

## PEM Fuel Cell Degradation Analysis Based on Joint Experimental and Simulation Techniques

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### Abstract

The research presented in this paper is aimed at the analysis and quantification of degradation processes in the membrane-electrode-assembly (MEA) of low-temperature PEM fuel cells based on a joint experimental / simulation based approach.

For this purpose the PEM fuel cell catalyst layer model available in a multi-physics simulation environment is extended from a zero-dimensional interface treatment to a three-dimensional agglomerate approach. The three-dimensional agglomerate catalyst layer model serves as the basis for modelling the effects of degradation on MEA performance and durability by taking into account the fundamental aspects of chemical kinetics, mechanics and physics. Model development and verification is supported by experimental studies of degradation in laboratory cells under well-defined accelerated-stress-test conditions.

Catalyst layer and degradation modeling details are presented together with results of the experimental / simulation based analysis of cells with idealized and industrial flow fields under degradation relevant conditions.

*Keywords:* digital tools in vehicle & vessel design; polymer electrolyte fuel cell; virtual testing; materials degradation; modelling; accelerated-stress-tests

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## Nomenclature

$b_i$	exponent for partial pressure of species $i$ , –	$r_{agg}$	agglomerate radius, m
$c_i$	concentration of species $i$ , mol/m <sup>3</sup>	$R$	universal gas constant, $R=8.314$ J/mol K
$E_a$	activation energy, J/mol	$T$	temperature, K
$F$	Faraday constant, $F=96485$ As/mol	$U$	voltage, V
$H_i$	Henry coefficient of species $i$ , m <sup>3</sup> Pa/mol	$V_{agg}$	agglomerate radius, m
$i$	current density, A/m <sup>2</sup>	$\alpha_g$	gas volume fraction, –
$i_r$	volumetric reaction current, A/m <sup>3</sup>	$\varepsilon$	porosity, –
$i_0$	volumetric exchange current, A/m <sup>3</sup>	$\eta$	activation overpotential, V
$k_a$	anodic transfer coefficient, –	$\phi_{ele}$	electronic potential, V
$k_c$	cathodic transfer coefficient, –	$\phi_{eq}$	equilibrium potential, V
$p$	pressure, Pa	$\phi_{ion}$	ionic potential, V

## 1. Introduction

Fuel-cell powered electric vehicles are highly efficient and when fueled with H<sub>2</sub> do not emit any harmful pollutants. However, the costs of the fuel cell systems are still too high and cannot be reduced sufficiently by scale effects of the beginning serial production. Still, the material costs of the platinum required for the cells play a significant role besides the costs for the proton-conducting membrane. A reduction of the platinum content, especially on the more performance critical cathode side of the membrane-electrode-assembly (MEA), however, exerts a direct impact on the activity of the catalyst layer and hence on the performance and the cell degradation characteristics. In general, degradation of cell components mainly occurs via i) active layer reduction, ii) carbon corrosion and iii) membrane degradation (Zhang et al. (2009); Inaba et al. (2006)).

In order to run fuel cells close to their maximum power output, operating parameters are chosen such that they may result in local temperature maxima, regions of low relative humidity and high local current densities leading to accelerated degradation. Hence, a detailed insight into the spatially resolved species concentration distributions, the local temperature conditions as well as the related species conversion rates in the MEA is decisive for the understanding of the interaction of the different transport and reaction processes and hence for the assessment and quantification of their individual contributions to the local and overall MEA degradation characteristics.

The present work presents the progress in the development and application of a joint experimental / simulation-based methodology that enables the space- and time-resolved assessment of the processes governing degradation in the MEA of low-temperature PEM fuel cells. In the following, the individual elements of the joint simulation / experimental methodology are briefly outlined, comprising details regarding experimental degradation studies, chemical kinetic based degradation modelling, multi-physics 3D-CFD simulation and degradation characterization / quantification in laboratory cells with idealized and industrial flow fields. Results of the experimental analysis are presented and discussed together with related computational results obtained by applying the newly developed simulation models. Finally, an outlook on the further planned activities is provided.

## 2. Degradation Analysis

In order to obtain a fundamental understanding of the lifetime limiting degradation mechanisms and to enable model development, experimental data is required. However, in real systems, multiple different mechanisms are overlapping and thus, highly specific tests are required to permit selective parameterization.

### 2.1. Accelerated stress test protocol development

A large variety of accelerated-stress-test (AST) protocols - such as those proposed by the US Department of Energy (US DoE) or the Joint Research Centre (JRC) - are available. These tests either aim to selectively induce component degradation in order to allow comparison of material characteristic and durability, or make an attempt to realistically portray detrimental conditions, as they can occur during fuel cell operation. These can again be classified by the dominant degradation mechanisms as reviewed in Table 1 (Fuel Cell Technologies Office (2017); Tsotridis et al. (2015)).

ASTs aimed at specific failure modes are based on fundamental knowledge of the respective underlying mechanisms. They do not aim to include realistic operation conditions, but serve as means to ensure comparability.

Degradation of the polymer electrolyte is either caused by mechanical or chemical stressors. Mechanical stress is induced by changing relative gas humidity and thus the expansion or shrinkage of the ionomer. Chemical degradation on the other hand is caused by the presence of harmful radicals, able to decompose the polymer electrolyte. Whereas the first mechanism mainly results in the formation of cracks and pinholes, the latter causes an increased membrane resistance towards ion conduction (Bodner, Rami et al. (2016); Bodner et al. (2015)). In order to induce platinum catalyst degradation, the US Department of Energy proposed an accelerated stress test, which includes voltage cycling between 0.6 and 1.0 V with triangle sweeps and a sweep rate of 50 mV s<sup>-1</sup>. Even though carbon corrosion occurs at a potential of 0.207 V vs. reversible hydrogen electrode (RHE), it is expected to have a minor contribution due to slow reaction kinetics. At a potential above 1.1 V vs. RHE carbon dioxide dissociates and a protective PtO layer is formed, protecting the catalyst from degradation. This effect is made use of in the catalyst support specific AST proposed by the US DoE in which the voltage is cycled between 1.0 and 1.5 V (de Bruijn et al. (2008); Fuel Cell Technologies Office (2017)).

ASTs aimed at portraying specific, but real failure modes usually result in complex and strongly interacting degradation mechanisms. Therefore, these tests tend to be highly application oriented. During start-up / shut-down (SUSD), the fuel cell can be exposed to critical conditions, inducing degradation of the electrodes and limiting the durability. Initially, air is present at both anode and cathode. During start up, the air is purged out by hydrogen on the anode. This gradient has, however, been proven to be harmful and leads to significant carbon corrosion due to cathode polarization. Carbon corrosion is especially an issue in mobile and automotive applications, as these face far more SUSD cycles than fuel cells in stationary systems. Mitigation strategies are mainly based on engineering solutions, such as purging of the anode with an inert gas, minimizing dwell times by using high gas flow rates or applying an external load to avoid cathode polarization (Brightman and Hinds (2014)). The highly fluctuating load changes are portrayed in the fuel cell dynamic load cycle (FC-DLC). This test was issued by the Joint Research Centre, is based on the new European driving cycle (NEDC) and includes cycling between 0% and 100% of the fuel cell's nominal load (Tsotridis et al. (2015)).

## *2.2. Degradation issues in PEMFCs for automotive application*

Polymer electrolyte fuel cells for automotive applications are exposed to a variety of harmful conditions, most deriving from strongly fluctuating power demand. Even if performance peaks during acceleration are compensated by hybridization, the fuel cell will still be facing sudden load changes. Despite the harmfulness of a high number of start-up / shut-down cycles, these attribute only to approximately 33% of the reported degradation, whereas dynamic load changes were identified to cause 56.6% in PEMFC busses under real driving conditions (Pei et al. (2008)).

Voltage over- and undershoot behavior occurs when the load changes are caused by the time delay needed by the system in order to equilibrate. This is happening due to the response time for the media supply, inhomogeneous concentration distribution, flooding issues or membrane dry out. A decrease in current density results in a shorter time until equilibration, as the membrane humidification is initially better. A sudden increase of power demand, however, leads to extensive water production on the cathode and results in water management issues and flooding. Liquid water can block channels and pores, which causes reactant starvation (Enz et al. (2015)).

