Modeling and simulation of transient scanning electrochemical microscopy response of electrodes with porous filling

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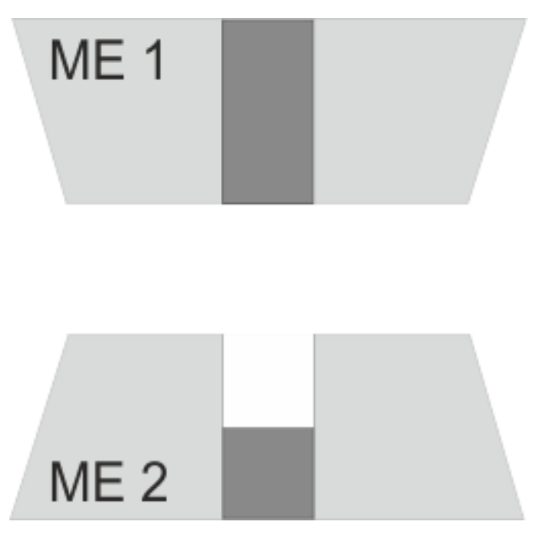
Introduction:

Highly porous nanostructured materials have been investigated and used for a large variety of applications, such as catalysis, energy conversion/storage, optics, sensing and more [1]

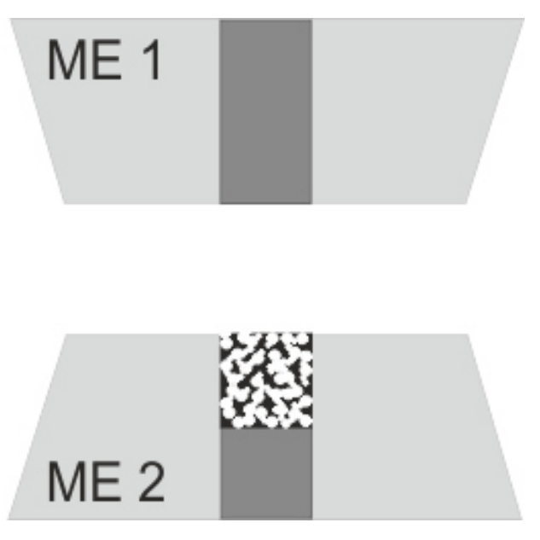
- scanning electrochemical microscopy (SECM) investigations require comparison to reaction-transport models
- a 2D axisymmetric geometry was used to describe the system depicted in the experimental SECM (scanning electrochemical microscopy) setup below
- ➢ *Aim of this work*: evaluation of mass transport of the porous structure and its effect on the current response
- ➢ *Approach*:
- treatment of porous materials as homogeneous medium with apparent lower diffusion coefficient (void volume, tortuosity)
- explicit treatment of solid and liquid parts in porous media using a 2D axisymmetric geometry

Experimental setup:

- the setup on the left side considers a flat electrode (interrogator, ME1) aligned on top of a recessed electrode (sample, ME2)
- the setup on the right side has the cavity of the ME2 filled with an initially passive porous material
- linear sweep voltammetry at the ME1 is simulated for the reduction of a mediator with the ME2 set at negative and positive feedback condition
- two different approaches for the simulation of the porous filling were don)
- ➢ COMSOL's transport of diluted species module (input: porosity factor 0.5, tortuosity factor 1)
- ➢ model of pores defined as longitudinal rectangles alongside the vertical axis (100 nm wide, porosity 0.5)



cavity electrode



cavity filled with passive porous material

Boundary conditions:

- diffusion in the electrolyte for cylindrical geometry (1)

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

- diffusion in the porous media using porosity and tortuosity factors (2)

$$D_e = \frac{\epsilon}{\tau} D_i \qquad \tau = \epsilon^{-\frac{1}{2}}$$

- tip and substrate Butler-Volmer electrode kinetics (3)

$$-D_O \nabla C_O = -k^\circ e^{-\alpha f(E-E^\circ)} C_O(0,r) + k^\circ e^{(1-\alpha) f(E-E^\circ)} C_R(0,r)$$

- ME tip current (4)

$$i_T = \int_{r=0}^{r=a} 2\pi n F D_O r \frac{\partial C_O(r,0)}{\partial z} dr$$

