

Upscaled model for diffusion and serial reduction pathways in porous electrodes

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Abstract

Multiscale modelling of coupled diffusion and serial reduction reactions in porous micro-electrodes is developed in this work. The governing coupled equations at the pore scale in the case of two reduction reactions, as for instance, the serial reaction pathway for oxygen reduction to hydrogen peroxide and subsequently to water, are upscaled to obtain a macroscopic model describing the process in an effective medium at the electrode scale. This new macroscopic model, obtained from the volume averaging technique, is validated through comparisons with results of 3D Direct Numerical Simulations of the pore-scale model. The excellent agreement between the two approaches proves the relevance of the macroscale model which reduces to a 1D problem in the configuration under concern, providing a drastic speedup in the computation of the solution. Numerical results obtained with the macroscopic model are successfully compared to experimental data obtained by voltammetry with porous gold electrodes of different thicknesses operating the serial pathway of oxygen reduction to water. Results highlight the ability of this new macroscopic model to predict the electrode behavior and show that the second reduction reaction of hydrogen peroxide plays an important role in the current production.

Keywords: Porous micro-electrode, Oxygen reduction reaction, Diffusion reaction macroscopic model, Upscaling, Volume averaging method

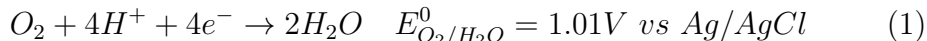
1. Introduction

The use of porous electrodes for *in vivo* implantable active or passive electro-devices is a very promising way for an efficient *in situ* production of electric energy [1, 2, 3]. The main advantage of using a porous material lies in its very large specific area (pore surface to volume ratio) which favours the heterogeneous electro-chemical reactions of interest [4, 5, 6]. As a consequence, the macroscopic size of the electrode can be significantly reduced and the current can be enhanced by an order of magnitude or more in comparison to a flat electrode of the same size [7, 8].

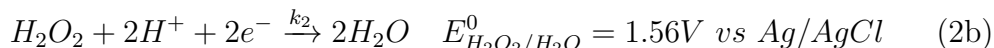
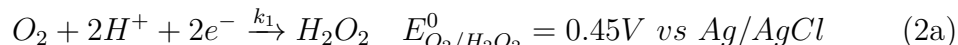
Important efforts have been dedicated to a better understanding and characterization of such devices operating in different regimes, with the purpose of improving their overall efficiency. Nevertheless, modelling at the macroscopic scale can be quite difficult in particular when catalytic enzymes are embedded in the porous structure [1] for the Direct Electron Transfer

15 [9, 10] and Mediated Electron Transfer [11, 12] modes. An optimal design
16 of the architecture of the electrode may be achieved by an analysis of the
17 correlation of the macroscopic current delivered by the electrode with the
18 underlying microscopic structure, electrochemical and mass transfer param-
19 eters. Although this might be achieved from Direct Numerical Simulation
20 (DNS) carried out on the pore-scale model, a much more tractable procedure
21 relies on macroscopic modelling [13, 14]. However, even in the simplest case
22 where no enzyme is present, macroscopic modelling has been widely relying
23 on empirical approaches since the early work of Levie [15], later extended
24 by Barcia *et al.* [16]. For instance, Barnes *et al.* [17] considered a disk
25 covered by spherical pores operating a single reaction involving one electron
26 and empirically derived a macroscopic model. A similar system (cylindrical
27 pillars regularly distributed and orthogonally positioned on a plane surface),
28 with the same reactional scheme, was recently investigated [18, 19], assum-
29 ing again an additive contribution of each pore (*i.e.* independence of the
30 pillars in the diffusion/reaction process). The latter hypothesis was relaxed
31 in the empirical homogenized model proposed by Ender [20] in which the
32 effective diffusivity dependence upon the pore geometry was however not
33 explicitly provided, as in Ferguson and Bazant [21]. An empirical macro-
34 scopic model was also used to study a porous rotating disk electrode in the
35 convection- or diffusion-dominated regime [22, 23]. A more formal deriva-
36 tion of a macroscopic model for transport and reaction in a porous electrode,
37 taking into account the solid, fluid and gas phases, was reported by Vidts
38 and White [24], without however any closure allowing an accurate estimate
39 of the effective diffusivity. A new electrode kinetic equation for a non-porous
40 electrode was recently developed on the basis of a coupled model of elec-
41 tron transfer obeying a Butler-Volmer relationship and oxygen mass transfer
42 at steady-state in the case of direct oxygen reduction [25]. For a thorough
43 analysis of the macroscopic behavior and, further, in the perspective of an
44 optimization of the devices under concern, a rational approach, based on
45 a cautious derivation of appropriate macroscopic models from the physico-
46 electrochemical governing equations at the underlying microscopic scale is
47 of major importance. In this context, the volume averaging method was re-
48 cently employed to obtain a closed macroscopic model operating at the scale
49 of an entire porous electrode, coupling diffusion and reaction [13]. It was fur-
50 ther validated with experiments and used to determine the optimal electrode
51 thickness [14]. However, this model is limited to the relatively simple case of
52 a single reduction reaction.

Heterogeneous reduction reactions at a cathodic electrode immersed in an aqueous solution saturated by oxygen constitute a system of common and wide interest [26, 4]. In this configuration, the oxygen reduction shall be considered in different reaction pathways [27]. The first one is the so-called “direct” four-electron reaction



(E_{O_2/H_2O}^0 being the standard potential of the O_2/H_2O couple). The second one involves two-successive bi-electronic reactions with the intermediate production of hydrogen peroxide. This mechanism is often referred to as a serial (or indirect) reaction pathway. It is such that



53 where, k_1 and k_2 denote the electron transfer rate constants, $E_{O_2/H_2O_2}^0$ and
 54 $E_{H_2O_2/H_2O}^0$ the standard potentials of the couples O_2/H_2O_2 and H_2O_2/H_2O
 55 respectively. Depending on the electrode surface material and the solution,
 56 one or the other pathway, a combination of the two, or even the reaction
 57 limited to the oxygen reduction to hydrogen peroxide (2a), may be privi-
 58 leged [26, 28, 29]. In particular, at gold surfaces, the serial pathway seems
 59 to be the relevant one in the presence of acidic solutions (e.g. 0.5M H_2SO_4)
 60 [29, 30]. Nevertheless, the same pathway was observed for gold electrodes
 61 in neutral [26] or alkaline solutions [31]. Beyond the pH value, other de-
 62 terminant parameters are to be considered, including the crystallographic
 63 structure of gold as well as the existence and stability of hydroperoxyl OOH
 64 groups at the surface [28]. For the porous electrodes used in this work (see
 65 section 4.2), the pH was shown to be a key parameter. Indeed, experiments
 66 carried out at 0.5M H_2SO_4 revealed the existence of two distinct waves in
 67 the voltammogram which are characteristic for the serial reduction scheme
 68 whereas the same experiment, carried out at 0.05M, did not exhibit this fea-
 69 ture. Actually, in some configurations, although the potential values of the
 70 two couples for this pathway are well separated, the second reaction in (2b)
 71 may contribute significantly to the electronic exchange when $[H_2O_2]$ is not
 72 exceedingly small compared to $[O_2]$, as will be further highlighted in this
 73 work. This may occur even at cathodic potentials that are not much smaller
 74 than $E_{O_2/H_2O_2}^0$, O_2 and H_2O_2 being reduced at close potentials [26]. Under

75 such circumstances, ignoring the hydrogen peroxide reduction may lead to
76 erroneous interpretation of voltammetry results obtained at potentials that
77 could be thought to be such that the reaction (2b) is negligible *a priori*. As a
78 result, deriving a formal macroscopic model in which more than one reactive
79 species is involved is of considerable importance. The task is significantly
80 more complex than when only one reaction is involved as the series path-
81 way induces a coupling that needs to be carefully taken into account in the
82 derivation of the macroscopic model. To the best of our knowledge, this has
83 not been reported so far and the present work aims at such a task.

84 In this work, the series reduction of two species (namely O_2 and H_2O_2
85 for further comparison with experiments) is considered together with mass
86 transfer by diffusion yielding a new initial boundary value problem at the
87 pore-scale. Diffusion is supposed to obey Fick's law [32] and the Butler-
88 Volmer formalism is employed to describe the electrochemical kinetics [33].
89 The pore-scale model is subsequently upscaled using the volume averaging
90 method [34], carrying the coupling between the species to the final diffusion-
91 reaction macroscopic model for the series pathway of the oxygen reduction
92 reaction. The associated closure problems, which allow the determination
93 of the macroscopic coefficients (*i.e.* the effective diffusivities), are provided.
94 Numerical simulations of the initial 3D pore-scale model are employed to suc-
95 cessfully validate the 1D macroscopic model. Finally, experimental voltam-
96 metry results, obtained with porous gold electrodes in an aqueous acid solu-
97 tion, are compared to the numerical predictions from the macroscopic model,
98 illustrating the performance of the present approach and highlighting the im-
99 portance of the second reduction reaction (2b) without which fitting the data
100 at low potential fails.