Suddenly changing load conditions also demand a highly dynamic response of the gas supply. If this cannot be accomplished, reactant starvation can occur. On the cathode, oxygen starvation leads to a potential drop and therefore to a reduction of protons, resulting in the emission of hydrogen, which poses a potential hazard. Furthermore, platinum oxides are reduced, thus initially increasing the active surface area of the catalyst and enhancing the performance. However, in the presence of residual oxygen, the oxygen reduction reaction still takes place. This induces a strongly inhomogeneous current distribution and hence also locally increased temperatures, which in turn lead to an accelerated platinum agglomeration rate in the respective areas. Oxygen starvation therefore causes a shortened durability despite the initially positive effect (Bodner et al. 2017; Bodner, Schenk, et al. 2016)).

On the anode, reactant deprivation results in an increase of potential and the oxidation of the carbon support. This leads to the emission of carbon dioxide, the detachment of platinum catalyst nanoparticles and thus a loss of both electrical conductivity of the electrode and a decreased electrochemically active surface area (Bodner et al. (2015)).

Table 1. List of accelerated stress tests

Type of test	Dominant degradation mode	Description	Given system parameters	Expected duration (h)	Source	Interruptions
Degradation specific	Electrocatalyst degradation	Square wave voltage cycling, 0.6 V (3 s) -0.95 V (3 s)	Cell temperature: 80 °C, rH(anode and cathode): 100%, hydrogen (100 sccm) /Nitrogen (37.5 sccm), atmospheric pressure	50	DoE (2017)	Polarization curves after 0, 1k, 5k, 10k, 30k cycles; cycling voltammetry after 10, 100, 1k, 3k, 10k, 20k and 30k
Degradation specific	Catalyst support degradation	Triangle sweep (500 mV/s), 1.0 V -1.5 V	Cell temperature: 80 °C, rH(anode and cathode): 100%, hydrogen/Nitrogen, atmospheric pressure	2.78	DoE (2017)	Polarization curves and cycling voltammetry after 0, 10, 100, 200, 500 1k, 2k and 5k
Degradation specific	Chemical MEA degradation	Steady state open circuit voltage	Cell temperature: 90 °C, rH(anode and cathode): 30%, hydrogen ( $\lambda = 10$ at 0.2 A/cm <sup>2</sup> equ. flow) /air ( $\lambda = 10$ at 0.2 A/cm <sup>2</sup> equ. flow), 1.5 bara	500	DoE (2017)	Effluent water sampling, hydrogen cross over, electrochemical impedance spectroscopy every 24 h
Degradation specific	Mechanical membrane degradation	2 min 0% rH / 2 min dew point 90°C	Cell temperature: 80 °C, air (2 SLPM) /air (2 SLPM), atmospheric pressure	1333.33	DoE (2017)	Hydrogen cross over and electrochemical impedance spectroscopy every 24 h
Simulation of real operation	Mixed - membrane and electrode	50 s 0.3 V, 10s OCV	Hydrogen/air (dry, $\lambda = 2.0$ at max. current equ. flow)	n.k.	ZBT	n.d.
Relative humidity cycling	Mechanical membrane degradation	E.g. 24 h 80% rH, 24h 0% rH	Hydrogen/air	n.k.	TUG CEET	n.d.
Anode starvation	Anode catalyst	Different modes possible (load cycling/gas flow cycling)	Hydrogen/air	n.k.	TUG CEET	n.d.
Cathode starvation	Cathode catalyst	Different modes possible (load cycling/gas flow cycling)	Hydrogen/air	n.k.	TUG CEET	n.d.
Simulation of real operation	Mixed	FC-DLC, relative load cycling (0-100% nominal load) adapted for NEDC	Hydrogen/air	n.k., 20 min./cycle	JRC (2015)	n.d.

