



HIGHLANDER  
HIGH performing uLtrA-durable membraNe electroDe assEmblies for tRucks

## HIGH PERFORMING ULTRA-DURABLE MEMBRANE ELECTRODE ASSEMBLIES FOR TRUCKS

**Grant agreement no.: 101101346**

**Start date:** 01.01.2023 – **Duration:** 36 months.

**Project Coordinator:** D. J. Jones, CNRS

*The HIGHLANDER project is supported by the Clean Hydrogen Partnership and its members Hydrogen Europe and Hydrogen Europe Research.*

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## DELIVERABLE REPORT

<b>D2.2: BASIC PARAMETERISATION STRATEGY FOR THE INTEGRATED MODEL</b>		
Due Date	30th June 2024	
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Workpackage	WP2	
Workpackage Leader	FZJ	
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Date released by WP leader	14th August 2024	
Date released by Coordinator	14th August 2024	
<b>DISSEMINATION LEVEL</b>		
<b>PU</b>	Public	<b>X</b>
<b>SEN</b>	Sensitive, limited under the conditions of the Grant Agreement;	
<b>NATURE OF THE DELIVERABLE</b>		
<b>R</b>	Document, report	
<b>DEM</b>	Prototype demonstrator	
<b>DEC</b>	Website	
<b>DMP</b>	Data management plan	
<b>OTHER</b>	Software, algorithms, models	<b>X</b>

<b>SUMMARY</b>	
<b>Keywords</b>	<i>Degradation model, parameterisation, sensitivity analysis</i>
<b>Abstract</b>	<i>For the previously developed basic degradation model (Deliverable 2.2), the minimum set of parameterisation experiments was determined through sensitivity analyses of the model. Through discussions with experienced experimental partners, valuable additional parameterisation experiments and alternative routes to access parameters were identified. For the current, advanced model iteration, the additional parameters and possibilities for their extraction are discussed. Furthermore, for the anticipated full model at the end of HIGHLANDER, all anticipated parameters and preliminary ideas for their extraction were discussed.</i>
<b>Public abstract for confidential deliverables</b>	A/A

<b>REVISIONS</b>			
<b>Version</b>	<b>Date</b>	<b>Changed by</b>	<b>Comments</b>
<b>0.1</b>			

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## **D2.2 BASIC PARAMETERISATION STRATEGY FOR THE INTEGRATED MODEL DEVELOPED AND PASSED ON TO TASK 6.2**

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## 1 INTRODUCTION

HIGHLANDER aims at developing an integrated model framework to predict the performance of a 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 parameterization 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. It is crucial to investigate the sensitivity of all of these parameters to understand their impact on model predictions. The experimental determination of non-sensitive parameters can be deprioritized compared to highly sensitive parameters. Furthermore, if multiple experimental methods exist for measuring a particular parameter, sensitivity analysis can guide the selection of the most appropriate experimental method, aiding in the design of an experimental plan.

## 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 has been presented. The code was made available as open source, editable and extendible via a Git repository. D2.2 focused on the development of a strategy to parameterise the model and enable predictions supporting the design and health monitoring of a FC stack and its components.

## 3 DISCUSSION

### 3.1 General Discussion of the Relevant Parameters

In this section, we discuss the critical parameters necessary for accurately modelling of a PEMFC. These parameters significantly impact performance and durability predictions. They can be categorized as materials, composition, structure, operation, and performance parameters.

#### Materials Parameters:

Focusing on the materials of a catalyst layer (CL), the electrocatalyst is essential for the efficiency and longevity of the cell. Platinum and its alloys, such as PtCo, are known for their high activity in key reactions. The composition of the electrocatalyst material impacts the relevant reaction mechanisms and pathways and thereby activity and stability. The mass specific activity and the catalyst loading are critical in view of cost and performance optimization.

