Electronic Supplementary Information

3D Electrochemical and Ion Current Imaging using Scanning Electrochemical-Scanning Ion Conductance Microscopy

Yasufumi Takahashi[1,2,3,4,*], Hiroki Ida[2], Yoshiharu Matsumae[2], Hirokazu Komaki[2], Yuanshu Zhou[4], Akichika Kumatani[2], Makoto Kanzaki[5], Hitoshi Shiku[6], and Tomokazu Matsue[1, 2,*]

[1]WPI-Advanced Institute for Materials Research, Tohoku University, 980-8577, Japan

[2]Graduate School of Environmental Studies, Tohoku University, 980-8579, Japan

[3]Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), Saitama 332-0012, Japan

[4]Division of Electrical Engineering and Computer Science, Kanazawa University, 920-1192, Japan

[5]Graduate School of Biomedical Engineering, Tohoku University, 980-8579, Japan

[6]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Tel: (+81)-076-234-4866

*Corresponding author: yasufumi@se.kanazawa-u.ac.jp, matsue@bioinfo.che.tohoku.ac.jp

Numerical Simulation of Scanning Electrochemical Microscopy

In order to evaluate standard rate constant for electron-transfer (k^0) on unbiased conductive substrate, we simulated the SECM current response on unbiased conductors by numerical simulation software of COMSOL multiphysics. We used the same simulation model as described in the previous work.[1] In this simulation, the redox reaction was simulated to be happened on unbiased conductive substrate because the tip-generated species is supposed to diffuse and react at the surface of the conductive substrate directly under the tip. The point was to find the boundary condition of unbiased conductor, which the net current on unbiased conductive is approximately zero (Fig. S1).

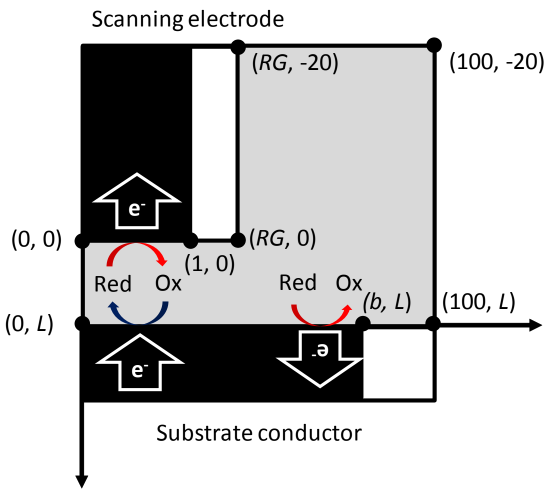

Fig. S1 Model geometries of the scanning electrochemical microscopy (SECM) simulation.

Dimensionless parameters are defined by:

$$R = r/a \qquad \text{(S1)}$$

$$Z = z/a \qquad \text{(S2)}$$

$$RG = r_g/a \qquad \text{(S3)}$$

$$L = d/a \qquad \text{(S4)}$$

$$C(R,Z) = c(r,z)/c_0 \qquad \text{(S5)}$$

$$\tau = 4Dt/a^2 \qquad \text{(S6)}$$

$$K = k^0 a/D \qquad \text{(S7)}$$

where a is tip radius, r_g is insulater thickness, d is the tip-sample distance, c is concentration, D is the diffusion coefficient of the mediator, r and z are the spatial coordinates in directions radial and normal to the UME surface, respectively, measured from the center of the electrode, and t is time.

The time-dependent diffusion equation solved was

$$\frac{\partial C(R,Z)}{\partial \tau} = 0.25\left[\frac{\partial^2 C(R,Z)}{\partial R^2} + \frac{1}{R}\frac{\partial C(R,Z)}{\partial R} + \frac{\partial^2 C(R,Z)}{\partial Z^2}\right] \quad \text{(S8)}$$

The boundary conditions are expressed as follows:

$$C(R,0) = 0 \quad 0 < R < 1 \ (scanning\ electrode\ surface) \quad \text{(S9)}$$

For a quasi-reversible substrate reaction, the unbiased conductor surface boundary condition in given by

$$\left[\frac{\partial C(R,Z)}{\partial R}\right]_{Z=L} = \frac{K(1+\theta)}{\theta^{\alpha}}\left(\frac{\theta}{\theta+1} - C(R,Z)\right) \ 0 < R < b \quad (conductor\ substrate\ surface)(S10)$$

(α is transfer coefficient, in this simulation we set $\alpha = 0.5$)

With $$\theta = exp\left[\frac{F}{RT}(E - E^{0'})\right] \quad \text{(S11)}$$

$$\left[\frac{\partial C(R,Z)}{\partial R}\right]_{Z=0} = 0, \ \ 1 < R < RG \ (insulator) \quad \text{(S12)}$$

$$\left[\frac{\partial C(R,Z)}{\partial Z}\right]_{R=RG} = 0, \ \ -20 < Z < 0 \ (insulator) \quad \text{(S13)}$$

$$C(R,Z) = 1, \ RG < R < 100, \ Z = -20 \ (simulation\ space\ limits) \quad \text{(S14)}$$

$$C(R,Z) = 1, \ R = 100, \ -20 < Z < D \ \ (simulation\ space\ limits) \quad \text{(S15)}$$

$$\left[\frac{\partial C(R,Z)}{\partial R}\right]_{R=0} = 0, \ 0 < Z < D \ \ (axis\ of\ symmetry) \quad \text{(S16)}$$