### 2.3. Characterization of degradation

Notwithstanding that some accelerated stress tests are designed to address and distinguish different degradation mechanisms, a periodical characterization of the fuel cell is necessary to identify and quantify the resulting degradation of the stress test. Different electrochemical methods are available:

- quasi-stationary potentiometry (polarization curve): the current-voltage behavior of the fuel cell over the complete operation range is measured under typical operating conditions; the measurement provides the sum of all voltage losses
- electrochemical impedance spectroscopy (EIS): the DC load of the fuel cell is superimposed by a well-defined sinusoidal AC current wave of systematically varied frequencies; measuring the current and related voltage reply, the different voltage losses can be separated due to their specific time constants; a renowned result is the high frequency resistance that directly indicates the ohmic resistance of the cell, as well as the charge transfer and diffusion resistances
- cyclic voltammetry (CV): purging with an inert gas (N<sub>2</sub>, Ar, etc.) on the cathode side of the fuel cell, the anode can be used as a reference electrode; voltage sweeps with different speeds can then be used to measure the electrochemical surface area of the cathode (fast sweep) or the hydrogen crossover (slow sweep)

While the polarization curve can be measured with the ordinary fuel cell test rig equipment, special measurement devices and additional test rig features are necessary to measure the EIS and CV. Alternatively, a model based polarization curve analysis can be used to quantify the different voltage losses, respectively degradation mechanisms. For this purpose a fast model is used that can be automatically calibrated to the polarization curves.

Within this project a model has been developed that is based on the analytical model from Kulikovsky (2014). The model calculates the individual losses for the reaction kinetics ( $U_{act}$ ), ohmic losses ( $U_{ohm}$ ), losses caused by oxygen diffusion limitations and limited ionic conductivity in the cathode catalyst layer ( $U_{CCL}$ ) and losses caused by the limited oxygen diffusion rate in the GDL ( $U_{GDL}$ ).

$$U = U_{ideal} - U_{act}(i+i_n) - U_{ohm}(i+i_n) - U_{CCL}(i+i_n) - U_{GDL}(i+i_n) \quad (1)$$

An exemplary model calibrated to a measured polarization curve is presented in Fig. 1. By using the calibrated model it is possible to identify and quantify the different losses.

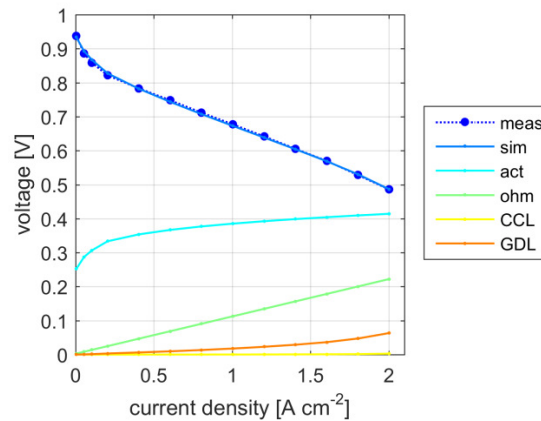


Fig. 1 Exemplary measured polarization curve compared to the calculated polarization curve including the separately calculated voltage losses

Applying this model based analysis it is possible to get detailed and valuable information from the polarization curves. The computational requirements are negligible and series of polarization curves can be analyzed via standard computer configurations within seconds. The information about the quantity of the different voltage losses can be also applied to accelerate the calibration of CFD simulations that will further allow to get a detailed and spatially resolved view of the local species distributions, thermal and electrochemical conditions and related transport processes in the cell at different degradation states.

### 3. Degradation Modelling

In the last decade, numerous degradation models have been published, with a brief overview of existing theoretical approaches proposed to predict durability of PEM fuel cells provided in Karpenko et al. (2016). In accordance with the utilized theory and the level on which degradation phenomena are described, the degradation models are divided into the following categories: 1) micro-scale, 2) macro-scale, 3) multi-scale models. Unfortunately, most of the existing models consider degradation phenomena in only one single component of the fuel cell, i.e. either in the membrane, in the catalyst or in the gas diffusion layer.

