

# Fast and Reliable State-of-Health Model of a PEM Cathode Catalyst Layer

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Long-term stability of polymer electrolyte membrane fuel cells under dynamic operation still has a high potential for optimization, specifically for use in the automotive industry. This stability is especially affected by the degradation processes taking place in the cathode catalyst layer and hence should be fully understood. In this work, we develop a fast and reliable state-of-health model of the cathode catalyst layer, incorporating the electrochemical degradation processes related to anodic and cathodic platinum dissolution, oxidation, Pt loss due to ion diffusion, carbon corrosion and place exchange mechanisms as well as their interaction. For the purpose of validation, the model is developed alongside a comprehensive experimental data set. A detailed parameter study taking into account temperature, relative humidity and load profile dependency was carried out. A good agreement between model and experiment was found for load ranges between 0.6 and 0.95 V. Further, good approximation of the active surface area loss for cell temperatures between 60°C and 90°C and relative humidity between 30% and 100% were achieved.

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Polymer electrolyte membrane (PEM) fuel cells are increasingly regarded as the alternative for combustion engines in the transportation sector. Their successful market introduction depends on their reliability in terms of lifetime and operation under various conditions. One of the main contributors to power loss over the lifetime of these cells is the loss of the electrochemically active electrode surface (ECSA) of the cathode catalyst layer. The catalyst layer typically consists of agglomerates of Pt nanoparticles on a carbon support, encased by a PFSA ionomer.

If the PEM fuel cell is used in vehicles, it must be able to withstand thousands of operating hours under changing load conditions. The cathode potential can range between 0.6 and 0.95 V, with the potential even rising temporarily above 1.35 V during startup and shutdown of the vehicles.<sup>1</sup> Under such conditions, platinum displays an electrochemically unstable behavior, resulting in what is commonly known as Pt dissolution. With increasing potential,  $Pt^{2+}$  ions dissolve from the cathode catalyst layer into the electrolyte, and from there can diffuse into the membrane, preventing a possible re-deposition. If the potential continues to rise, degradation of the carbon catalyst support occurs, namely known as carbon corrosion. Parallel to these two degradation mechanisms, the oxidation of Pt can also take place. The dissolution and oxidation of Pt are commonly assumed to follow Reactions 1–3.

$$Pt \leftrightarrow Pt^{2+} + 2e^{-} \quad \phi_{eq,a,Diss}^{ref} = 1.19 V$$
<sup>[1]</sup>

$$Pt + H_2O \leftrightarrow PtO + 2H^+ + 2e^- \quad \phi_{ea,Ox}^{ref} = 0.98V$$
<sup>[2]</sup>

$$PtO + 2H^+ \leftrightarrow Pt^{2+} + H_2O$$
[3]

The direction in which the reactions take place depends on the applied potential  $\phi$  and the respective equilibrium potential  $\phi_x^{ref}$  of the reaction. At low potentials in the range of 0.27–0.85 V, H<sub>2</sub>O molecules initially adsorb on the Pt surface. Once the potential is in the range of 0.85–1.15 V, half a monolayer of H<sub>2</sub>O is discharged, leaving half a monolayer of PtO (Fig. 1a). At potentials larger than 1.15 V, further discharge of H<sub>2</sub>O molecules occurs and chemisorbed oxygen completely covers the catalyst site.<sup>2</sup> The oxidized Pt atoms can no longer

dissolve according to Reaction 1, hence, Pt oxide actively counteracts catalyst degradation. Nevertheless, various experiments show that even with long holding time on increased potential in a cyclic stress, Pt dissolution takes place.<sup>3</sup>

Since protective PtO can form parallel to the dissolution of Pt, anodic Pt dissolution becomes inhibited after a short polarization time at a given high potential and can finally completely stop. The mechanism of Pt dissolution as a degradation process has been extensively examined in various publications.<sup>2–6</sup>

The loss of the active surface area of the catalyst layer due to Pt dissolution is mainly associated with a change in the catalyst layer particle size distribution. Shao-Horn et al. described this change to occur mainly due to Pt grain migration on the carbon support, Pt dissolution and the reappearance on larger particles (Ostwald ripening), Pt dissolution and removal into the membrane and the detachment of Pt particles due to carbon corrosion.<sup>7</sup>

The electrochemical Ostwald ripening (Fig. 1e) is defined by the dissolution and re-deposition of  $Pt^{2+}$  ions. If there is a potential at which Pt dissolution occurs, then smaller particles dissolve faster than larger particles, due to their higher chemical potential.<sup>8,9</sup> The dissolved  $Pt^{2+}$  ions can re-deposit in the case of a reduced potential, preferably onto larger particles.<sup>2</sup> The accelerated dissolution with smaller particles leads to permanent particle growth and an increase in the mean particle size. This enlargement of the particle volume leads to a reduction of the ECSA, since the surface to volume ratio decreases with  $\frac{1}{r}$ . Various studies, therefore, hypothesize that Ostwald ripening is the driving process for particle growth in high potential ranges.<sup>10</sup> Dissolved Pt can also diffuse into the membrane and result in an irreversible degradation of the catalyst layer as it can no longer participate in the reaction (Fig. 1f).

Further, dissolution of Pt can occur via the so-called placeexchange mechanism<sup>4</sup> (Fig. 1b) as described by Equations 4 and 5. During the anodic Pt dissolution described in Equation 1, as the potential rises above the equilibrium potential, an oxide layer on the catalyst forms and the anodic Pt dissolution diminishes. Further increase in the potential or holding the potential constant for a sufficient time leads the adsorbed O-atoms to undergo a place exchange from surface to sub-surface positions, exposing the Pt atoms once again. At this point, new oxides can adsorb on top of the exposed platinum. As this process of place exchange continues, the oxides begin to build deeper into the platinum lattice.<sup>4</sup> A subsequent cathodic potential sweep will now not only reduce the formed oxides, but additionally lead to a

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**Figure 1.** Pt degradation mechanisms considered in the model: (a) Pt oxidation and PtO surface coverage; (b) Place exchange between Pt lattice and adsorbed O atoms; (c) Oxide reduction and cathodic dissolution of exchanged Pt; (d) Carbon corrosion; (e) Electrochemical Ostwald-Ripening; (f) Pt<sup>2+</sup> ion dissolution into the membrane.

cathodic dissolution of the exchanged platinum (Fig. 1c) as described in Equation 5.

$$PtO \leftrightarrow O - Pt$$
 [4]

$$O - Pt + 2H^+ \leftrightarrow H_2O + Pt^{2+}$$
<sup>[5]</sup>

Carbon corrosion is also a major degradation mechanism of the catalyst layer where the carbon support is electrochemically dissolved (Fig. 1d). A loss of the carbon leads to an electrical insulation and further loss of the platinum catalyst.<sup>2</sup> In aqueous solutions, the dissolution follows<sup>11</sup>:

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad \phi_{eq,CC}^{ref} = 0.207 V$$
 [6]

