Methodology for Evaluation of Contributions of Ostwald Ripening and Particle Agglomeration to Growth of Catalyst Particles in PEM Fuel Cells

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Abstract

The degradation of the catalyst layer represents one of the main limiting factors in a wider adoption of fuel cells. The identification of the contributions of different mechanisms of catalyst degradation, namely the Ostwald ripening and particle agglomeration, is an important step in the development of mitigation strategies for increasing fuel cell reliability and prolonging its life time. In this paper, the degradation phenomena in high temperature polymer electrolyte membrane fuel cell (HT-PEMFC) are analyzed using a physically-based model of fuel cell operation and catalyst degradation, describing carbon corrosion, platinum dissolution and consequent growth of catalyst particles. The model results indicate significantly different time dependence of catalyst particle growth resulting from different mechanisms: linear growth in the case of particle agglomeration and root-like time dependence for the Ostwald ripening. Based on these results, a new analytic method is proposed, performed by the fitting of a test root-function to the time profile of the particle size growth and using best-fit parameters to identify the prevailing growth mechanism. Using this method on a particle growth time trace deduced from in situ cyclic voltammetry measurement during HT-PEMFC degradation, we are able to identify the agglomeration as the main mechanism of catalyst particle grow.

Keywords: Agglomeration, Catalyst Layer, Degradation, Fuel Cells, High Temperature, Modeling, Ostwald Ripening, Supported Catalysts

1 Introduction

In a world of increasing awareness about environmental issues, fuel cells emerge as one of the most promising future technologies for clean and efficient energy conversion [1, 2]. While low-temperature polymer electrolyte membrane fuel cells (LT-PEMFC) are mostly aimed at the transport sector, high-temperature PEMFC (HT-PEMFC) are more suitable for small scale stationary power generation, and because of their simple design and resistance to CO poisoning, offering the possibility of using reformed hydrocarbons instead of pure hydrogen [3].

Despite significant development in recent years, the degradation of fuel cell components remains the main limiting factor in a wider adoption of this technology. Several degradation mechanisms, deteriorating the performance of crucial fuel cell components, are shared between the LT and the HT-PEMFCs, most notable among them being the degradation of the proton conducting membrane [4] and the catalyst layer [5]. While the membrane degradation mechanisms differ significantly between LT- and HT-PEMFC because of the difference in the membrane materials used [3], the characteristics of the catalyst layer, and consequently the relevant degradation mechanisms,
are similar for both. The nanoscopic particles of platinum (Pt) or a similar noble metal, dispersed on a high-surface carbon support, featuring high specific surface for the catalyst reaction, are prone to several degradation phenomena, initiated by electric potential, elevated temperature and humidity present in the catalyst layer [6].

These detrimental conditions lead to two distinctly different mechanisms of catalyst degradation. The first mechanism, the so-called Ostwald ripening, is driven by Pt dissolution, which is more prominent for smaller particles than for larger ones because of the surface energy effects. This results in a dissolution of Pt from smaller particles and its redeposition on larger Pt particles, resulting in a net growth of particle size in the catalyst layer [7, 8]. On other hand, the corrosion of carbon support, also significant in the catalyst environment, leads to particle detachment from their support, their migration, and potential agglomeration with other particles [9]. Both Ostwald ripening and particle agglomeration lead to a gradual increase of mean particle size in the catalyst layer, resulting in a lower specific surface area and thus also to a lower electrochemical surface area (ESA) and consequent decrease in fuel cell efficiency [5].

Mitigation strategies to reduce the degradation rate of the catalyst range from the development of new materials, to better withstand the harsh conditions in the catalyst layer, over optimized MEA, flow field and stack design to improved control strategies for fuel cell operation, aimed at avoiding the conditions most detrimental to the fuel cell components [10]. Nowadays, these development tasks can be supported by increasingly capable physically-based models of both fuel cell operation and degradation, describing the entire causal chain of interconnected degradation mechanisms, e.g., [11, 12]. The correct identification of individual degradation processes and their causes, however, is a crucial step in both the development of sufficiently detailed degradation models and the resulting mitigation strategies.

In the case of catalyst degradation, the experiments indicate that the carbon corrosion is typically more pronounced at high temperatures [13], while high electric potential leads to a higher Pt dissolution [14], which is further enhanced for small particles [7]. These two phenomena can be relatively easily distinguished in the short term experiments by measuring the CO2 emissions from the fuel cell [15] or the concentration of dissolved Pt in the catalyst layer [14]. In real-life applications, however, where the fuel cell is exposed to uncontrolled conditions, which can only be tracked to a certain degree during the life-time, the identification of various degradation modes proves to be a much more challenging task. The catalyst degradation is in this case typically studied based on a post mortem measurement of the particle size distribution (PSD), obtained by transmission electron microscope (TEM) imaging of the aged catalyst sample [16, 17].

The theoretical models of particle growth due to Ostwald ripening suggest the development of asymmetric PSD with the maximum on the large-particle side and the “tail” towards the small-particle side [8], while the models of particle agglomeration, based on the Smoluchowski equation [18], predict the opposite, a PSD with the maximum on the small-particle side and the “tail” towards the large-particle side [19]. The contribution of either of the two degradation modes can, therefore, be determined based on the skewness of the measured PSD. This sort of analysis was done based on small-angle X-ray scattering (SAXS) [20] and TEM imaging [17] of the aged catalyst. Vion-Dury proposed a more complex analysis of TEM images based not only on the size, but also on the shape of catalyst particles, which provides deeper insight into the mechanism of their growth [21]. While all these established approaches are to some degree capable of distinguishing between Ostwald ripening and agglomeration contributions to particle growth, they are all based on the analysis of the detailed shape of the PSD, which is difficult to measure and can only be obtained after the end of life of the fuel cell.

In this paper we study the distinction between both processes, i.e., particle agglomeration and Ostwald ripening, using our recently developed model of fuel cell operation and degradation [11, 12]. The model is calibrated based on the experimental data on the HT-PEMFC recently published in [16, 22] and used to model particle growth during long-term fuel cell operation. The analysis of particle growth, based on the results of the model, indicates a significant difference in the mean particle size growth when caused by either Ostwald ripening or particle agglomeration. In the case of particle growth because of the agglomeration, the mean particle size grows linearly with time, while in the case of the Ostwald ripening, the growth is described by a root function of time [7].

