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Electrochemical microreactor and gas-evolving reactions

Jiří Křišt'ál [a], Roman Kodým [b], Karel Bouzek [b,*], Vladimír Jiřičný [a]

[a] *Institute of Chemical Process Fundamentals, AS CR, Rozvojova 135, 165 02 Prague, Czech Republic*
[b] *Institute of Chemical Technology Prague, Technicka 5, 166 28 Prague, Czech Republic*

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Abstract

Present study addresses a problem of utilization of electrochemical microreactors for a system containing gas-evolving electrode reaction. Impact of the interelectrode distance reduction on the local current density distribution is treated in parallel with the influence of a single gas bubble present in the interelectrode space. Subsequently, the bubble size distribution is experimentally determined by flow visualization and image processing. The effect of bubbles on current density distribution is predicted on the base of the numerical simulation results.

Keywords: Electrochemical microreactor; Interelectrode distance; Bubble size distribution; Current density distribution

1. Introduction

Application of microstructured devices in the laboratory practice has been well known already for several decades. In recent period, great effort has been made to utilize this type of equipment also in the industrial practice [1,2]. The main advantages of the microstructured units reside in a precise control of the local values of the operational parameters and reduction of the potential hazards to the environment. An additional advantage represents a possibility to reach a high degree of conversion in the single pass through the cell. This is thanks to the interelectrode distance being of the same order of magnitude as the thickness of the Nernst diffusion layer.

Microstructured approach has been used intuitively in the design of the cells for electroorganic synthesis already since 1960s. The main reason represents extremely low conductivity of the organic solvents resulting in unacceptably high energy costs when using classical electrochemical cell arrangement. The typical representative of the construction optimized for such a type of process represents the so-called thin capillary gap cell. A typical example of a process utilizing this type of cell represents electrochemical methoxylation of 4-methylanisole developed and utilized by BASF [3]. Due to the extremely low interelectrode distance, reaching typically 0.5–1.0 mm, this cell may be nearly recognized as a microstructured one.

The distinction of the process is the hydrogen evolution reaction taking place at the cathode surface. Up to now, no study is known to the authors providing the more detailed information allowing for the better understanding of the processes taking place in the microstructured electrochemical reactor with the gas evolution.

The aim of this communication is to document the influence of the reduced interelectrode distance and the presence of the gas phase on the accuracy of the local current density control for an electrochemical cell with a segmented electrode, and to experimentally determine the size distribution of electrochemically generated bubbles in such a narrow gap cell for different electrolyte flow rates and current densities. Electrochemical microreactor proposed by Rode et al. [4] was used as an example.

2. Mathematical model

A mathematical model was developed describing the secondary local potential and current density distribution

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[*] Corresponding author. Tel.: +420 22044 4019; fax: +420 22044 4410.
E-mail address: Karel.Bouzek@vscht.cz (K. Bouzek).

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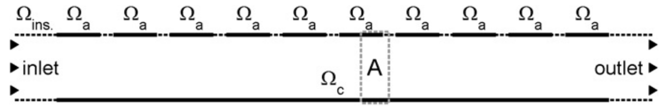

Fig. 1. The schematic sketch of the segmented cell geometry: Ω_a – anode segment; Ω_c – cathode; $\Omega_{ins.}$ – insulation; A – model domain.

(CDD) in the microstructured cell with segmented anode. Sketch of used model system is depicted in Fig. 1. The two-dimensional model consists of a rectangular channel, with segmented anode at the top and non-segmented cathode at the bottom. The segmented anode is divided into 10 sections, Ω_a, of identical length (10.0 mm), separated by insulations, Ω_{ins}, 1.0 mm thick. The cathode, Ω_c, forms the cell wall opposite to the anode.

Due to the symmetry of the cell geometry, the domain for potential field calculation can be reduced to the central part of the cell while preserving sufficient accuracy. The selected part is shown in the Fig. 1 as a rectangle labeled A, and consists of a half of the anode segment, half of the insulation segment and corresponding part of the cathode.

