Highly disparate activity regions due to non-uniform potential distribution in microfluidic devices: Simulations and experiments

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ABSTRACT

In a microfluidic flow cell activity pattern can occur along a thin band electrode due to the potential distribution in the cell. For quantitative characterization of the pattern formation exclusively due to electric effect and for elimination of interactions of reaction sites from concentration distribution along the flow channel, a partial differential equation model is formulated for the spatiotemporal variation of electrode potential with Butler–Volmer kinetics limited by mass transfer. At constant applied circuit voltage, with increase of the electrode size a limiting current is achieved because of the spatial pattern formation. The limiting current arises due to the formation of high activity at the downstream edge, and low (nearly open circuit potential) activity at the upstream edge. The spatial pattern (e.g., ratio of active vs. inactive region) depends on the electrode size, the applied voltage, the conductivity of the electrolyte, and the distance from the downstream electrode edge to the reservoir. It is also shown that by placing equally spaced insulating stripes on the electrode much of the activity can be retained and the current does not decrease significantly due to the lessened surface area (as long as the surface area of the insulating stripes is less than about 50% of the entire electrode area). The model simulations are interpreted with a coupled ordinary differential equation model of segmented electrodes and the occurrence of the strong edge effects is confirmed with experiments of a four-electrode electrode array in a microfluidic flow cell with ferrocyanide oxidation.

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1. Introduction

Microfluidic devices that incorporate electrochemical flow-through cells gained considerable interest in electroanalytical chemistry [1–3], where one electrode can be used as a detector, or multiple electrodes can be integrated in a generator–collector detector system [4–6]. In addition, the devices can be used as kinetic probes [7–10], in miniaturized biological and electrochemical fuel cells as portable, renewable energy generators [11,12], for electrosynthesis [13,14], or as template device in materials science [15]. The mathematical modeling and theoretical analysis of electrochemical systems, which are often required for the description and optimization of the microfluidic devices, are challenging tasks because of the presence of multiscale, integrated processes [16,17]. Detailed descriptions for mass transfer, reactions kinetics, and potential drop in the electrolyte are often required for characterization of the spatiotemporal response of the cell in terms of concentration and current density profiles [18,19].

Modeling efforts have been often focused on considering one or two dominant types of processes (e.g., mass transport and chemical reaction); even with such simplifications, a wide variety of responses are possible. For example, modeling of convective flow, diffusion, and mass-transfer limited (quasistationary) charge-transfer chemical reactions led to identification of six different zones of different mass transfer characteristics of a single electrode [20], and three major (sequential, coupling, and crosstalk) operational regions in dual electrode configurations [21]. Flow profiles have been simulated computationally for various experimental techniques such as chronoamperometry, linear and cyclic sweep voltammetry [22–25] and, with similar approach, limitations on experimentally measurable kinetic rate constants were obtained as a function of cell geometry [7].

In addition to mass transfer, potential drop in the electrolyte also has a great impact on the behavior of electrochemical cells. In traditional macrocells potential drops can cause ohmic losses resulting in bistability and oscillations [26], can impact explosive growth of metastable pitting corrosion [27] and can induce coupling resulting in stationary patterns [28,29], traveling and standing waves [18], and synchronization patterns [30]. In traditional configurations one of the simplest manifestation of
pattern formation is the ‘edge effect’ when the shape of the electrodes imposes a pattern because of the high activity of the edges [31]. The presence of potential drop distribution in the flow channel proves to be a great challenge in the modeling of microfluidic devices. On one hand, ohmic drops can be considered as a necessary nuisance that could be avoided by non-traditional design of counter [32] and reference [33] electrodes. In some examples, modeling studies can help designing of cell geometry as it was done with microfluidic electrokinetics [34] or with interdigitated electrode arrays [35]. On the other hand, nonuniform potential field can be advantageous, e.g., for bipolar electrode focusing [36] or microelectrochemical gates and integrated circuits [37]. In microfluidic settings the potential drop in the flow channel can be very large because of the small volume of the conducting electrolyte. For example, this ohmic potential drop can result in non-uniform conducting polymer growth on a single electrode [15] or in strong electrical coupling that can drive synchronous variations of currents with electrocatalytic [38] and corrosion [39] systems.

