



PROJECT FINAL REPORT

Stationary PEM fuel cells with lifetimes beyond five years

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Publishable summary – STAYERS

Stationary PEM fuel cells with lifetimes beyond five years

0. Executive summary

Economical viability of PEM fuel cell power for stationary applications demands a fuel cell lifetime of at least 5 years, or over 40,000 hours of continuous operation. In contrast to automotive use, which is focused on low cost and practical lifetimes of 5,000 hours, for stationary use robustness, reliability, and longevity are as important as the initial investment cost, especially for applications in the chemical industry and in remote areas. Continuous operation implies higher yearly costs of maintenance and overhaul than for intermittent applications such as automotive- and back-up power.

The STAYERS objective of 40,000 hours of PEM fuel cell lifetime was defined by the time elapsed until 10% of the initial voltage is lost. To reach this ambitious goal, basic material research was given maximum attention. The durability of all components of a PEM fuel cell stack have been investigated and improved where necessary, to reach the target lifetime of 40,000 hours: the membrane, membrane electrode assembly (MEA), rim, seals, cell (bipolar) plates, flow fields, and stack housing. This has been done in an iterative approach evaluating the components via extensive field testing as well as specific accelerated stress tests (AST's). All activities were coordinated in WP-1.

In WP-2, Solvay Specialty Polymers developed improved membranes and a new production route, which allowed the introduction of radical scavengers. These improved membranes showed a 5.6 times higher durability in AST, while the baseline membrane already lasted over 10,000 hs in field tests.

In WP-3, Solvicore developed over 50 MEA variations. Detailed comparison of field performance as well as post-mortem analysis revealed that the predominant decay mechanisms are mainly related to cathode degradation. Field tests showed that reversible decay plays an important role and is most probably related to air contaminants. Considering irreversible decay rates only, lifetimes beyond 40,000 hs are achievable for the best performers of the final iterations.

In WP-4, Nedstack operated a 70 kW power plant using hydrogen from a chlor-alkali plant. Over 40,000 hr of system lifetime with high reliability and low maintenance was shown. Stack hardware components were analyzed for lifetimes up to 23,000 hs. Improved seal materials and stack housing were developed to reach the project lifetime. Actual stack lifetimes of over 20,000 hs were reached using external reference MEA's, with extrapolated lifetimes beyond 40,000 hs.

In WP-5, Sintef developed a cathode AST and performed contaminant and recovery studies on the different MEA iterations, giving more insight in the reversible and irreversible degradation behavior as observed during field tests.

In WP-6, JRC developed a CFD model based on experimentally determined material characteristics, to assess the relative contributions of the different degradation mechanisms. Loss of cathode catalyst surface area was confirmed to play a dominant role.

These promising results for extended fuel cell stack lifetime, as well as the achieved 40,000 hr system lifetime, enable an important next step towards the large scale deployment of PEM Power Plant technology. In particular, these advances have led to the FCH-JU Demcopem-2MW project, where a 2 MW PEM fuel cell generator will be integrated with an existing chlorine production plant, converting waste hydrogen into electricity. In addition, the insights in degradation mechanisms as obtained within Stayers, will be used for further fuel cell (component) development in other FCH-JU projects, such as Second Act and MATISSE. Finally, the obtained knowledge will be applied in commercial product development by the different partners involved.

1. Introduction

Economical use of PEM fuel cell power for stationary applications demands a lifetime of the fuel cells of at least 5 years, or more than 40,000 hours of continuous operation. The prospect of large scale application for automotive use has focused PEM research on low cost production techniques with practical lifetimes of the fuel cells of 5,000 hours. For the stationary use, especially in the chemical industry and in remote areas, robustness, reliability, and longevity are as important as the initial investment cost. For stationary generators the yearly cost of maintenance and overhaul are expected to be much larger than for intermittent applications such as automotive- and back-up power.

To reach the high goals of the project, basic material research was given maximum attention. The durability of all components of a stack of PEM fuel cells, especially that of the Membrane Electrode Assembly (MEA), rims and seals, cell (bipolar) plates, and flow field is of paramount importance for a stationary power generator.

Project STAYERS was dedicated to the goal of obtaining 40,000 hours of PEM fuel cell lifetime employing the best technological and scientific means. Apart from materials research it also required a detailed investigation of degradation mechanisms and their mitigation during continuous operation. Operating conditions that are favorable for longevity have been applied (e.g. a high relative humidity of 85%). The effect of possible contaminants also has been investigated. A lifetime of 40,000 hours, if defined as the time elapsed until 10 % of the initial voltage is lost, is equivalent with an average voltage decay rate of $1.5\mu\text{V}/\text{h}$. To establish this lifetime within the 26,000 hours of a three years project advanced materials research and development has been combined with models and accelerated tests.

During the Stayers project it was concluded that at least 4-8 khs of operation are required for a proper lifetime evaluation. Together with the production time of the materials, both BOL+EOT characterization and post-mortem analyses this implies that at least 18 months are required per iteration, or not more than 2 iterations per 3-year project. The initial project approach of developing 4 iterations, each based on the results of the previous was very ambitious and unrealistic in the original time frame. It is recommended to limit the number of iterations for future FCH-JU projects.

2. Membrane Development (WP-2) – Solvay Specialty Polymers

1. Introduction

Solvay Specialty Polymers S.p.A (formerly Solvay Solexis S.p.A.) is, in the frame of Stayers project, the leader of Work Package (WP) 2. This WP is aimed to develop advanced membranes to be used to manufacture long-lasting MEAs and stacks (the durability target is 40,000 hrs).

Membranes developed in the frame of Stayers and made available to the partners along the project have been produced with Aquivion® PerFluoroSulfonic Acid (PFSA) having Equivalent Weight (EW) of 790 g/mol and were reinforced with an expanded PolyTetraFluoroEthylene (ePTFE) support. The overall thickness is about 22 μ m.

Aquivion® PFSA, when compared with its congeners, features higher glass transition temperature (*i.e.* higher softening temperature), higher capability to retain and absorb cathode product water (*i.e.* self-humidification ability) and high conductivity and water mobility especially in low humidity conditions.

2. Membranes Developed

In Figure 1 the developmental activity carried out in Solvay is roughly sketched.

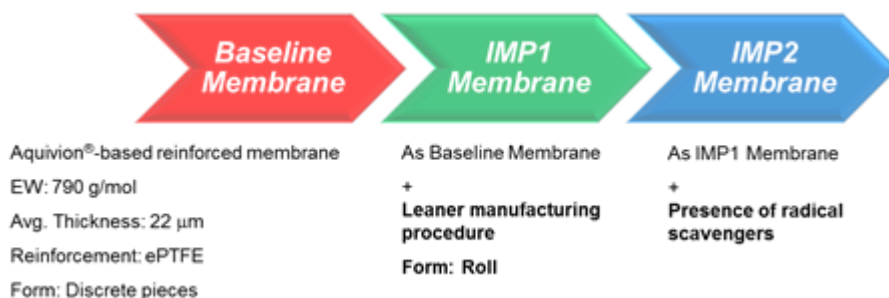


Figure 1: Resuming chart of membrane development carried out by Solvay Specialty Polymers in the frame of Stayers project.

2.1 Baseline R79-02SX Membrane

As discussed above, Baseline membrane was the first grade injected into Stayers. It was a ePTFE reinforced Aquivion® PFSA-based membrane having EW of 790 g/mol and thickness about 22 μ m. Baseline membrane was delivered to the partners as discrete sheet (18x18 cm) till M6 (June 2011).

After the initial internal and within the consortium evaluation of Baseline membrane, Solvay started the development of IMP1 generation.

2.2 IMP1 Membrane

Such membrane has the same physical (thickness, EW, kind of reinforcement) and electrochemical (conductivity) properties of Baseline grade but its production process was improved reducing the number of steps, the complexity of the process, costs, amount of scraps and production time.

Indeed, the newly developed process avoids the need for membrane final washing (water + acid) which was mandatory for Baseline membrane. The aim of this treatment was to remove pollutants, impurities and solvent residual from the membrane which, if present, strongly increase the membrane conditioning time (Figure 2) thus increasing the operational costs of the stack.

Moreover, this new process allowed the production and the delivery of membrane in roll form. IMP1 samples were delivered to the partners since M12 (December 2011) and were also used to prepare the MEAs for the final SC-4 stack.

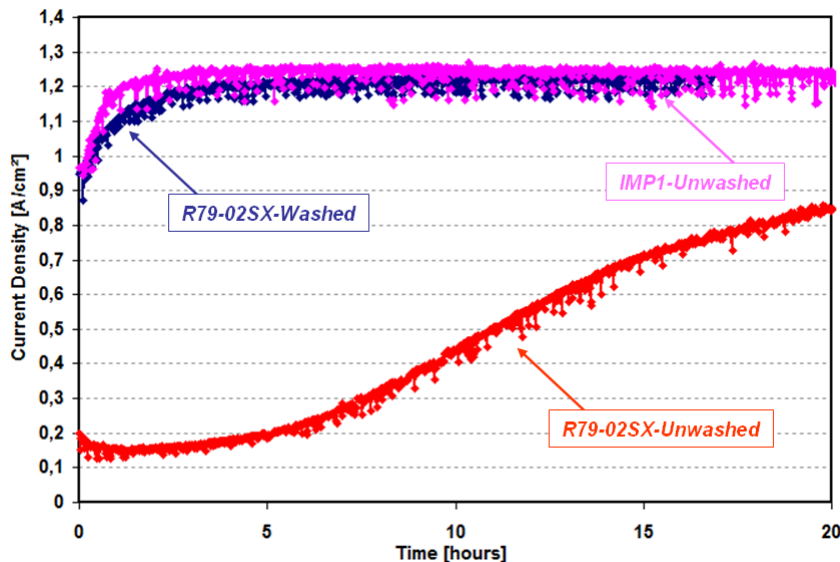


Figure 2: Conditioning time of novel IMP1 (unwashed) membrane (purple) compared with R79-02SX baseline washed (blue) and unwashed (red). It's clearly evident that IMP1 and washed Baseline membrane are fully conditioned after few hours whereas the unwashed Baseline isn't completely conditioned after 20 hrs. Testing conditions: Cell voltage: 0.6 V; T: 75°C; RH: 85%; feed: H₂/O₂ and P: 1 barA (either side).

2.3 IMP2 Membrane

In order to reach the Stayers challenging target of 40,000 hrs of durability, Solvay decided to develop a second generation of membranes able to exceed lifetime of the previously sampled grades. To do that, a second membrane generation, namely IMP2, containing radical scavengers was developed.

It's well known both in open and in patent literature that the introduction of radical scavengers (in general cations of transition metals) is very effective in increase the fuel cell membrane lifetime. Indeed, chemical degradation is thought to be strongly affected by the radical production within the cell through different pathways (such as the two electron oxygen reduction at the cathode, gas crossover and surface reactions on the platinum particles).

A water-soluble salt of a selected radical scavenger was added to Aquivion® PFSA dispersion and starting from that, a reinforced membrane was produced taking advantage from the technology developed for IMP1. Worth to be underlined is the fact that the possibility to avoid the acid washing introduced with IMP1 paved the way to the scavenger introduction. Indeed, being the scavengers added as cations and forming ionic bonds with the polymer, an acid treatment would wash them away from the membrane.

Durability of IMP2 was checked using an internal Accelerated Stress Test (AST) protocol finding a sharp increase in IMP2 lifetime vs. IMP1 (about 1400 hrs vs. about 250 hrs) (Figure 3).