With especially short jumps to higher potentials, such as in the start-stop operation of a vehicle, carbon corrosion is known to occur on a larger scale. Further, it cannot be ruled out that even the long term operation at lower potential damages the carbon support.<sup>2</sup> Aside from the potential at which the cell is run, the operating temperature and the gas relative humidity can also have a significant influence on the degradation rate of the catalyst layer. The effects of operating parameters have been extensively investigated experimentally in literature.<sup>12–19</sup>

Modeling has also been used to further our understanding of degradation within the catalyst layer and its overall effects on the cell lifetime and performance. Rinaldo et al.<sup>20</sup> developed a model to de-convolute Pt migration mechanisms contributing to ECSA loss. The model comprised Pt dissolution/re-deposition, detachment and coagulation based on the radius-scaled Smoluchowski particle size evolution.<sup>21</sup> Modeling the latter process makes the model rather time-expensive. The loss of Pt surface area including both Pt dissolution/precipitation and oxide formation and removal was modelled by Holby et al.<sup>22</sup> This work is pioneering in that an oxide model was validated against the behavior of multiple sets of cyclic voltammetry data with varying upper potential limit. Li et al.<sup>23</sup> used a one-dimensional model to investigate Pt degradation across the cathode catalyst layer to elucidate the influence of  $H_2/N_2$  vs. H<sub>2</sub>/Air on Pt degradation. Young et al.<sup>24</sup> introduced a semi-empirical model of carbon corrosion that was used to fit reaction rate constants and specific capacitances of carbon and platinum. Although much work is found in literature focusing on modeling degradation in the catalyst layer, these studies usually focus on one type of degradation mechanism and are computationally expensive.

Degradation of the catalyst layer due to catalyst and support degradation is a complex and significant problem in determining the lifetime of the fuel cell. Comprehensive understanding of the underlying mechanisms is crucial to design the cell and its control mechanism. In this work, we develop a model to predict the state of health of the PEM fuel cell based on the degradation of the cathode catalyst layer. The motivation is to build a model with a reduced complexity/weak coupling, which can still describe the measured data in a specific operating regime. Thus, non-dominating processes are omitted and modelled as lumped functions. The model accounts for Ostwald ripening, Pt loss into the membrane, carbon corrosion and for the first time (as per the authors' knowledge) place-exchange mechanism without compromising the capability of simulating hours of fuel cell operation in "real" time or even faster. The model is, hence, fast, reliable and flexible in various operating ranges and describes the dominating degradation processes in the catalyst layer. In the next sections, we describe this model and validate it against measured and published experimental data.

## **Model Description**

The aim of the model proposed in this work is to mathematically describe the state of health (SoH) of the catalyst layer as a function of the potential to which the cathode catalyst layer is exposed. Specifically, we aim to introduce a model that can be used as a tool for fast prediction of the health of the catalyst layer based on limited computational performance resources. Hence, structural changes in the ionomer and the gas diffusion layer are not considered, but rather the SoH is characterized only by the change in the electrochemical active surface area of the cathode catalyst layer. The main assumption on which the model is based is that the ECSA is directly coupled to the particle size distribution (PSD) of the platinum catalyst and its change in size is the driving mechanism of the degradation. Due to calculation limitation, a zero-dimensional model with constant time discretization, based on the on-board data acquisition rate capability, was developed, as opposed to a multi-dimensional model with highly coupled equations.

The electrode configuration is represented as a finite number of particle groups, categorized by particle radius and corresponding particle amounts. All particles of one group undergo the same transition, either they shrink or they grow. Since no coalescence between differently sized particles is considered, particles neither change into another group nor are new groups generated, which allows a separate simulation of the radius evolution of each particle group. Hence, this also allows for parallelization and therefore significant speed-up of calculations. This approach is valid as long as coalescence has a negligible impact on degradation. Literature data show that this is the case for the AST protocols we use for the model validation, where Ostwald ripening and support corrosion are dominant.

The catalyst degradation is modelled in terms of the reaction rates of the corresponding platinum morphology change. The reaction pathways considered in this work are described in Equations 1-6.

To describe the rates of each of the electrochemical reactions, a variation of the Butler-Volmer equation is used, which was first established by Darling and Meyers.<sup>6</sup>

The applied electrode potential  $\phi^n$  at time  $t_n$  is the driving force for the degradation processes. Whether a Pt particle of the particle radius group "i" dissolves, grows or is protected by an oxide layer depends on the conditions and state variables of the system such as oxide surface coverage  $\theta_{PtO}^{i,n}$  and Pt ion concentration  $c_{Pt2+}^n$  in the electrolyte, in which the first is a function of particle size (indicated by radius group "i") and the seconds act as a Pt reservoir for re-deposition to all particle sizes.

From now on, the model equations are written in terms of the raised index "i" to indicate the currently observed particle radius group, and the raised index "n" to indicate the corresponding time  $t_n$ , which is only noted when it deviates from the current time step. For the reaction rate of Pt dissolution, the following equation is applied:

$$R_{a.Diss}^{i} = k_{a.Diss} \theta_{vac}^{i,n-1} \left[ \exp\left(\frac{\alpha_{a,a.Diss} n_{a.Diss} F}{R T} \left(\phi - \phi_{eq,a.Diss}^{i}\right)\right) - \left(\frac{c_{p_{t}^{2+}}^{n-1}}{c_{p_{t}^{2+}}^{ref}}\right) \exp\left(-\frac{\alpha_{c,a.Diss} n_{a.Diss} F}{R T} \left(\phi - \phi_{eq,a.Diss}^{i}\right)\right) \right]$$

$$\left[ 71 \right]$$

Equation 7 consists of anodic and cathodic exponential terms, where the anodic term describes the dissolution of Pt and the cathodic term defines the re-deposition of dissolved Pt<sup>2+</sup> ions depending on the overpotential of this reaction. In addition to the electrode potential  $\phi$  and equilibrium potential  $\phi_{eq,a.Diss}$ , the reaction direction (forward/backward) also depends on the concentration of dissolved Pt,  $c_{Pt^{2+}}$  and the parameter  $\theta_{vac}$  describing the vacant part of the catalyst surface area, which is not covered with oxides. Hence, for instance, if there is no dissolved  $Pt^{2+}$  in the electrolyte, the anodic term will always dominate the reaction, leading to dissolution independent of the electrode potential. The parameter  $\theta_{vac}^{i,n-1}$ , can be described by:

$$\theta_{vac}^{i,n-1} = 1 - \theta_{PtO}^{i,n-1}$$
[8]

where  $\theta_{PtO}^{i,n-1}$  is the PtO surface coverage in which 0 means no coverage, and 1 a full monolayer. Since Pt dissolution is promoted by a higher humidification of the electrode,<sup>12</sup> we assume a correlation between the reaction constant  $k_{a.Diss}$  and the relative gas humidity RH, described by a simple power law:

$$k_{a.Diss} = k_{a.Diss}^{ref} \left(\frac{\text{RH}}{\text{RH}_0}\right)^{\text{v}}$$
[9]

