Reduced models for the cathode catalyst layer in PEM fuel cells

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27. September 2006

Abstract: We study a pore scale model for the catalyst layer on the cathode side of a fuel cell, where hydrogen and oxygen combine at catalyst sites. Our model distinguishes microscopically the phases of rigid structure, electrolyte, pore-space, and catalyst. The oxygen concentration and the protonic potential are described by diffusion equations with reaction terms on the catalyst's surface. For the limit of a vanishing pore size we derive homogenized equations of reaction-diffusion type and provide formulae for the effective coefficients. A dimensional reduction shows that a thin catalyst layer can be replaced by a boundary condition. We furthermore analyze the effect of a doubling of the Tafel slope for high protonic potentials and determine effective constants.

1   Introduction

A fuel cell is an electrochemical device that converts chemical energy into electrical energy, having water and heat as by-products. The proton exchange membrane (PEM) fuel cell is among the most favorable candidates for replacing the internal combustion engine in automobiles and batteries in portables. The reactant gases are hydrogen and oxygen, where the latter is provided by ambient air. A typical fuel cell consists of an anode flow channel, anode diffusion layer, anode catalyst layer, membrane, cathode catalyst layer, cathode diffusion layer and cathode flow channel (see Figure 1). The principal mechanism is that a hydrogen molecule splits into two electrons and two hydrogen ions on the anode side, the ions travel through the PEM while the electrons are conducted through the external circuit, providing the electrical energy. In the cathode catalyst layer, hydrogen ions, electrons and oxygen combine to water molecules.

One of the main sources of energy loss in a PEM fuel cell is the slow kinetic of the oxygen reduction reaction (ORR) at the catalyst particles in the cathode catalyst layer. The description of the fuel cell cathode, especially the modeling of the mass and charge transfer limitations within the active cathode layer, is therefore of particular importance. In literature, different models are suggested to describe

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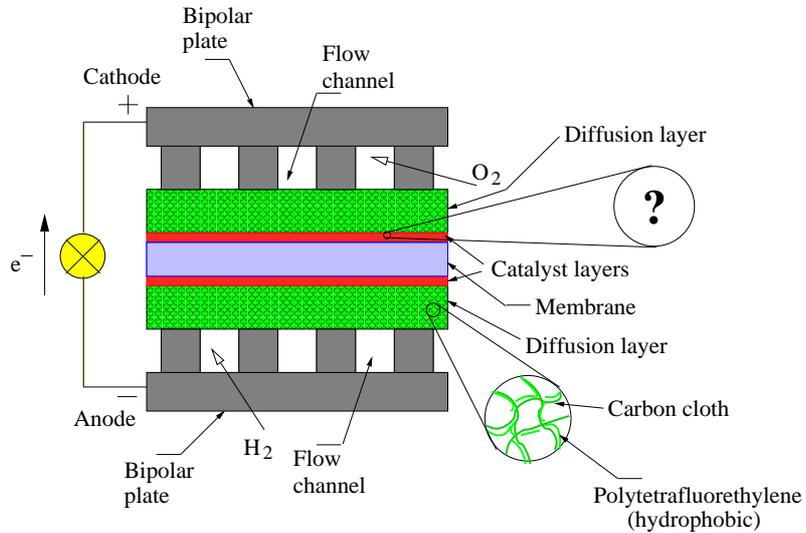
Figure 1: Sketch of a proton exchange membrane (PEM) fuel cell.

the cathode. A compact overview of these models is given e.g. in [15]. In the next subsection we give a description of the three principal models.

1.1   Three simplified models for the cathode active layer

The catalyst layer as a homogeneous region

In the simplest model (described e.g. in [1], [3], [4], [10]), the microscopic structure of the catalyst layer is neglected and the layer is replaced by a homogeneous material (see Figure 2(a)). This meta-material is permeable for gas as if there was pore space, conducting protons like the electrolyte, conducting electrons like the carbon based structure, and oxygen reduction is everywhere possible as if catalyst particles were homogeneously distributed. The kinetics are often described in one-dimensional models, z being the coordinate across the layer, and the ohmic drop for electrons is neglected. For an isothermal system under steady state conditions, local mass and charge balances then lead to the equations

$$D\frac{\partial^2 C}{\partial z^2} - \frac{\gamma}{L}\frac{1}{qF}i_0\frac{C}{C_0}\exp\left(\frac{2.3\eta}{b}\right) = 0,$$

$$\kappa\frac{\partial^2 \eta}{\partial z^2} - \frac{\gamma}{L}i_0\frac{C}{C_0}\exp\left(\frac{2.3\eta}{b}\right) = 0,$$

where C is the oxygen concentration and η is the protonic potential, for the meaning and for typical values of the physical constants see appendix B. The neighboring layers of the catalyst layer are not modeled but rather replaced by boundary conditions, $C = C_0$ and $\partial_z\eta = 0$ at $z = 0$ (the gas diffusion layer interface), and $\eta = \eta_0$ and $\partial_z C = 0$ at $z = L$ (the PEM interface). The exponential expression in η reflects the Tafel law which models the multistep reaction mechanism of oxygen reduction.
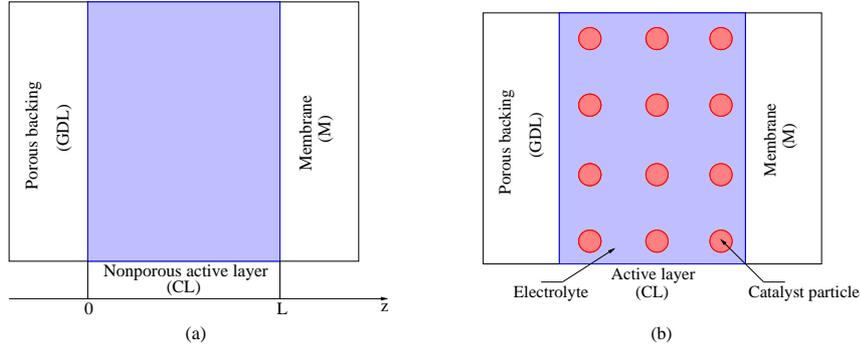
Figure 2: (a) The catalyst layer as a homogeneous meta-material. (b) Catalyst particles included in the electrolyte.

Catalyst particles immersed in electrolyte

Bultel et al. [3] propose a modified model in which spherical catalyst particles are distributed in a regular hexagonal three-dimensional fashion within the electrolyte (Figure 2(b)). The equations to describe the oxygen concentration and the protonic potential are $\nabla \cdot (D\nabla C) = 0$ and $\nabla \cdot (\kappa \nabla \eta) = 0$ away from the spherical inclusions, with the electrochemical Tafel law as the boundary condition for $i = \kappa \partial_n \eta$ along the electrolyte-particle interface,

$$i = i_0 \left[\frac{C}{C_0} \exp\left(\frac{2.3\eta}{b} \right) \right]. \tag{1.1}$$

The main feature of the modified model is its sensitivity to diffusion resistance – at high reaction rates, it is possible that the oxygen concentration is significantly different far from the catalyst particles and at the particle boundaries, where it is consumed. The numerical comparison between the two models reveals good agreement at moderate reaction rates. Instead, when the reaction is concentrated in a region of few particles, the models provide different profiles in that region (see Figure 10 in [3]).

In this work we show with mathematical rigour that, in the limit of a vanishing particle size, the homogeneous model describes well the behavior of the solution of the particle model. The only modification regards the coefficients in the homogeneous model, which must be adapted in a way that involves the local geometry. We mention already here that our model is three dimensional, that it is general enough to include additionally the pore-space and the carbon-based structure, and that it is not limited to spherical catalyst particles.

Catalyst-electrolyte agglomerates distributed in pore space

The drawback of the previous model is the absence of gas pores, which is not realistic, see [8]. In the agglomerate model, the catalyst and the electrolyte are in fine mixture to form an agglomerate, much as the meta-material in the homogeneous model (see Figure 3). Agglomerate particles of cylindrical [4] or spherical [5], [7] shape are then distributed to leave the pore space for fast transport of gas.
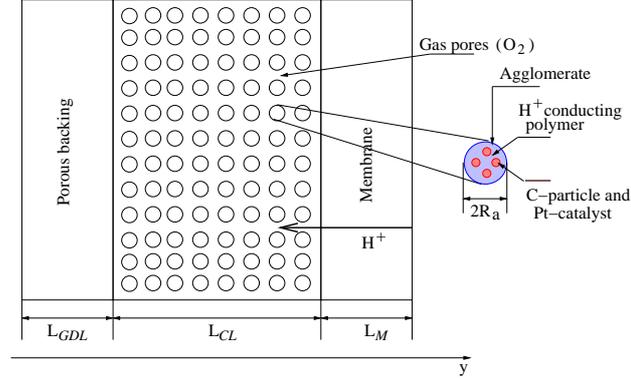
Figure 3: Agglomerates distributed in pore space.

The agglomerate model introduces a new effect for high protonic potentials. The oxygen reaching the single agglomerate reacts, due to the fast kinetics, in the vicinity of the boundary, and the interior catalyst particles can not contribute to the reaction. A dimensional analysis shows that the active layer has a size of order $1/\sqrt{e^{2.3\eta/2b}}$ for high potentials η. This leads to a production rate which is proportional to $e^{2.3\eta/2b}$ or, in other words, to a doubling of the Tafel slope b. The effect is studied e.g. in [7], where also a doubling of the Tafel slope due to the limitation of proton migration across the active layer is discussed. In [5], a similar agglomerate model is studied in the time-dependent case. Our analysis does not show the doubling of the Tafel slope due to pore scale transport limitations. On the other hand, we find a doubling of the Tafel slope as a consequence of transport limitations through the catalyst layer. The result is made precise in Section 3.2, where also the effective constant is determined.

1.2   The general pore-scale model and effective equations

In the present paper, we derive effective equations for the catalyst layer. Starting from a three-scale microscopic model with a periodic geometry and using equations for the oxygen concentration and the overpotential with boundary conditions at the catalyst particle − electrolyte interface, we deduce the effective equations for the averaged concentration and the averaged overpotential as ε tends to zero, ε being the small parameter describing the typical pore size.

We base our model on the modified equations proposed in [3] and the other models described before. Our model concentrates strictly on the cathode catalyst layer, it is single-phased and isothermal. The starting point is a surface reaction law which reads, in physical units,

$$D\partial_n C = \frac{i_0}{qF}\frac{C}{C_0}e^{2.3\eta/b} \qquad\qquad \text{molar flux, unit } \frac{mol}{sm^2}$$

$$\kappa\partial_n\eta = i_0\frac{C}{C_0}e^{2.3\eta/b} \qquad\qquad \text{protonic flux, unit } \frac{A}{m^2}$$

In order to non-dimensionalize the equations, we introduce $C^\varepsilon = \frac{C}{C_0}$, $\eta^\varepsilon = \frac{2.3\eta}{b}$, and permeabilities $\mu_\eta = \frac{2.3 i_0}{\kappa\cdot b}\cdot m$, $\mu_C = \frac{i_0}{D\cdot qF\cdot C_0}\cdot m$, where m stands for the unit of

one meter. We prove that the non-dimensional effective equations are (2.6)–(2.9). Transforming them back into physical units they read

$$D\nabla \cdot (M_C \nabla C) = |\partial\mathcal{K}|i_0 \frac{1}{qF}\frac{C}{C_0}\mathrm{e}^{2.3\eta/b} \qquad (1.2)$$

$$\kappa\nabla \cdot (M_\eta \nabla \eta) = |\partial\mathcal{K}|i_0 \frac{C}{C_0}\mathrm{e}^{2.3\eta/b} \qquad (1.3)$$

where $|\partial\mathcal{K}|$ stands, in dimensionalized units, for the total surface of catalyst particles per unit volume, a number which must be compared with γ/L from [3]. The effective diffusion matrix $M_\eta = (m_{ij})_{ij} \in \mathbb{R}^{n\times n}$ can be calculated from the cell-problem

$$m_{ij} := \int_{\mathcal{E}}(\nabla w_i^* + e_i)_j = \int_{\mathcal{E}}(\partial_j w_i^* + \delta_{ij}), \qquad (1.4)$$

where w_i^* are solutions of the diffusion problem (2.22) in the single cell. A similar expression with the solutions w_i^* of cell problem (2.27) determines M_C. In particular, all constants of the effective equation are determined. Hence the result of our analysis is an effective equation which is similar to the simplified model with a homogeneous layer, with coefficients adjusted according to the geometry of the single cell.