First IMP2 laboratory samples were supplied in M20 (August 2012) and its industrialization till the pilot plant scale allowed the delivery of a roll (several sq. m) in M31 (July 2013) which was used to produce MEAs for SC-4 stack.

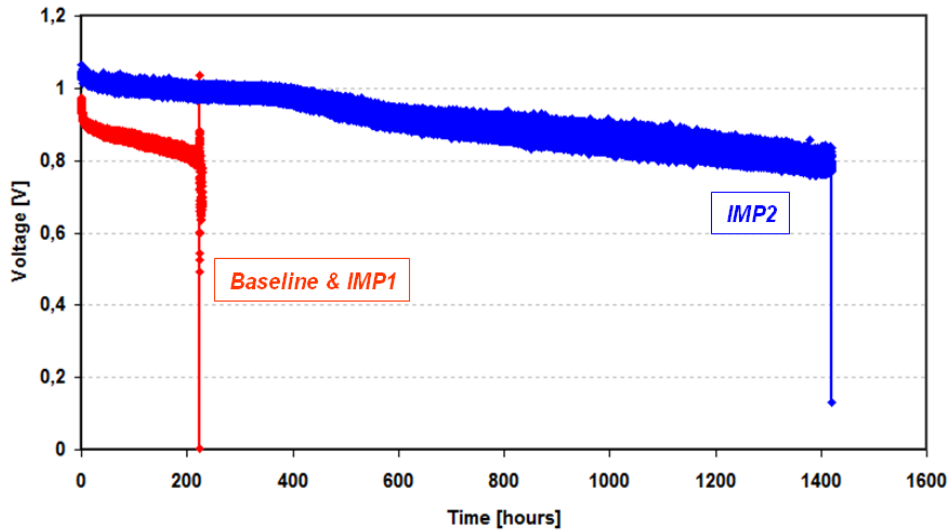


Figure 3: Durability in AST of baseline, IMP1 and IMP2 membranes. Conditions: j : 0 A/cm²; T : 90°C; RH: 30%; feed: H₂/O₂ and P : 1 barA (either side). Failure criteria: Cell voltage below 0.70 V.

3. Membrane Lifetime Extrapolation

Membrane contribution to the device durability can be roughly extrapolated considering that in AST carried out in lab, membrane IMP2 has a lifetime about 5.6-fold higher than that of baseline and IMP1. Furthermore, baseline membrane lasted about 10,000 hrs in real operating conditions of Delfzijl power plant; thus, applying the durability factor found in AST (5.6) to this test duration, we obtain a membrane extrapolated lifetime long enough to satisfy the Stayers durability criteria (Figure 4).

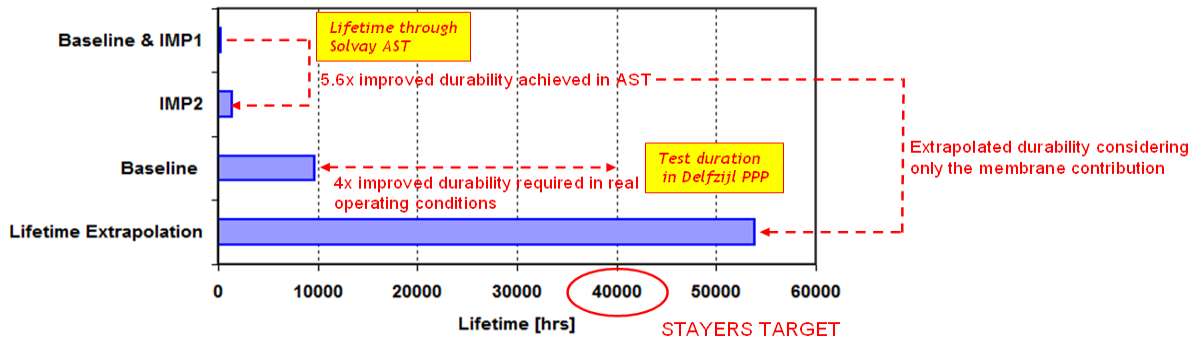


Figure 4: Extrapolated durability considering only the membrane contribution

4. Conclusions

- i. Solvay Specialty Polymers developed three different generations (called Baseline, IMP1 and IMP2) of Aquivion[®] PFSA-based ePTFE-reinforced thin membranes.
- ii. Such membranes were made available to the partners upon request. The amount of *Figure 1* supplied material was enough to allow the production of the right quantity of MEAs to nurture the project.
- iii. Each iteration showed improvements when compared to the previous one: IMP1 was supplied in roll and its production was simplified with respect to Baseline and IMP2 (delivered in roll, too) contains radical scavengers able to increase membrane lifetime (Figure 3). Such improvements were achieved without drops in electrochemical performances.
- iv. Extrapolation (Figure 4) of IMP2 durability reached the Stayers target (40.000 hours).
- v. The process to produce the radical scavenger-containing IMP2 membrane was successfully scaled-up.

3. MEA Development (WP-3) – SolviCore

Within the frame of the STAYERS project, SolviCore GmbH & Co. KG has been in charge of work package 3 (WP3), “MEA development”.

- First objective of this work package was to develop an MEA fit for 40000 hours of operation within Nedstack stack hardware under stationary operating conditions.
- Second objective was to develop an improved understanding of the interactions between MEA and system and degradation mechanisms involved.

Towards this target, a number of successive MEA generations (SC-0 to SC-4) have been developed and provided for the project. They have been operated in test environments ranging from laboratory tests to a field employed PEM power plant. Test data have been collected and analysis performed on aged MEAs and their components after operation, with the intention to evaluate MEA degradation mechanisms, contributing to the next step of MEA development. Thus, a loop-type development cycle has been realized.

Individual development cycles have put the focus on different aspects of MEA manufacturing to improve its durability, namely materials improvements and process improvements.

The project planning anticipated a continuous improvement of MEA lifetime from one MEA generation to the other.

Overview of MEA development loops

The membrane used has significant influence on the MEA lifetime achievable. In course of the STAYERS project, SolviCore used Aquivion® membranes developed and supplied by Solvay Specialty Polymers.

Other aspects besides the membrane need to be considered in MEA development, as additional requirements beside performance and slow electrochemical degradation have to be satisfied. To be commercially viable, its manufacturing process has to suit mass manufacturing. Interactions between MEA and stack hardware (e.g. assembly, compression...) have to be considered, too. MEA development loops realized in STAYERS need to reflect this. Table 1 gives a simplified overview of the changes incorporated within the different MEA generations SC-0 to SC-4.

MEA generation	Membrane	Electrodes	Rim Type
SC-0	old Solvay baseline	CCB (Type 1+3)	4-Layer
SC-1	new Solvay baseline	CCB (Type 3)	2-Layer
SC-2	IMP1	CCM (one variation derived from CCB Type 3)	simplified 2-Layer
SC-3	IMP2 beside IMP1	CCM (numerous variations; "rainbow stacks")	simplified 2-Layer
SC-4	IMP1 and/or IMP2	CCM (few variations)	simplified 2-Layer

Table 1: Simplified overview of MEA changes for individual MEA generations SC-0 through SC-4
Explanation: CCB = catalyst coated backing, CCM = catalyst coated membrane, IMP = Improved next generation membrane

SC-0 and SC-1: Baseline MEAs

Both SC-0 and SC-1 served to provide a degradation baseline. These MEAs have been catalyst coated backing (CCB)-based, employing two qualities of Aquivion® R79-02SX membrane.

Baseline MEAs from several stacks field-operated for up to 10.000 hours served to establish and investigate MEA degradation mechanisms.

It was observed early in the project that different decay rates can be observed depending on test environment employed. *Figure 1* visualizes decay rates for both SolviCore’s laboratory testing environment and Delfzijl PEM power plant field-testing. Both initial performance level and the decay pattern observed differ with operating environment. This constituted proof for two important findings:

1. Influence of environmental factors on performance and decay, yet to be identified
2. More than one degradation mechanism applies.

Results of the investigation helped in focusing on topics of importance for the next development loops:

- OCV decay and H2 crossover indicate membrane degradation is not an issue for durability at this stage
- Cathode catalyst layer needs to be the development focus to achieve lifetime improvement
- Certain areas of the MEA suffer more during operation than others; 10cm² single cell testing is method of choice for an in-depth investigation.
- Good agreement of results at different partners allows for cross-check of results

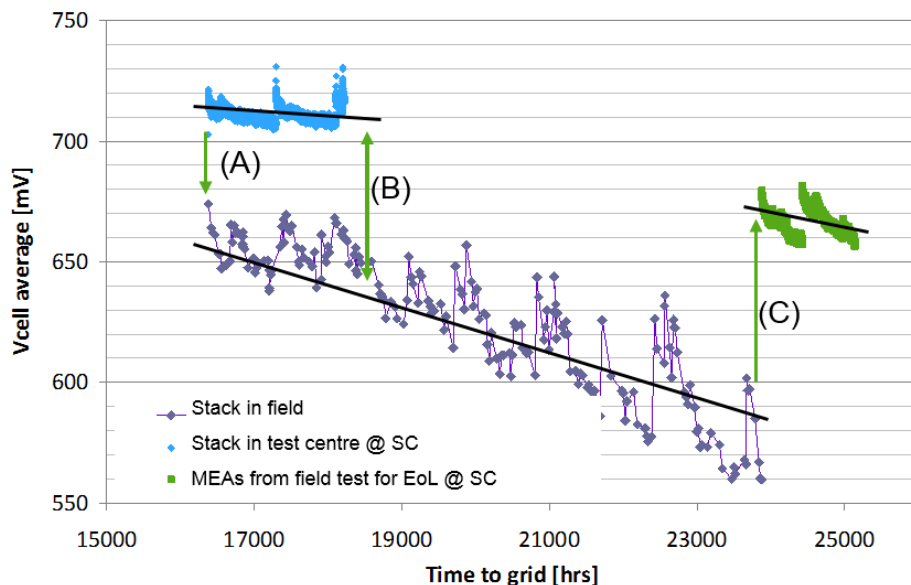


Figure 1: Importance of test environment observed on SC-1 decay. More than one degradation mechanism applies with (A) Performance gap at BoL; (B) Differences in degradation trends; (C) EoL performance gain in Lab. Blue curve: Stack in SolviCore test center, violet curve: stack in field, green curve: MEAs from field stack in SolviCore test center

SC-2: Improve manufacturing process

Subsequent development loops and the future need for large scale manufacturing necessitated a transfer from CCB to CCM (Catalyst Coated Membrane) manufacturing technology. It simplifies the overall manufacturing process and a higher degree of automation can be applied. CCM technology is suited for continuous processes. It also allows for quick adaption to new raw materials.

A prerequisite towards a CCM-based MEA is roll-good membrane material available on commercial scale and with quality sufficient to feed a continuous process. This requirement was met by Solvay’s IMP1 membrane, which was therefore integrated into MEA generation SC-1.

Results obtained with SC-2 in laboratory environment presented a slight advantage for CCM variation. Also effect of different air feed method had been tested by introducing a pump directly in front of the test station. Some additional decay could be observed, but similar for SC-1 and SC-2.

This MEA type was consequently introduced in field, but it did not translate well to the results obtained in laboratory test: In field operation, an increase in degradation rate was observed rather than a decrease.

SC-3: Towards step change in MEA degradation

This development loop was planned to further improve MEA durability and provide quicker conditioning. As the previous development loop SC-2 did not yield the intended increase in MEA lifetime, SC-3 and SC-4 needed to demonstrate a step-change.

The original development approach was altered to this purpose: Rather than supplying individual MEA variations after a down-selection process based on lab testing, a broader selection of MEA variations is provided for field testing.

