

# Modeling and Simulation of Redox Titration of Metal Oxides at Porous Microelectrodes

Luis Balboa\*, Michael Hänsch, Johannes Behnken, Gert Wittstock  
 Institute of Chemistry, Carl von Ossietzky University of Oldenburg, Oldenburg, Germany  
 \*email: luis.humberto.balboa.blanco@uni-oldenburg.de

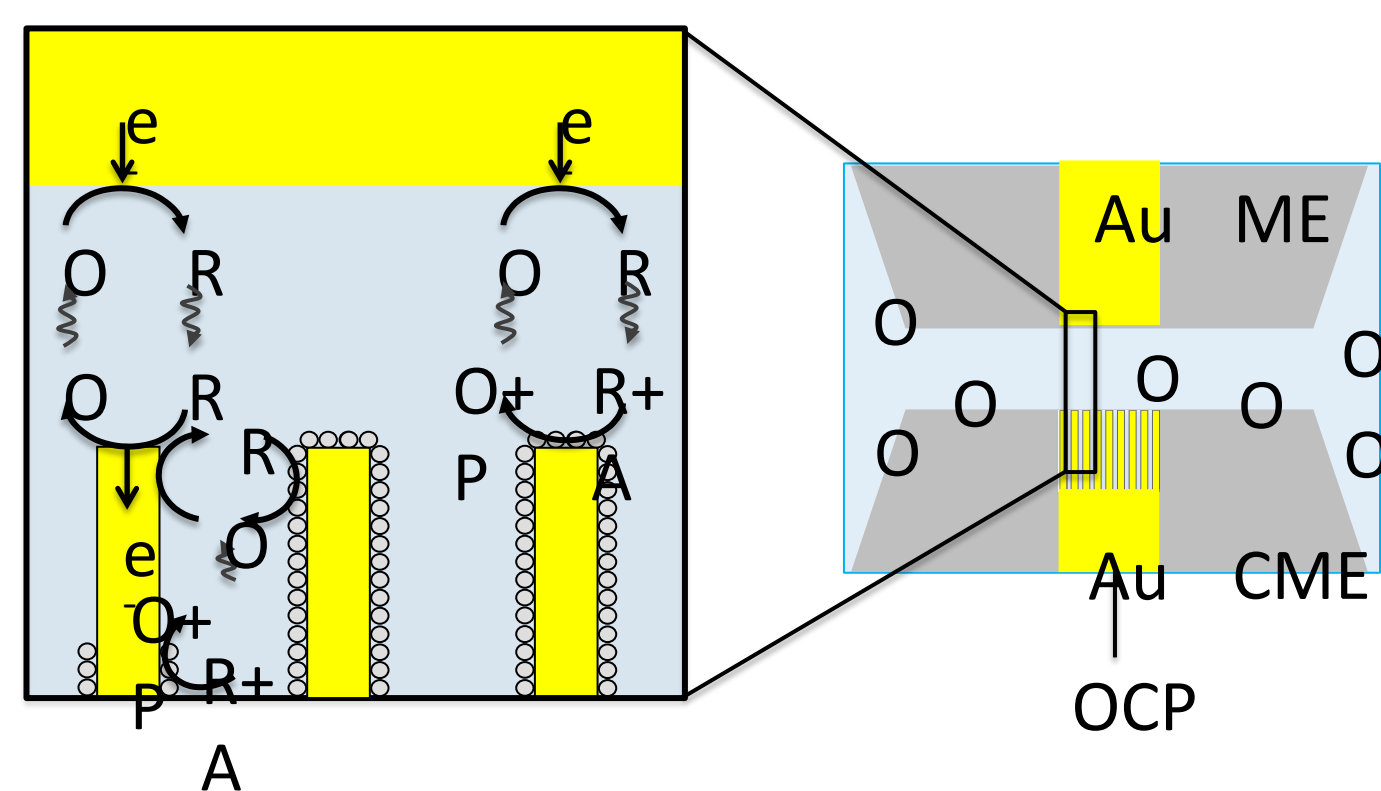
## Introduction:

