Soft Stylus Probes for Scanning Electrochemical Microscopy

-- Electronic Supporting Information --

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S1: Details of the Boundary Element Method (BEM) Simulations

The sample surface was assumed as 1600 µm × 1600 µm. The total boundary of the simulation domain was represented by 4966 triangles for simulation of conducting samples and 11493 triangles for insulating surfaces (Figure S1-1). After touching, the tilted soft stylus probe produces an almost linear concentration profile on an insulating sample. Therefore, a higher mesh density was used for insulating samples. Otherwise the simulation results showed some scattering.

a) **b)**

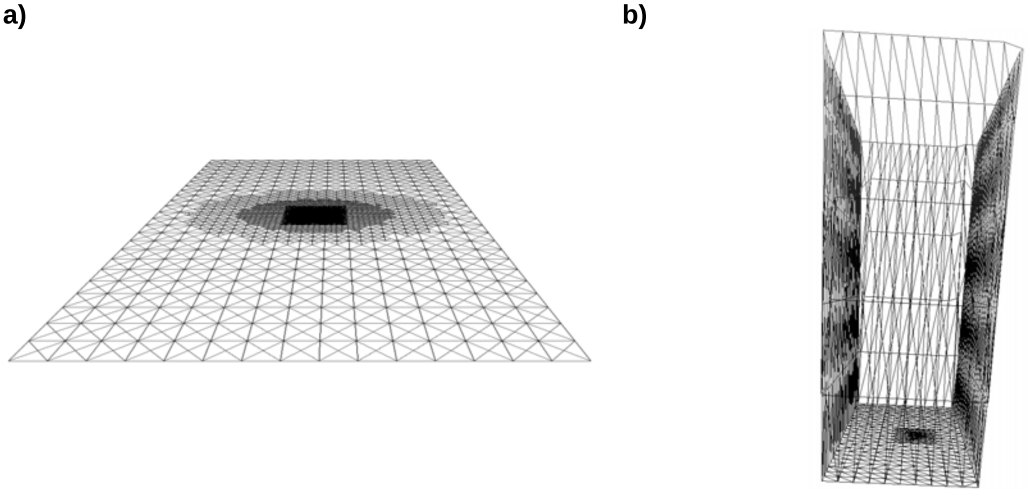

Figure S1-1: a) Used grid for the substrates corresponding to 1600 µm × 1600 µm. The size of the elements is reduced under the active electrode area. The total number of elements is 3484 (conducting sample) and 7725 (insulating sample). b) Grid of the lower part of the soft stylus probe with a height equal to 520 µm. The polished cross section corresponds to 480 µm × 200 µm. The electrode body and the active area is represented by 1482 triangles (conducting sample) or 3768 triangles (insulating sample).

The electrode geometry was taken from a microphotograph of the particular electrode (similar to Figure 1c) and slightly idealized to the shape shown in Figure S1-2. The total polished area of the soft stylus probe was taken as 480 µm × 200 µm (Figure S1-1), the quarter-moon shaped active electrode area fits into an rectangle of 40 µm × 17 µm. Simulations have been performed for several α. The paper reports about the simulation with $\alpha = 3°$.

a) **b)**

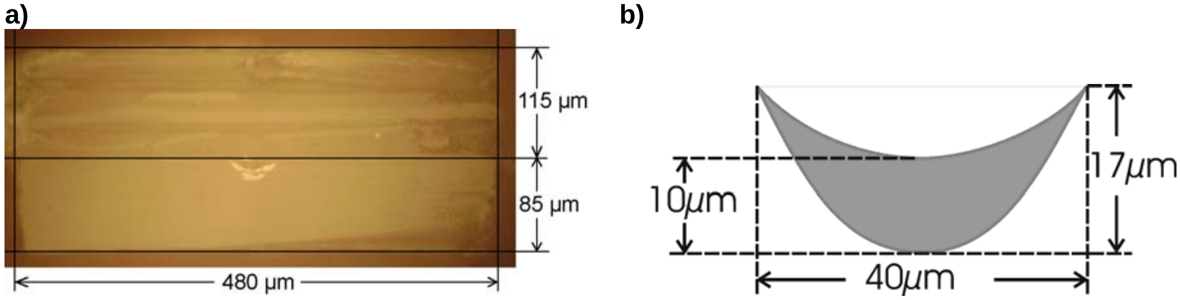

Figure S1-2: a) Optical microphotograph of the polished cross section of the soft stylus probe. b) Shape and extension of the active electrode area considered for the BEM simulation.

