NOVEL

Fraunhofer ISE

NOVEL PROJECT

DELIVERABLE D6.2

PUBLIC REPORT WITH CONDENSED FINDINGS AND CONCLUSIONS FROM ORGANISED INTERNATIONAL WORKSHOP ON PEM ELECTROLYSIS

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ABBREVIATIONS

AFM	Atomic Force Microsopy
AST	Accelerated Stress Test
BoP	Balance of Plant
BPP	Bipolar Plate
CV	Cyclic Voltammetry
CuCo	Current Collector
EIS	Electric Impedance Spectroscopy
HFR	High Frequency Resistivity
MEA	Membrane Electrode Assembly
R&D	Research and development
S(T/R)EM	Scanning (Transmission/Raster) Electron Microscopy

1 INTRODUCTION

The aims of the NOVEL project, as stated in Annex I – Description of Work (DoW), are to gain an improved understanding of degradation processes in PEM electrolysers and develop accelerated stress test protocols for lifetime evaluation in order to design more cost competitive, high efficiency PEM electrolyser stacks at costs below € 2,500 / (Nm^3 H_2/h) and no impact on lifetime (>40,000h).

It will therefore take advantage of the progress made during its progenitor, the NEXPEL project, by further long-term-testing of stacks developed therein, post-mortem analysis of degradation effects and feeding the gained knowledge into the development of novel stack materials and designs.

As measures to disseminate the results of the project, two international workshops are to be organised of which the first was held on March 12th and 13th 2013 in Freiburg/Germany and the second will be organized in January 2015.

Accordingly, deliverable D6.2 consists of two parts due at the end of months 8 and 30, each summarizing the findings and conclusions of the respective workshop. This report will therefore deal with the first workshop, starting with a short general overview and a rundown on the given talks. Opinions of the attendants on several aspects regarding electrolysis, which have been acquired via a questionnaire, will be presented and conclusions from it made.

1.1 Attendance

The 1st international Workshop on Durability and Degradation Issues in PEM Electrolysis Cells and its Components was organised and hosted by Fraunhofer ISE in the facilities of the solar info center GmbH in Freiburg/Germany. It was attended by 111 guests from 15 different countries and with various types of affiliation with electrolysis. The beforehand unexpectedly high interest for the workshop and the wide approval regarding the organisation made it a great success.

Figure 1.1: Magnus Thomassen (SINTEF, left) and Tom Smolinka (Fraunhofer ISE, right).

Figure 1.2: The audience of the workshop.

Figure 1.4 shows the distribution of the home countries of the workshop participants. The audience was attracted from as far as North America, South Africa and Russia. Naturally however, due to the geographic proximity, about half of the audience came from Germany, the majority of the rest from Central and Western Europe.

A cross-section of the professional background of the audience was obtained from the 46 filled questionnaires received. The distribution of the affiliations stated therein is shown in Figure 1.3. Taking this as a significant sample, half of the audience is involved in Research & Development and 35% are manufacturers of electrolysers or their components.

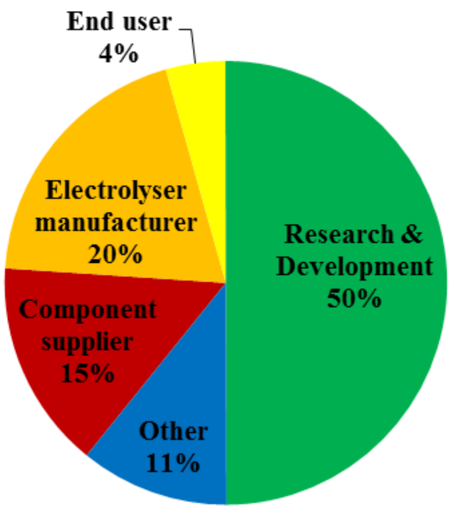


Figure 1.3: Distribution of the affiliations of the participants after the questionnaire results.