Based on these results, this paper presents an insightful and simple analytic method aimed at distinguishing individual contributions of both particle growth mechanism, based solely on the time trace of a mean radius of particles in the catalyst layer. The method consists of fitting of a variable-order root-function to the measured time trace of mean particle size, with the best fit root-order being used as an indicator of the prevalent catalyst degradation mechanism. The advantage of this innovative method over established approaches lies in its ability to identify the main degradation mechanism solely from the cyclic voltammetry measurement during fuel cell operation, without the need for detailed post mortem particle size measurement, making it simpler, faster and potentially more useful in real world applications. The method is tested on the time trace of mean particle size, calculated from the catalyst surface area measured by cyclic voltammetry [17].

2 Experimental
2.1 Methods
The coupled fuel cell operation and degradation model, used in the presented analysis, was already extensively presented in [12], therefore we only briefly present the most important aspects, crucial for understanding the contributions of this paper. In the coupled model, the local conditions in the catalyst layer, initiating the degradation processes, namely the
local electric potential, temperature and humidity, the so-called degradation stimuli, are calculated using an advanced hybrid analytical-numerical (HAN) approach [23–25]. In the direction perpendicular to the channel, the concentrations and velocity profiles of the gases in the feed channels and in the gas diffusion layer (GDL) are calculated analytically with the solutions coupled numerically along the length of the channel [23]. The resulting gas concentrations at the catalyst are used to determine the relation between the voltage and the current generation based on the Butler–Volmer equation and voltage drop across the membrane.

The local conditions in the catalyst layer, calculated by the HAN model, are used as the inputs to the recently developed catalyst degradation model [11]. The model combines several verified models of individual steps in the catalyst degradation, namely the particle size dependent Pt and carbon oxidation [26, 27], Pt dissolution [28], and the corrosion of carbon support [26]. The contributions of these effects are used as inputs of the detailed model of particle size redistribution because of both Ostwald ripening [29] and particle agglomeration [9, 29]. In the following subsections, individual processes included in the degradation model are presented in detail. The interactions between the processes and their effect on the overall particle growth in the catalyst is also explained, followed by the description of the model calibration, based on the experimental data found in literature. Note that the same catalyst degradation processes also occur in the LT-PEMFC and, provided the proper calibration of reaction rate parameters, the same model could also be used in this kind of fuel cell system [26].

2.1.1 Pt and Carbon Surface Oxidation Model

The local catalyst voltage, temperature and humidity determine the dynamics of Pt and carbon surface oxidation, the first step in catalyst degradation. As proposed by Pandy [26], the surface oxides start forming on the Pt and carbon surface in the presence of water at sufficiently high voltage. In our model, very similar to the one proposed by Pandy [26] and Macauley [27], we assume at most a monolayer coverage of oxides of two kinds: unstable hydroxyl groups (C−OH and Pt−OH) and stable oxide groups (C=O and Pt=O) on the defect sites on carbon (C*) and Pt surface (Pt*), as described by reversible electrochemical reactions:

\[ C^* + H_2O \rightarrow C − OH + H^+ + e^-; \quad E_{C1} = 0.29 \text{ V RHE} \]  
\[ C − OH = C = O + H^+ + e^-; \quad E_{C2} = 0.80 \text{ V RHE} \]  
\[ Pt^* + H_2O \rightarrow Pt − OH + H^+ + e^-; \quad E_{Pt1} = 0.79 \text{ V RHE} \]  
\[ Pt − OH = Pt = O + H^+ + e^-; \quad E_{Pt2} = 0.80 \text{ V RHE} \]

The equilibrium potentials \( E_i \) are given for a flat reaction surface, in relation to the reversible hydrogen electrode (RHE) and at typical temperature of HT-PEMFC operation \( T = 160^\circ \text{C} \). Note that the equilibrium potential of the reactions taking place on the Pt particle surfaces is shifted by the Kelvin term, decreasing the potential on surfaces of particles with smaller radius \( r \) [28]:

\[ E_{Pt1}(r) = E_{Pt1} + \frac{1}{2F} \left( \frac{\sigma_{PtOH}M_{PtOH}}{\rho_{PtOH}} - \frac{\sigma_{PtM}}{\rho_{Pt}} \right) \]  
\[ E_{Pt2}(r) = E_{Pt2} + \frac{1}{2F} \left( \frac{\sigma_{PtM}M_{PtOH}}{\rho_{Pt}} - \frac{\sigma_{PtOH}M_{Pt}P_{PtOH}}{\rho_{PtOH}} \right) \]

where \( \sigma, M, \) and \( \rho \) denote the surface tension, molar mass and density, respectively, of Pt and Pt surface hydroxyl and oxide groups, and \( F \) denotes the Faraday constant. The rates of the reactions depend on the degradation stimuli: the temperature \( T \), the relative humidity \( a_{H_2O} \), the local electric potential between the catalyst and adjacent ionomer \( U_{cat} \), and the proton activity \( a_{H^+} \), related to the pH value, as well as the percentage of clean Pt (\( \Theta_{Pt} \)) and carbon surface (\( \Theta_{C} \)) and the percentage of surface being covered in oxides: \( \Theta_{PtOH} \) and \( \Theta_{PtO} \) for Pt−OH and Pt=O groups, respectively, and \( \Theta_{COH} \) and \( \Theta_{CO} \) for C−OH and C=O groups:

\[ r_{C1}(r) = k_{C1} \left[ \frac{a_{H_2O} \Theta_{C}(r)e^{\alpha_{C}(U_{cat}−E_{C})/b}}{a_{H_2O} \Theta_{COH}(r)e^{\alpha_{COH}(U_{cat}−E_{CO})/b}} \right] \]  
\[ r_{C2}(r) = k_{C2} \left[ \frac{\Theta_{COH}(r)e^{\alpha_{COH}(U_{cat}−E_{CO})/b}}{\Theta_{COH}(r)e^{\alpha_{COH}(U_{cat}−E_{CO})/b}} \right] \]  
\[ r_{Pt1}(r) = k_{Pt1} \left[ \frac{a_{H_2O} \Theta_{Pt}(r)e^{\alpha_{Pt}(U_{cat}−E_{Pt})/b}}{k_{reeq\alpha_{Pt}} \Theta_{PtOH}(r)e^{\alpha_{PtOH}(U_{cat}−E_{PtOH})/b}} \right] \]  
\[ r_{Pt2}(r) = k_{Pt2} \left[ \frac{\Theta_{PtOH}(r)e^{\alpha_{PtOH}(U_{cat}−E_{PtOH})/b}}{k_{reeq\alpha_{Pt}} \Theta_{PtOH}(r)e^{\alpha_{PtOH}(U_{cat}−E_{PtOH})/b}} \right] \]

with the \( R \) denoting the general gas constant. The temperature dependence of reaction rates is expressed implicitly in the Tafel slope, \( b = RT/F \), and also in the reaction rates \( k_r \), which also strongly depend on the temperature [12].

