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Numerical analysis of Debye screening effect in electrode surface potential mapping by scanning electrochemical potential microscopy

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ABSTRACT

We investigate the effects of the probe apex geometry, overlap of the electric double layers (EDLs) and Debye screening on surface potential mapping with scanning electrochemical potential microscopy (SECPM). The simulation consists of scanning a tip parallel to the electrode surface over a charged hemispherical nanoparticle adsorbed on the electrode surface. As expected, a clear dependence of the apparent size of the imaged particle on the probe apex geometry has been noticed. The Debye screening has a significant effect on the probe sensitivity, while the electrolyte concentration affects the observed size of the imaged particles.

1. Introduction

Significant progress has been made in the development of new scanning probe microscope (SPM) techniques during the last decades. The emergence of new SPM techniques based on the use of new concepts allowed scientists to gather more knowledge in surface and interface science. The use of the electrochemical scanning tunneling microscope (EC-STM) or the atomic force microscope (AFM) in electrolyte environment was a great innovation for *in situ* investigations. Both permitted significant progress in several research fields as, e.g., biology and bio-electrochemistry in investigating and understanding mechanisms, which were inaccessible by conventional methods.

The lateral and the normal potential distribution at the electrode|electrolyte interface define the charge distribution at the interface and hence, all the related electrochemical processes. This has been one of the major objectives of a new SPM technique named scanning electrochemical potential microscopy (SECPM). Inspired by the EC-STM, this technique is assumed to profile the potential at the electric double layer (EDL) if the probe is scanning in a direction normal to the electrode surface, referred to as *z*-direction [1], and to map the surface potential if a 2D scan parallel to the electrode (in the *x*-*y* plane) is used [2]. The latter allows imaging of electrode surfaces, with and without adsorbed species, e.g., metallic nano-clusters and biological species. However, few scientific articles using SECPM technique exist in the literature as the theoretical understanding is still under development.

In a recent numerical study, we have shown the applicability of the SECPM in probing the EDL at equilibrium, for an electrode|electrolyte interface [3]. We demonstrated the dominant effect of the metallic nano-probe geometry, i.e., apex sharpness or curvature on the EDL potential profiling. The effect of nano-electrode curvature on the EDL properties has also been reported by Dickinson and Compton recently [4]. The probe and electrode EDLs overlap and Debye screening also affect the probe potential. This led us to conclude that the EDL potential profile obtained with SECPM is a direct consequence of electrode/probe EDLs overlap [3].

Recently, Baier and Stimming have shown for the first time an interesting advantage of the SECPM in imaging non-conductive adsorbed biological species, which could not be resolved with EC-STM [2]. However, a theoretical understanding of the SECPM in mapping mode is needed because, e.g., an unexplained difference in size of the enzyme imaged by SECPM and EC-STM has been observed [2].

The main aim of this communication is to provide an explanation of contrast formation and the parameters affecting SECPM mapping mode. We investigate the effects of the probe apex geometry, EDLs overlap and electrolyte concentration on the resolution of the SECPM in potential mapping mode.

2. Model and simulation

The details of the geometry, equations, modeling, boundary conditions and materials have been described elsewhere [3]. Briefly, the 3D SECPM model consists of a cylindrical cell with electrolyte and a flat electrode on its bottom. The coated probe has a metallic apex, which is not coated, nevertheless electrochemically inert. The EDL is

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modeled using the modified Poisson-Boltzmann equation proposed by Wicke and Eigen [6,7]. For dilute solutions, this takes into account the finite ion size effect and prevents steric effects near highly charged surfaces. We considered a restricted symmetric 1:1 electrolyte solution (i.e., same radii for cation and anion) with a concentration of 0.1 mM, which corresponds to an EDL Debye length of 30 nm at room temperature.

Here, we added a metallic hemispherical nano-particle (diameter of 10 nm, height 5 nm) adsorbed on the surface of the flat electrode (see Fig. 1). A constant potential of 200 mV vs. the potential of zero charge (our reference point) was applied to the working electrode and nano-particle. The probe scan is simulated at constant distance (6 nm) from the electrode plane. Therefore, the variation of the probe potential in the vicinity of the charged particle does not directly provide information on the height of the particle (in contrast to constant potential mode), but it is correlated to the sample topography. Using a finite element method package [8] and based on our earlier work [3], we have simulated line scans over the hemispherical nano-particle and *x-y* scans in order to get a 2D image. The potential topography has been realized by computing the probe potential at different particle positions in the *x-y* plane.

3. Results and discussion

In order to demonstrate numerically the ability of the SECPM to image electrode surfaces on a nanometer scale, we have simulated a scan for a simple case, in which we considered an adsorbed hemispherical particle having the same potential as the electrode. We assumed that the sharp metallic probe has an open circuit potential (OCP) equal to 20 mV, when it is located far away from the electrode. The OCP represents the shift from the potential of zero charge (PZC = 0 V) of the probe, which is chosen as our reference in this study [3]. The assumption of a non-zero probe potential is based on the fact that most studies are carried out under ambient conditions where the oxygen is known to lead to slight positive charging of inert probes such as platinum or gold. Regarding the role of the OCP on the potential measurement by SECPM see Ref. [3].

In Fig. 2b (black curve), we show the obtained scan line over the charged particle and the 2D image in Fig. 2a, obtained by *x-y* scanning with step size of 1 nm in both directions. We note that the full width at half maximum (FWHM) of the bell shaped curve is larger than the actual diameter of the hemispherical particle, as it was also observed experimentally [2] and will be discussed in the next sections.

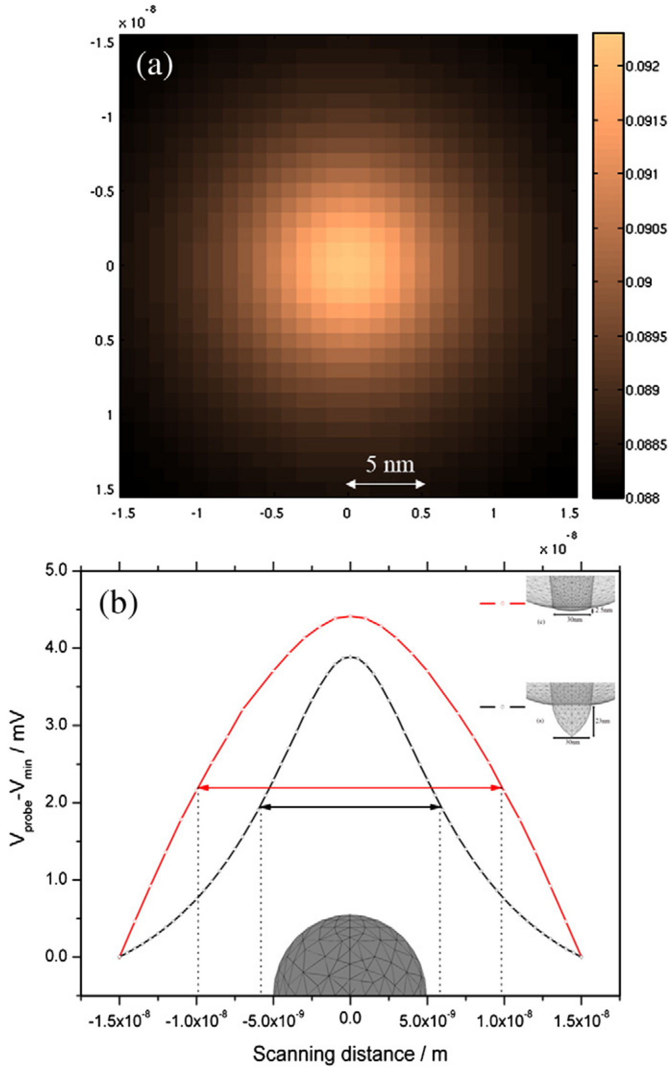

Fig. 2. (a) 2D image obtained by *x-y* scanning: colors represent the potential contrast (in V). The black curve in panel (b) represents the corresponding scan line over the hemispherical nano-particle. (b) Effect of the probe apex geometry on the apparent particle size in SECPM images. For comparison, the nano-particle is superimposed on the same scale.

3.1. Effect of the probe apex

It is important to note that the two modes of SECPM – vertical EDL profiling and horizontal *x-y* mapping – have completely different requirements regarding the optimum shape of the probe apex. In a recent study of the EDL profiling mode, we showed that the probe apex has to be flattened and not sharp, even if the apex protrusion is smaller than the investigated EDL Debye length. A sharp apex would create a non-uniform charge density distribution along the metallic boundary and hence the EDL distortion and Debye screening effects would be enhanced, leading to a decrease in probe sensitivity. The result is a steeper EDL potential profile close to the surface as compared to the unperturbed EDL potential [3].

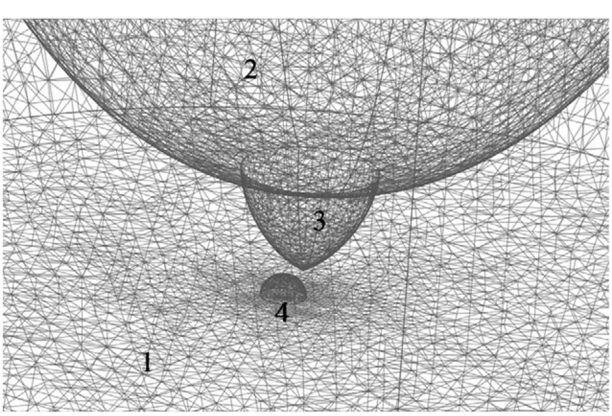

Fig. 1. SECPM cell model: (1) working electrode surface, (2) dielectric coating, (3) metallic probe and (4) hemispherical particle.

In the mapping mode, the probe is measuring the potential in the *x-y* plane. As the potential contrast between adjacent points is of interest and exact values of potential are less important, one may expect that the use of a sharp apex would give better resolution.

A comparison of the resulting scan lines calculated for a sharp and for a flattened probe is shown in Fig. 2b. Indeed, the sharp apex gives better resolution reflected by its smaller FWHM compared to the flattened apex. Decreasing the apex radius by using a sharp protruding shape increases the SECPM resolution. However, the non-classical behavior of curved EDLs, which was shown recently by Dickinson and Compton [4], and the voltammetric response of a nano electrode reported by Liu et al. [5] have to be kept in mind for the EDL probe.