In this paper, we explore the effect of potential distribution on total current and current density distribution in a flow channel for electrochemical reactions with Butler–Volmer kinetics with mass transfer limitation on both single and segmented electrodes. The primary goal of the model is to shed light on contributions of non-uniform potential distribution to the unusually disparate activity of the electrode edges. To eliminate interactions among reacting sites due to concentration distribution, we consider uniform concentrations of analytes along the flow channel, and a thin Nernst diffusion layer across the height of the flow channel. Numerical simulations of the model equations are carried out with a single electrode to explore the effect of electrode size and electrolyte conductivity on quasistationary linear sweep voltammograms, in particular, to the onset potential and current density of limiting currents with large electrode widths. The role of edge effects is elucidated for electrode configurations with single (one-sided) and double (two-sided) counter/reference electrode placements as well as for segmented working electrodes. The numerical findings of separation of high and low activity regions in the partial differential equation model are interpreted with a coupled ordinary differential equation model of segmented electrodes. Finally, the findings of model equations are compared to an experimental measurement with four segmented electrodes in microfluidic flow channel with the ferrocyanide oxidation reaction on Pt.

2. The distributed system: model

The cell geometries used in this model are depicted in Fig. 1. All of them represent two-dimensional approximation of a three-dimensional microfluidic flow cell geometry, where the lateral extension of the microcell was neglected. In the simplest geometry from Fig. 1a, the working electrode (WE) of length \( W \) is embedded in insulator, on the bottom side of the cell of length \( D \) and height \( H \), while \( L \) denotes the distance from the WE to the Reference Electrode (RE). Both RE and the Counter Electrode (CE) are modeled as an equipotential plane on the right side of the cell. (The reference and counter electrode are typically placed at the reservoir, which has minimal ohmic potential drop because of the large size.) Fig. 1b represents a more symmetrical situation, when both left and right walls of the cell are described by equipotential planes kept at the applied voltage; this would correspond to a cell geometry with two CEs. Here \( L_1 \) and \( L_2 \) represent the distances from the edges of the WE to the equipotential planes. Fig. 1c describes a segmented WE, where active electrode stripes alternate with insulating regions.

At the WE, the charge balance equation reads:

\[
\dot{i}_{\text{muc}} = \dot{i}_{\text{cap}} + \dot{i}_{\text{i}}
\]

![Fig. 1. Electrochemical cell geometries. (a) 3-electrode flow cell, (b) Two counter electrode (CE) cell and (c) Segmented working electrode (WE) cell. e.p. marks the equipotential plane(s).](image-url)
WE kinetics, we used a simple Butler–Volmer kinetics with mass transfer contribution [41]. The dimensionless reaction current density is:

\[ i_R = e^{\beta \phi_{\text{RE}}} - e^{-\beta \phi_{\text{WE}}} \]  

(9)

where \( \beta = 0.5 \) is the transfer coefficient. The dimensionless Faradaic current density \( i_F \) (assuming a renormalized mass transfer limiting current of 1) is given by:

\[ \frac{1}{i_F} = \frac{1}{i_R} + 1 \]  

(10)

which leads to

\[ i_F = \frac{e^{\beta \phi_{\text{RE}}} - e^{-\beta \phi_{\text{WE}}}}{e^{\beta \phi_{\text{RE}}} - e^{-\beta \phi_{\text{WE}}} + 1} \]  

(11)

The potential of the metal of the WE is taken as reference and thus the following relationship is valid between the drop of potential across the electrical double layer in front of WE and the electrostatic potential in front of WE:

\[ \phi_{\text{DL}} = -\phi_{\text{WE}} \]  

(12)

In stationary state, according to Eq. (7) the capacitive current density vanishes and the migration current density equals the Faradaic current density. The total current at the WE will be:

\[ I_{\text{tot}} = \int_0^W i_F \, dx \]  

(13)

The potential at the right wall of the cell – in case of Fig. 1a and c geometries – or at both lateral walls for Fig. 1b is equal to the applied voltage \( V_{\text{appl}} \) in a classical three electrode setup with potentiostatic control:

\[ \phi_{\text{RE},-CE} = V_{\text{appl}} \]  