2.1.2 Carbon Corrosion Model

The surface oxidation affects the degradation of catalyst particles in two ways. Firstly, the unstable carbon surface group C−OH is the main initiator of the carbon corrosion, resulting in a reaction with either water (reaction C3) or Pt surface group Pt−OH (reaction PtC) via electrochemical reactions:

\[ C − OH + H_2O \rightarrow C * + CO_2 + 3H^+ + 3e^-; \quad E_{C3} = 0.96 \text{ V RHE} \]  
\[ Pt − OH + C − OH \rightarrow C * + Pt * + CO_2 + 2H^+ + 2e^-; \quad E_{PtC} = 0.62 \text{ V RHE} \]

with reaction rates:
\[ r_{PtC}(r) = k_{PtC} \Theta_{COH}(r) \Theta_{PiOH}(r) e^{2\tau_{Pt}(U_w - E_{PtC}(R))/b} \] (13)

\[ r_{C3}(r) = k_{C3} \Theta_{C(OH)}(r) e^{3\tau_{C}(U_w - E_{C3}(R))/b} \] (14)

The reaction rates in Eqs. (7)–(10), (13), and (14) are used to determine the temporal dynamics of the oxide coverage on the carbon and the Pt surface:

\[ \frac{d \Theta_{PiOH}(r)}{dt} = \frac{F}{\Gamma_{Pt}} [r_{Pt1}(r) - r_{Pt2}(r) - r_{PtC}(r)] \] (15)

\[ \frac{d \Theta_{PiOH}(r)}{dt} = \frac{F}{\Gamma_{Pt}} r_{Pt2}(r) \] (16)

\[ \frac{d \Theta_{C2}(r)}{dt} = \frac{F}{\Gamma_{C}} [r_{C1}(r) - r_{C2}(r) - r_{C3}(r) - r_{PtC}(r)] \] (17)

\[ \frac{d \Theta_{COH}(r)}{dt} = \frac{F}{\Gamma_{C}} r_{C2}(r) \] (18)

where \( \Gamma_{Pt} \) and \( \Gamma_{C} \) denote the surface density of the defect sites on the Pt and carbon surface, suitable for the formation of the oxide groups. The proportion of clean surface of Pt and carbon is calculated as \( \Theta_{Pt} = 1 - \Theta_{PiOH} - \Theta_{PiOH} \) and \( \Theta_C = 1 - \Theta_{C(OH)} - \Theta_{COH} \), respectively. Note that the carbon surface coverages refer only to the area around the attached Pt particle of roughly the same surface as that of the particle, which is most relevant for the catalyst degradation. This is argued, firstly by the assumption that most of the carbon corrosion occurs in this region because of the spillover of Pt oxide groups to carbon (reaction PtC in Eq. (12)), and secondly by the fact that only the carbon corrosion in the region surrounding Pt particles contributes to their detachment and further agglomeration.

2.1.3 Pt Detachment and Agglomeration Model

Since the carbon corrosion via pathway PtC occurs because of the interaction of carbon and Pt surface groups, it is most pronounced around the particles. This results in a reduced junction between the particle and its support, and eventually in a detachment of the particle, as schematically shown in Figure 1a. Note that the rate of corrosion (Eq. (13)) is determined by the production of oxides on both carbon and Pt surface (Eqs. (7) and (9)), which is affected by the Kelvin term (Eq. (5)), and is therefore size dependent. The proposed model further takes into account that because of the smaller contact area between the Pt particle and the carbon, smaller particles are more likely to detach, which is described by the term \( 1/r \).

The size distribution of the detached particles \( \frac{df_{N,det}(r,t)}{dt} \) is, therefore, related to current PSD \( f_N(r,t) \) as [12]

\[ \frac{df_{N,det}(r,t)}{dt} = k_{det} \frac{M_c}{\rho_C} \frac{r_{C3}(r) + r_{PtC}(r)}{r} f_N(r,t) \] (19)

Note that the rate of detachment is proportional to the additional factor \( k_{det} \), taking into account the microscopic properties of the boundary between Pt and carbon support. The resulting size-dependent particle detachment rate, proportional to the current PSD \( f_N(r,t) \), is used as the first term in the Smoluchowski equation (20), describing the particle size redistribution because of the agglomeration. The second term in Eq. (20) describes the loss of particles, with which the detached particles are merged, from PSD, assuming the probability for merging is independent of particle size. The third term describes the emergence of new particles formed by agglomeration under the assumption of a spherical shape of particles and the conservation of mass during their merging:

\[ \frac{df_{N,det}(r,t)}{dt} = \frac{df_{N,agg}(r,t)}{dt} - \frac{df_{N,det}(r,t)}{dt} \frac{f_N(r,t)}{N_0(t)} \]

\[ \int_{0}^{r} \left[ \frac{df_{N,agg}(r,t)}{dt} \right] dr + \frac{1}{N_0(t)} \int_{0}^{r} \left[ \frac{df_{N,det}(r,t)}{dt} \right] \left[ \frac{f_N(r,t)}{\sqrt{r^3 - r^3}} \right] dr \] (20)

The total number of particles is denoted as \( N_0(t) = \int_{0}^{r} f_N(r,t) dr \). A similar equation was used by Urchaga [29] to model the degradation of the catalyst layer. In his model, however, the detachment of particles was assumed to be independent of size, not taking into account the size dependence of carbon corrosion (Eq. (13)), and particle detachment (Eq. (19)).