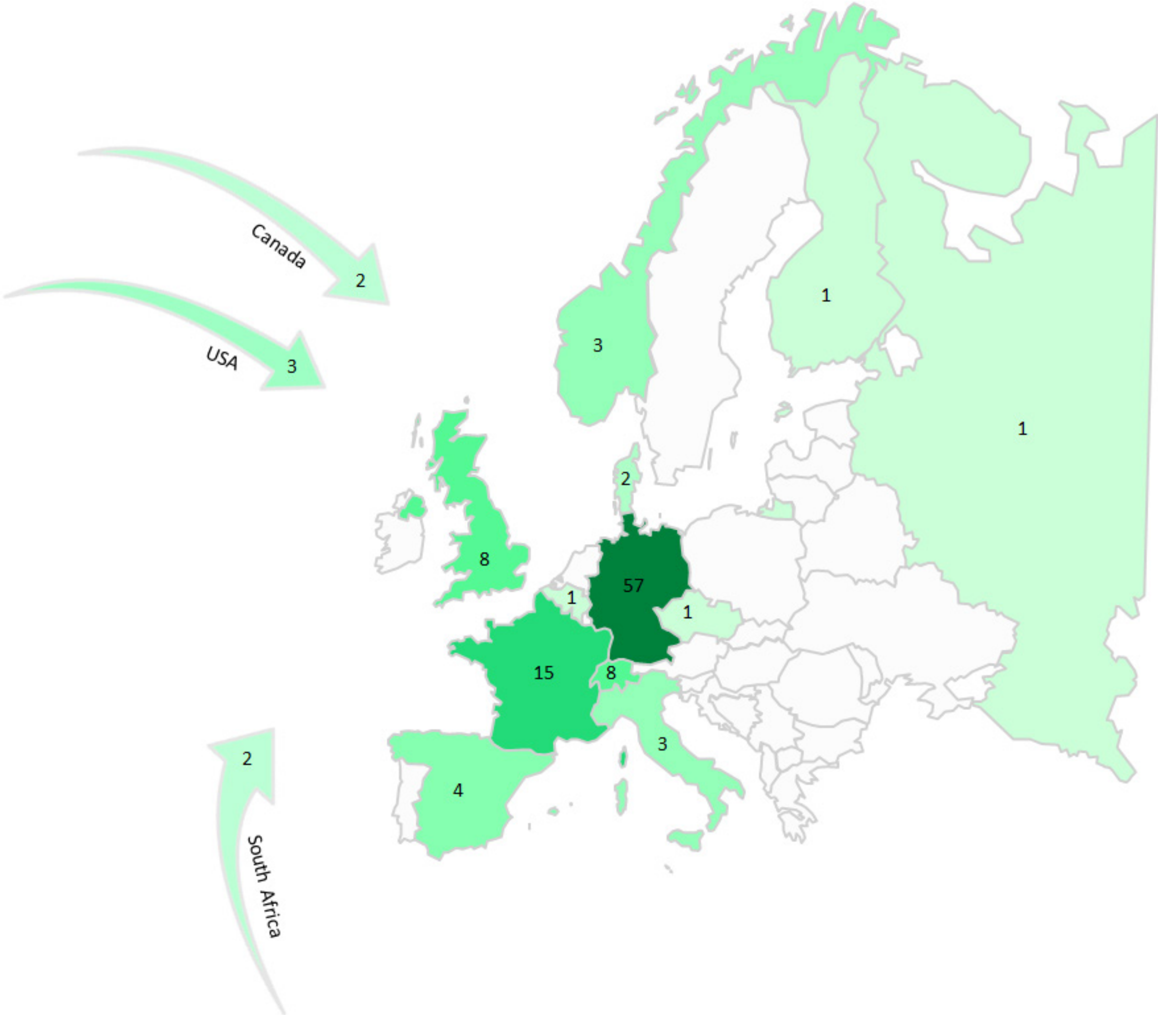


Figure 1.4: Map of origins of the workshop participants.

2 SESSIONS

The workshop consisted of three sessions discussing the lifetime and degradation issues of PEM electrolysers with foci on the industrial view, the scientific perspective and accelerated stress tests. The presentations shown will be summarized in the following section. A panel discussion concluded each session.

2.1 Session 1: Industrial view on life-time of PEM electrolysers

2.1.1 R&D Focus Areas Based on 60,000 hr Life PEM Water Electrolysis Stack Experience (Everett Anderson | Proton OnSite | USA)

From Proton's market experience in water electrolyser systems, the stack is the most reliable component. Though increasing use in combination with renewable energy sources comes with challenges regarding reliability, cost, varying load and load range efficiency and the scale-up to megawatt-systems.
Reliability has been demonstrated in commercial stacks with life times of 60,000h without detectable voltage decay. To reduce the costs, low cost membranes, lower catalyst loading and new stack designs with less metal are investigated. New process methods and coatings for bipolar plates are evaluated. To increase the efficiency, higher temperatures and thinner membranes are aimed at. Accelerated stress tests are conducted by a combination of potential-, pressure- and temperature cycling. Varying load and load range showed to be no issue due to the rapid response of the PEM electrolyser to the current signal and its tolerance to variable power input.

2.1.2 PEM Electrolyser Degradation Mechanisms and Practical Solutions (Nick van Dijk | ITM Power | Great Britain)

Besides the presentation of ITMs product range in electrolysis and the used tools to measure their degradation, a raw summary of the degradation mechanisms in focus of investigation and conclusions was given:
Poisoning of the membrane due to impurities in the water may be reversible. Accelerated stressing was observed to be connected to current density, pressure and temperature. ITM has means of degradation prevention, though possibly expensive.

2.1.3 Recent Advances in PEM Water Electrolysis (Joseph Cargnelli | Hydrogenics| Canada)

As a worldwide leader in water electrolysis, Hydrogenics is committed to the development and commercialization of Power-to-Gas. Focus of its activities therefore lies in scale-up, cost-reduction, efficiency-improvement and performance in dynamic operation. Tests regarding long-term stability, operation with high current density, full load cycling and dynamic cycling on the base of PV-profiles have been undertaken with promising results (e.g. 400 PV duty cycles without degradation).
From Hydrogenics' experience accelerated stress test protocols which mainly affect the membrane could involve high temperature and current density, as well as On/Off-cycles.
The most crucial challenges are the still too high material costs and catalyst loadings (progress like for PEM fuel cells necessary) and the need for faster testing and validation (AST).