101 The article is organized as follows. The pore-scale model characterized
102 by diffusion and a serial pathway of two reduction reactions is first devel-
103 oped in section 2. The upscaling procedure to derive the macroscopic model
104 is briefly summarized in section 3, while more details of the derivation are
105 provided in Appendix A. Section 4 is first dedicated to the validation of the
106 upscaled model through comparisons of simulations of its 1D version with
107 the 3D-DNS of the pore-scale model. Secondly, predictions of the current-
108 to-potential relationship obtained from the macroscopic model are compared
109 to experimental voltammetry data. The improvement of the prediction from
110 the new model including the two reduction reactions developed in the present
111 work with respect to the one reported earlier [13] is clearly highlighted. Con-
112 cluding remarks are drawn in section 5.

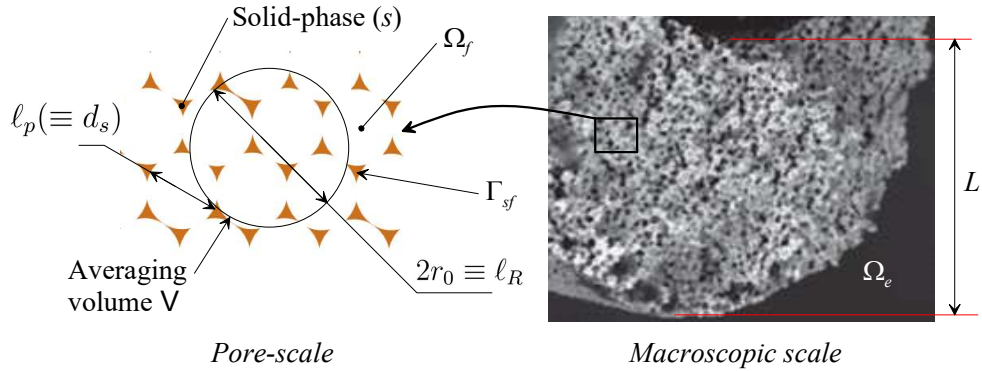


Figure 2.1: Schematic representation of the configuration under study showing the fluid domains inside (Ω_f) and outside (Ω_e) the electrode and the characteristic lengths at the pore-scale (ℓ_p) and at the macroscopic scale (L). The right picture is a SEM image of a cross section of a cylindrical porous electrode of thickness L . V represents the averaging volume, of radius r_0 , used to upscale the pore-scale problem; d_s and ℓ_R are respectively the size of the spherical pores and the size of the periodic unit cell in the special case of a FCC structure (see section 4).

113 2. Pore-scale model

The system under study is schematically represented in Fig. 2.1, showing the pore and macroscopic scales and the associated characteristic lengths. The development starts with the statement of the microscopic model at the pore-scale involving a pair of serial electrochemical reactions coupled with diffusion of the reactive species within a porous electrode. Let A and B denote these two species (*e.g.* respectively O_2 and H_2O_2 in the reaction pathway (2)) and c_A and c_B their molar concentrations in the liquid aqueous solution saturating the pores and in which the electrode is immersed. The reaction rates associated to these two reactions are given by the Butler-Volmer relationship [33]

$$R_A = -k_1 \alpha_A c_A \quad (3a)$$

$$R_B = -k_2 \alpha_B c_B + k_1 \alpha_A c_A \quad (3b)$$

with

$$\alpha_A = \exp\left(\frac{-\alpha_1 n_1 F(E - E_{O_2/H_2O_2}^0)}{RT}\right) \quad (4a)$$

$$\alpha_B = \exp\left(\frac{-\alpha_2 n_2 F(E - E_{H_2O_2/H_2O}^0)}{RT}\right) \quad (4b)$$

114 where α_1 and α_2 denote the electron transfer coefficients, n_1 and n_2 the
 115 numbers of transferred electrons, for reactions (2a) and (2b) respectively, R ,
 116 F and T being the ideal gas constant, Faraday's constant and the absolute
 117 temperature. It should be noted that both reduction reactions in (2) are con-
 118 sidered to be irreversible so that only the forward Butler-Volmer's equation
 119 is used and the process takes place under isothermal conditions.

The diffusion mechanism of the two species occurring within the porous electrode is considered as a Fickian process. Together with the solid/fluid interface, initial and boundary conditions, this leads to write the governing equations for the transport and reaction of species $i = A, B$ under the form of the following initial boundary value problem

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (\mathcal{D}_i \nabla c_i) \quad \text{in } \Omega_f \quad (5a)$$

$$-\mathbf{n} \cdot (\mathcal{D}_i \nabla c_i) = -R_i \quad \text{at } \Gamma_{sf} \quad (5b)$$

$$c_i = \mathcal{F}_i(\mathbf{r}) \quad \mathbf{r} \in \Omega_f, t = 0 \quad (5c)$$

$$c_i = \mathcal{G}_i(\mathbf{r}, t) \quad \mathbf{r} \in \mathbf{A}_{fe}, \forall t \quad (5d)$$

120 Here \mathcal{D}_i denotes the molecular diffusion coefficients of species i , \mathbf{n} the normal
 121 unit vector at the solid/fluid interface, Γ_{sf} , pointing out of the fluid phase.
 122 In addition, $\mathbf{A}_{fe} = \Omega_f \cap \Omega_e$ is the entrance and/or exit boundary of the fluid
 123 phase occupying the domain Ω_f inside the electrode from/into the diffusion
 124 layer occupying the region Ω_e outside the electrode, next to it (see Fig. 2.1).
 125 It should be noted that in the diffusion layer surrounding the electrode, the
 126 diffusion mechanism of both species is governed by Fick's second law given in
 127 Eq. (5a). It must be noted that the formal set of assumptions and restrictions
 128 for this model to be valid is not easy to identify. However, detailed analyses
 129 indicate that if the system is such that species are dilute, the total density
 130 and total molar concentration of the mixture are constant, and when the
 131 molar fluxes of both species are the same order of magnitude, Eq. (5a) is
 132 a reasonable approximation [35, 36]. These restrictions and constraints are
 133 retained here.

134 For a given structure, macroscopic geometry and operating conditions,
 135 the system of equations (5) can be solved by making use of a DNS in order
 136 to compute the concentrations and, consequently, the current available at
 137 the electrode which is given by

$$I = -n_1 k_1 F \alpha_A \int_{\Gamma_{sf}} c_A d\Gamma - n_2 k_2 F \alpha_B \int_{\Gamma_{sf}} c_B d\Gamma \quad (6)$$

138 Such a solution will be investigated in section 4. However, for practical
 139 purposes, a closed macroscopic model is requested, the derivation of which
 140 is provided in section 3.

141 3. Upscaled model

In this section, our aim is to obtain a macroscopic model by upscaling the above pore-scale problem given in Eqs. (5), using the volume averaging method [34]. The difficulty here lies in the coupled multi-reactions and multi-diffusive species problem, yielding a much more complex procedure than the one carried out in [13]. For the sake of conciseness, only the result of the upscaling process is provided below. Details on how to obtain this result are reported in Appendix A. Let $\langle c_i \rangle^f$ ($i = A, B$) represent the intrinsic average concentration in the fluid phase defined by

$$\langle c_i \rangle^f = \frac{1}{V_f} \int_{V_f(\mathbf{x})} c_i dV \quad (7)$$

where V_f (of volume V_f) is the region occupied by the fluid phase within the averaging domain. The macroscopic model, coupling the concentration evolution of both species, is given by

$$\varepsilon \frac{\partial \langle c_A \rangle^f}{\partial t} = \nabla \cdot (\varepsilon \mathcal{D}_A \mathbf{D}_{eff}^* \cdot \nabla \langle c_A \rangle^f) - k_1 \alpha_A a_v \langle c_A \rangle^f \quad (8a)$$

$$\varepsilon \frac{\partial \langle c_B \rangle^f}{\partial t} = \nabla \cdot (\varepsilon \mathcal{D}_B \mathbf{D}_{eff}^* \cdot \nabla \langle c_B \rangle^f) + k_1 \alpha_A a_v \langle c_A \rangle^f - k_2 \alpha_B a_v \langle c_B \rangle^f \quad (8b)$$

where ε and a_v are the porosity and specific area (see their formal definition in Appendix A) whereas \mathbf{D}_{eff}^* denotes the effective diffusivity tensor given in (A.17a), namely

$$\mathbf{D}_{eff}^* = \mathbf{I} + \frac{1}{V_f} \int_{A_{sf}} \mathbf{n} b dA \quad (9)$$

Here, \mathbf{A}_{sf} represents the solid-fluid interface contained in the averaging domain, considered as the Representative Elementary Volume (that will be restricted to a unit cell) of the pseudo periodic structure within which the vector \mathbf{b} is solution of the following intrinsic closure problem (see Eqs. (A.12))

$$\nabla^2 \mathbf{b} = 0 \quad \text{in } \mathbf{V}_f \quad (10a)$$

$$\mathbf{n} \cdot \nabla \mathbf{b} = -\mathbf{n} \quad \text{at } \mathbf{A}_{sf} \quad (10b)$$

$$\langle \mathbf{b} \rangle^f = 0 \quad (10c)$$

$$\mathbf{b}(\mathbf{r}) = \mathbf{b}(\mathbf{r} + \ell_i \mathbf{e}_i) \quad i = 1, 2, 3 \quad (10d)$$

Here, $\ell_i \mathbf{e}_i$ ($i = 1, 2, 3$) are the periodic lattice vectors of the unit cell. When complemented with the initial and boundary conditions for $\langle c_A \rangle^f$ and $\langle c_B \rangle^f$, Eqs. (8) form the effective macroscopic model for the coupled diffusion and serial reduction reactions of species A and B . It must be emphasized that its validity is subject to three constraints. The first one is on the length-scales, *i.e.*, $\ell_p \ll L$ (ℓ_p is the characteristic pore-size and L the macroscopic length-scale of the medium, see Fig. 2.1). The second one, on the kinetic number expressed as $Ki = \ell_p \max(k_1 \alpha_A / \mathcal{D}_A, k_2 \alpha_B / \mathcal{D}_B)$, is given by $Ki \ll 1$. The last one is on the time scale at which the process is observed which must be such that $t / \ell_p^2 \min(\mathcal{D}_A, \mathcal{D}_B) \gg 1$ [34, 13]. The macroscopic concentration fields of $\langle c_i \rangle^f$ ($i = A, B$), solution of the macroscopic model, allows the determination of the current available at the electrode which takes the form

$$I = -n_1 k_1 F \alpha_A a_v \int_{\Omega} \langle c_A \rangle^f dV - n_2 k_2 F \alpha_B a_v \int_{\Omega} \langle c_B \rangle^f dV \quad (11)$$

142 Ω representing the entire domain occupied by the electrode.

