Clean Hydrogen Partnership

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# HIGH PERFORMING ULTRA-DURABLE MEMBRANE ELECTRODE ASSEMBLIES FOR TRUCKS

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## DELIVERABLE REPORT

| ***D2.3 ADVANCED TEST PROTOCOLS DERIVED FROM THE INTEGRATED MODEL AND AVAILABLE FOR TASK 6.3*** | |
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| ***DISSEMINATION LEVEL*** | | |
|---|---|---|
| **PU** | *Public* | *x* |
| **SEN** | *Sensitive, limited under the conditions of the Grant Agreement;* | |

| ***NATURE OF THE DELIVERABLE*** | | |
|---|---|---|
| **R** | *Document, report* | *x* |
| **DEM** | *Prototype demonstrator* | |
| **DEC** | *Website* | |
| **DMP** | *Data management plan* | |
| **OTHER** | *Software, algorithms, models* | *x* |

| **SUMMARY** | |
|---|---|
| **Keywords** | *Degradation model, parameterisation, test protocol* |
| **Abstract** | *For the full version of the degradation model (Deliverable 2.4, currently under development), the set of parameterisation experiments was devised and planned. Through discussions with experienced experimental partners in the project, useful additional parameterisation experiments and alternative routes to access parameters were identified. An advanced test protocol for the HIGHLANDER project was developed and will be passed on to Task 6.3 for use in the remainder of the project.* |
| **Public abstract for confidential deliverables** | *For the full version of the degradation model (Deliverable 2.4, currently under development), the set of parameterisation experiments was devised and planned. Through discussions with experienced experimental partners in the project, useful additional parameterisation experiments and alternative routes to access parameters were identified. An advanced test protocol for the HIGHLANDER project was developed and will be passed on to Task 6.3 for use in the remainder of the project.* |

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# D2.3 Advanced test protocols derived from the integrated model and available for Task 6.3

## Contents

1 Introduction ....4
2 Scope ....4
3 Discussion ....4
3.1 Test protocol and derived parameters ....4
3.2 Test variants for enhanced validation and predictive capabilities ....6
4 Conclusions and future work ....7
5 References ....7

# 1 Introduction

HIGHLANDER aims at developing an integrated model framework to predict the performance of a proton exchange membrane (PEM) fuel cell over its lifetime. The framework incorporates structure-dependent processes across various scales, bridging microscopic local reaction conditions, mechanisms, and rates at interfaces with macroscopic transport phenomena. Supplemented with a comprehensive and reliable parameterisation approach, the model becomes a powerful tool to delineate and quantify the impact of degradation mechanisms on performance over time.
Parameters can be chosen and validated based on experimental insights. Some parameters are a priori known and controlled by experimentalists, some can be measured directly, some can be derived from physical relationships with other, measurable parameters, and others must be extracted from multiple experimental setups. In D2.2, we investigated the sensitivity of all the parameters of the basic version of the model, to understand their impact on model predictions. The experimental determination of non-sensitive parameters can be deprioritised compared to highly sensitive parameters. Furthermore, if multiple experimental methods exist for measuring a particular parameter, sensitivity analyses can guide the selection of the most appropriate experimental method, aiding in the design of a concise and expedient experimental plan. In this work, the parameterisation strategy of the full degradation model for HIGHLANDER was assembled into an advanced test protocol and is critically discussed, especially focussing on practical applicability through discussions with experimental partners.

# 2 Scope

In WP2, the aim is to develop a physics-based model framework for the prediction of performance over lifetime of a PEM fuel cell. In D2.1, a basic version of this model was presented. The code was made available as open source, editable and extendible via an open access modelling platform. D2.2 has focused on the development of a strategy to parameterise the basic version of the model and enable predictions supporting the design and health monitoring of a FC stack and its components. D2.3 presents a parameterisation strategy for the full model developed in HIGHLANDER, which will be implemented in Task 6.3 throughout the rest of the project.

# 3 Discussion

The following sections explain the methodology used to merge the insights from our previous work (WP2) on modelling with experimental activities in WP3, 4, 5 and finally WP6, and describe how data from the tests are systematically mapped to model parameters. This approach enables further evolution of the model's analytical and predictive capabilities based on new experimental evidence.

## 3.1 Test protocol and derived parameters

Building on the basic model from D2.1 and the parameterisation strategy of the basic model and the anticipated full model from D2.2, a set of experiments together with an advanced test protocol were developed to feed into model-based degradation studies, as depicted in Figure 1. The advanced test protocol is derived from test protocols used in WP6 adapted to the specific needs of model validation in WP2. It is based on an accelerated stress test (AST) with 1,000 voltage cycles between 0.6 V and 0.95 V under $H_2/N_2$ followed by another 1,000 cycle sets between 0.6 V and 0.9 V under $H_2$/air conditions. Before and after these 2,000 cycles, an extensive performance test protocol, listed in Table 1, is conducted. Subsequently, the same loop of voltage cycles and performance tests is carried out repeatedly, for a total of 14,000 cycles.