2.1.4 CETH$_2$'s Technology Roadmap and Life-time Expectations in PEM Electrolysis (Fabien Auprêtre| CETH$_2$ | France)

With 15 years' experience in PEM hydrogen generation focus will over the next decade shift significantly from the needs for industrial to those for mobility and energy storage applications, for which higher and more cost-effective rates of hydrogen production are necessary. From the state of the art stack (5000 € per Nm³/h, 35,000h test with 10% efficiency loss) tested those necessities are approached by increasing the number of cells per stack, the active cell area and the current density.
Challenges for the first two approaches will mainly regard the heat, pressure and water distribution profiles and the sealing. The last two will mostly focus on new materials and designs for those components responsible for the electrical distribution: Current collectors and bipolar plates.

2.2 Session 2: Scientific perspective on degradation and endurance

2.2.1 Corrosion Resistant Metallic Components for Electrochemical Devices (Conghua Wang | TreadStone Technologies | USA)

In electrolyser systems the costs are driven by the stack and in the stack by the bipolar plates, which is TreadStone's focus for technology development. Since nickel and stainless steels are unstable in the aggressive electrolyser environment and the stability of titanium comes along with bad conductivity due to its protective oxide layer, another approach is presented:
A conductive substrate with a corrosion resistant but poorly conductive layer is connected to the current collectors by gold vias. As presented all the DOE 2015 targets regarding the plate properties are met by this technology whilst being of low costs.
Currently, the durability is tested in cooperation with Ford.

2.2.2 Degradation issues in NEXPEL and NOVEL (Magnus Thomassen | SINTEF | Norway)

Based on a brief overview of the NEXPEL and NOVEL projects, degradation mechanisms and AST protocols for membranes and catalysts were presented.
Mechanical degradation of the membrane due to known causes is supposed to lead to early life failure. On the other side chemical degradation in the form of peroxide formation is yet under investigation. Its detection was made possible by cyclic voltammetry measurements via a µ-electrode.
As for catalyst dissolution and diffusion into the membrane supported and unsupported layers have been examined and AST protocols proposed.
Although much can be learned from procedures for fuel cells, differences in the degradation mechanisms make it crucial to develop proper ASTs for electrolysers.

2.2.3 The BBC Membrel Process - A retrospective view (Günther Scherrer | Paul Scherrer Institute | Switzerland)

Presented was a historic review of the progress in electrolyser development made by BBC between 1980 and 1987. Starting with the oil crisis in 1973 and growing awareness of climate and resources, electrolysis came back to attention and testing of different electrolyser concepts has been started. With the discovery of the Nafion membrane PEM electrolysers similar to those being common today have been developed and their degradation studied. Due to missing market development and loss in interest in this knowledge the Membrel Project had to be terminated.

2.2.4 Endurance of PEM electrolysis cells and stacks (Pierre Millet | Université Paris-Sud | France)

Provided was an overview of electrochemical techniques that can be used to characterize and optimize PEM water electrolysis cell components. Explanations of the methods and examples were given for polarization curve measurement as simple in-situ method, cyclic voltammetry for e.g. the determination of the roughness of an electrode and electrochemical impedance spectroscopy as in-situ tool for measuring real and imaginary contributions of the cell impedance.
From those methods and the experience earned in durability tests the main limitations mentioned for electrolysers are cost, durability and scale-up.

2.2.5 High pressure PEM electrolysers: efficiency, life-time and safety issues (Vladimir Fateev | NRC "Kurchatov Institute“ | Russia)

Most hydrogen applications require a high pressure of the gas. The question addressed in this presentation was whether it is more efficient to pressurize the hydrogen electrochemically inside the cell or mechanically on the outlet.
Although there are disadvantages of electrochemical compression which regard gas purity, current efficiency, platinum metals loading and life-time, costs seem to be the same for both systems at large scale production and there might even be an advantage at decentralized energy supply for < 1 MW.

2.3 Session 3: Accelerated stress tests for PEM electrolysis

2.3.1 Approaches and methodology on accelerated stress tests in fuel cells (Nada Zamel | Fraunhofer ISE | Germany)

Since degradation testing is time-consuming and expensive accelerated stress tests are designed to mimic failure under real life conditions. For PEM fuel cells the different degradation mechanisms of the membrane, electrodes, GDLs and bipolar plates are known well enough to establish general AST protocols for ageing essentially the component under investigation only.
DOE Standards for ASTs are used as standard procedures and commonly used.
Different degradation protocols for the catalyst and catalyst-support have been tested successfully.