(14)

We assume that the electrolyte is concentrated enough such that at any point in the electrolyte electroneutrality condition is valid and thus Laplace equation is satisfied:

\[ \Delta \phi = 0 \]  

(15)

On all the walls, excepting the electrode areas, a no-flux boundary condition was used, which describes an insulating area:

\[ \nabla \phi|_C = 0 \]  

(16)

Because the local current density in Eq. (11) is a unique function of the drop of potential across the electrical double layer, the concentration distribution in the flow channel does not affect the solutions. This approximation is equivalent to the assumption that there is no change of concentration along the flow channel (in the x direction); the only concentration change occurs across the height of the flow channel (in the y direction) in the form of a Nernst diffusion layer that gives an overall kinetic expression shown in Eq. (11). An investigation on the impact of concentration distribution along the flow channel on the amperometric response will be the subject of future work.

2.1. Numerical aspects

Laplace Eq. (15) was discretized using space centered finite difference schemes for considered cell geometries with a fixed grid size of 0.01 \times 0.01. The resulted algebraic systems were solved using the HSL 2002 library [42]. The stability of the numerical solutions were confirmed with comparisons of potential distributions with smaller grid sizes of 0.005 \times 0.005 and comparisons of cell resistance to a variable grid size (with 5825 nodes and 11,264 triangles) solution obtained previously [43]. The time dependent boundary condition (7) was integrated using a fourth order Runge–Kutta algorithm.

3. The distributed system: numerical simulation results

Fig. 2 shows the current density–voltage characteristics for three different cases. The continuous line corresponds to the point-like system and was obtained plotting \( i_F \) from Eq. (11) as a function of \( \phi_{\text{DL}} \). For low \( \phi_{\text{DL}} \) values, \( \beta \phi_{\text{DL}} \ll 1 \) and, from Eq. (11), \( i_F \approx 2 \beta \phi_{\text{DL}} \), i.e., the Faradaic current will increase linearly with \( \phi_{\text{DL}} \), while for large potential drops the current saturates, \( i_F \rightarrow 1 \). The dots correspond to a spatially distributed system, where the WE is short – the electrode length \( W = 0.1 \). (The other parameter values are \( D = 12, L = 1, \) and \( \sigma = 10 \); these parameters correspond to a fairly conducting electrolyte with a relatively close placement of WE to the reservoir). The applied voltage was fixed at different values, and the stationary value of the WE current density was determined. As it can be noticed from Fig. 2, the current–voltage characteristic for a short WE is identical to that for a point-like system and saturation is reached for applied voltages around 10. This result implies that a small electrode has uniform current distribution that represents a point-like electrode.

In contrast, when the WE is long enough (here, \( W = 8 \), triangles on the plot), the potential drop in the microchannel has significant impact; the current increases with the applied voltage only gradually and current plateau is achieved at very large applied voltage (here, over 40).

Fig. 3 illustrates the dependence of the total current as a function of the WE length \( W \), for different values of the operational parameters: dimensionless conductivity \( \sigma \), lateral position of the WE, \( L \), and applied voltage, \( V_{\text{appl}} \).

The cell geometry with the WE embedded in insulator prevents the onset of uniform electrode states [16]. However, if the WE is short enough, the potential distribution on the inner part of the WE will be approximately uniform and Eq. (13) reduces to:

\[ I_{\text{tot}} = W I_{\text{F}} \]  

(17)

i.e., total current at the WE will be proportional to the electrode length. This is visible in Fig. 3a for a cell with far WE placement \( L = 8 \). For small \( W \) values, \( I_{\text{tot}} \) increases linearly with \( W \). Fig. 4a1 shows the vertical component of the potential gradient, \( \frac{\partial \phi}{\partial y} \), in the vicinity of the WE. In these plots, lower part of the colorbar means large values of the migration current (active), while upper part means inactive (close to zero potential gradient), and the lateral extension of the cell is marked by the line at the bottom of the plot. When the WE is short \( (W = 0.1) \), the vertical potential gradient is nearly uniform at the WE.

