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Simulations of Scanning Electrochemical Microscopy Experiments in Pure Negative and Positive Feedback Mode with Ring Microelectrodes

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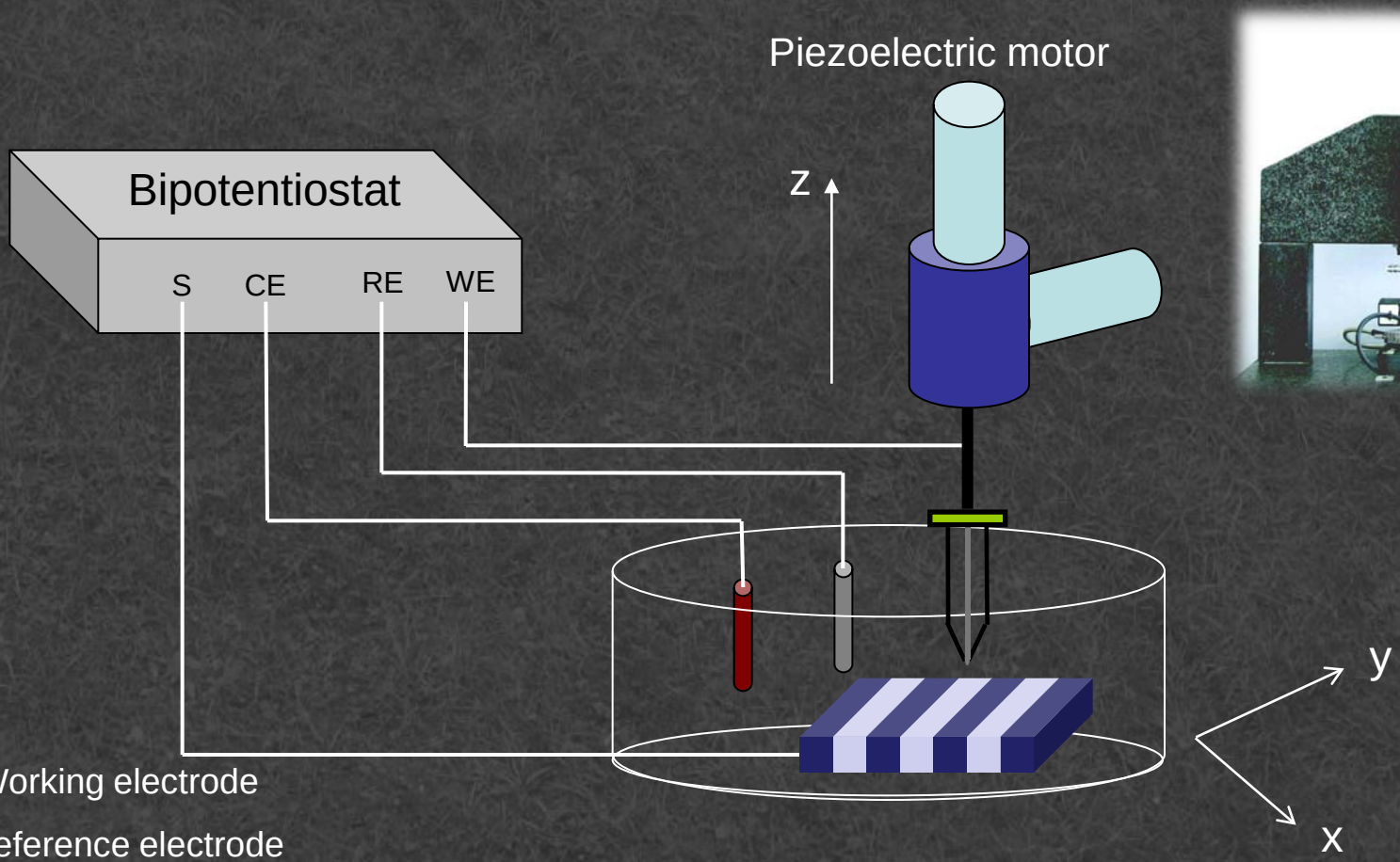
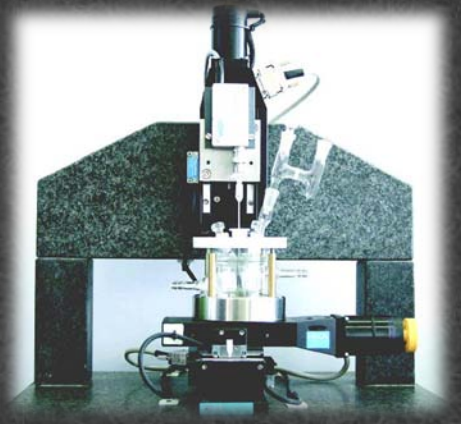
SECM instrument