2.3.2 Accelerated stress tests in PEM fuel cells: What can we learn from it? (David Wilkinson | University of British Columbia | Canada)

Many advances for PEM fuel cells are - where the requirements are similar - applicable to electrolysers and thus are the diagnostic methods and durability tests.
Of the lifetime issues known, those dealt with in this presentation were low/excess humidification and low reactant flows which have been examined by overpotential measurement via built-in reference electrodes, CO stripping voltammetry and impedance spectroscopy. Segmented fuel cells allow determining the spatial distribution of parameters like current density and reactant transport in the operating cell. In plane gradients have been observed.

3 QUESTIONNAIRE

During the workshop a questionnaire was handed out to the audience which contained questions – partially of the multiple-choice kind – about the professional background, and on opinions regarding the requirements for the operation of electrolysers, degradation issues and opportunities of accelerated stress test.

Of the 111 participants, 46 returned a filled or at least party filled questionnaire. This is sufficiently large share to get an idea of the general opinion of the audience present. This chapter will serve to show and interpret the obtained results.

3.1 Expertise of the audience

How the experience of the audience was distributed in the fields of PEM electrolysis, fuel cells and hydrogen technology according to the self-assessment of all the respondents is shown in figure 3.1. While classifying the data according to the affiliations is not meaningful in most cases due to low statistics, for members of the R&D sector there is one interesting thing to note. A significant portion of the R&D members classified themselves as "Experts" in PEM fuel cell technologies, whereas for electrolysers the distribution is more homogenous around the "advanced" level. This might indicate a growing interest in PEM electrolysis technology within the fuel cell experts, or it could indicate that the R&D representatives generally think that the overall knowledge-level of PEM electrolysers is lower than that of PEM fuel cells.

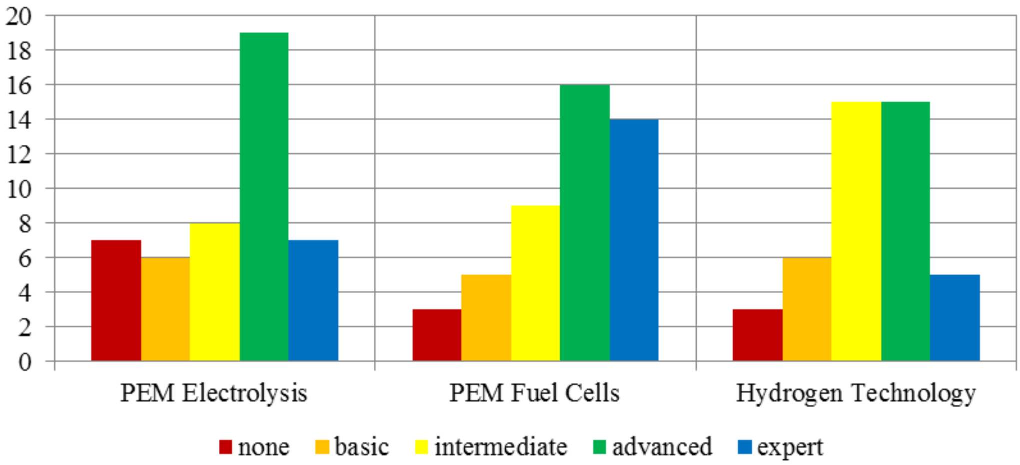


Figure 3.1: How would you grade your experience with ...

3.2 Requirements for electrolysers

This section of the questionnaire aimed at estimating the typical working conditions, meaning its field of application and the working parameters, from the short and long term point of view

3.2.1 Fields of application

The opinions on the importance of water electrolysis applied in mobility, stand-alone systems, grid scale load balancing and (chemical) industry in the near and distant future are plotted in figure 3.2.

In short term vision the general opinion is quite indifferent. From the long term standpoint, however, huge importance, especially in the sectors of mobility and load balancing is being attributed to this technology. Expected growth for industrial use is rather negligible.