The dimensionless tip current is given by

$$I_T = \frac{i_T}{i_{T,\infty}} = \frac{\pi}{2}\int_0^1 R\left[\frac{\partial C(R,Z)}{\partial Z}\right]dR \quad \text{(S17)}$$

The dimensionless substrate current is given by

$$I_S = \frac{\pi}{2}\int_0^b R\left[\frac{\partial C(R,Z)}{\partial Z}\right]dR \quad \text{(S18)}$$

(b is the dimensionless radius of unbiased conductor.)

We used parametric sweep, which was the function of COMSOL Multiphsics for changing the parameter (dimensionless radius of unbiased conductor (b), tip-sample distance (L), K, and θ) automatically and sequencally during simulation, to find the suitable θ with different K. We used normalized model and defined the threshold of net current of I_s to be less than 0.01. Then we fitted the experimental approach curves to the numerical simulated approach curves to estimate the k^0.

An example of the simulation result for a quasi-reversible substrate reaction of different size unbiased substrate conductors is attached (Fig. S2).

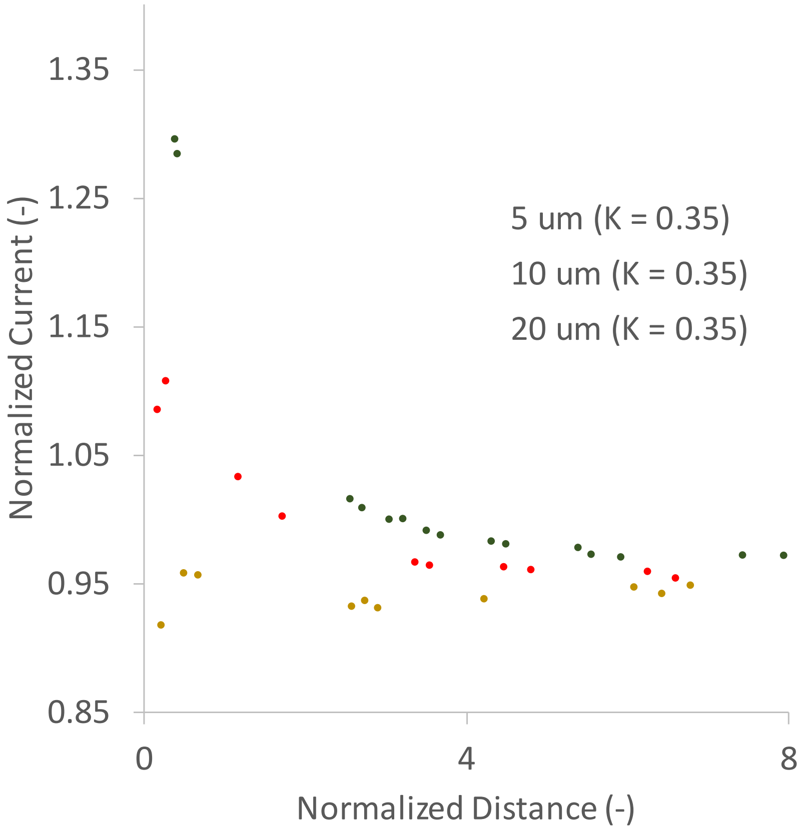

Fig. S2 Simulated approach curves of different size unbiased substrate conductors.

The diameters of unbiased conductors are 5, 10, and 20 μm. a = 278 nm. RG=1.1, K = 0.35.

The faradaic current signal was decreased to 87% during electrochemical imaging due to the fouling of the carbon electrode during imaging process. Figure S3 shows the faradaic current signal change during imaging.

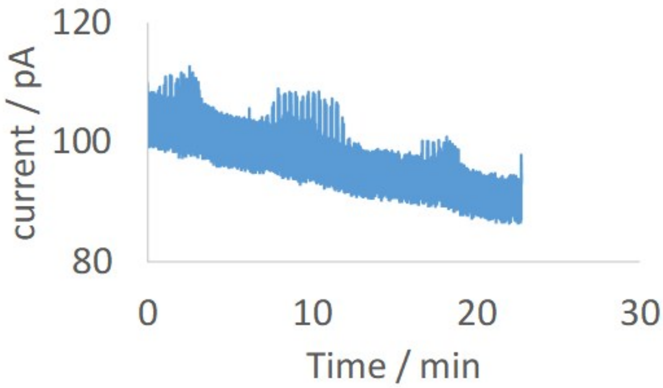

Figure S3 Current decrease during SECM-SICM imaging of unbiased Pt conductors.

Reference

1. Xiong, H., Guo, J.D. & Amemiya, S. *Anal. Chem.* **79**, 2735 (2007).