

Electrochemical Characterisation Of The Graphite Microband Electrodes.

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Introduction: The monitoring of phenolic compounds in raw waters and wastewaters is of great importance for environmental control due to their wide use in industry and natural occurrence in various compounds. A general drawback of previously reported biosensors for phenol detection is their insufficient limits of quantification for phenols in water samples. One way to improve the quantification limit is by the use of microelectrodes, which exhibit a better signal/noise ratio than conventional-sized electrodes because they minimize the active surface area and the concomitant noise associated with the double layer capacitance, while enhancing mass transfer via multidimensional diffusion along axes where the electrode dimensions are small relative to the diffusion layer thickness[1]. In this work we perform numerical and experimental characterization of screen printed graphite microband array electrodes. Such microband electrode system with immobilized laccase has been used for phenols detection in weakly supported media.

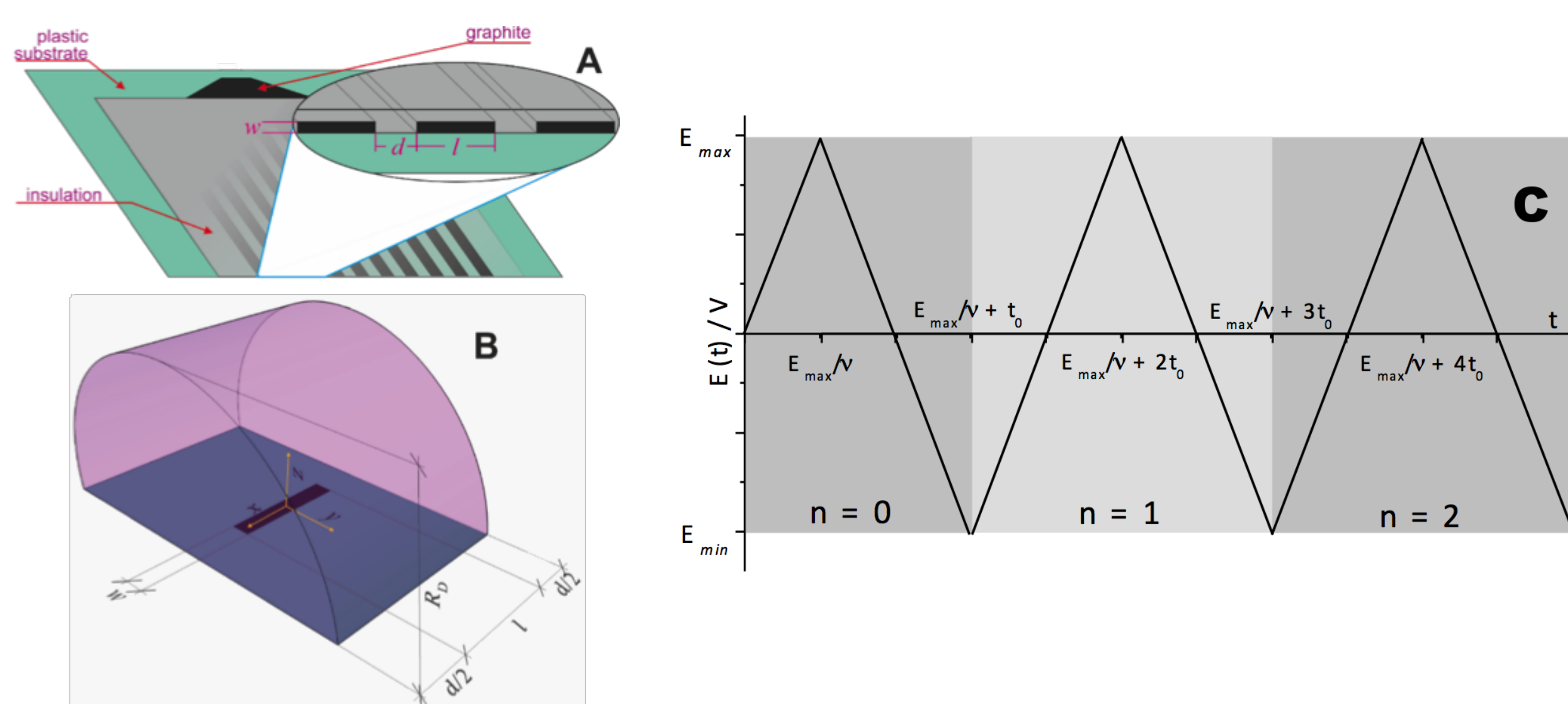
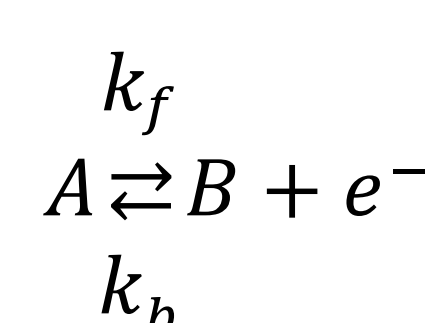