2.1.4 Pt Dissolution and Ostwald Ripening Model

In the model of equilibrium Pt dissolution, based on the work of Darling [28] and later used by Urchaga [29], the Pt can only dissolve from the part of Pt surface not covered by

![Fig. 1 Schematic representation of the modeled particle growth mechanisms](image-url)
the oxides. The dissolution rate further depends on the size of the particle via Kelvin term $E_{\text{diss}}(r) = E_{\text{diss}} - \frac{1}{2} \sigma_{\text{PtMpt}}$, and the concentration of the dissolved Pt$^{2+}$ ions in the catalyst ionomer $c_{\text{Pt}^{2+}}$, resulting in a change of particle size:

$$\frac{dr}{dt}(r) = -k_{\text{diss}} \frac{M_{\text{Pt}}}{\rho_{\text{Pt}}} \left( e^{\frac{E_{\text{diss}}}{Rt}} - c_{\text{Pt}^{2+}} e^{\frac{E_{\text{diss}}}{Rt}} \right)$$

$$\Theta_{\text{Pt}}(r) = e^{\frac{E_{\text{diss}}}{Rt}}$$

(21)

This electrochemically driven dissolution process leads to the shrinkage of small particles and the growth of large particles [7, 29] (show schematically in Figure 1b), very similar to the one in case of classical diffusion driven Ostwald ripening [8]. The resulting particle size redistribution is calculated as [30]:

$$\frac{dN_{\text{aggl}}(r, t)}{dt} = -\frac{\partial}{\partial r} \left[ \frac{dr}{dt}(r) f_{\text{N}}(r, t) \right]$$

(22)

In addition to the equilibrium dissolution, described by Eq. (21), more complex mechanisms of Pt dissolution during voltage cycling have been reported in literature [31, 32], explained by the detachment of Pt surface oxide layer during the cathodic part of the voltage sweep. The mathematical model of this mechanism has recently been published [33]. However, since this mechanism causes a significant degradation of Pt catalyst only during the fast voltage cycling at high voltage, not typically encountered during HT-PEMFC operation, the mechanism was not considered in our model.

2.1.5 Mean Particle Size Growth

The combined effect of particle agglomeration (Eq. (20)) and Ostwald ripening (Eq. (22)) results in a total particle size redistribution, calculated as:

$$\frac{dN_{\text{tot}}(r, t)}{dt} = \frac{dN_{\text{aggl}}(r, t)}{dt} + \frac{dN_{\text{OR}}(r, t)}{dt}$$

(23)

In the present study, we aim at calculating the time profile of the growth of mean particle size $\langle r \rangle(t)$, calculated as

$$\langle r \rangle(t) = \frac{\int_0^\infty r f_N(r, t) dr}{N_0(t)}$$

(24)

where $f_N(r, t)$ is changing with time based on Eq. (23):

$$f_N(r, t) = f_N(r, 0) + \int_0^t \frac{dN_{\text{tot}}(r, t)}{dt} dt$$

(25)

For easier analysis of individual contributions of both particle growth processes, the change in mean particle size can be split to individual contributions:

$$\langle r \rangle(t) = \langle r \rangle_0 + \Delta \langle r \rangle_{\text{aggl}}(t) + \Delta \langle r \rangle_{\text{OR}}(t)$$

$$= r_0 + \int_0^t \Delta r_{\text{aggl}}(t) dt + \int_0^t \Delta r_{\text{OR}}(t) dt$$

(26)

with the time derivatives of Ostwald ripening and agglomeration contributions calculated from the contributions of each process to the particle redistribution $\frac{dN_{\text{aggl/OR}}(r, t)}{dt}$ from Eqs. (20) and (22):

$$\frac{dN_{\text{aggl/OR}}(r, t)}{dt} = \frac{1}{N_0(t)} \left[ \int_0^\infty \frac{dN_{\text{aggl/OR}}(r, t)}{dt} dr - \langle r \rangle(t) \int_0^\infty \frac{dN_{\text{aggl/OR}}(r, t)}{dt} dr \right]$$

(27)

For the case of Ostwald ripening, it was elaborated in [7] that the contribution takes the form of a root-function of time,

$$\langle r \rangle_0 + \Delta \langle r \rangle_{\text{OR}}(t) = \sqrt{\langle r \rangle_0^3 + Bt}$$

(28)

However, the effect of Pt oxide coverage was not taken into account in [7] and the given result most likely cannot be directly applied to the newly proposed model. For the case of particle agglomeration, no similar study stating the explicit time profile of the mean particle size growth could be found. This raises several questions: can contributions from Ostwald ripening and particle agglomeration be distinguished based solely on the growth of mean particle size of PSD? Can potential differences between both processes be exploited to identify the predominant degradation mode in a real fuel cell system? To answer these questions, the degradation model [12] was used to replicate the results of two degradation experiments on HT-PEMFC and analyze the resulting particle growth profiles. To reproduce the experimental measurements, however, the model first needs to be properly calibrated, as explained in the next section.

2.1.6 Model Calibration

The model contains a wide array of parameters, which need to be properly calibrated in order for the model to generate plausible results. Some of the parameters, such as material densities, molar masses and general physical constants, are well known and can be easily obtained from the literature, i.e., [26, 28, 34–36]. These parameters are listed in Table A1 in the Appendix A. The reaction rate parameters in Eqs. (7)–10), (13), (14), (19), and (21), on the other hand, are more difficult to determine. Their values differ between sources (e.g., [26, 27]), and are also known to strongly depend on the temperature (e.g., electrochemical reaction rate constants) and on the detailed material properties of catalyst components (e.g., particle detachment rate in Eq. (19)) [11, 12]. To properly determine the values of these parameters, the model was calibrated based on
the experimental data, found in literature. Two different experiments were used in the calibration.