143 4. Numerical results

144 In this section, the macroscopic model is first validated from comparisons
 145 with pore-scale DNS on a given model structure. Predictions of the current
 146 delivered by an electrode during voltammetry tests from the macroscopic
 147 model are further compared to experimental data.

148 4.1. Pore-scale model DNS and numerical solutions of the macroscopic model

149 To carry out 3D DNS of the pore-scale model (Eqs. (5)) and compare the
 150 results with those obtained from the 1D solution of the macroscopic model
 151 derived in section 3, a model configuration is considered. It is represented in

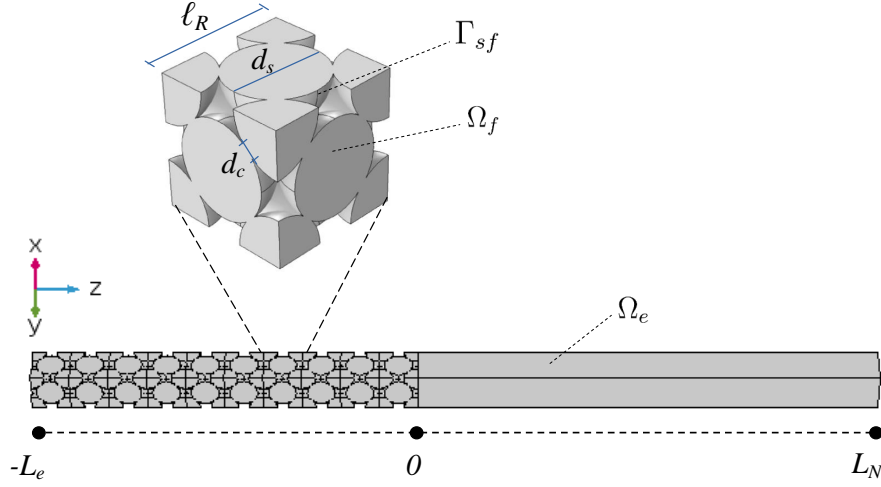


Figure 4.1: 3D domain for DNS and unit cell of the porous structure. All fluid domains are represented in gray; the solid phase is not depicted

152 Fig. 4.1 where the computational domain for the DNS and the periodic unit
 153 cell, of size ℓ_R , of the porous structure are reported. The electrode, of thick-
 154 ness L_e , is supposed to be composed of a face-centered-cubic (FCC) arrange-
 155 ment of spherical pores of diameter $d_s = \ell_p$ connected to each other through
 156 a circular window of diameter d_c . Its extensions in the x - and y -directions
 157 are supposed to be large enough for periodicity to be a valid approximation
 158 in both directions. For this approximation to hold, it is first assumed that
 159 the electrode length is much larger than ℓ_R . Second, the electrode is sup-
 160 posed to be either a plane one, with a very large lateral extension compared
 161 to ℓ_R , or is circular with a thickness L_e much smaller than its mean radius.
 162 As a consequence, the 3D computational domain for the pore-scale DNS is
 163 restricted to a single unit cell in the x - and y -directions (see Fig. 4.1).

164 The electrode, positioned between $z = -L_e$ and $z = 0$, lies on its solid
 165 impermeable and electrically conducting support at $z = -L_e$ so that a zero
 166 diffusive flux for both species is applied at this location. Moreover, the elec-
 167 trode is in contact with the bulk solution at $z = 0$ where a Nernstian diffusion
 168 layer, between $z = 0$ and $z = L_N$, settles down. At the free extremity of the
 169 diffusion layer, a Dirichlet boundary condition is applied for the two species,
 170 *i.e.* $c_i = c_i^0$, $i = A, B$ at $z = L_N$. Finally, periodic boundary conditions on
 171 c_i , $i = A, B$ (and their gradients) are applied in the x - and y -directions. The
 172 initial concentrations are supposed to be uniform, equal to c_i^0 , $i = A, B$.

The system of pore-scale equations (5) is made dimensionless using ℓ_R , ℓ_R^2/D_A and c_A^0 as the reference quantities for length, time and concentrations respectively. Denoting dimensionless quantities with the superscript *, this yields the following initial boundary value problem to be solved

$$\frac{\partial c_A^*}{\partial t^*} = \nabla^{*2} c_A^*, \quad \text{in } \Omega_f \cup \Omega_e \quad (12a)$$

$$\frac{\partial c_B^*}{\partial t^*} = \frac{\mathcal{D}_B}{\mathcal{D}_A} \nabla^{*2} c_B^*, \quad \text{in } \Omega_f \cup \Omega_e \quad (12b)$$

$$\text{B.C.1} \quad -\mathbf{n} \cdot \nabla^* c_A^* = \frac{\ell_R}{\mathcal{D}_A} k_1 \alpha_A c_A^* \quad \text{at } \Gamma_{sf} \quad (12c)$$

$$\text{B.C.2} \quad -\mathbf{n} \cdot \nabla^* c_B^* = \frac{\ell_R}{\mathcal{D}_B} (k_2 \alpha_B c_B^* - k_1 \alpha_A c_A^*) \quad \text{at } \Gamma_{sf} \quad (12d)$$

$$\text{B.C.3} \quad -\mathbf{n} \cdot \nabla^* c_i^* = 0, \quad i = A, B \quad \text{at } z^* = -L_e^* \quad (12e)$$

$$\text{B.C.4} \quad c_A^* = 1 \quad \text{at } z^* = L_N^* \quad (12f)$$

$$\text{B.C.5} \quad c_B^* = c_B^0/c_A^0 \quad \text{at } z^* = L_N^* \quad (12g)$$

$$\text{I.C.1} \quad c_A^* = 1 \quad \text{in } \Omega_f \cup \Omega_e \quad \text{at } t^* = 0 \quad (12h)$$

$$\text{I.C.2} \quad c_B^* = c_B^0/c_A^0 \quad \text{in } \Omega_f \cup \Omega_e \quad \text{at } t^* = 0 \quad (12i)$$

$$c_i^*(x^*, y^*, z^*) = c_i^*(x^* + 1, y^* + 1, z^*), \quad i = A, B \quad \text{in } \Omega_f \quad (12j)$$

$$\mathbf{n} \cdot \nabla^* c_i^*(x^*, y^*, z^*) = \mathbf{n} \cdot \nabla^* c_i^*(x^* + 1, y^* + 1, z^*), \quad i = A, B \quad \text{in } \Omega_f \quad (12k)$$

173

174 The software COMSOL Multiphysics (version 5.2a) was used to solve this
 175 3D problem. Careful attention was paid to the mesh convergence and we used
 176 a physics-controlled mesh including extremely fine grid blocks composed of
 177 9×10^6 tetrahedral elements in the overall domain represented in Fig. 4.1.