Figure 1. A: The layout of the screen printed graphite microband electrode arrays; **B:** Simulation domain at a single microband electrode; **C:** The time dependence of the electrode potential utilized for modelling.

Computational Methods:

A rectangular form of each microband electrode in the array (Fig. 1A) was assumed with a microband width w of 7 μm [2], a length l of 0.4 mm and a distance between the electrodes in the array d of 0.4 mm. In order to describe the voltammetric response of the MBA, a single electrolyte domain (Fig. 1B) bound to a single graphite microelectrode and the surrounding in-plane insulator were chosen.

Both species A and B involved in mass transport undergo a one-electron redox reaction at the electrode surface:



where k_a and k_b are the forward and backward rate constants. Only species A is present in the bulk solution. If the electrode reaction follows Butler-Volmer kinetics, the rate constants can be defined as:

$$k_f = k^\circ \exp \left\{ \frac{(1-\alpha)F(E(t)-E^\circ)}{RT} \right\}$$

$$k_b = k^\circ \exp \left\{ \frac{-\alpha F(E(t)-E^\circ)}{RT} \right\}$$

where k° is the standard electron transfer rate constant, $\alpha=0.5$ is the transfer coefficient, F is the Faraday constant, E° is the formal potential of the redox couple, $E(t)$ is the potential applied to the microband electrode, R is the gas constant and T (298 K) is the temperature.

The mass transport of species in Cartesian coordinates is described by Fick's second law of diffusion:

$$\frac{\partial c_A}{\partial t} = \nabla^2(D_A \nabla c_A)$$

$$\frac{\partial c_B}{\partial t} = \nabla^2(D_B \nabla c_B)$$

where D_A and D_B are the diffusion coefficients, c_A and c_B are the concentrations of the species, respectively.

The boundary condition at the electrode surface[3]

$$-D_A \nabla c_A = D_B \nabla c_B = k_f c_A - k_b c_B$$

A constant bulk concentration ($c_A=1$ mM, $c_B=0$ M) has been assumed on the top surface of the domain. A periodic boundary condition has been set along the x direction in order to take into account the periodic structure of the microband array.

In the CV simulation the electrode surface potential is imposed to vary back and forth between two potentials with constant scan rate (Fig. 1C)

Results: Voltammetric responses of the ferrocenedimethanol redox probe ($D_A=D_B=7 \times 10^{-6}$ cm²/s, $k^\circ=2 \times 10^{-2}$ cm/s, $E^\circ=0.255$ V) were studied on the graphite screen printed electrodes (Fig. 1C). The microband array (MBA) showed pronounced sigmoidal voltammetric responses, typical for micro-scale electrodes with enhanced mass transport of the redox material to/from the electrode, due to convergent diffusion. The transition from redox peak currents obtained at the macro-scale electrode (Inset of Fig. 2) to the wave-shaped response of the micro-scale electrode, is due to the enhancement of rates of reactant and product mass transfer to and from the electrode surface respectively [4], as a result of convergent diffusion. Assuming a microband electrode width of 7 μm [2], more than two orders of magnitude larger current density for the redox process was obtained with the micro-scale electrode, which illustrates the sensitivity increase achieved due to convergent diffusion.