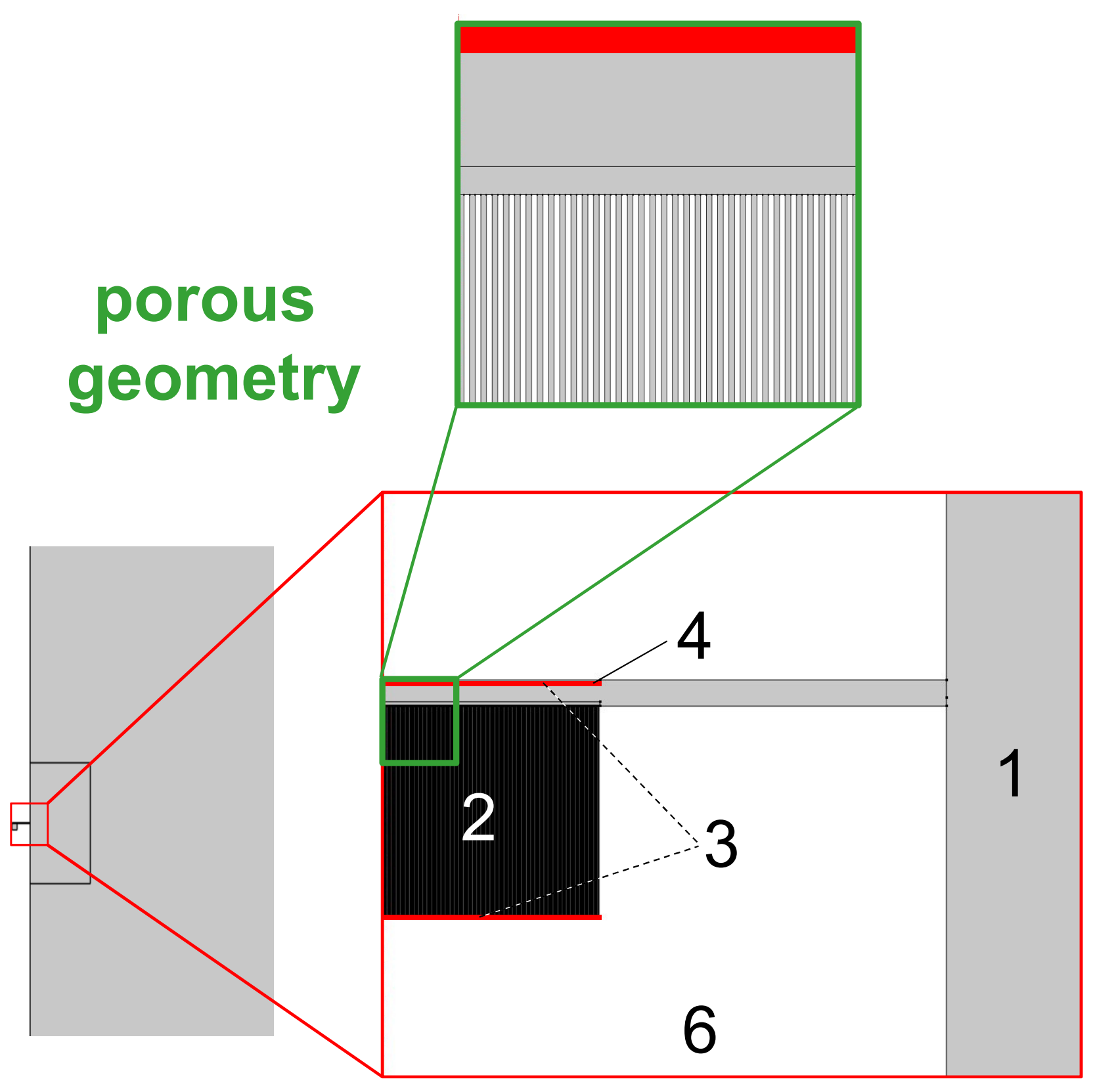
- concentration outside simulation box (5)

$$C_i = C_{Bulk}$$

- insulating glass (6)

$$-D_O \nabla C_O = 0$$

symbol list	**description**
C_i	concentration of o/r species in the solution
*D*i	diffusion coefficient
C_{bulk}	initial bulk concentration
α	transfer coefficient
f	F/nRT
E	electrode potential
E°	standard potential
k°	standard electrochemical reaction constant
r_t	electrode tip radius
D_e	effective diffusion coefficient
τ	tortuosity
F	faraday constant



