

# Screening Effects in Probing the Electric Double Layer by Scanning Electrochemical Potential Microscopy (SECPM)

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**Abstract:** A computational method is developed to study probing the electric double layer by Scanning Electrochemical Potential Microscopy. The model is based on a modified Poisson-Boltzmann equation, which takes into account steric effects. We investigated the effect of metallic apex protrusion and the open circuit potential (OCP) of the tip on the probed potential. A clear electrostatic screening effect was observed when varying the OCP of the probe. Steeper potential profiles were noticed for high OCPs, which is due to screening effect. The dependence of the measured potential on the metallic apex shape was also observed.

**Keywords:** Electric double layer, SECPM, Debye screening.

## 1. Introduction

Scanning electrochemical potential microscopy (SECPM) has been introduced by C. Li *et al.* (Veeco Inst. Inc.) [1]. It was primarily designed to probe the electric double layer (EDL) by approaching a metallic probe towards a charged surface immersed in an electrolyte solution. The electrochemical potential can be measured, allowing the identification of the charge distribution and the potential gradient in the normal direction of the EDL. It is a promising technique, because it allows direct access to the EDL properties rather than measuring the capacitance by impedance spectroscopy or surface forces measurement with, e.g. atomic force microscopy.

In addition, SECPM offers the possibility to map surface potential of an electrode/electrolyte interface [2]. This can have an interesting advantage compared to the electrochemical scanning tunneling microscopy (EC-STM) in imaging non-conductive samples, e.g. biological species adsorbed on the surface.

However, this technique seems to be not intensively used by electrochemists. Few

scientific articles exist in the literature, which are concerned with the use of the SECPM for electrochemical investigation. The first published work using the SECPM concept appeared in 2004 [3], in which a modified EC-STM setup was used to probe the EDL potential. The authors showed the possibility to measure the potential on the nanometer scale for an electrode/electrolyte interface. Based on the linear superposition approximation (LSA), a simplified interpretation was given for the measurement principle and for the EDLs overlap that can occur between the tip and the sample.

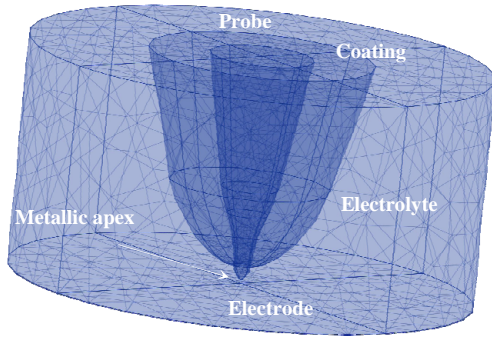
Later, Hurth *et al.* [4] reported their EDL potential profile measurements with the SECPM, and concluded for different situations that the data did not fit the classical Gouy-Chapmann-Stern (GCS) model. They suggested the need for a theoretical model, which explains the measurement process and the effect of the EDL overlap between the tip and the sample on the probed potential.

To our knowledge, a comprehensive theory of SECPM has not been developed, and consequently this technique to probe the electric double layer is hardly applied yet. A theoretical model needs to be developed in order to interpret the experimental data, and in particular to explain the physical mechanism of the measurement and the parameters affecting it. We believe that a computational method will help addressing this need.

## 2. The model

The geometry of the SECPM model is represented by a cylindrical cell containing an electrolyte solution. The cell has a flat electrode on its bottom, see Fig (1). The metallic probe is coated with an insulator except near its apex, and is located in the axial position. There is no reference electrode in this configuration since all the potentials are set against zero potential in the

bulk due to electro-neutrality (on top of the cylinder).



**Figure 1.** The 3D SECPM model

## 2.1 Governing equations

One of the most widely used model for describing the potential distribution in the EDL is the Poisson-Boltzmann (PB) equation. It is a continuum mean field approach considering non-interacting ions as point charges in a uniform dielectric background, which represents the polar solvent. However, it is well known that this approach fails to describe properly the ionic distribution near the electrode for large applied potential [5]. The concept of the Stern layer was the first model to reflect the effect of the ion size. In more refined picture, an effective ion size was introduced to the PB equation in order to constrain the distance separating two solvated ions [5]. This can prevent the crowding effect and fix a maximal concentration that can be reached under high applied potential. Equation 1, represents the modified PB

$$\nabla^2 V = \frac{zeC_b}{\varepsilon \varepsilon_0} \frac{2 \sinh\left(\frac{zeV}{kT}\right)}{1 + 2\nu \sinh^2\left(\frac{zeV}{2kT}\right)} \quad (1)$$

Where  $\nu = 2a^3C_b$  is the volume fraction occupied by the ions, and  $a$  is the limiting distance between two solvated ions.  $C_b$  is the bulk concentration of the solution, and  $\varepsilon$  is the dielectric constant of the solution chosen uniform in the electrolyte and equal to 78.5 for water at a room temperature. The bulk

concentration was set to 0.1mM and the applied potential to the working electrode was 300mV.