We wish to verify the underlying assumption of the particles being small compared to typical dimensions. We note that in [3] a particle size of order 10^{-8} is assumed, while the thickness of the layer is of order 10^{-6}. The comparison yields the desired result. It is important to note that the order of the non-dimensional coefficients is $\mu_C \sim 10^{-2}$ and $\mu_\eta \sim 10^0$. A relevant question concerns the size of the quantity $|\partial\mathcal{K}|$ which is, comparing with the effective equation in [3], of order 10^6. In our analysis, this quantity is assumed to be fixed, while the small quantity $\varepsilon \sim 10^{-8}$ is sent to zero. We emphasize that some constants must be kept fixed and large, since we are deriving an equation which contains a large coefficient — a fact that is exploited in the next step to perform a dimensional reduction.

1.3 Dimensional reduction

We consider two regimes. The first regards the case of catalyst layers of small width $L = \delta$, where we assume that the relative production rates can be written as $|\partial\mathcal{K}|\mu_C = \frac{1}{\delta}\mu_C^*$ and $|\partial\mathcal{K}|\mu_\eta = \frac{1}{\delta}\mu_\eta^*$. This assumption is met, since both $1/\delta$ and $|\partial\mathcal{K}|$ are of the order of $10^6\frac{1}{m}$. Starting from time dependent equations, we show that, in the limit $\delta \to 0$, the oxygen concentration satisfies the effective equations

$$\tau\frac{\partial C}{\partial t} - D\Delta C = 0 \qquad\qquad \text{in } \Omega_0 \qquad (1.5)$$

$$D\partial_n C = \delta|\partial\mathcal{K}|i_0\frac{1}{qF}\frac{C}{C_0}\mathrm{e}^{2.3\eta_0/b} \qquad\qquad \text{on } \Sigma_0 \qquad (1.6)$$

where Ω_0 stands for the gas diffusion layer (GDL) and Σ_0 for the GDL-PEM interface, $\tau > 0$ is a constant. The equations are derived in their dimensionless form in (3.9)-(3.10).

If, instead, the potential is large in comparison with the layer thickness, then

the effective equation for the oxygen concentration in the gas diffusion layer is

$$\tau\frac{\partial C}{\partial t} - D\Delta C = 0 \qquad\qquad\qquad \text{in } \Omega_0 \qquad (1.7)$$

$$D\partial_n C = \frac{\kappa\, b}{2.3qF}\beta_1^*\sqrt{\frac{C}{C_0}}\mathrm{e}^{2.3\eta_0/(2b)} \qquad\qquad \text{on } \Sigma_0 \qquad (1.8)$$

We refer to Proposition 1 from Section 3.2 for the definition of $\beta_1^* \approx 1.413$. The effective equation is derived in the one-dimensional setting with a constant oxygen concentration in the layer in (3.21). Interpreted in physical terms, β_1^* expresses a slope and has the unit $1/m$.

Which of the two above models, (1.6) or (1.8), is adequate for the description of the catalyst layer depends on the two quantities $e^{-2.3\eta_0/2b}$ and δ, the latter measured in meter. In the example of [3], the two quantities are comparable, the first with a range of $10^{-5} - 10^{-3}$ (depending on the Tafel slope), the second 10^{-6}. For a more precise estimate one has to take into account the large coefficient $|\partial\mathcal{K}| \sim 10^6$, which makes the penetration depth smaller by a factor of 10^3. With this factor, $10^{-3}e^{-2.3\eta_0/2b}$ can indeed be considerably smaller than δ, hence the doubling of the Tafel slope becomes visible.

A simple possibility to take into account both limiting behaviors over a range of η_0-values would be to couple the equation for the oxygen concentration with the minimum of the two expressions of (1.6) and (1.8).

2   Homogenization of the pore scale model

2.1   Pore scale geometry

Our analysis concerns boundary value problems in macroscopic domains $\Omega = (0, L_1) \times (0, L_2) \times (0, L_3) \subset \mathbb{R}^3$. We restrict here to the physically interesting case of three space dimensions. In lower dimensional cases the connectedness of the two components can not be realized; higher dimensions could be treated with our methods.

The microscopic structure of the medium is assumed to be periodic with periodicity cell $Y = (0, 1)^3$. For a sequence of small parameters $\varepsilon > 0$ we assume that the macroscopic domain is decomposed as

$$\Omega = \bigcup_{k\in I_\varepsilon} Y_k^\varepsilon + N, \quad I_\varepsilon \subset \{k \in \mathbb{Z}^3 : \varepsilon k \in \bar\Omega\}, \quad Y_k^\varepsilon = \varepsilon(k + Y),$$

where N denotes a subset of boundaries, $N \subset \bigcup_k \partial Y_k^\varepsilon$. We note that the order of the index set is $|I_\varepsilon| \sim \varepsilon^{-3}$.

The microscopic structure in a single cell Y_k^ε is sketched in Figure 4. Three major components are present in each cell, the carbon-based structure $\mathcal{S}$, the electrolyte $\mathcal{E}$, and the pore space $\mathcal{P}$. In our model we assume that $\mathcal{S}, \mathcal{E}, \mathcal{P} \subset Y$ are open and pairwise disjoint subsets such that $\bar Y = \bar{\mathcal{S}} \cup \bar{\mathcal{E}} \cup \bar{\mathcal{P}}$. We denote the structure phase in the single cell by $\mathcal{S}_k^\varepsilon := \varepsilon(\mathcal{S} + k) \subset Y_k^\varepsilon$, and the total contribution of the structure to the macroscopic domain by $\mathcal{S}^\varepsilon \subset \Omega$, the interior of the union $\bigcup_k \bar{\mathcal{S}}_k^\varepsilon$. In the same way we define $\mathcal{E}_k^\varepsilon$, $\mathcal{E}^\varepsilon$, and $\mathcal{P}_k^\varepsilon$, $\mathcal{P}^\varepsilon$. We assume that the boundaries $\partial\mathcal{S}^\varepsilon \setminus \partial\Omega$ and $\partial(\bar{\mathcal{E}}^\varepsilon \cup \bar{\mathcal{P}}^\varepsilon) \setminus \partial\Omega$ are of class $\mathcal{C}^2$ and that $\mathcal{E}^\varepsilon$ is connected.
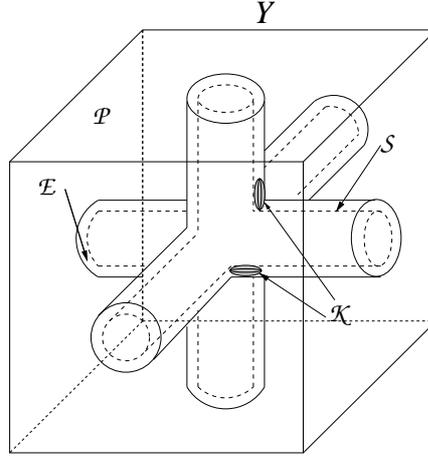
Figure 4: Sketch of a possible unit cell in the detailed pore scale model. $\mathcal{P}$ denotes the pore space, $\mathcal{E}$ the electrolyte, $\mathcal{S}$ the carbon based structure, $\mathcal{K}$ are catalyst incluions.

Responsible for the electrochemical reactions in each cell is the catalyst. It appears in form of small inclusions of platinum surrounded by electrolyte. Since the relative diameter of the catalyst inside each cell depends on ε, we do not treat the catalyst as an independent phase but rather assume that there is a point $y_c \in \mathcal{E}$ which describes the position of the center of the catalyst inclusion. The relative diameter of the catalyst particles is denoted by $r_\varepsilon > 0$. We model the situation that the total surface of the catalyst remains of order 1 when $\varepsilon \to 0$. Since, in three dimensions, the total surface is of order $|I_\varepsilon| \cdot (\varepsilon r_\varepsilon)^2$, we set $r_\varepsilon = \sqrt{\varepsilon}$. The shape of catalyst is given by an open and bounded set $\mathcal{K} \subset B_1(0) \subset \mathbb{R}^3$ with Lipschitz boundary. We set

$$\mathcal{K}_k^\varepsilon = \varepsilon(k + y_c + r_\varepsilon \mathcal{K}), \quad \mathcal{K}^\varepsilon = \bigcup_{k \in I_\varepsilon} \mathcal{K}_k^\varepsilon.$$

We will always consider ε small enough to have $\mathcal{K}^\varepsilon \subset \mathcal{E}^\varepsilon$.

Other notations are as follows. $\mathcal{H}^2$ denotes the two-dimensional Hausdorff measure and $\mathcal{L}^3$ the three-dimensional Lebesgue measure, in integrals we also write dx or dy instead of $d\mathcal{L}^3$. For sets Q, the symbol $\mathbf{1}_Q$ denotes the characteristic function which equals 1 on Q and vanishes elsewhere. The average of a function f over a set Q is denoted by $\fint_Q f := |Q|^{-1} \int_Q f$. The letter c denotes constants that are independent of ε, its value may change from one line to the next.

2.2   Pore scale equations

We introduce the domain Ω_C^ε as the subset of Ω with presence of oxygen. This is the interior of the set $\bar{\mathcal{P}}^\varepsilon \cup \bar{\mathcal{E}}^\varepsilon \backslash \mathcal{K}^\varepsilon$. The variable describing the oxygen concentration is denoted by $C^\varepsilon : \Omega_C^\varepsilon \to \mathbb{R}$. Similarly, we denote the set with the presence of protons by Ω_η^ε, defined as the interior of the set $\bar{\mathcal{E}}^\varepsilon \backslash \mathcal{K}^\varepsilon$. The exterior normal vector to Ω_η^ε is denoted by n, n points into $\mathcal{K}^\varepsilon$ on $\partial \mathcal{K}^\varepsilon$. The variable describing the protonic

potential is denoted by $\eta^\varepsilon : \Omega_\eta^\varepsilon \to \mathbb{R}$, it satisfies

$$
\begin{aligned}
\Delta\eta^\varepsilon &= 0 && \text{in } \Omega_\eta^\varepsilon \\
\partial_n\eta^\varepsilon &= -\mu_\eta C^\varepsilon \mathrm{e}^{\eta^\varepsilon} && \text{on } \partial\mathcal{K}^\varepsilon \\
\partial_n\eta^\varepsilon &= 0 && \text{on } \partial\mathcal{E}^\varepsilon \backslash \partial\Omega
\end{aligned}
\tag{2.1}
$$

The equations for the oxygen concentration C^ε are coupled to the protonic potential as follows:

$$
\begin{aligned}
\nabla \cdot (D^\varepsilon(x)\nabla C^\varepsilon) &= 0 && \text{in } \Omega_C^\varepsilon \\
D^\varepsilon(x) &= \begin{cases} D_1 & \text{if } x \in \mathcal{P}^\varepsilon \\ D_2 & \text{if } x \in \mathcal{E}^\varepsilon \end{cases} \\
(D^\varepsilon\nabla C^\varepsilon) \cdot n &= -\mu_C C^\varepsilon \mathrm{e}^{\eta^\varepsilon} && \text{on } \partial\mathcal{K}^\varepsilon \\
(D^\varepsilon\nabla C^\varepsilon) \cdot n &= 0 && \text{on } \partial\mathcal{S}^\varepsilon \setminus \partial\Omega
\end{aligned}
\tag{2.2}
$$

Here, μ_η and μ_C are the coefficients that relate the flux with the concentration.

