Operational strategies," *Applied Energy*, pp. 582-592, 2015.

¹⁹ N. S. Khattra, Z. Lu, A. M. Karlsson, M. H. Santare, F. C. Busby, and T. Schmiedel, "Time-dependent mechanical response of a composite PFSA membrane," *J. Power Sources*, vol. 228, pp. 256–269, Apr. 2013.

²⁰ F. Xu, S. Mu, and M. Pan, "Mineral nanofibre reinforced composite polymer electrolyte membranes with enhanced water retention capability in PEM fuel cells," *J. Memb. Sci.*, vol. 377, no. 1–2, pp. 134–140, Jul. 2011.

used to improve CO tolerance but which can be easily dissolved leading to Ru precipitates in the membrane or in the electrodes²¹.

As mentioned above, start-up and shut down cycles can cause cathode corrosion if air enters the anode when the cell is off. Upon the next start-up, local presence of oxygen increases the anode potential and the catalyst carbon support on the cathode side stands corrosion conditions. Fuel cells stack are required to work also in very cold conditions. A lot of attention has been devoted to cold start up, mostly pushed by the automotive sector. Ice formation results in catalysts layer cracking roughly parallel to the membrane surface (delamination²²) due to increased volume of water from liquid to solid state. To mitigate this effect water purge from the GDL when switching off the device is a possible solution.

²¹ P. a. Henry, L. Guétaz, N. Pélissier, P.-A. Jacques, and S. Escribano, "Structural and chemical analysis by transmission electron microscopy of Pt–Ru membrane precipitates in proton exchange membrane fuel cell aged under reformat," *J. Power Sources*, vol. 275, pp. 312–321, Feb. 2015.

²² Q. Yan, H. Toghiani, Y.-W. Lee, K. Liang, and H. Causey, "Effect of sub-freezing temperatures on a PEM fuel cell performance, startup and fuel cell components," *J. Power Sources*, vol. 160, no. 2, pp. 1242–1250, Oct. 2006.

5. ANNEXES

Table 3 summarizes some characteristic of commercial PEM fuel cells stacks. Information is taken from manufacturers' flyers. Figures with * are computed from available data and sometimes cannot be directly compared. For example, power density on mass basis in some cases includes also the chassis or the auxiliaries in addition to the fuel cells stack itself. It is worth noting that all the stacks are designed to work also at freezing conditions, as discussed above, with ad hoc equipment. However very few information or feed-back is available about real operation of these stacks and systems.



D7.1
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 Date: 27/05/2015
 Page N°: 20 of 20

Table 3 Commercial fuel cells stacks

Manufacturer; Model	Power kW	Fuel	Voltage V/cell	# cells	Power density*		Uf* %	Efficiency (H2 LHV*)	Pressure; ΔPa; ΔPc barg; mbar	Coolant	Environment °C	Notes
					W/cm ²	W/kg						
PowerCell; S1	1-6	H2; reformat	0.95-0.55	10-60					-;70; 300	DI water; anti freezing	-30 – 70	
Ballard; FCgen 1020ACS	0.3-3	>99.95% H2	0.683		0.7	230		50	-;16;56	Air	-10 - 52	Self humidified
Ballard; FCgen 1300	2.4 – 10.5	>80% H2	0.65	27-120		290-470		50		DI water; anti freezing	-5 – 70	
Ballard; Electragen H2	1.7-5	>99.95% H2	48-55			30-45		40-42				
Nedstack; XXL series	2-9.5	>99.95% H2; <0.2ppm CO	0.8-0.41	20-100	0.18	100-240	80	44-46	-; 50;120	DI water; G20		Continuous operation
Nedstack; HP series	2- 10	>99.95% H2; <0.2ppm CO	0.8-0.43	20-100	0.18	130-290	80	45-47	-; 50;120	DI water; G20		Back up power
Nuvera; Orion	10- 30	H2	1.1-0.56	48-128	0.35	520-880					-40 - 60	Passive recirculation
Pragma; ProRD	0.2-0.47	H2	0.95-0.4	3-7	0.67		66		<2;-;-			
Horizon; H serie	1. - 5	99.995% H2		50-120		150-170		40	-; 0.45-055	air	5-30	
Horizon; H1000XP	1	99.995% H2	0.6	50		200		48	-; 0.45-055	air	5-35	
Schunk Bahn; FC HLC	0.08-0.36	>99.99% H2	0.57-0.67	8-42		150-180		40-41		anti freezing	5 – 70	self humidified and external humidified