The support material is needed to provide structural stability and effective catalyst dispersion. The properties of the porous network it forms (pore size distribution, wettability of internal surfaces) determine the water distribution and the transport properties of the CL, including diffusion coefficients of gaseous species (oxygen, water vapour and inert gases), liquid water permeability and proton conductivity (since excess protons, bound in complexes with water such as hydronium, Eigen, or Zundel ions, acquire their mobility from being surrounded by water). Excess protons are generated by the

dissociation of functional acidic groups of the ionomer upon contact with water. The ionomer, by virtue of its ion exchange capacity (IEC), therefore, controls the proton density in water-filled pores, exerting a direct impact on proton conductivity and reaction kinetics. The ionomer, i.e., its hydrophilic-hydrophobic chemical structure and IEC, determine the wettability of interfaces and pores in the CL. Emerging fluorine-free ionomers, such as high-oxygen permeability ionomers (HOPI), offer improved performance and environmental benefits.

### **Composition Parameters:**

Composition parameters of the model include the Pt loading, Pt:C ratio, I:C ratio and the total porosity. Using these parameters, expressions for volume fractions of the different interpenetrating phases can be obtained, that determine the effective physical properties of the layer, such as exchange current density, oxygen and vapor diffusion coefficients, liquid water permeability and effective vaporization exchange rate. Structure-based modelling of physical properties can be refined by considering pore size and wettability distributions as well as the shapes of primary and secondary pores. Relations among parameters can serve parameter cross-validation. For example, from knowing Pt loading, Pt:C ratio and I:C ratio, it is possible to infer the thickness of the CL, if the porosity is known and vice versa.

### **Structure Parameters:**

For a reliable prediction of changes in performance over time, further structural parameters are needed. The Pt particle radius distribution (PRD), provided at the beginning of life (mean particle size and standard deviation of distribution) is essential input for the degradation model. It is the basis for predicting the evolution of the PRD, the Pt mass, and the electro-chemical surface area (ECSA) with time. As we strive to refine the degradation approach by accounting for specific local reaction conditions, an important distinction must be made between electrocatalyst particles attached to the outer agglomerate surface (in close proximity to ionomer, exposed to a low pH environment) or at pore surface inside of agglomerates (outside of ionomer double layer region, exposed to a high pH environment). This distinction impacts the proton access to and thus the electrocatalytic activity at the catalyst. To be able to analyse the kinetics of catalyst degradation processes, it is important to measure Pt mass loss, carbon loss and ECSA change. Data on changes in PRD and CL thickness over time provide vital complementary information for the parameterisation of the degradation model.

For the ionomer, the thickness and coverage of the thin ionomer film on the agglomerate significantly impact proton conduction, the local reaction environment and overall cell efficiency. However, these parameters are challenging to measure directly, necessitating the development of new experimental methods or the use of model-based correlation models to obtain their values indirectly. Additionally, the local pH value within the microstructure is vital for accurate modelling of the local reaction environment but cannot be measured directly. Thus, simulating the pH value as a variable through intrinsic material parameters, structural composition, and PRD degradation remains a key goal.

Further, the thickness of each layer in the PEMFC is crucial for accurate modelling, including proton exchange membrane (PEM), cathode catalyst layer (CCL), gas diffusion layer (GDL) and, if present, cathode microporous layer (MPL). The thicknesses of these layers affect mass and charge transport processes within the cell. Additionally, the overall cell area plays a significant role in determining the fuel cell's power output.

### Operation Parameters:

Operating parameters are essential for the realistic simulation of performance. These include, temperature, relative humidity (RH), and partial pressures of reactants. Temperature and RH influence the proton conductivity of the ionomer and the reaction kinetics. Partial pressures of hydrogen and oxygen directly determine the rates of electrochemical reactions. For a given set of operating parameters, the physical performance model will yield the distributions of local variables throughout the CL, including oxygen concentration or particle pressure, vapour pressure, liquid pressure, and electrolyte phase potential (metal phase potential assumed constant).

The Accelerated Stress Test (AST) protocols, determined by the lower potential limit (LPL), upper potential limit (UPL) and the potential sweep rate, provide critical data on the durability and degradation behaviour under various operational conditions.