WE : Working electrode

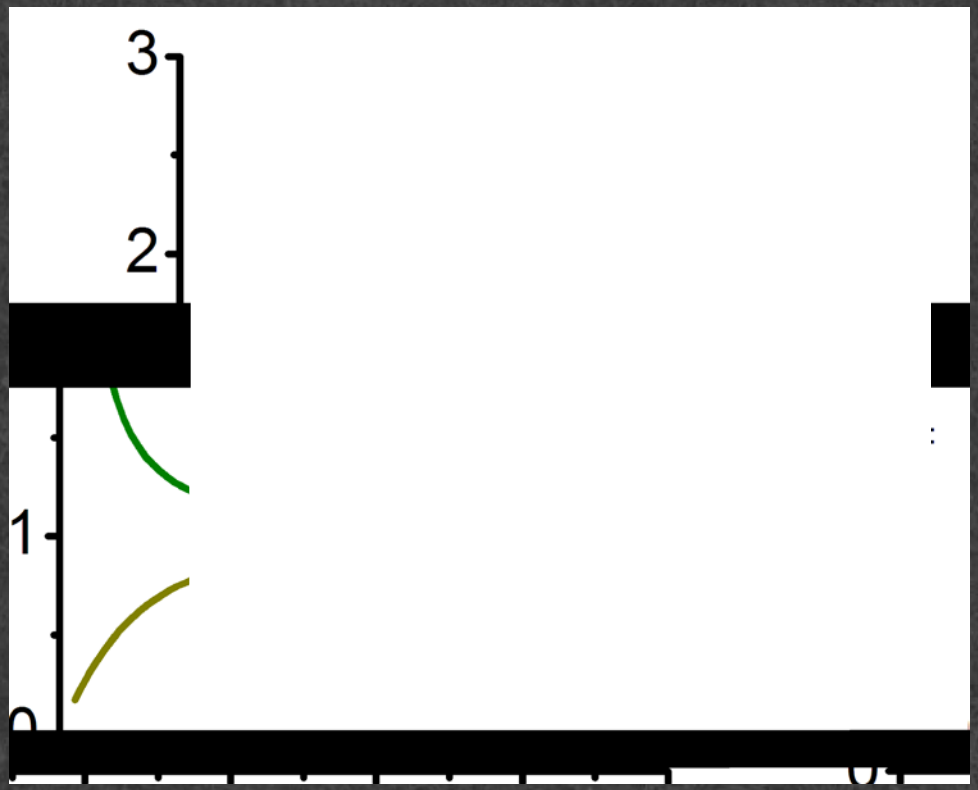
RE : Reference electrode

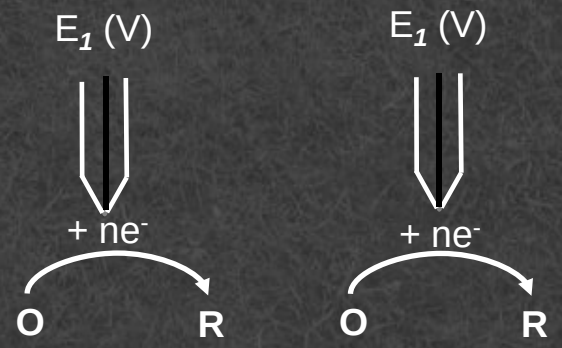
CE : conter electrode

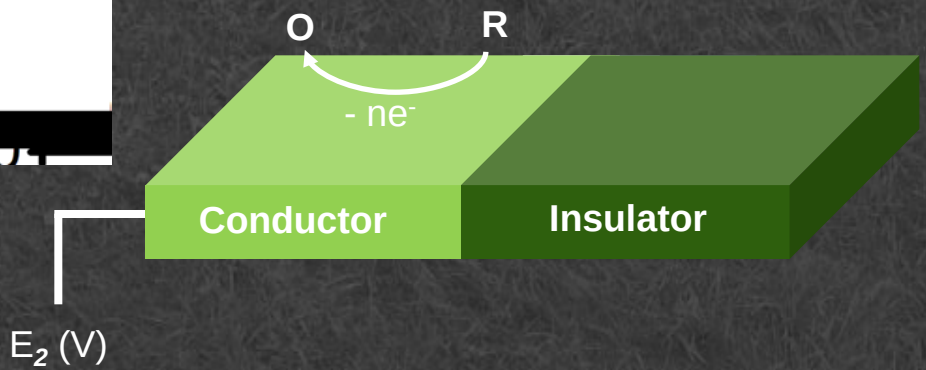
S : Substrat

Positive and negative feedback

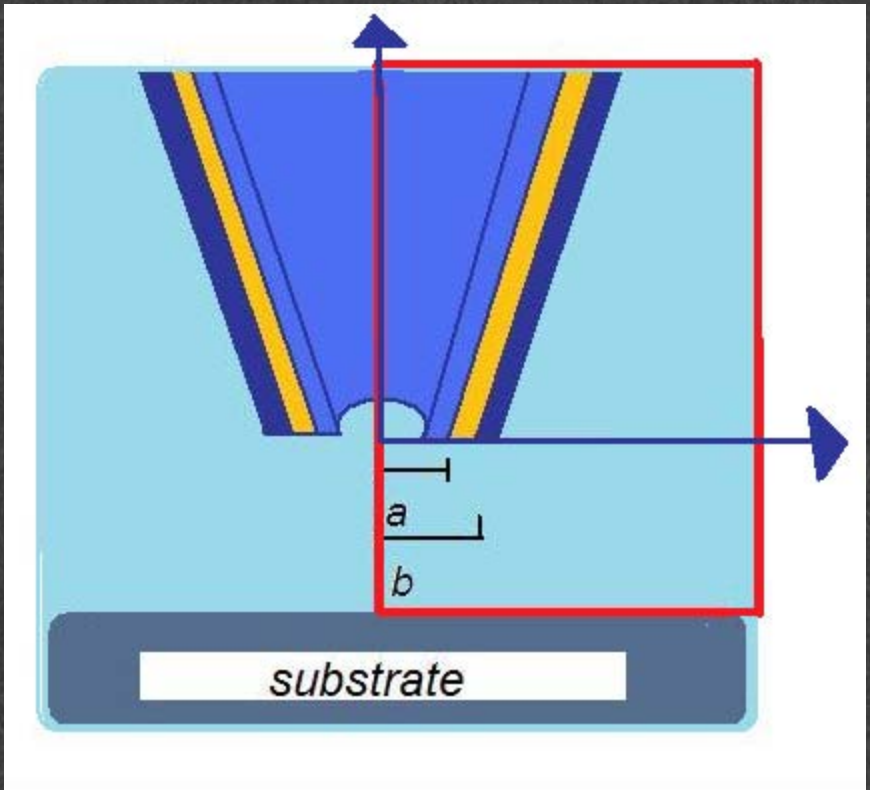
$$I_n = 4nFDrC$$

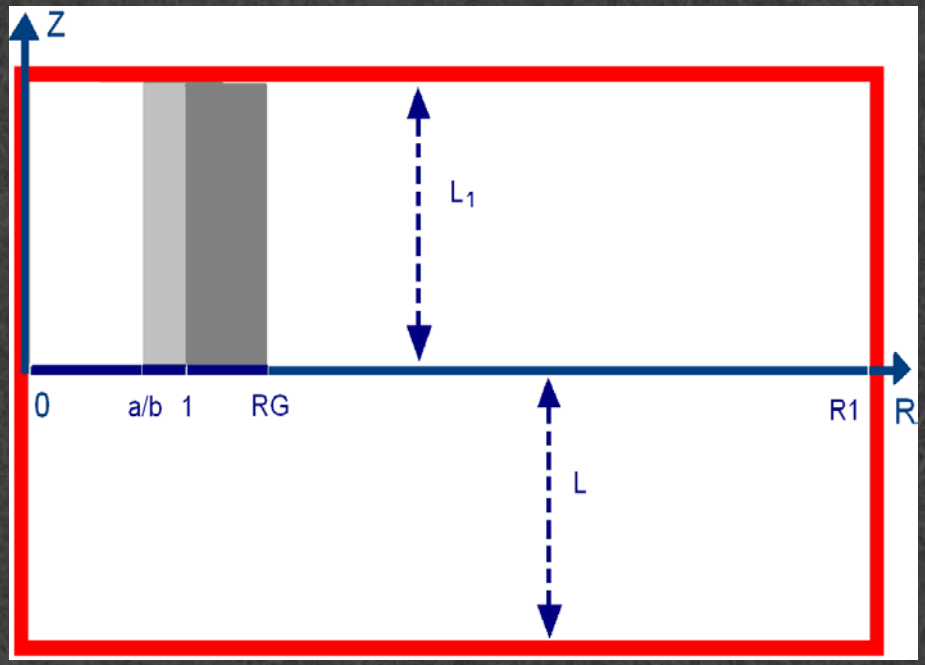






Ring Microelectrode Problem





Normalized simulation domain (R and Z dimensionless cylindrical coordinates