The approach started at a distance of h_P = 100 µm and 20 simulation points were calculated until touching the surface, where h_P is the distance measured from surface to the lowest point of the soft stylus probe. The working distance *d* of the *unbent* probe is then

$$d = h_P + 85\ \mu\text{m}\ \sin(\alpha) \qquad \text{(S1-1)}$$

To have more simulation points near the sample surface, the distances of consecutive points were adjusted quadraticly.

After touching the sample, the tilt angle α between the sample surface and the polished cross section was increased from 3° to 20° using a quadraticly growing step width.

For the plot in Figure 4b of the main manuscript, h_p was determined with the help of a calibration curve (Eq. S1-2) constructed from angles α (in degree) determined from microscopic images and the positional information of the vertical motor.

$$h_p = -5.52\ \mu\text{m}\ \text{grad}^{-1}\ \alpha \qquad \text{(S1-2)}$$

S2: Contactless Mode Imaging

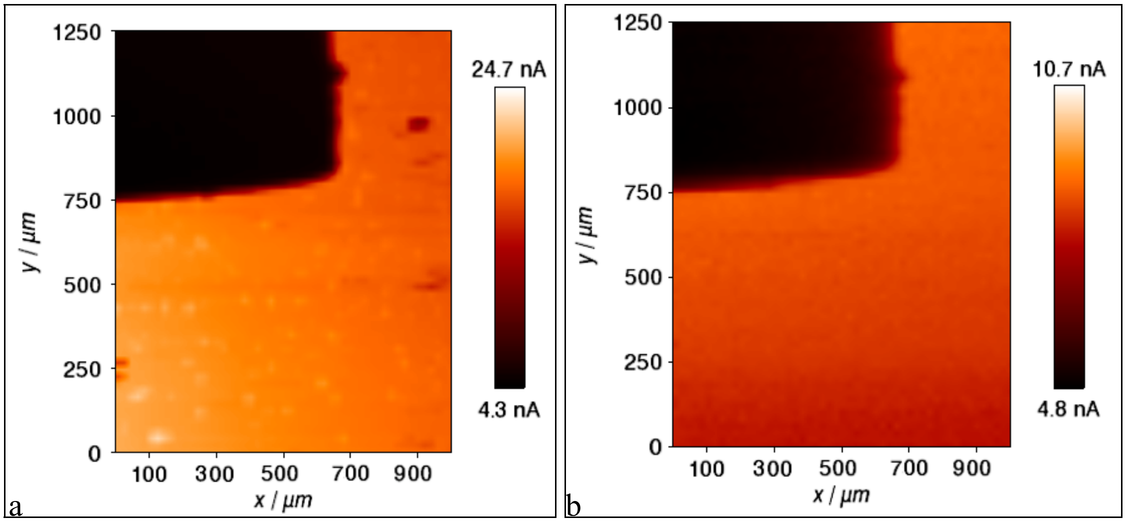

Figure S2-1. Constant height SECM image of glass partially covered by gold in 2.0 mM $FcCH_2OH$, 0.1 M KNO_3. Working electrode a) Pt microdisc (r_T = 10 µm, *RG* = 3 - 4) and b) soft stylus probe (exposed by laser ablation, thickness 6 µm, width 32 µm). Imaging conditions: E_T = 0.25 V, *d* = 5 µm, step size = 20 µm and translation rate v_T = 20 µm/s.

A SECM image of a portion of glass partially covered with gold was recorded using either a common Pt microdisk (r_T = 10 µm, *RG* = 3 - 4, Figure S2-1a) or a soft stylus probe (thickness 6 µm, width 32 µm, Figure S2-1b) as working electrode with 2 mM $FcCH_2OH$ as mediator. In both cases, a recycling of the redox mediator takes place on the unbiased gold electrode, thereby generating higher current values in Figures S2-1a and S2-1b. The contrast between the responses over insulating and over conducting surfaces differs between both probe types. This difference comes from the fact the Pt microdisc has a smaller *RG* = 3 – 4 than the soft stylus probe, thus a closer probe-substrate distance can be obtained with the microdisc electrode. Despite this, no significant loss in resolution is observed and almost the same information can be extracted from both images.