## 3. Use of COMSOL Multiphysics

The Multiphysics model is based on combining the Poisson equation (electrostatic mode) with the ionic Boltzmann distribution. We used the modified PB, which takes into account the size effects of ions and prevents steric effects near the charged electrode. The coated probe was modeled as a perfect insulator governed by the Poisson equation with a dielectric permittivity in the same range as the Apiezon wax that is used in the experiment.

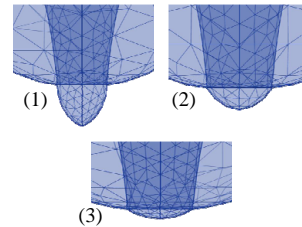
We assigned a vertical speed of 10 nm/s to the probe by using the moving mesh (ALE) application mode.

For simplicity, we used an axial symmetric geometry for the  $z$  scanning case, and a full 3D model for the  $x$ - $y$  scanning mode.

## 4. Results and discussions

### 4.1 Effect of the metallic apex shape

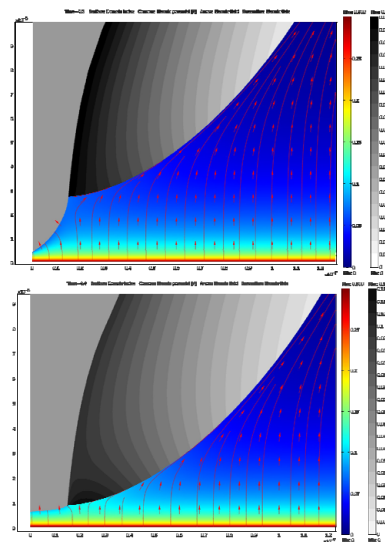
In this study, we simulated the SECPM scan for three different metallic apex geometries. The height of the protrusion was changed gradually till obtaining a flattened apex. See figure 2.



**Figure 2.** The different apex protrusion used in the simulation.

We considered a nil OCP for the probe when it is located far away from the electrode. This means that the probe is not surrounded by an EDL. The scanned distance starts from 100 nm and stops at 2 nm in order to avoid inverted mesh and to keep a correct physical description at this scale. The resulting probed potential profiles are shown in figure 3(a). We can see clearly that the height of the protrusion affects dramatically the probed potential. The effect is characterized by a steeper probed potential profile than the unperturbed

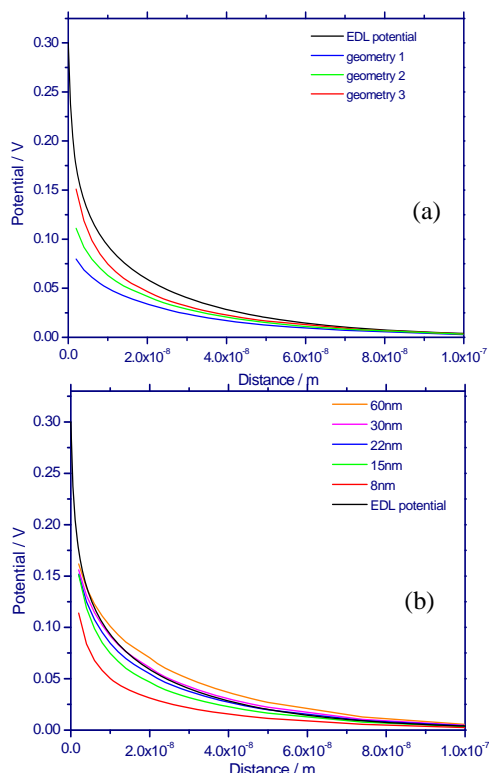
EDL potential. Decreasing the protrusion of the metallic apex tends to reduce the steepness of the probed potential. The flattened apex yields the closest curve to the EDL potential profile. This effect is essentially due to the distortion of the iso-potential surfaces of the EDL, which have to be parallel to the surface of the metallic protrusion. This can cause a deformation of the EDL and shift the probed potential, see figure 4. The second reason for this effect is the non-uniform surface charge distribution on the metallic apex, caused by the sharpness of tip. This can generate a high surface charge density and electric field on the apex. The electric field coming from the electrode will be screened and the potential in the vicinity of the metallic apex is decreased. Note that changing the surface area of the circular flattened surface apex also has an effect on the probed potential. This is shown in figure 3(b), in which we can see clearly that small surface area (low radius) produces a huge charge density, and hence a high electric field that can screen the potential.



