FEM Simulation of the Scanning Electrochemical Potential Microscopy (SECPM)

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Abstract: The present work focuses on modeling a new experimental technique: Scanning Electrochemical Potential Microscopy (SECPM), used to probe the potential profile of the electric double layer (EDL). We used an electrostatic approach to compute the EDL potential measured within the metallic probe. Also, we are investigating the effect of the interaction of the electrode/probe double layers on the distribution of the ions. Mapping the concentration gradient between the probe and the working electrode along the approach, could give insight into the charge distribution and the potential at the probe.

Keywords: Scanning electrochemical potential microscopy (SECPM), electric double layer.

1. Introduction

The electric double layer at the metal/electrolyte interface is an important topic in interface science. Electric double layers (EDL) play a central role in physical chemistry, biology, energy storage, engineering and many industrial processes. The microscopic model of the electric double layer was developed during the last century, and different theoretical approaches were used to describe the distribution of ions and the potential profile at the interface. The classical model of the electric double layer has been developed by Gouy, Chapmann and Stern in the early twentieth century.

The SECPM has been introduced recently as a new experimental technique. It was designed to measure the potential profile at the interface by approaching a metallic probe toward the working electrode in the electrolyte. The experimental setup is presented in Figure 1. It was inspired from the electrochemical STM technique, but instead of measuring the tunneling current, the tip is probing the potential at the EDL. In SECPM the metallic probe is at open circuit and connected to a high input impedance voltmeter. The probe is scanning in z direction from the bulk electrolyte toward the working electrode. It is assumed that during the approach, the probe does not perturb the double layer, and measures the EDL potential without passing current. This hypothesis is based on the use of an inert metallic probe e.g. gold. Special preparation processes are applied to avoid chemical reactions and strong interactions with the electrolyte environment [1]. Besides the EDL potential to be measured, the probe has its own potential, the open circuit potential, which is independent of the approach and has to be measured far away from the working electrode in order to subtract it.

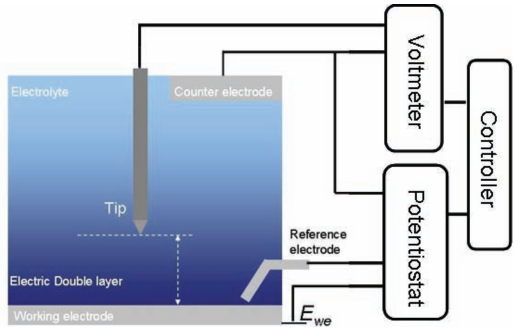

Figure 1. SECPM experiment setup

To our knowledge, a comprehensive theory of SECPM has not been developed, and experimentally this technique to probe the electric double layer is hardly ever applied. C. Hurth and A.J. Bard [1] reported their measurements with the SECPM, and found that the data did not fit the classical Gouy-Chapmann-Stern theory. They suggested, the assumption that the tip does not perturb the double layer is inaccurate, and proposed to consider a theoretical treatment, which takes the real boundary conditions encountered in SECPM into account. One of the major effects expected is an interaction of the double layers between the probe and the working electrode, which can affect and disturb the distribution of the ions in the diffuse double layer. This is studied in this work. The second effect, which can have a significant effect on the distribution of the ions, is the presence of electron transfer caused by electrochemical reactions at the tip. We will investigate this issue in the near future in order to understand how much this can affect the ion concentration and the potential at the probe.

2. Theory

As mentioned earlier, the most widely used theoretical model to describe the physical properties of the EDL is the Gouy-Chapmann (GC) Model [2,3]. It is based on the combination of the Poisson and Boltzmann (PB) equations (Eq.1); this model can give a reasonable prediction of the EDL properties for dilute solutions of point charges and for low potentials. For low concentration it is assumed that the ions are not interacting with each other and they are like a point charge in a continuum dielectric (water) of permittivity ε. The Poisson equation is used to calculate the potential in the EDL from the charge distribution in the diffuse layer, which is given by a Boltzmann distribution where electrostatic and thermal energies balance each other. For a binary electrolyte, the PB equation can be written as:

$$\begin{aligned} &-\nabla\left(\varepsilon_o \varepsilon \nabla V\right) = \rho \\ &= NzqC_{bulk}\left[exp\left(\frac{-zqV}{kT}\right) - exp\left(\frac{zqV}{kT}\right)\right] \end{aligned} \quad (1)$$

Where ρ is the free charge density, N the Avogadro number, z the charge number, ε_0 the vacuum permittivity, q the elemental charge, C_{bulk} the bulk molarity of the electrolyte, T the absolute temperature and k the Boltzmann constant.

Different approaches exist to solve the PB equation. The first approach is the linearization by taking into account the Debye-Hückel theory, which assumes that the electrostatic energy is small compared to the thermal energy. An analytical solution exists for binary symmetrical electrolytes.

An alternative is to use a finite element method, but since the equation is highly non-linear, a limitation appears in the applied electrode potential due to non-convergence and unphysical solutions.

The limited applicability of the GC model encouraged many scientists to propose modifications of the PB equation [4,5]. These models take into account the finite size of the ions and the steric effect caused by the application of a high potential to the electrode.

An equivalent and more flexible approach than the GC model exists, which is based on the use of the Nernst-Planck-Poisson NPP equations in the steady state. The Nernst-Planck (NP) equation expresses the relationship between the ionic flux and the electric potential.

$$J_i = -D_i \nabla C_i - D_i \frac{zF}{RT} C_i \nabla V \quad (2)$$

Where D_i is the diffusion constant of the species, F the Faraday constant, R the ideal gas constant. The total ionic flux is the sum of two contributions, the first one is coming form the concentration gradient, i.e., the diffusive part, and the second is due to the electro migration of the species.

Considering the steady state and inserting the (NP) equation into the mass conservation

$$\frac{\partial C_i}{\partial t} = -\nabla J_i \quad (3)$$

Leads to set of equations for each species:

$$(4)\ \begin{cases} D_1 \nabla^2 C_1 + D_1 \frac{zF}{RT} \nabla\left(C_1 \nabla V\right) = 0 \\ D_2 \nabla^2 C_2 + D_2 \frac{zF}{RT} \nabla\left(C_2 \nabla V\right) = 0 \\ -\nabla\left(\varepsilon_o \varepsilon \nabla V\right) = \rho = \sum N C_i z q \end{cases}$$

To solve the (NP) equation for a binary electrolyte we need the Poisson equation, which relates the potential to the charge density.

Solutions of the NPP model (Eq.4) are simple for the steady state, low potential, and dilute solution. However in general, the equations need a numerical solution using the finite element method. We should mention that the NPP model also fails to describe correctly the EDL properties for high concentration and for large applied electrode potential. Note that integrating the Nernst-Planck equations in the steady state and for zero ion fluxes, will give a Boltzmann distribution of ions as a function of the electric potential as in the PB model. For this study we restricted our self to use dilute concentration and low potential. Also we are assuming that there is no specific adsorption on the electrode and on the metallic probe, which can affect the considerations taken to define the potential drop in the EDL.

3. The model

Our approach is based on using the Multiphysics Modeling tools of Comsol™, considering the model as coupled field problem. The electric double layer and the coated metallic probe are described as explained in the following.

3.1 Geometry

We considered a binary symmetrical *1:1* dilute electrolyte in the steady state, in contact with an ideally polarized electrode, i.e., no electron transfer or electrochemical reactions occur. A coated probe is immersed in the electrolyte near the diffuse layer (Fig.2). The probe has an uncoated metallic apex which is considered totally inert. The system is modeled in 2D axis symmetrical coordinates. Revolving the geometry and extrusion of the solution, allowed us to get the full 3D model of the SECPM simulation.

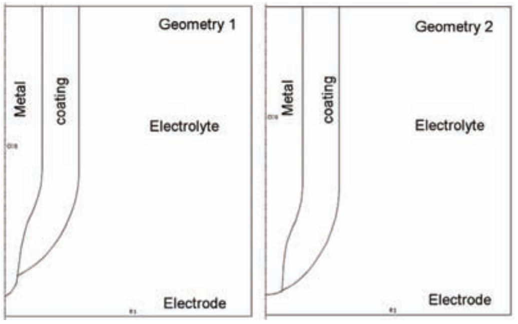

Figure 2. Geometrical description of the model

We investigated the effect of the shape of the probe comparing a tip with protruding apex (geometry1) with a non-protruding apex (geometry 2), as shown in Fig.3. For sufficient resolution in the SECPM experiment, the metallic protrusion of the apex should be smaller than the Debye length of the diffuse layer, which is dependent on the electrolyte concentration.