The concept of “rainbow stacks” has been employed to that purpose. Repeating MEA groups ensure decay rates observed are not artefacts. A total of 3 rainbow stacks has been operated within the SC-3 generation.

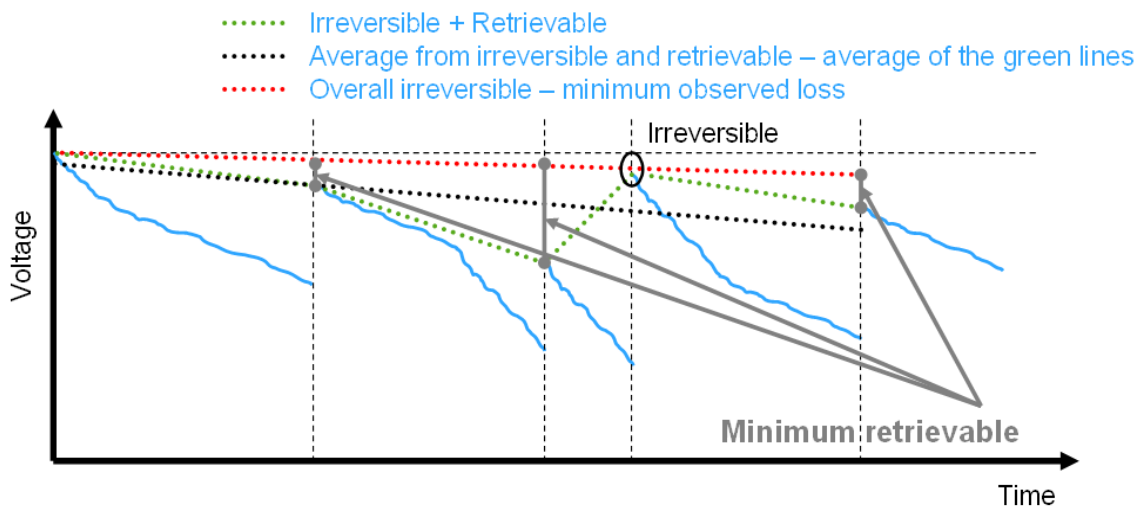
The method allowed identifying both primary and secondary effects on MEA lifetime for subsequent incorporation within SC-4. Rainbow stacks contained systematic variations to anode and cathode catalyst functionalities, non-catalyst variations (catalyst layer composition) as well as processing variations.

Different methods to perform lifetime prediction had been introduced and compared to existing field results to prove their efficiency. The most important was to be able to take into account the effect of possible impurities on the MEA degradation, as well as the recoveries possible by a start/stop event on the power plant.

Two methods were validated as meaningful to obtain results compatible with real lifetime:

- Case 2: From linear regression over integral operation history (black line below)
- Case 4: From best recovery obtained during stop/restart of the power plant (red line)

These methods were approaching good prediction after at least 4.000 runtime hours.



The “end of test” analysis performed on these variations helped to gain understanding in the possible correlations in between degradation mechanisms:

- Irreversible losses such as irreversible EPSCA or ohmic resistance are observed but not correlated to the field sensitivity, which is indicated by the saw tooth behaviour – see violet line in *Figure 1*
- Some unassigned losses, mass transfer resistance and reversible ECSCA losses, could be linked to field sensitivity in combination with the not identified impurities
- All variations are losing more performance in contact with the deliberately added pollutants. The best variations identified did not change their irreversible sensitivity to pollutants with ageing (i.e. are able to get back to their initial performance as soon as the pollutant is

removed, or upon a stop/start). Moreover, cathode contaminant tolerant type also showed reduced reversible decay during field tests

SC-3 also incorporated Solvay Specialty Polymers' second membrane improvement, IMP2. A few variations of the SC-3 MEAs tested exhibited potential for the required step change in MEA lifetime, and they were applied to SC-4 either individually or in combination with others.

SC-4: Confirmation of the approaching target

In this fourth development loop the most promising variations of previous generations have been introduced. The most promising variations have been combined in order to clarify the impact of single variations, such as membrane generation, anode CO-tolerance and/or loading.

MEA lifetime demonstrated by field test results from the Delfzijl PEM power plant is presented in Figure 2.

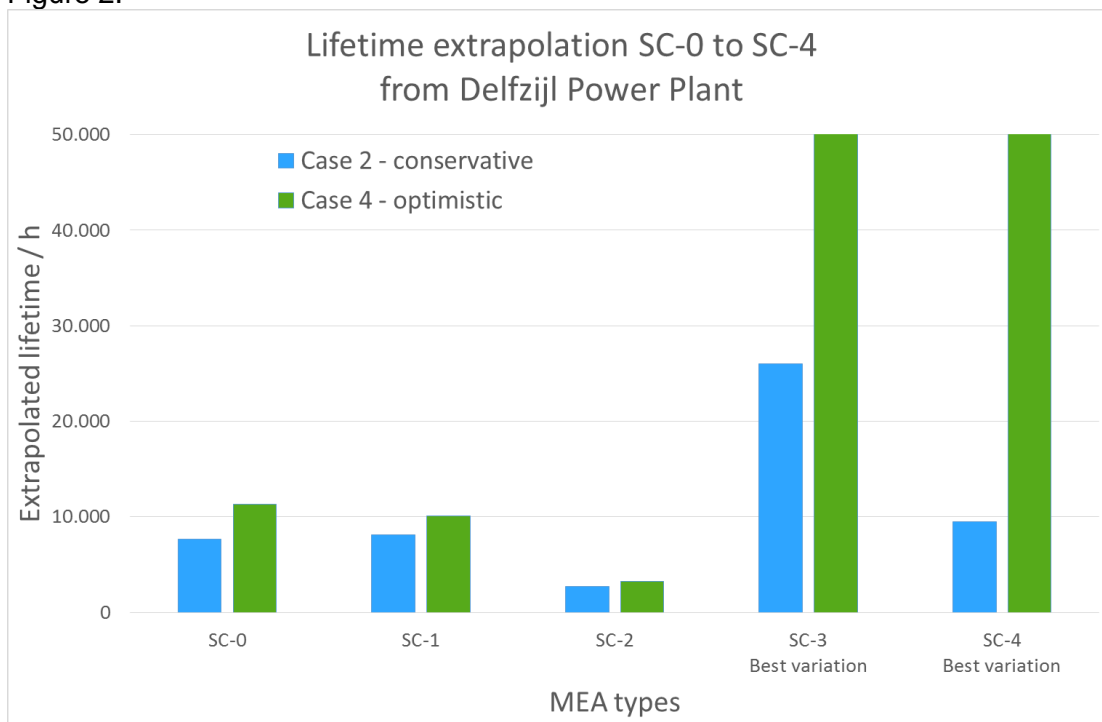


Figure 2: MEA lifetime achieved in the Delfzijl PEM power plant for MEA generations SC-0 to SC-4, status as of M42. Typical operating time: SC-0 = 10.000h; SC-1 = 10.000h; SC-2 = 6.000h; SC-3 = 7 to 9.000h; SC-4 = 4.000h

The “end of test” analysis performed on the aged MEAs from field tests at the very end of the project confirmed most of the trends extracted from SC-3 analysis (improved Cathodes show biggest improvement). Predominant degradation mechanisms as observed from our field tests can be listed as follows:

1. Cathode loss of active surface area by poisoning - reversible
2. Cathode increase in mass transfer resistance, possibly related to loss of hydrophobicity either from material degradation (irreversible) or changes in surface functional groups (reversible)
3. Cathode loss of active surface area by particle growth (and carbon corrosion) - irreversible
4. Anode loss of active surface area by poisoning assisted by irreversible loss of active surface area (particle growth/dissolution, carbon corrosion) - reversible
5. Cathode increase of proton resistance – irreversible

Obviously the reversible decay on cathode is strongly limiting lifetime in practice and further research is required to identify the responsible component.

4. Stack - and Balance-of-Plant development (WP 4) - Nedstack

Work package 4 has focused on lifetime improvements for stack components, system conditions, and the actual durability testing in Nedstack's PEM Power Plant using the hydrogen from a chlor-alkali plant.

4.1 Flow field development

The first topic to be addressed was the flow field as two aspects of the reference flow field may potentially be limiting lifetime:

- a) Uneven temperature distribution (hot spots) over the cell area as determined by the coolant flow field
- b) Fuel starvation as a result of insufficient condensate removal, determined by the anode flow field design

a) Coolant flow field

CFD calculations using COMSOL initially indicated an excessive temperature rise ($> 10^{\circ}\text{C}$) near the cathode inlet. However, measurements showed only limited temperature differences ($< 4^{\circ}\text{C}$) in comparison with the average outlet temperature. These are not expected to limit lifetime and efforts were directed towards evaluation of the anode flow.

b) Anode flow field

Partial flooding in the anode may provoke local fuel starvation conditions, which are detrimental for lifetime. Hence, improvement of the anode flow field should be directed towards elimination of these flooding conditions providing stable cell voltages under standard conditions for all commercial MEA-types. Flooding was studied via cell voltage instabilities provoked by reducing anode stoichiometry to as low as 1.1 for a known sensitive MEA type. No cell instabilities could be observed, nor with other MEA types indicating this feature is not critical.

4.2 Evaluation of stack hardware

Besides the MEA, also the following stack components must be able to guarantee operation times over 40,000 hs:

- I. Cell plates
- II. Seals
- III. Stack housing

Functional properties of above components have been evaluated, both by evaluation of in situ aged samples (aged up to 23,000 hs in real operation) and by specifically designed Accelerated Stress Tests (AST's) :

I. Cell plates

For maximum lifetime, in Nedstack stacks exclusively composite type cell plates are used. There have not been any indications that the reference cell plate as used from the start of Stayers may be lifetime limiting. Therefore focus has been to characterize all functional properties and to monitor them after ageing. The results are summarized below:

- Dimensional stability (i.e. creep effects): though a minimal increase in cell plate thickness was observed, for critical dimensions such as the MEA-chamber no significant differences are observed over 23.000 hs of operation. Relaxation actually results in a flatter cell plate (reduced spread in intra-cell plate thickness), which mostly seems to occur within the first 10,000hs after which it slows down. This is confirmed with density measurements in the

area of maximum relaxation, where a minor reduction of was measured after 10,000 hs, after which it remains stable.

- Permeability: during standard leak testing no significant difference was observed between new and aged (up to 23,000 hs) cell plates, confirming that the localized relaxation has no noticeable effect
- Electrical conductivity: Electrical resistance of cell plates is measured for over 23,000 operating hours. It decreases substantially (improving performance) while the strongest reduction again takes place in the first 10,000 hs. As the thickness of the plates increases slightly, the decrease of the resistance is probably caused by changes of the surface properties of the plates.
- Surface properties have been characterized by measuring the change in contact angle (degree of hydrophobicity) over operating time and by electrochemical degradation (AST). The importance of changing surface properties for real life operation has been determined by analyzing stack performance containing in-situ aged cell plates
 - Contact angle measurements: While anode cell plates do not reveal a significant change in contact angle up to 18,000 hs of operation, cathode cell plates show a significant reduction of hydrophobicity. This occurs especially at the gas inlet area where the contact angle reduced from approx. 80° down to 0°.
 - Electrochemical degradation: It was confirmed by impedance spectroscopy (EIS) that aged cathodes show a reduced impedance. This is probably caused by increased wetting and possibly an increased surface roughness due to carbon oxidation. An AST was developed for artificial ageing of carbon composite cell plates via electrochemical surface oxidation. Within 24 hr ageing to a similar extend as for 18 khr cathodes was achieved, showing similar increases in hydrophilicity and OCV, and decrease in impedance. Excessive ageing by AST did not show a further deterioration of surface properties suggesting this is not a critical factor in reaching 40,000 hs lifetime
 - The loss of hydrophobicity as observed for aged cathodes may affect stack performance due to increased mass transport problems. Whether this is limiting should be detectible from 18,000 hs of in situ ageing, since beyond this time no further deterioration of surface properties is expected to occur. Hence a stack with different sections of new and aged (23,000 hs) cell plates has been investigated. No negative effects of aged cell plates (anode and cathodes) could be observed. On the contrary, used anodes have slightly lower ohmic resistance.