### Performance Parameters:

Effective physicochemical parameters are critical for evaluating the functional effectiveness of PEMFC components. For the membrane, high-frequency resistance, water permeability and electro-osmotic drag are crucial for a model-based performance prediction. In the CCL, parameters such as proton conductivity, oxygen diffusivity, volumetric exchange current density, Tafel slope, vaporization exchange rate, and water retention curve play essential roles. The cathode diffusion media require consideration of oxygen and vapor diffusivity, as well as vaporization-condensation rates and liquid permeability to assess performance under various operating conditions.

### 3.2 Parameterisation Strategy of the Basic Model

The basic model is outlined in the Deliverable Report D2.1. and consists of a combination of a statistical model for catalyst particle degradation [Rinaldo et al. 2010, Rinaldo et al. 2012, Urchaga et al. 2015, Baroody et al. 2018] with a macrohomogeneous performance model [Eikerling and Kulikovskiy 2014, Kulikovskiy 2014]. The model parameters, their extraction method and the relative local sensitivity are given in Table 1. Here, the relative local sensitivity describes the change of the voltage loss at the end of life (here chosen as 30.000 h),  $\Delta U_{EOT}$ , upon a small change of a model parameter,  $\Delta p$ , with respect to a chosen reference parameter set  $p_{ref}$ . It is calculated as

$$S_R = \frac{\left| \frac{\Delta p}{p_{ref}} \right|}{\left| \frac{\Delta U_{EOT}}{U_{EOT,ref}} \right|}$$

For a basic parameterisation of the model, only a few measurements are necessary. The parameters of the degradation sub-model can be obtained from the evolution of the ECSA over the analysed lifetime of the cell. To extract the parameters from the ECSA evolution, the fitting routine implemented in D2.1 can be used. Additionally, the radius distribution of the catalyst particles at the beginning of life is needed, which can be obtained from TEM imaging, analysed with the tools presented in [Colliard-Granero et al. 2022]. For the parameterisation of the performance sub-model, a measured polarization curve can be fitted with the tool developed in D2.1. Additional parameters are the thickness of the components, i.e., GDL and CL, which are either measured with SEM or estimated from the CL composition and porosity.

When analysing parameter sensitivities, almost all parameters have a sensitivity in the same order of magnitude, around 1. This is not surprising, as the basic model contains a minimum set of physically relevant processes, i.e., none of the considered processes is negligible or could be further simplified.

Remarkable is only the low sensitivity of the dissolution rate constant. Further analysis revealed that there are two regimes of catalyst particle degradation, in which the value of the redeposition rate is insensitive: first, if the redeposition rate is very low compared to the dissolution rate, degradation is dominated by the dissolution of the particles. In this regime, overall mass of active catalyst is lost. This could occur if the dissolved catalyst forms a Pt band in the membrane or is otherwise removed from the cell. Secondly, if the redeposition rate is very high then all dissolved catalyst gets redeposited, i.e., the total mass of catalyst is conserved, and strict Ostwald ripening occurs. Only in intermediate regimes, in which particles undergo dissolution and only partially redeposit, the redeposition rate is sensitive.

## 4 CONCLUSIONS AND FUTURE WORK

### 4.1 Parameterisation Strategy of the next model iteration

In Table 2, we list additional parameters from an advanced model [Heitz et al. 2024]. In this model, illustrated in Figure 1, we distinguish two populations of electrocatalyst nanoparticles: particles in close proximity (in the order of the thickness of the electrochemical double layer of protons) of the ionomer and particles outside of the double layer region at the ionomer film. The latter population of electrocatalyst nanoparticles are for instance located inside of water-filled pores in the ionomer-free interior of Pt/C agglomerates. As particles of the first population (close proximity to ionomer film) are exposed to local reaction conditions with markedly lower local pH, we anticipate different degradation kinetics. The additional parameters needed for this model extension as well as their extraction method are listed in Table 2.