Porous nanostructured materials have been investigated and used for a large variety of applications like batteries, fuel cells, sensing and more [1]

- Surface interrogation scanning electrochemical microscopy (SI-SECM) investigations require comparison to reaction-transport models [2]
- a 2D axisymmetric geometry was used to describe the system depicted in the experimental SI-SECM setup below
- Aim of this work:** simulation of mass transport and surface reactions in the porous structure and its effect on the current response for oxide titration experiments
- Approach:**
  - explicit treatment of solid and liquid parts in porous media using a 2D axisymmetric geometry

## Experimental setup:

- schematic of the SECM setup simulated using COMSOL Multiphysics
- the setup considers a flat electrode (interrogator, ME1) aligned on top of a cavity electrode (sample, CME) filled with porous gold and platinum
- Surface oxides at the CME are reduced by the redox mediator (R) generated at the ME, the mediator in the electrolyte which is in turn oxidized (O). O diffuses back to ME where it is reconverted into R. As long as there are oxides adsorbed at the sample a current is registered at the ME which can be used to calculate the oxide coverage of the sample



## Boundary conditions:

### Diffusion in the Electrolyte

$$\frac{\partial c_i}{\partial t} = D_i \left( \frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2} \right)$$

### (1) Tip Microelectrode

$$\frac{\partial c_O}{\partial t} = -c_O k_0 e^{-\frac{\alpha F}{RT}(E-E_0)} + c_R k_0 e^{-\frac{(1-\alpha)F}{RT}(E-E_0)}$$

### Current at the tip

$$i_{tip} = 2\pi D_0 \int_{r=0}^{r=rt} \frac{\partial c_O}{\partial z} r dr$$

### (2) Porous electrode

$$\frac{\partial c_O}{\partial t} = (\theta_1 - \theta_2) k_{ox1} c_R + \theta_2 k_{ox2} c_R$$

$$\frac{\partial c_R}{\partial t} = -((\theta_1 - \theta_2) k_{ox1} c_R + \theta_2 k_{ox2} c_R)$$

$$\frac{\partial \Gamma_1}{\partial t} = (\theta_1 - \theta_2) k_{ox1} c_R + D_{ox1} \nabla^2 \Gamma_1$$