The potential distribution was calculated by solving the Laplace equation (Eq. (1)), where φ represents the Galvani potential and σ means the conductivity of the electrolyte being in this particular case assumed constant in the whole calculation domain. The conductivity value of 2.85 S m^{-1} was used.

$$\nabla(\sigma\nabla\varphi) = 0 \tag{1}$$

The Laplace equation was solved by the Finite Element Method (FEM) in the COMSOL Multiphysics™ environment.

The zero potential gradient in the direction normal to the surface (Eq. (2)) was used as a boundary condition for the insulation embedded between the anode segments, and at the planes of symmetry.

$$\frac{\partial\varphi}{\partial n} = 0 \tag{2}$$

The Butler–Volmer type polarization curve (Eq. (3)) was used at the electrode–electrolyte interface

$$j_n = 10^{(E-n_a)/m_a} - 10^{-(E-n_c)/m_c} \tag{3}$$

where j_n represents current density normal to the electrode surface, E the electrode potential, and m and n the Tafel slope and intercept coefficients, respectively. Subscripts a and c refer to anode and cathode, respectively. The Tafel slopes $m_a = 0.076$ V dec^{-1}, $m_c = 0.63$ V dec^{-1} and intercepts $n_a = 1.31$ V, $n_c = -0.955$ V were determined experimentally for the system under study.

3. Experimental

The geometry of the experimental electrochemical microreactor was of a rectangular channel with dimensions: length × width × depth (interelectrode distance) $150.0 \times 10 \times 0.1$ mm^3. Orientation was vertical. The microchannel walls were made of glass with embedded glassy carbon electrodes. To ensure the homogeneous mechanical and electrochemical conditions, the whole electrode surface was polished by diamond paste. The inlet was situated at the bottom and the outlet on the top of the microreactor. The reaction mixture for electrochemical alkoxylation [3] was used as a liquid phase. It consisted of 4-methylanisole (0.01 mol dm^{-3}) solution in methanol. Because of low conductivity of the solution, sodium perchlorate (0.4 mol dm^{-3}) was added as a supporting electrolyte. Gas phase (hydrogen) was generated electrochemically on the cathode directly inside the microchannel.

Flow inside the thin-gap microchannel was visualized by digital camera and images processed using Matlab Image Processing Toolbox. Bubble size distribution was evaluated based on the projected area and equivalent diameter of bubbles.

The used range of liquid velocities and current densities corresponded to the conditions suitable for the electrochemical reaction (liquid flow rates: 3×10^{-9} –5×10^{-7} m^3 s^{-1}, current densities: 100–7000 A m^{-2}). Galvanostatic regime was used. Liquid was supplied with a syringe pump and the cell outlet was open to the atmosphere.

4. Results

4.1. Local current density distribution

The homogeneity of the local CDD inside the cell characterizes its ability to work within the narrow distribution of the working electrode potential (close to the optimal one), thus ensuring the high process selectivity. This aspect becomes even more important when using segmented electrode characterized by the relatively high number of edges.

The calculated local anodic CDD inside the electrochemical cell for the interelectrode distance from 1.0 mm down to 0.1 mm is shown in Fig. 2. The reduction of the interelectrode distance had an important effect on the homogeneity of the CDD. The reason resides in the significant reduction of the space available for the widespreading of the current lines with decreasing of the interelectrode distance. In agreement with general theory, the widespreading effect became less significant with slower electrode reaction rates. From the primary CDD point of view, as the interelectrode distance was decreased from 1.0 to 0.1 mm the maximum current density at the anode-insulation interface dropped down from 10,000 to 4000 A m^{-2}. A more important parameter is the electric charge (q_a) passing through the system in the anode part with current density higher by 10% than average. The charge q_a represents an extent of the side reaction proceeding at higher anode potential, and thus potentially diminishing the selectivity. For interelectrode distance of 1.0 and 0.1 mm, the charge q_a passing through the non-homogeneous regions reached for the primary CDD 11% and 2% of the total charge, respectively.