In the experiment by Bandlamudi et al. [22], the accelerated stress test was performed by feeding the HT-PEMFC with synthetic air on the cathode and hydrogen on the anode side while keeping it at a constant potential of 0.9, 1.0, 1.1, and 1.2 V using an external potentiostat. The CO2 emissions were measured for a period of 30 min at each voltage, resulting in the time traces of CO2 concentrations $c_{CO2,exp}(t)$, shown as dashed line in Figure 2, with index $i$ denoting each of the four experiments. The process of using the HAN model to calculate the operation conditions and the degradation stimuli, used as an input of the degradation model, is described in [12]. The resulting modeled CO2 concentration time traces $c_{CO2,mod,i}(t)$ are calculated based on the carbon corrosion rates $r_C$ and the gas flow through the cathode channel. The chi-squared parameter $\chi^2_{PSD}$, related to PSD, was calculated by summing the square of differences between the measured and the modeled data, was determined by integrating over time and summing over all four experiments the square of difference between modeled and measured time traces:

$$\chi^2_{CO2} = \frac{\int \left( c_{CO2,exp}(t) - c_{CO2,mod,i}(t) \right)^2 dt}{c_{CO2,exp}(t)} (29)$$

The chi-squared parameter $\chi^2_{PSD}$ related to PSD, was calculated by comparing the experimentally measured and modeled PSD, resulting from the long-term degradation experiment on the HT-PEMFC, presented by Hangee et al. in [16]. In this experiment, two identical fuel cells were aged in their standard operating conditions, at temperature 160°C and current density 0.2 Am m^2 (relating to the fuel cell voltage $U = 0.6$ V), one for 2,700 h (MEA_t1) and one for 4,800 h (MEA_t2). After the tests, the cells were dismantled and the PSD in the catalyst layer was measured using TEM and compared with the fresh catalyst (MEA_t0). The measured PSD are shown as black lines in Figure 4. The PSD during the degradation was modeled using HAN generated inputs with discretized size of particles divided into $M = 30$ size classes with radius $r_i$ ranging from 0.25 to 7.25 nm. The value of $\chi^2_{PSD}$ was calculated by summing the square of differences between measured ($f_{N,exp}(r_i, t)$) and modeled ($f_{N,mod}(r_i, t)$) PSD over both degraded samples (t1, t2) and over all particle sizes ($r_i$):

$$\chi^2_{PSD} = \sum_{i=1}^{M} \sum_{t=1}^{T} \frac{f_{N,mod}(r_i, t) - f_{N,exp}(r_i, t)}{f_{N,exp}(r_i, t)} (30)$$

The total chi-squared value $\chi^2 = \chi^2_{CO2} + \chi^2_{PSD}$ was minimized by varying the values of 8 reaction rate constants $k_{Pt1}$, $k_{Pt2}$, $k_{C1}$, $k_{C2}$, $k_{PtC}$, $k_{dis}$, $k_{det}$, $k_{dis}$ (from Eqs. (7)–(10), (13), (14), (19), and (21)) using a combination of a differential evolution minimization method [37] to identify the global minimum in parameter space and Nelder-Mead minimisation [38] to refine the solution.

### 3 Results and Discussion

#### 3.1 Calibrated Parameters

The best-fit values of the calibration parameters, calculated as described in Section 2.6, are listed in Table 1. The reliability of the calibrated parameters was determined by numerical calculation of the sensitivity of $\chi^2$ to the change of parameters $k_i$, $\alpha_k = \frac{1}{2} \frac{\partial^2 \chi^2}{\partial k_i^2}$, with the relative error of the parameter being $k_i / \alpha_k$. Most of the parameters were determined with reasonably small errors below 10%, with the exception being the reaction rates $k_{Pt2}$ and $k_{C2}$, for which only the lower limit could be determined. The increase of these two parameters does not significantly change the modeled results and the value $\chi^2$. This can be explained by the fact that all hydroxyl surface groups on Pt and carbon are consumed by the corrosion reactions C3 and PtC before they could be transformed into stable oxide surface groups by the reactions C2 (Eq. (2)) and Pt2 (Eq. (4)), making the exact values of the parameters $k_{Pt2}$ and $k_{C2}$ less relevant in the process of carbon corrosion and particle growth.

Table 1. Calibrated values of reaction rate constants.

| Parameter | Calibrated value |
|-----------|-----------------|
| $k_{Pt1}$ | $4.7 \times 10^{-4} \pm 0.1 \text{ mol m}^{-2} \text{s}^{-1}$ |
| $k_{Pt2}$ | $1.6 \times 10^{-4} \text{ mol m}^{-2} \text{s}^{-1}$ |
| $k_{C1}$  | $1.6 \times 10^{-1} \pm 0.02 \text{ mol m}^{-2} \text{s}^{-1}$ |
| $k_{C2}$  | $1.6 \times 10^{-1} \text{ mol m}^{-2} \text{s}^{-1}$ |
| $k_{PtC}$ | $1.17 \times 10^{-3} \pm 0.08 \text{ mol m}^{-2} \text{s}^{-1}$ |
| $k_{dis}$ | $9.3 \times 10^{-3} \pm 0.02 \text{ mol m}^{-2} \text{s}^{-1}$ |
| $k_{det}$ | $3.4 \times 10^{-3} \pm 0.08 \text{ mol m}^{-2} \text{s}^{-1}$ |
| $k_{dis}$ | $2.13 \times 10^{-3} \pm 0.03 \text{ mol m}^{-2} \text{s}^{-1}$ |

![Fig. 2](image-url) Experimentally measured (dashed line) and modeled (solid line) time traces of CO2 emissions during stress test of the HT-PEMFC at voltages 0.9 V (orange), 1.0 V (green), 1.1 V (red), and 1.2 V (black). The significant decrease of CO2 emissions during the high voltage test ($U = 1.2$ V) is caused by the particle size growth, resulting in a decreasing rate of carbon corrosion via reaction PtC.
3.2 Carbon Dioxide Emissions

The modeled CO₂ emissions, calculated using the best-fit calibration parameters, are shown as solid lines in Figure 2, alongside dashed line representing the experimental data. Good agreement between both sets of data indicates the successful calibrating procedure and the capability of the degradation model to properly describe the corrosion of carbon support in the catalyst layer. The results of the degradation model also provide additional insight into the underlying processes, causing different time dependences of CO₂ emissions at different voltages, especially a significant decline of CO₂ emissions during the test at $U = 1.2$ V. According to the model, the reason for the decline lays in the increase in Pt particle size during the test, resulting in slower production of OH surface groups on Pt surface (see Eqs. (5) and (9)) and consequently a slower rate of reaction PtC (Eq. (12)). At lower voltages, the degradation is much slower, leading to only a small decrease in CO₂ emissions during the 30-minutes test. The validity of this explanation is confirmed by a similar increase in mean particle size during degradation tests, predicted by the degradation model, $\Delta \bar{r}_{\text{mod}} = 1.40 \text{nm}$, to the one reported by Bandlamudi [22], $\Delta \bar{r}_{\text{exp}} = 1.45 \text{nm}$. These results clearly indicate the importance of coupled degradation modeling, comprising several individual mechanisms from the surface oxidation to the particle growth, in explaining the results of degradation experiments on the HT-PEMFC.