As it is shown in Fig. 3a, beyond a critical electrode length, \( W_c \), the current saturates at a value \( I_{\text{sat}} \). The origin of this saturation is
shown in Fig. 4a2 with $W = 3.98 > W_c$. Compared to the small electrode in Fig. 4a1, the stationary state changes dramatically. The vertical component of the potential gradient at upstream edge ($3 < x < 4$) has similar values as for the uniform electrode. However, for $x < 3$ the magnitude of the gradient drops and at the upstream electrode parts the gradient (that produces the migration current) diminishes. We thus see that the electrode surface is strongly nonuniform with coexisting active (downstream) and inactive (upstream) regions.

Because of the dependence of the Faradaic current on $\phi_R$, the saturation current, $I_{sat}$, will depend on the applied voltage, $V_{appl}$. When $V_{appl}$ is decreased to 10 (Fig. 3a) the saturation current and the critical width $W_c$ decrease; the lower applied voltage is capable of maintaining smaller active region. When the electrode is placed closer to the reservoir, both the critical width and the limiting current increase (see Fig. 3b for $L = 1$); higher portion of active region can be achieved with close WE placement. Therefore, we see that by closer placement of the WE, the spatial profile of the potential distribution can be affected, perhaps because of the stronger coupling in the system due to the decrease in total solution resistance [18]. Note also that for small electrode widths the slope of total current vs. electrode width is the same (one) as expected for the mass transfer limited activity. From Fig. 3a–c, the lateral position of the WE, $L$, is kept constant, while the conductivity, $\sigma$, is decreased ten times. Consequently the cell resistance, $R_{cell}$, increases with one order of magnitude and both the saturation current and the critical length strongly decrease.

According to Christoph and Eiswirth [44], the local charge balance equation at the WE, (3), can be written using the coupling function method as:

$$\frac{\partial \phi_R}{\partial t} = -i_f(\phi_R) + \frac{V_{appl} - \phi_R}{\rho} + const \cdot \int_0^W H_0(|x-x'|) \cdot (\phi_R(x', t) - \phi_R(x, t)) \, dx'$$

(18)

where $\rho(x)$ is the local resistance felt at the position $x$ on the WE, $H_0$ is the coupling function and the constant in front of the integral depends on the electrolyte conductivity $\sigma$ and cell geometry. Taking a spatially uniform initial condition at the WE, the integral vanishes in the r.h.s. of Eq. (12), allowing the calculation of the local resistance, $\rho(x)$:

$$\rho = \lim_{\Delta x \to 0} \frac{V_{appl} - \phi_R}{H_0(0) i_f(\phi_R)}$$

(19)

Then logarithm of the local resistance $\rho$ is plotted function of the horizontal coordinate along WE (see Fig. 4b1 and b2).

For a small electrode width (Fig. 4b1) the downstream edge of the electrode has the lowest resistance. Although the vertical component of the potential gradient has a maximum value at the center of the WE, the maximum of $\rho$ is closer to the upstream edge of the WE because of the geometrical asymmetry of the cell. The values of $\rho$ decrease at the WE edges, in a similar way to that described by Newman for a disk WE embedded in insulator [16]. However, in our case, the geometry of the microcell leads to a more complex local resistance distribution.

In Fig. 4b2, we kept constant all the parameter values from Fig. 4b1 (including the lateral WE position) and the WE length, $W$, was increased to 3.98. Compared to the previous case, the stationary state changes dramatically. Due to the microchannel properties, the local resistance $\rho$ increases from low values at the downstream WE edge to extremely high values for the remaining part of the WE, including the upstream edge. These high $\rho$ values render most of the WE in an inactive state, where the values of $\frac{d^2 \phi}{dx^2}$ are very low. Thus we see that the reason for the strongly nonuniform current distribution is the quickly (exponentially) growing local resistance into the flow channel from the downstream edge.

We investigated the effect of a change in the cell geometry, from Fig. 1a, to a more symmetrical one, with 2 CEs, depicted in Fig. 1b on the features of the spatial pattern formation. The parameter values for these simulations are the same as in Fig. 3b, and $V_{appl} = 10$. Under these circumstances, curve 1 from Fig. 5a coincides with the curve from Fig. 3b, for $V_{appl} = 10$, presenting the total WE current, $I_{tot}$, as a function of the WE length, $W$.

