

Electrocatalysis and direct electron transfer simulations at heterogeneous surfaces using the finite element method

Rafael A. L. Chioquetti¹, João V. S. Vital¹, Wellington L. Santana¹, Raphael P. Bacil¹, Silvia H. P. Serrano*¹

rafaelchioquetti@usp.br; shps@iq.usp.br

¹Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo (USP)

Keywords: Heterogeneous surfaces, Electrocatalysis, Mass transport, Finite Element Method

Highlights

A MATLAB-based simulation using the finite element method was developed to study electrocatalysis and electron transfer on heterogeneous surfaces, modeling kinetic variations, radial diffusion, and catalyst dispersion.

Abstract

Voltammetry on heterogeneous surfaces is crucial for environmental electrochemistry, particularly for green energy production, pollutant degradation, and sensing technologies. Here, we present a MATLAB-based simulation model for studying electrocatalytic and direct electron transfer processes on heterogeneous surfaces, considering kinetic diversity and radial diffusion effects. This model can provide valuable insights into mass transport efficiency on experimental and preparative scales, making electrocatalysis more viable for environmental and industrial applications. Finite element method (FEM) was used for calculations involving systems of partial differential equations, modeled and solved with MATLAB 2022b 'PDE Toolbox.' The simulation script was entirely developed by our group.

For direct electron transfer, exponential distributions of electrode kinetics were modeled. Electroactive species react with varying kinetics across the surface, with increasing overpotential activating different electrode areas, creating distinct voltammetric profiles. These profiles can be experimentally verified in chemically modified electrodes and applied in sensor development. Kinetic distribution can follow a known function or be random, allowing diverse heterogeneous surfaces to be simulated.

Additionally, electrocatalysis at non-homogeneously coated electrodes was modeled. Considering an electrochemically activated catalyst bound to an electrode surface, where its reactive form converts a free-moving substrate, we compared catalytic efficiency at film-coated electrodes and those with varied catalyst dispersions. For heterogeneously coated electrodes, radial diffusion toward "kinetic islands" enhances mass transport and increases catalytic efficiency. The model also allows the study of kinetic dispersion, surface dynamics, and electrode geometry on catalyst efficiency.

This simulation tool offers new possibilities for optimizing electrochemical processes in environmental and industrial applications. It is especially valuable for designing efficient systems for green hydrogen production and CO₂ reduction, crucial for sustainable energy and environmental remediation. Our model enhances catalytic and sensing technologies, supporting cleaner, greener solutions for the future.

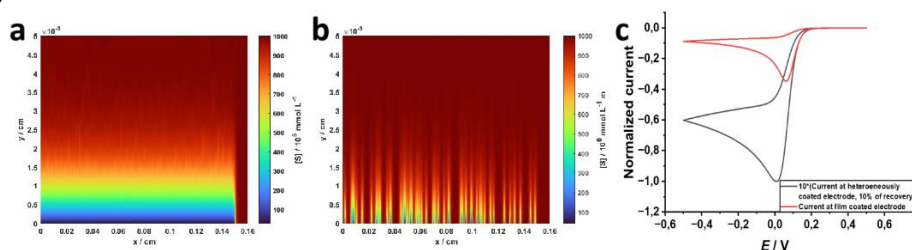


Figure 1. Concentration profiles at 0 V near homogeneously (a) and non-homogeneously, 10% coated (b) electrode performing the catalytic conversion of a substrate in solution (electrode radius: 0.15 cm). (c) Normalized voltammograms generated in simulations including homogeneous and heterogeneous models shown in figures (a) and (b), accounting for the different surface concentrations of catalyst.

[1] G. Acosta-Santoyo, J. Treviño-Reséndez, I. Robles, L.A. Godínez, J.D. García-Espinoza, A review on recent environmental electrochemistry approaches for the consolidation of a circular economy model, *Chemosphere* 346 (2024) 140573. <https://doi.org/10.1016/j.chemosphere.2023.140573>.

[2] R.A. L. Chioquetti, D.P.C. da Silva, S.H.P. Serrano, Modification of carbon paste electrodes for the selective determination of adenosine in the presence of phosphate adenylic derivatives, *Journal of Solid State Electrochemistry* (2024). <https://doi.org/10.1007/s10008-024-05972-w>.

[3] C. Costentin, J.-M. Saveant, Cyclic Voltammetry Analysis of Electrocatalytic Films, *The Journal of Physical Chemistry C* 119 (2015) 12174–12182. <https://doi.org/10.1021/acs.jpcc.5b02376>.

Acknowledgments