3.3 Particle Size Redistribution

The particle growth in the catalyst layer is even more significant in the case of long-term degradation, observed by Hangee et al. [16]. Due to the well measured PSD after different stages of degradation, this system was used as the basis for our model analysis of the time profile of the mean particle size in the catalyst layer. The comparison between measured (black) and modeled (orange) PSD, using the model with best-fit calibration parameters, listed in Table 1, is shown in Figure 4. Good matching between both sets of data indicates that the particle size distribution processes in the degradation model are properly described. Furthermore, the relatively low fitting error of parameters $k_{\text{dis}}$ and $k_{\text{det}}$ (see Table 1) suggests that the processes of Ostwald ripening and particle agglomeration are well distinguishable by the model, and that significantly different PSD is to be expected if different sets of parameters are used.

To provide a further insight into the process of particle growth, the parameters $k_{\text{dis}}$ and $k_{\text{det}}$, controlling the relative contributions of both growth mechanisms, were recalibrated using the following procedure. The value of $k_{\text{det}} = k_{\text{det,fit}}$ was set to a constant value, determined by the parameter $k_{\text{det}}$ taking values between 0 and 1, where $k_{\text{det,fit}}$ is the best-fit value from Table 1. Using this constant rate of particle detachment and agglomeration, only the parameter $k_{\text{dis}}$, controlling the rate of Ostwald ripening was adjusted to minimize the value of $\chi^2_{\text{PSD}}$, while keeping the other parameters intact. This procedure results in a controlled ratio between contributions of both mechanisms, allowing for a clearer distinction between both effects.

The plot of the best-fit value of calibration parameter $k_{\text{dis}}$ obtained by the procedure explained above, and the corresponding $\chi^2_{\text{PSD}}$ as a function of fixed $k_{\text{det}}$ is shown in Figure 3. Increasing the detachment parameter $k_{\text{dis}}$ results in a decrease of the best-fit value of $k_{\text{dis}}$, which can be easily explained by the interplay of both particle growth mechanisms. When agglomeration gets more prominent with the increase of $k_{\text{det}}$, the contribution of Ostwald ripening decreases to preserve the total net growth effect of both processes. What is more interesting is that the minimal value of $\chi^2_{\text{PSD}}$ corresponding to the best overall fit, reaches its minimum only when the dissolution rate $k_{\text{dis}}$ drops to practically zero. This indicates that in the studied degradation experiment [16], the catalyst degradation is to a large degree caused by the particle agglomeration, initiated by the carbon corrosion.

This conclusion was tested by the standard procedure of analyzing the shape of the PSD to determine the primary source of particle growth. In case of particle agglomeration, a small number of large particles forms relatively fast, which leads to a formation of PSD with long “tail” towards the large-particle side (i.e., significantly with positive skewness) [20]. In case of Ostwald ripening, on the other hand, a fast dissolution of small particles and relatively slow redeposition of Pt on large particles results in large particles being significantly more numerous than small particles. Therefore, the resulting PSD has a “tail” towards the small-particle side and negative skewness [20]. The analysis of the shape of PSD after the catalyst degradation therefore enables one to determine the main mechanism of particle growth. The skewness of the measured PSD was quantitatively determined, using the expression [7]

$$\lambda = \frac{\langle (r - \bar{r})^3 \rangle}{\sigma^3}$$

(31)

![Graph](image)

Fig. 3 The results of the fitting of parameter $k_{\text{dis}}$ at fixed value of $k_{\text{det}}$. The decrease in best fitted value $k_{\text{dis}}$ (blue) with increased $k_{\text{det}}$ indicates the interplay between the processes of Ostwald ripening and particle agglomeration in describing the particle growth. The minimal value of $\chi^2_{\text{PSD}}$ is achieved only when the value of $k_{\text{dis}}$ drops nearly to zero, indicating the process of particle agglomeration being mostly responsible for the particle growth in the studied experiment [16].
where $\mu$ denotes a mean value and $\sigma$ is the standard deviation of PSD. The negative value of skewness $\lambda$ indicates that particle growth is caused by Ostwald ripening, while the positive value is an indicator of particle agglomeration. The values $\lambda$ for the PSD of fresh and both aged samples of catalyst from the experiment by Hengge et al. [16] are positive, being 1.16, 0.69, and 0.46, respectively. This result was compared to the values obtained from the analysis of PSD, measured during a 520 h long term degradation test of HT-PEMFC with non-humidified hydrogen and oxygen as inlet gases, at temperature of 150 °C and a current density of 700 mA cm–2, presented by Zhai et al. [17]. In this experiment the particle agglomeration was identified as the main mechanism of catalyst degradation. The values $\lambda$ for PSD, measured on fresh sample and aged samples after 100, 300, and 520 h of degradation, are 0.6, 0.51, 0.73, and 0.47, respectively, comparable to the values of PSD used in the calibration of our model. From this we can deduce that in the long-term degradation experiment, reproduced by our model, the particle growth is also caused mostly by the particle agglomeration, as correctly discerned from the results of the degradation model calibration.