Mathematical Formulation

- Reduction Reaction:

$$O + ne^- \rightarrow R$$

- Convection and Migration effects are neglected

Then: Only diffusion occurs

- Simulation of the steady-state diffusion controlled current
- Simulation considering spatially uniform flux

Mathematical Formulation

Dimensionless parameters:

Radial distance (R)

$$R = \frac{r}{b}$$

Normal distance (Z)

$$Z = \frac{z}{b}$$

Concentration of O

$$C_O = \frac{c_O(r,z,t)}{c_O^o}$$

Time (T)

$$T = t\frac{D_O}{b^2}$$

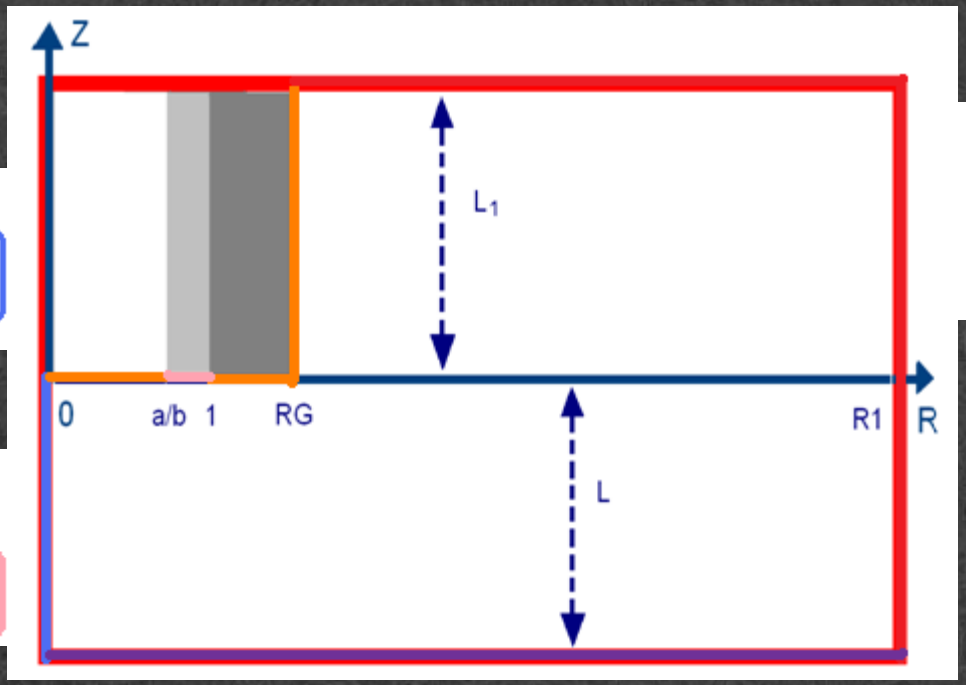
Diffusion eq. in cylindrical coordinates

$$\frac{\partial^2 C_O}{\partial R^2} + \left(\frac{1}{R}\right)\left(\frac{\partial C_O}{\partial R}\right) + \frac{\partial^2 C_O}{\partial Z^2} = 0$$

Current :

$$\frac{I_T}{I_{T,\infty}} = \frac{\int_0^{2\pi}\int_{\frac{a}{b}}^{1} J(R,0,L)\cdot dS}{\int_0^{2\pi}\int_{\frac{a}{b}}^{1} J(R,0,100)\cdot dS}$$

