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Research Paper

Analysis of Fully On-Chip Microfluidic Electrochemical Systems under Laminar Flow

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ABSTRACT

We demonstrated a functional on-chip multi-microelectrode array within a microfluidic channel as a fully on-chip electrochemical cell under laminar flow. A pair of working electrode (WE) and counter electrode (CE) with the small aspect ratio of width to length were parallel placed along the axial direction of flow, relying on the laminar nature of microscale flows to maintain sufficient separation of WE and CE. Thanks to the on-chip integrated reference electrode, the ohmic potential drop for the facing WE-CE configuration was experimentally examined to be negligible. Using a quasi-reversible probe, the COMSOL simulated diffusion limited voltammetric current was observed to deviate from the Levich equation when ignoring the lateral diffusion, as a result of the relatively high ratio of mass transfer to kinetics in the microfluidic chip compared to the disk electrode. The lateral diffusion was found to compensate the current distortion such that the limiting voltammetric response resembles the current predicted from the Levich equation. By considering these effects, the Koutecky-Levich method was used for the kinetic analysis of the microfluidic chips.

1. Introduction

Microfluidic electrochemical cells (μECs) have received considerable interest as a promising integrated microfluidic system which is often included in the broad scope of lab-on-chip applications [1–3]. The microfluidic devices can be used for biosensors [4,5], fuel cells [6], droplet manipulation [7], flow focusing platform [8] and miniaturized fluidic pump [9]. These devices have many benefits, such as reduced reagent and analyte consumption, shortened detection time and enhanced sensitivity. MEMS technologies enable the integration of microelectrodes into microfluidic chips and the continual advances in the miniaturization of the entire system [10,11]. However, the development of an analytical solution turns out to be not straightforward for the miniaturized systems. Such that the mass transport and the electrode response in confined systems have been extensively investigated [11–18]. Under stagnant solutions, the electrode response is modified by the spatial confinement of microchannel [18], as well as the redox cycling between paired electrodes [11]. In the presence of hydrodynamic flows, the electrode response has been extensively studied as a function of geometrical and hydrodynamic conditions [12–17]. Some transitions from thin-layer behavior to semi-infinite diffusion were established, where the voltammetric response is in accordance with Levich analysis, in spite of edge effects near channel walls. In these systems, the electrode (typically with a large aspect ratio of width to length) is stretched across the entire width of the channel. The counter electrode is placed at downstream from the working electrode (WE) [12] or in a separate channel [20], in order to prevent unwanted side-products. In addition, a reference electrode (RE) integrated in microfluidic channels enables to accurately control the potential of working electrode (WE) [21]. A platinum pseudo-RE provides a good option due to its longevity [22] and easy fabrication, as long as the user is well aware of its sensitivity to changes in the local chemical environment, e.g., by the redox species diffused out from the channel region [11].

In a previous work, we already found the interaction between closely-spaced WE-CE pairs induced the so-called redox cycling, as a result of the overlap of their diffusion regions under stagnant conditions [11]. For microfluidic chips under laminar flow, Levich equation well models the semi-infinite diffusion on the single band electrode with a large aspect ratio of width to length, for edge effects being ignoring. In this work, a pair of WE-CE with the small aspect ratio was parallel placed within a microfluidic chip, relying

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on the laminar flow to minimize the chemical coupling. This parallel electrode configuration enables to apply multi-streams on WE and CE within a single fluidic channel for the construction of devices in various fields, e.g., microfluidic fuel cells. Special attention will be paid to the understanding of the effects of mass transport on the voltammetric response at this particular electrode configuration. The quasi-reversible Fe^{3+}/Fe^{2+} redox couple was chosen as a sensitive indicator of the change in mass transport. The flow was pressure-driven and strictly laminar regime (characterized by low Reynolds numbers $Re < 1$). The oxidation and reduction kinetics at the microelectrode were modeled using COMSOL to validate the experimental results. Next to simulation of the voltammetric responses, it provides valuable insights into the build-up of the concentration profiles.

2. Experimental

2.1. Cell fabrication

The microfluidic chip consists of a multi-microelectrode array and a microfluidic working channel (Fig. 1a). The fabrication procedure has been published previously [11]. Briefly, the microfluidic channel is fabricated in poly(dimethoxy)silane (PDMS) by using the soft-lithography technique. The microfluidic channel had a height of 20 μm and width of 200 μm for the main channel and 100 μm for the four inlet/outlet branches. To produce the mold, SU-8 2015 photoresist was patterned on a clean gallium arsenide wafer by using the standard photolithography technique. Then the liquid PDMS prepolymer (Sylgard 184, Dow Corning) was mixed at the recommended 1:10 ratio of crosslinking to base polymer, degassed, cast against the positive relief. After curing at room temperature for 24 hours, the PDMS replica was peeled from the mold and thus a PDMS microchannel was generated. The Pt microelectrode array was fabricated using standard electron beam evaporation and lift-off techniques on a 4-inch silicon wafer according to the layout in Fig. 1c. Next, a 600 nm SiO_2 layer was deposited over the metal stack using chemical vapor deposition. Then the SiO_2 layer was cleared by selective etching with a buffered hydrofluoric acid (BHF); the remaining SiO_2 layer will be formed a permanent bonding with PDMS in the following steps. After the BHF etching, the geometrical area of each electrode exposed to electrolytes is designed to be $850 \times 40\ \mu m^2$, the gap between the two electrode columns is 100 μm. The WE/CE dimensions are $850 \times 40\ \mu m^2$, the gap between the two electrode columns is 100 μm, and the vertical pitch is 50 μm.