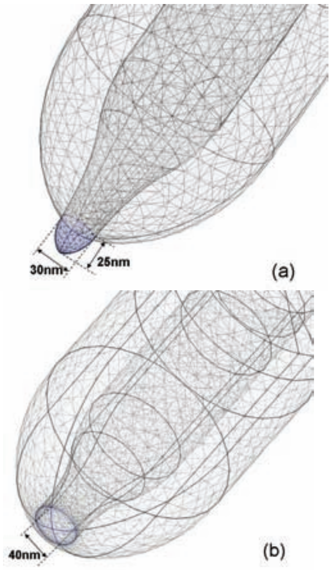

Figure 3. 3D Geometrical description of the probe (a) protruding probe, (b) non-protruding probe

3.2 Physics

For modeling the electric double layer under steady state conditions, we used the NPP model described in the previous section. This is done by using the Nernst-Planck equation available in the electrokinetic flow application mode with the Poisson equation in the electrostatic mode.

The metallic part of the probe was modeled by using the Laplace equation, which is available in the conductive media DC mode. The dielectric coating is acting as a dielectric shield and is governed by the Poisson equation available in the electrostatic mode. In the experiment, the coating used is low-density polyethylene (LDPE), which is preferred over apiezon wax for its high bonding to the metal. In the simulations we used two different values (ε=2.3 and 4.5) for the dielectric permittivity of the coating in order to analyze its effect on the potential measured.

We used a dilute solution (0.05 mM) and low working electrode potential (0.05 V), in order to make sure that the diffuse layer extends as far as possible from the electrode surface, which corresponds to a Debye length equal to $\lambda \approx 43$ nm.

3.3 Boundary conditions

For the electrolyte boundaries, we assumed a constant potential at the working electrode and zero potential in the bulk, due to electroneutrality. We used the Integration Coupling Variables to calculate the charges surrounding the metallic apex and the coating at different positions of the probe in the electrolyte. By using Gauss's law it was possible to get the electric potential at the boundaries of the metallic protrusion and the coating of the probe.

4. Results

4.1 Effect of the geometry

As mentioned previously, the effect of geometry was studied in order to see which geometry of the metallic apex gives a profile closer to the unperturbed potential of the EDL. We started scanning by positioning the probe in the electrolyte bulk, and computing the solution for each distance to the working electrode. In Fig.4 the probe potential for both geometries is plotted together with the unperturbed potential of the EDL. Note that the protruding geometry gives a profile closer to the unperturbed potential of the EDL, while the non-protruding one shows large deviation.

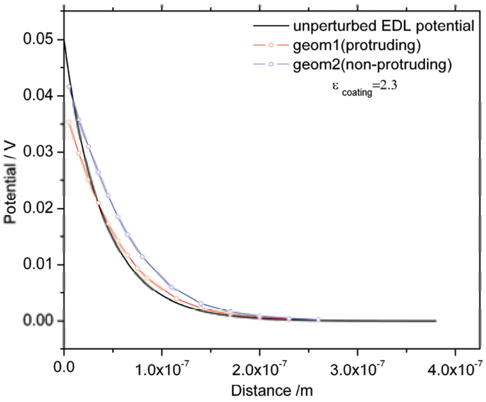

Figure 4. Probe and EDL potentials for both geometries with $\varepsilon_{coating}$=2.3

The source of the electric potential in the probe are the ions surrounding it. For a detailed analysis, the distribution of the ions is plotted in the region between the probe and the working electrode for different probe/electrode distances. Fig.5a and 5b show these distributions for both geometries. These plots demonstrate the presence of a tip EDL. Its effect is more pronounced near the positive working electrode. The tip EDL is constituted by a cation excess due to the negative polarization of the metallic tip. During the approach of the tip, the cation excess is increasing while the anions are depleted continuously from the tip. There is an electroneutral region between the metallic apex and electrode. This region is characterized by an equal concentration of cations and anions, which are coming from both double layers. This result can be attributed to the interaction of the two double layers.

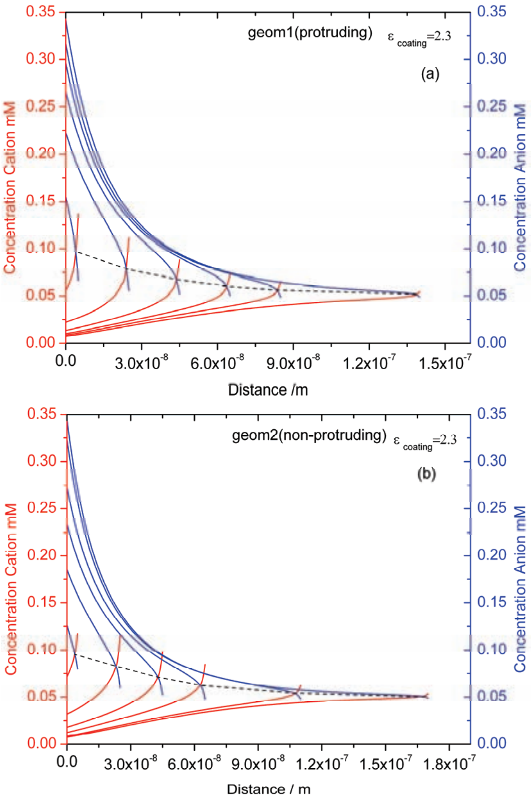

Figure 5. Ion distributions for different probe/electrode distances with $\varepsilon_{coating}$=2.3: (a) protruding apex, (b) non-protruding apex

