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Multi-scale modeling of coupled diffusion-electrochemical reaction for porous micro-electrodes with enzymatic catalysis

T. D. Le^a, D. Lasseux^a, A. Kuhn^b, N. Mano^c, G. Vignoles^d

^a*Institut de Mécanique et d'ingénierie (I2M), Bordeaux.*

^b*Institute of Molecular Science (IMS), Bordeaux.*

^c*Centre de Recherche Paul Pascal (CRPP), Bordeaux.*

^d*Laboratoire des Composites Thermostructuraux (LCTS), Bordeaux.*

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1. Introduction

Porous electrodes with high specific surface area have been efficiently applied to design miniaturized electro-devices such as bio-batteries, bio-captors, etc. Such electrodes may provide much higher electrical current than classical flat electrodes of the same macroscopic size [4]. In a previous work [2], a multi-scale model of diffusion and electrochemical reaction in porous electrodes has been developed for a simple oxygen reduction reaction so that oxygen is reduced to hydrogen peroxide by directly consuming electrons at the cathode. In order to improve the efficiency of such devices, redox reactions may be catalyzed by enzymes which are immobilized within a polymer layer in the vicinity of the solid surface [3]. In the present work, we develop a multi-scale model of coupled transport and electrochemical reaction in porous electrodes operating in the enzymatic Direct Electron Transfer regime where complex reactions induced by the enzymes together with their mass balance are taken into account.

At the microscopic pore-scale, an electrochemical model for complex redox enzymatic reactions at the solid-fluid interface is developed, considering the oxygen reduction reaction which is catalyzed by the bilirubin oxidase enzyme (BOD) at the cathode. In this scenario, the Butler-Volmer equation is used to relate the potential and reaction rates with the current. This electrochemical model is further coupled with the mass transfer of oxygen governed by Fick's law and the mass balance of enzymes to form the microscopic coupled model in a transient regime. By making use of the volume averaging method [5], the above mentioned microscopic problem is upscaled to obtain a macroscopic model. This model is characterized by a macroscopic coupled diffusion-reaction equation in the porous electrode involving an effective diffusion coefficient that can be computed from the solution of an intrinsic closure problem.

Using a model pore geometry, 3D direct numerical simulations of the microscopic model are carried out and compared to 1D numerical simulations of the macro-model. Excellent agreement between the oxygen concentration profiles within the electrodes obtained from the two models is observed while a speed-up of about 21600 is achieved with the 1D macro-model illustrating the capability of the multi-scale approach. Such a model is capable of predicting the electrical current density with respect to the pore-space architecture providing a useful tool for electrode microstructural optimization. A successful comparison between the model and experiments is also reported.

2. Numerical results

2.1. Pore-scale model

The pore-scale diffusion/reaction model is written at the microscale for the enzymatic direct electron transfer regime. In this context, an electrochemical model based on Butler-Volmer equation [1] for the reduction reaction of oxygen catalyzed by the BODs is proposed and coupled with the diffusive mechanism of oxygen and mass balance of enzyme under non steady-state condition. The 3D numerical experiments for voltametry were performed on a computational domain represented in Fig. 1(a). The porous electrode is composed of 10 periodic FCC unit cells in the z -direction between $z = -L_e$ (where L_e is the electrode's thickness) and $z = 0$ and periodic boundary conditions are applied along x and y

directions. In addition, at $z = 0$ the electrode is in contact with the diffusion fluid layer (the bulk fluid) between $z = 0$ and $z = L_N$ where molecular diffusion takes place. A zero flux condition at $z = -L_e$, and constant concentration, $c_{O_2}^0$ at $z = L_N$ are imposed. The initial concentration of oxygen is supposed to be uniform equal to $c_{O_2}^0$. Dimensionless concentration fields obtained from DNS are represented in Fig. 1(b) at $t = 10s, 41s$ and $71s$ highlighting the coupled diffusion-reaction process inside the porous electrode. We may observe the decrease of oxygen concentration during the voltametry.

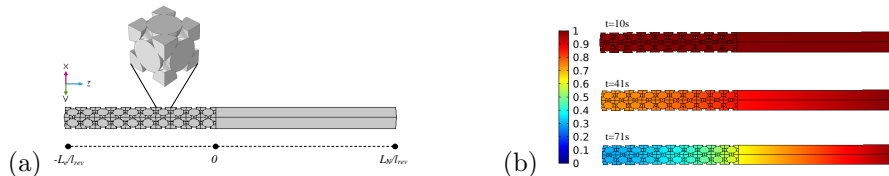


Figure 1: (a) 3D domain for the direct numerical simulation; (b) Normalized concentration fields $c_{O_2}^*$ at $t = 10s, 41s$ and $71s$

2.2. Macroscopic model

The pore-scale model is upscaled to the macroscale by using the volume averaging method [5]. In Fig. 2(a), the current curve obtained from the simulation of macroscopic model is compared to the results of 3D DNS with different mesh refinements defined in Comsol Multiphysics: finer, extra fine and extremely fine. A very good agreement is obtained between the two models with the extremely fine mesh, validating the macroscopic model whose simulation requires only 1 second in contrast to 6 hours for 3D DNS. Furthermore, these results also validate our upscaling approach providing a powerful tool to study the physical and electrochemical properties of a porous electrode modified by enzymes. In Fig. 2(b), we have represented the intensity versus the scanning potential obtained from our numerical simulation using the upscaled model together with the experimental results. The agreement of our simulation results with measurements on the different electrodes is very satisfactory.

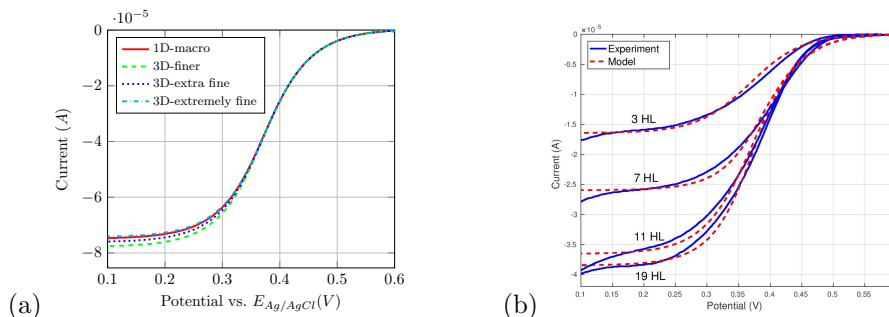


Figure 2: Comparisons between (a) the current curves during voltametry obtained from 3D DNS for different mesh refinements and 1D macroscopic simulation; (b) the macroscopic model numerical simulation and experimental data

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