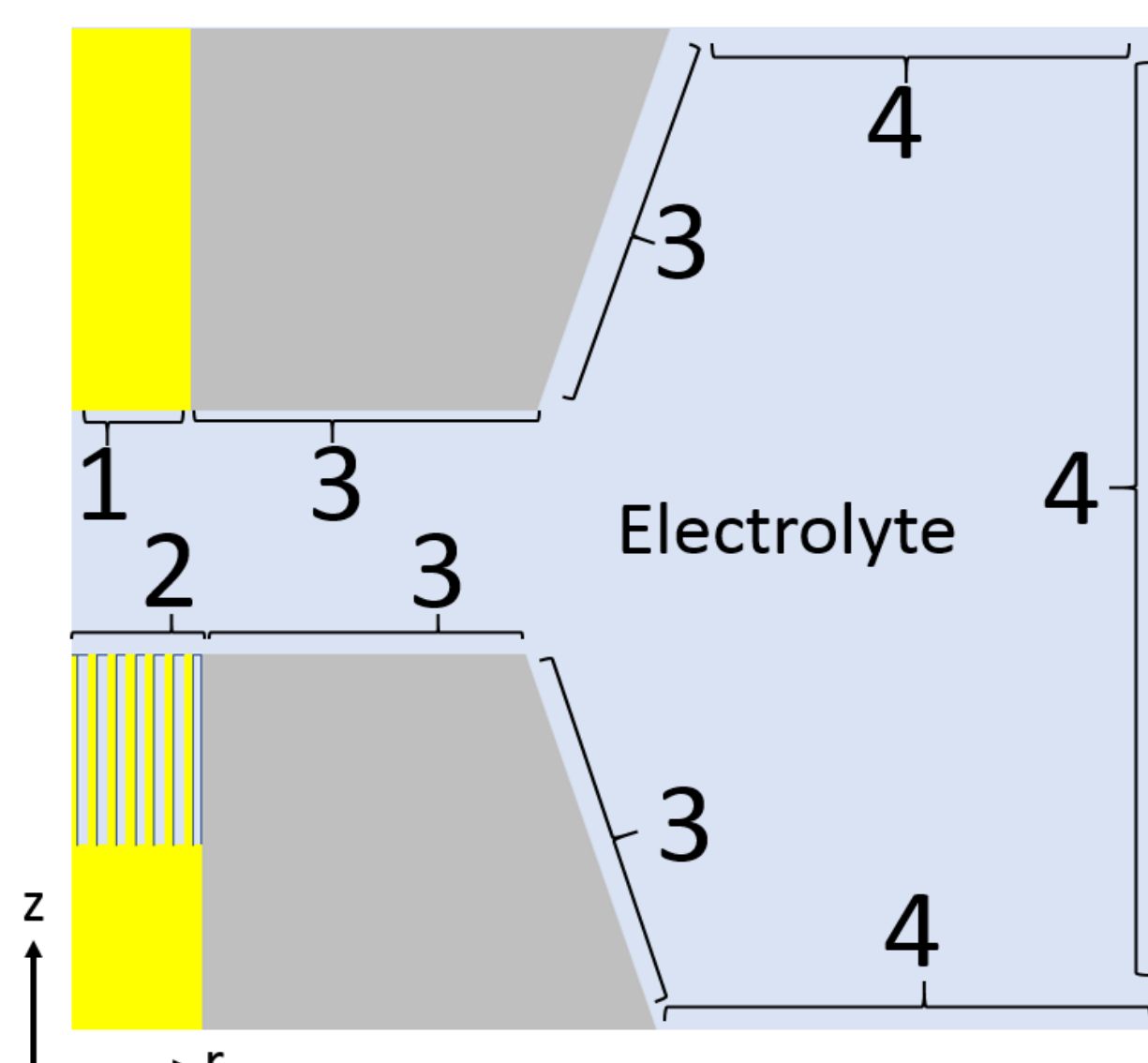
$$\frac{\partial \Gamma_2}{\partial t} = \theta_2 k_{ox2} c_R + D_{ox2} \nabla^2 \Gamma_2$$

$$\theta_1 = \min\left(\frac{\Gamma_1}{\Gamma_{max}}, 1\right)$$

$$\theta_2 = \min\left(\frac{\Gamma_2}{\Gamma_{max}}, 1\right)$$

### (3) Insulator Glass

$$\frac{\partial c_O}{\partial t} = 0 \quad \frac{\partial c_R}{\partial t} = 0$$