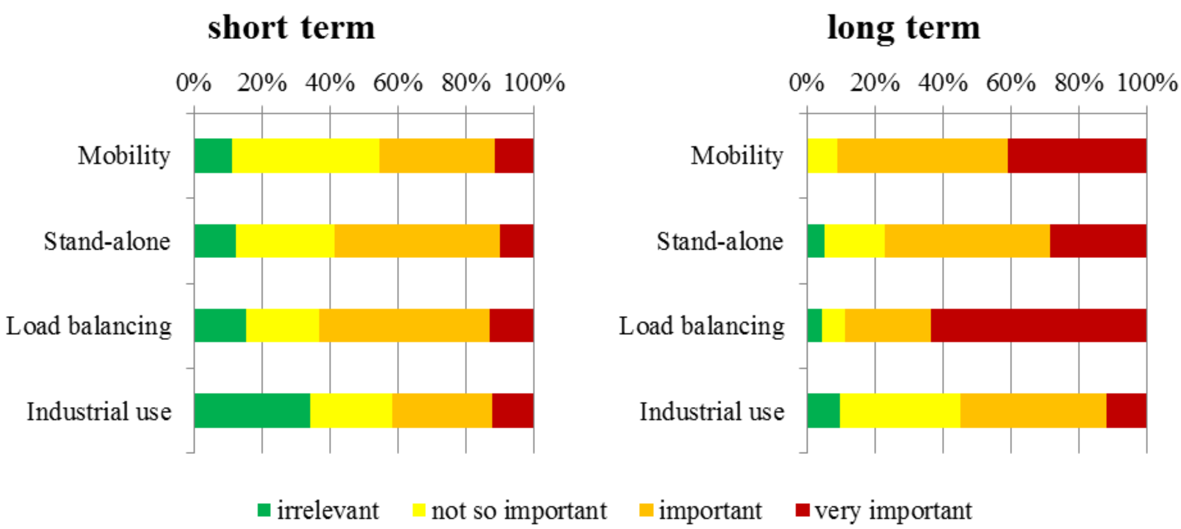


Figure 3.2: Where do you see the most relevant fields of application for PEM electrolysers?

3.2.2 Working conditions

It has been asked for the values regarded as typical for the operating pressure, temperature and number of start/stop-cycles during the electrolyser lifetime in short term and long term. The answers are displayed in the figures 3.3 to 3.5. Typical working conditions for now and the near future are expected to be working pressures between 20 and 30 bars, a temperature of 60 to 80°C and a variety of underwent on/off-cycles, probably depending on the field of application.

For the more distant future an increase in the values of all three working parameters is expected: A temperature shift of to 80°C or more, increased cycling number by about one magnitude and working pressures of about 50 bars and 100 bars or more, again depending on the field of application (e.g. higher pressures for the mobile sector).

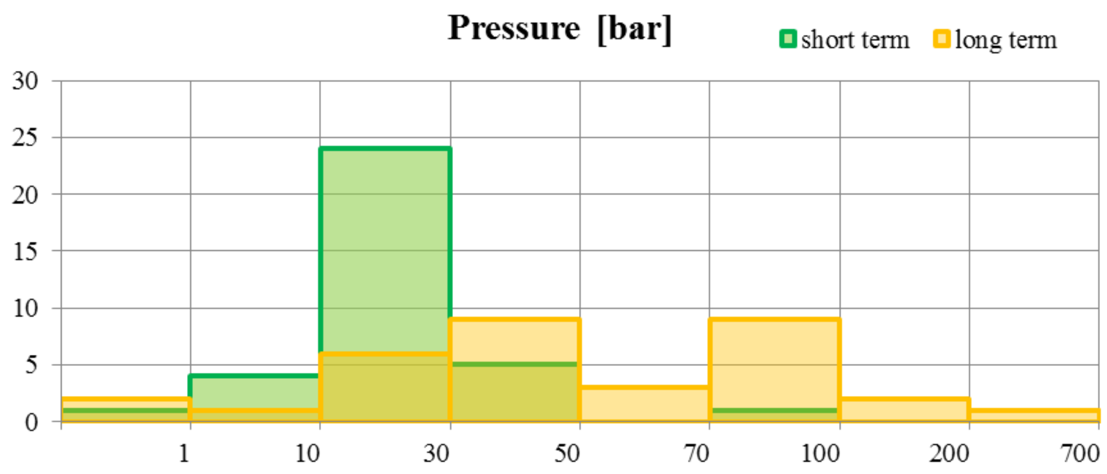


Figure 3.3: What is in your opinion the typical operating pressure for the most relevant applications?

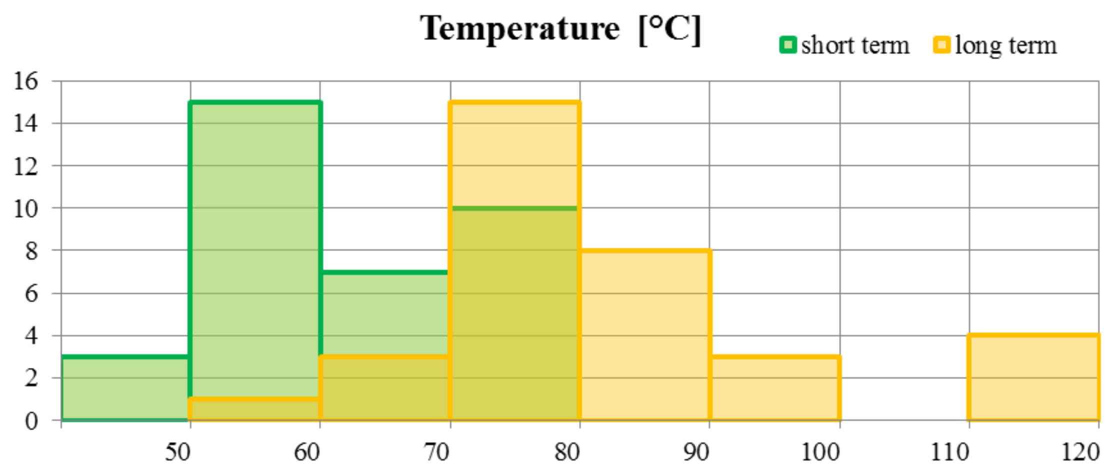


Figure 3.4: What is in your opinion the typical operating temperature for the most relevant applications?