Summarizing it is concluded that even though ageing of cell plates, especially cathodes, changes the surface properties (wetting, electrochemical impedance) this is not noticeable in normal stack operation for cell plates operated up to 23 khrs. Combined with the results obtained from cell plate AST's it is believed that the surface properties will not be limiting up to 40.000 hs.

- Mechanical properties: Flexural strength has been determined on in situ aged cell plate samples (from 0 up to 23,000 hs). Although there is a tendency towards increased stiffness with ageing, there is no significant difference in strength observed at room temperature or at operating temperature (70°C) between the different operating times.

Extensive analyses of functional properties of aged cell plates strongly suggests that at least up to 40,000 hs of operation this component is not limiting lifetime.

II. Seals

In contrast to cell plates, the reference seal material does require improvements in order to be able to achieve 40,000 hs operating time. Even though stacks have operated for 20,000 hs, upon return obvious deterioration of sealing properties was observed. The lifetime of the Stayers reference material has been defined based on historical data from stack leakage tests as shown in fig 4.1. The residual pressure % is shown in the left graph for the gas compartment and on the right for the coolant channel. It can be seen that seal degradation is much more severe in the coolant channel. Assuming a pressure decay limit of 50% is acceptable, a seal lifetime of 12 khs is obtained for the coolant channel (35 khs for the gas compartment), which corresponds fairly well with observations in practice.

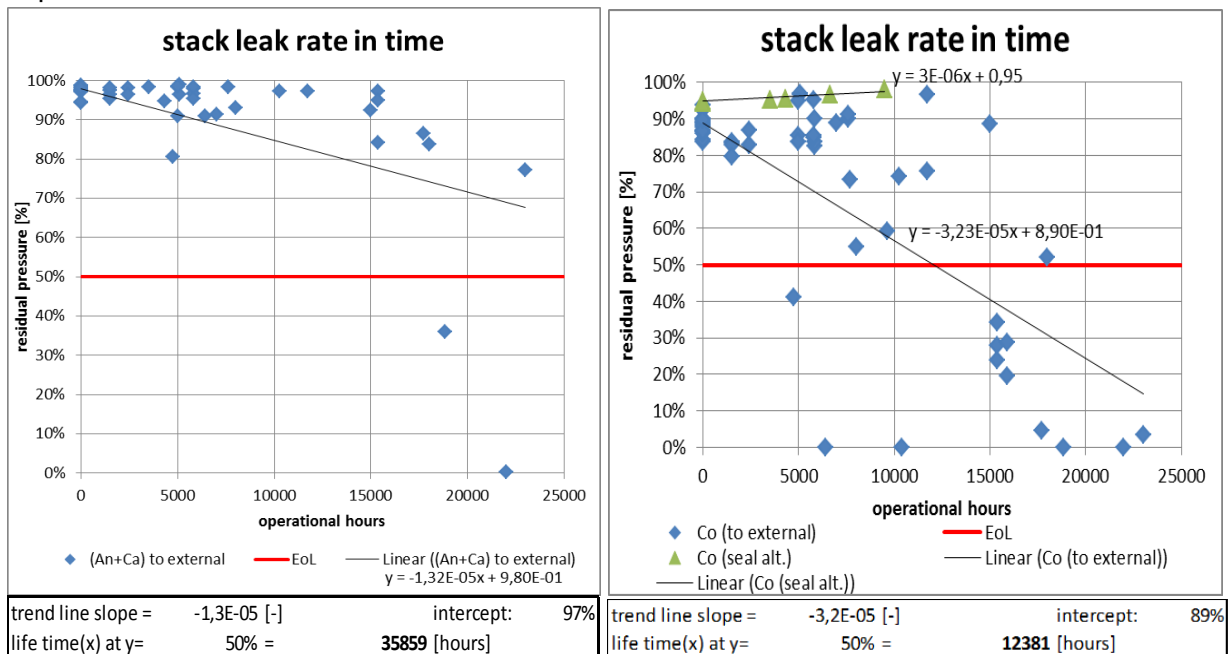


Fig 4.1 - stack leak rate in time; left: combined anode+cathode compartment, right: coolant.

During the Stayers project, three improved seal materials have been selected, and tested in situ for up to 10 khs. AST's have been used which allowed to estimate the lifetime of the improved materials in relation to the reference seal. The reference and improved materials have been exposed to harsh oxidizing conditions. Visual evaluation of the reference after 24 hs showed a level of seal degradation comparable with 20,000 hs of operation in the power plant, while improved material A-1 required a three times longer test time for the same visual effect. The other alternative materials (B-2 and 3) showed only minor discoloration after 3 days (B-2) or similar degradation to the reference (B-3). In order to quantify the expected lifetimes in a better way, tensile tests were performed on in situ aged reference material (20,000 hs), and AST-aged reference, and improved seal materials. The reference allowed determination of an AST factor of approx. 300 based on residual tensile strength. Lifetime predictions for the improved seal materials were 31, 47, and 150 khs for the materials B-3, A-1 and B-2 respectively, which corresponds to the trend observed during the visual observation. At the end of the project this rather rough method was verified by measuring the leak rates of stacks equipped with improved seals (green markers in Fig 4.1). As can be seen from Fig. 4.1 a spectacularly improved trend is visible supporting estimated lifetimes beyond 40,000 hs for at least two of the improved materials.

III. Stack housing & assembly procedures

At the start of the Stayer project a new stack housing design (GEN 2.5) was launched and applied together with the SC-1 MEA deliveries being the first formal SC-1 iteration to be field tested. Also one stack with a 20% reduced assembly force was tested. It was concluded that:

- Reduced assembly force clearly had a negative effect on MEA lifetime (increased decay)
- Field test results, tensile tests, and reassessment of the Gen 2.5 design prompted the need for further improvements (e.g. elimination of shear stress on bolts, compensation of creep effects in aluminium at elevated temperatures, corrosion resistance)

A new stack housing was designed – the GEN 2.6 40 khr, using a more corrosion resistant anodized aluminium type and several proto-types were manufactured for extensive mechanical (rupture, deflection, creep tests at elevated temperatures) and corrosion testing. The new GEN 2.6 design indeed showed drastically improved mechanical properties and met all design requirements for operation over 40,000 hrs. Moreover, for used GEN 2.5 tension plates after 18,000 hrs of operation it was shown that creep with the expected strain softening does not occur. On the contrary, strain hardening occurs, resulting in an increased strength in comparison to the BOL properties.

Corrosion properties were studied by electrochemical analyses of aluminum materials in a salt solution. The selected anodized material showed strongly reduced corrosion densities and absence of pitting.

4.3 Test set-up for duration tests at chlor-alkali plant

Before the start of the Stayers project Nedstack's fuel cell system connected to Akzo Nobel's chlor-alkali plant in Delfzijl, the Netherlands, was upgraded with a new stack module with improved flow (U-flow). Throughout the project, operating conditions favorable for longevity have remained unchanged and are summarized in Table 4.1

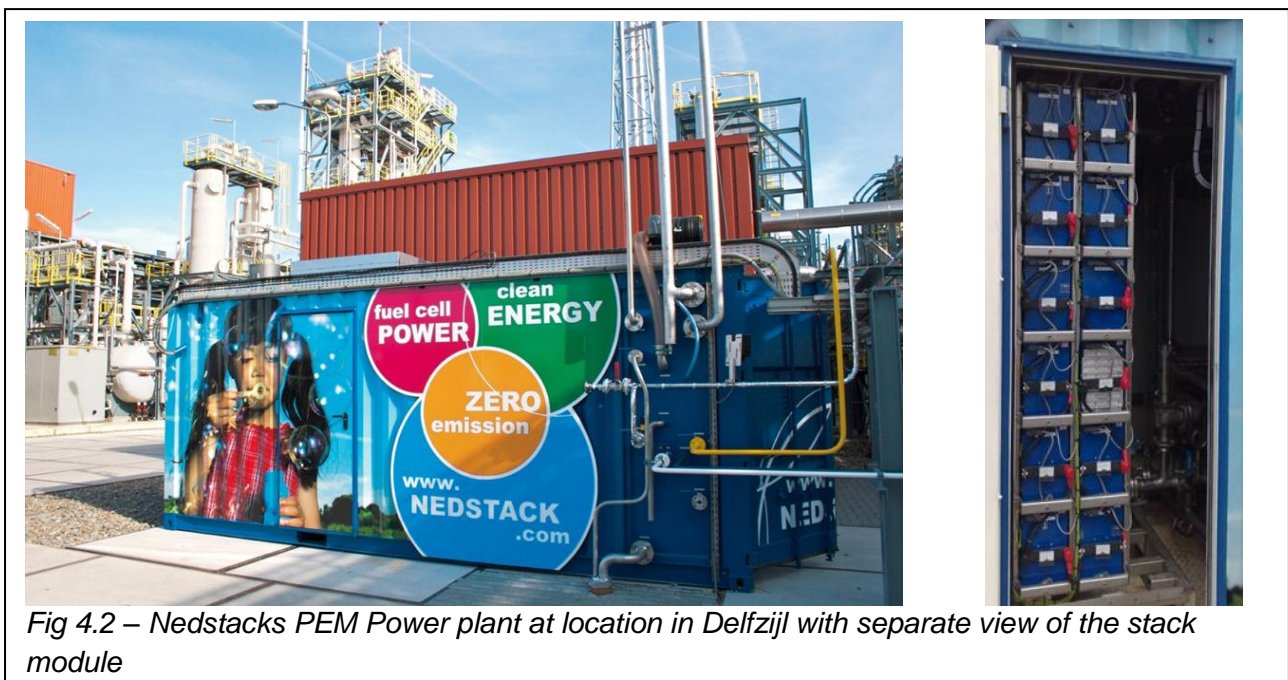


Table 4.1 – Operating conditions PEM power plant

System	J [A/cm ²]	Stoich. ratio Cathode	Stoich. ratio Anode	T stack [deg. C]	RH cathode [%]	RH anode [%]
Power plant Delfzijl	0,5	3.3	2.4	65	85	85

At the start of the project a powerful Cell Voltage Monitoring (CVM) tool was implemented, which allowed detailed evaluation of individual cell decay, which proved especially useful for the SC-3 and 4 rainbow stacks. During the Stayers project over 25,000 hs of durability test data have been generated by the power plant giving extremely valuable information and allowing for comparison of the numerous MEA types that have been tested.

In the final part of the project period, the important milestone of 40.000 hs of operation of the power plant has been reached. This has been achieved without replacement of any of the main system components. The system has shown an uptime > 85%, while no Nedstack maintenance personnel is present on site proving the technology is very robust and reliable.

Feed stream analyses has shown sub-ppm levels of CO in the hydrogen and 15 ppb NO_x and 1 ppb SO₂. It was found during the project that for sensitive MEA types (low catalyst loadings) such levels may contribute to reversible decay but generally this is not the case. Improved air filtration showed no effect.