### (4) Bulk

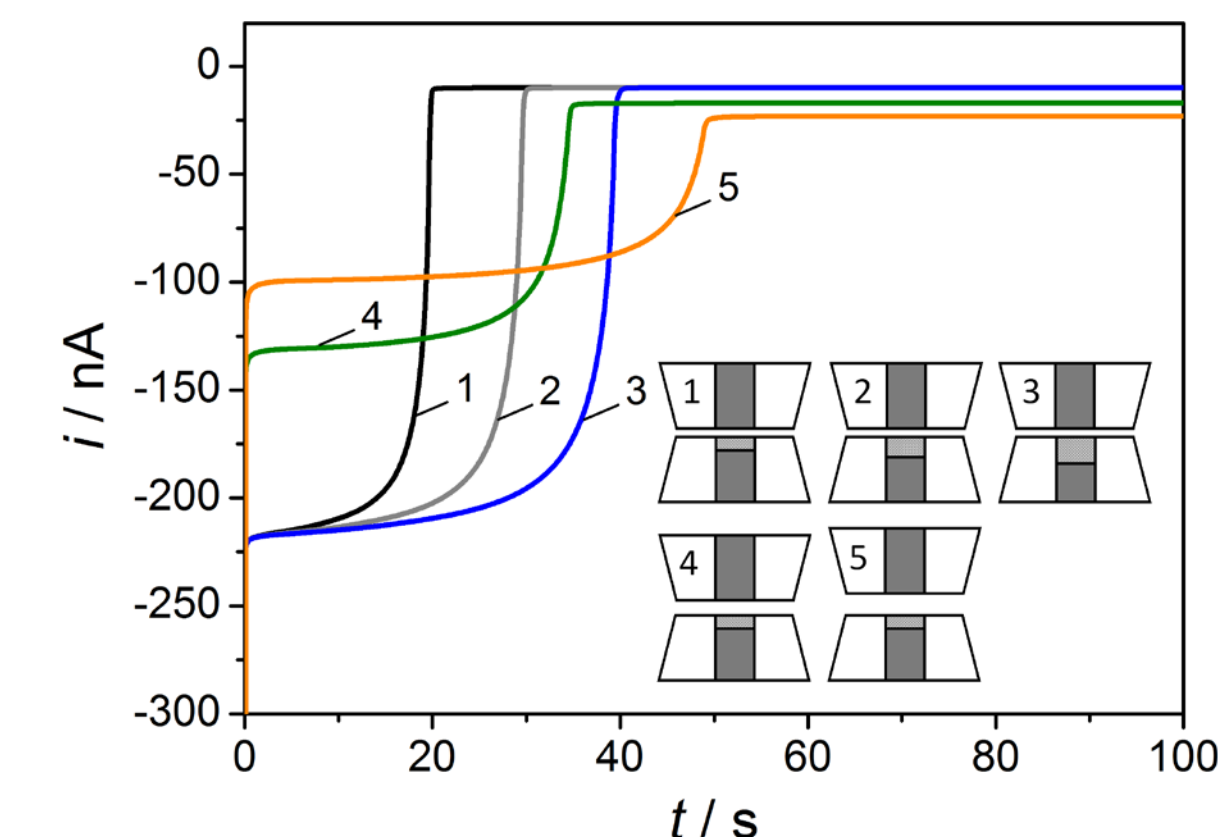
$$c_O = c_O^{bulk}$$

$$c_R = 0$$

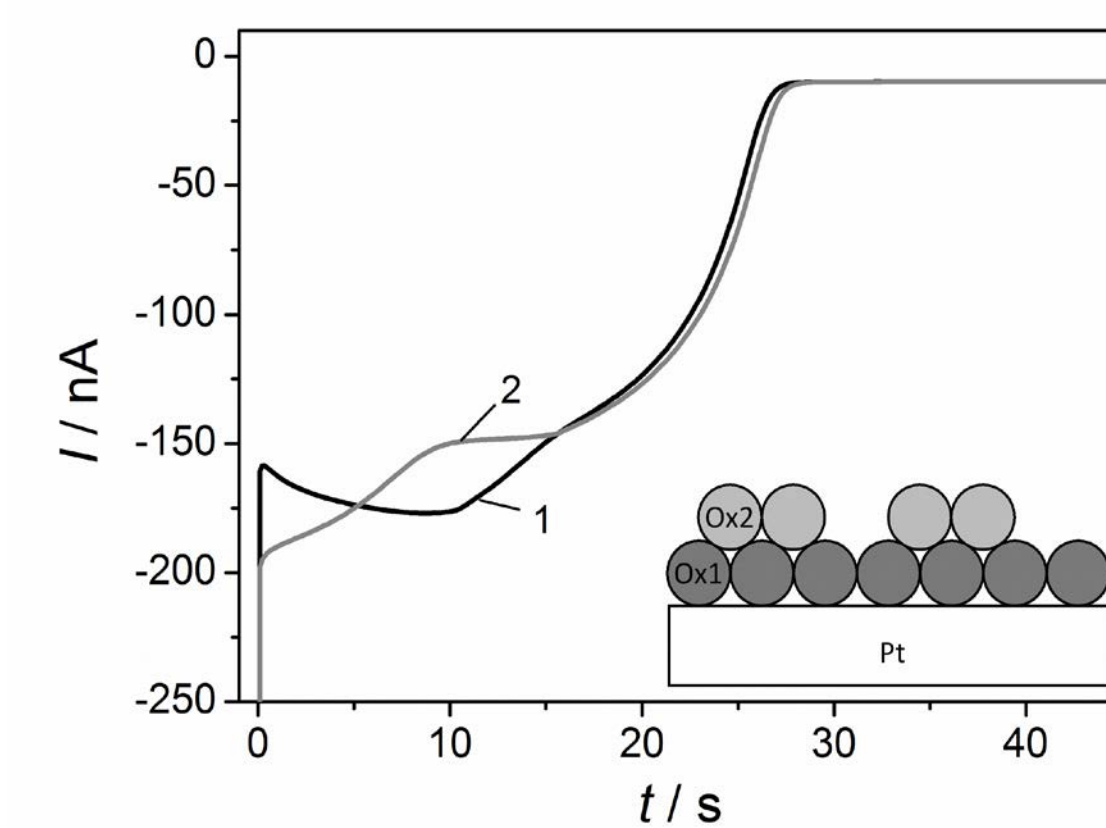
- c mediator concentration
- D diffusion coefficient
- k rate constant
- E potential
- Θ surface coverage
- Γ surface concentration
- i=O,R oxidized/reduced form of mediator