Note that there is a difference between the two geometries in terms of ion distributions. This effect is due to the shape of the metallic part of the probe. The non-protruding metallic apex has strong interaction with the coating surrounding it. This can affect the ion distributions near this region and also the probe potential.

At the positively charged electrode, there is an excess of anions. During the approach, the surface region in front of the tip gradually looses its anion surface excess, while the concentration of cations is increasing. This is due to the excess of cations in the diffuse layer of the tip. The tip EDL is not confined to the metallic part of the probe, but it is enveloping the coating also with a low cation excess. This is due to the electric polarization at the coating/electrolyte interface, as shown in Fig.6.

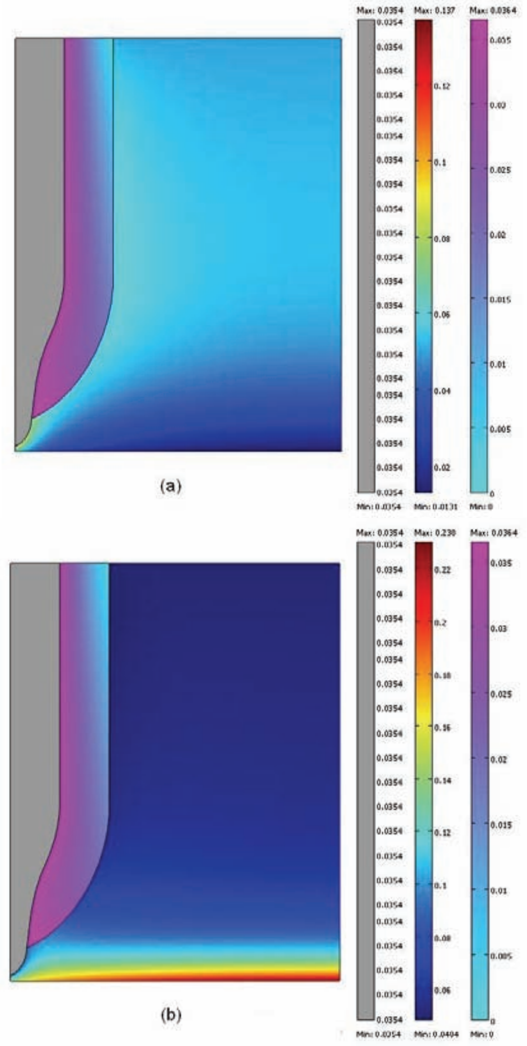

Figure 6. Ion distributions at tip/electrode distance of 5 nm and $\varepsilon_{coating}$=2.3 (a) cation, (b) anion

4.2 Effect of the coating dielectric permittivity

For the same conditions, we computed the solution after changing the dielectric permittivity of the coating for both geometries. The potential profile of the probes and the unperturbed potential are plotted in Fig.7.

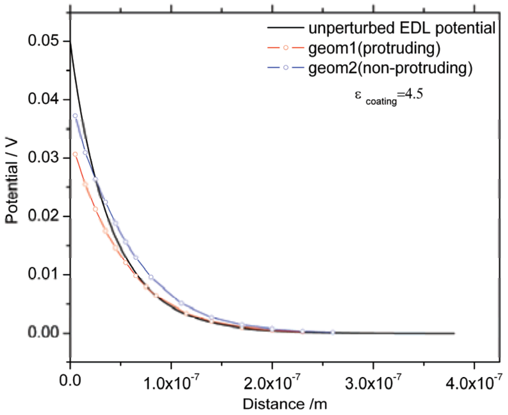

Figure 7. Probe and EDL potentials for both geometries with $\varepsilon_{coating}$=4.5

There is a significant effect of the coating permittivity: the probe potential is shifted to lower values for both geometries. This effect can be explained by the decrease of the ion surface excess at the metallic tip, which is shown in Fig.8.