4.4 CVM data analyses stack characterization

I. BOL/MOL/EOL analyses of SC Iterations

Detailed electrochemical BOL/MOL/EOL analyses for all SC-0 to 4 iterations have been performed. Some general conclusions:

- The magnitude of the reversible decay rate observed in field tests within a run correlates with initial ECSA: lower catalyst loadings show stronger reversible decay; When over lifetime the ECSA reduces irreversibly this also corresponds with a steeper decline of cell voltage within a run in comparison with the initial decline, at BOL.
- The stop-start procedure of the power plant results in a substantial recovery of the reversible part of the decay. A constant decay in the order of 100 mV can be observed after for example 1000 hs of continuous operation for SC-2, while most of this decay is recovered after a short stop. The different time scales suggest a different mechanism than gradual flooding, such as catalyst contamination.
- Ex-situ electrochemical MOL analyses and in particular an additional recovery procedure enhance this recovery of retrievable decay even more. To a large extend this seems related to ECSA regain which occurs e.g. after release of contaminants upon cell voltage excursions > 1.0 V, though also a reduction of mass transport resistance is obtained.
- Cathode contamination was found for specific SC-3 MEA's after field operation by cyclic voltammetry. Ex-situ determination of reversible ECSA loss is difficult though, since partial recovery already takes place during the stop procedure of the plant, transport to the lab, and preceding preparation and analyses.
- The irreversible decay is mainly caused by irreversible cathode ECSA loss, while reversible decay is due to cathode contamination. In addition, the mass transfer resistance increases probably due loss of hydrophobicity in GDL and catalyst layer. Anode ECSA loss also occurs, but at normal levels this is not expected to contribute to cell voltage loss. Low anode ECSA increases the sensitivity towards CO and may increase reversible decay (especially at CO levels > 0.2 ppm).

II. Nedstack XXL reference stacks

Nedstack's commercial FCS XXL stacks have also been operating in the power plant and have achieved lifetimes over 26,000 hs while still in operation. These MEA's have also been applied to allow lifetime determination for the improved seals. When evaluating the decay rates of the latest XXL generation, extrapolated lifetimes (based on a simple linear regression of collected operating data) are obtained meeting the Stayers target of 40,000 hs as can be seen in Fig 4.3 and table 4.2. The decay rates are very consistent and operating times are considered sufficient (7 to 16 khs) to justify the conclusion that the XXL catalyst indeed is able to reach the stayers target of 40,000 hs.

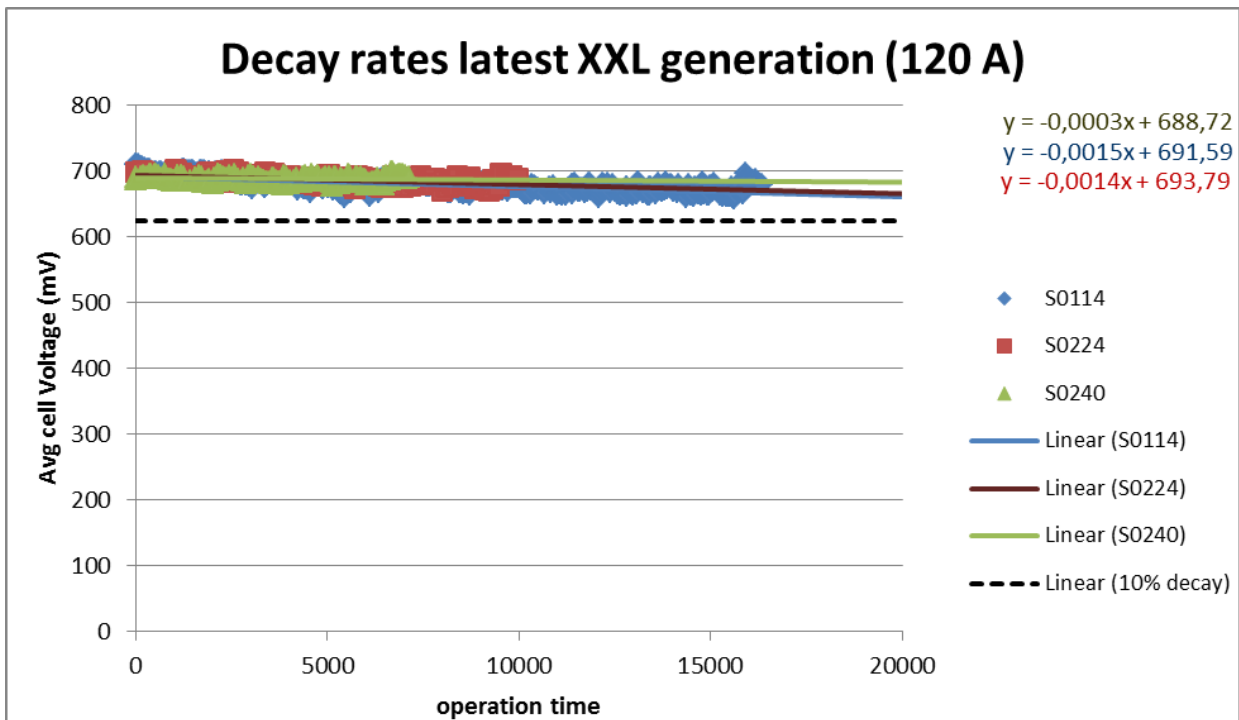


Fig. 4.3 Performance of the latest generation XXL MEA's

Table 4.2 - lifetime data latest XXL stack generation

stack	actual lifetime khs	CV_BOL mV	decay rate $\mu\text{V/h}$	estimated lifetime khs
S0114	16,4	692	1,55	44,6
S0224	10	693	1,43	48,3
S0240	7,1	689	0,32	216,0
avg	11,2	691	1,1	103,0

From the WP-4 results it can be concluded that 40,000 hs lifetime is possible for stacks (catalyst, cell plates, seals and housing) and Balance of Plant. With these results, large scale implementation of the PEM Power Plant technology can now take a big step forward!

5. WP5 Accelerated Durability Investigations (WP-5) - Sintef

Introduction

Stiftelsen SINTEF (Norway) has been work package leader of WP 5. The objective of this work package was to evaluate degradation of the most important components of the fuel cell stacks by designed Accelerated Stress Tests (ASTs). Focus of the activities in this WP was therefore mainly oriented towards degradation AST and contamination experiments on single cells to study the reversible (both anode and cathode), retrievable (cathode) and irreversible (cathode) performance losses of the MEAs.

In the first phase of the project, several different AST protocols that could mimic the real life degradation of the stack at Delfzijl plant were developed and tested on single fuel cell units at SINTEF that contained MEAs similar to Delfzijl stacks. Once an AST protocol was selected, it was implemented to different types of MEAs for comparing the results of cathode degradation with ASTs to that of the real life degradation. At the next stages of the project, effect of contaminants like CO, NO₂ and SO₂ on both the fresh and stress tested electrodes was determined. A table showing the performance of MEAs during AST and poisoning studies is summarized at the end of this summary.

Test station at SINTEF

The fuel cell test station at SINTEF for large cell/electrode areas, as well as its software, see *Figure 3*, were adapted to the requirements of partners' test cells and testing procedures and to the requirement of automated long term complex AST test cycles.

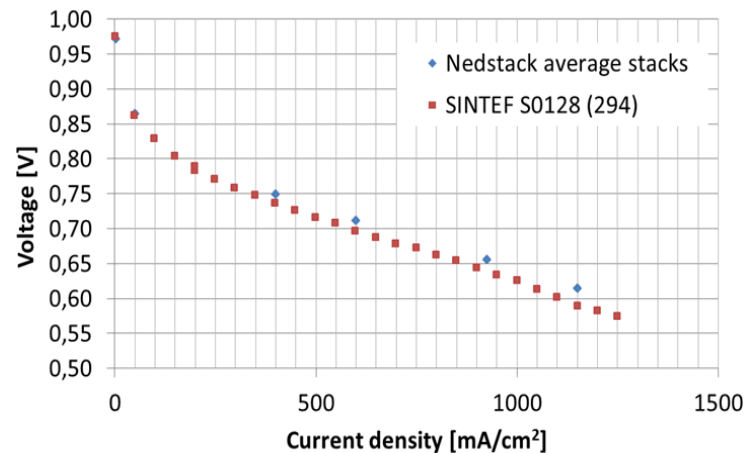


Figure 3: Test station for large cell areas at SINTEF and performance curves for SC0.

Irreversible degradation – cathode

For the irreversible degradation, initially several AST protocols were evaluated. Based on results from post-mortem analysis performed on SC0 MEAs operated at Delfzijl, which showed that the cathode catalyst was the main degrading component of the MEA, the following AST protocol was selected (*Figure 2*):

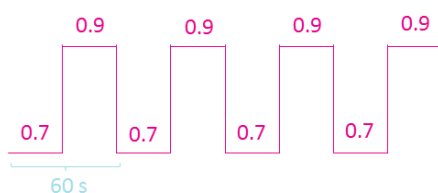


Figure 2: Voltage cycling between 0.7 and 0.9 V.

The performance curves before and after applying the test protocol on MEA 297 (SC1) is shown in Figure 3.

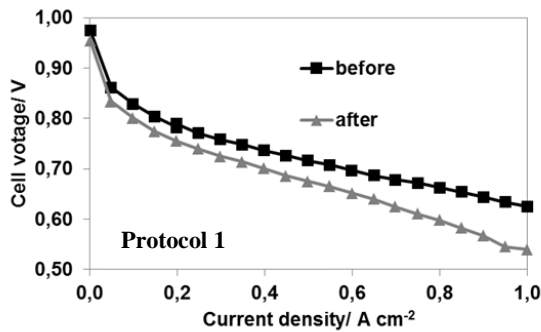


Figure 3: Performance curves of the cells before and after performing AST protocol 1.

Figure 4 indicates that the MEA tested with Protocol 1 lost about 30 % of the cathode active Pt electrochemical surface area (ECSA) after 900 hours of operation. A second protocol (2), which included a period at 1.2 V, lost about 70 % of the ECSA after only about 200 hours of operation. The reason for this difference is due to the 1.2 V step which causes heavy carbon (support) corrosion. As the stress test Protocol 2 proved to be too detrimental and not representative for the stacks at the Delfzijl plant, protocol 1 has been used for all the MEAs tested at SINTEF. Post mortem analysis, comparison with the stacks operated at Delfzijl and an MEA initially used at Delfzijl plant and subsequently tested at SINTEF for its EoL confirmed about 5-6 times accelerated degradation of the cathode catalyst with Protocol 1, making it a very useful for evaluation and lifetime prediction of the last MEA iterations.

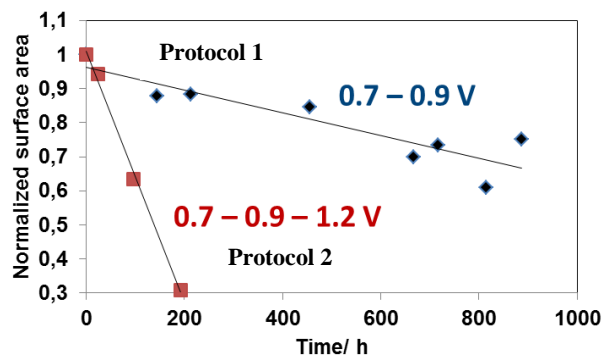


Figure 4: Normalized active cathode catalyst surface area measured during AST, SC1.