After dicing of wafer, a single die (8 mm × 8 mm) was attached onto the cavity of a ceramic dual in-line package (CERDIP); gold bond wires electrically connected the peripheral Pt die pads to the copper lead frame of the package; the bonding wires were encapsulated in PDMS Sylgard 3140 (3145 RTV, Dow Corning) (schematically shown in Fig. 1b). Afterwards, a PDMS microchannel was bonded to a chip by the covalent Si-O-Si bonds between the PDMS and the SiO_2 layer of the chips activated by means of oxygen plasma, making microfluidic chips with tight sealing. Then this packaged device was soldered onto a printed circuit board (PCB). Afterwards, polyimide tubing (OD: 0.236 mm,

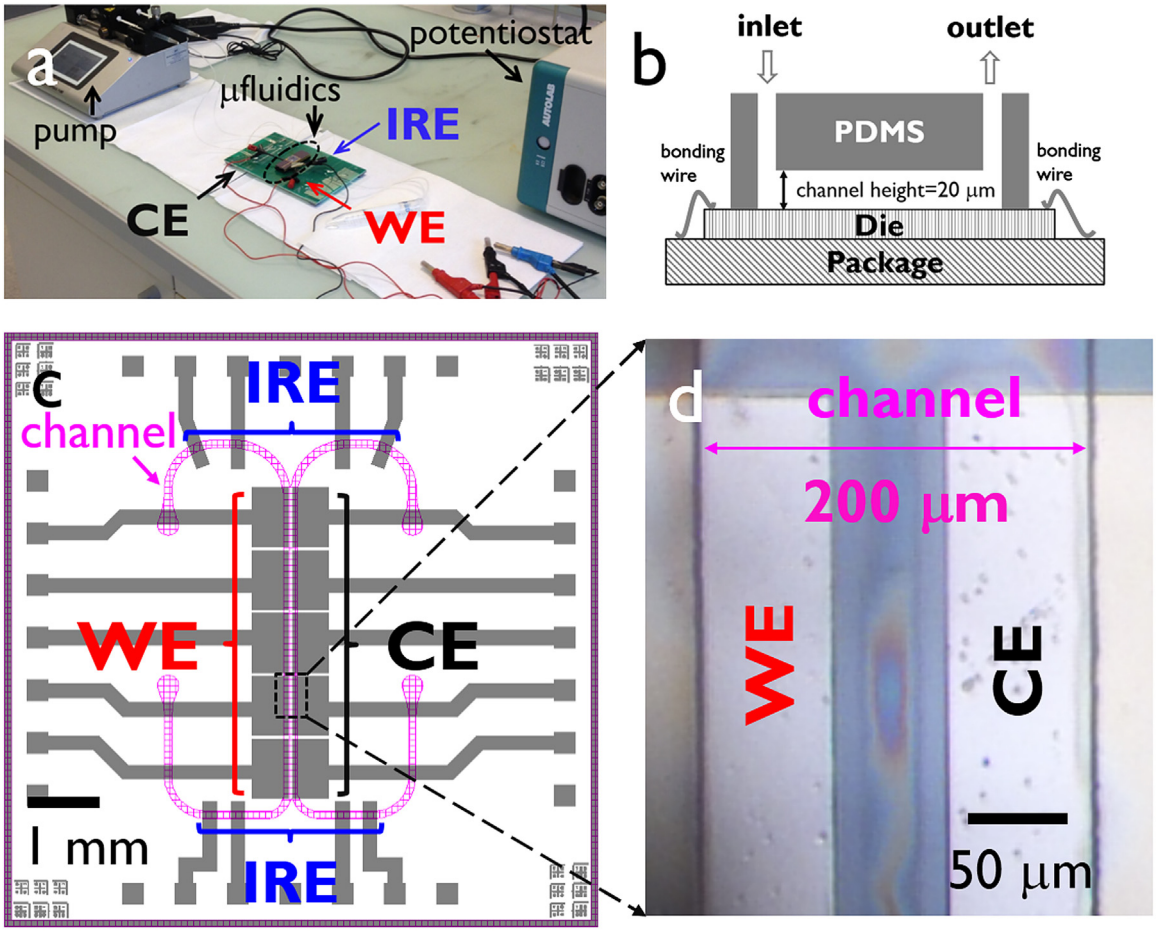

Fig. 1. (a) The measurement set-up for microfluidic electrochemical chips; (b) schematic cross-section of the device; (c) the layout of the multi-microelectrode array includes 5 electrode pairs (used as working electrode (WE) and counter electrode (CE)) and 8 electrodes located at the inlet and outlet (used as internal reference electrode (IRE)); (d) optical microscopic image of the region indicated in (c).