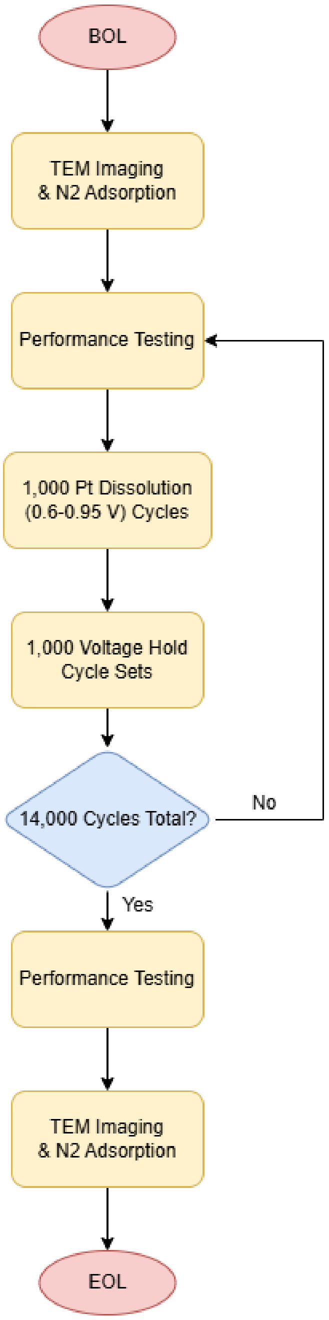


*Figure 1 Flowchart of test protocol*

| |
|---|
| 1. Initial Conditioning |
| 2. Condition Before BOL (CV) 100% RH |
| 3. 10 min Purge |
| 4. $H_2$ & CO CV 100% RH |
| 5. $H_2$ Permeation 100% RH |
| 6. $H_2/N_2$ EIS Sweep 100% RH |
| 7. Condition Before BOL (CV) 30% RH |
| 8. 10 min Purge |
| 9. $H_2$ & CO CV  30% RH |
| 10. $H_2$ Permeation 30% RH |
| 11. $H_2/N_2$ EIS Sweep 30% RH |
| 12. Conditioning |
| 13. Recovery |
| 14. Conditioning |
| 15. Wet Mass Activity ($O_2$ Polarization) |
| 16. Recovery |
| 17. Conditioning |
| 18. Dry Mass Activity ($O_2$ Polarization) |
| 19. Recovery |
| 20. Conditioning |
| 21. EU Reference Air Polarization |
| 22. Conditioning |
| 23. Air Polarization 100% RH |
| 24. Conditioning |
| 25. Air Polarization 30% RH |
| 26. (BOL only) Conditioning |
| 27. (BOL only) Temperature Sweep |
| 28. (BOL only) Conditioning |
| 29. (BOL only) Pressure Sweep |
| 30. (BOL only) Recovery |
| 31. (BOL only) Conditioning |
| 32. (BOL only) EU Reference Air Polarization |
| 33. (BOL only) Conditioning |

*Table 1 Performance testing protocol. Steps 26 to 33 are done only once at BOL.l*

However, before the AST cycles are carried out, a wide range of model parameters can already be extracted from data on materials properties, structure and composition (see D2.2 report). To capture the particle radius distribution (PRD) of the Pt particles within the catalyst layer, TEM imaging is applied. With the help of image analyses and additional algorithms, locations of particles in the microstructure can be obtained. This detailed assessment is necessary to distinguish particles in the two different populations, as intended in the modelling framework. PRDs can be extracted for particles located on the surface of the agglomerate (assumed to be in proximity to ionomer) and particles in the primary pores (therefore not in proximity to ionomer). This experiment is conducted both at beginning of life (BOL) and end of life (EOL) to quantify the change in particle radius influenced by the location of the particles. Using SEM imaging, performed both at BOL and EOL as well, the thicknesses catalyst layer, membrane, and GDL are determined.

Moving from imaging characterisation to adsorption techniques, with the help of N2 adsorption, ionomer coverage on the agglomerate surface can be determined. This is done at BOL and EOL.