There is only a limited number of models available aimed at predicting performance and durability of a complete fuel cell or stack. One of the most powerful methods utilized to study and to support the development of fuel cells is computational-fluid-dynamics. The CFD simulations allow monitoring of the most important transport phenomena inside the cell which is practically impossible by using current experimental methods. In previous work (Karpenko et al. (2016), Fink et al. (2016)) the development of semi-empirical degradation models of the polymer electrolyte membrane and catalyst, and the coupling of these models with a CFD approach for application to low-temperature PEM fuel cells is reported. This coupled approach takes into account the effect of local operating conditions, such as temperature, humidity and voltage on the local degradation processes. The simulation shows that the cell current density decreases faster by lowering relative humidity and increasing temperature (Karpenko et al. (2016)). Because the adopted degradation models are of semi-empirical character, they are not applicable to simulate changes in the chemical compositions of the Pt/C catalyst and the ionomer and do not support the prediction of HF and CO<sub>2</sub> concentrations released during fuel cell operation.

One of the main goals of the work presented here is to develop largely refined models that take into account chemical degradation proceeding in the ionomer and Pt/C catalyst in low-temperature PEM fuel cells operating under steady-state conditions and accounting for mechanical durability of the membrane under cycling voltage conditions. The developed models are based on the fundamentals of radical kinetics, physics and mechanics and consider the following degradation phenomena:

- chemical destruction of the perfluorinated sulfonated ionomer in the catalyst layer and in the polymer electrolyte membrane
- Pt oxidation and Pt dissolution in the catalyst, Pt diffusion and deposition in the membrane
- C corrosion in the catalyst layers
- CO<sub>2</sub> and HF concentrations released during the PEM fuel cell operation
- mechanical durability of the membrane under voltage cycling conditions

In the following, a model for describing the ionomer chemical degradation is introduced. Table 2 provides a comparison of some available degradation models of the perfluorinated ionomer in fuel cells. Interestingly, the analyzed models largely differ in the assumption regarding the location of the hydrogen peroxide formation. Some authors assume the H<sub>2</sub>O<sub>2</sub> formation to occur only at the anode, other authors take into account the peroxide emergence at both electrodes, i.e. at the anode as well as at the cathode. Also, the different authors consider various mechanisms of ionomer degradation. Shah et al. (2009) and Gummalla et al. (2010) take into account only destruction of the main chains of the ionomer, while others, e.g. Goulon et al. (2010), Wong et al. (2014), Quiroga et al. (2016) assume degradation of the side chains only.

Table 2. Comparative analysis of the degradation models

Authors and Year	Location of the H <sub>2</sub> O <sub>2</sub> formation		Considered mechanism of Nafion degradation	
	At the anode	At the cathode	Unzipping of the main chain	Splitting of the side chain with sulfo-groups
Shah et al. (2009)	+	+	+	-
Gummalla et al. (2010)	+	+	+	-
Coulon et al. (2010)	+	-	-	+
Wong et al. (2014)	+	+	-	+
Quiroga et al. (2016)	+	-	-	+

Degradation of the main chains is initiated on carboxylic groups, which are situated at the end of the polymer chains. The hydroxyl radicals reacting with the carboxyl groups build CO<sub>2</sub>, HF and a new carboxylic group at the end of the main chain. This process, known as unzipping mechanism, shortens the main chains and destroys the

polymer electrolyte. In this way, the membrane is getting thinner. Another mechanism of the ionomer degradation is an attack of the side chains by the hydroxyl radicals. In this case, the radicals break chemical bonds between the oxygen and carbon atoms of the side chains splitting the part of the chain containing the proton-conducting groups. The splitting mechanism leads not only to a decrease in the membrane thickness, but also to a reduction in the membrane conductivity, which dramatically affects the fuel cell performance (Karpenko et al. (2015)). The newly developed model takes into account the chemical kinetics of the ionomer degradation in both the catalyst layers and the membrane (Karpenko et al. (2017)).

