Carbon Nanotube Fiber Microelectrodes Show a Higher Resistance to Dopamine Fouling

Wolfgang Harreither,[†,§] Raphaël Trouillon,[†] Philippe Poulin,[‡] Wilfrid Neri,[‡] Andrew G. Ewing,[†,#] Gulnara Safina[†,∗]

In this file of Supporting Information, we describe the steady-state oxidation model for a partially blocked electrode and we show additional analytical details (background CV scans) of the CNTF electrodes.

1 Model of electrode fouling

The effect of partial blocking of the electrode on the diffusion limited current i_{dl} was simulated using finite element modeling. The finite element modeling simulations were performed using Comsol Multiphysics 4.0 a. The system was simplified to facilitate the computation by drawing a square (edge length: 16 μm) partially blocked by insulating squares of edge d, as shown on Figure S1A, at the bottom of a cylinder (radius: 500 μm, height: 500 μm) of liquid, containing 1 mM of analyte at t= 0 s, representing the electrochemical cell (the diffusion coefficient D was 6 10^{-10} $m^2 s^{-1}$, as previously measured for dopamine).[1] The system was run for t_{max}= 20 s, and assuming that the distance x_{max} affected by the electrode is described by[2]

$$x_{max} = \sqrt{6Dt_{max}} = 300\ \mu m \tag{1}$$

the defined electrochemical cell is large enough to ensure the boundaries are not reached over the course of the simulation time.

This geometry allowed for the use of a regular square pattern, mimicking the formation of patches of insulating materials on the electrode surface. In this case, several patches of insulating material, of characteristic size d, were evenly positioned at the surface of the electrode. Because of the micrometric scale of the system, the shape discrepancy between the model and the actual device was not expected to have a significant effect on the relative variations in the diffusion limited current generated at the partially blocked surface.

The geometry was meshed with a tetrahedral pattern (maximum size: 35 μm, minimum size: 1.5 μm, maximal element growth rate: 1.35, resolution of curvature: 0.3, resolution of narrow regions: 0.85). To accomodate the geometry defining the electrode, a finer mesh was used in a cylinder (radius: 30 μm, height: 30 μm) centered over the electrode (maximum size: 5 μm, minimum size: 0.05 μm).

This model assumes that the insulating film initially inactivates discrete patches whose size then increases as the polymer grows. The diffusion-limited current i_{dl} was calculated for different values of d, from a fully active to a fully blocked electrode. In our simulations, i_{dl} was obtained by running the model for 20 s, and the current computed at t= 20 s was used as an approximation of i_{dl}. Practically, it was observed that a quasi-steady state was reached after 2-3 s.

The system was solved, and the normal flux of analyte at steady state at the surface of the electrode was obtained for increasing values of d. The calculations and fitting routines were perfomed with Igor Pro (Wavemetrics, US).

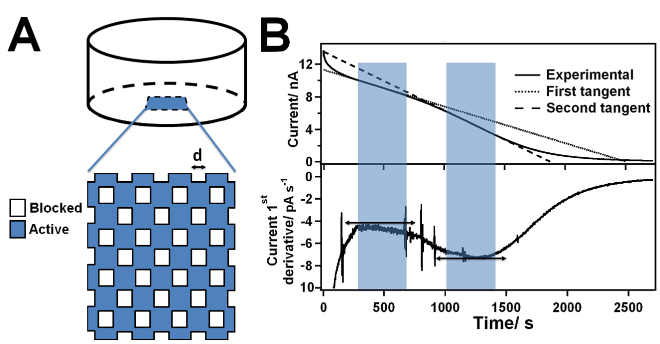

Figure S1. Model of the fouling process and kinetics. A: description of the model for the finite element simulation showing the partially blocked electrode located at the bottom of a cylinder of analyte; B: Average amperometric trace obtained for a CNTF in 1 mM DA, and its first order derivative. The linear sections of the amperogram are highlighted in blue, and the corresponding tangents are displayed.

The experimental data was then analyzed as presented on Figure S1B. The first order derivative was calculated, showing two regions were the trace can be approximated by its tangent. In particular, using the second tangent, the one describing the fast decay between 1000 and 2000 s, the electrode can be considered as completely blocked after 1882.6 s.

†*: Department of Chemistry and Molecular Biology, University of Gothenburg, S-41296, Gothenburg, Sweden*

‡*: Centre de Recherche Paul Pascal, CNRS, Université de Bordeaux, Pessac 33600, France*

#*: Department of Chemical and Biological Engineering, Chalmers University of Technology, S-41296 Gothenburg, Sweden*

∗*: To whom correspondence should be addressed: phone +46 766 22 90 61; email gulnara.safina@chem.gu.se*

§*: Present address: Lohmann & Rauscher GmbH, 2525 Schönau an der Triesting, Austria*

To simulate the growth of the insulating patches, the experimental data was normalized to its initial value, and fitted with the simulated trace. As detailed in the text, a d linearly increasing with time ($d = kt$) was found to return the best fit, thus supporting the possibility of an insulation scheme in growing patches. The growth coefficient k was found to be characteristic of the polymerization reaction, and is an indicator of the resistance to fouling of the electrode.

It is important to note that this fitting strategy is valid only if the system can be considered at steady state at every instant. In other words, if the growth of the patches is much slower than the characteristic time defining the formation of the depletion layer.

2 Background scans of CF and CNTF

Backgrounds CVs were performed for the CNTF and CF microelectrodes, in PBS and 0.1 M H_2SO_4 (Figure S2).

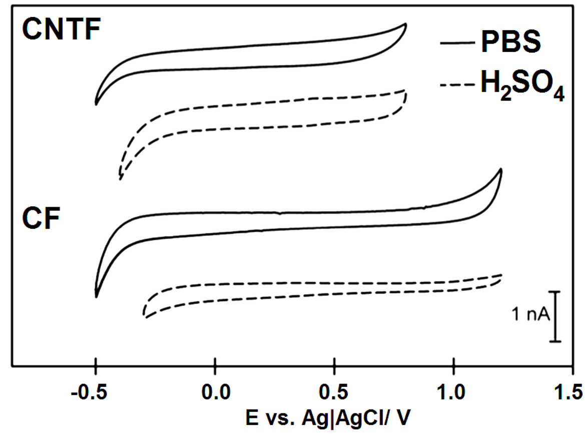

Figure S2. Background scans of the CNTF microelectrode (upper CVs) and CF microelectrode (lower CVs) in PBS buffer pH 7.4 (solid line) and 0.1 M H_2SO_4 (broken line), scan rate was 100 mV s^{-1}.

References

1 G. Gerhardt and R. N. Adams, *Anal. Chem.*, 1982, **54**, 2618–2620.

2 T. J. Schroeder, J. A. Jankowski, J. Senyshyn, R. W. Holz and R. M. Wightman, *J. Biol. Chem.*, 1994, **269**, 17215–17220.