



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

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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 current regions with large electrode widths. The role of edge effects is clarified 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:

$$i_{\text{mig}} = i_{\text{cap}} + i_{\text{F}} \quad (1)$$

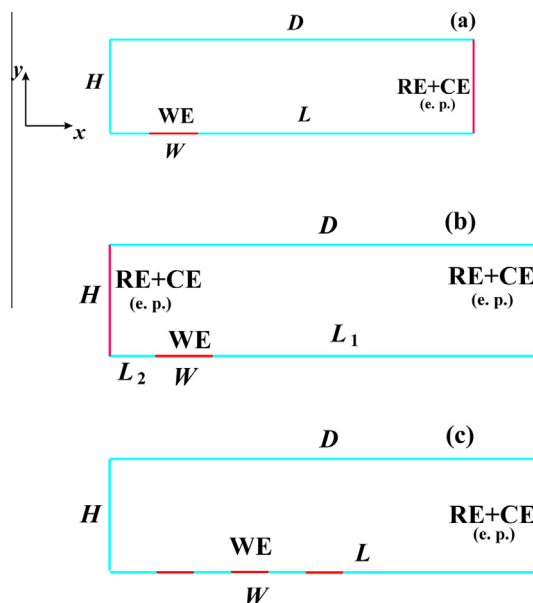


Fig. 1. Electrochemical cell geometries. (a) 3-electrode flow cell, (b) Two counter electrode (CE) cell and (c) Segmented working electrode (WE) cell. e.p. marks the equipotential plane(s).

The migration current density (i_{mig}) is the sum of capacitive (i_{cap}) and Faradaic (i_{F}) terms. As a consequence:

$$C_{\text{DL}} \frac{\partial \phi_{\text{DL}}}{\partial t} = -\sigma \frac{\partial \phi}{\partial y} \Big|_{\text{WE}} - i_{\text{F}}(\phi_{\text{DL}}) \quad (2)$$

where ϕ is the electrostatic potential in the electrolyte, t the time, y the vertical coordinate, ϕ_{DL} is the potential drop across the electric double layer in front of the WE, σ is the electrical conductivity, and C_{DL} is the double layer capacitance per unit area of the WE [40]. We define dimensionless quantities:

$$\varphi' = \frac{F}{RT} \varphi \quad (3)$$

where $F = 96,500 \text{ C/mol}$, $R = 8.314 \frac{\text{J}}{\text{mol K}}$ and T is the absolute temperature. The ϕ_{DL} is rescaled in the same manner to give ϕ'_{DL} . The dimensionless Faradaic current density is:

$$i'_{\text{F}} = \frac{i_{\text{F}}}{j_0} \quad (4)$$

where j_0 is the exchange current density. The dimensionless time is:

$$t' = \frac{Fj_0}{C_{\text{DL}}RT} t \quad (5)$$

and the dimensionless coordinates are:

$$x' = \frac{x}{L_0}; \quad y' = \frac{y}{L_0} \quad (6)$$

where $L_0 = 0.1 \text{ cm}$. Replacing Eqs. (3)–(6) in (2), we obtain the dimensionless charge balance equation:

$$\frac{\partial \phi'_{\text{DL}}}{\partial t'} = -\sigma' \frac{\partial \varphi'}{\partial y'} \Big|_{\text{WE}} - i'_{\text{F}}(\phi'_{\text{DL}}) \quad (7)$$

where the dimensionless conductivity is:

$$\sigma' = \sigma \frac{RT}{FL_0j_0} \quad (8)$$

For the simplicity of notation, we drop the prime, and all quantities referred from this point on, related to the spatially distributed system modeling, are dimensionless. In order to model the

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