The stated values for the equilibrium potential of the Pt dissolution reaction are valid only for bulk Pt material. Since the catalyst is present in the form of nanoparticles, the equilibrium potential needs to be adapted for the spherical structure. To this end, a Gibbs-Thompson correction is used, which describes the correlation between particle radius and the surface energy of a curved surface.

$$\phi^{i}_{eq,a.Diss} = \phi^{ref}_{eq,a.Diss} - \frac{\Delta \mu^{i}_{Pt}}{2F}$$
[10]

$$\Delta \mu_{P_t}^i = \frac{\sigma_{P_t} M_{P_t}}{r_{P_t}^{i,n-1} \rho_{P_t}}$$
[11]

The parameter  $\phi_{eq,a.Diss}^{ref}$  defines the equilibrium potential of the reaction of the Pt bulk material, while  $\Delta \mu_{Pt}^{i}$  describes the effect of particle surface tension on the equilibrium potential. With increasing particle radius, the shift in the equilibrium potential diminishes, and  $\phi^i_{eq,a,Diss}$ converges to the value for bulk material  $\phi_{eq,a,Diss}^{ref}$ . The rate of Pt oxidation of Equation 2 also follows the Butler-

Volmer equation<sup>6</sup> as given by:

$$R_{Ox}^{i} = k_{Ox} \cdot \left[ \exp\left(-\frac{\omega_{PtO} \ \theta_{PtO}^{i,n-1}}{R \ T}\right) \cdot \exp\left(\frac{\alpha_{a, \ Ox} n_{Ox} \ F}{R \ T} \left(\phi - \phi_{eq, Ox}^{i}\right)\right) - \theta_{PtO}\left(\frac{c_{H^{+}}}{c_{H^{+}}^{ref}}\right)^{2} \exp\left(-\frac{\alpha_{c, Ox} \ n_{Ox} \ F}{R \ T} \left(\phi - \phi_{eq, Ox}^{i}\right)\right) \right]$$
[12]

Again, the applied potential governs the reaction direction. The first term describes the formation of an oxide layer, assuming the presence of a sufficient amount of water for the reaction to take place. The second term describes the reduction of the formed Pt oxides. Since H<sup>+</sup> ions take part in the reduction, the cathodic oxide reduction is also governed by the proton concentration  $c_{H^+}$ . The concentration is assumed to be constant and is calculated according to:6

$$c_{H^+} = \frac{1}{\frac{EW}{\rho_{Nafion}} + \frac{\lambda M_{H2O}}{\rho_{H2O}}}$$
[13]

EW describes the equivalent weight of the ionomer,  $\rho_{Nafion}$  the density of the ionomer material Nafion, and  $\lambda$  the amount of water molecules per acid group, which correlates to the water activity  $a_w$ , and can be calculated by Equation 14 described by Springer et al.<sup>25</sup> The water activity equals the relative humidity of the participating gases and can assume values ranging from 0 to 1.

$$\lambda = 0.043 + 17.81a_w - 39.85a_w^2 + 36.0a_w^3$$
[14]

The equilibrium potential of the Pt oxidation is likewise corrected for the Pt particle radius.<sup>6</sup>

$$\phi_{eq,Ox}^{i} = \phi_{eq,Ox}^{ref} - \frac{\Delta \mu_{P_{t}}^{i}}{2F} + \frac{\Delta \mu_{P_{t}O}^{i}}{2F}$$
[15]

$$\Delta \mu_{PtO}^{i} = \Delta \mu_{PtO}^{ref} + \frac{\sigma_{PtO}M_{PtO}}{r_{Pt}^{i,n-1}\rho_{PtO}}$$
[16]

Besides the potential-driven reduction of a formed oxide layer, PtO can chemically dissolve according to Equation 3. The reaction is not an electrochemical reaction, hence, the reaction rate is described by a chemical equilibrium constant,  $K_{Chem}^i$  as<sup>6</sup>

$$R_{Chem}^{i} = k_{Chem} \left( \theta_{PtO}^{i,n-1} \cdot c_{H^{+}}^{2} - \frac{c_{Pt^{2+}}}{K_{Chem}^{i}} \right)$$
[17]

with the equilibrium constant defined as

$$K_{Chem}^{i} = \exp\left(\frac{F}{R T} \left(n_{a,Diss} \phi_{eq,a,Diss}^{i} - n_{Ox} \phi_{eq,Ox}^{i}\right)\right)$$
[18]

Two empirical Equations 19, 21 are introduced to describe the mechanisms of place exchange and cathodic Pt dissolution. The reaction rate for the transition between Pt oxides and place-exchanged oxides is defined as:

$$R_{PE}^{i} = \left(k_{PE,for} \; \theta_{PtO}^{i,n-1} \exp\left(\frac{\omega_{PE,for} \; \theta_{PtO}^{i,n-1}}{R \; T}\right) \\ \exp\left(\frac{\beta_{PE} \; F \; \left(\phi - \phi_{eq,PE}^{i}\right)}{R \; T}\right)\right) \\ - k_{PE,back} \; \theta_{O-Pt}^{i,n-1} \exp\left(\frac{\omega_{PE,back} \; \theta_{O-Pt}^{i,n-1}}{R \; T}\right)$$
[19]

where  $k_{PE,for}$  and  $k_{PE,back}$  describe the kinetics of the forward/ backward reaction,  $\theta_{O-Pt}^{i,n-1}$  the normalized Pt sites with an embedded oxygen atom and  $\phi_{eq,PE}^{i}$  the equilibrium potential of the place exchange mechanism. Similar to the oxide formation in Equation 11 we introduced the interaction parameters  $\omega_{PE, for}$  and  $\omega_{PE, back}$  between the exchanged species, which diminish the reaction after a specific amount of oxides have exchanged positions. The reaction rate is formulated with a potential-dependent exponential term that causes a higher electrode potential to promote a higher ratio of place-exchanged oxides. In case of a cathodic potential change, the (sub-surface) oxide present in the platinum lattice can either flip back to a surface oxide via the backward direction of reaction Equation 4 or can be reduced, which in turn leads to free Pt ions that can no longer sit atop of the oxygen atom. To formulate this oxygen reduction step mathematically, the maximal stable sub-surface oxide coverage  $\theta^i_{O-Pt,lim}$  for the new potential value is calculated by setting  $R_{PE}^{i}$  to zero and solving for  $\theta_{Q-Pt}^{i}$ . In order to solve this equation, the Lambert function W(x) was used, leading to the following expression:

$$\theta_{O-Pt,lim}^{i} = \frac{RT}{\omega_{PE,back}} W\left(\frac{k_{PE,for} \ \theta_{PtO}^{i,n-1} \ \omega_{PE,back}}{k_{PE,back} \ R \ T} + \frac{\theta_{PtO}^{i,n-1} \ \omega_{PE,for}}{R \ T}\right)\right) [20]$$

The reaction rate of the cathodic Pt dissolution triggered by the subsurface oxygen reduction step is modelled by the following equations:

$$R_{c.Diss}^{i} = k_{c.Diss} \left( \theta_{O-Pt}^{i,n-1} - \theta_{O-Pt,lim}^{i} \right) \quad \text{for} \quad \theta_{O-Pt}^{i,n-1} > \theta_{O-Pt,lim}^{i}$$
[21]

$$R_{c.Diss}^{i} = 0 \qquad \text{for} \quad \theta_{O-Pt}^{i,n-1} \le \theta_{O-Pt,lim}^{i}$$
[22]

where the reaction constant  $k_{c.Diss}$ , describes the rate of the cathodic reduction. Since not much is known about the kinetics of this reaction mechanism,  $k_{c.Diss}$  acts as a simple tuning parameter between the scenario of a back-flipping sub-surface oxide (no Pt loss) and the oxide reduction leading to a free Pt ion into the electrolyte.