### 3.4 Mean Particle Size Growth Analysis

The distinction between both particle growth mechanisms is further highlighted in Figure 4 by plotting two additional PSD, obtained from the degradation model using the best-fit value of calibration parameter $k_{\text{det}}$ at fixed $k_{\text{det}}$ corresponding to $K_{\text{det}} = 0$ (green line, pure Ostwald ripening) and $K_{\text{det}} = 0.5$ (purple line, combination of Ostwald ripening and particle agglomeration). The modeled PSD in Figure 4 show a narrower distribution in the case of more prominent particle agglomeration (larger values of $k_{\text{det}}$), which more closely resembles the measured PSD from [16]. What is even more interesting is that for more prominent Ostwald ripening (smaller values of $k_{\text{det}}$), the separation between the peaks of the PSD of aged samples MEA_t1 and MEA_t2 seems to be smaller than expected from the experiments. This leads to a conclusion that the relative increase in the particle size between measured samples is affected by the relative contributions of either Ostwald ripening or particle agglomeration towards the overall particle growth.

This revelation was further explored by a closer look into how the mean size of particles in the modeled PSD changes with time. The results are plotted in Figure 5 for three values of $K_{\text{det}} = [0,0.5,1]$, which are the same as those used in Figure 4. As we can see from the black dashed line in Figure 5, the mean particle size, determined from the experiment by Hengge et al. [16], increases almost linearly with time. The modeled growth of particles in the case when the Ostwald ripening is the only growth mechanism ($k_{\text{det}} = 0$ $k_{\text{det},\text{fit}}$, red line in Figure 5a), on the other hand, shows a root-function dependence. This is an expected result, compatible with theoretical studies on the Ostwald ripening [7], but such a time profile of the mean particle size is distinctly different from the one obtained in the experiment (black dashed line and dots in Figure 5a). In Figure 5b ($k_{\text{det}} = 0.5$ $k_{\text{det},\text{fit}}$), where contributions of both the Ostwald ripening (green line, $r_0 + \Delta r_{\text{Ost}} (t)$, calculated based on Eqs. (26) and (27)) and the particle agglomeration (orange, $r_0 + \Delta r_{\text{agg}} (t)$, calculated based on Eqs. (26) and (27)) are present, the modeled growth more closely resembles the measured results, but still shows a significant root-function dependence. The modeled result using the best calibration parameters is shown in Figure 5c ($k_{\text{det}} = k_{\text{det},\text{test}}$). It clearly indicates that the modeled growth is practically linear, aligning perfectly with the experimental results, and the Ostwald ripening is negligible.

Several conclusions can be drawn from this observation. Firstly, we see that the Ostwald ripening, as implemented in the degradation model, results in a root-function dependence of mean particle size growth with time, predicted both theoretically [7] and experimentally [39, 40]. The shape of the modeled time profiles $\langle r \rangle (t)$ is analyzed using a test fitting function, similar to Eq. (28), with the root-order $p$ being a variable fitting parameter:

$$r_p(t) = \left( r_0^p + a t \right)^{1/p}$$  \hspace{1cm} (32)  

Fitting of function (Eq. (32)) to the modeled $\langle r \rangle (t)$ for the case when only Ostwald ripening contributes to the particle growth (red line in Figure 5a), $k_{\text{det}} = 0$ results in the best-fit parameter being $p_f = 4.6$, comparable to $p = 3$, predicted in theoretical studies of Ostwald ripening [7]. The difference is most probably caused by the inclusion of Pt surface oxide coverage effects in Eq. (21), not taken into account in [7,8]. Furthermore, a clear distinction between the contribution of Ostwald ripening and particle agglomeration can be seen from the shape of particle growth profiles in Figure 5. In contrast to Ostwald ripening, the growth because of agglomeration (orange) dis-
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...the particle growth profile because of the Ostwald ripening and the particle agglomeration indicates the possibility of using the fitted value of $p$ in the test function (Eq. (32)) as an indicator to distinguish between the contribution of both processes.

### 3.5 Identification of Particle Growth Mechanism based on the Fitting Function

Our newly proposed analytic method for catalyst degradation analysis is performed by fitting the test function (Eq. (32)) to the experimentally measured time trace of mean size of particles in the fuel cell catalyst layer during degradation. As explained in previous sections, significantly different time profile is expected for different particle growth mechanisms, resulting in different values of best fitted value of parameter $p$ in test function (Eq. (32)), which can therefore be used to identify the prevalent degradation mode.

To calibrate the method, the test function (Eq. (32)) was fitted to the modeled particle size growth profile at several values of $k_{\text{det}}$ between 0 and $k_{\text{det,fit}}$, with the corresponding calibrated parameter $k_{\text{dis}}$ shown in Figure 3. The best-fit values of $p$ are plotted in Figure 6 as a function of the relative contributions of the Ostwald ripening to the overall increase in the particle size at the end of the experiment at time $t_2$ from [16], calculated from Eqs. (26) and (27) as

$$X_{\text{OR}} = \frac{\Delta(r)_{\text{OR}}(t_2)}{\Delta(r)_{\text{OR}}(t_2) + \Delta(r)_{\text{agg}}(t_2)}$$

(33)

The plot shows a steady increase of $p$ with the ratio $X_{\text{OR}}$, with value $p = 1.13$ at $X_{\text{OR}} = 0$, and $p = 4.5$ at $X_{\text{OR}} = 1$. The monotonicity of $p$ as a function of $X_{\text{OR}}$ indicates that the fitted $p$ value could indeed be used as a qualitative indicator capable of distinguishing the relative importance of individual particle growth mechanisms, with higher values indicating the prominence of Ostwald ripening and values close to 1 indicating the importance of particle agglomeration.
The applicability of this identification test lies in a fact that it relies solely on the fitting of a relatively simple analytic function (Eq. (32)) and does not require a complex degradation modeling framework, as used in this paper for the development and validation of the proposed analytic method. The mean particle size, in the present study calculated from the full PSD, can also be obtained by several other, much simpler methods, for example calculated from the ESA, measured by cyclic voltammetry [17]:

\[
\langle r \rangle_{ESA} = \frac{p_{fit}}{3ESA}
\]

(34)

To test the proposed method, the values of ESA, measured every few hours during the long-term degradation test by Zhai et al. [17] (already presented in Section 3.3) were used to first calculate the time trace of mean particle size \( \langle r \rangle_{ESA} (t) \) and then the test function (Eq. (32)) was fitted to the data. The result of this procedure is shown in Figure 7, with the values of \( \langle r \rangle_{ESA} \) shown in red and the best fitted test function shown in dashed black. Although the time trace of mean particle size \( \langle r \rangle_{ESA} \) does not display particularly linear or root-like behavior, the best-fit value of \( p_{fit} = 1.3 \) suggest the prevalence of the particle agglomeration as the main mechanism of catalyst degradation. This result agrees with the analysis done by Zhai et al., who also claim that particle agglomeration is responsible for the particle growth [17], thus confirming the applicability of the proposed testing procedure.