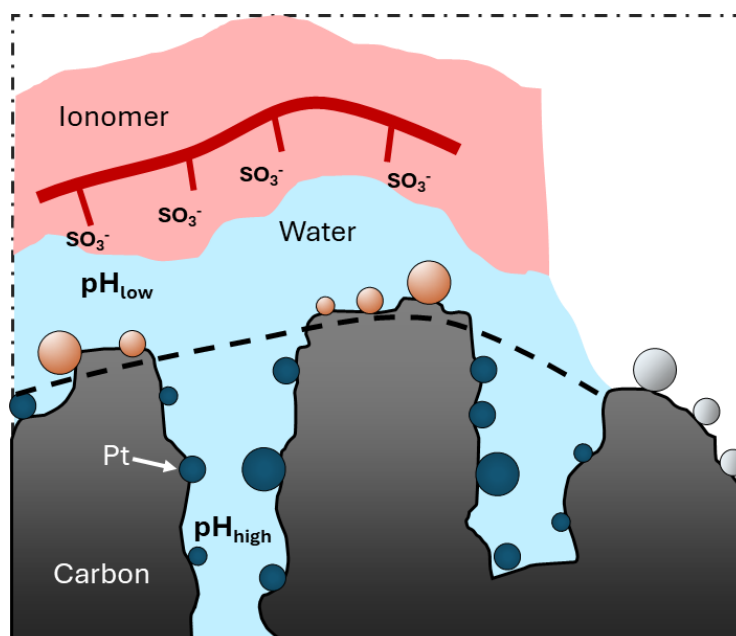


Figure 1 Distinction of Pt particles depending on their position: in contact with ionomer (red), inside of micropores (blue), inactive and therefore neglected (grey)

## 4.2 Preliminary Parameterisation Strategy of the Anticipated Full Model

The advanced model that is to be developed in HIGHLANDER, as outlined in Figure 2, will combine catalyst structure degradation with a microstructural CL model [Olbrich et al. 2022], which considers changes in structure and wetting properties over the lifetime of the cell. Based on these changes, correlated changes in effective transport properties (proton conductivity, oxygen permeability, liquid water permeability) with liquid saturation and operating conditions will be obtained. These properties are fed into a more detailed macrohomogeneous model that includes liquid water transport in a self-consistent manner [Zhang et al. 2023]. While the exact parameters of the model are not yet clear, we anticipate a set of parameters as outlined in Table 3. These parameters include properties of the ionomer in the catalyst layer, parameters describing the interaction of the ionomer with the catalyst (important in order to determine the local reaction environment) and the substrate, as well as structural parameters of the GDL (in order to refine the description of liquid water through the GDL).