## Computational Results:

SI-SECM was used to detect different amounts of surface oxides on porous gold and platinum CME. Figure A shows the titration curves of the three CMEs with increasing electrochemical area, the titrated amount of oxides increases and therefore the detection time increases. Curves 1, 2 and 3 shows simulated titration curves for varying cavity depths h and curves 4 and 5 two different working distances d according to the experiments conducted on nanoporous gold-CMEs. Four features changes with increasing d are observed: the background current increases, the overall current decreases, longer detection times are required to transfer the same charge from the NPG sample, the current decays more slowly after completion of the titration



In order to further investigate the influence of two different oxide species distinguished by the rate constants for the chemical reaction with the mediator. The amount of Ox1 were initially set to 1 monolayer and for Ox2 0.5 monolayer while the rate constant was set 10 times faster for Ox1 than for Ox2 for curve 1 and the other way around for curve 2. Ox1 can only react if Ox2 was already partly removed. Curve 1 shows an initial decrease in current due to the slow reaction of Ox2 followed by an increase in current due to the faster reaction of Ox1 until the oxides are consumed and the current drops to the current controlled by hindered mediator diffusion. In curve 2, the current transient shows an initially higher current, due to the faster reaction rate of Ox2 which drops to a current plateau due to the slower rate constant of the underlying Ox1 before decreasing to the current controlled by hindered mediator diffusion. This simulation shows that depending on the reaction rates of two different oxide species, qualitatively different current transients may result for the same total charge. These results agree with the observed behavior in the experiments when comparing oxides adsorbed on porous gold and platinum electrodes



## Conclusions:

While the exact shape of the current transient obtained in the experiments could not be reproduced, the four features described were also observed experimentally. By setting a diffusion coefficient of the adsorbed oxides to a value 100 times larger than the diffusion coefficient of the mediator, the mediator does not have to diffuse into the pore volume to reduce the surface oxides. Instead the oxide concentration equilibrates over the whole surface very quickly similar to an electron transport over the entire porous network. The simulation emulates the "vertical electron transfer" within NPG-CME and agrees qualitatively with the experimental curves and support the proposed titration mechanism [3]

## References:

- Schwager, P., Dongmo, S., Fenske, D., & Wittstock, G. (2016). Reactive oxygen species formed in organic lithium-oxygen batteries. *Physical Chemistry Chemical Physics*, 18(16), 10774-10780.
- Rodríguez-López, J., Minguzzi, A., & Bard, A. J. (2010). Reaction of various reductants with oxide films on Pt electrodes as studied by the surface interrogation mode of scanning electrochemical microscopy (SI-SECM): Possible validity of a Marcus relationship. *The Journal of Physical Chemistry C*, 114(43), 18645-18655.
- Haensch, M., Behnken, J., Balboa, L., Dyck, A., & Wittstock, G. (2017). Redox titration of gold and platinum surface oxides at porous microelectrodes. *Physical chemistry chemical physics: PCCP*.

## Acknowledgements:

The authors would like to thank Carl von Ossietzky University of Oldenburg for the financial support.