Boundary conditions



Axis of symmetry

$$\frac{\partial C_O(0,Z)}{\partial R} = 0 \quad for \; -L \le Z \le 0$$

Simulation space limits

$$C_O(R_1,Z) = 1 \quad for \; -L \le Z < L_1$$

$$C_O(R,L_1) = 1 \quad for \; RG \le R < R_1$$

Tip Surface

$$C_O(R,0) = 0 \quad for \; \frac{a}{b} \le R < 1$$

Insulator regions

$$\frac{\partial C_O(RG,Z)}{\partial R} = 0 \quad for \; 0 \le Z \le L_1$$

$$\frac{\partial C_O(R,0)}{\partial Z} = 0 \quad for \; 0 \le R < \frac{a}{b} \quad or \; for \quad 1 \le R < RG$$

Conductor

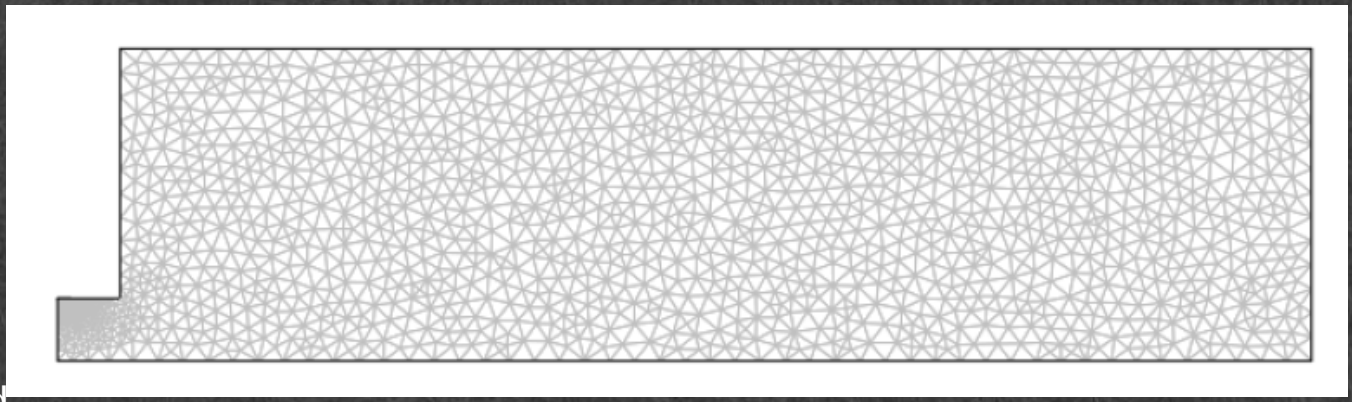
$$C_O(R,-L) = 0 \quad for \; 0 \le R < R_1$$