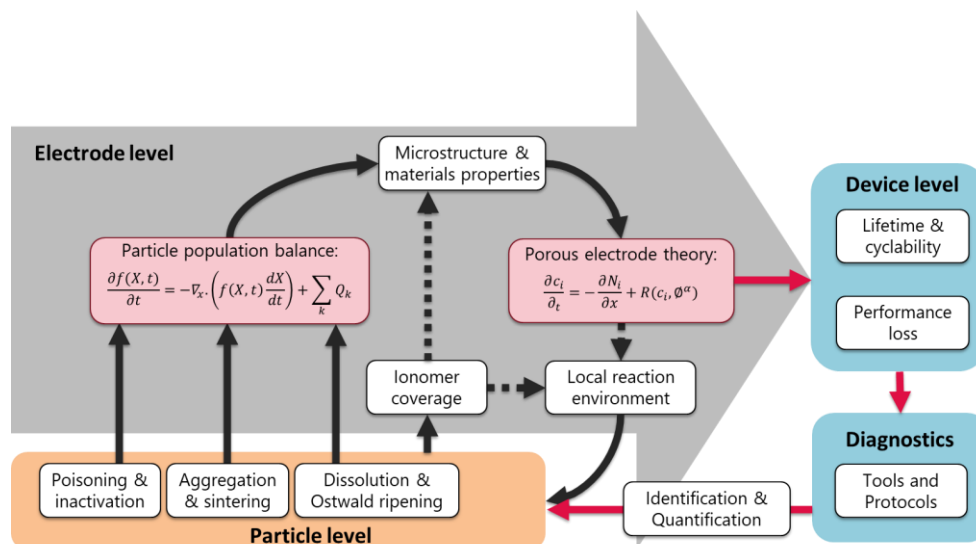


Figure 2 Advanced model framework

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## 6 APPENDIX

Table 1: Minimal parameterisation strategy of the basic model

Parameter	Unit	Extraction method	Relative local sensitivity
Pt molar mass	[g m <sup>-3</sup> ]	Literature	$1.79 \cdot 10^{-7}$
Pt loading	[g m <sup>-2</sup> ]	Ink recipe, mass spectrometry	$1.79 \cdot 10^{-7}$
BOL particle radius distribution	[-]	TEM	Mean radius of the PRD: 0.144 Standard deviation of the PRD: $4.45 \cdot 10^{-7}$
Dissolution rate constant	[mol m <sup>-2</sup> s <sup>-1</sup> ]	Fitting of ECSA(t)	$4.34 \cdot 10^{-2}$
Redeposition rate constant	[m s <sup>-1</sup> ]	Fitting of ECSA(t)	$1.79 \cdot 10^{-7}$
Catalyst surface tension (or critical radius)	[J m <sup>-2</sup> ]	Fitting of ECSA(t)	0.146
Thickness of the GDL	[m]	SEM or calculate from composition and porosity	2.75
Thickness of the CL	[m]	SEM or calculate from composition and porosity	1.20
Effective diffusion coefficient in the GDL	[cm s <sup>-1</sup> ]	Fitting of polarization curve	2.79
Effective diffusion coefficient in the CL	[cm s <sup>-1</sup> ]	Fitting of polarization curve	1.173
Effective proton conductivity on the CL	[S cm <sup>-1</sup> ]	Fitting of polarization curve	0.184
Intrinsic volumetric exchange current density	[A cm <sup>-3</sup> ]	Fitting of polarization curve	0.151
Tafel slope	[V]	Fitting of polarization curve	3.50
Ohmic resistance	[Ω cm <sup>2</sup> ]	High frequency resistance, EIS	1.08
Open circuit voltage	[V]	Direct measurement	5.77
Oxygen concentration at inlet	[mol m <sup>-3</sup> ]	Operating parameter	7.30

Table 2: Parameterisation strategy for advanced model considering two Pt population balances

Parameter	Unit	Extraction method
Ionomer coverage	[-]	TEM, indirect via BOL Pt particle distribution, Pt loading and ECSA, considering uncovered Pt is inactive
BOL and EOL particle radius distribution inside micropores	[-]	TEM 180°-measurements [Kobayashi et al. 2022]
BOL and EOL particle radius distribution on surface	[-]	TEM 180°-measurements [Kobayashi et al. 2022]
Proton concentration on surface between agglomerate and ionomer	[mol m <sup>-3</sup> ]	Indirect fitting of Pt particle radius distribution on surface at EOL
Proton concentration inside micropores	[mol m <sup>-3</sup> ]	Indirect fitting of Pt particle radius distribution inside micropores at EOL

Table 3: Parameterisation strategy for anticipated performance model

Parameter	Unit	Extraction method
Ionomer to carbon ratio	[-]	Ink recipe
Ionomer dispersion parameter	[-]	Fitting of ionomer coverage and I:C ratio
Degree of alignment of ionomer on Pt, C	[-]	Assumption, indirect fitting, Molecular Dynamics Simulation
Molar mass ionomer side chain	[g mol <sup>-1</sup> ]	Ionomer structure
Density of ionomer, Pt, C	[g m <sup>-3</sup> ]	Literature
Pore size distribution in CL	[-]	Mercury intrusion porosimetry, N <sub>2</sub> adsorption
CL porosity	[-]	Fitting of CL thickness and ionomer, Pt and C loading and density, Fitting of CL thickness and pore size distribution
Pore size distribution in GDL	[-]	Mercury intrusion porosimetry, N <sub>2</sub> adsorption
GDL porosity	[-]	Fitting of GDL thickness and C loading and density, Fitting of GDL thickness and pore size distribution
Water contact angle	[°]	Water retention curve, vapor sorption curve
Oxygen Diffusivity through flooded CL and GDL	[m s <sup>-2</sup> ]	Assumption, indirect fitting
Relative Humidity	[%]	Operating parameter
Temperature	[K]	Operating parameter
Pressure at inlet	[bar]	Operating parameter