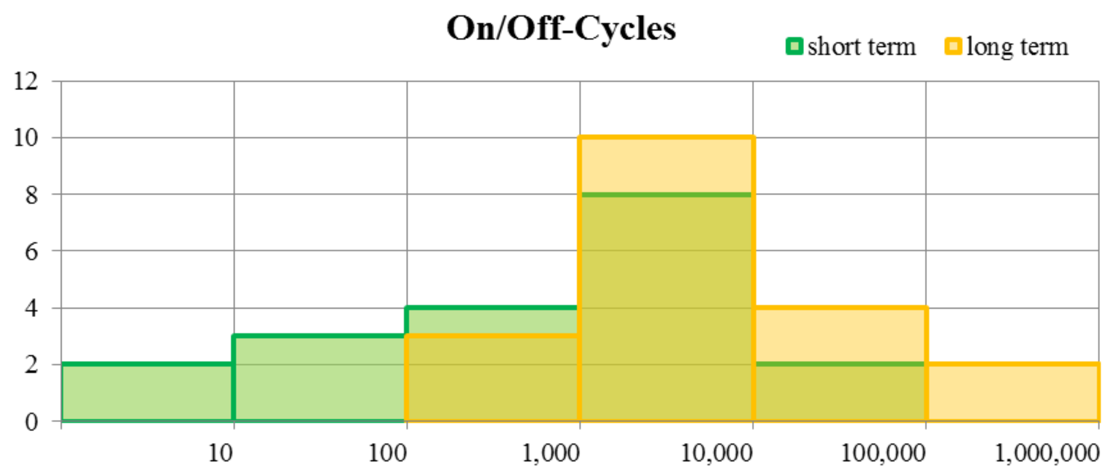


Figure 3.5: What is in your opinion the typical number of on/off-cycles for the most relevant applications?

As can be learned from the ranking of the most limiting parameters for the electrolyser operation figure 3.6 increasing the temperature is the most urgent issue. This was already indicated in the rise of temperature seen between short and long term operating conditions but was not to be expected in this dimensions. This might at least partly be an artifact of the questionnaire due to mentioning "temperature" as an example.

The next urgent issues in this ranking are increasing the operating pressure and the part-load compatibility (in combination with renewables). Increasing the current density to gain a higher H_2 output and acceptance of overload are furthermore to mention. Minor roles are attributed to the ability to tolerate On/Off, pressure, current density and temperature cycles, which would be more crucial in mobile applications.

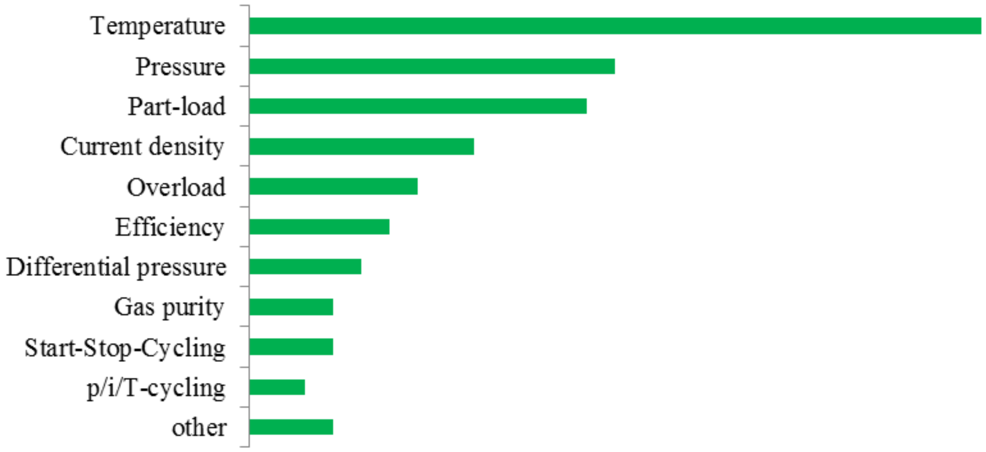


Figure 3.6: From the point of application: Which operating conditions are the most limiting today?

3.3 Technical Questions

The questions summarized under the category "technical questions" were to give an impression of the participants' daily experience with reliability, durability and degradation of electrolyser systems and components.

3.3.1 Most crucial components

As can be seen in figure 3.7 on cell level the most crucial factor is the durability. However, an even smaller concern about the reliability was expected since usually the cell components either work and slowly degrade or don't work but are not prone to unexpectedly fail. The issues regarding the BoP, on the other hand, are seen to be mostly concerning reliability, which clearly makes sense.
As for the distribution for the cell-components it has to be mentioned here, that, since this question was not of a multiple-choice type, an entry of the components "current collector" and "catalyst" without the cell side thought of was assigned to both possibilities. Keeping this distortion in mind (probably an excessively estimated contribution of the cathode side parts), the ranking is basically the same as that in figure 3.8, displaying the (multiple choice) answers of the most important components to be improved.