To complete the system of equations we have to impose exterior boundary conditions on $\partial\Omega$. We decompose this macroscopic boundary as $\partial\Omega := \Gamma_M \cup \Gamma_{GDL} \cup \Gamma_{per}$ with $\Gamma_M := (0, L_1) \times (0, L_2) \times \{L_3\}$ the membrane interface, $\Gamma_{GDL} := (0, L_1) \times (0, L_2) \times \{0\}$ the gas diffusion layer interface, and $\Gamma_{per} := \partial\Omega \backslash (\Gamma_M \cup \Gamma_{GDL})$ the lateral boundaries. We impose as macroscopic boundary conditions

$$
\begin{aligned}
&\text{on } \Gamma_M: \ \eta^\varepsilon = \eta_0 \text{ given}, \ (D^\varepsilon\nabla C^\varepsilon) \cdot n = 0 \\
&\text{on } \Gamma_{GDL}: \ C^\varepsilon = C_0 \text{ given}, \ \partial_n\eta^\varepsilon = 0 \\
&\text{on } \Gamma_{per}: \ C^\varepsilon, \ \eta^\varepsilon \text{ periodic}
\end{aligned}
\tag{2.3}
$$

The periodicity assumption is made for simplicity, no-flux conditions can be treated with the same results. We assume here that η_0 and C_0 are real numbers and, since C^ε models a concentration, additionally $C_0 \geq 0$. Our results remain valid for $C_0, \eta_0 \in H^{1/2} \cap L^\infty$ with $C_0 \geq 0$.

2.3   Effective equations

We derive effective equations for our three-scale model for the catalyst layer using the method of oscillating test-functions. In order to have the unknown variables defined on all of Ω we identify the functions η^ε and C^ε with their trivial extensions. We define the volume fractions $V_\eta := \frac{|\mathcal{E}|}{|Y|}$ and $V_C := \frac{|\mathcal{P} \cup \mathcal{E}|}{|Y|}$, and the effective reaction constants $\bar{\mu}_\eta := \mu_\eta |\partial\mathcal{K}|$ and $\bar{\mu}_C := \mu_C |\partial\mathcal{K}|$.

Theorem 1. *For a subsequence holds:*

$$
\frac{1}{V_\eta}\eta^\varepsilon \rightharpoonup \eta^0 \ \ and \ \ \frac{1}{V_C}C^\varepsilon \rightharpoonup C^0 \ \ weakly \ in \ L^2(\Omega) \tag{2.4}
$$

$$
i^\varepsilon := -\mathbf{1}_{\Omega_\eta^\varepsilon}\nabla\eta^\varepsilon \rightharpoonup i^0 \ \ and \ \ j^\varepsilon := -\mathbf{1}_{\Omega_C^\varepsilon}D^\varepsilon(x)\nabla C^\varepsilon \rightharpoonup j^0 \ \ weakly \ in \ L^2(\Omega). \tag{2.5}
$$

The averaged protonic potential $\eta^0 : \Omega \to \mathbb{R}$ with flux i^0 and the averaged oxygen

concentration $C^0 : \Omega \to \mathbb{R}$ with flux j^0 satisfy, in the distributional sense in Ω,

$$\nabla \cdot i^0 + \bar{\mu}_\eta C^0 e^{\eta^0} = 0 \qquad (2.6)$$

$$i^0 = -M_\eta \nabla \eta^0 \qquad (2.7)$$

$$\nabla \cdot j^0 + \bar{\mu}_C C^0 e^{\eta^0} = 0 \qquad (2.8)$$

$$j^0 = -M_C \nabla C^0, \qquad (2.9)$$

where the effective coefficients M_η and M_C are determined with (2.24) and (2.28) below. The boundary conditions on $\partial\Omega$ remain unchanged, in the weak sense holds

$$\eta^0 = \eta_0, \; j^0 \cdot n = 0 \quad \text{on } \Gamma_M \qquad (2.10)$$

$$C^0 = C_0, \; i^0 \cdot n = 0 \quad \text{on } \Gamma_{GDL} \qquad (2.11)$$

$$C^0, \eta^0 \quad \text{periodic on } \Gamma_{per}. \qquad (2.12)$$

2.4 Proof of Theorem 1

This section is devoted to the proof of the homogenization result. We use the method of oscillating test-functions, since this method is more flexible than two-scale convergence: it is applicable, e.g., in stochastic problems [9] or in differential inclusion problems [11]. In the present setting we need the flexibility to treat the catalyst inclusions of size $\varepsilon^{3/2}$. There are two technical ingredients that are not standard: One is a result comparing averages on the catalyst surfaces with averages in the cell, exploiting the property of a finite flux (Lemma 2). The second is a modification of the lemma on compensated compactness in the setting of measure convergence (Lemma 3).

A-priori estimates

We start by collecting a priori estimates for the sequence $(C^\varepsilon, \eta^\varepsilon)$ of solutions.

1. Maximum principles. We first note that the oxygen concentration is non-negative everywhere, $C^\varepsilon \geq 0$. Indeed, the function C^ε is harmonic in the pore-space $\mathcal{P}^\varepsilon$ and in the electrolyte $\mathcal{E}^\varepsilon \setminus \bar{\mathcal{K}}^\varepsilon$. We can apply the maximum principle and find that a negative minimum must be attained on the boundary. It can not lie on $\partial\mathcal{P}^\varepsilon \cap \partial\mathcal{E}^\varepsilon$ by the continuity of the normal flux and the Hopf lemma, and not on other boundaries by the boundary conditions. The same argument implies also the upper bound,

$$0 \leq C^\varepsilon \leq C_0.$$

The function η^ε is harmonic in its domain of definition $\Omega_\eta^\varepsilon = \mathcal{E}^\varepsilon \setminus \bar{\mathcal{K}}^\varepsilon$. The maximum principle implies that the maximum of η^ε must be attained on $\partial\Omega \cup \partial\mathcal{K}^\varepsilon$. Equation (2.1)b) implies that $\partial_n \eta^\varepsilon$ is negative on $\partial\mathcal{K}^\varepsilon$, hence the maximum of η^ε can not be on this boundary, the Hopf lemma excludes a maximum on $\partial\mathcal{E}^\varepsilon \setminus \partial\Omega$. We conclude

$$\sup_{\Omega_\eta^\varepsilon} \eta^\varepsilon = \max_{\bar{\Omega}_\eta^\varepsilon} \eta^\varepsilon = \eta_0.$$

We emphasize that, at this point, we have only an upper bound for η^ε, but this is sufficient for the uniform bound of the exponential term, $\sup e^{\eta^\varepsilon} \leq e^{\eta_0}$.

2. Energy estimates. We multiply equation (2.2)a) for C^ε with $C^\varepsilon - C_0$ and integrate over the domain Ω_C^ε. The boundary integrals at the macroscopic boundaries vanish and we find

$$\int_{\Omega_C^\varepsilon} D^\varepsilon \nabla C^\varepsilon \cdot \nabla C^\varepsilon + \int_{\partial \mathcal{K}^\varepsilon} \mu_C C^\varepsilon e^{\eta^\varepsilon} (C^\varepsilon - C_0) d\mathcal{H}^2 = 0.$$

Since the diffusion coefficient is strictly positive, we find

$$\int_{\Omega_C^\varepsilon} D|\nabla C^\varepsilon|^2 + \int_{\partial \mathcal{K}^\varepsilon} \mu_C |C^\varepsilon|^2 e^{\eta^\varepsilon} \leq c \int_{\partial \mathcal{K}^\varepsilon} \mu_C C^\varepsilon e^{\eta^\varepsilon} C_0,$$

and conclude the boundedness of the left hand side. We exploited here the uniform boundedness of the two-dimensional volume of $\partial \mathcal{K}^\varepsilon$,

$$|\partial \mathcal{K}^\varepsilon| = \sum_{k \in I_\varepsilon} (\varepsilon r_\varepsilon)^{n-1} |\partial \mathcal{K}| = \frac{L_1 L_2 L_3}{\varepsilon^3} \varepsilon^2 r_\varepsilon^2 |\partial \mathcal{K}| \leq c.$$

Similarly, by a multiplication of equation (2.1)a) with $\eta^\varepsilon - \eta_0$, we find

$$\int_{\Omega_\eta^\varepsilon} |\nabla \eta^\varepsilon|^2 + \int_{\partial \mathcal{K}^\varepsilon} \mu_\eta C^\varepsilon \eta^\varepsilon e^{\eta^\varepsilon} \leq \int_{\partial \mathcal{K}^\varepsilon} \mu_\eta C^\varepsilon e^{\eta^\varepsilon} \eta_0,$$

therefore the boundedness of the left hand side and, in particular, the boundedness of $\nabla \eta^\varepsilon$ in $L^2(\Omega_\eta^\varepsilon)$, since the function ξe^ξ is bounded from below for $\xi \in \mathbb{R}$. For the L^2-estimate of η^ε we exploit the boundary condition $\eta^\varepsilon = \eta_0$ on Γ_M and Poincaré's inequality for the connected set Ω_η^ε.

We can now choose subsequences and limit functions such that $(C^\varepsilon, \eta^\varepsilon)$ together with their gradients converge weakly. For a physical normalization we use the volume fractions $V_\eta := \frac{|\mathcal{E}|}{|Y|}$ and $V_C := \frac{|\mathcal{P} \cup \mathcal{E}|}{|Y|}$ and choose limit functions η^0, C^0, i^0, and j^0 in order to have the weak convergences of (2.4)–(2.5).

Conservation laws (2.6) and (2.8)

Our aim is to derive the conservation law (2.6),

$$\nabla \cdot i^0 + \bar{\mu}_\eta C^0 e^{\eta^0} = 0. \tag{2.13}$$

Let $\varphi \in C_0^1(\Omega)$ be an arbitrary test-function. Exploiting that η^ε is harmonic in Ω_η^ε, we find

$$0 = \int_{\Omega_\eta^\varepsilon} \Delta \eta^\varepsilon \varphi = -\int_{\Omega_\eta^\varepsilon} \nabla \eta^\varepsilon \cdot \nabla \varphi + \int_{\partial \Omega_\eta^\varepsilon} \partial_n \eta^\varepsilon \varphi$$
$$= \int_\Omega i^\varepsilon \cdot \nabla \varphi - \mu_\eta \int_{\partial \mathcal{K}^\varepsilon} C^\varepsilon e^{\eta^\varepsilon} \varphi.$$

The convergence $i^\varepsilon \rightharpoonup i^0$ weakly in $L^2(\Omega)$ provides the limit of the first term. We set $u^\varepsilon := C^\varepsilon e^{\eta^\varepsilon}$ and $u^0 := C^0 e^{\eta^0}$ and note that (2.13) follows once we verify

$$\frac{1}{|\partial \mathcal{K}|} \int_{\partial \mathcal{K}^\varepsilon} u^\varepsilon \varphi \to \int_\Omega u^0 \varphi \tag{2.14}$$

for $\varepsilon \to 0$ and test-functions $\varphi \in C^0(\bar{\Omega})$. Both functions C^ε and e^{η^ε} have an L^2-bounded gradient in their domain of definition. In Lemma 5, (A.2) and (A.3) from appendix A we show that this fact implies the weak convergence of the product,

$$\frac{1}{V_\eta} u^\varepsilon \mathbf{1}_{\Omega_\eta^\varepsilon} \rightharpoonup u^0 = C^0 e^{\eta^0} \quad \text{in } L^2(\Omega).$$