Fig. 2 shows the spatial distribution of hydrogen peroxide in a low-temperature PEM fuel cell under typical operating conditions. The simulation is carried out at  $c_{O_2} = 16 \text{ mol/m}^3$  at the cathode catalyst layer. This value is correlated to the oxygen concentration in real PEMFC operation at open circuit voltage, when the electrical load is absent. Because the oxygen at the anode can occur only due to the cross-over diffusion across the membrane, the oxygen concentration at the anode usually is very low (10, 5 and 2 ppm). The considered ratio between the oxygen concentrations in the cathode and anode catalyst layers is 5-6 orders of magnitude. In the simulated case, the dominant formation of the hydrogen peroxide is observed when in the anode CL  $c_{O_2}$  shows a maximum value of  $1.6 \cdot 10^{-4} \text{ mol/m}^3$ . With decreasing oxygen concentration in the anode CL, the hydrogen peroxide concentration in the anode drops, and the peroxide formation dominates in the cathode CL. Numerous papers have been devoted to the analysis of degradation of the Nafion membrane in PEMFCs. Some researchers have detected higher degradation at the cathode side, others have reported on predominant degradation at the anode side. In accordance to the present model, the speed of the membrane degradation depends on the hydrogen peroxide concentration which is a function of the operating condition of the cell.

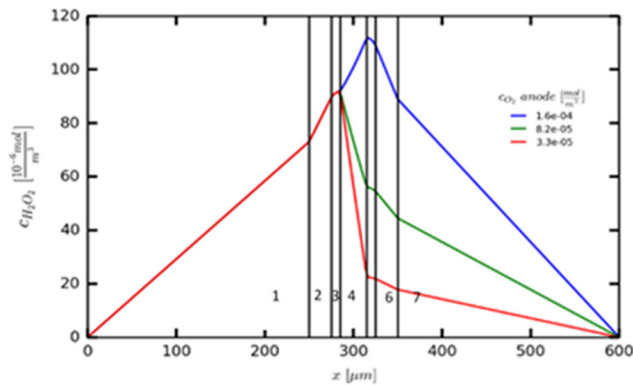


Fig. 2. Spatial distribution of hydrogen peroxide in the different domains of a LT-PEMFC

1, 7 – macroporous substrate layers; 2, 6 – microporous layers;  
 3 – cathode catalyst layer; 4 – membrane; 5 – anode catalyst layer.  
 The calculation is performed at  $T=70^\circ\text{C}$ ,  $p_a=p_c=1 \text{ bar}$ ;  $RH_c=RH_a=90\%$ .

The present model enables monitoring of time-dependent changes in the ionic conductivity of the membrane and catalyst layers, their thickness, acid group concentration as well as the amount of HF and  $\text{CO}_2$  released. In a next step, this model will be coupled with the CFD approach described in the next section and applied to analyze local degradation phenomena in laboratory and industrial fuel cells.

## 4. Simulation Methodology

### 4.1. Three-dimensional Catalyst Layer Model

In order to utilize the degradation models in a multi-physics 3D-CFD framework, the zero-dimensional interface model available in AVL FIRE™ is extended to a full three-dimensional treatment of the catalyst layers. The three-dimensional model is able to describe the transport processes of all relevant quantities (e.g. gas species, liquid water, electrons, ions, heat) through the catalyst layers, and additionally to provide information about the catalyst layer structures. A good choice for such a model is a *thin-film agglomerate model*. Agglomerate models for PEM fuel cells have been developed since approximately 20 years (Antoine et al. (1998); Weber and Newman (2004); Shah et al. (2006); Xing et al. (2014)). In contrast to most of the agglomerate models presented in the literature, the agglomerate model adopted in this work solves the diffusion equation in the agglomerates *numerically* rather than *analytically* allowing for a more general formulation of the diffusion processes and the electrochemical

reactions. Below, a short overview of the implemented agglomerate model is presented whereas a more rigorous theoretical description can be found in Fink et al. (2017).

A schematic sketch for both catalyst layer models, e.g. the interface and the three-dimensional agglomerate model, is shown in Fig. 3. In the agglomerate model, the catalyst layer is assumed to consist of spherical agglomerates of platinum dispersed carbon particles embedded in ionomer covered by a thin ionomer film. In the interface model, the catalyst layer is modelled as a two-dimensional interface. The agglomerate model accounts for transport in the catalyst layers and local electrochemical reactions in the agglomerates in all three space-dimensions, whereas the interface model neglects the transport processes and provides boundary conditions for the adjacent gas diffusion layers and membrane via surface reaction sources.