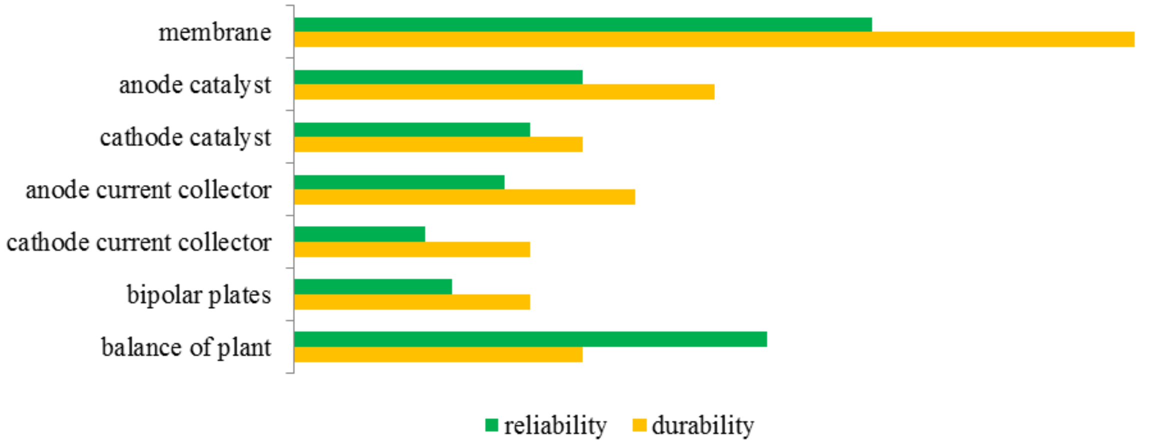


Figure 3.7: What are the most critical components of concern regarding reliability and/or durability?

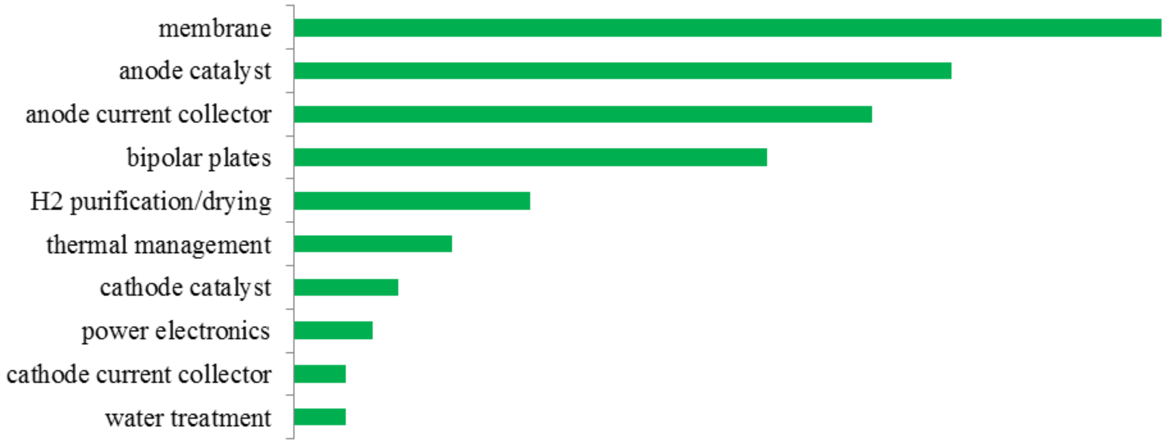


Figure 3.8: What are the most important components to be improved for a PEM electrolyser?

All together the membrane is regarded as the most liable component to fail and therefore bears the biggest urge for improvement. Another crucial block of components consists of the catalyst and current collector on the anode side together with the bipolar plates. Of less importance seem to be system components outside the cell stack, i.e. the periphery of the electrolyser system.

3.3.2 Degradation mechanisms

Information about the known degradation effects for each component and possible means for their measurement or monitoring were collected. The results are summarized in table 3.1 and shall neither be complete nor entirely relevant or important but serve as a source of inspiration for further research activities within the NOVEL project.

Component	Degradation effect	Measurement method
Membrane	Thinning	Increase in permeation
		Ohmic resistance via ref. Electrode
		Crossover measurement
		SEM
		Gas purity measurement
	Permeation	Gas purity measurement
		Water analysis (fluoride release)
	Overpotential	HFR
		Ion exchange capacity
	Contamination	-
	Mechanical	Post mortem
Bipolar Plates	Oxide layer, Corrosion	Ohmic resistance
		EIS
		Post mortem
Catalyst	Erosion/Agglomeration	OCP evolution
		HFR
		EIS
		Post mortem
		CV
		SEM, TEM, AFM
		tafel plot
		Pt dissolution methods
	Contamination	Water conductivity
Current collectors	Oxide layer	Ohmic resistance
		Spectroscopy
		EIS
Gasket	Gas leakage	Pressure drop
		H_2 detection

Table 3.1: What are the main degradation effects for these components and suitable techniques for measuring/monitoring?