Also the function u^ε has a L^2-bounded gradient in Ω_η^ε,

$$\nabla u^\varepsilon = \nabla C^\varepsilon e^{\eta^\varepsilon} + C^\varepsilon e^{\eta^\varepsilon} \nabla \eta^\varepsilon \quad \text{bounded in } L^2(\Omega_\eta^\varepsilon),$$

since C^ε and e^{η^ε} are uniformly bounded in L^∞. This fact allows to compare averages over cells with averages over small spheres inside the cells. More precisely, Lemma 1 below yields the weak convergences as measures

$$\frac{\varepsilon^3}{|\partial B_{\varepsilon\delta}|} \sum_{k \in I_\varepsilon} u^\varepsilon \; \mathcal{H}^2 \lfloor \partial B_{\varepsilon\delta}(\varepsilon(k + y_c)) - \frac{1}{V_\eta} u^\varepsilon \; \mathcal{L}^3 \lfloor \Omega_\eta^\varepsilon \rightharpoonup 0,$$

$$\frac{\varepsilon^3}{|\partial B_{\varepsilon r_\varepsilon}|} \sum_{k \in I_\varepsilon} u^\varepsilon \; \mathcal{H}^2 \lfloor \partial B_{\varepsilon r_\varepsilon}(\varepsilon(k + y_c)) - \frac{1}{|\partial \mathcal{K}|} \sum_{k \in I_\varepsilon} u^\varepsilon \; \mathcal{H}^2 \lfloor \partial \mathcal{K}_k^\varepsilon \rightharpoonup 0,$$

for $\varepsilon \to 0$ and all δ that are sufficiently small to satisfy $B_\delta(y_c) \subset \mathcal{E}$. Finally, Lemma 2 below implies that the difference of the leftmost terms above vanishes in the limit, and hence results (2.14). We remark that Lemmas 1 and 5 are very general and apply to all H^1-bounded sequences in homogenization problems, while Lemma 2 is specific to the problem and exploits the pointwise gradient bound on the interior boundaries.

Lemma 1. *Let u^ε satisfy a uniform bound $\int_{\Omega_\eta^\varepsilon} |\nabla u^\varepsilon|^2 \leq c_0$. Then, with the exponents $q_1 = 2$ and $q_2 = 3/2$, the averages*

$$\bar{u}_k^\varepsilon := \fint_{\mathcal{E}_k^\varepsilon \setminus \mathcal{K}_k^\varepsilon} u^\varepsilon, \quad \tilde{u}_k^\varepsilon := \fint_{\partial \mathcal{K}_k^\varepsilon} u^\varepsilon$$

satisfy for some constant $c = c(c_0)$

$$\sum_{k \in I_\varepsilon} \int_{\mathcal{E}_k^\varepsilon \setminus \mathcal{K}_k^\varepsilon} |u^\varepsilon - \bar{u}_k^\varepsilon|^2 \leq c\varepsilon^{q_1}, \tag{2.15}$$

$$\sum_{k \in I_\varepsilon} \int_{\partial \mathcal{K}_k^\varepsilon} |u^\varepsilon - \tilde{u}_k^\varepsilon|^2 \leq c\varepsilon^{q_2}. \tag{2.16}$$

The same result holds for the averages

$$\bar{u}_k^\varepsilon := \fint_{\partial B_{\varepsilon\delta}(\varepsilon(k+y_c))} u^\varepsilon, \quad \tilde{u}_k^\varepsilon := \fint_{\partial B_{\varepsilon r_\varepsilon}(\varepsilon(k+y_c))} u^\varepsilon.$$

The estimates are standard, for the convenience of the reader we include the proof in appendix A. Much more interesting is the following comparison, which fails for general H^1-bounded sequences u^ε due to a vanishing capacity of $\mathcal{K}^\varepsilon$.

Lemma 2. *Let u^ε be harmonic in the ball $B_{\varepsilon\delta}(\varepsilon(k+y_c))$ for every k. Furthermore, let u^ε satisfy the uniform bound $\int_{\Omega_\eta^\varepsilon} |\nabla u^\varepsilon|^2 \le c$ and let the normal flux be uniformly bounded, $|\partial_n u^\varepsilon|_{\partial\mathcal{K}^\varepsilon}| \le c$. Then averages over boundaries can be compared with each other:*

$$M_\varepsilon := \frac{\varepsilon^3}{|\partial B_{\varepsilon\delta}|} \sum_{k\in I_\varepsilon} u^\varepsilon \; \mathcal{H}^2 \lfloor \partial B_{\varepsilon\delta}(\varepsilon(k+y_c)) - \frac{\varepsilon^3}{|\partial B_{\varepsilon r_\varepsilon}|} \sum_{k\in I_\varepsilon} u^\varepsilon \; \mathcal{H}^2 \lfloor \partial B_{\varepsilon r_\varepsilon}(\varepsilon(k+y_c))$$

(2.17)

satisfies $M_\varepsilon \rightharpoonup 0$ in the weak sense of measures.

Proof. We first consider a rescaled solution $u(x) = u^\varepsilon(\varepsilon x)$ and a single rescaled cell. We investigate balls $B_\rho(y_c)$ with center in the catalyst position, and radii $\rho \in [r_\varepsilon, \delta]$, such that $r_\varepsilon \mathcal{K} \subset B_\rho(y_c) \subset \mathcal{E}$. We study the averages

$$U(\rho) := \fint_{\partial B_\rho(y_c)} u = \fint_{\partial B_1(0)} u(y_c + \rho x) \, d\mathcal{H}^2(x).$$

(2.18)

For harmonic functions in $\mathcal{E}$, the mean value theorem implies that this quantity does not depend on ρ. Instead, since the function u is harmonic only outside $\mathcal{K}$, we must do a calculation for the derivative of $U(\rho)$,

$$\frac{\partial U(\rho)}{\partial \rho} = \frac{1}{|\partial B_\rho(0)|} \int_{\partial B_\rho(y_c)} \frac{\partial u}{\partial \nu} \, d\mathcal{H}^2.$$

(2.19)

Since u is harmonic in $\mathcal{E} \setminus \mathcal{K}$, the total flux is independent of ρ,

$$\int_{\partial B_\rho(y_c)} \frac{\partial u}{\partial \nu} \, d\mathcal{H}^2 - \int_{y_c + r_\varepsilon \partial \mathcal{K}} \partial_n u \, d\mathcal{H}^2 = \int_{B_\rho(y_c) \setminus (y_c + r_\varepsilon \mathcal{K})} \Delta u = 0$$

(2.20)

by the Gauß theorem. We now scale by ε and make use of the boundedness of the flux along $\partial\mathcal{K}^\varepsilon$,

$$F^\varepsilon := \int_{\varepsilon(y_c + r_\varepsilon \partial \mathcal{K})} \partial_n u^\varepsilon \, d\mathcal{H}^2, \qquad |F^\varepsilon| \le c\,|\partial\mathcal{K}|\,|\varepsilon r_\varepsilon|^2 \le c\varepsilon^3.$$

(2.21)

We now integrate the rescaled version of (2.19) between $\varepsilon r_\varepsilon$ and $\varepsilon\delta$ to obtain

$$|U(\varepsilon\delta) - U(\varepsilon r_\varepsilon)| = \left| \int_{\varepsilon r_\varepsilon}^{\varepsilon\delta} \left(\frac{1}{\rho^{n-1}|\partial B_1|} \int_{\partial B_\rho(\varepsilon y_c)} \frac{\partial u^\varepsilon}{\partial \nu} \, d\mathcal{H}^2 \right) d\rho \right|$$

$$= \left| \int_{\varepsilon r_\varepsilon}^{\varepsilon\delta} \frac{F^\varepsilon}{\rho^{n-1}|\partial B_1|} \, d\rho \right| \le c\varepsilon^{3/2}.$$

With this estimate we can apply M_ε to a continuous function φ,

$$M_\varepsilon(\varphi) = \sum_{k\in I_\varepsilon} \frac{\varepsilon^3}{|\partial B_{\varepsilon\delta}|} \int_{\partial B_{\varepsilon\delta}(\varepsilon(k+y_c))} u^\varepsilon \; \varphi - \sum_{k\in I_\varepsilon} \frac{\varepsilon^3}{|\partial B_{\varepsilon r_\varepsilon}|} \int_{\partial B_{\varepsilon r_\varepsilon}(\varepsilon(k+y_c))} u^\varepsilon \; \varphi$$

$$= \sum_{k\in I_\varepsilon} \varepsilon^3 \varphi(\varepsilon k) \left[\frac{1}{|\partial B_{\varepsilon\delta}|} \int_{\partial B_{\varepsilon\delta}(\varepsilon(k+y_c))} u^\varepsilon - \frac{1}{|\partial B_{\varepsilon r_\varepsilon}|} \int_{\partial B_{\varepsilon r_\varepsilon}(\varepsilon(k+y_c))} u^\varepsilon \right] + o(1),$$

to conclude

$$|M_\varepsilon(\varphi)| \le c\varepsilon^{3/2} + o(1),$$

and thus the result $M_\varepsilon \rightharpoonup 0$. □

Proceeding in the same way as described above, we obtain the conservation law (2.8),

$$\nabla \cdot j^0 + \bar{\mu}_C C^0 \mathrm{e}^{\eta^0} = 0.$$

The flux relations (2.7) and (2.9)

Our aim now is to derive from the flux definition in the ε-problem $i^\varepsilon = -\mathbf{1}_{\Omega_\eta^\varepsilon} \nabla \eta^\varepsilon$ the upscaled law $i^0 = -M_\eta \nabla \eta^0$ for some geometry dependent matrix M_η. The method will be that of oscillating test-functions and compensated compactness. Some additional considerations are necessary due to a vanishing capacity of the inclusions $\mathcal{K}^\varepsilon$, as we will see below.

We start with the construction of oscillating test-functions. On the periodicity cell Y we define functions $w_j^* : Y \to \mathbb{R}$ in two steps. We first solve on $\mathcal{E}$ the problem

$$
\begin{aligned}
\nabla \cdot (\nabla w_j^* + e_j) &= 0 \text{ in } \mathcal{E} \\
n \cdot (\nabla w_j^* + e_j) &= 0 \text{ on } \partial\mathcal{E}\backslash\partial Y \\
w_j^* &\text{ is } Y\text{-periodic.}
\end{aligned}
\tag{2.22}
$$

Here e_j is the j'th unit vector in $\mathbb{R}^n = \mathbb{R}^3$. We note that, due to a constant diffusivity, there is no change of the equation if e_j is omitted in the first line. We emphasize that the second line refers to the traces on the boundary taken from the domain $\mathcal{E}$. We now continue w_j^* to all of Y by solving the problem

$$
\begin{aligned}
\Delta w_j^* &= 0 \text{ in } Y\backslash\bar{\mathcal{E}} \\
w_j^* &\text{ continuous on } \partial\mathcal{E}\backslash\partial Y \\
w_j^* &\text{ is } Y\text{-periodic.}
\end{aligned}
\tag{2.23}
$$

We note that w_j^* is bounded due to the $\mathcal{C}^2$ property of the periodic extension of $\partial\mathcal{E}$. We define the effective diffusion matrix $M_\eta = (m_{ij})_{ij} \in \mathbb{R}^{3\times3}$ as

$$m_{ji} := \int_\mathcal{E} (\nabla w_j^* + e_j)_i = \int_\mathcal{E} (\partial_i w_j^* + \delta_{ij}).
\tag{2.24}$$

The functions w_j^* allow to define, for an arbitrary function $\psi_0 = (\psi^j)_{j=1,2,3} \in \mathcal{C}_0^2(\Omega, \mathbb{R}^3)$, the family of oscillating test-functions

$$\psi_\varepsilon(x) = \sum_{j=1}^3 \psi^j(x)[\nabla_y w_j^*(x/\varepsilon) + e_j].$$

The idea now is to consider the integral

$$J_\varepsilon := \int_\Omega i^\varepsilon \cdot \psi_\varepsilon = -\int_{\Omega_\eta^\varepsilon} \nabla\eta^\varepsilon \cdot \psi_\varepsilon = \int_{\Omega_\eta^\varepsilon} \eta^\varepsilon \nabla \cdot \psi_\varepsilon - \int_{\partial\Omega_\eta^\varepsilon} \eta^\varepsilon n \cdot \psi_\varepsilon.$$

We claim the two convergences

$$J_\varepsilon = \int_\Omega i^\varepsilon \cdot \psi_\varepsilon \to \int_\Omega i^0 \cdot \psi_0, \tag{2.25}$$

$$J_\varepsilon = \int_{\Omega_\eta^\varepsilon} \eta^\varepsilon \nabla \cdot \psi_\varepsilon - \int_{\partial\Omega_\eta^\varepsilon} \eta^\varepsilon n \cdot \psi_\varepsilon \to \int_\Omega \eta^0 \, M_\eta : \nabla\psi_0, \tag{2.26}$$

where $M_\eta : \nabla\psi_0 = \sum_{ij} m_{ji}\partial_i\psi_0^j$. Once this is shown, we have derived the flux-gradient relation $i^0 = -M_\eta \cdot \nabla\eta^0$.