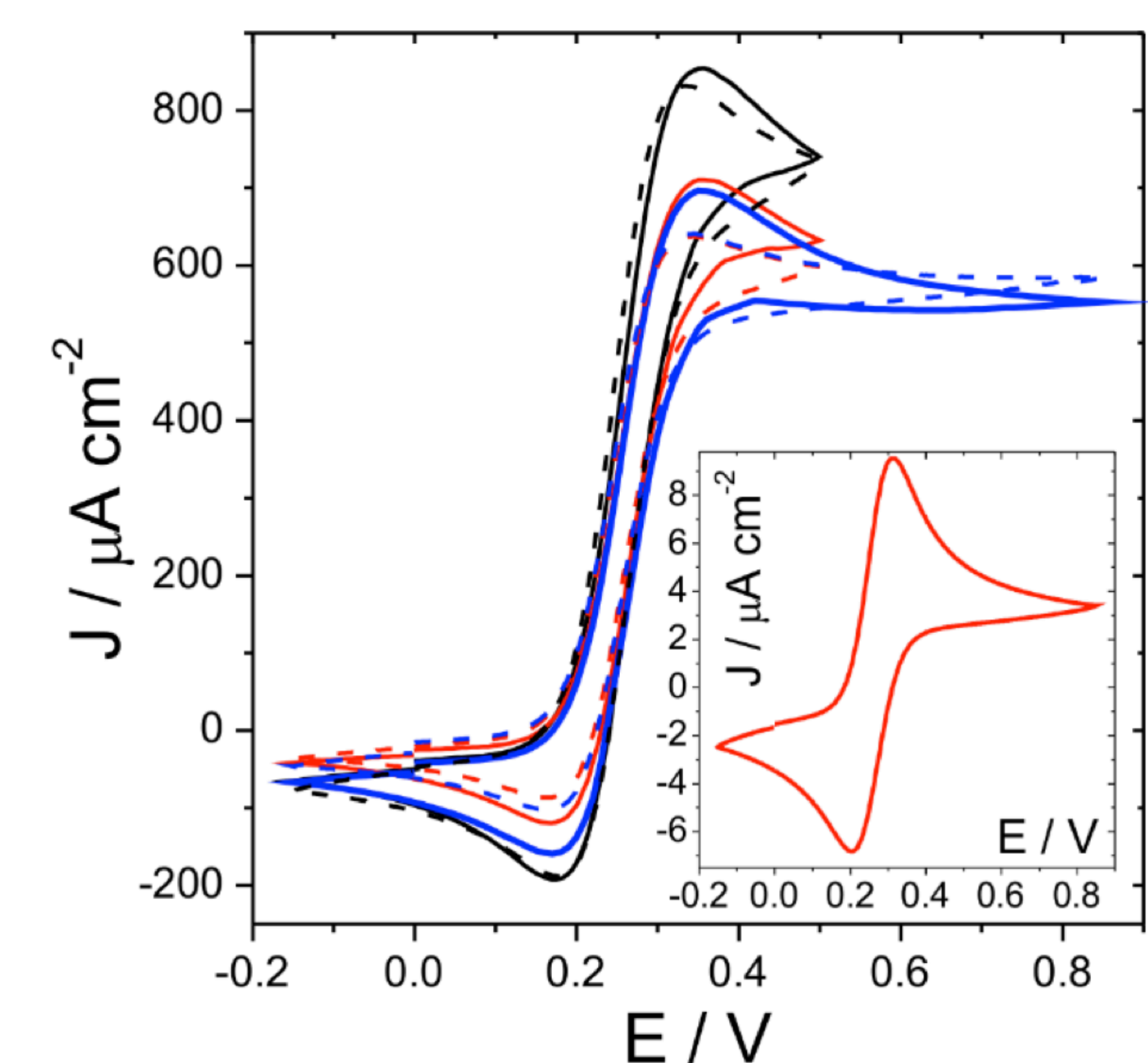


Figure 2. Experimental and simulated voltammetric responses (solid and dashed curves, respectively) of ferrocenedimethanol at the graphite microband electrode (0.1 M HCl, 1 mM FcDM, scan rates: 50 mV/s (red and blue curves) and 200 mV/s (black curves); Inset: voltammetric response at the graphite disk electrode.