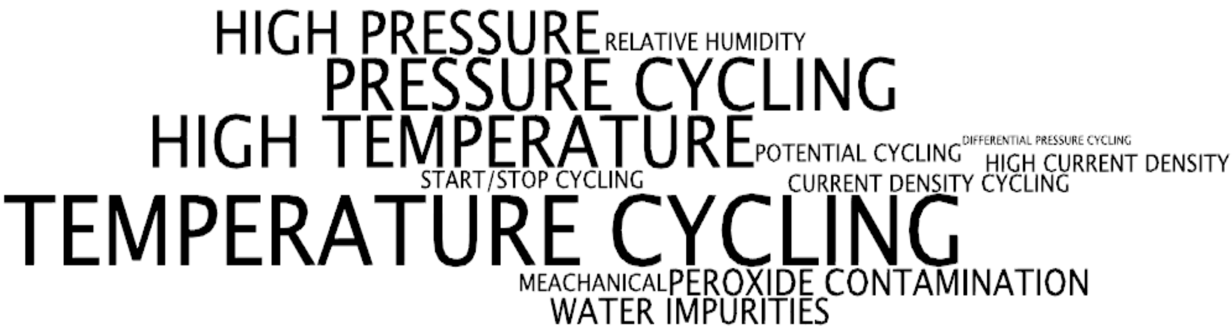
The inquiry for the main lack of understanding was answered with a long list of various keywords, which shall not be given here in its entirety. A clustering of the comments in certain categories, however, could be observed:

- Oxide layer formation, properties and prevention of BPP & CuCo degradation
- Membrane degradation mechanism
- Cross-linking of degradation (e.g. poisoning, …), BoP influence
- Effects of dynamic working conditions and cycling
- (Electro-) chemical effects (surface, H_2O_2 attacks, …)
- Permeation and cross-over
- System and periphery (control, system integration, …)

3.4 Accelerated Stress Test

Accelerated stress tests were considered useful mostly for membranes and catalysts (mentioned 31 and 25 respectively) but also for current collectors and bipolar plates (14 and 12 resp.). The following word-clouds depict the frequency of the suggested AST methods for each component.

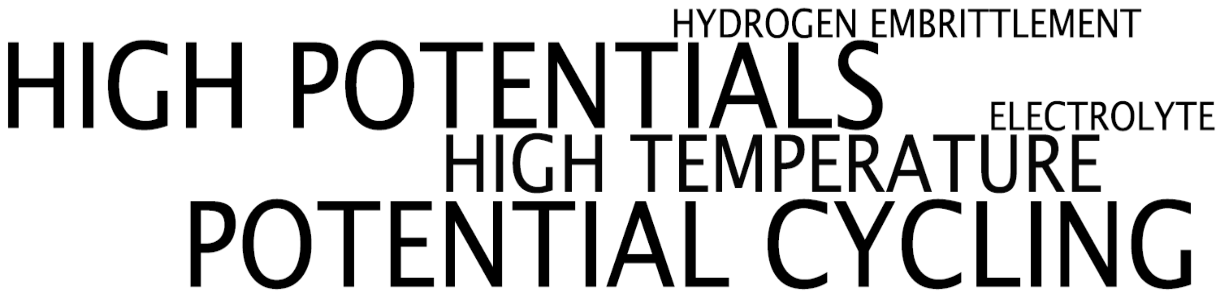
Membrane



Catalyst

Current collectors

Bipolar plates



4 CONCLUSIONS AND OUTLOOK

The 1st international Workshop on Durability and Degradation Issues in PEM Electrolysis Cells and its Components was the first of its kind and was an overall success. Exclusively positive feedback was received from the participants. The presentations as well as the results from the questionnaire yielded valuable input for the NOVEL project although the latter has, from today's point of view, to be considered as not perfectly designed.

A wide overview on the activities of industry and research facilities in the fuel cell and electrolyser field was obtained and insights into new methods and findings were provided.

The opportunities of PEM water electrolysis for the future seem to have been recognised which is leading to growing interest. There is a general consensus that the importance of this technology will grow, especially in applications of load balancing in connection with renewables and H_2-mobility. The expertise and the advantage in knowledge in the fuel cell technology can and will play an important role in further development into this direction.

Current limitations are seen in rising the working temperature and pressure which would increase the overall efficiency of the systems but also the proneness to degradation and failure of the cell components. Being the central component especially the membrane is considered to be the most limiting for the cell's lifetime and thus the most urgent to be improved. Efforts are also expected and being made regarding the catalysts, the current collectors and bipolar plates.

Although various degradation effects are known well, others still have to be studied to answer the open questions.

To save time and costs doing so, accelerated stress tests for the cells and components are necessary. They base on working conditions that are known to be the most degrading: Basically High temperature and pressure and their cycling for the membrane and high potential and its cycling for the catalyst, current collectors and bipolar plates.

Concluding, the just said shows that the NOVEL project chose its main goals correctly and the appropriate approach with tasks 1.2 and 1.3 to fulfil these exact needs and to live up to the expectations on the PEM water electrolysis technology for the short and long term future.

Results of the project tasks and findings of further research activities of the project partners will be presented on a second workshop at the beginning of 2015.