The following conservation equations describe the calculation of the mass balances. The kinetic equations involve the following species: Pt, PtO, O-Pt, Pt<sup>2+</sup>, H<sup>+</sup> and H<sub>2</sub>O, with the proton and water concentrations assumed to be constant.

The Pt particle radius  $r_{P_t}^i$  can be calculated by the following expression:

$$\frac{dr_{P_t}^i}{dt} = -\frac{M_{P_t}}{\rho_{P_t}} \left( R_{a.Diss}^i + R_{Chem}^i + R_{c.Diss}^i \right)$$
[23]

There are three kinetic reaction rates which influence the change of particle radius, the anodic Pt dissolution/re-deposition  $R_{a,Diss}^i$ , the chemical PtO dissolution  $R_{c,hem}^i$ , and the cathodic Pt dissolution  $R_{c,Diss}^i$ . The calculated mass loss in the catalyst layer corresponds to the concentration of Pt<sup>2+</sup> ions  $c_{Pt^{2+}}$  in the electrolyte, which can be described by the following expression:

$$\epsilon \frac{dc_{Pt^{2+}}}{dt} = 4 \pi \sum_{i} r_{Pt}^{i} n_{Pt}^{i} \left( R_{a.Diss}^{i} + R_{Chem}^{i} + R_{c.Diss}^{i} \right)$$
$$-q_{PtLoss}$$
[24]

Since the cathode catalyst particles are discretized into finite groups, categorized by their radius, the overall ion concentration is calculated by the sum of the reaction rates  $R_i$  multiplied with the corresponding particle surface  $4 \pi r_{p_1}^{i_2} n_{p_1}^i$  over all particle groups.

As the concentration of dissolved ions in the catalyst layer rises, a concentration gradient toward the membrane causes ions to diffuse into the membrane, forming a so-called Pt band. The Pt loss  $q_{Pt,loss}$  in the catalyst layer with thickness  $h_{CL}$  can be described by Fick's first law,

$$q_{PtLoss} = -D_{Diff} \frac{c_{Pt^{2+}}^{n-1}}{L_x \cdot h_{CL}}$$
[25]

with the diffusion coefficient  $D_{Diff}$  and the diffusion length  $L_x$  to the Pt-band. The Pt ion concentration in the Pt-band is assumed to be zero. For simplicity, no concentration gradient of Pt ions within the catalyst layer is assumed (0D-model). For the diffusion coefficient  $D_{Diff}$  we assume a dependence on temperature and relative humidity of the gas, as described by:

$$D_{Diff} = D_0 \cdot \left(\frac{T}{T_0}\right)^2 \cdot \left(\frac{RH}{RH_0}\right)^2$$
[26]

with the reference values for temperature  $T_0$  and relative humidity  $RH_0$  corresponding to the diffusion constant  $D_0$ .

The evolution of the oxide coverage,  $\theta_{PtO}^{i}$  of the catalyst layer was adapted from Ref. 6 with the addition of a term for the place exchange:

$$\frac{d\theta_{PtO}^{i}}{dt} = \left(\frac{R_{Ox}^{i} - R_{Chem}^{i} - R_{PE}^{i}}{\Gamma_{max}}\right) - \left(\frac{2}{r_{Pt}^{i}}\right)\frac{dr_{Pt}^{i}}{dt} \qquad [27]$$

where the first term on the right-hand side describes the formation/reduction of oxides by the reaction paths introduced above and the second term accounts for a changing particle size that leads to a changing oxide coverage.  $\Gamma_{max}$  is the number of moles of active sites per unit of platinum area.

A similar equation is used to describe the partial change of the place-exchanged oxide species.

$$\frac{d\theta_{O-Pt}^{i}}{dt} = \left(\frac{R_{PE}^{i} - R_{c.Diss}^{i}}{\Gamma_{max}}\right) - \left(\frac{2}{r_{Pt}^{i}}\right)\frac{dr_{Pt}^{i}}{dt}$$
[28]

In addition to the change in radius of each particle group, particles can be permanently detached by carbon corrosion, causing a change in the amount of particles. At potentials above  $\sim 1.1$  V, the catalyst support material is attacked in terms of Reaction 6, causing a reduced

adhesion of the Pt and leading to a loss of particles. This mechanism is implemented in the model by the following equation:

$$\frac{dn_{P_t}^i}{dt} = -k_{CC} \exp\left(\beta_{CC} \left(\phi - \phi_{eq,CC}\right)\right) \frac{n_{P_t}^i}{r_{P_t}^i}$$
[29]

where  $\beta_{cc}$  describes the potential dependency of the carbon corrosion,  $k_{cc}$  the reaction constant, and  $\phi_{eq,CC}$  the equilibrium constant of the reaction. The ratio  $\frac{n_{P_t}^i}{r_{P_t}^i}$  accounts for the effect that Pt itself catalyzes carbon corrosion and smaller particles have a smaller contact surface, leading to less adhesion.

The ECSA can be calculated by summing up the number of particles  $n_{Pt}^i$  multiplied with their surface (spherically shaped with radius  $r_{Pt}^i$ ) for all particle radius groups:  $ECSA = 4 \pi \sum_{i} r_{Pt}^{i}^2 n_{Pt}^i$ 

*Limiting equations.*—Since the model is developed without adaptive time discretization, unrealistic reaction rates can be calculated due to the exponential terms which are very sensitive to large potential changes. One of the main aspects of this model was the reduction of calculation time, which cannot be guaranteed with a discretization into variable time steps. For this reason, the reaction rates  $R_{a.Diss}^i$ ,  $R_{o.Diss}^i$ ,  $R_{ox}^i$  and  $R_{PE}^i$  have been physically limited separately for every particle group.