The 1D macroscopic model was also solved in the same conditions. In that case, the computational domain reduces to the two sub-domains Ω and Ω_e as depicted in Fig. 4.2. At the boundary between the electrode and the diffusion

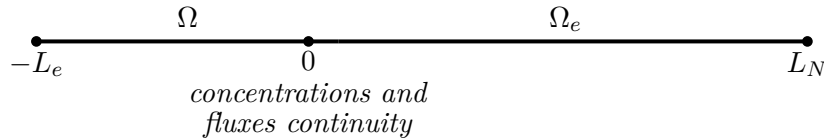


Figure 4.2: 1D reduced domain for the simulation of the macroscopic model layer, *i.e.* at $z = 0$, continuity of both the concentrations and diffusive fluxes

of each species is considered. This choice for the boundary conditions at the macroscopic porous-fluid interface was shown to be an appropriate one in the framework of the underlying hypotheses for the problem under consideration [13]. Using the same reference quantities, the dimensionless form of the macroscopic problem to be solved can be stated as follows

$$\frac{\partial \langle c_A^* \rangle^f}{\partial t^*} = \mathbf{D}_{eff}^* \frac{\partial^2 \langle c_A^* \rangle^f}{\partial z^{*2}} - \frac{a_v \ell_R^2}{\varepsilon \mathcal{D}_A} k_1 \alpha_A \langle c_A^* \rangle^f \quad \text{in } \Omega \quad (13a)$$

$$\frac{\partial \langle c_B^* \rangle^f}{\partial t^*} = \frac{\mathcal{D}_B}{\mathcal{D}_A} \mathbf{D}_{eff}^* \frac{\partial^2 \langle c_B^* \rangle^f}{\partial z^{*2}} + \frac{a_v \ell_R^2}{\varepsilon \mathcal{D}_A} \left(k_1 \alpha_A \langle c_A^* \rangle^f - k_2 \alpha_B \langle c_B^* \rangle^f \right) \quad \text{in } \Omega \quad (13b)$$

$$\text{B.C.1} \quad \langle c_i^* \rangle^f = c_i^*, \quad i = A, B \quad \text{at } z^* = 0 \quad (13c)$$

$$\text{B.C.2} \quad \varepsilon \mathbf{D}_{eff}^* \frac{\partial \langle c_i^* \rangle^f}{\partial z^*} = \frac{\partial c_i^*}{\partial z^*}, \quad i = A, B \quad \text{at } z^* = 0 \quad (13d)$$

$$\frac{\partial c_A^*}{\partial t^*} = \frac{\partial^2 c_A^*}{\partial z^{*2}}, \quad \text{in } \Omega_e \quad (13e)$$

$$\frac{\partial c_B^*}{\partial t^*} = \frac{\mathcal{D}_B}{\mathcal{D}_A} \frac{\partial^2 c_B^*}{\partial z^{*2}}, \quad \text{in } \Omega_e \quad (13f)$$

$$\text{B.C.3} \quad \frac{\partial \langle c_i^* \rangle^f}{\partial z^*} = 0, \quad i = A, B \quad \text{at } z^* = -L_e^* \quad (13g)$$

$$\text{B.C.4} \quad c_A^* = 1 \quad \text{at } z^* = L_N^* \quad (13h)$$

$$\text{B.C.5} \quad c_B^* = \frac{c_B^0}{c_A^0} \quad \text{at } z^* = L_N^* \quad (13i)$$

$$\text{I.C. 1} \quad \langle c_A^* \rangle^f = 1 \quad \text{in } \Omega \text{ at } t^* = 0 \quad (13j)$$

$$\text{I.C. 2} \quad \langle c_B^* \rangle^f = \frac{c_B^0}{c_A^0} \quad \text{in } \Omega \text{ at } t^* = 0 \quad (13k)$$

$$\text{I.C. 3} \quad c_A^* = 1 \quad \text{in } \Omega_e \text{ at } t^* = 0 \quad (13l)$$

$$\text{I.C. 4} \quad c_B^* = \frac{c_B^0}{c_A^0} \quad \text{in } \Omega_e \text{ at } t^* = 0 \quad (13m)$$

178 In the above equations, \mathbf{D}_{eff}^* is such that, due to isotropy of the unit cell,
 179 $\mathbf{D}_{eff}^* \mathbf{1} = \mathbf{D}_{eff}^*$. It was computed prior to the solution of Eqs. (13) by solving the
 180 closure problem in Eqs. (10). Both problems were also solved with COMSOL
 181 Multiphysics.

182 The micro- and macroscale simulations correspond to a voltammetry
 183 numerical experiment carried out with a scanning potential ranging from
 184 $E = 0.4V$ to $0V$ at a constant scan rate $r_E = 5mV/s$. Parameters used

Parameter	Symbol	Value	Unit
Ideal gas constant	R	8.314	$J/(molK)$
Faraday's constant	F	96485	C/mol
Temperature	T	298	K
Number of transferred electrons	n_1, n_2	2	—
Electron transfer coefficient	α_1	0.58	—
Electron transfer coefficient	α_2	0.482	—
Electron transfer rate constant	k_1	$1.2 \cdot 10^{-7}$	cm/s
Electron transfer rate constant	k_2	$1.7 \cdot 10^{-17}$	cm/s
Standard potential vs. $E_{Ag/AgCl}^0$	$E_{O_2}^0$	0.45	V
Standard potential vs. $E_{Ag/AgCl}^0$	$E_{H_2O_2}^0$	1.56	V
Initial and bulk concentration of O_2	c_A^0	1.2	mol/m^3
Initial and bulk concentration of H_2O_2	c_B^0	0	mol/m^3
Diffusion coefficient of O_2	D_A [37]	$1.9 \cdot 10^{-9}$	m^2/s
Diffusion coefficient of H_2O_2	D_B [37]	$1.4 \cdot 10^{-9}$	m^2/s
Dimensionless effective diffusivity	D_{eff}^*	0.493	—
Spherical pore diameter	d_s	1.2	μm
Connecting window-size	d_c	$0.15d_s$	μm
Size of the periodic unit cell	ℓ_R	1.678	μm
Porosity	ε	0.763	
Specific area	a_v	3.567×10^6	$1/m$

Table 4.1: Parameters used in the simulations

185 in the simulations are provided in Table. 4.1. The electrode thickness was
186 chosen to be $L_e = 10\ell_R$ which corresponds to 40 half layers (HL) of spheri-
187 cal pores. The diffusion layer thickness, L_N , was taken equal to $30\mu m$. It
188 must be noted that, because of a pseudo-elementary rate determining step, a
189 single electron transfer is to be considered [38], even though both reduction
190 reactions occur with two electrons [39]. As a consequence, the values of n_1
191 and n_2 were taken equal to 1 in the exponential term of the driving force in
192 the Butler-Volmer relationships (4).

193 In Fig. 4.3 the O_2 concentration profiles within the electrode during
194 voltammetry obtained from the solution of the 1D macroscopic model (Eqs.
195 (13)) and 3D DNS of the pore-scale model (Eqs. (12)) are represented at
196 three different times. Clearly, the agreement between the two approaches is

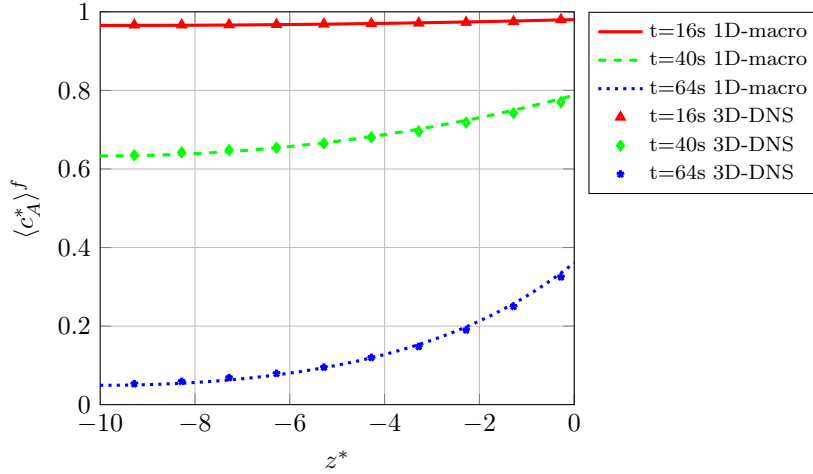


Figure 4.3: Dimensionless O_2 concentration profiles within the porous electrode obtained from the solution of the 1D macroscopic model and from 3D DNS of the pore-scale model

197 excellent. This is further confirmed in Fig. 4.4 in which evolutions of the
 198 dimensionless mean concentrations, $\overline{c_i^*}$, $i = A, B$, over the entire electrode
 199 domain are represented. The mean concentrations are given by the averages
 200 $\frac{1}{|\Omega|} \int_{\Omega} \langle c_i^* \rangle^f dV$ and $\frac{1}{|\Omega_f|} \int_{\Omega_f} c_i^* dV$, for the 1D macroscopic approach and 3D
 201 DNS at the pore-scale respectively, $|\Omega|$ and $|\Omega_f|$ denoting the volume of Ω and
 202 Ω_f . Again, results obtained from the pore-scale DNS and from the solution
 203 of the macroscopic model match perfectly.

204 For completeness, a final comparison is made on the current delivered
 205 by the electrode versus the applied potential obtained from the macroscopic
 206 and pore-scale approaches, the current, I , being computed from Eqs. (11)
 207 and (6) respectively. The voltammogram is represented in Fig. 4.5 showing
 208 again the excellent agreement between the two results. These very successful
 209 comparisons prove the validity of the new upscaled model.

210 The net advantage of the macroscopic approach lies in the gain in terms
 211 of computational resources and time required to obtain the (average) concen-
 212 tration fields and the current. In fact, for the case under study, the compu-
 213 tational time is only 9s for the 1D macroscopic model while 108 minutes are
 214 needed for a 3D DNS of the pore-scale model (on a Dell PowerEdge 430-2
 215 processors Intel Xeon E5-2630v3), leading to a speed-up of about 720. In

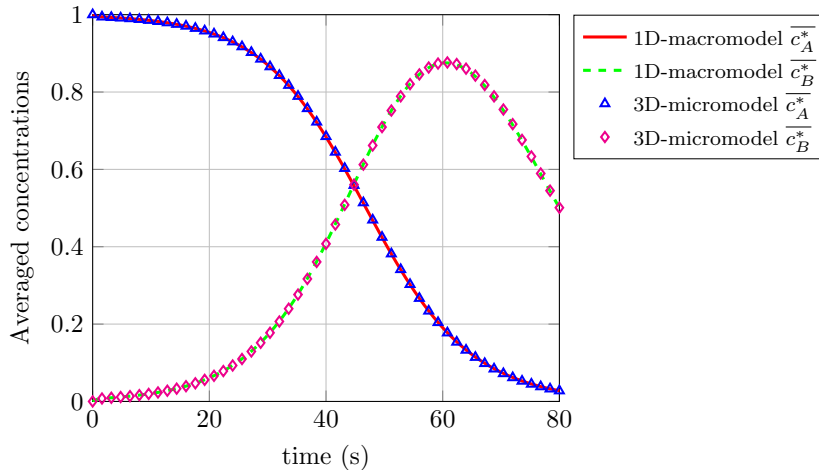


Figure 4.4: Dimensionless mean concentrations of O_2 and H_2O_2 within the porous electrode obtained from the simulation of the 1D macroscopic model and from 3D DNS of the pore-scale model

216 addition, the upscaling procedure provides a comprehensive model operating
 217 at the macroscopic scale and the link with the microscale parameters.