We start with the verification of (2.26). For the boundary integral we calculate, using the summation convention,

$$-\int_{\partial\Omega_\eta^\varepsilon} \eta^\varepsilon n \cdot \psi_\varepsilon = -\int_{\partial\mathcal{E}^\varepsilon} 0 - \int_{\partial\mathcal{K}^\varepsilon} \eta^\varepsilon(x)\psi^j(x)n(x) \cdot (\nabla w_j^*(x/\varepsilon) + e_j) \, d\mathcal{H}^2(x)$$

$$= \sum_{k \in I_\varepsilon} \int_{\partial\mathcal{K}_k^\varepsilon} \left[\eta^\varepsilon(x)\psi^j(x) - \fint_{\partial\mathcal{K}_k^\varepsilon} \eta^\varepsilon\psi^j \right] n(x) \cdot (\nabla w_j^*(x/\varepsilon) + e_j) \, d\mathcal{H}^2(x) \to 0$$

for $\varepsilon \to 0$. Here, the average can be inserted since the boundary integral vanishes as a consequence of the Gauß theorem and $\nabla \cdot (\nabla w_j^* + e_j) = 0$ in $\mathcal{K}_k^\varepsilon$. The convergence follows from the lemma on averages, inequality (2.16) in Lemma 1.

For the volume integral in (2.26) we calculate with the summation convention

$$\int_{\Omega_\eta^\varepsilon} \eta^\varepsilon \nabla \cdot \psi_\varepsilon = \int_{\Omega_\eta^\varepsilon} \eta^\varepsilon(x)\partial_i\psi^j(x)[\delta_{ij} + \partial_{y_i} w_j^*(x/\varepsilon)] \, dx$$

$$= \sum_{k \in I_\varepsilon} \int_{\mathcal{E}_k^\varepsilon \setminus \mathcal{K}_k^\varepsilon} [\eta^\varepsilon(x) - \bar{\eta}_k^\varepsilon]\partial_i\psi^j(x)[\delta_{ij} + \partial_{y_i} w_j^*(x/\varepsilon)] \, dx$$

$$+ \sum_{k \in I_\varepsilon} \bar{\eta}_k^\varepsilon \int_{\mathcal{E}_k^\varepsilon \setminus \mathcal{K}_k^\varepsilon} \partial_i\psi^j(x)[\delta_{ij} + \partial_{y_i} w_j^*(x/\varepsilon)] \, dx$$

$$\to \int_\Omega \eta^0(x)\partial_i\psi^j(x) \int_\mathcal{E} [\delta_{ij} + \partial_{y_i} w_j^*] \, dx = \int_\Omega \eta^0(x)m_{ji}\partial_i\psi^j(x) \, dx,$$

again by Lemma 1. We have thus shown the limit (2.26).

Concerning (2.25), we observe that we do have the $L^2(\Omega)$ weak convergences $i^\varepsilon \rightharpoonup i^0$ and $\psi_\varepsilon \rightharpoonup \psi_0$, where the latter follows from $\fint_Y \nabla_y w_i^*(y) \, dy = 0$. The key idea is now to use the method of compensated compactness in order to conclude the correct limit for the product $i^\varepsilon \cdot \psi_\varepsilon$.

Let us try to use compensated compactness in its standard form, as e.g. in [9], Lemma 4.3. Then we have to show that not only the curl of the second factor, but also the divergence of the first factor converges strongly in $H^{-1}(\Omega)$. But we have

$$\text{div } i^\varepsilon = -\mu_\eta C^\varepsilon \mathrm{e}^{\eta^\varepsilon} \mathcal{H}^2 \lfloor \partial\mathcal{K}^\varepsilon,$$

and this expression does not converge strongly in $H^{-1}(\Omega)$, since the capacity of the holes $\mathcal{K}^\varepsilon$ vanishes. We can therefore not conclude with the standard argument.

Nevertheless, $\nabla \cdot i^\varepsilon$ does converge in the weak sense of measures. More precisely, it converges weakly to $-\mu_\eta C^0 e^{\eta^0} |\partial\mathcal{K}|$ by Lemma 1 and Lemma 2. In order to introduce the product of i^ε with a gradient, we use the sequence of functions X_j^ε :

$\Omega \to \mathbb{R}$, $X_j^\varepsilon(x) := x_j + \varepsilon w_j^*(x/\varepsilon)$, with $X_j^\varepsilon \to X_j$ uniformly in Ω, where $X_j : x \mapsto x_j$ is the j'th coordinate function. Using $W^\varepsilon := \sum_{j=1}^3 \psi^j X_j^\varepsilon$ we may write

$$\int_\Omega i^\varepsilon \cdot \psi_\varepsilon = \int_\Omega i^\varepsilon \cdot \left[\nabla W^\varepsilon - \sum_{j=1}^3 X_j^\varepsilon \nabla \psi^j \right].$$

The uniform convergence $W^\varepsilon \to W^0 = \sum_{j=1}^3 \psi^j X_j$ allows to use the version of compensated compactness from Lemma 3 below. Since ψ_0 is compactly supported, we conclude

$$\int_\Omega i^\varepsilon \cdot \psi_\varepsilon \to \sum_{j=1}^3 \int_\Omega i^0 \cdot \left[\nabla(\psi^j X_j) - X_j \nabla \psi^j \right] = \int_\Omega i^0 \cdot \psi_0.$$

This shows (2.25) and thus $i^0 = -M_\eta \nabla \eta^0$.

The flux relation (2.9), $j^0 = -M_C \nabla C^0$, follows with the same calculations. With $D_0 := D_1 \mathbf{1}_\mathcal{P} + D_2 \mathbf{1}_\mathcal{E}$, one uses the cell solutions

$$\begin{aligned}
\nabla \cdot (D_0(\nabla w_j^* + e_j)) &= 0 \text{ in } \mathcal{E} \cup \mathcal{P} \cup (\partial\mathcal{E} \cap \partial\mathcal{P}) \\
n \cdot (D_0(\nabla w_j^* + e_j)) &= 0 \text{ on } \partial\mathcal{E} \backslash \partial Y \backslash \partial\mathcal{P} \\
w_j^* &\text{ is } Y\text{-periodic,}
\end{aligned} \tag{2.27}$$

and defines the effective diffusion matrix $M_C = (m_{ij})_{ij} \in \mathbb{R}^{3\times3}$ by

$$m_{ji} := \int_{\mathcal{E}\cup\mathcal{P}} (D_0(\nabla w_j^* + e_j))_i = \int_{\mathcal{E}\cup\mathcal{P}} D_0(\partial_i w_j^* + \delta_{ij}). \tag{2.28}$$

Regarding the last equality, we recall that in our application D is scalar-valued with two different values in $\mathcal{P}$ and $\mathcal{E}$, respectively.

With this result, the proof of Theorem 1 is complete. The verification of the macroscopic boundary conditions for the weak limits is a standard calculation; for the flux boundary conditions one uses a test-function φ which does not vanish on all boundaries in the derivation of the conservation law.

Lemma 3. *[A version of compensated compactness] Let $i^\varepsilon \rightharpoonup i^0$ weakly in $L^2(\Omega)$ such that div i^ε is a bounded sequence of measures. Let furthermore $\nabla W^\varepsilon \rightharpoonup \nabla W^0$ weakly in $L^2(\Omega)$ with*

$$W^\varepsilon \to W^0 \text{ uniformly in } \Omega.$$

Then $i^\varepsilon \cdot \nabla W^\varepsilon \rightharpoonup i^0 \cdot \nabla W^0$ in the sense of distributions.

Proof. We first observe that it suffices to consider $W^0 = 0$, since for $\psi \in C_0^\infty(\Omega)$

$$\int_\Omega i^\varepsilon \cdot \nabla W^\varepsilon \, \psi = \int_\Omega i^\varepsilon \cdot \nabla(W^\varepsilon - W^0) \, \psi + \int_\Omega i^\varepsilon \cdot \nabla W^0 \, \psi,$$

and the second integral converges to the desired limit. We now calculate, for $W^0 = 0$ and $\psi \in C_0^\infty(\Omega)$,

$$\int_\Omega i^\varepsilon \cdot \nabla W^\varepsilon \, \psi = -\int_\Omega \text{div } i^\varepsilon \, W^\varepsilon \, \psi - \int_\Omega W^\varepsilon \, i^\varepsilon \cdot \nabla \psi \to 0$$

by the $C^0(\Omega)$-convergence $W^\varepsilon \to 0$ and the boundedness of div i^ε in the dual space $C^0(\Omega)'$. $\qquad\square$

3   Effective equations for catalyst layers

In numerical calculations it is very time consuming to resolve the catalyst layer. Since the catalyst layer is much thinner than the gas diffusion layer and the membrane, in numerics it is very often treated as an infinitely thin interface between the gas diffusion layer and the membrane [1], [12].

In this section we derive two reduced models, one for moderate production rates and thin catalyst layers, the other for high potentials, in which the problem on the compound object diffusion layer plus catalyst layer is replaced by an effective equation in the gas diffusion layer which includes the effect of the catalytic reactions in its boundary condition.