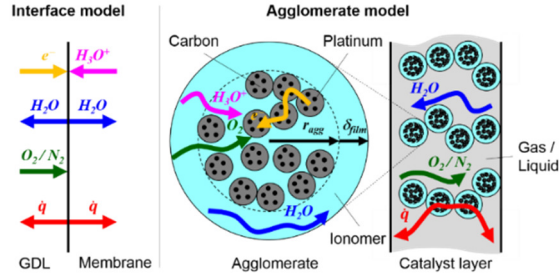


Fig. 3 Assumed catalyst layer structure and transport quantities for interface and agglomerate model, Fink et al. (2017)

The redox reactions are described with the Butler-Volmer equation

$$i_r = i_{0,ref} f(c_i) \left( \frac{p_w}{p_{ref}} \right)^{b_w} \frac{\alpha_g}{\varepsilon} \exp \left[ -\frac{E_{a,i_0}}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \left[ \exp \left( \frac{2k_a F \eta}{RT} \right) - \exp \left( -\frac{2k_c F \eta}{RT} \right) \right] \quad (3)$$

with the activation overpotential  $\eta = \phi_{ele} - \phi_{ion} - \phi_{eq}$ , where  $\phi_{eq}$  is the equilibrium potential calculated with the Nernst equation. The reactant concentration function  $f(c_i)$  reads

$$f(c_i) = \begin{cases} \left( \frac{H_i}{p_{ref}} \right)^{b_i} \frac{3}{4\pi r_{agg}^3} \int c_i^{b_i} dV \\ \left( \frac{p_i}{p_{ref}} \right)^{b_i} \end{cases} \text{ in } \begin{cases} \text{agglomerate} \\ \text{interface} \end{cases} \text{ model for } i = O_2, H_2 \quad (4)$$

In the agglomerate model the reactant concentrations are calculated from the transport in the ionomer phase of the agglomerates whereas in the interface model the reactant concentrations are taken from the gas phase in the GDL.

#### 4.2. Model Verification and Application to Industrial Cell

Before applying the model to a real industrial fuel cell, it is verified on a simple test cell with straight channels. A comprehensive parameter study is conducted from which only the variation of the agglomerate radius is shown here. Fig. 4 presents the influence of agglomerate radius variations on cell potential and O<sub>2</sub> concentration.

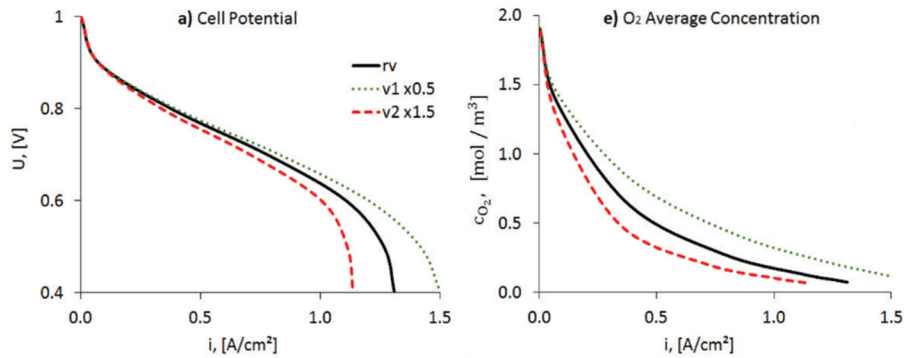


Fig. 4. Influence of agglomerate radius on the cell potential (left) and average O<sub>2</sub> concentration in the agglomerates (right)



The agglomerate radius is varied from its reference value of 500 nm to plus/minus 50%, i.e. the same amount of ionomer and platinum is redistributed to larger but less agglomerates. Larger particles exhibit a stronger diffusion resistance for the reactant transport leading to a performance drop and smaller average oxygen concentrations in the agglomerates.

