



# Multi-scale modeling of diffusion and electrochemical reactions in porous micro-electrodes



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## HIGHLIGHTS

- A diffusion and electrochemical reaction model in a porous electrode is proposed.
- A macroscale model operating at the electrode scale is obtained by upscaling.
- The macroscale model is validated by direct numerical simulation and experiments.

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## ABSTRACT

A multi-scale model of diffusion/reaction at play in a porous electrode is developed and solutions to the physico-electro-chemical coupled problem are provided. This represents a key step to progress in the optimization of new efficient and innovative micro-electro-devices that needs to be addressed from a chemical engineering point of view. The pore-scale model based on Fickian diffusion in the porous medium and Nernstian layer and the electrochemical reaction governed by the Buttlar-Volmer equation is upscaled using volume averaging to obtain a macroscopic model that describes the process on an effective equivalent medium. The validity and accuracy of the macroscopic model is successfully checked through the comparison with direct numerical simulations of the initial microscale model for amperometry tests. Predictions obtained from the upscaled model on the current intensity versus the scanning potential during voltammetry reveal to be in very good agreement with experimental results reported in the literature. These results show the capability of the macroscopic model to analyze the behavior of the porous electrode. In particular, it provides an efficient tool to study the dependence of the current intensity on the microstructure of the porous material and on the electrochemical parameters with the perspective of optimizing the electrode efficiency.

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## 1. Introduction

Porous electrodes have become a privileged solution for miniaturized and potentially *in vivo* implantable active and passive electro-analytical devices such as biosensors, bioactuators, batteries, etc. thanks to their high specific surface area which allows efficient *in situ* electrical energy production through the use of rather well-controlled redox couples. Indeed, for a given over-potential, such electrodes may provide electrical current at least one order

of magnitude higher than classical flat electrodes of the same size (Walcarius and Kuhn, 2008; Szamocki et al., 2006) making possible a reduction of the overall macroscopic size of electrodes down to a few tens of micrometers in thickness and a few millimeters in extent. For the past two decades, porous electrodes have often been synthesized by self-assembly and electrodeposition (Reclusa and Ravaine, 2003) using the Langmuir-Blodgett technique (Blodgett, 1935). These techniques allow to create a wide range of porous microstructures with tunable porosity as well as controllable architecture (Karajić et al., 2015).

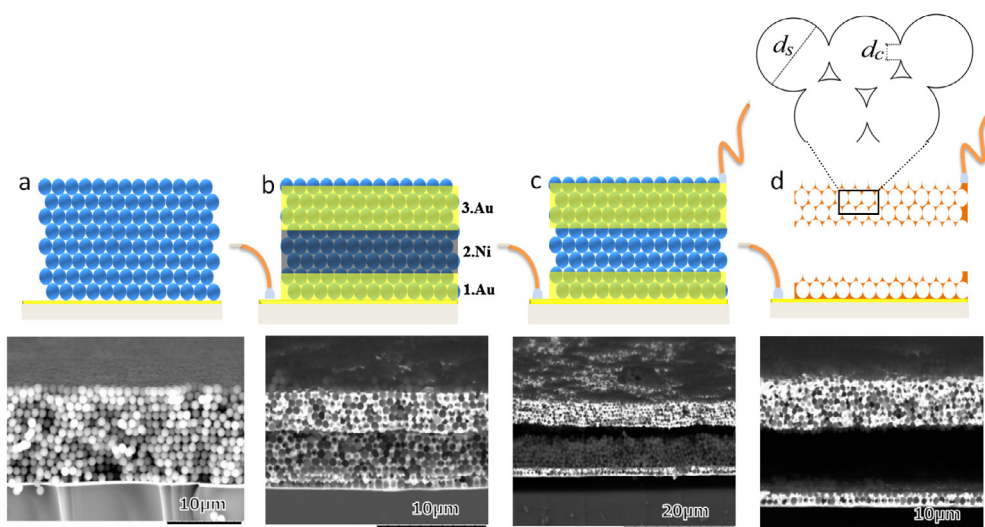
An illustration of the overall procedure, inspired from Bartlett et al. (2000), is sketched in Fig. 1.1 representing the four main steps to obtain a miniaturized two-electrode electrochemical cell using this technique (Karajić et al., 2015). The first step consists in the