S3: Topographic artifacts in line scans over tilted surfaces

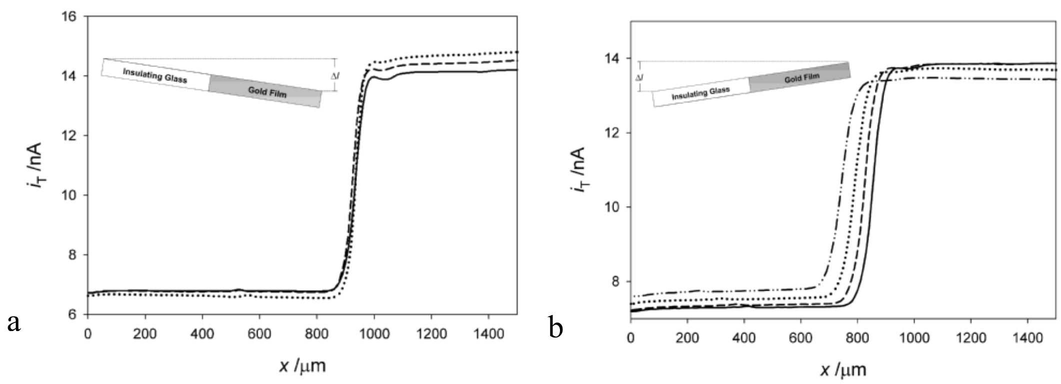

Figure S3-1. Lateral SECM line scans in feedback mode with a polished soft stylus probe over a glass partially covered by gold in 2.4 mM $FcCH_2OH$, 0.1 M KNO_3. The sample was tilted from the glass towards the gold region a) downhill b) uphill. The height difference (Δl) between the starting (over glass) and final (over gold) points was varied; 20 µm (continuous line), 30 µm (dashed line), 50 µm (dotted line) and 90 µm (dashed-dotted line). E_T = 0.3 V, step size = 10 µm and v_T = 10 µm/s, h_P = -75 µm.

Under the conditions tested (i.e. $\Delta l \leq 90$ µm for a scan length ≥ 2000 µm), the probe can tolerate height differences $\Delta l \leq h_P$ (Figure S3-1a). If the probe scans uphill, the increased bending of the probe increased the distance between the active electrode and the sample. This causes a decrease of the contrast between signals over insulating region and conducting regions (Figure S3-1b).

S4: Derivatization of SECM Line Scans

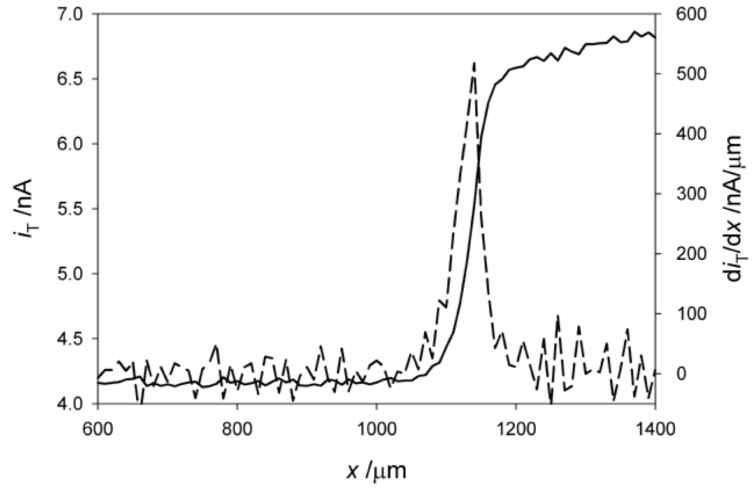

Figure S4-1. Lateral SECM line scan in feedback mode (continuous line) with a soft stylus probe prepared by mechanical polishing over a glass–gold boundary in 2.1 mM $FcCH_2OH$, 0.1 M KNO_3. Numerical differentiation of the line scan presented (dashed line). h_P = –5 µm, E_T = 0.3 V, step size = 10 µm and translation rate v_T = 10 µm/s.

The average value of highest point obtained from the numerical differentiation of 8 line scans was employed in equation 2 of the main manuscript to determine the resolution achieved with the soft stylus probe exposed by mechanical polishing.