In a second step, the model is applied to a single cell with an industrial flow field. Fig. 5 shows ionic current density in a mid-plane of the membrane as well as activation overpotential, O<sub>2</sub> concentration in the agglomerates and liquid water volume fraction in a mid-plane of the cathode catalyst layer for an operating point of 0.6 V / 1.4 A/cm<sup>2</sup>. Overall, the current density decreases from cathode inlet towards outlet due to the O<sub>2</sub> concentration decrease. In the region close to the air inlet the current density maximum is located below the channel lands due to the low electrical conductivity of the GDL and larger amount of available O<sub>2</sub>. After approximately a quarter of the cathode channel length, the current density maximum is shifted towards the region below the air channels. Now, O<sub>2</sub> access becomes the dominating factor. The influence of the anode flow field can also be seen in the current density. From the anode side, the dominating effect is the better electron access below the lands. Membrane humidity seems to have a minor effect on the current density distribution and there is only a small amount of liquid water.

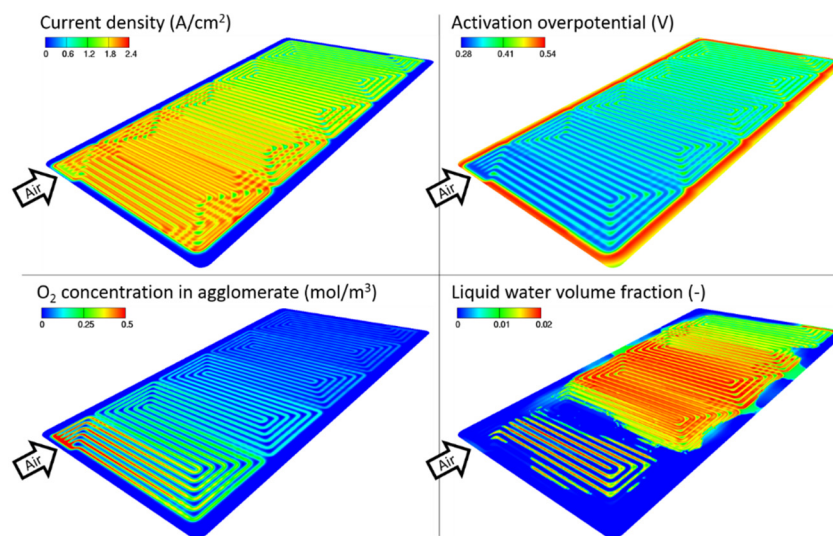


Fig. 5. Current density in the mid-plane of the membrane and several quantities in the mid-plane of the cathode catalyst layer for an operating point of 0.6 V / 1.4 A/cm<sup>2</sup>

## 5. Summary and Outlook

The progress in the development and application of a joint experimental / simulation-based methodology that enables the analysis and assessment of the processes governing degradation in the membrane-electrode-assembly of low temperature PEM fuel cells is presented. Comprehensive accelerated-stress-test protocols aimed at covering the diverse degradation processes in low-temperature PEM fuel cells are derived. The experimental results and model-based derived data enable a deeper understanding of the individual degradation phenomena and their interaction. In addition, the results form the basis for the development of advanced degradation models for use within the context of a multi-physics 3D-CFD simulation approach. The chemical kinetics based membrane degradation model fully takes into account the hydrogen-peroxide and radical formation within the polymer-electrolyte-membrane. The catalyst layer degradation modelling approach covers processes such as the temporal changes of Pt/C and Ionomer-phase as well as the catalyst layer thickness. Forming the basis for coupling the degradation models with the CFD simulation approach, a newly developed catalyst layer model represents the three-dimensional transport of electrons, ions, mass and heat by simultaneously taking into account agglomerates of carbon, platinum and ionomer covered by an ionomer film. Within this modelling concept, the diffusion of reactants across the ionomer phase and towards the catalytic layers as well as the electrochemical reactions within the agglomerates are taken as functions of the local concentration of reactants. In the further work the joint experimental / simulation-based approach will be refined and applied to the detailed analysis and assessment of the processes governing degradation in the membrane-electrode-assembly of low-temperature PEM fuel cells with idealized and industrial flow fields under the derived accelerated-stress-test conditions.

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