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## Nomenclature

$A_{sf}$	solid/fluid interface in the averaging volume	$n$	number of transferred electrons
$A_{sf}$	measure of $A_{sf}$ ( $m^2$ )	$\mathbf{n}$	unit normal vector to the solid-fluid interface pointing out of the fluid phase
$A_{fe}$	interface between the fluid phase in the electrode and the external bulk fluid	$\mathbf{r}$	position vector (m)
$a_v$	specific area ( $m^{-1}$ )	$R$	Ideal gas constant (J/K/mol)
$\mathbf{b}$	closure variable that maps $\nabla\langle c_A \rangle^f$ onto $\tilde{c}_A$ (m)	$r_0$	characteristic size of the averaging volume (m)
$c_X$	concentration of species $X$ ( $X = A$ or $B$ ) ( $mol/m^3$ )	$r_E$	potential scan rate (V/s)
$c_A^0$	bulk concentration of species $A$ ( $mol/m^3$ )	$R_{red}$	reduction reaction rate ( $mol/m^2/s$ )
$\langle c_A \rangle$	superficial average of $c_A$ ( $mol/m^3$ )	$s$	closure variable that maps $\langle c_A \rangle^f$ onto $\tilde{c}_A$
$\langle c_A \rangle^f$	intrinsic average of $c_A$ ( $mol/m^3$ )	$T$	temperature (K)
$\langle c_A \rangle_{sf}$	area average of $c_A$ ( $mol/m^2$ )	$\mathbf{u}$	effective vector associated with the chemical reaction (m/s)
$\tilde{c}_A$	concentration deviation ( $mol/m^3$ )	$V$	averaging volume
$\overline{c}_A$	dimensionless concentration averaged over the fluid domain	$V$	measure of $V$ ( $m^3$ )
$D_A$	molecular diffusion coefficient of species $A$ ( $m^2/s$ )	$V_f$	domain occupied by the fluid phase within the averaging volume
$\mathbf{D}_{eff}$	effective diffusion tensor ( $m^2/s$ )	$V_f$	measure of $V_f$ ( $m^3$ )
$D_{eff}$	effective diffusion coefficient in the isotropic case ( $m^2/s$ )	$V_s$	domain occupied by the solid phase within the averaging volume
$d_s, d_c$	diameter of spherical pore, pore connection window size (m)	$V_s$	measure of $V_s$ ( $m^3$ )
$E, E^0$	potential, standard potential (V)	$\mathbf{x}$	position vector of the centroid of the averaging volume (m)
$F$	Faraday's constant (C/mol)	$\mathbf{y}$	relative position vector locating points in the fluid phase (m)
$\mathcal{F}_A$	initial concentration of species $A$ ( $mol/m^3$ )	$x, y, z$	directions in cartesian coordinate system
$\mathcal{G}_A$	concentration of species $A$ at the interface $A_{fe}$ ( $mol/m^3$ )	$(\ )^*$	dimensionless quantity
$i_v$	current per unit volume at the scale of the representative unit cell ( $A/m^3$ )	$\alpha$	electron transfer coefficient
$I$	total current intensity (A)	$\alpha_A$	potential dependent term, $\alpha_A = \exp\frac{-z_nF(E-E^0)}{RT}$
$\mathbf{I}$	unit tensor	$\nabla \cdot$	divergence operator
$\mathcal{I}_{sf}$	solid/fluid interface	$\varepsilon_f$	porosity of the electrode
$j$	current density ( $A/m^2$ )	$\Omega$	domain occupied by the electrode
$k_0$	electron transfer rate constant (cm/s)	$\Omega_e$	domain occupied by the external bulk fluid (Nernstian layer)
$K_{eff}$	effective reaction rate coefficient (m/s)	$\Omega_f$	domain occupied by the fluid phase within the electrode
$Ki$	pore-scale kinetic number, $Ki = \frac{k_0 \alpha_A \ell_p}{D_A}$	$\Omega_s$	domain occupied by the solid phase within the electrode
$L_{elec}$	electrode thickness (m)	$\nabla$	gradient operator
$L_N$	Nernstian layer thickness (m)		
$\ell_i$	periodic lattice vector in the $i$ th-direction (m)		
$\ell_p$	characteristic pore size ( $\ell_p \equiv d_s$ ) (m)		
$\ell_{REV}$	size of the periodic representative unit cell (m)		



**Fig. 1.1.** Two-coaxial electrochemical cell synthesis (from Karajić et al., 2015). *Top*: schematic representation of the different steps. *Bottom*: Corresponding cross-sectional SEM images of the material.

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