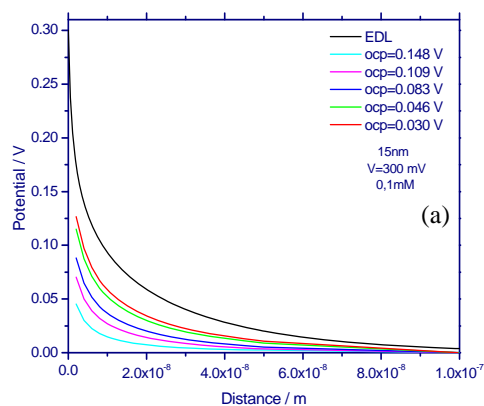
**Figure 4.** Electric field and potential distribution between the probe and the electrode.

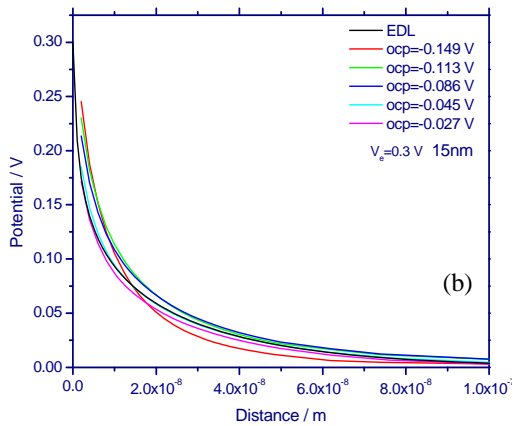
#### 4.2 Effect of the open circuit potential

In this second part, we were interested in the interaction of the probe and the electrode EDLs, and its effect on the probed potential. We considered a circular flattened metallic apex with a radius of 15nm (geometry 3). The scanning of the probe was operated under the same conditions as before. Different negative and positive OCPs were applied to the probe in order to see the effect of strength and the polarity of the EDLs on the probed potential. Subtracting the OCP from the probe potential at different positions leads to the resulting potential profiles shown in figure 5.