218 4.2. Comparison with experimental data

219 The aim of this section is to test the ability of the new macroscopic model
 220 developed here to accurately predict the current-to-potential characteristics
 221 obtained from voltammetry experiments carried out with porous electrodes
 222 for the serial oxygen reduction reactions to water as described by (2). Three
 223 porous electrodes were prepared according to a protocol that has been widely
 224 described in the literature [40, 41, 42, 43]. This protocol mainly consists of
 225 three steps: *i*) deposition of layers of organized colloidal self-assembled sil-
 226 ica beads is first performed on a gold wire of $250\mu m$ in diameter using the
 227 Langmuir-Blodgett method. Multiple silica particle layers were obtained by
 228 repeating the dipping and withdrawing (1.2 mm/min) process. Spherical
 229 silica beads of $1.2\mu m$ in diameter were employed here; *ii*) filling the bead
 230 assembly with gold is carried out by electrodeposition (Elevate® Gold 7990,
 231 $-0.6 V$); *iii*) beads are dissolved with hydrofluoric acid, leaving an electrically
 232 conducting porous structure which pore diameter, $d_s(= \ell_p)$, corresponds to
 233 the bead diameter. Since gold electrodeposition does not lead to a complete
 234 filling of the gaps between the beads, connecting windows between the

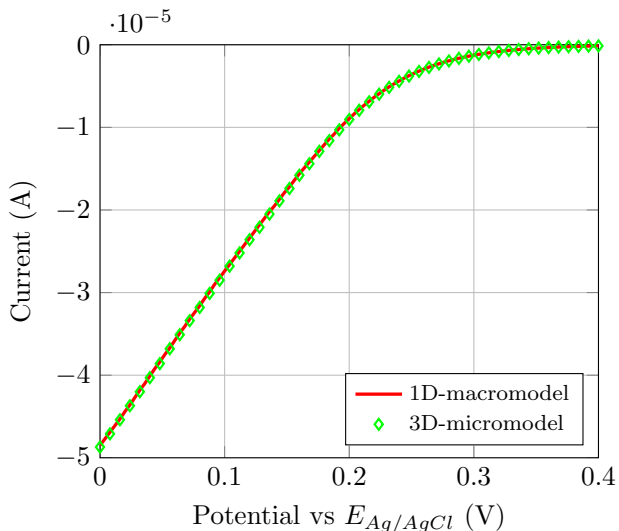


Figure 4.5: Current available at the electrode versus the applied scanning potential computed with the 1D macroscopic (Eq. (11)) and 3D microscopic (Eq. (6)) models

235 spherical pores remain, yielding an inverse opal-like percolating porous struc-
 236 ture. The connecting window-size, d_c , was characterized to be approximately
 237 $0.15d_s$. As a result of the self-assembling mechanism, the structure is very
 238 compact and can reasonably be represented by an FCC structure (see Fig.
 239 4.1). The three electrodes are made of 5, 11 and 19 half-layers of spherical
 240 pores respectively (referred to as 5HL, 11HL and 19HL in the following). It
 241 should be noted that a 4HL structure corresponds to 1 FCC unit cell for
 242 modelling.

243 The electrodes were immersed in a 0.5M H_2SO_4 solution saturated by
 244 oxygen in order to carry out voltammetry experiments at a constant temper-
 245 ature $T = 298K$ and a constant scan rate of $5mV/s$ with a decreasing po-
 246 tential in the range from $0.4V$ to $0V$. All the electrochemical measurements
 247 were carried out with an Autolab PGSTAT101 potentiostat. A cylindrical
 248 flexible carbon sheet was used as counter electrode, and Ag/AgCl (3M KCl)
 249 was used as a reference electrode. Electrochemical measurements were car-
 250 ried out inside a sealed cell, the 0.5M H_2SO_4 solution was always purged with
 251 O_2 for 15min before the measurement, and a slow O_2 flow was kept above the
 252 0.5M H_2SO_4 solution in order to maintain the constant O_2 concentration.

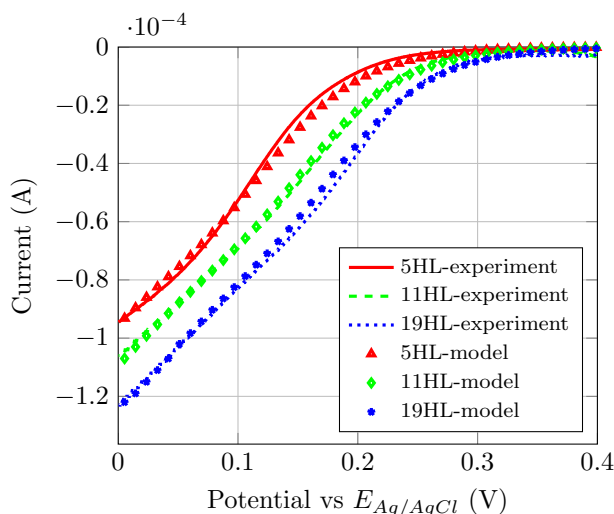


Figure 4.6: Experimental voltammogram obtained with the three electrodes in a 0.5M H_2SO_4 solution saturated with oxygen at a $5mV/s$ scan rate. Comparison with predictions obtained from the macroscopic model in Eqs. (13)

253 Experimental results obtained with the three electrodes are reported in Fig.
 254 4.6. It should be noted that all the experiments were repeated at least three
 255 times to check repeatability.

256 The electron transfer rate constants, k_1 and k_2 , and electron transfer
 257 coefficients, α_1 and α_2 , together with the diffusion layer thickness, L_N , are
 258 not accurately known *a priori*. For this reason, these parameters were fitted
 259 in the macroscopic 1D model given in Eqs. (13) and the current expressed
 260 in Eq. (11) in the least square sense. This was performed on the curve
 261 obtained with the 11HL electrode and optimal values for k_1 , k_2 , α_1 and α_2
 262 (together with all the other required data for the solution of the macroscopic
 263 model) are reported in Table 4.1. The diffusion layer thickness yielding the
 264 best fit was found to be $L_N = 130\mu m$. Values of the parameters fitted on
 265 the voltammogram obtained with the 11HL electrode were then kept the
 266 same for the simulations of the 1D macroscopic model for the 5HL and 19HL
 267 electrodes. Numerical results are reported in Fig. 4.6 as a comparison with
 268 experimental data, showing an excellent agreement. In fact, as reported in
 269 Fig. 4.7, the absolute value of the relative error on the current over the
 270 whole range of scanning potential is less than 5% for all the electrodes. This

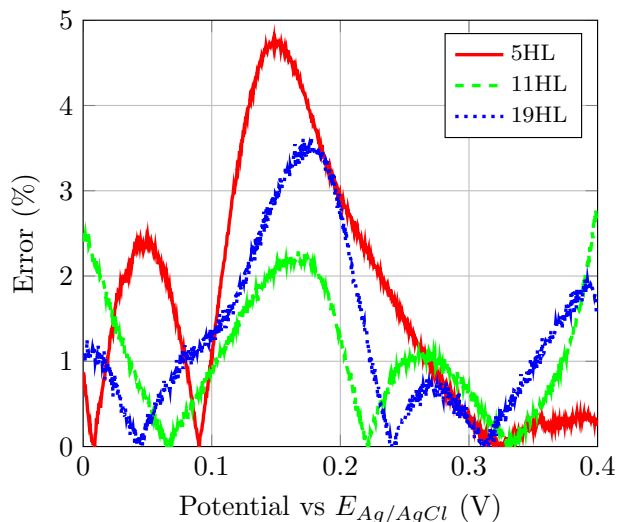


Figure 4.7: Absolute value of the relative error on the current between simulation results and experimental data. The experimental data set of Fig. 4.6 for the 11HL electrode was employed to fit the parameters (see text) which were used to perform simulations of the 1D macroscopic model for the 5HL and 19HL electrodes

271 demonstrates the ability and the accuracy of the new macroscopic model
 272 derived in this work to predict the behavior of a porous electrode in the
 273 case of a serial reaction pathway. In order to appreciate the role of the
 274 reduction reaction (2b) of H_2O_2 to water that is often neglected, a one-
 275 reaction version of the macroscopic model was solved, taking into account
 276 only the reduction reaction (2a) of O_2 to H_2O_2 , as in [13]. Parameters for the
 277 solutions of this reduced model were kept the same as those employed with
 278 the full model for the complete serial pathway. Current versus the scanning
 279 potential results are reported in Fig. 4.8. From this figure, it can be observed
 280 that the reduced model correctly predicts the current in the upper range of
 281 the potential values. However, for potentials smaller than 0.2V to 0.1V,
 282 depending on the electrode thickness, the second reaction plays obviously a
 283 key role in the electronic exchange. This can be explained by the fact that,
 284 at the early stage of the experiments, *i.e.* at large values of the potential,
 285 $[H_2O_2]$ is not significant since the amount of oxygen that has already reacted
 286 remains small. More quantitatively, the contribution of the second reduction
 287 reaction to the overall current production can be estimated from the analysis

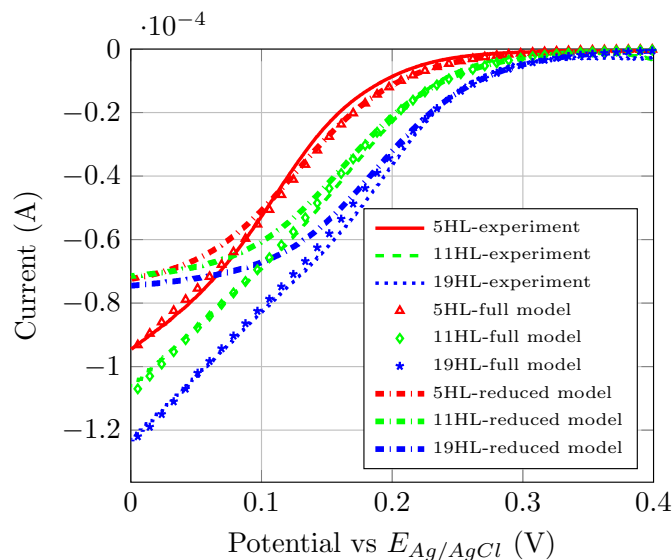


Figure 4.8: Comparison of the voltammetry curves obtained by simulations of the reduced model considering a single reduction reaction O_2 to H_2O_2 and the full coupled model of the complete serial pathway

288 of the ratio between the two terms in the right hand side of Eq. (11), which
 289 is simply given by $k_2\alpha_B\bar{c}_B^*/(k_1\alpha_A\bar{c}_A^*)$. This ratio is represented versus the
 290 scanning potential in Fig. 4.9. It can be clearly seen that around 10% of the
 291 total current delivered by the electrode is produced by the second reaction
 292 for potentials smaller than 0.1V, 0.14V and 0.17V for the 5HL, 11HL and
 293 19HL electrodes respectively. This is perfectly consistent with the values
 294 of the threshold potentials in Fig. 4.8 at which the reduced model fails to
 295 accurately predict the current observed experimentally. This threshold value
 296 increases with the electrode thickness and this is due to the fact that, while
 297 decreasing the potential, $[H_2O_2]$ is larger for a thicker electrode as a result of a
 298 larger reacting surface. This behavior is further confirmed by the fact that the
 299 contribution of the second reduction reaction becomes larger as the electrode
 300 thickness increases. For instance, at 0 V, the second reaction contributes to
 301 around 33%, 45% and 58% of the total current produced with the 5HL, 11HL
 302 and 19HL electrodes respectively. In the latter case, the second reaction is
 303 even the dominant one. This clearly highlights that this second reaction
 304 must not be omitted in the interpretation of the electrochemical behavior of
 305 an electrode during oxygen reduction in an aqueous solution.

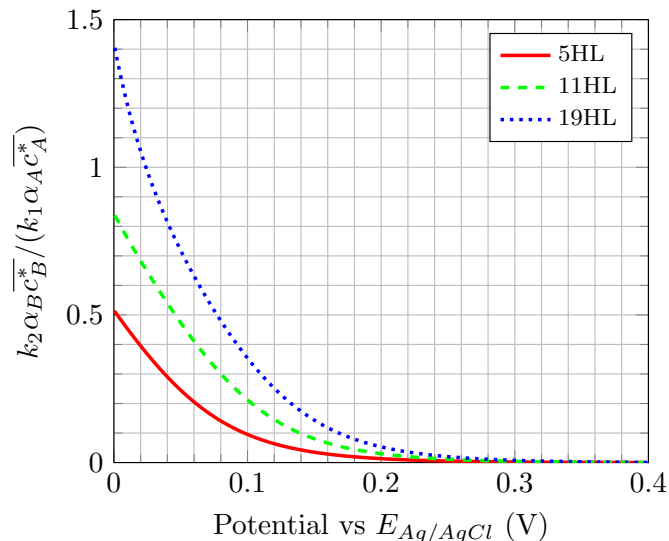


Figure 4.9: Ratio of the current contribution from each of the two serial reduction reactions versus the scanning potential

306 5. Conclusions

307 In this article, a physico-electrochemical multiscale model of two reduction
 308 reactions within a porous electrode via a serial pathway including the
 309 diffusion of the two reactive species was developed. The initial boundary
 310 value problem at the pore-scale was stated and upscaled to formally derive
 311 a new macroscopic model using the volume averaging method. It provides
 312 an accurate prediction of the coupled evolution of both molar species con-
 313 centrations. The associated closure problem allowing the determination of
 314 the effective coefficients (more particularly the effective diffusivity) appear-
 315 ing in this model was provided. A validation of the macroscopic model was
 316 carried out with a thorough comparison with the results obtained from Di-
 317 rect Numerical Simulations of the pore-scale model in the case of the serial
 318 pathway of oxygen reduction to water, clearly assessing the accuracy of the
 319 macroscopic model. A very significant computational speed-up is achieved
 320 with the macroscopic model.

321 Voltammetry experiments were carried out on three different porous gold
 322 electrodes of different thicknesses immersed in an aqueous acid solution. The
 323 macroscopic model was used to predict the current-to-potential relationship
 324 after parameters such as the electron transfer rate constants, the electron

325 transfer coefficients of both reactions and the diffusion layer thickness have
326 been fitted on the experimental data of only one of the three electrodes.
327 The agreement between the experimental results and the prediction from
328 the model is excellent, showing less than 5% of error over the whole range
329 of scanning potential and proving the relevance of the macroscopic model.
330 Moreover, simulations showed the importance of the second reduction reac-
331 tion of hydrogen peroxide to water. It indicates that this reaction very sig-
332 nificantly contributes to the overall current available at the electrode when
333 the potential becomes smaller than $0.2V$ to $0.1V$, depending on the electrode
334 thickness. On the basis of its performance, the macroscopic model derived
335 here opens interesting perspectives in terms of the optimization of sophis-
336 ticated electrode architectures. More generally, this model maybe of major
337 interest in chemical engineering applications, far beyond the context of the
338 present work, whenever a series of heterogeneous reactions is to be consid-
339 ered involving more than one diffusing dilute species. A generalization to
340 reactions involving n species ($n > 2$) may also be envisaged following the
341 same approach to obtain a macroscopic description.

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348 Appendix A Volume averaging and derivation of 349 the upscaled model

350 In this Appendix, the upscaling procedure to derive the macroscopic dif-
351 fusion/reaction equations by making use of the volume averaging method is
352 presented. The development is similar to the one described in [34] with an
353 extension to a more complex problem where multiple species and reactions
354 are involved.

The upscaling is carried out by means of the superficial and intrinsic vol-
ume averaging operators over a volume \mathbf{V} (of measure V and radius r_0) (see
Fig. 2.1) embedding a domain occupied by the fluid phase \mathbf{V}_f (of measure

V_f) and the solid-fluid interface A_{sf} (of measure A_{sf}). V_f and A_{sf} are the restrictions of Ω_f and Γ_{sf} to V and $r_0 \ll L$. The two operators are respectively defined as

$$\langle c_i \rangle = \frac{1}{V} \int_{V_f} c_i dV \quad i = A, B \quad (\text{A.1a})$$

$$\langle c_i \rangle^f = \frac{1}{V_f} \int_{V_f} c_i dV = \varepsilon^{-1} \langle c_i \rangle \quad i = A, B \quad (\text{A.1b})$$

Here, ε represents the porosity, $\varepsilon = \frac{V_f}{V}$. Permutation of the average and the time and space derivative requires the use of the Reynolds transport and averaging theorems which can be respectively expressed as follows [44, 45],

$$\left\langle \frac{\partial c_i}{\partial t} \right\rangle = \frac{\partial \langle c_i \rangle}{\partial t} \quad (\text{A.2a})$$

$$\langle \nabla c_i \rangle = \nabla \langle c_i \rangle + \frac{1}{V} \int_{A_{sf}} \mathbf{n} c_i dA \quad (\text{A.2b})$$

355 and a straightforward form for the latter for the divergence operator. It
 356 should be noticed that while writing Eq. (A.2a), V was assumed to be inde-
 357 pendent of time due to a non-deformable porous medium.

