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Research paper

Characterization of slug flow of two aqueous phases by electrochemical impedance spectroscopy in a fluidic chip

Petr Polezhaev[a], