Influence of scanning probe geometry on the imaging of diffusional processes at the nanoscale

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Summary

Imaging diffusional profiles is important in many different areas ranging from life sciences to materials. Combined scanning electrochemical - atomic force microscopy (SECM-AFM) probes allow simultaneous investigation of surface topography and reactivity at higher resolution and improved precision than with SECM alone. For this technique, it is crucial that the disturbance of the diffusion profile by the tip is minimal. Simulations were carried out to test the effect of different AFM probe designs on diffusion to support experimental results.

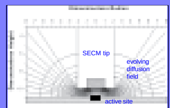

***Figure 1.1**: The impact of a conventional SECM tip on a diffusion field from an active site.*

(1) Introduction

Imaging diffusional transport at interfaces is important in the study of biological processes such as ion transport across membranes or the release of neurotransmitters at the synapse.

Scanning electrochemical microscopy (SECM) is a powerful technique used to image interfacial kinetics and concentration profiles over active diffusional sites, though its resolution is usually limited to the micron scale. Atomic force microscopy (AFM) is capable of measuring topographical information of the substrate at the nanometer scale. Recently combined SECM-AFM tips have been developed to simultaneously gain information on the topography and concentration profiles at high resolutions and with much more precision at active sites than with SECM alone[1].

Finding reliable estimates on the disturbance of the probe on the diffusion process and using probes that minimise this disturbance are crucial for these imaging techniques. While it is generally known that a smaller electrode size improves the image resolution and minimises disturbance, the influence of the probe design is less well studied.

References

[1] Gardner, C. E., Macpherson, J. V., *Anal. Chem.* **2002**, 74,576A.

[2] Dobson,P.S., Weaver, J.M.R., Holder, M.N., Unwin, P.R., Macpherson, J.V., *Anal. Chem.* **2005**, 77, 424-434.

[3] Kwak, J., Bard, A.J., *Anal. Chem.* **1989**, 61, 1221-1227.

Acknowledgement

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(2) Typical Probe Geometries

2.1 Electron microscopy images

This indicates the position of the electrode in a combined SECM-AFM tip.

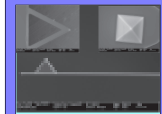


***Figure 2.1:** Electron microscopy images of the **Si_3N_4** type AFM probe (triangular cantilever).*

***Figure 2.2:** Electron microscopy images of the **LoT-FESP** type AFM probe (single beam cantilever).*

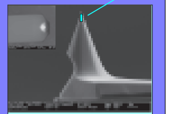
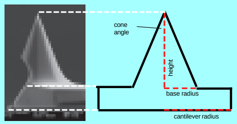


***Figure 2.3:** Electron microscopy images of the **MM-FESP** type AFM probe (single beam cantilever).*

2.2 Probe representation for the simulation



2.3 Probe Dimensions

	Si_3N_4	LoT-FESP	MM-FESP
Height	3.3 µm	15 µm	18 µm
Cone angle	40°	24°	24°
Base radius	2.7 µm	6.7 µm	6.5 µm
Cant. radius	6 µm	25 µm	10 µm

(3) Background

The influence of an approaching probe on the concentration profile evolving around an active site (modelled as a disc electrode) embedded in an insulating substrate can be investigated by measuring the current at the electrode as the probe tip is brought close and into contact with the substrate (at the center point of the embedded electrode).

The current at the disc electrode is the result of a diffusion-limited reduction of Ru $(NH_3)_6^{3+}$. An AFM probe approaching the disc electrode from the top (z direction) or from the side (x,y direction) hinders the diffusion of the reacting species to the electrode and reduces the resulting current.

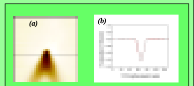


***Figure 3.1: (a)** Substrate current image (white = no hindering, black = strong hindering) resulting from scanning an AFM probe (Si_3N_4) across an insulating surface with an electrode embedded in its center. The triangular shape of the cantilever is reflected in the current profile (**cmp. Figure 2.1**). The normalised current profile along the horizontal line is shown in **(b)**.*

(4) Simulations:

4.1 Software

The simulations were carried out using the software package FEMLab, which implements the Finite Element Method to solve systems of partial differential equations (PDE), which describe the diffusion process. For a given geometry the concentration profile of the species diffusing away from the active site was computed.

4.2 The Model

The model consisted of a 2D box with a disk electrode (an ideal active site) embedded in the bottom boundary, from where the reduced species diffuse (**Figure 4.1**). The probe was treated as a cone and the cantilever as a disk "floating" in the solution.

Boundary conditions: At the electrode the species concentration was maximal, the embedding surface and the probe were usually insulating. At the extreme boundaries of the domain the species concentration was assumed to be zero, while the left boundary was set to satisfy a symmetry condition (**Figure 4.2**).

Mesh: The geometry was meshed using a quadratic mesh growing exponentially away from critical edges (**Figure 4.3**).

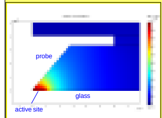


***Figure 4.1:** Concentration profile for the Si_3N_4 tip close to the active site.*

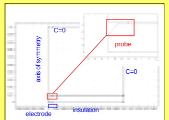


***Figure 4.3:** Geometry of the "floating probe" model.*

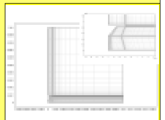


***Figure 4.2:** The system was solved on a quadratic mesh growing exponentially away from critical edges.*

4.3 Fitting the simulation results to experiment

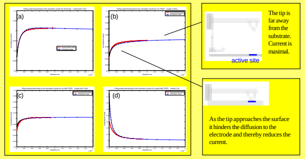


***Figure 4.4:** The figures show the simulation approach curves in comparison with experimental results. The currents are normalised with respect to the theoretical current for a disk-shaped electrode in bulk solution. **(a)** Si_3N_4 probe, **(b)** LoT-FESP, **(c)** MM-FESP (oxidised), **(d)** MM-FESP (metal coated)*

4.4 Influence of different probe geometries on the diffusion to the disk electrode.

Height of the probe: Increasing the height of the approaching tip while keeping its base radius constant decreases the hindering of the diffusion and in turn results in a higher current (**Figure 4.5**).

Base radius of the probe: Increasing the base radius (or equivalently the angle) of the tip cone decreases the diffusion to the electrode and therefore reduces the current (**Figure 4.6.**).

Radius of the cantilever: A large cantilever leads to a reduction of the current by blocking the diffusion. This effect is more pronounced for probes with a small tip height such as the Si_3N_4 probe (**Figure 4.7**).

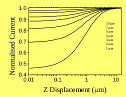


***Figure 4.5**: Influence of probe height on the diffusion to the electrode.*

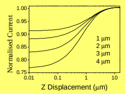


***Figure 4.6**: Influence of the probe base radius.*

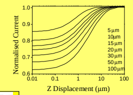


***Figure 4.7**: Influence of the cantilever (modelled as a floating disc) radius.*

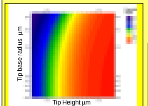


***Figure 4.8**: The current at the electrode (colour coded) when the probe is very close to the electrode (maximal hindering of the diffusion) as a function of the probe height and its base radius.*

(5) Conclusions

- Hindering of the diffusion to the electrode is minimal for high and narrow probe tips. From **Figure 4.8** it can be concluded that the height of the tip is the determining factor.
- The design of the cantilever affects diffusion more significantly when the probe has a small cone height, for example the Si_3N_4 probe (see **Figure 4.7**).