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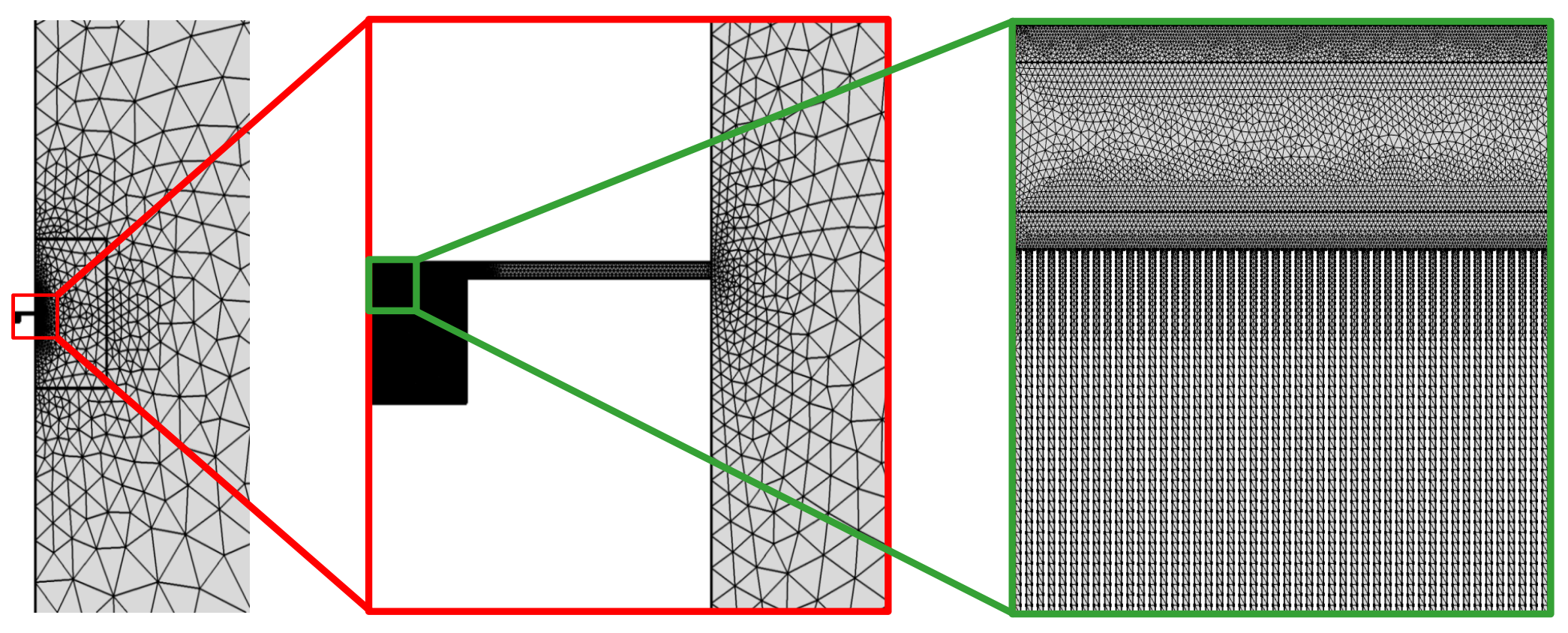
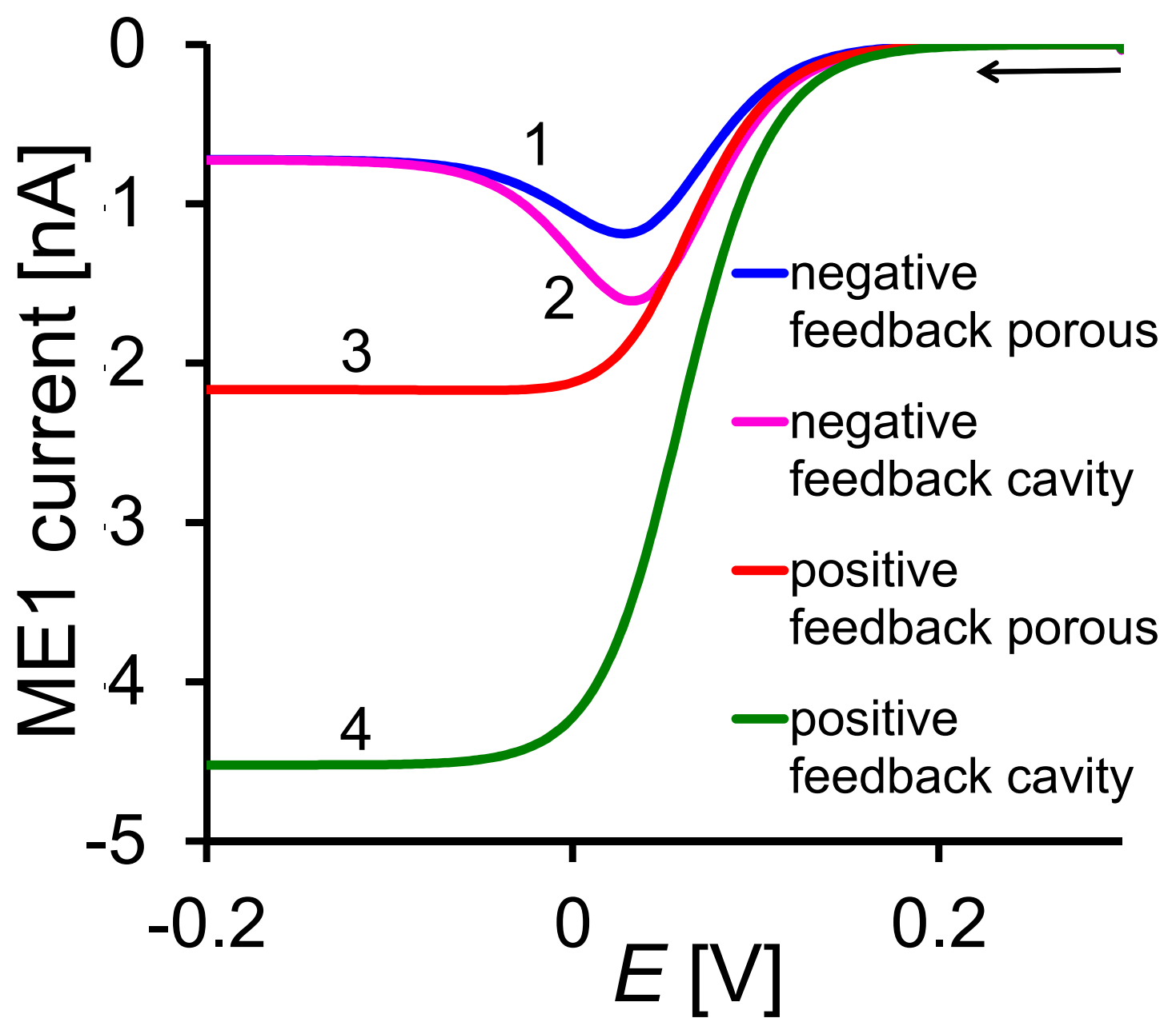
Meshing:

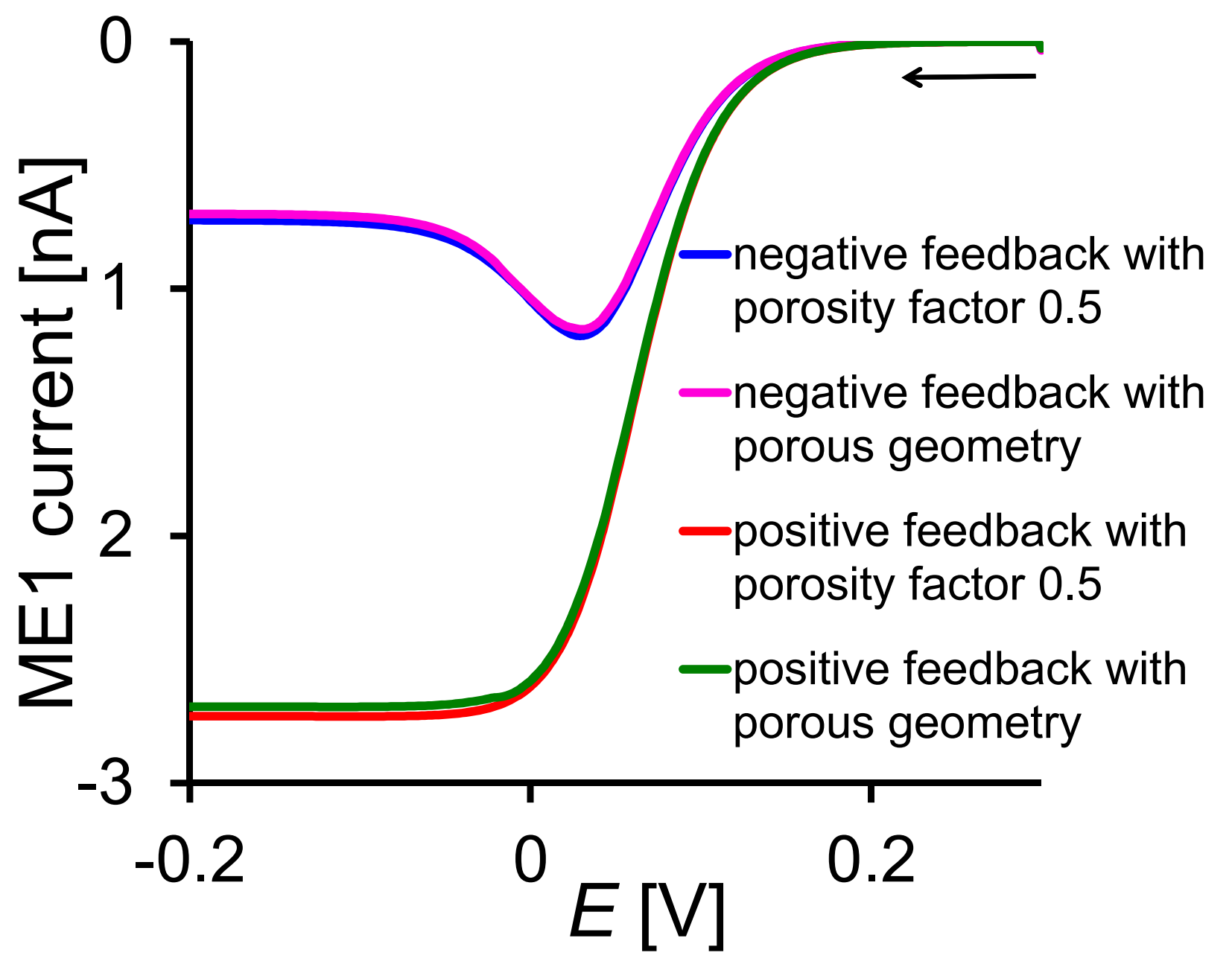
- the volume surrounding ME1 and ME2 are very finely meshed (boundaries maximum element size of 10 nm and for the electrolyte near the reaction zone a maximum of 0.5 µm)
- mesh for bulk electrolyte is defined more coarsely