The maximum dissolution and re-deposition rate for every radius group i is introduced based on the limiting Pt ion concentration in the current time step  $c_{p_l^{2+},lim}^i$ . In case of re-deposition, the limiting concentration is  $c_{p_l^{2+},lim}^i = 0$ , since the re-deposition shuts down when there are no Pt ions left in the ionomer. The limiting concentration in case of Pt dissolution is calculated as the concentration  $c_{p_l^{2+}}$  for which the dissolution shuts itself down. This is realized by solving the equation  $R_{a,Diss}^i = 0$  for  $c_{p_l^{2+}}$ .

$$c_{Pt^{2+},lim}^{i} = c_{Pt^{2+}}^{ref} \cdot \frac{\exp\left(\frac{\alpha_{a,a,Diss} R_{a,Diss}F}{RT} \left(\phi - \phi_{eq,a,Diss}^{i}\right)\right)}{\exp\left(-\frac{\alpha_{c,a,Diss} R_{a,Diss}F}{RT} \left(\phi - \phi_{eq,a,Diss}^{i}\right)\right)}$$
[30]

The limiting borders for reaction rate  $R_{a.Diss}^i$  are calculated as the ratio between the remaining dissolvable/redepositionable Pt concentration  $c_{Pt^{2+},lim}^i - c_{Pt^{2+}}$ , the particle surface  $4 \pi r_{Pt}^{i,n-1^2}$ , and the overall amount of Pt particles  $\sum n_{Pt}^i$  per time step.

$$R_{a.Diss,lim}^{i} = \frac{c_{P_{l}2^{+},lim}^{i} - c_{P_{l}2^{+}}^{n-1}}{4 \pi r_{P_{l}}^{i,n-1^{2}} \Delta t \sum n_{P_{l}}^{i}}$$
[31]

The maximum PtO coverage is calculated by solving the equation  $R_{Ox}^i = 0$  for  $\theta_{PtO}^i$ 

$$= \frac{RT}{\omega_2} \cdot W\left(\frac{c_{H^+}^{ref^2}\omega_2}{c_{H^+}^2 R T} \cdot \exp\left(\frac{(\alpha_{a,2} + \alpha_{c,2}) F n_2 \left(\phi - \phi_{eq,Ox}^i\right)}{R T}\right)\right)$$
[32]

The maximum place exchange coverage is calculated correspondingly by solving  $R_{PE}^i = 0$  for  $\theta_{O-Pt}^i$  as described earlier in Equation 20.

Since the reaction rates are limited, but not the partial coverages, the maximum PtO and O-Pt coverages are transferred into limiting rates by the following equations:

$$R_{Ox,lim}^{i} = \frac{\theta_{PtO,lim}^{i} - \theta_{PtO}^{i,n-1}}{\Delta t} \Gamma_{max}$$
[33]

$$R_{PE,lim}^{i} = \tau_{PE} \frac{\theta_{O-Pt,lim}^{i} - \theta_{O-Pt}^{i,n-1}}{\Delta t} \Gamma_{max}$$
[34]

$$R_{c.Diss,lim}^{i} = (1 - \tau_{PE}) \frac{\theta_{O-Pt,lim}^{i} - \theta_{O-Pt}^{i,n-1}}{\Delta t} \Gamma_{max}$$
[35]

The parameter  $\tau_{PE}$  controls how much of the exchanged species can be reversed, and how much is undergoing a cathodic dissolution. The ordinary differential equations are solved by an explicit Euler method with fixed time step.

## Experimental

The model parameters were validated through a comprehensive experimental investigation of catalyst degradation. Several tests were performed under variation of temperature, relative humidity and potential range for 500 operation hours, with the exception of the support aging protocol (Set 4), which only required 3 hours. The materials and experimental apparatus used are described in detail in Ref. 26.

A total of four measurement sets were carried out as outlined below:

• Set 1 follows the DoE AST protocol for catalyst degradation, where the potential was cycled in rectangular sweep between 0.6 and 0.95 V, holding each potential step for 3 s. The anode was fed with hydrogen, while nitrogen was fed on the cathode side. 300,000 potential cycles were carried out and after fixed numbers of cycles, the ECSA was characterized by cyclic voltammetry. Under the given potential conditions, the cell temperature was also varied between 60, 80 and 90°C at a constant RH of 100%.

• For Set 2, the RH was varied between 30, 60 and 100% at a constant cell temperature of 80°C, otherwise using the same operating conditions as Set 1.

• To investigate the impact of different potential profiles on the catalyst degradation, in measurement Set 3, rectangular and triangular potential cycles between 0.6 and 0.9 V/0.95 V were applied at a cell temperature of 80°C and RH of 100%, while feeding the anode with hydrogen and the cathode with air. The applied load profiles are

- $\circ$  Square wave between 0.6 and 0.95 V (6 s cycle) SW 0.95 V
- Square wave between 0.6 and 0.90 V (6 s cycle) SW 0.90 V
- Triangular wave between 0.6 and 0.90 V (6 s cycle) TW 0.90 V

• The focus in measurement Set 4 was to degrade the catalyst support following the corresponding DoE AST protocol. For this purpose, 5000 fast triangular potential sweeps, 2 s per cycle, between 1.0 and 1.5 V were applied at a cell temperature of 80°C and RH of 100%. The anode was fed with hydrogen, while nitrogen was fed on the cathode side.

#### **Results and Discussion**

An initial PSD is given as a model input. The initial distribution consists of a finite number of particle groups, categorized by their particle radius and number of particles within each group. Figure 2 shows the assumed PSD discretized into 32 groups with a mean particle radius of 5.5 nm and an initial ECSA of  $40 \text{ m}^2/\text{g}_{pt}$ , which is the measured beginning of life ECSA of our fresh membrane electrode assembly. For every particle group, the equation sets are solved in every time step using the parameters given in Table I.

An example of the simulated evolution of Pt oxide coverage for three potential cycles between 0.6 and 0.95 V and for three different particle radius groups (2, 4 and 6 nm) is given in Figure 3. It is clear that as the potential rises, oxidation of the Pt sets in, forming an oxide layer covering the catalyst surface. After 3 s dwell time at 0.95 V, the oxide reaches a maximum of 0.3 partial coverage. Smaller particles reach a higher total coverage, due to the shift in the equilibrium potential (Equations 10 and 15).

The corresponding evolution of Pt dissolution and re-deposition rates for the three particle groups of different sizes as a function of the applied cyclic potential is given in Figure 4. As the potential increases from 0.6 to 0.95 V, the Pt dissolution rapidly sets in. It is found that smaller particles dissolve much faster compared to larger particles due to their lower equilibrium potential. While the dissolution continues, the concentration of  $Pt^{2+}$  ions in the ionomer of the catalyst layer rises. Due to the increased  $Pt^{2+}$  ion concentration, the dissolution of



Figure 2. Calculated initial particle size distribution of 32 particle radius groups with a mean particle radius of 5.5 nm and an initial ECSA of  $40 \text{ m}^2/g_{pt}$ .

large particles shifts, despite the high potential, to a re-deposition. The emerging concentration difference between the catalyst layer and the membrane causes an ion flux (Equation 24) into the Pt band, leading to an irreversible loss of Pt. Figure 5 shows the evolution of  $Pt^{2+}$  concentration in the ionomer as well as the subsequent  $Pt^{2+}$  loss into the membrane over three potential cycles.