The second curve from Fig. 5a corresponds to the same lateral distance as before (here, with $L_1 = L_2$), but for geometry depicted in Fig. 1b. As a result, the transition from linear dependence to saturation occurs for larger $W$, and the saturation current doubles its value compared to the previous case. The reason of these changes can be noticed in Fig. 5b and c. Compared to the results from Fig. 4, due to the symmetry of the cell geometry 2, the local resistance $\rho$
decreases to low values on both up and downstream edges of the WE. Thus, the active region on the WE doubles its ‘active’ surface, as it can be seen on the stationary vertical gradient distribution from Fig. 5b, where the two active edges are clearly visible.

The consequences of the edge effect are studied further by using the microcell geometry from Fig. 1c. Here, on the WE, conducting and insulating regions alternate. The parameter values are the same as in Fig. 3c, with $W = 2$, as a low conductivity value enhances the edge effect. The total WE length, $W$, as well as its lateral position, $L$, are kept constant while a number of $n_{\text{ins}}$ identical stripes of insulators, each of length 0.09, are placed on the WE with equal spacing. Assuming a uniform spatial distribution of the migration current at the WE, the total current $I_{\text{tot}}$ would linearly decrease with $n_{\text{ins}}$, reaching its zero value when the entire WE surface would be covered with insulator. This variation corresponds to the dashed line in Fig. 6a.

The values obtained from simulations are represented on the same plot by points. Due to the edge effect, the observed decrease in $I_{\text{tot}}$ when increasing $n_{\text{ins}}$ is much smaller than the previous one. In fact, the total current remains almost constant as long as the surface area of the insulators is kept less than 50% of the total surface area. As a consequence, the total current density, $i$, plotted on Fig. 6b, increases with $n_{\text{ins}}$. Some of the corresponding vertical gradient distributions in the electrolyte, in the WE area, are plotted in Fig. 7.

In Fig. 7a, there is no insulating stripe on the WE, the extension of which is marked with a line at the bottom of the figure. In this plot is visible the active region located on the downstream edge of the WE. Fig. 7b and c correspond to one and nine insulating stripes, respectively. While for $n_{\text{ins}} = 1$ the change in the migration current distribution is small compared to the case when no insulator is present, for $n_{\text{ins}} = 9$, the maximum absolute value of $\partial u/\partial y$ increases from 0.25 to 0.33, contributing to the raise of the total current density at the WE. For comparison, Fig. 7d presents the vertical gradient distribution for a continuous WE with the same active surface and lateral position as in Fig. 7c.

4. Demonstration of pattern formation with electrode arrays: numerical simulations and experiments

In order to further analyze and characterize the edge induced pattern formation in the distributed system, we perform an analysis of behavior of segmented electrode arrays in numerical simulations and experiments.

4.1. Numerical simulations

Let us consider a four-electrode array in a flow channel shown in Fig. 8a. To derive equation for the electrical coupling among the electrodes, and equivalent circuit was constructed, shown in Fig. 8b.

Each electrode is represented with a parallel combination of a capacitive ($C$) and a nonlinear Faradaic component. The four electrodes are coupled through the resistive elements of the electrolyte (four resistors $r$). The potentiostat sets circuit potential of each electrode to circuit potential $\psi$, therefore:

$$
\begin{align*}
\psi_1 &= e_1 + r(i_1 + i_2 + i_3 + i_4) \\
\psi_2 &= e_2 + r(i_2 + i_3 + i_4) \\
\psi_3 &= e_3 + r(i_3 + i_4) \\
\psi_4 &= e_4 + ri_4
\end{align*}
$$

where $e_1 \cdots e_4$ and $i_1 \cdots i_4$ are the electrode potentials and the currents of the four electrodes, respectively. The currents of the four electrodes are obtained from capacitive, Faradaic, and coupling terms:
\[
\begin{align*}
\dot{i}_1 &= c_1 a \frac{\partial e_1}{\partial x} + a j_f(e_1) + \frac{e_1 - e_2}{r} \\
\dot{i}_2 &= c_2 a \frac{\partial e_2}{\partial x} + a j_f(e_2) + \frac{e_2 - e_3}{r} \\
\dot{i}_3 &= c_3 a \frac{\partial e_3}{\partial x} + a j_f(e_3) + \frac{e_3 - e_4}{r} \\
\dot{i}_4 &= c_4 a \frac{\partial e_4}{\partial x} + a j_f(e_4) + \frac{e_4 - e_5}{r} 
\end{align*}
\]