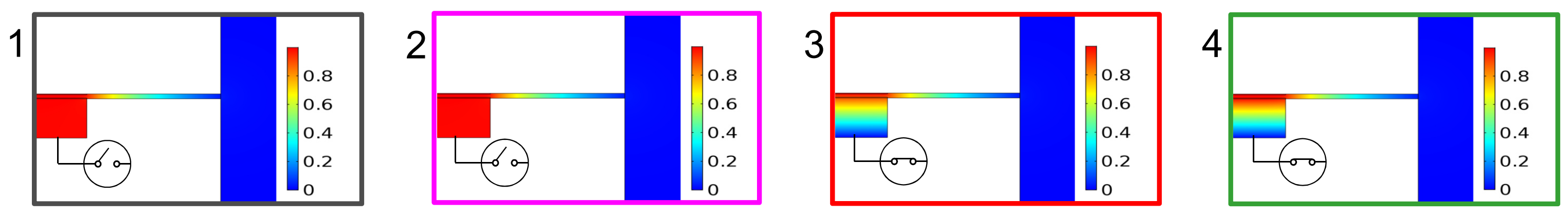


Computational Results:

- linear sweep voltammograms (LSVs) on the left represents the cavity electrode with and without porous material under positive and negative feedback conditions
- the porous filling was simulated using porosity and tortuosity factors of 0.5 and 1 respectively (insets show the concentration gradient at the end of the sweep)
- the right LSV compares both approaches for simulating the porous filling
- The four insets at the bottom show the concentration profile of the reduced species at the end of the sweep







- negative feedback: the current response at the ME1 is moderately lower than the current for the open cavity
- as the electrode potential becomes more negative, the current decreases to almost the same values regardless of the presence of porous material in the cavity
- positive feedback: transport of species is hindered by the porous filling of the cavity → much lower currents at ME1
- results agree independent of particular implementation of geometry (right diagram)

Conclusions:

- positive feedback is strongly influenced by the presence of the porous material in the cavity
- ➢ NEXT:
- expansion to simulate not only a porous passive material but a porous electrode
- consideration of adsorption at inner surface
- pore size → pore size distribution

References:

1. E. Seker, M. Reed, M. Begley, Materials 2 (2009) 2188.
2. J. Rodríguez-López, M.A. Alpuche-Avilés, A. J. Bard, J. Am. Chem. Soc. 130 (2008) 16985.
3. http://www..comsol.com

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