The ECSA loss of further MEA cathodes tested with Protocol 1 is shown in Figure 5. It was found that MEA type SC1 (CCB version) shows a slightly lower ECSA loss than all the other MEAs (about 10% loss vs. 17-19%, after 400 hours of AST). However, the ECSA losses after this procedure are in the same range for all tested MEA. Thus, by increasing the absolute loading (=ECSA), longer lifetimes can be achieved. The linear trend found by this AST experiments was also implemented in the modelling activities in WP6. Loss in anode ECSA was only found for SC3-CCV4A, but as expected it reduced only marginally (~5%).

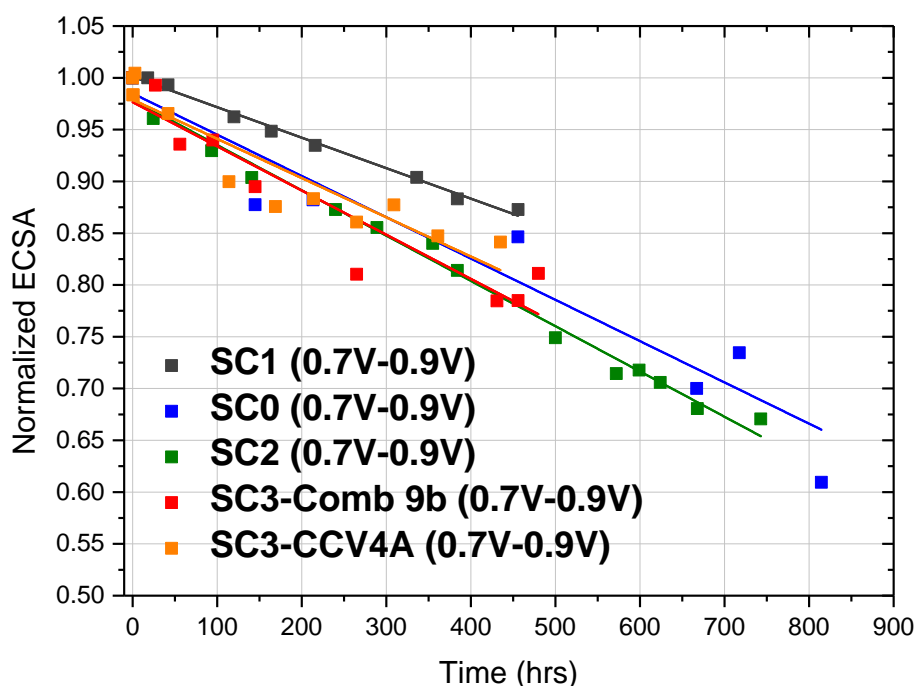


Figure 5: Normalized active cathode catalyst surface area measured during AST with Protocol 1 on different MEAs.

Poisoning of the catalyst

The effect of poisoning of the electrocatalysts on both anode (CO) and cathode (NO₂ and SO₂) were determined before and after cathode AST. Depending on whether the MEA recovered from the performance loss due to poisoning effect after only removal of the impurity from the feed, the degradation state was categorized as reversible (no additional actions besides changing to neat feed streams) or retrievable (some recovery procedure required). An example on the fuel cell performance on one MEA type from the project (SC-3 Comb 9b) with poisoning before and after cathode AST is shown in Figure 6. Results from post-mortem testing at SolviCore show different behavior, where aged MEAs have similar tolerance at BoL and after several thousands of hours in operation. The contradiction in these results is not understood but may be related to partial recovery during IV measurements at Nedstack and subsequent shipping of MEAs to SC.

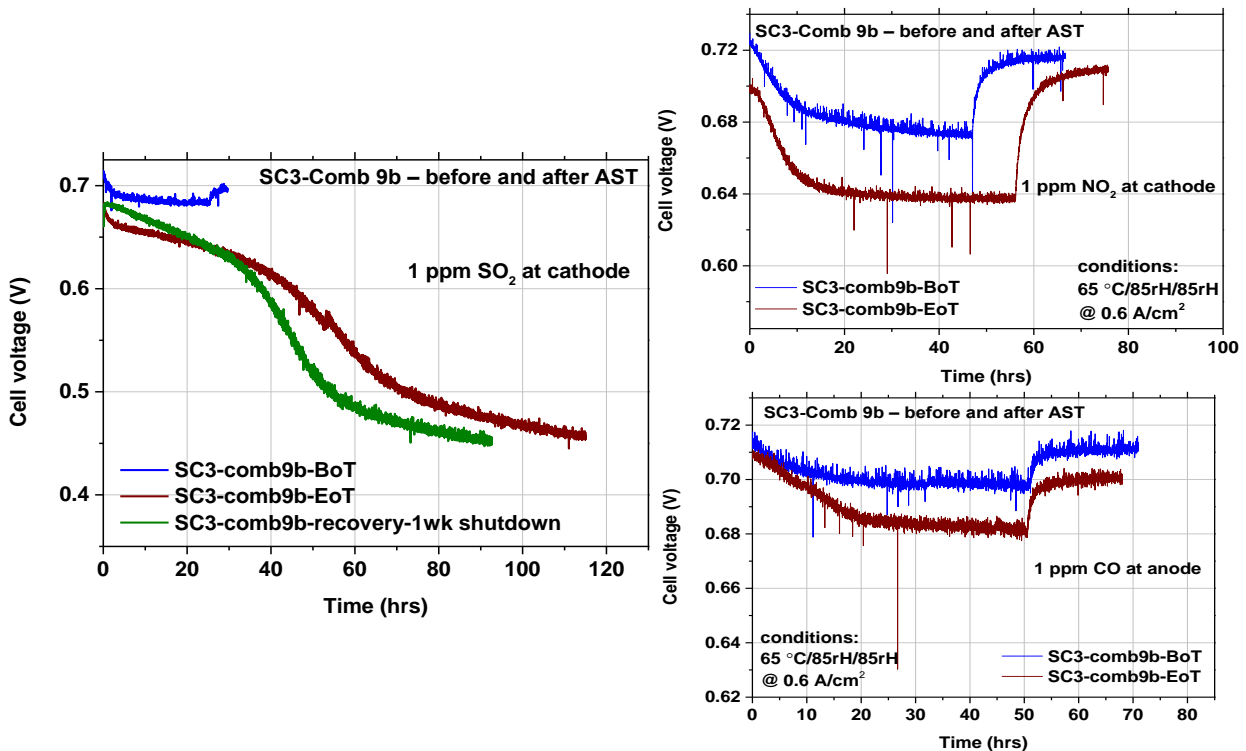


Figure 6: Effect of anode and cathode poisoning of MEA SC3-Comb 9b before and after 400h AST.

Reversible degradation (CO and NO₂):

Referring to the two graphs to the right in figure 6: The effect of 1.0 ppm CO in the anode feed over time on MEA types SC1, SC2, SC3-CCV4A and SC3-Comb 9b were determined. This degradation was fully reversible, i.e. the performance was completely recovered once the CO supply was removed from the anode feed. It was observed that the CO tolerance of SC3-Comb 9b was much higher than the other MEAs, while SC1 was second best. This can be explained by the fact that SC2 and SC3-CCV4A anodes were of similar type and they contained about 25% less Pt on the anode compared to SC1, whereas the anode of SC3-comb9b was designed to be CO tolerant. The reversible degradation rate increased after cathode AST, whereas the voltage decay rate of SC2 and SC3-Comb 9b increased by about 3 and 1.5 times respectively after cathode AST. MEA type SC3-Comb 9b was found to be more tolerant towards CO-poisoning than the others both before and after cathode AST. These CO experiments indicated that the AST applied not only degraded the cathode, but also influenced the anode electrode, even though anodes only showed a marginal decrease in ECSA (about 5%) after the AST. The different trends as observed in field tests for SC3-Comb 9 in comparison with e.g. CCV-6 indicate that CO levels in Delfzijl are not significant.

The effect of 1 ppm NO₂ in the cathode feed on MEA performance of types SC3-CCV4A (from different batches) and SC3-Comb 9b before and after cathode AST was validated. It was found that the performance of MEA type SC3-Comb 9b was about the same as SC3-CCV4A under the influence of NO₂, although variations in tolerance was seen with different MEAs of type SC3-CCV4A. The voltage decay rate of SC3-CCV4A was increased by more than 3 times after cathode AST, while that of SC3-Comb 9b increased by only about 1.25 times, although the BoT performance of both these MEAs were very similar. In summary, MEA type SC3-Comb 9b was found to be more tolerant towards NO₂ than the other MEAs even after cathode AST. As with the CO-poisoning effect, the cell performance was fully reversible, i.e. the performance was completely recovered once the NO₂ supply was removed from the cathode feed.

Retrievable degradation (SO₂):

Referring to the graph to the left in figure 6: The effect of 0.5 ppm SO₂ on the cathode of MEAs types SC3-CCV4A and SC3-Comb9b before and after cathode AST was evaluated. From the measurements it was found that (unlike with CO and NO_x) the cell performance was only partially recoverable even though the SO₂ supply was cut off and clean air fed after the cell attained saturation (at about 40 hours). Different recovery protocols were tried to recover the initial fuel cell performance. Of all the protocols, a complete shutdown of the test station for at least a day was found to be the most efficient way to retrieve the cell performance. Records of the cell voltage and the residing time during cell shutdown and start up, along with cyclic voltammetry studies on the cathode, showed that recovery requires the cell voltage to be at least 1.0 V for a limited time to remove sulfur species from the catalyst layer. However, as these high potentials may set off other degradation mechanisms to cathode and membrane, care should be taken with this recovery protocol. At the present scenario, occasional shutdown of stacks at Delfzijl plant will actually act as a recovery procedure for cleaning the cathode from sulfur or SO₂-like contaminants. Nedstack indeed demonstrated that cell voltage excursions above 1.0 V occur upon a stop/start in the plant. The subsequent recovery of retrievable decay shows very similar voltage recovery trends between the plant and SINTEF tests for SO₂ recovery.

Summary tables with results from AST and contamination experiments:

The poisoning effects at the beginning of tests for those MEA variations tested at SINTEF are ranked in Table S1. SC1 is used as baseline (0), + and – indicates better or worse performance relative to this. As expected, SC3-Comb 9b, which is developed as a CO-tolerant MEA, shows much better tolerance to CO. Furthermore, MEAs with low Pt content at the anode such as SC2 and SC3-CCV4A performed poorly with 1 ppm CO, when compared to both high-loaded SC3-Comb 9b alloy catalyst and SC1 (Pt only). This observation clearly shows the effect of Pt loading on CO-poisoning, i.e. the higher the Pt content, the better the CO tolerance.

On comparing the effect of cathode contaminants on the electrode performance, SC3-Comb 9b which contains high loaded alloy catalyst showed better tolerance towards both 1 ppm NO₂ and 0.5 ppm SO₂ than the others. Similarly, SC3-CCV4A with high Pt loading cathode showed superior tolerance to NO₂ poisoning. Nevertheless, this MEA is not as good as SC3-Comb 9b when it comes to SO₂ contamination which suggests that the Pt-alloy has a positive effect on SO₂ poisoning. Surprisingly, SC1 with a standard Pt loading (less than SC3-CCV4A) is as good as SC3-CCV4A on SO₂ tolerance. Another difference of SC1, as previously mentioned, is that the catalyst is coated directly onto the backing layer (CCB-based).