As the potential decreases again, the re-deposition of dissolved Pt ions sets in immediately and the ion concentration declines within a few time steps. As shown in Figure 4, larger particles can accept redepositing ions from the electrolyte much faster than smaller particles, leading to a preferable growth of large particles. In combination with the higher dissolution of small particles, this causes an overall shift in the PSD toward larger particles, hence, resulting in an ECSA loss due to the effect of Ostwald ripening. This effect is accompanied by a particle radius evolution as shown in Figure 6a, where small particles decrease in size, while large particles feed from the dissolved ions and expand in size. To prevent the particles from getting infinitely small, and thus causing numeric calculation errors, a lower limit has been introduced with  $r_{Pt,min} = 7 * 10^{-10} m$ . As soon as a particle group reaches this limit, it gets erased from the electrode model. In addition to the radius change of the particles, the amount of particles in each group diminishes due to carbon corrosion (not shown) as described in Equation 29. The ECSA can be calculated as the total surface area of all Pt particles remaining on the carbon support, resulting in a



**Figure 3.** Evolution of PtO coverage over three potential cycles between 0.6 and 0.95 V for three particle radius groups of 2, 4 and 6 nm.

# Table I. Model Parameters.

Parameter	Description	Value	Unit	Comments
$\sigma_{Pt}$	Surface tension	$237 \times 10^{-6}$	J/cm <sup>2</sup>	Ref. 6
$\sigma_{PtO}$		$0.1 \times 10^{-3}$	J/cm <sup>2</sup>	Ref. 6
$h_{CL}$	Electrode thickness	$12 \times 10^{-4}$	cm	Assumed
$k_{a Diss}^{ref}$	Reaction constant	$1 \times 10^{-10}$	mol/(cm <sup>2</sup> s)	Fitted
$k_{Ox}$		$1.4 \times 10^{-11}$	mol/(cm <sup>2</sup> s)	Fitted
k <sub>Chem</sub>		$3 \times 10^{-24}$	mol/(cm <sup>2</sup> s)	Ref. 6
$k_{PE,for}$		$1 \times 10^{-22}$	mol/(cm <sup>2</sup> s)	Fitted
k <sub>PE,back</sub>		$1 \times 10^{-20}$	mol/(cm <sup>2</sup> s)	Fitted
k <sub>c.Diss</sub>		$1.4 \times 10^{-9}$	mol/(cm <sup>2</sup> s)	Fitted
k <sub>CC</sub>		$1.5 \times 10^{-20}$	mol/(cm <sup>2</sup> s)	Fitted
$\alpha_{a,a.Diss}$	Transfer coefficient	0.3	-	Fitted
$\alpha_{c,a.Diss}$		0.5	-	Ref. 6
$\alpha_{a,Ox}$		0.35	-	Ref. 6
$\alpha_{c,Ox}$		0.5	-	Fitted
n <sub>a.Diss</sub>	Number of electrons	2	-	Ref. 6
$n_{Ox}$		2	-	Ref. 6
$\beta_{PE}$	Fit parameter	0.5	-	Fitted
$\beta_{CC}$		19	-	Fitted
$\phi_{ea,a,Diss}^{ref}$	Equilibrium potential	1.188	V	Ref. 17
$\phi_{eq,Ox}^{ref}$		0.98	V	Ref. 17
$\phi_{eq,PE}^{ref}$		1.2	V	Assumed
$\phi_{eq.c.Diss}^{ref}$		0.98	V	Assumed
$\phi_{ea,CC}^{ref}$		0.2	V	Ref. 2
$\Delta \mu_{PtO}^{ref}$	Chemical potential	$-42.3 \times 10^{3}$	J/mol	Ref. 6
$c_{Pt2+}^{ref}$	Reference concentration	$1 \times 10^{-3}$	mol/cm <sup>3</sup>	Ref. 24
$c_{n+}^{ref}$		$1 \times 10^{-3}$	mol/cm <sup>3</sup>	Ref. 24
$\omega_{PtO}$	PtO interaction parameter	$27 \times 10^{3}$	J/mol	Ref. 6
$\omega_{PE, for}$	ľ	$10 \times 10^{3}$	J/mol	Fitted
$\omega_{PE,back}$		$90 \times 10^{3}$	J/mol	Fitted
EW	Equivalent weight of ionomer	1100	g/mol	Ref. 24
$\Gamma_{max}$	Maximum Pt surface coverage	$2.18 \times 10^{-9}$	mol/cm <sup>2</sup>	Ref. 6
8	Electrode porosity	1.6	-	Fitted
$T_0$	Reference temperature	80	°C	Fitted
$RH_0$	Reference humidity	100	%	Fitted
$\tau_{PE}$	Ratio cathodic dissolution/reverse place exchange	0.5	-	Assumed
ϑ	fitting parameter RH	1.7	-	Fitted

specific ECSA evolution for each particle group (Figure 6b). The overall ECSA evolution of the catalyst layer is calculated by summing up the ECSA evolution of each radius group as given in Figure 6c. The ECSA evolution shows distinctive



Figure 4. Pt dissolution and redeposition rates over three potential cycles between 0.6 and 0.95 V for three particle radius groups of 2,4 and 6 nm.

"bends", which occur every time a particle group reaches the lower limit and gets erased. Increasing the amount of calculated particle groups leads to a denser PSD, and thereby to a more continuous ECSA evolution. The impact of the amount of



Figure 5. Concentration of  $Pt^{2+}$  ions dissolved in the ionomer and the subsequent  $Pt^{2+}$  loss into the membrane over three potential cycles between 0.6 and 0.95 V.



**Figure 6.** (a) Particle radius evolution with time for initial particle radius groups from 2–9 nm; (b) Corresponding ECSA evolution of each particle group; (c) Overall ECSA evolution of the whole catalyst layer.

calculated particle groups on the final ECSA evolution is depicted in Figure 7.

As Figure 7 shows, a deviation in the simulated ECSA evolutions can be noted, which diminishes with higher amount of particle groups. Since an increase in particle groups also leads to a proportionally higher calculation time, 8 to 16 particle groups were found to lead to reasonable results. For the simulation of long-term degradation, it should be noted that there is a minimum amount of necessary particle groups. The ECSA evolution with 4 particle groups over 500 operating hours shows that there seems to be no visible degradation in the last 100 operating hours. Since particle groups are completely erased from the electrode model when reaching the radius limitation, the degradation through Ostwald ripening shuts down at the point where only one radius group is left, letting the dissolution and re-deposition of Pt ions occur in the same particle group. To ensure reliable simulations results,



**Figure 7.** Impact of the amount of calculated particle groups on the ECSA evolution over 300k potential cycles between 0.6 and 0.95 V (6s), simulations were carried out with PSD of 4, 8, 16 and 32 initial particle radius groups.

it should be guaranteed there is always a minimum of 2 particle groups available.