where \(a\) is the surface area of the electrodes, and \(j_f(e)\) is the Faradaic current density of the electrodes. By combining Eqs. (20) and (21) we obtain a set of ordinary differential equations for the electrode potentials:

\[
\dot{e}_1 = \frac{1}{a} \left( j_f(e_1) + \frac{e_1 - e_2}{r} \right) \\
\dot{e}_2 = \frac{1}{a} \left( j_f(e_2) + \frac{e_2 - e_3}{r} \right) \\
\dot{e}_3 = \frac{1}{a} \left( j_f(e_3) + \frac{e_3 - e_4}{r} \right) \\
\dot{e}_4 = \frac{1}{a} \left( j_f(e_4) + \frac{e_4 - e_5}{r} \right)
\]

These equations show that the electrode segments are coupled with strength \(1/\theta\); the coupling can be enhanced by using small electrodes and strongly conducting electrolytes with small \(\theta\)-values. The ODE system has two trivial approximate solutions. When the coupling is strong (small \(\theta\)-values), the coupling terms will dominate and thus for stationary solutions (\(de_1...dt = 0\)) \(e_1 = e_2 = e_3 = e_4 = e_5\); this solution corresponds to the uniform potential distribution solution in the distributed system. When the coupling between the electrodes is weak, (large \(\theta\)-values) the coupling terms in the equations will be small, therefore the upstream electrode will be inactive exhibiting open circuit potential \(e_{oc}\): \(e_2 = e_3 = e_4 = e_5 = e_{oc}\), and the currents of these electrodes are zero \(j_f(e_{oc}) = 0\). However, for the most downstream electrode, because of the \(\frac{e_1 - e_4}{r}\) term, a high current state can be established at potential \(e_1\) that corresponds to \(\frac{e_1 - e_4}{r} = j_f(e_1)\). This solution thus corresponds to the strong edge effects seen in the distributed system where the downstream electrode behaves as if it were alone in the flow channel, while the upstream electrodes are inactive.

The effect of electrode size on the appearance of uniform and non-uniform current distribution can be demonstrated with numerical simulations using a general kinetic formula that incorporates Butler–Volmer kinetics and mass transfer limitations:
\[
\frac{1}{f_F} = \frac{1}{j_L} + \frac{1}{2j_0 \sinh(0.5\sigma f)}
\]

where \( j_L = 10 \text{ mA/cm}^2 \) is the limiting current, \( j_0 = 10^{-3} \text{ mA/cm}^2 \) is the exchange current density, \( f = nF/RT = 38.95 \text{ 1/V} \), and the symmetry factor is assumed to be 0.5.

With relatively small electrode size of \( 10^{-5} \text{ cm}^2 \), the (quasistationary) linear sweep voltammetry is shown in Fig. 8c (The coupling resistance \( r \) is set to 10 kΩ). Because of the strong coupling the currents of the electrodes are almost identical at any potential values. However, when the size of the electrodes is increased to \( 10^{-3} \text{ cm}^2 \), the edge effects become prevalent, as it can be seen in Fig. 8d: the downstream electrode reaches limiting current at about \( v = 1.0 \text{ V} \); at this circuit potential the most upstream electrode is largely inactive because it produces only 34% of the limiting current. Note also that the electrodes closer...
Each electrode segment is 0.1 mm (see Fig. 9a). The electrolyte solution is 0.01 M ferrocyanide/0.1 M potassium nitrate pumped through the 100 \( \mu \text{m} \times 200 \mu\text{m} \) microfluidic channel at flow rate \( Q = 1.5 \mu\text{L/min} \). Each electrode segment is numbered, with the corresponding color denoting the current level at \( V = 1.0 \text{V} \) (color code is same as in panel d). RE: Ag/AgCl/3 M NaCl reference electrode, CE: Pt counter electrode. (b) Optical microscope image of PDMS-based flow channel sealed over the four Pt band electrodes. Scan rate: 10 mV/s, \( Q = 1.5 \mu\text{L/min} \). Each electrode segment is plotted, denoted by the corresponding electrode segment number. (c) Colormap of current profile across each individual Pt band WE during ferrocyanide oxidation at \( V = 1.0 \text{V} \), corresponding to the scan in panel (c).