The superficial average operator is applied to the microscale equations (5a) and, after making use of the interfacial boundary conditions (5b) together with the hypothesis that the pore and macroscopic characteristic length-scales ℓ_p and L are well separated, *i.e.* $\ell_p \ll L$, this yields

$$\begin{aligned} \varepsilon \frac{\partial \langle c_A \rangle^f}{\partial t} = \nabla \cdot \left[\mathcal{D}_A \left(\varepsilon \nabla \langle c_A \rangle^f + \langle c_A \rangle^f \nabla \varepsilon + \frac{1}{V} \int_{A_{sf}} \mathbf{n} c_A dA \right) \right] \\ - k_1 \alpha_A a_v \langle c_A \rangle_{sf} \end{aligned} \quad (\text{A.3a})$$

$$\begin{aligned} \varepsilon \frac{\partial \langle c_B \rangle^f}{\partial t} = \nabla \cdot \left[\mathcal{D}_B \left(\varepsilon \nabla \langle c_B \rangle^f + \langle c_B \rangle^f \nabla \varepsilon + \frac{1}{V} \int_{A_{sf}} \mathbf{n} c_B dA \right) \right] \\ + k_1 \alpha_A a_v \langle c_A \rangle_{sf} - k_2 \alpha_B a_v \langle c_B \rangle_{sf} \end{aligned} \quad (\text{A.3b})$$

where a_v is the specific area given by $a_v = \frac{A_{sf}}{V}$ and $\langle c_i \rangle_{sf}$ the area average of c_i defined by

$$\langle c_i \rangle_{sf} = \frac{1}{A_{sf}} \int_{A_{sf}} c_i dA, \quad i = A, B \quad (\text{A.4})$$

The averaged equations (A.3) contain both intrinsic average and point-wise concentrations. To remove the latter, the spatial decomposition

$$c_i = \langle c_i \rangle^f + \tilde{c}_i, \quad i = A, B \quad (\text{A.5})$$

is introduced [46], where \tilde{c}_i is the deviation of concentration which fluctuates at a typical length-scale ℓ_p while $\langle c_i \rangle^f$ experiences significant variations at the scale L . A consequence of the fact that $r_0 \ll L$ is that $\langle \tilde{c}_i \rangle^f \simeq 0$. Inserting the above decomposition into Eqs. (A.3) leads to

$$\begin{aligned} \varepsilon \frac{\partial \langle c_A \rangle^f}{\partial t} = & \nabla \cdot \left[\mathcal{D}_A \left(\varepsilon \nabla \langle c_A \rangle^f + \langle c_A \rangle^f \nabla \varepsilon + \frac{1}{V} \int_{\mathbf{A}_{sf}} \mathbf{n} \langle c_A \rangle^f dA \right. \right. \\ & \left. \left. + \frac{1}{V} \int_{\mathbf{A}_{sf}} \mathbf{n} \tilde{c}_A dA \right) \right] - k_1 \alpha_A a_v \left(\langle \tilde{c}_A \rangle_{sf} + \langle \langle c_A \rangle^f \rangle_{sf} \right) \end{aligned} \quad (\text{A.6a})$$

$$\begin{aligned} \varepsilon \frac{\partial \langle c_B \rangle^f}{\partial t} = & \nabla \cdot \left[\mathcal{D}_B \left(\varepsilon \nabla \langle c_B \rangle^f + \langle c_B \rangle^f \nabla \varepsilon + \frac{1}{V} \int_{\mathbf{A}_{sf}} \mathbf{n} \langle c_B \rangle^f dA \right. \right. \\ & \left. \left. + \frac{1}{V} \int_{\mathbf{A}_{sf}} \mathbf{n} \tilde{c}_B dA \right) \right] + k_1 \alpha_A a_v \left(\langle \tilde{c}_A \rangle_{sf} + \langle \langle c_A \rangle^f \rangle_{sf} \right) \\ & - k_2 \alpha_B a_v \left(\langle \tilde{c}_B \rangle_{sf} + \langle \langle c_B \rangle^f \rangle_{sf} \right) \end{aligned} \quad (\text{A.6b})$$

The intrinsic average, $\langle c_i \rangle^f$, $i = A, B$, in the area integral terms may be developed around the centroid of the averaging domain using a Taylor expansion. The 0^{th} -order terms of these expansions cancel with the terms $\langle c_i \rangle^f \nabla \varepsilon$ while order of magnitude estimates can be employed to show that the higher order terms are much smaller than $\varepsilon \nabla \langle c_i \rangle^f$ (see Chapter 1 in [34] for the details). In addition, it can be shown that, whenever the pore-scale kinetic number $Ki = \ell_p \max \left(\frac{k_1 \alpha_A}{\mathcal{D}_A}, \frac{k_2 \alpha_B}{\mathcal{D}_B} \right)$ satisfies the constraint $Ki \ll 1$, then $\tilde{c}_i \ll \langle c_i \rangle^f$, $i = A, B$ at \mathbf{A}_{sf} [34]. Moreover, by estimating the orders of magnitude of $\langle \langle c_i \rangle^f \rangle_{sf}$, it can be proven that $\langle \langle c_i \rangle^f \rangle_{sf} \approx \langle c_i \rangle^f$, $i = A, B$ [34]. As a consequence Eqs. (A.6) are reduced to the following forms

$$\varepsilon \frac{\partial \langle c_A \rangle^f}{\partial t} = \nabla \cdot \left[\mathcal{D}_A \left(\varepsilon \nabla \langle c_A \rangle^f + \frac{1}{V} \int_{\mathbf{A}_{sf}} \mathbf{n} \tilde{c}_A dA \right) \right] - k_1 \alpha_A a_v \langle c_A \rangle^f \quad (\text{A.7a})$$

$$\begin{aligned} \varepsilon \frac{\partial \langle c_B \rangle^f}{\partial t} = & \nabla \cdot \left[\mathcal{D}_B \left(\varepsilon \nabla \langle c_B \rangle^f + \frac{1}{V} \int_{\mathbf{A}_{sf}} \mathbf{n} \tilde{c}_B dA \right) \right] + k_1 \alpha_A a_v \langle c_A \rangle^f \\ & - k_2 \alpha_B a_v \langle c_B \rangle^f \end{aligned} \quad (\text{A.7b})$$

At this stage, the model remains unclosed since \tilde{c}_i is still present in the averaged mass balance equations. The aim is now to develop a closure, *i.e.* relationships between \tilde{c}_i and $\langle c_i \rangle^f$. This can be achieved by subtracting Eqs. (A.7) from the initial pore-scale equations (5a) together with the interfacial boundary conditions in order to derive an initial boundary value problem for \tilde{c}_i . When order of magnitude estimates are employed and under the constraint that the process is considered at a time scale such that

$$\frac{t}{\ell_p^2} \min(\mathcal{D}_i) \gg 1 \quad i = A, B \quad (\text{A.8})$$

it is not hard to deduce that the closure problems on \tilde{c}_A and \tilde{c}_B can be simplified to

$$\nabla^2 \tilde{c}_A = - \underbrace{\frac{\varepsilon^{-1} k_1 \alpha_A a_v}{\mathcal{D}_A} \langle c_A \rangle^f}_{\text{reactive volume source}} \quad \text{in } \mathbf{V}_f \quad (\text{A.9a})$$

$$-\mathbf{n} \cdot \mathcal{D}_A \nabla \tilde{c}_A = \underbrace{\mathbf{n} \cdot \mathcal{D}_A \nabla \langle c_A \rangle^f}_{\text{diffusive surface source}} + \underbrace{k_1 \alpha_A \langle c_A \rangle^f}_{\text{reactive surface source}} \quad \text{at } \mathbf{A}_{sf} \quad (\text{A.9b})$$

$$\langle \tilde{c}_A \rangle^f = 0 \quad (\text{A.9c})$$

$$\tilde{c}_A(\mathbf{r}) = \tilde{c}_A(\mathbf{r} + \ell_i \mathbf{e}_i) \quad i = 1, 2, 3 \quad (\text{A.9d})$$

$$\nabla^2 \tilde{c}_B = \underbrace{\frac{\varepsilon^{-1} k_1 \alpha_A a_v}{\mathcal{D}_B} \langle c_A \rangle^f}_{\text{reactive volume source from species A}} - \underbrace{\frac{\varepsilon^{-1} k_2 \alpha_B a_v}{\mathcal{D}_B} \langle c_B \rangle^f}_{\text{reactive volume source from species B}} \quad \text{in } \mathbf{V}_f \quad (\text{A.10a})$$

$$-\mathbf{n} \cdot \mathcal{D}_B \nabla \tilde{c}_B = \underbrace{\mathbf{n} \cdot \mathcal{D}_B \nabla \langle c_B \rangle^f}_{\text{diffusive surface source}} - \underbrace{k_1 \alpha_A \langle c_A \rangle^f}_{\text{reactive surface source from species A}} + \underbrace{k_2 \alpha_B \langle c_B \rangle^f}_{\text{reactive surface source from species B}} \quad \text{at } \mathbf{A}_{sf} \quad (\text{A.10b})$$

$$\langle \tilde{c}_B \rangle^f = 0 \quad (\text{A.10c})$$

$$\tilde{c}_B(\mathbf{r}) = \tilde{c}_B(\mathbf{r} + \ell_i \mathbf{e}_i) \quad i = 1, 2, 3 \quad (\text{A.10d})$$

358 Since the objective is not to solve these closure problems over the whole
359 structure of size L , and with the idea that the boundary condition at \mathbf{A}_{fe}

360 plays a significant role at a distance of the order of ℓ_p , the solution can
 361 be sought on a Representative Elementary Volume of the medium that is
 362 considered as periodic with a period $\ell_i \mathbf{e}_i$ in the i^{th} -direction ($i = 1, 2, 3$)
 363 so that the external boundary condition is replaced by periodic conditions
 364 expressed in Eqs. (A.9d) and (A.10d). It should be noted that periodicity is
 365 introduced as convenient boundary conditions at the closure level but does
 366 not restrict the applicability of the macroscopic model to periodic structures.