The performance tests carried out around the AST cycles, as described in Table 1, enable further parameter extraction. The electrochemically active surface area (ECSA) is determined by CO stripping with cyclic voltammetry (CV), both under 100 % RH and 30 % RH. Determining ECSA at 100% RH assumes to capture the surface of all utilizable Pt particles. Proton transport to the particles is realized through ionomer and water, as the interplay results in a dense network of proton transport pathways to all particles in the layer. In contrast, determining ECSA by CO stripping at 30 % RH, particles not in proximity to ionomer are assumed to be protonically disconnected and thus inactive, as protonic conductivity is decreased drastically outside the ionomer network. Building on previous analyses of measurements, ECSA at 30 % RH is fully ascribed to particles in close proximity to the ionomer. Expecting a nearly complete ionomer coverage on the surface of the agglomerate [Olbrich et al. 2022], the ratio of Pt particles on the surface of the agglomerate to particles located in primary pores can be determined. At BOL this distinction is necessary to parameterise the model; at EOL the distinction can then be used to validate the model.

Using the performance tests, further parameters can be extracted. A fitting routine was established based on Ref. [Kulikovsky 2014] to determine the effective diffusion coefficients of GDL and CL, the effective proton conductivity of the CL, the ohmic resistance including membrane proton transport, the intrinsic volumetric exchange current density and the Tafel slope from polarization curves. To validate parameters, independent additional measurements can be used. Limiting current measurements combined with the usage of appropriate models can be employed to assess the effective oxygen diffusion coefficient. Electrochemical impedance spectroscopy (EIS) measurements can be used for the determination of ohmic resistance, as well as in combination with geometric properties of the CL to extract and validate the effective proton conductivity of the CL. Another parameter extracted from the test protocol is the open circuit voltage (OCV), e.g., during a recovery procedure. The model uses the OCV to describe hydrogen crossover, which can be validated with H2 permeation measurements.

## 3.2 Test variants for enhanced validation and predictive capabilities

To enhance the accuracy of the model, this extensive test protocol is carried out for multiple MEA configurations. Variants of the configuration help to validate the consistency of the model and the fitting routines, enhance accuracy and robustness, as well as increase the understanding about the influence of specific parameters on degradation and performance. After an extensive exchange with WP6, a set of configurations was determined as optimal between innovation, significance, comparability and feasibility. Variations from the baseline are: 1. changes in ionomer coverage by reducing the I/C ratio, and 2. the location of Pt particles by preventing particles to deposit in the primary pores in the fabrication process. Additionally, data from the preceding project IMMORTAL can be used for comparison and validation.

As a first sample in WP6.3, the baseline configuration with catalyst X was already tested and analysed in WP2. Building up on the expertise collected in the analysis, the next sample in WP6.3 will contain a configuration with catalyst X with much lower I/C ratio, around half of the current value. The exact value is determined later by experts in WP6 to ensure feasibility. This test will give insights on changes in ionomer coverage over time, and thus on degradation or stability of particles in different location in the microstructure.

Subsequently, another configuration will be prepared based on catalyst X with Pt placed primarily on the outside of the support. To ensure similar Pt particle sizes and density of the particles on the surface at BOL, a reduced Pt assay is used, ultimately resulting in a lower Pt loading. This configuration is expected to perform significantly worse, therefore it is primarily investigated on the decay of ECSA rather than performance.

Using these configurations, the extended modelling framework can be parameterised robustly, accurately and comprehensively. Additionally, using the methods discussed above the model can be validated.

# 4 Conclusions and future work

An advanced test protocol and specific configurations of test variants have been presented. The test protocol can be used to determine all relevant model parameters. Additionally, it includes methods to validate the model. At BOL and EOL, imaging tests and adsorption techniques are used, to get insights into the structure of the CL. During the AST cycles, an extensive performance test protocol is applied to extract both ECSA at 100 % RH and 30 % RH to assess the influence of ionomer on catalyst degradation, as well as further tests to extract performance parameters needed for the holistic coupled framework.
Testing different sample configurations with this test protocol, a robust set of modelling parameters as well as model validation and further insights and predictive capabilities can be gained.

This deliverable report is passed to Task 6.3 for the experiments to be conducted. In collaboration with Task 6.3, the measurements are analysed and further discussed. A comprehensive advanced parameter set is extracted for the model.

# 5 References

[Kulikovsky 2014] A. A. Kulikovsky. A Physically–Based Analytical Polarization Curve of a PEM Fuel Cell. J. Electrochem. Soc. 161 (3) F263-F270, 2014

[Olbrich et al. 2022] W. Olbrich, U. Sauter, T. Kadyk, M. Eikerling. Modeling of wetting phenomena in cathode catalyst layers for PEM fuel cells. Electrochimica Acta 431, 140850, 2022