The downstream edge have monotonically larger current values along the flow channel.

### 4.2. Experiments

To demonstrate the edge effect in an experiment, the oxidation of potassium ferrocyanide was studied in a four-electrode array in a microfluidic flow cell. A schematic of the four-electrode microfluidic flow cell is shown in Fig. 9a.

The electrolyte solution is a 0.01 M ferrocyanide/0.1 M potassium nitrate solution pumped through a 100 \( \mu \text{m} \times 200 \mu\text{m} \) poly-dimethyl-siloxane linear microfluidic channel at flow rate \( Q = 1.5 \mu\text{L/min} \), which corresponds to a linear velocity of 0.125 cm/s. The electrolyte flows over the four Pt band electrodes to the reservoir, which contains the Ag/AgCl/3 M NaCl reference electrode (–35 mV vs. standard calomel electrode) and Pt wire counter electrode (All potentials are given with respect to the applied reference electrode.) The Pt electrodes were fabricated with soft lithography technique described in a previous publication [38]. The width of each Pt electrode is 0.5 mm, the distance to the reservoir containing the RE and CE is 1.1 mm, and the spacing between each electrode segment is 0.1 mm (see Fig. 9b).

The linear sweep voltammogram with four electrodes in the flow channel is shown in Fig. 9c and d. With all four electrodes in the flow channel, the more active downstream electrodes reach the limiting current at \( V = 1.0 \text{V} \); at the same time the current of the upstream electrode, \( \text{WE}_1 \), is suppressed due to the edge effect. At 1.0 V circuit potential where the downstream electrode already reached the limiting current, the most upstream electrode reached only 52% of the limiting current. Similar to the numerical predictions, the currents of the electrodes monotonically decrease with increasing the distance from the most downstream electrode.

The simulations and experiments with segmented electrodes thus demonstrate the prevalence of the pattern formation effects with the segmented electrodes. It is expected that the patterns will become dominant with large electrode sizes and weakly conducting electrolytes. Note that the numerical simulations and experiments contradict common expectation that the upstream electrode would be the most active due to the oxidation of the fresh electrolyte. In contrast, the downstream electrode was found to be the most active due to the potential distribution effects.

### 5. Conclusions

The simulation results predict the coexistence of active and inactive regions when the length of the electrode in a flow channel exceeds a critical value. Above the critical length the total current does not increase anymore with increasing the size of the electrode because of the extremely high local resistance of the upstream edge of the electrode. The model was constructed to explore the potential drop effects and to eliminate contributions from variations of concentrations along the channel due to diffusion and convection. (The model does consider a thin Nernst diffusion layer across the channel height that has impact on the current obtained from the electrode through Butler–Volmer kinetics limited by mass transfer in Eq. (11). Because of assumptions on concentration distribution, quantitative comparison could be possible only in (i) micropolarization region where the surface concentration is the same as bulk concentration, (ii) in reactions that are under kinetic control (e.g., transpassive Ni electrodeposition [43]) where the flow rate does not affect the behavior and (iii) in flow cells at large flow rates where there are no concentration variations along the flow channel. Since the interactions among reacting sites due to concentration effects were discarded, the contributions from potential drop effects can be clearly identified. For example, activity of the electrode does not decrease dramatically by incorporating equally placed insulators on the electrode; this feature may contribute to the effectiveness of multi-electrode based detectors that can enhance mass transfer to segmented electrodes [4] without inactivating the electrode surface due to the suppressed edge effects. Future studies will be directed toward considering diffusion/convection that could add further complexity and the...
possibility of non-monotonic variations of the current along the flow channel due to the counteracting potential drop and concentration shielding effects.

Conflict of Interest

The authors declare that there is no conflict of interest with any financial organization regarding the material discussed in the manuscript.

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