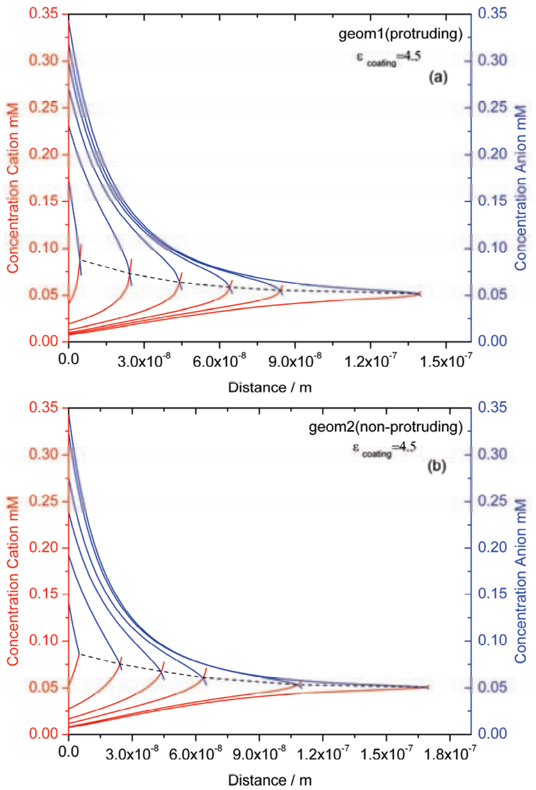

Figure 8. Ion distributions for different probe/electrode distances with $\varepsilon_{coating}$=4.5
(a) protruding apex, (b) non-protruding apex

Comparing with the ion distributions of Fig.5 ($\varepsilon_{coating}$=2.3) shows that the cation excess on the metallic apex is reduced for $\varepsilon_{coating}$=4.5. This can be explained by the extension of the tip EDL toward the probe coating, which is shown in Fig.9. The coating surface has a higher potential due to the increase of the dielectric permittivity. The electroneutral region is still present between the probe and electrode, but with a lower concentration value than in the first case.

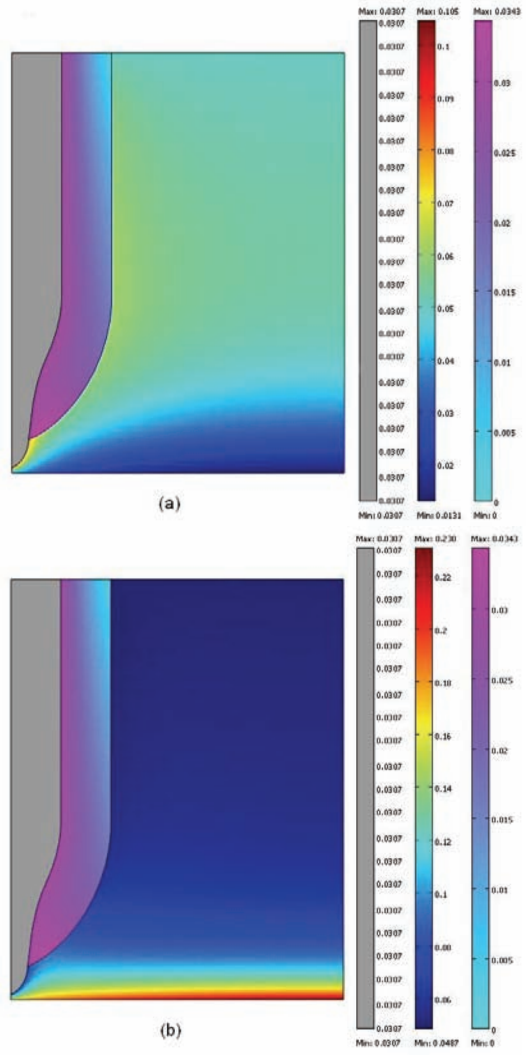

Figure 9. Ions distribution for $\varepsilon_{coating}$=4.5
(a) cation, (b) anion

5. Conclusion

Simulation of the SECPM with Comsol™ allowed us to explain how the potential is measured by the metallic tip in the experiment. The presence of the tip EDL and its interaction with the working electrode was analyzed. An electroneutral region was found between the probe and the working electrode. The geometry and the coating permittivity were demonstrated to have an effect on the probe potential. The potential of the SECPM probe was found to follow the EDL potential for sufficiently large tip-electrode distances (>5 nm) for a probe with protruding metallic apex. A low dielectric permittivity of the coating reduces the perturbations by the probe.

The above model reflects the ideal case, when the probe is totally inert without redox reactions at the metallic apex. This model will be further improved by adding other effects, as the electron transfer at the tip, and the ion size effect in order to apply higher potential to the electrode. Different cases will be studied to check the applicability of this experimental technique by a validation with experiment.

6. References

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