Table S1: Ranking of MEAs based on their tolerance towards contaminants at BoT

MEA type	Tolerance@ BoT		
	CO	NO ₂	SO ₂
SC1	0	n/a	0
SC2	-	n/a	n/a
SC3-CCV4A	-	+	0
SC3-Comb 9b	+	+	+

The MEAs were ranked in Table S2 according to their AST performance and contamination tests after the cathode AST. Standard Pt-loaded CCB-based SC1 has lost relatively less cathode Pt

ECSA compared the others with both low and high Pt loaded MEAs after 400 hrs of AST. No major difference in the Pt ECSA loss is found between high Pt and high Pt-alloy loaded SC3-CCV4A and Comb 9b.

The contaminant tolerant SC3-Comb 9b performed better with both anode and cathode poisons, even after the AST, followed by SC3-CCV4A (SC 0, 1 and 2 were not tested for tolerance after AST). Notably this corresponds with a reduced reversible decay as observed in Delfzijl for MEA's with specifically the same contaminant tolerant cathode, one more indicating the influence of air contaminants on reversible decay.

Table S2: Ranking of MEAs based on their tolerance towards contaminants at BoT

MEA type	AST protocol	% ECSA loss @ 400 hrs	Tolerance@ EoT		
			CO	NO ₂	SO ₂
SC0	0.7-0.9 V	17	n/a	n/a	n/a
SC1	0.7-0.9 V	12	n/a	n/a	n/a
SC1	0.7-0.9-1.0 V	9	n/a	n/a	n/a
SC2	0.7-0.9 V	19	-	n/a	n/a
SC3-CCV4A	0.7-0.9 V	17	n/a	0	0
SC3-Comb 9b	0.7-0.9 V	19	+	+	+
SC3-CCV4A EoL RB1	6700 hrs at Delfzijl	46	n/a	-	-

Summarized, the AST protocol applied at SINTEF was found to accelerate the fuel cell degradation by 5-6 folds compared to the real time operation. The cathode Pt ECSA loss for all the MEA variations was very similar, except for MEA type SC-1. Poisoning studies revealed that MEA type SC3-Comb 9b is most tolerant towards the contaminants applied at SINTEF.

6. MEA modelling and data analysis (WP 6) - JRC

This is the summary of the efforts made in this work package 6 on modelling and analysis of PEM fuel cell degradation issues.

In order to predict the long term behaviour of PEM fuel cells the components and their identified mechanisms of degradation have been included into the mathematical model of a fuel cell (CFD).

The mathematical model of the PEM fuel cells consists of conservation equations which are solved for mass, momentum, species, energy and charge with electrochemical reactions. Special attention is given to water management in PEM fuel cells (the two-phase flow in the cathode channel, co-transport of water molecules and protons in the membrane).

The identified degradation mechanisms can be taken into account in the mathematical model through the following most important parameters responsible for PEM degradation (having effect on I-V polarization curves): thermal conductivity, electric conductivity, protonic conductivity, diffusivity, permeability, porosity, tortuosity and specific catalyst surface area.

The CFD fuel cell model was used to predict the relative contribution due to the change (degradation) of each individual physical property to the overall performance (I-V curves) of the cell. It is shown some parameters have significant influence on voltage decay namely ECSA for cathode/anode, electrical conductivity of GDLs/CLs, porosity of GDLs, contact angle of GDLs or protonic conductivity of the membrane.

It turned out that the catalyst properties (especially ECSA) are influencing also the kinetics (low current densities domain of an I-V curve) and in a less extent the mass transfer. The GDL properties are mainly responsible for the decay at high current densities, and show limited influence at low current densities.

6.1 Water saturation effect at cathode side

Four mechanisms are responsible for water transport across MEA: (1) electro-osmosis from the

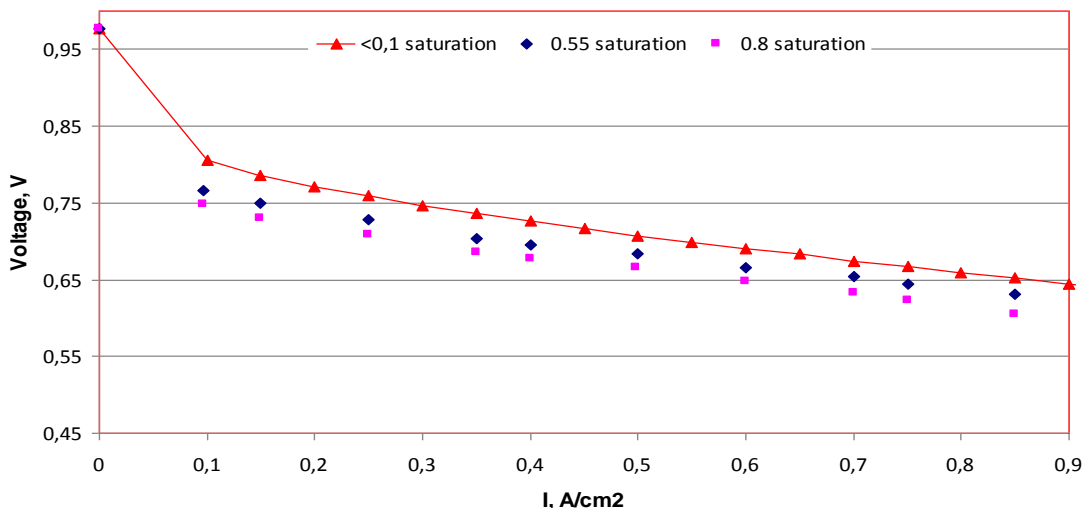


Figure 4 Influence of water accumulation in cathode GDL on the I-V curve

anode to cathode side; (2) back diffusion from the cathode to the anode side; (3) hydraulic permeation (pressure driven), mostly from cathode to anode, and (4) thermo-osmotic drag, typically small due to small temperature gradients. The water content inside membrane and catalyst layers is calculated based on equations describing these four phenomena. The liquid water is introduced in the model through the saturation in the porous layers. The influence of water accumulation in the GDL cathode was studied and a decrease of the voltage lower than 10 % was found when increasing the saturation level from 0.1 to 0.8.

Experimentally a net water transfer across the membrane from cathode side to anode side has been observed. Calculations of water mass flow rates evidenced that about 20% of the water produced at the cathode side is transported to the anode side (for 0.8 A/cm² and co-flow configuration).

To assess the influence of water accumulation in the cathode several polarisation curves were calculated for different cases corresponding to different saturation levels in cathode GDL layer. A decrease of the voltage around 10 % was found when increasing the saturation level from 0.1, corresponding to the beginning of the operation of the cell to 0.8 corresponding to a highly saturated porous layer.

6.2 Voltage decay prediction due to air/fuel contamination

A preliminary study of the influence of impurities present in the air (namely SO₂) or in the hydrogen (namely CO) streams was realised using kinetic models published in the literature and adapting them to the working conditions used within the project (where possible). In order to describe the voltage decrease due to contamination, the source terms at the cathode/anode side were modified accordingly to account contaminant adsorption effect on the kinetics and in the CO case voltage recovery due to CO electrochemical oxidation. This study showed lower calculated voltage decay than experimentally measured (about 0.76 mV/h for 5 ppm SO₂ calculated and 11.4 mV/h calculated, for 10 ppm CO). The limitations in modelling the effects of impurities on PEM fuel cell performance are mainly due to inaccurate reaction kinetics found in literature and to the measuring of cumulated degradation effects in the experiments.

Figure 5 presents the influence of 10 ppm CO in hydrogen on voltage decay showing equilibrium reached after about two hours of operation and subsequent voltage recovery by electrochemical oxidation of adsorbed CO when the hydrogen is free of CO.

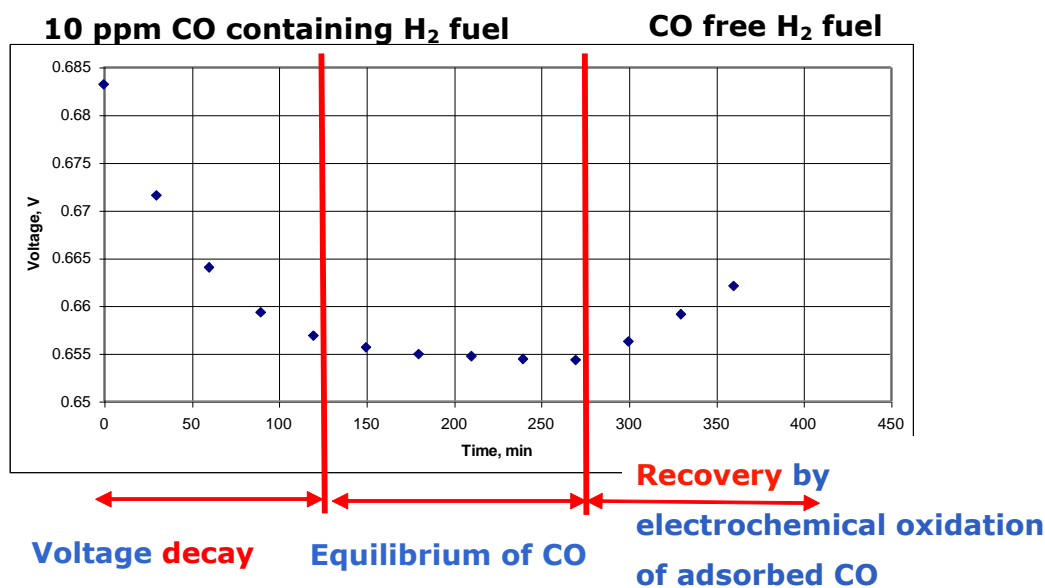


Figure 5 Voltage decay due to CO contamination of hydrogen

6.3 Parametric study

A set of physical parameters was identified to be responsible for performance degradation of PEMFC. The effect of these parameters is studied by extrapolating the experimentally obtained results for durations of up to 10,000 hours.

The physical parameters that were tested are: (1) electrical conductivity of bipolar plates; (2) ECSA, permeability, electrical conductivity, porosity and contact angle for the catalyst; (3) protonic conductivity; (4) electrical conductivity, porosity and contact angle for the GDL.

From the studied parameters some have significant influence on voltage decay namely ECSA for cathode/anode, electrical conductivity of GDLs/CLs, porosity of GDLs, contact angle of GDLs, proton conductivity.

The mechanisms responsible for ECSA decrease are mainly loss of active area by carbon corrosion, particle growth, detachment, dissolution and precipitation (in the membrane/ionomer) or migration of noble metal. Another cause is loss of catalytic activity, by blockage of the active sites (by noble metal surface coverage and modification) due to the presence of gas impurities.

To study the influence of ECSA, a linear decay of $a_{i,s}$ in below expressions was assumed based on experimental characterization at EOL performed by the project partners. In Fig 6 the results for both cathode and anode ECSA decrease are given corresponding to different operating times (6,400 h, 10,000 h and 15,000 h).