Because the two above problems on \tilde{c}_A and \tilde{c}_B are linear, their solutions can be sought in terms of linear combinations of the sources identified in Eqs. (A.9) and (A.10). This allows writing the formal solutions as

$$\tilde{c}_A = \mathbf{b} \cdot \nabla \langle c_A \rangle^f + s_1 \langle c_A \rangle^f \quad (\text{A.11a})$$

$$\tilde{c}_B = \mathbf{b} \cdot \nabla \langle c_B \rangle^f + s_2 \langle c_A \rangle^f + s_3 \langle c_B \rangle^f \quad (\text{A.11b})$$

367 where \mathbf{b} , s_1 , s_2 and s_3 are the closure variables. When these formal solutions
 368 are introduced in the closure problems in Eqs. (A.9) and (A.10), and when
 369 the contributions from each source are separated, the closure variables are
 370 found to obey the four following closure problems

Problem I

$$\nabla^2 \mathbf{b} = 0 \quad \text{in } \mathbf{V}_f \quad (\text{A.12a})$$

$$\mathbf{n} \cdot \nabla \mathbf{b} = -\mathbf{n} \quad \text{at } \mathbf{A}_{sf} \quad (\text{A.12b})$$

$$\langle \mathbf{b} \rangle^f = 0 \quad (\text{A.12c})$$

$$\mathbf{b}(\mathbf{r}) = \mathbf{b}(\mathbf{r} + \ell_i \mathbf{e}_i) \quad (\text{A.12d})$$

371

Problem II

$$\nabla^2 s_1 = -\frac{\varepsilon^{-1} k_1 \alpha_A a_v}{\mathcal{D}_A} \quad \text{in } \mathbf{V}_f \quad (\text{A.13a})$$

$$\mathbf{n} \cdot \nabla s_1 = -\frac{k_1 \alpha_A}{\mathcal{D}_A} \quad \text{at } \mathbf{A}_{sf} \quad (\text{A.13b})$$

$$\langle s_1 \rangle^f = 0 \quad (\text{A.13c})$$

$$s_1(\mathbf{r}) = s_1(\mathbf{r} + \ell_i \mathbf{e}_i) \quad (\text{A.13d})$$

Problem III

$$\nabla^2 s_2 = \frac{\varepsilon^{-1} k_1 \alpha_A a_v}{\mathcal{D}_B} \quad \text{in } \mathbf{V}_f \quad (\text{A.14a})$$

$$\mathbf{n} \cdot \nabla s_2 = \frac{k_1 \alpha_A}{\mathcal{D}_B} \quad \text{at } \mathbf{A}_{sf} \quad (\text{A.14b})$$

$$\langle s_2 \rangle^f = 0 \quad (\text{A.14c})$$

$$s_2(\mathbf{r}) = s_2(\mathbf{r} + \ell_i \mathbf{e}_i) \quad (\text{A.14d})$$

Problem IV

$$\nabla^2 s_3 = -\frac{\varepsilon^{-1} k_2 \alpha_B a_v}{\mathcal{D}_B} \quad \text{in } \mathbf{V}_f \quad (\text{A.15a})$$

$$\mathbf{n} \cdot \nabla s_3 = -\frac{k_2 \alpha_B}{\mathcal{D}_B} \quad \text{at } \mathbf{A}_{sf} \quad (\text{A.15b})$$

$$\langle s_3 \rangle^f = 0 \quad (\text{A.15c})$$

$$s_3(\mathbf{r}) = s_3(\mathbf{r} + \ell_i \mathbf{e}_i) \quad (\text{A.15d})$$

Inserting the representations of \tilde{c}_A and \tilde{c}_B into the average equation (A.7) finally yields the closed macroscopic mass balance equations

$$\begin{aligned} \varepsilon \frac{\partial \langle c_A \rangle^f}{\partial t} &= \nabla \cdot (\varepsilon \mathcal{D}_A \mathbf{D}_{eff}^* \cdot \nabla \langle c_A \rangle^f) + \nabla \cdot (\mathbf{u}_1 \langle c_A \rangle^f) \\ &\quad - k_1 \alpha_A a_v \langle c_A \rangle^f \end{aligned} \quad (\text{A.16a})$$

$$\begin{aligned} \varepsilon \frac{\partial \langle c_B \rangle^f}{\partial t} &= \nabla \cdot (\varepsilon \mathcal{D}_B \mathbf{D}_{eff}^* \cdot \nabla \langle c_B \rangle^f) + \nabla \cdot (\mathbf{u}_2 \langle c_B \rangle^f) \\ &\quad + \nabla \cdot (\mathbf{u}_3 \langle c_B \rangle^f) + k_1 \alpha_A a_v \langle c_A \rangle^f - k_2 \alpha_B a_v \langle c_B \rangle^f \end{aligned} \quad (\text{A.16b})$$

with the effective parameters \mathbf{D}_{eff}^* , \mathbf{u}_1 , \mathbf{u}_2 and \mathbf{u}_3 given by

$$\mathbf{D}_{eff}^* = \mathbf{I} + \frac{1}{V_f} \int_{\mathbf{A}_{sf}} \mathbf{n} b dA \quad (\text{A.17a})$$

$$\begin{aligned} \mathbf{u}_1 &= \frac{\mathcal{D}_A}{V} \left(\int_{\mathbf{A}_{sf}} \mathbf{n} s_1 dA \right); \quad \mathbf{u}_2 = \frac{\mathcal{D}_B}{V} \left(\int_{\mathbf{A}_{sf}} \mathbf{n} s_2 dA \right); \\ \mathbf{u}_3 &= \frac{\mathcal{D}_B}{V} \left(\int_{\mathbf{A}_{sf}} \mathbf{n} s_3 dA \right) \end{aligned} \quad (\text{A.17b})$$

From Eqs. (A.13b), (A.14b) and (A.15b), the order of magnitude estimates of the closure variables s_1 , s_2 and s_3 at \mathbf{A}_{sf} can be extracted to give

$$s_1 = \mathbf{O} \left(\frac{l_p k_1 \alpha_A}{\mathcal{D}_A} \right); \quad s_2 = \mathbf{O} \left(\frac{l_p k_1 \alpha_A}{\mathcal{D}_B} \right); \quad s_3 = \mathbf{O} \left(\frac{l_p k_2 \alpha_B}{\mathcal{D}_B} \right) \quad (\text{A.18a})$$

Once introduced in Eqs. (A.17b), this leads to the following order of magnitude estimates

$$\begin{aligned} \nabla \cdot (\mathbf{u}_1 \langle c_A \rangle^f) &= \mathbf{O} \left(\frac{k_1 \alpha_A}{L} \langle c_A \rangle^f \right); & \nabla \cdot (\mathbf{u}_2 \langle c_A \rangle^f) &= \mathbf{O} \left(\frac{k_1 \alpha_A}{L} \langle c_A \rangle^f \right); \\ \nabla \cdot (\mathbf{u}_3 \langle c_B \rangle^f) &= \mathbf{O} \left(\frac{k_2 \alpha_B}{L} \langle c_B \rangle^f \right) \end{aligned} \quad (\text{A.19})$$

However, the order of magnitude estimates for the macroscopic reactive terms are

$$k_1 \alpha_A a_v \langle c_A \rangle^f = \mathbf{O} \left(\frac{k_1 \alpha_A}{\ell_p} \langle c_A \rangle^f \right); \quad k_2 \alpha_B a_v \langle c_B \rangle^f = \mathbf{O} \left(\frac{k_2 \alpha_B}{\ell_p} \langle c_B \rangle^f \right) \quad (\text{A.20})$$

In the latter, a_v was estimated to be $a_v = \mathbf{O}(\ell_p^{-1})$. From Eqs. (A.19) and (A.20), and due to the length-scale hierarchy $\ell_p \ll L$, it follows that the macroscopic diffusion/reaction equations (A.16) can be written in their final simplified forms as

$$\varepsilon \frac{\partial \langle c_A \rangle^f}{\partial t} = \nabla \cdot (\varepsilon \mathcal{D}_A \mathbf{D}_{eff}^* \cdot \nabla \langle c_A \rangle^f) - k_1 \alpha_A a_v \langle c_A \rangle^f \quad (\text{A.21a})$$

$$\begin{aligned} \varepsilon \frac{\partial \langle c_B \rangle^f}{\partial t} &= \nabla \cdot (\varepsilon \mathcal{D}_B \mathbf{D}_{eff}^* \cdot \nabla \langle c_A \rangle^f) + k_1 \alpha_A a_v \langle c_A \rangle^f \\ &\quad - k_2 \alpha_B a_v \langle c_B \rangle^f \end{aligned} \quad (\text{A.21b})$$

372 It is worth noting that, after the simplifications resulting from the order of
 373 magnitude estimates, the macroscopic mass balance equations (A.21) for the
 374 two species only require the solution of the closure problem I in Eqs. (A.12)
 375 yielding the effective diffusivity tensor \mathbf{D}_{eff}^* given by Eq. (A.17a).

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