**Figure 3.** Probed potential profiles: (a) different protrusions, (b) different surface areas.



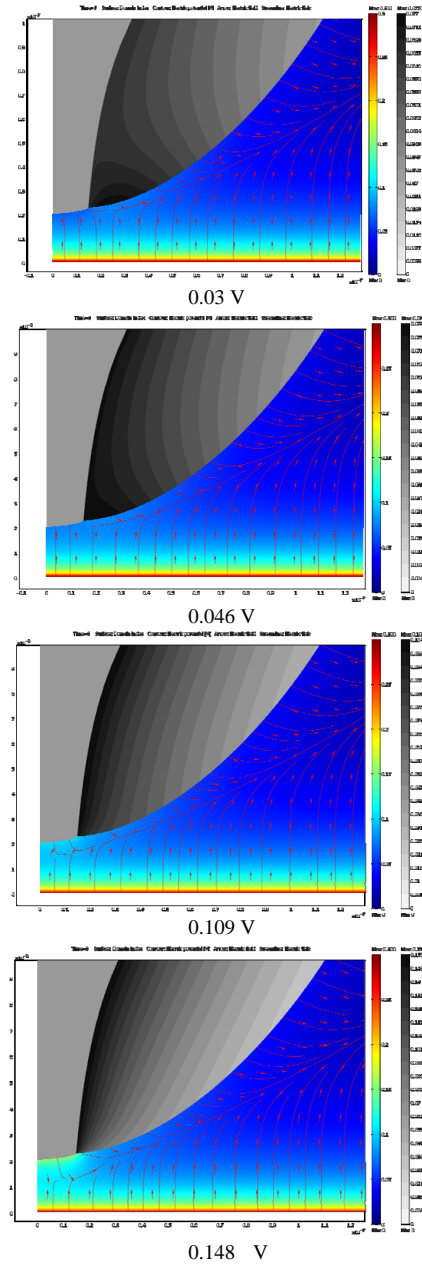


**Figure 5.** Probed potential profiles: (a) positive OCP, (b) negative OCP.

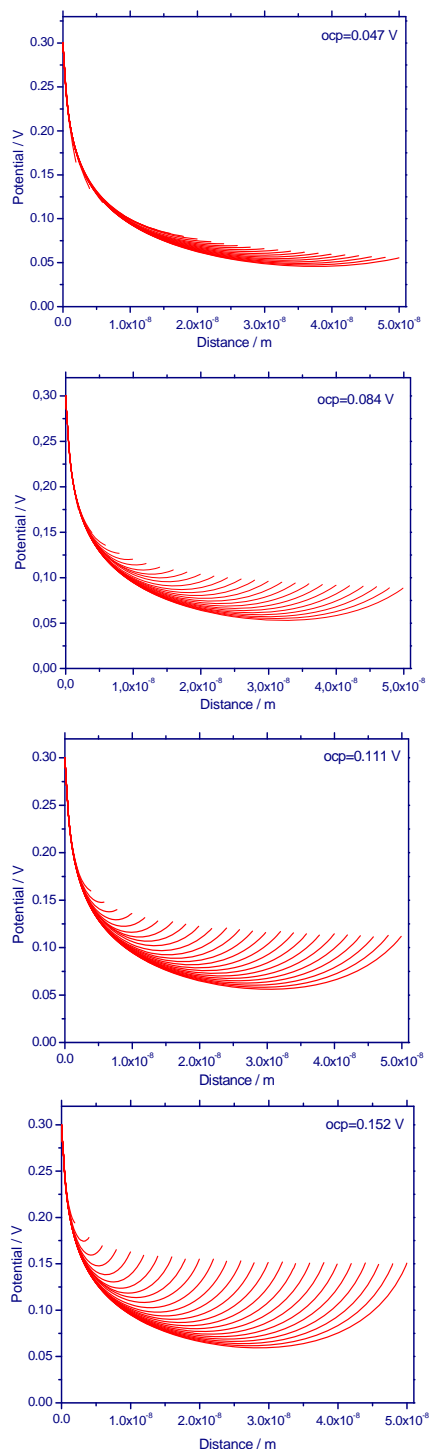
For the case of EDLs with the same polarity, the screening effect is well distinguished. This is due to the presence of the EDL at the probe, characterized by a negative volume charge density and electric field oppositely oriented to the one coming from the electrode. The EDL at the probe screens and deviates the electric field lines coming from the electrode, see figure 5. Depending on the strength of the electric field generated at the probe and the surrounding volume charge density, the potential can be affected severely. This is shown in fig.6, which represents the potential profiles between the electrode and the probe for different separating distances and OCPs. Increasing the OCP leads to decrease the sensitivity of the probe to the potential gradient of the EDL electrode, and hence reproduces a steeper probed potential profile during its approach. The effect of the EDLs overlap is characterized by a change of the surface charge density of the metallic apex along the scanning distance. The polarization of the metallic apex and hence its potential depends on the carried charges representing its OCP in the bulk region. The sensitivity of the probe to the potential gradient is directly related to the change of the surface charge density of the metallic apex.

Inversing the polarity between the electrode and the probe can reduce this effect since that the both electric fields are oriented in the same direction. At a certain extent, the screening effect can be lowered by the presence of an opposite

volume charge densities for the probe and the electrode, leading to a potential profile closer to the unperturbed EDL potential of the electrode.



**Figure 5.** Electric field and potential distribution between the probe and the electrode for different OCPs



**Figure 6.** Potential profile between the probe and the electrode for different separating distances.

## 5. Conclusions

This study allowed us to conclude that a flattened surface apex has to be used for a correct EDL potential probing with the SECPM. The overlap of the EDLs leads to decrease the probed potential. This is due the screening effect related to the presence of the EDL at the probe. If a weak EDL with inverse charge density is present at the probe, the screening effect is reduced. A theoretical model has to be combined with the experiment results, in order to extract the unperturbed EDL potential profile from the probed potential, which is a consequence of the EDLs overlap.

## 6. References

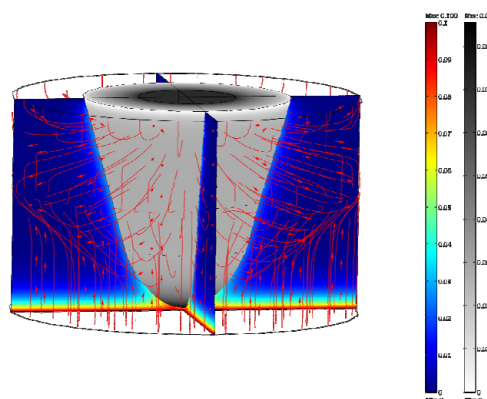
- [1]. Chunzeng Li, Kevin J. Kjoller, “*Scanning electrochemical potential microscopy*”, US Patent No: US 7.156.965 B1, Veeco Instrument Inc (2007)
- [2]. C. Baier, U. Stimming, *Angew. Chem. Int. Ed.* (2009), **48**, 5542–5544
- [3]. D.H. Woo, J.S. Yoo, S.M. Park, I.C. Jeon, H. Kang, *Bull Korean Chem. Soc.* 2004, **25**, 577
- [4]. C. Hurth, C. Li, and Allen J. Bard, *J. Phys.Chem. C*, **111**, 4620-4627 (2007)
- [5]. I. Borukhov, D. Andelman and H. Orland, *Phys. Rev. Lett.* **79**, 435 - 438 (1997)

## 7. Acknowledgements

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## 8. Appendix

For illustrative purpose, we plotted the 3D SECPM model, in which the electric field and the potential distribution are shown.



**Figure 7.** Electric field and potential distribution between the probe and the electrode, in the 3D model.