The enhancement of the sensitivity at the MBA was larger than obtained for charged redox probes (ferro/ferricyanide and hexaamineruthenium) [2], which probably illustrates the different contributions of surface states to the electrode reaction kinetics. The observed voltammetric responses on the MBA were still characterized by peak redox currents and a dependence of the currents on the scan rate. This illustrates that the observed current plateaus are not true steady-state currents. Thus, although having enhanced mass transfer, leading to a current density increase, the microband arrays showed mixed diffusional behavior over the time domain of the recorded cyclic voltammograms.

The experimental data collected at different scan rates and anodic limits showed good agreement with simulated voltammetric responses obtained with the use of the new model developed for the MBA. The concentration profiles of the reactant species (Fig. 3) obtained at potentials of steady-state currents, show highly nonlinear diffusion, which spreads mostly in the radial direction. Being the critical dimension of the microscale electrode [5], the microband electrode width limits the observed current density.

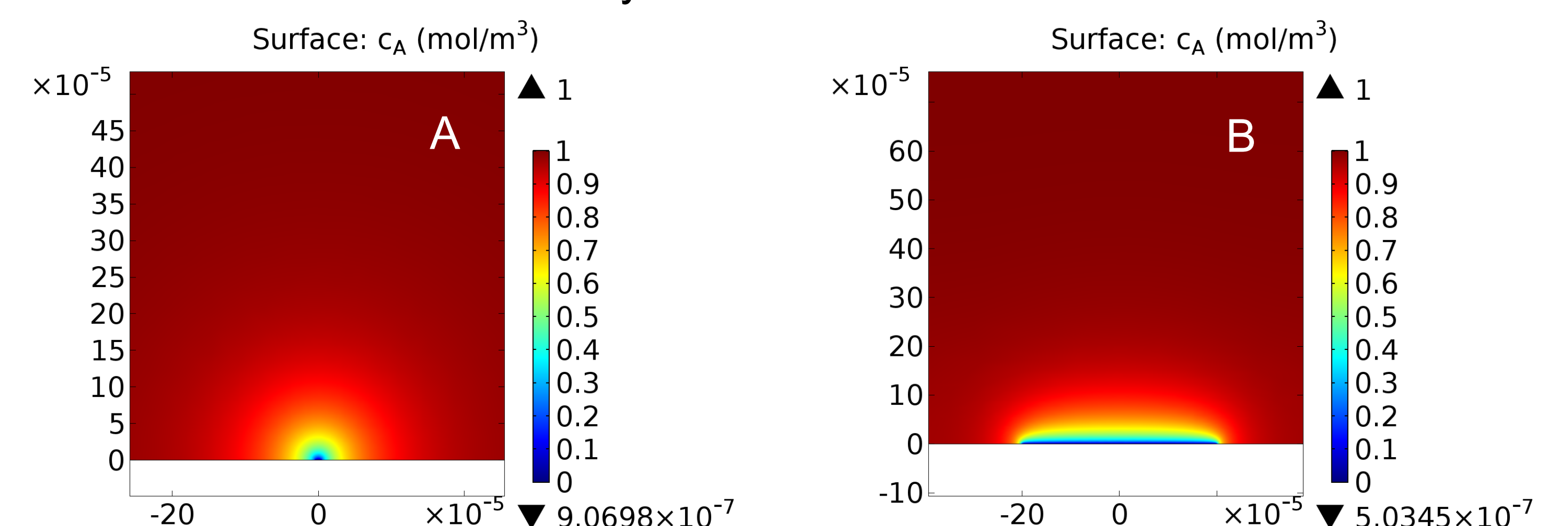


Figure 3. A: zx cross section and **B:** zy cross section of product concentration profile at $E=0.85$ V, scan rate is 50 mV/s

Conclusions: We developed modified diffusion domain approach for simulation electrochemical process at graphite microbands array electrode.

We found that current density in the considered microelectrode array more than two orders of magnitude larger than current density for macro electrode. This sensitivity increase achieved due to convergent diffusion.

References:

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