Insulator

$$\frac{\partial C_O(R,-L)}{\partial Z} = 0 \quad for \; 0 \le R < R_1$$

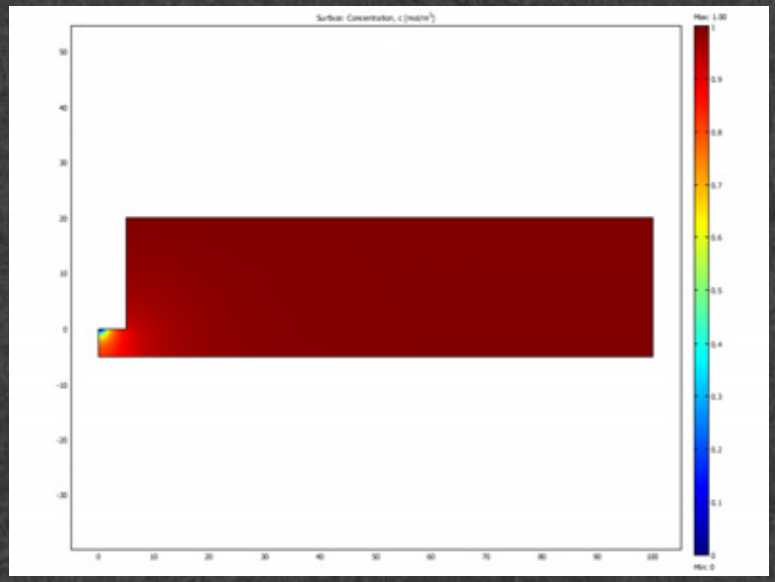
Determination of the current value

- Meshing



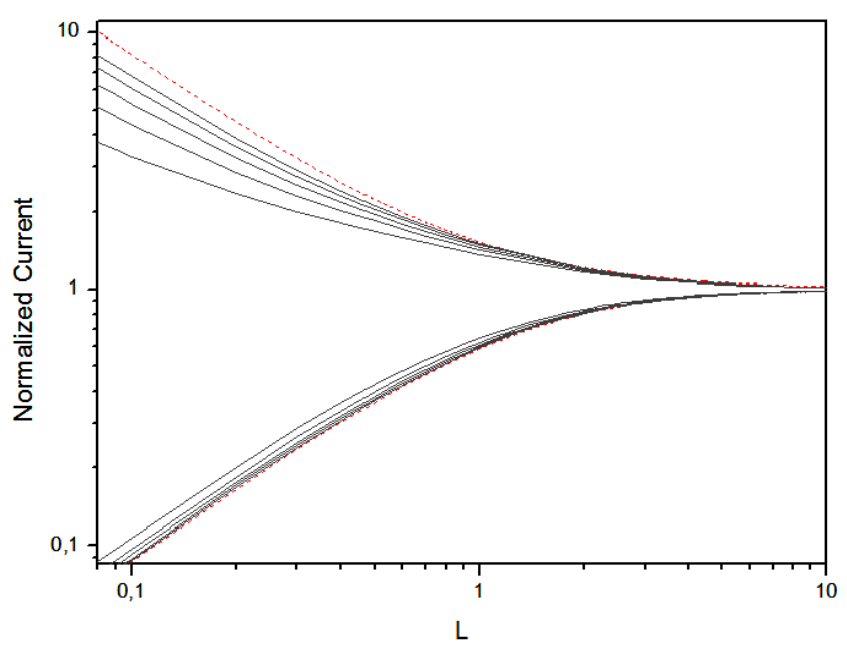
Exponential distributed meshing

- Simulation



Results

- Ring electrode approach curves. RG=5



Results and discussion

TABLE XIV. Deviation considering a height h of solution inside the micropipet.

h	1	3	6	10
Relative error (%)	0.33	0.54	0.17	0.23

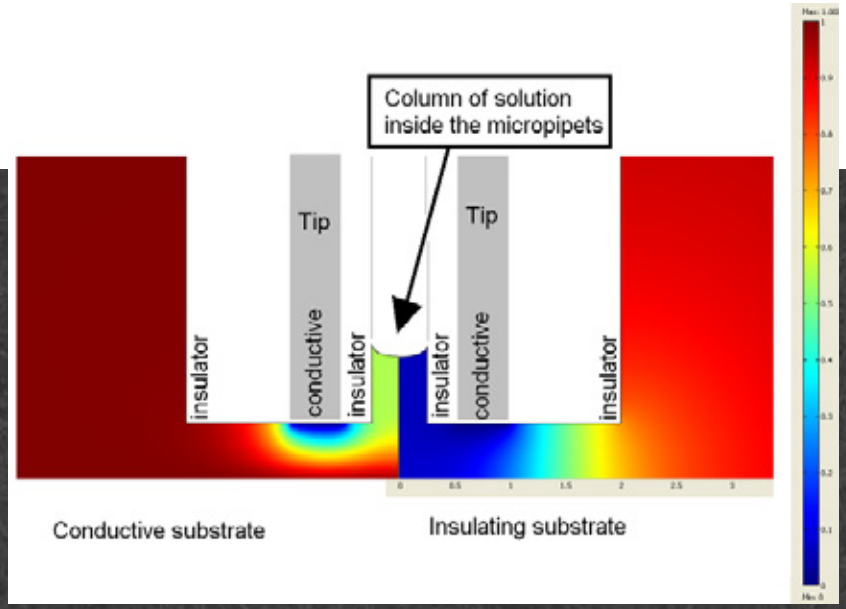


Figure 4. Comsol representation of the effect of a column of solution inside the micropipets. Simulations are realized for conductive and insulating substrate, where a/b=5, RG=2, L=0.5. Concentration is between 0 and 1 (in colour scale).

Conclusions

- The dimensionless time-independent SECM approach curves in positive and negative feedback mode for a reversible electrochemical reaction that were obtained for a ring microelectrode have been validated with existing literature.

  A 1% tolerance level has been maintained consistently and extensive tables of these curves have been reported.

  The simulation is well behaved for a/b ratios ranging from 0.5 to 0.9 and at the left limit where their behavior is that of the corresponding microdisk.

  Since few SECM approach curves are performed with band microelectrodes, the right limit, where a/b is 1, was not investigated..

  Is there no difference in the SECM response if the pipette is filled by solution or by air.

Acknowledgements

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