Model validation through ECSA evolution.-In this work, we use the ECSA evolution as a validation metric. The ECSA was simulated for the four experimental data sets and compared to the measured data as shown in Figure 8. Simulating 500 real-time operating hours, under reasonable numerical conditions (8 particle radius groups, 50 data points per second) on a default Desktop PC (CPU: Intel Core i7, 3.20 GHz) takes a calculation time of around 9 hours. The effect of temperature on catalyst degradation is shown in Figure 8a. In this figure, the measured and simulated ECSA evolution over 300,000 rectangular potential cycles (each cycle time is 6 s) between 0.6 and 0.95 V are shown for different operating temperatures (Set 1). The experimental trend of increasing ECSA loss with higher operating temperatures is comparable with literature results.<sup>18,19</sup> A good agreement between simulated and measured ECSA is reported here, particularly for operating temperatures of 60 and 80°C, while an overestimation by the model can be observed for 90°C in the first 200 operating hours. Since the simulations were processed by a restricted model, there may be temperature effects, such as increased ionomer degradation, that are not calculated, and thus can lead to the shown deviation. As it is clear from both experiment and simulation, the temperature can highly impact the ECSA loss.

Figure 8b shows the effect of relative humidity on the measured and simulated ECSA evolution. Both experiment and model show that higher humidification leads to an increase in ECSA loss, which was also reported by Uchimura et al.<sup>14</sup> The simulated data are in very good agreement with the experimental data, particularly for an RH of 100% and 30%. An RH of 60% shows good comparability up to 100 operating hours after which the model slightly deviates from the experiment, which can be attributed to the lumped model approach regarding the RH dependency ( $D_{Diff} \sim RH^2$ , Eq. 26), leaving room for optimization.

The potential load profile dependent ECSA was also calculated and is compared to experimental data in Figure 8c. The highest ECSA loss is found for SW up to 0.95 V and lower losses are shown to occur with a decreased upper potential limit (UPL) of 0.90 V for both SW and TW. Again, good agreement between experiment and model is seen.

Finally, the effect of catalyst support degradation by carbon corrosion is investigated. Its impact on ECSA loss is shown in Figure 8d. At high potential levels, the catalyst itself does not degrade due to a full protection by surface oxides, but rather the carbon support corrodes. To validate the reaction rate of the carbon corrosion, parameter variation of the reaction constant  $k_{cc}$  has been carried out.

From our results it is evident that the model can predict the ECSA loss with satisfying accuracy within the investigated operating range.

**Detailed analysis of the AST simulation results.**—To further understand the effects of operating conditions on catalyst degradation, the model was used to calculate the Pt dissolution for the four sets described earlier. The effect of temperature was investigated via the simulation of one cycle of an applied load profile as given in Figure 9. Pt dissolution into the ionomer is found to increase with higher temperatures, in turn leading to a higher possible re-deposition and hence higher degradation due to Ostwald ripening. Further, higher concentration of  $Pt^{2+}$  in the catalyst layer leads to a higher diffusion into the membrane, thus, Pt loss increases with rising temperatures. This also stems from the fact that the diffusion process itself is highly temperature dependent. Figure 9d shows the simulated amount of platinum in the membrane (PITM) after one cycle for three temperatures. TEM images from Ref. 19 also show higher amounts of PITM for higher operating temperatures.

In Figure 10, the impact of relative humidity on the catalyst degradation was investigated. Pt dissolution into the ionomer increases with higher relative humidity due to fast kinetics (Equation 9), reaching the same maximum after a dwell time of 3 s for all investigated RH. Since the maximum concentration persists for a longer time at a



Figure 8. Experimentally measured (points) and simulated (lines) ECSA evolution over 500 operating hours, investigating the effect of (a) temperature; (b) relative humidity; (c) applied load profile; (d) DoE AST protocol for catalyst support degradation on the ECSA loss over time.



**Figure 9.** Simulative investigation of the impact of temperature on catalyst degradation: Potential load profile for one applied cycle (black); The evolution of  $Pt^{2+}$  ion concentration in the ionomer in nmol per electrode volume (blue); The corresponding ion diffusion flux into the membrane in nmol per electrode volume per second (red) for operating temperatures (RH = 100%) (a) T = 90°C, (b) T = 80°C, (c) T = 60°C, (d) Platinum in the membrane after one potential cycle.



**Figure 10.** Simulative investigation of the impact of RH on catalyst degradation: Potential load profile for one applied cycle (black); The evolution of  $Pt^{2+}$  ion concentration in the ionomer in nmol per electrode volume (blue); The corresponding ion diffusion flux into the membrane in nmol per electrode volume per second (red); for relative humidities (T = 80°C) (a) RH = 100%, (b) RH = 60%, (c) RH 30%, (d) Platinum lost into the membrane after one potential cycle.

higher RH, the corresponding ion diffusion increases proportionally, leading to higher Pt losses into the membrane as depicted in Figure 10d. This finding is also reported by Uchimura et al. who detected via TEM imaging higher amounts of PITM as the gas humidity was increased.<sup>12</sup>

Figure 11 shows a more detailed view of single potential cycles applied in the experiments of Set 3. Comparing both square wave profiles, it can be seen that a 50 mV higher UPL causes a 15 times higher concentration of the dissolved platinum in the ionomer. This increase in concentration leads to a significantly higher re-deposition and thus higher ECSA loss due to Ostwald ripening and a significantly higher platinum loss into the membrane. Comparing SW 0.90 V and TW 0.90 V, it is found that a triangular load profile causes slower platinum dissolution due to the slower increase in potential. Further,  $Pt^{2+}$  concentration peaks at the UPL and re-deposition sets in directly after the potential decreases again. A triangular load profile leads to less dissolved and re-deposited platinum, hence, lower degradation and Ostwald ripening. Further, a shorter dwell time at high  $Pt^{2+}$  concentration causes lower ion flux into the membrane, leading to a lower platinum loss into the membrane.

The impact of carbon corrosion on the ECSA is investigated in more detail as shown in Figure 12. The ECSA loss is divided into losses due to anodic Pt dissolution and carbon corrosion after 20 and 5,000 cycles. As the potential is cycled between 1.0 and 1.5 V, the PtO evolution quickly reaches a full oxide monolayer, causing Pt dissolution to shut down. As the potential cycling occurs in a high potential range, the oxides cannot be reduced and hence the dissolved Pt ions cannot be re-deposited. However, a decrease in the dissolved Pt<sup>2+</sup> concentration due to ion diffusion into the membrane is still observed. Figure 12b shows that after the first 20 cycles, the anodic Pt dissolution largely contributes to the overall ECSA loss, which diminishes after 5,000 cycles, leaving the carbon corrosion to be the major degradation mechanism, Figure 12c.