Due to absence of published data, the method could not be further tested on the experimental data from HT-PEMFC degradation for which the Ostwald ripening would be identified as the main degradation mechanism. Among several studies on catalyst degradation in the HT-PEMFC [41–44], reported in a recent review paper by Araya et al. [45], none report the Ostwald ripening as being a significant factor in the catalyst particle growth. To further validate the proposed analytic method, the degradation model will need to be additionally tested on the data from the LT-PEMFC systems, where the Ostwald ripening might be more pronounced compared to the particle agglomeration [46].

4 Conclusion

In the present study we used a recently developed coupled fuel cell operation and catalyst degradation model to analyze the individual contributions of Ostwald ripening and particle agglomeration to the overall growth of particles in the fuel cell catalyst layer during its degradation. The model was calibrated based on the results of two degradation experiments on high temperature polymer electrolyte membrane fuel cell, measuring CO₂ emissions because of the corrosion of the carbon support [22], and particle size redistribution during a 4,800 h long-term degradation of a commercial fuel cell [16]. The ability of the model to simultaneously reproduce the results of two distinct experiment using the same parameters confirms the plausibility of the modeling approach used in the study.

The results of the model show a significantly different profile of particle size growth depending on the predominant degradation regime. The Ostwald ripening regime induces a typical root-function dependence, known from the established literature [7, 8], confirming the validity of the model. The linear growth of mean particle size, observed in the particle agglomeration regime, on the other hand, could not be found in literature and represents a new insight into the mechanism of the catalyst degradation. Based on these significant differences in the time-dependence of mean particle size, a new identification method was developed and tested based on the fitting of a root function on the experimental data, using the best-fit root order as an indicator of predominant degradation mechanism. The proposed method might be of great use especially in cases where the size distribution of particles in the catalyst, traditionally used to determine the main degradation mechanism, is not known, while the mean particle size can still be determined \( \text{via} \), i.e., cyclic voltammetry experiment [17].

The proposed analytical method identifies a carbon corrosion induced particle agglomeration as a predominant mode of catalyst degradation in long-term HT-PEMFC degradation test, used in model calibration [16], which is in line with the established knowledge on HT-PEMFC degradation, suggesting that the carbon corrosion is the main initiator of degradation processes in catalyst layer [13]. The use of the proposed method was also tested on the time trace of mean particle size, calculated from the cyclic voltammetry data. The result, suggesting the particle agglomeration as the main degradation mechanism, is in agreement with the analysis of the data in the original paper [17]. However, further testing of the proposed method is planned for the future to establish its reliability, aimed at the analysis of the long term fuel cell degradation test in various controlled operating conditions, known to initiate either more Ostwald ripening or more particle agglomeration.
If proved successful, the proposed novel method for the identification of the catalyst degradation mechanism could represent an important step in the analysis of fuel cell degradation, and in the future development of more efficient mitigation strategies.

The result of the proposed method agrees with the explanation of the catalyst degradation provided by the authors in [17], identifying the particle agglomeration as the predominant particle growth mechanism in the HT-PEMFC degradation experiment analyzed. Since no experimental data, identifying the Ostwald ripening as the main degradation process in HT-PEMFC, could be found in the established literature [45], further testing of the method is proposed on the LT-PEMFC systems, where both processes contribute more equally to the overall catalyst particle growth method [46].

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Appendix A: Degradation Model Parameters

The values of various degradation model parameters, such as material densities, surface tensions and molar masses, obtained from the literature, are listed in Table A1, alongside with the source from which the value was taken.

Table A1: List of model parameters obtained from the literature.

| Parameter | Value | Units | Description | Source |
|-----------|-------|-------|-------------|--------|
| $\rho_{\text{Pt}}$ | 21,090 | kg m$^{-3}$ | Pt density | [34] |
| $\rho_{\text{PtOH}}$ | 14,170 | kg m$^{-3}$ | Pt–OH density | Calc. from [34] |
| $\rho_{\text{PtO}}$ | 14,100 | kg m$^{-3}$ | Pt=O density | [34] |
| $\rho_{\text{C}}$ | 2,000 | kg m$^{-3}$ | Carbon support density | – |
| $\sigma_{\text{Pt}}$ | 2.73 | J m$^{-2}$ | Pt surface tension | [34] |
| $\sigma_{\text{PtOH}}$ | 1.34 | J m$^{-2}$ | Pt–OH surface tension | Calc. from [34] |
| $\sigma_{\text{PtO}}$ | 1 | J m$^{-2}$ | Pt=O surface tension | [34] |
| $M_{\text{Pt}}$ | 0.195 | kg mol$^{-1}$ | Pt molar mass | [34] |
| $M_{\text{PtOH}}$ | 0.212 | kg mol$^{-1}$ | Pt–OH molar mass | Calc. from [34] |
| $M_{\text{PtO}}$ | 0.211 | kg mol$^{-1}$ | Pt=O molar mass | [34] |
| $M_{\text{C}}$ | 0.012 | kg mol$^{-1}$ | Carbon molar mass | – |
| $M_{\text{H}_{2}O}$ | 0.018 | kg mol$^{-1}$ | Water molar mass | – |
| $r_{\text{Ox}}$ | 30,000 | J mol$^{-1}$ | Pt oxide interaction | [34] |
| $k_{\text{rev}}$ | 0.3 | – | Pt oxidation reversibility | [28] |
| $\Gamma_{\text{Pt}}$ | 2.15 | As m$^{-2}$ | Pt surface site density | [34] |
| $\Gamma_{\text{C}}$ | 4.6 | As m$^{-2}$ | Carbon surface site density | [35, 36] |
| $C_{\text{Pt}^{2+}, \text{ref}}$ | 1,000 | mol m$^{-3}$ | Reference Pt$^{2+}$ concentration | [34] |

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