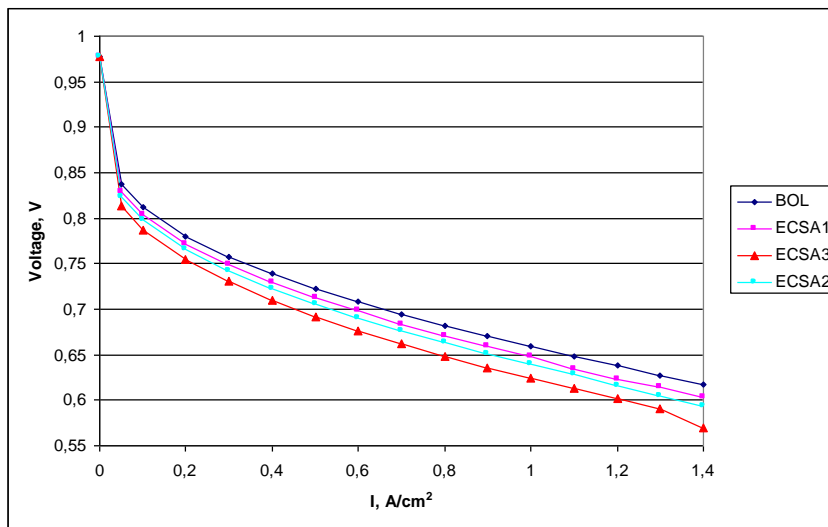


Figure 6. Influence of catalyst (cathode & anode) electrochemical surface area - Linear decay (ECSA 1 – 6,400 h, ECSA2 – 10,000 h, ECSA3 – 15,000 h)

6.4 GDL properties

Determination of the effective transport properties for GDL in PEM fuel cells is very critical due to the anisotropy of the porous material and different compression areas. Because some physical properties affect the PEM fuel cell modelling results significantly so they should be predicted in a trusted way. In order to estimate the effective transport properties, the 3D structure of the GDL is required. Several MEA samples (fresh as well as after ~3500h of operation) were analyzed by X-ray computed tomography.

The 3D image consisting of grey voxels was processed in order to assign voxels to each material in function of its grey value. The resulted 3D image contains black voxels attributed to solid material, respectively white voxels attributed to void space is presented in **Figure 7** (right).

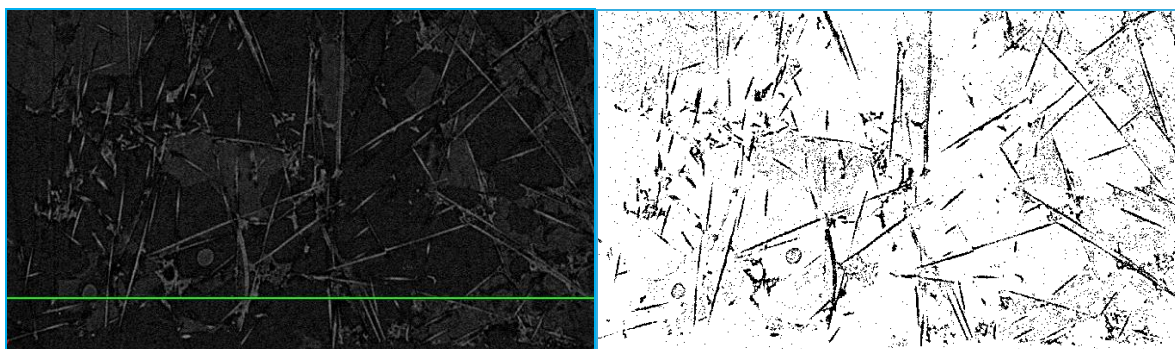


Figure 7. Fiber localization 2D slices: filtered and after segmentation.

Several properties were calculated based on the 3D structure of the GDL: pore size distribution, effective thermal conductivity, effective diffusivity, electrical conductivity and saturation dependent properties like capillary pressure by accounting the influence of contact angle; permeability; relative gas diffusivity and relative thermal conductivity

The wettability of the GDL is changing during the PEM FC lifetime because of the loss of PTFE coating, which has an important impact on water removal. The more liquid water is accumulating in the GDL, the higher the fuel cell performance decrease due to several reasons: the most evident is the blockage of the gas diffusion from the gas channel to the catalyst layer; a second one is the transport of radicals responsible for PTFE degradation that can take place only through liquid water; there is no local degradation of PTFE in the presence of water vapours.

The capillary pressure dependence on the liquid saturation is used to account for the mass transport limitations in the GDL. The wettability of the porous GDL is quantitatively introduced in the model by the value of the contact angle, in order to understand how water is transported in samples with different wettability.

From the capillary pressure variations with saturation (Figure 8), it is seen that at constant saturation that the lower the contact angle is, the lower the pressure that is necessary to introduce water inside the pore, resulting in a faster accumulation of water in the GDL.

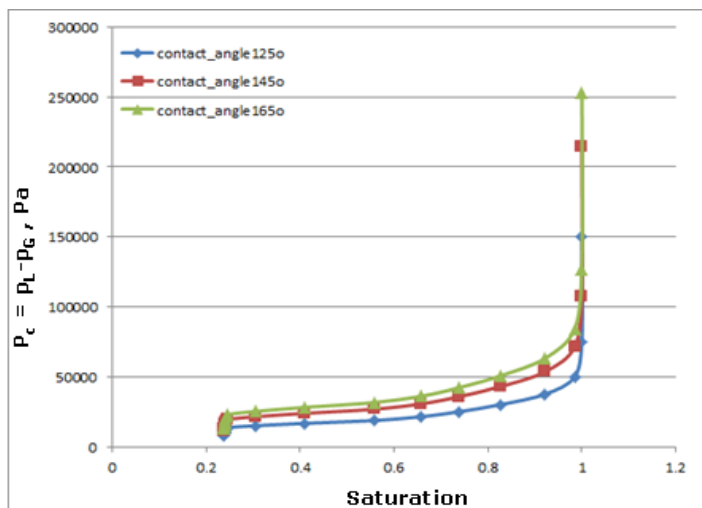


Figure 8. Capillary pressure inside cathode GDL for different contact angles (freshly conditioned, under land).

6.5 Cumulated effect of parameters

A worst case scenario in which all the properties were modified was also simulated (Figure 9) and the results were compared with the experimental data (stack operated for 6,400 hours).

The differences at low current density between modelling and experimental data (higher experimental voltages than simulated data) are the consequence of the fact that in worse scenario case the ECSA was decreased further from 23% (cathode), respectively 14% (anode) corresponding to 6,400h, to 54% respectively 33% (15,000 hours of operation). Experimental results obtained within the project showed a cathode ECSA irreversible decrease of about 50% after 13,000 hours of operation while Anode ECSA did not decrease so fast as it was assumed in modelling. Both experimental and modelling results are supporting the conclusion that cathode ECSA decrease is the most dominant decay mechanism for these MEA's.

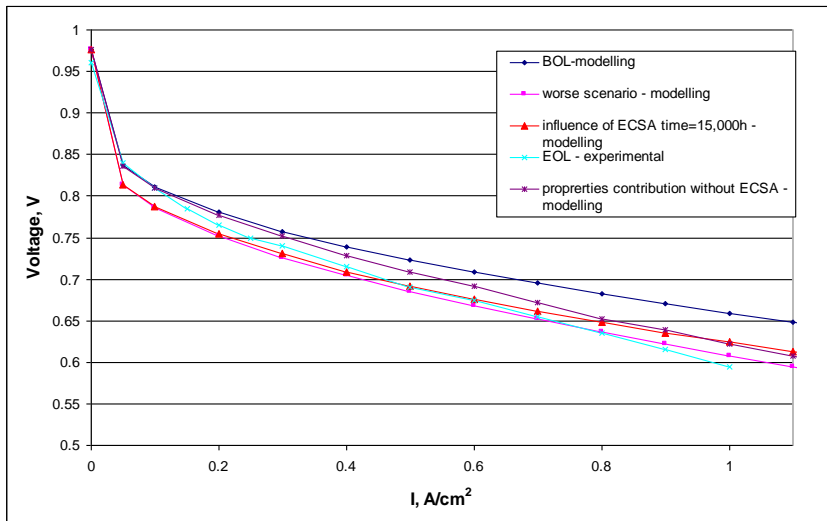


Figure 9. Cumulated effect of all the properties.

6.6 Conclusions

The degradation mechanisms of the MEA were included in the mathematical model through changes in the values of several identified parameters, of which properties were found to change during the lifetime.

From the studied parameters significant impacts have ECSA, the GDL properties and the proton conductivity. ECSA for anode side showed a lower decay rate and effect on I-V curve compared with cathode ECSA.

Using an ex-situ characterization technique (CT scans) for 3D reconstruction of GDLs it was possible to evaluate the state of the anisotropic GDL under channel and under land regarding the compression and porosity.

Two phase simulations in the anisotropic GDL cathode showed a high impact of the contact angle; water accumulation increases significantly for contact angles lower than 125°.

Capillary pressure dependencies on saturation for different contact angles were calculated. Results showed that a larger amount of water will be present in the GDL with higher porosity. Also when the contact angles decreases from 165° at values lower than 125° the level of water saturation is almost doubled.

The effective and relative (to liquid water saturation) thermal conductivity in the three directions was also evaluated for the anisotropic GDL. Because of the anisotropic structure of the GDL, the values of thermal conductivity are very different in plane and through plane. Also because of different compression levels under channel and under land the thermal conductivity is slightly improving under land.

Overall, the experimental and modelling results support the conclusion that cathode ECSA decrease is the most dominant decay mechanism.

STAYERS - Stationary PEM fuel cells with lifetimes beyond five years
FCH JU Grant Agreement number: 256721
Period covered: from 01-01-2011 to 30-06-2014

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Dissemination

Activity type	Description of activities/achievements
Dissemination	
Conference presentations	<p>Results were presented at the following conferences:</p> <ol style="list-style-type: none"> 1. Fuel Cells 2012: Science & Technology - A Grove Fuel Cell Event, Berlin; "PFSA Aquivion® membranes: general features and degradation mechanisms". - Luca Merlo*, C. Oldani, M. Apostolo, V. Arcella (Solvay Specialty Polymers SPA) 2. Workshop“ Progress in PEMFC Stack Testing Procedures”, 28th – 29th January 2014, Oldenburg, Germany. “Test protocols for commercial fuel cell stacks”, M. Smit, Nedstack 3. Workshop“ Progress in PEMFC Stack Testing Procedures”, 28th – 29th January 2014, Oldenburg, Germany. “AST in PEM Fuel Cells”, K. Jayasayee, A. Ødegård, Sintef 4. Fuel Cells 2014 Science & Technology – A Grove Fuel Cell Event - April 2014, Amsterdam; “research interests for PEM FC from perspective of a commercial stack manufacturer”, M. Smit, Nedstack Fuel Cell Technology 5. Carisma conference 2014, Cape Town, South Africa, “Degradation evaluation by accelerated stress testing and effect of contaminants in PEM fuel cells for stationary applications”, K. Jayasayee, SINTEF
Workshops (Co-)organized by the project	<ol style="list-style-type: none"> 1. 2nd international workshop on degradation issues of uel cells, 21-23 Sept 2011, Thessaloniki, Greece <ul style="list-style-type: none"> • Presentation, "PEMFC Lifetime and Durability an overview". -Frank de Bruijn, Nedstack • Presentation “Experiences from AST in PEMFC”. - Anders Ødegård, SINTEF 2. Degradation of PEM Fuel Cells – experience exchange and discussion, 3-4 April 2013, Oslo, Norway <ul style="list-style-type: none"> • Presentation “Comparison lab test - field test, reversible - retrievable - irreversible decay, contaminants investigation” T. Martin, Solvicore • Presentation, “30,000 hours of PEMFC system operation at a chlor-alkali plant”, J. Coolegem, Nedstack • Presentation “AST protocol vs. real life operation and CO contamination”, K. Jayasayee, SINTEF
Publications and Patents	
Publications	<p>Publications in peer-reviewed journals</p> <ul style="list-style-type: none"> • A. Verhage, J. Coolegem, M.Mulder, H. Yildirim, F. de Bruijn, “30,000 h operation of a 70 kW stationary PEM fuel cell system using hydrogen from a chlorine factory”, int. J. hydrogen energy 38 (2013) pp. 4714-4724 • M. Smit. “Towards 40,000 operational hours for Nedstack’s FCS XXL PEM fuel cell stacks, Fuel Cells Bulletin, August 2014