3.1   Thin catalyst layers at moderate production rates

The assumption in this subsection is that the catalyst layer has a thickness δ, and that the production rates μ_η, μ_C are large, more precisely, that they are of order $1/\delta$. We have seen in the introduction of the present paper that this assumption is met in fuel cells and we write $\mu_\eta = \mu_\eta^*/\delta$ and $\mu_C = \mu_C^*/\delta$. We analyze here the limit $\delta \to 0$ and derive an effective law for the oxygen concentration. A cross section of the geometry is shown in Figure 5. The domain of interest is composed of the homogenized catalyst layer $\Omega_\delta = (0, L_1) \times (0, L_2) \times (0, \delta)$ of thickness δ, and the gas diffusion layer $\Omega_0 = (0, L_1) \times (0, L_2) \times (-L_3, 0)$. The reactions are confined to the layer Ω_δ, in the limit $\delta \to 0$ we expect an effective equation posed on the domain Ω_0 with a non-homogeneous boundary condition on $\Sigma_0 = (0, L_1) \times (0, L_2) \times \{0\}$. As additional notations we use $\Omega_{0\delta} = (0, L_1) \times (0, L_2) \times (-L_3, \delta)$ for the entire domain, $\Sigma_\delta = (0, L_1) \times (0, L_2) \times \{\delta\}$ for the boundary at the reactive side and $\Sigma_1 = (0, L_1) \times (0, L_2) \times \{-L_3\}$ for the non-reactive boundary. We always impose periodicity conditions on the lateral boundaries.
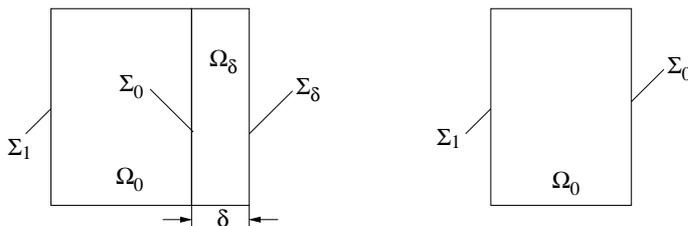
Figure 5: Geometry of the δ-problem and the effective domain.

We study the macroscopic equations that were obtained in the previous section for the overpotential η and the oxygen concentration C. To emphasize the dependence on δ we write $\eta^\delta : \Omega_\delta \to \mathbb{R}$ for the overpotential and $C^\delta : \Omega_{0\delta} \to \mathbb{R}$ for the oxygen concentration. We study the time dependent equations for C since transport limitations become important in the gas diffusion layer, which is much thicker than the catalyst layer. We therefore analyze the following equations for

the overpotential

$$-\nabla \cdot (M_\eta \nabla \eta^\delta) = -\frac{1}{\delta} \mu_\eta^* C^\delta \mathrm{e}^{\eta^\delta} \qquad \text{in } \Omega_\delta \qquad (3.1)$$

$$\eta^\delta = \eta_0 \qquad \text{on } \Sigma_\delta \qquad (3.2)$$

$$n \cdot (M_\eta \nabla \eta^\delta) = 0 \qquad \text{on } \Sigma_0 \qquad (3.3)$$

and, for the oxygen concentration,

$$\frac{\partial C^\delta}{\partial t} - \nabla \cdot (M_C \nabla C^\delta) = -\frac{1}{\delta} \mu_C^* C^\delta \mathrm{e}^{\eta^\delta} \mathbf{1}_{\Omega_\delta} \qquad \text{in } \Omega_{0\delta} \qquad (3.4)$$

$$n \cdot (M_C \nabla C^\delta) = 0 \qquad \text{on } \Sigma_\delta \qquad (3.5)$$

$$C^\delta = C_0 \qquad \text{on } \Sigma_1 \qquad (3.6)$$

In order to derive effective equations rigorously, we introduce an averaged overpotential as

$$\bar{\eta}^\delta = \int_0^\delta \eta^\delta(x_1, x_2, y)\, dy, \qquad \bar{\eta}^\delta : \Sigma_0 \to \mathbb{R}.$$

We will identify every function $\varphi : \Sigma_\delta \to \mathbb{R}$ with $\varphi : \Sigma_0 \to \mathbb{R}$.

Theorem 2. *[Effective equations in thin catalyst layers] Let η^δ, C^δ be a weak solution of (3.1)–(3.6) on a time interval $(0, T)$ with smooth initial values, and let the boundary conditions be given by $\eta_0 \in L^2(0, T; H^1(\Sigma_0)) \cap L^\infty((0, T) \times \Sigma_0)$ and $C_0 \in L^2(0, T; H^1(\Omega_0)) \cap L^\infty((0, T) \times \Omega_0)$. Then, for every sequence $\delta \to 0$ there holds*

$$\bar{\eta}^\delta \to \eta_0 \quad \text{strongly in } L^2(0, T; L^2(\Sigma_0)) \qquad (3.7)$$

$$C^\delta \Big|_{\Omega_0} \rightharpoonup C^0 \quad \text{weakly in } L^2(0, T; H^1(\Omega_0)) \qquad (3.8)$$

where C^0 satisfies weakly the effective equations

$$\frac{\partial C^0}{\partial t} - \nabla \cdot (M_C \nabla C^0) = 0 \qquad \text{in } (0, T) \times \Omega_0 \qquad (3.9)$$

$$n \cdot (M_C \nabla C^0) = -\mu_C^* C^0\, e^{\eta^0} \qquad \text{on } (0, T) \times \Sigma_0 \qquad (3.10)$$

with the other boundary conditions remaining unchanged.

Proof. We start with the a priori estimates for the sequence (C^δ, η^δ) of solutions. The maximum principle implies the boundedness of C^δ in L^∞ and an upper bound for η^δ.

We identify the boundary values η_0 with a function $\eta_0(x_1, x_2, y) = \eta_0(x_1, x_2)$ and multiply (3.1) with $\eta^\delta - \eta_0$. An integration over Ω_δ yields, at any time instance,

$$\int_{\Omega_\delta} M_\eta \nabla \eta^\delta \cdot \nabla \eta^\delta + \frac{1}{\delta} \int_{\Omega_\delta} \mu_\eta^* C^\delta \mathrm{e}^{\eta^\delta} \eta^\delta \leq \int_{\Omega_\delta} M_\eta \nabla \eta^\delta \cdot \nabla \eta_0 + \frac{1}{\delta} \int_{\Omega_\delta} \mu_\eta^* C^\delta \mathrm{e}^{\eta^\delta} \eta_0.$$

The maximum principle provides the boundedness of the second integrals of both sides and we conclude that the $L^2(0, T; H^1(\Omega_\delta))$-norm of η^δ is bounded. In particular, by Poincaré's inequality and the trace theorem, we have, at any time instance,

$$\|\bar{\eta}^\delta - \eta_0\|_{L^2(\Sigma_0)} \leq c\delta \|\eta^\delta\|_{H^1(\Omega_\delta)},$$

and therefore the strong convergence of $\bar{\eta}^\delta$, i.e. (3.7).

We now multiply (3.4) with $C^\delta - C_0$ and integrate over $\Omega_{0\delta}$. Using a cut-off function we may assume that C_0 vanishes on $\bar{\Omega}_\delta$ and we obtain

$$\int_{\Omega_{0\delta}} \frac{\partial C^\delta}{\partial t}(C^\delta - C_0) + \int_{\Omega_{0\delta}} M_C \nabla C^\delta \cdot \nabla C^\delta$$
$$+ \int_{\Omega_\delta} \frac{1}{\delta}\mu_C^* C^\delta \mathrm{e}^{\eta^\delta} C^\delta = \int_{\Omega_0} M_C \nabla C^\delta \cdot \nabla C_0.$$

This yields the $L^2(0,T; H^1(\Omega_0))$ boundedness of $C^\delta|_{\Omega_0}$. In particular, we can select a weakly convergent subsequence with a limit as in (3.8).

The equations for C^0. Multiplication of (3.4) with $\varphi \in \mathcal{D}((0,T) \times (0,L_1) \times (0,L_2) \times (-L_3,1))$ and an integration over $(0,T) \times \Omega_{0\delta}$ yields

$$-\int_0^T \int_{\Omega_{0\delta}} C^\delta \partial_t \varphi + \int_0^T \int_{\Omega_{0\delta}} M_C \nabla C^\delta \cdot \nabla \varphi + \int_0^T \int_{\Omega_\delta} \frac{1}{\delta}\mu_C^* C^\delta \mathrm{e}^{\eta^\delta} \varphi = 0. \quad (3.11)$$

For the first two integrals, the limits exist and coincide with the formal limits; this is an immediate consequence of the boundedness and the weak convergence of C^δ. Lemma 4 below provides the nontrivial limit

$$\int_0^T \int_{\Omega_\delta} \frac{1}{\delta}\mu_C^* C^\delta \mathrm{e}^{\eta^\delta} \varphi \to \int_0^T \int_{\Sigma_0} \mu_C^* C^0 \mathrm{e}^{\eta^0} \varphi$$

for $\delta \to 0$. Thus, the limit equation of (3.11) is

$$-\int_0^T \int_{\Omega_0} C^0 \partial_t \varphi + \int_0^T \int_{\Omega_0} M_C \nabla C^0 \cdot \nabla \varphi + \int_0^T \int_{\Sigma_0} \mu_C^* C^0 \mathrm{e}^{\eta^0} \varphi = 0,$$

which is the weak form of (3.9)-(3.10). $\qquad\qquad\qquad\qquad\qquad\qquad\qquad \Box$

In the above proof we used a convergence result which is the consequence of the fact that η^δ has small variations in the thin layer Ω_δ.

Lemma 4. *Let η^δ, C^δ be the solutions of (3.1)–(3.6) as in Theorem 2 with limits η^0 and C^0, and let $\varphi \in C_0^0((0,T) \times (0,L_1) \times (0,L_2) \times (-L_3,1))$. Then*

$$\int_0^T \fint_{\Omega_\delta} C^\delta e^{\eta^\delta} \varphi \to \int_0^T \int_{\Sigma_0} C^0 e^{\eta_0} \varphi \qquad \text{for } \delta \to 0.$$

Proof. First step. We claim that the averages of C^δ converge weakly,

$$\fint_0^\delta C^\delta(.,y)\, dy \rightharpoonup C^0\Big|_{\Sigma_0} \quad \text{weakly in } L^2((0,T) \times \Sigma_0) \text{ for } \delta \to 0. \qquad (3.12)$$

Indeed, the trace theorem provides the boundedness of every restriction of C^δ to a two-dimensional subset $\Sigma_y := \{(x,y) : x \in \Sigma_0\}$ with the bound

$$\|\mathrm{trace}_{\Sigma_y} C^\delta\|_{L^2} \le c\|C^\delta\|_{H^1(\Omega_{0\delta})}.$$

Jensen's inequality implies that also the average of traces is bounded in L^2,

$$\left\|\fint_0^\delta C^\delta(.,y)\, dy\right\|_{L^2(\Sigma_0)} = \left\|\frac{1}{\delta}\int_0^\delta \mathrm{trace}_{\Sigma_y} C^\delta\right\|_{L^2(\Sigma_0)} \le \frac{1}{\delta}\int_0^\delta \|\mathrm{trace}_{\Sigma_y} C^\delta\|_{L^2(\Sigma_0)} \le c.$$

The boundedness of $\fint_0^\delta C^\delta$ in $L^2((0,T) \times \Sigma_0)$ allows to choose a subsequence and a function $g \in L^2((0,T) \times \Sigma_0)$ with

$$\fint_0^\delta C^\delta \rightharpoonup g \text{ weakly in } L^2((0,T) \times \Sigma_0) \text{ for } \delta \to 0.$$

It remains to identify $g = \text{trace}_{\Sigma_0} C^0$. To this end we let $\psi \in C_0^1((0,T) \times (0,L_1) \times (0,L_2) \times (-L_3, 1))$ be an arbitrary function and calculate

$$\int_0^T \int_{\Sigma_0} \left(\fint_0^\delta C^\delta \right) \psi = \int_0^T \frac{1}{\delta} \int_0^\delta \int_{\Sigma_y} C^\delta \psi + O(\delta)$$

$$= \int_0^T \frac{1}{\delta} \int_0^\delta \int_{(0,L_1) \times (0,L_2) \times (-L_3, y)} \frac{\partial}{\partial y} (C^\delta \psi) + O(\delta)$$

$$\to \int_0^T \int_{\Omega_0} \frac{\partial}{\partial y} (C^0 \psi) = \int_0^T \int_{\Sigma_0} C^0 \Big|_{\Sigma_0} \psi.$$

The left hand side converges to $\int_0^T \int_{\Sigma_0} g \psi(.,0)$, we have therefore identified g and (3.12) is shown.