Comparison to published data .- In this work, we also consider the place exchange mechanism as a possible path of catalyst degradation. To further understand this mechanism, we compare the model to published experimental data. The place exchange mechanism and the subsequent cathodic dissolution are investigated by considering the experiment carried out by Cherevko et al.<sup>28</sup> The simulated anodic and cathodic Pt dissolution data for the applied potential in Ref. 28 are given in Figure 13. To show the anodic and cathodic Pt dissolution and when they occur, Cherevko et al. carried out an experiment with Pt catalyst in 0.1 M HClO<sub>4</sub> solution by applying anodic and cathodic potentials sweeps up to 1.6 and 1.9 V. They measured Pt dissolution rates where two dissolution peaks were detected. The anodic peak occurs when increasing the potential and shuts down after Pt oxidation forms a full monolayer PtO. Due to full PtO coverage, the anodic peak does not increase when increasing the UPL to 1.9 V. The cathodic dissolution peak occurs while decreasing the potential again. Due to the place exchanged oxide species and exposed Pt, the reduction of PtO causes a cathodic Pt dissolution, which is affected further by the UPL. By respectively comparing the anodic and cathodic peaks for each potential cycle, the measured ratio C1/A1 and C2/A2 is calculated as 10 and 15 for UPL 1.6 V and UPL 1.9 V, respectively. An actual quantitative comparison between measured and simulated C1 and A1 can be difficult due to different materials for electrolyte and catalyst. The comparison is, therefore, carried out using the ratio C1/A1 with the simulated ratio being 10.48 and 14.67 for UPL 1.6 V and UPL 1.9 V, respectively, leading to a good qualitative comparability with the measured data.

A trapezoidal potential cycle is also used to investigate the validity of the model. Here, we use the data provided by Topalov et al.<sup>4</sup> In their study, they detected an anodic and a cathodic Pt dissolution peak when applying trapezoid potential cycles with 300 s dwell time at different upper potential limits (slope scan rates of 1.0 V/s). The cathodic dissolution peak increases with rising UPL, while anodic



**Figure 11.** Simulative investigation of the impact of the potential profile on catalyst degradation: One cycle of different applied potential profiles (black); Dissolved  $Pt^{2+}$  concentration in the ionomer in nmol per electrode volume (blue); Subsequent Pt ion diffusion flux into the membrane in nmol per electrode volume per second (red) for potential profiles (a) square wave 0.6–0.95 V; (b) square wave 0.6–0.90 V (6s) (c) triangular wave 0.6–0.90 V (6s); (d) Platinum lost into the membrane after one potential cycle.

dissolution seems not to be affected. This is mainly due to the fact that the high surface coverage of oxides on the catalyst at high potentials blocks the anodic dissolution, while it promotes the place exchange and hence the cathodic dissolution. Figure 14 shows the simulated anodic and cathodic dissolution as well as the measured dissolution peaks at the given potential from Topalov et al.<sup>4</sup> For a qualitative comparison, the dissolution rates from the experiment and the simulations have each been normalized to their maximum value. A good agreement between the experimental results and our model can be seen, which also shows the trend of increasing cathodic dissolution peaks



Figure 12. (a) 20 applied potential cycles (black): fast triangular sweeps (2s) between 1 and 1.5 V; evolution of PtO-coverage over time (red); Dissolved  $Pt^{2+}$  concentration in the ionomer (blue); (b) ECSA loss due to anodic dissolution and carbon corrosion after the first 20 cycles; (c) after 5000 cycles.



Figure 13. Simulated anodic and cathodic Pt dissolution rates for a triangular potential profile between 0 and 1.6V/1.9 V (30 min), corresponding to the experimental investigations given in Ref. 25.

with rising UPL, while the anodic dissolution peak remains constant. Further, the model accurately predicts the ratio between the anodic and cathodic dissolution peaks.

*Implications of model.*—In order to investigate the dominating degradation mechanism in different potential ranges, we simulated a rectangular load profile between a fixed lower potential limit, and a varying UPL between 0.8 and 1.65 V, with 30s dwell time at each potential. Figure 15a shows the calculated overall ECSA losses for an LPL of 0.7, 0.75 and 0.80 V as a function of the UPL after 100 cycles, whereas Figures 15b, 15c and 15d show the partial ECSA losses due to carbon corrosion, anodic and cathodic Pt dissolution. It can be noted that the anodic Pt dissolution dominates the ECSA loss while cycling up to potentials < 1.6 V. ECSA losses due to carbon corrosion and place exchange become only notable for cycles with higher upper potential limits.

By observing the evolution of the ECSA loss due to anodic dissolution, we can see that the loss increases with cycling to higher potentials up to around 1.1 V. Cycling down to lower LPL causes higher ECSA losses because of a higher PtO reduction and a consequently higher Pt dissolution. Increasing the UPL above 1.1 V will again lead to a lower



**Figure 14.** Simulated anodic and cathodic Pt dissolution rates for a trapezoidal potential profile from 0 to 1.25, 1.35, 1.45, 1.55 and 1.65 V, with 300s dwell time at each UPL, compared to the experimental dissolution peaks measured by Topalov et al.<sup>4</sup> The dissolution rates from the model and the experiments have each been normalized to their maximum value.

ECSA loss, which is related to the formation of a full monolayer of PtO, covering the Pt and shutting down the anodic dissolution. At this point, a stronger decrease in the ECSA loss can be noted for LPL of 0.75 and 0.80 V, since the reduction of PtO never proceeds far enough to reduce the PtO coverage below one monolayer, obtaining the catalyst protection. Conversely, cycling down to 0.70 V will reduce the PtO coverage down to around 0.7 and therefore again lead to an anodic Pt dissolution.

Increasing the UPL above 1.6 V causes the place exchange to become more dominant, leading to a higher amount of ECSA loss due to cathodic Pt dissolution. At the same time, the impact of carbon corrosion increases in the higher potential ranges. The simultaneously decreasing anodic Pt dissolution leaves the place exchange and carbon corrosion to be the dominating ECSA loss mechanisms in potential ranges above 1.6 V.

# Conclusions

In this work, we developed a zero-dimensional model to describe the state of health of a PEM fuel cell based on the degradation of the cathode catalyst layer. The model takes into account the underlying



Figure 15. Simulated ECSA loss after 100 potential cycles (60s) for an LPL of 0.70, 0.75 and 0.80 V and an UPL between 0.8 and 1.65 V; (a) Overall ECSA loss; (b) Partial ECSA loss due to carbon corrosion; (c) Partial ECSA loss due to anodic Pt dissolution; (d) Partial ECSA loss due to cathodic dissolution/place exchange.

degradation mechanisms, catalyst dissolution and oxidation and carbon corrosion as well as the place-exchange mechanism. The model is fast and reliable and hence can be used in the design of the cell and its control mechanism. Using measured and published experimental data we validated the model and illustrated its capability in understanding the degradation mechanisms within the catalyst layer under various operating conditions.

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