Second step. For the auxiliary function

$$u_\delta(t, x_1, x_2, y) = e^{\eta^\delta(t,x_1,x_2,y)} - e^{\bar{\eta}^\delta(t,x_1,x_2)}$$

we claim that

$$\int_0^T \frac{1}{\delta} \int_{\Omega_\delta} |u_\delta|^2 \leq c \int_0^T \delta \int_{\Omega_\delta} |\nabla u_\delta|^2 \longrightarrow 0. \tag{3.13}$$

It suffices to show the estimate from (3.13) for continuous functions η^δ which satisfy by Rolle's theorem

$$|u_\delta(x_1, x_2, y)| \leq \int_0^\delta |\nabla u_\delta(x_1, x_2, y')| \, dy'.$$

We can therefore calculate

$$\frac{1}{\delta} \int_{\Omega_\delta} |u_\delta|^2 \leq \frac{1}{\delta} \int_{\Omega_\delta} \left(\int_0^\delta |\nabla u_\delta| \right)^2 \leq \frac{1}{\delta} \int_{\Omega_\delta} \delta \int_0^\delta |\nabla u_\delta|^2 = \delta \int_{\Omega_\delta} |\nabla u_\delta|^2$$

which, together with the a priori estimate for $\eta^\delta \in L^2(0,T;H^1(\Omega_\delta))$ and the upper bound for η^δ, provides (3.13).

Third step. We can now conclude the calculation for the product.

$$\left(\fint_0^\delta C^\delta e^{\eta^\delta} \right)(x_1, x_2) = \fint_0^\delta C^\delta e^{\bar{\eta}^\delta} + \fint_0^\delta C^\delta [e^{\eta^\delta} - e^{\bar{\eta}^\delta}] = e^{\bar{\eta}^\delta} \fint_0^\delta C^\delta + \fint_0^\delta C^\delta u_\delta,$$

and therefore, by (3.13),

$$\int_0^T \int_{\Sigma_0} \left(\fint_0^\delta C^\delta e^{\eta^\delta} \right) \varphi = \int_0^T \int_{\Sigma_0} \left\{ \left(\fint_0^\delta C^\delta \right)(x_1, x_2) e^{\bar{\eta}^\delta(x_1,x_2)} \varphi(x_1, x_2) \right\} + o(1).$$

The weak $L^2((0,T) \times \Sigma_0)$-convergence of the C^δ-average of (3.12) together with the strong convergence of $\bar{\eta}^\delta$ provides the result. $\qquad\square$

3.2   Thin catalyst layers at high potentials

In order to verify the effect of a doubling of the Tafel slope in the limit of high potentials, we analyze the following one-dimensional system in which we assume a constant oxygen concentration $C \equiv C_0$ in the whole catalyst layer $(0, \delta)$. The equation for η then reads (see Figure 6):

$$\partial_x^2 \eta = C e^{\eta} \quad \text{in } (0, \delta) \tag{3.14}$$

$$\eta(0) = \eta_0 \tag{3.15}$$

$$\partial_x \eta(\delta) = 0. \tag{3.16}$$

We are interested in an expression for the production rate

$$F_{\eta_0} := -\partial_x \eta(0) = \int_0^{\delta} C e^{\eta} \tag{3.17}$$

in the limit $\eta_0 \to \infty$. The expression is given by (3.21) from Proposition 1 below. Note that we find the effect of a double Tafel slope, since the production rate F_{η_0} is proportional to $e^{\eta_0/2}$ rather than e^{η_0}.

Figure 6: Sketch of solutions of system (3.14)-(3.16)

Proposition 1. *Consider the ODE*

$$\partial_y^2 \theta - \frac{1}{\theta}(\partial_y \theta)^2 = C\theta^2 \tag{3.18}$$

$$\theta(0) = 1 \tag{3.19}$$

$$\partial_y \theta(0) = -\beta, \tag{3.20}$$

for $\theta = \theta(y)$ and $y \in \mathbb{R}_+$, with $\beta, C \in \mathbb{R}_+$ given. There exists $\beta^* \in (0, \infty)$ depending on C, $\beta^* = \beta^*(C)$, with the property:

1. *For $\beta > \beta^*$, the solution $\theta = \theta_\beta$ of (3.18)-(3.20) is monotonically decreasing.*

2. *For $\beta < \beta^*$, the solution $\theta = \theta_\beta$ of (3.18)-(3.20) is positive and unbounded.*

The dependence on C is given as $\beta^*(C) = \beta_1^* \sqrt{C}$ with $\beta_1^* := \beta^*(1) \approx 1.413$. The production rate F_{η_0} defined in (3.17) satisfies

$$\frac{F_{\eta_0}}{e^{\eta_0/2}} \longrightarrow \beta_1^* \sqrt{C} \quad \text{for } \eta_0 \to \infty. \tag{3.21}$$

Proof. Part 1: Existence of $\beta^* \in (0, \infty)$. We define

$$\beta^* := \sup\{\beta \geq 0 \mid \text{solution } \theta_\beta \text{ is unbounded}\}$$

The set is nonempty, since the solution for $\beta = 0$, i.e. $\partial_y \theta_\beta(0) = 0$ is monotonically increasing and unbounded. We verify $\beta^* < \infty$ with the following result.

Claim: There exists a number $\bar{\beta} > 0$ depending on C such that the solutions θ_β with $\beta > \bar{\beta}$ satisfy:

$$\theta_\beta(y) \leq \mathrm{e}^{-\frac{\beta}{2}y}, \qquad \forall y \in \mathbb{R}_+ \tag{i}$$

$$\left| \frac{\partial_y \theta_\beta}{\theta_\beta} \right| > \frac{\beta}{2}, \qquad \forall y \in \mathbb{R}_+. \tag{ii}$$

Proof of the claim. Assume that (i) is satisfied on $(0, y_0)$. We claim that this implies that also (ii) is satisfied until y_0. Indeed,

$$\partial_y \left(\frac{\partial_y \theta_\beta}{\theta_\beta} \right) = \frac{\partial_y^2 \theta_\beta}{\theta_\beta} - \frac{(\partial_y \theta_\beta)^2}{(\theta_\beta)^2} = C \theta_\beta \leq C \mathrm{e}^{-\frac{\beta}{2}y}$$

together with $\frac{\partial_y \theta_\beta}{\theta_\beta}(0) = -\beta$ yields (ii) for β large enough.

On the other hand, let (ii) be satisfied until y_0. Then

$$\partial_y \theta_\beta < -\frac{\beta}{2} \theta_\beta$$

implies that (i) is strictly satisfied until y_0 and is, by continuity, also satisfied on a larger interval. We conclude that (i) and (ii) are satisfied on $\mathbb{R}_+$ and have thus verified the claim.

The dependence $\beta^*(C) = \beta^*(1)\sqrt{C}$ follows immediately by a scaling argument with the substitution $z = \sqrt{C}y$.

Part 2: We have to clarify the relation between the θ - equation and the production rate F_{η_0} of the η - equation. We introduce the large number $m := \delta \mathrm{e}^{\eta_0/2}$ and denote by $\eta = \eta_m$ the solution of (3.14) - (3.16). Setting

$$\theta = \theta_m := \frac{\mathrm{e}^\eta}{\mathrm{e}^{\eta_0}}, \quad y := x \mathrm{e}^{\eta_0/2}$$

we can calculate

$$\partial_x^2[\eta] = \partial_x^2[\log(\theta \mathrm{e}^{\eta_0})] = \partial_x \left[\frac{\partial_x \theta}{\theta} \right] = \mathrm{e}^{\eta_0} \partial_y \left[\frac{\partial_y \theta}{\theta} \right] = \mathrm{e}^{\eta_0} \left[\frac{\partial_y^2 \theta}{\theta} - \frac{(\partial_y \theta)^2}{\theta^2} \right]$$

$$\overset{!}{=} C \mathrm{e}^\eta = C \theta \mathrm{e}^{\eta_0}.$$

We see that the η - equation is equivalent to (3.18). Therefore $\theta = \theta_m$ solves (3.18)-(3.20) with an unknown value of $\beta = \beta_m$, determined by the boundary condition $\partial_y \theta_m(m) = 0$. We note that $\theta_m \geq 0$ holds by definition of θ and that θ_m is monotonically decreasing, since $\partial_y \theta(y_0) = 0$ for some $y_0 < m$ implies $\partial_y \theta > 0$ on $(y_0, m]$.

Then $\partial_y \theta_m(m) = 0$ implies $\beta_m \leq \beta^*$, since the continuation of θ_m beyond m is necessarily unbounded. For a subsequence $m \to \infty$ and a limiting value $\beta_\infty \leq \beta^*$ we find $\beta_m \to \beta_\infty$, and $\theta_m \to \theta_\infty$ uniformly on compact subsets for some limiting function θ_∞, which is bounded by 1, since all θ_m are. This implies $\beta_\infty \geq \beta^*$ and we have thus verified $\beta_m \longrightarrow \beta_\infty$.
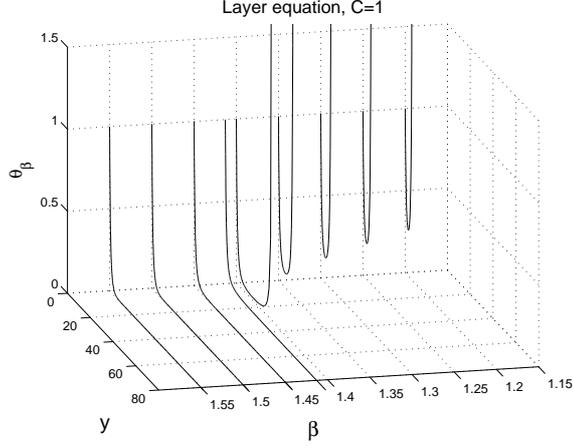
Figure 7: Numerical solutions of system (3.18)-(3.20)

The production rate is

$$F_{\eta_0} = -\partial_x \eta(0) = -\mathrm{e}^{\eta_0/2} \partial_y [\log(\theta_m \mathrm{e}^{\eta_0})] \Big|_{y=0} = -\mathrm{e}^{\eta_0/2} \frac{\partial_y \theta_m(0)}{\theta_m(0)},$$

hence

$$\frac{F_{\eta_0}}{\mathrm{e}^{\eta_0/2}} = -\partial_y \theta_m(0) = \beta_m \underset{m\to\infty}{\longrightarrow} \beta^*.$$

This was the claim. $\square$

Numerically, we determined the value $\beta_1^* = 1.413 \pm 0.002$. We refer to Figure 7 for the shape of solutions for various values of β.

A   Proof of the homogenization Lemmas

Proof of Lemma 1. Proof of (2.15).
    We study a domain of integration $\mathcal{E}_r := \mathcal{E} \setminus (y_c + r\mathcal{K})$ for real numbers $r > 0$ with $r \leq r_0$, where $y_c + r_0\mathcal{K} \subset \mathcal{E}$. For any $u \in H^1(\mathcal{E}_r)$ with average $\bar{u}$ the Poincaré-Wirtinger inequality states that

$$\int_{\mathcal{E}_r} |u - \bar{u}|^2 \, dy \leq c \int_{\mathcal{E}_r} |\nabla u|^2 \, dy.$$

In this inequality, c can be chosen independent of $r \leq r_0$, as can be seen by a simple contradiction argument exploiting compactness. By a change of variables $x = \varepsilon y$, we find for any function $u \in H^1(\mathcal{E}_k^\varepsilon \setminus \mathcal{K}_k^\varepsilon)$

$$\int_{\mathcal{E}_k^\varepsilon \setminus \mathcal{K}_k^\varepsilon} |u - \bar{u}_k|^2 \frac{dx}{\varepsilon^3} \leq c \int_{\mathcal{E}_k^\varepsilon \setminus \mathcal{K}_k^\varepsilon} \varepsilon^2 |\nabla u|^2 \frac{dx}{\varepsilon^3}.$$

Summing over all $k \in I_\varepsilon$ we obtain

$$\sum_{k \in I_\varepsilon} \int_{\mathcal{E}_k^\varepsilon \setminus \mathcal{K}_k^\varepsilon} |u - \bar{u}_k|^2 \, dx \leq c\varepsilon^2 \int_{\Omega_\eta^\varepsilon} |\nabla u|^2 \, dx,$$

which was the claim in (2.15).

Proof of (2.16). For any $u \in H^1(2\mathcal{K})$, the trace theorem yields for the average $\tilde{u} := \fint_{\partial \mathcal{K}} u$ the estimate

$$\int_{\partial \mathcal{K}} |u - \tilde{u}|^2 \, d\mathcal{H}^2 \leq c \int_{2\mathcal{K} \backslash \mathcal{K}} |\nabla u|^2 \, dy.$$

By a change of variables $x = \varepsilon(k + y_c + r_\varepsilon y)$ with $dx = (\varepsilon^{3/2})^3 dy$, we find

$$\int_{\partial \mathcal{K}_k^\varepsilon} |u - \tilde{u}_k|^2 \, \frac{d\mathcal{H}^2}{\varepsilon^3} \leq c \int_{\mathcal{E}_k^\varepsilon \backslash \mathcal{K}_k^\varepsilon} (\varepsilon^{3/2})^2 |\nabla u|^2 \, \frac{dx}{\varepsilon^{9/2}}.$$

Summing over all $k \in I_\varepsilon$ we obtain:

$$\sum_{k \in I_\varepsilon} \int_{\partial \mathcal{K}_k^\varepsilon} |u - \tilde{u}_k|^2 d\mathcal{H}^2 \leq \sum_{k \in I_\varepsilon} c\varepsilon^{3/2} \int_{\mathcal{E}_k^\varepsilon \backslash \mathcal{K}_k^\varepsilon} |\nabla u|^2 \, dx,$$

which was the claim in (2.16). The result for the other averages is shown with the same calculations. $\square$

Lemma 5. *Let v^ε be a sequence in $L^2(\Omega)$ which vanishes outside the set Ω_η^ε, a periodically perforated domain with a limiting relative volume $V_\eta = |\mathcal{E}|/|Y| = \lim_{\varepsilon \to 0} |\Omega_\eta^\varepsilon|/|\Omega|$. We assume a uniform H^1-bound and a weak convergence*

$$\int_{\Omega_\eta^\varepsilon} |\nabla v^\varepsilon|^2 \leq c, \qquad \frac{1}{V_\eta} v^\varepsilon \rightharpoonup v^0 \text{ weakly in } L^2(\Omega).$$

Given the sequence v^ε we may construct a piecewise constant interpolation $\bar{v}^\varepsilon \in L^2(\Omega)$ by setting, for $k \in I_\varepsilon \subset \mathbb{Z}^3$ and with $Y_k^\varepsilon = \varepsilon(k + Y)$,

$$\bar{v}_k^\varepsilon := \fint_{Y_k^\varepsilon \cap \Omega_\eta^\varepsilon} v^\varepsilon \in \mathbb{R}, \qquad \bar{v}^\varepsilon := \sum_{k \in I_\varepsilon} \bar{v}_k^\varepsilon \mathbf{1}_{Y_k^\varepsilon}.$$

An approximating sequence $\hat{v}^\varepsilon \in H^1(\Omega)$ can be constructed as a continuous and piecewise linear interpolation. We choose a regular grid of tetrahedra with vertices $\{\varepsilon k : k \in I_\varepsilon\}$, set $\hat{v}^\varepsilon(\varepsilon k) = \bar{v}_k^\varepsilon$ for all $k \in I_\varepsilon$ and define $\hat{v}^\varepsilon$ as the piecewise linear interpolation of these values.

Then there holds

$$\bar{v}^\varepsilon \to v^0 \text{ and } \hat{v}^\varepsilon \to v^0 \text{ strongly in } L^2(\Omega). \tag{A.1}$$

The above construction allows to conclude limits of nonlinear expressions. For a sequence v^ε as above, which is additionally bounded from above, there holds

$$\frac{1}{V_\eta} \mathbf{1}_{\Omega_\eta^\varepsilon} e^{v^\varepsilon} \rightharpoonup e^{v^0} \tag{A.2}$$

in the sense of measures. Furthermore, let $w^\varepsilon : \Omega \to \mathbb{R}$ be a sequence of functions that vanish outside Ω_C^ε, with ∇w^ε bounded in $L^2(\Omega_C^\varepsilon)$ and with weak limit $w^\varepsilon \rightharpoonup V_C w^0$ in $L^2(\Omega)$. For $\Omega_\eta^\varepsilon \subset \Omega_C^\varepsilon$ we find

$$\frac{1}{V_\eta} v^\varepsilon w^\varepsilon \rightharpoonup v^0 w^0 \tag{A.3}$$

in the sense of measures.

Proof. Jensen's inequality implies that the L^2-norm of $\bar{v}^\varepsilon$ is bounded. For a subsequence we may therefore assume the weak convergence to a limit $g \in L^2(\Omega)$. In order to identify the limit we calculate for a continuous function $\varphi : \bar{\Omega} \to \mathbb{R}$

$$\int_\Omega g\varphi \leftarrow \int_\Omega \bar{v}^\varepsilon \varphi = \sum_{k \in I_\varepsilon} \int_{Y_k^\varepsilon} \bar{v}^\varepsilon \varphi = \sum_{k \in I_\varepsilon} \varphi(\varepsilon k) \varepsilon^3 \fint_{Y_k^\varepsilon \cap \Omega_\eta^\varepsilon} v^\varepsilon + o(1)$$
$$= \frac{1}{V_\eta} \int_{\Omega_\eta^\varepsilon} v^\varepsilon \varphi + o(1) \to \int_\Omega v^0 \varphi,$$

and we therefore have $\bar{v}^\varepsilon \rightharpoonup v^0$ in $L^2(\Omega)$. In the proof of Lemma 1 we have seen an estimate for the difference $v^\varepsilon - \bar{v}^\varepsilon$,

$$\int_{\Omega_\eta^\varepsilon} |v^\varepsilon - \bar{v}^\varepsilon|^2 \leq c\varepsilon^2.$$

In the proof of this inequality we can also integrate over $3 \times 3 \times 3$ neighboring cells Y_k^ε and find, for $e \in \{0,1\}e_1 + \{0,1\}e_2 + \{0,1\}e_3$, the estimate

$$\sum_{k \in I_\varepsilon} \int_{Y_k^\varepsilon} \left| \frac{\bar{v}_{k+e}^\varepsilon - \bar{v}_k^\varepsilon}{\varepsilon} \right|^2 \leq c. \tag{A.4}$$

In particular, $\|\hat{v}^\varepsilon - \bar{v}^\varepsilon\|_{L^2}^2 \leq c\varepsilon^2$ and thus also $\hat{v}^\varepsilon \rightharpoonup v^0$ in $L^2(\Omega)$. Since the gradient of $\hat{v}^\varepsilon$ can be estimated by the difference quotients between nearest neighbors of the grid, we conclude the uniform bound $\int_\Omega |\nabla \hat{v}^\varepsilon|^2 \leq c$. This uniform $H^1(\Omega)$-estimate implies the strong convergence $\hat{v}^\varepsilon \to v^0$ in $L^2(\Omega)$. Since they are close to each other in norm, this also implies the strong convergence $\bar{v}^\varepsilon \to v^0$ in $L^2(\Omega)$ and thus (A.1).

We can now calculate nonlinear terms as follows. For a continuous function φ holds

$$\int_{\Omega_\eta^\varepsilon} e^{v^\varepsilon} \varphi = \sum_{k \in I_\varepsilon} \int_{Y_k^\varepsilon \cap \Omega_\eta^\varepsilon} e^{v^\varepsilon} \varphi(\varepsilon k) + o(1)$$
$$= \sum_{k \in I_\varepsilon} \int_{Y_k^\varepsilon \cap \Omega_\eta^\varepsilon} \left\{ (e^{v^\varepsilon} - e^{\bar{v}_k^\varepsilon}) \varphi(\varepsilon k) \right\} + \sum_{k \in I_\varepsilon} \int_{Y_k^\varepsilon \cap \Omega_\eta^\varepsilon} e^{\bar{v}_k^\varepsilon} \varphi(\varepsilon k) + o(1)$$
$$\to V_\eta \int_\Omega e^{v^0} \varphi,$$

since $|e^{v^\varepsilon} - e^{\bar{v}_k^\varepsilon}| \leq c|v^\varepsilon - \bar{v}^\varepsilon|$ by the boundedness of v^ε, and since the strong convergence of $\bar{v}^\varepsilon \to v^0$ implies the strong convergence $e^{\bar{v}^\varepsilon} \to e^{v^0}$. We have thus verified (A.2).

In order to show the convergence (A.3) of products, we calculate, for a continuous function φ,

$$\int_{\Omega_\eta^\varepsilon} v^\varepsilon w^\varepsilon \varphi = \sum_{k \in I_\varepsilon} \int_{Y_k^\varepsilon \cap \Omega_\eta^\varepsilon} v^\varepsilon w^\varepsilon \varphi(\varepsilon k) + o(1)$$
$$= \sum_{k \in I_\varepsilon} \int_{Y_k^\varepsilon \cap \Omega_\eta^\varepsilon} \{ (v^\varepsilon - \bar{v}_k^\varepsilon)(w^\varepsilon - \bar{w}_k^\varepsilon) \varphi(\varepsilon k) \} + \sum_{k \in I_\varepsilon} \int_{Y_k^\varepsilon \cap \Omega_\eta^\varepsilon} \bar{v}_k^\varepsilon \bar{w}_k^\varepsilon \varphi(\varepsilon k) + o(1)$$
$$= O(\varepsilon^2) + V_\eta \int_\Omega \bar{v}^\varepsilon \bar{w}^\varepsilon \varphi + o(1) \to V_\eta \int_\Omega v^0 w^0 \varphi.$$

This was the claim. $\qquad \square$

B List of symbols and typical values

Symbol	Meaning	Unit	Values
C	molar concentration of gas specie (O_2)	mol/m^3	
η	local overpotential	V	
i	transfer current density at cathode	A/m^3	
q	total number of electrons consumed in the ORR per oxygen molecule		4
F	Faraday's constant	As/mol	96487
C_0	reference molar concentration of O_2	mol/m^3	3.39 [4], 6.2 [2]
D	diffusion coefficient	m^2/s	$\sim 10^{-6}$ [2], 5.2197×10^{-6} [13]
κ	ionic conductivity in the electrolyte	A/Vm	1 [3], 0.3 [7]
i_0	reference current density	A/m^2	$10^{-6}-1.4\times10^{-2}$ [3] 10^{-2} [14], 4.4×10^{-7} [10]
γ	real catalyst area per geometric area	$m^2\, m^{-2}$	0.4 [3]
L	active layer thickness	m	10^{-6} [3], 0.287×10^{-4} [6], 10^{-5} [5]
$\dfrac{\gamma}{L}$	effective catalyst area per unit volume	$1/m$	4×10^5 [3]
η_0	total overpotential	V	0.6 [3]
b	Tafel slope	V	$0.06 - 0.12$ [3] 0.0529 [5], 0.0874 [5]
d	mean particle diameter	m	10^{-8} [3]
a	interparticle distance	m	10^{-7} [3]

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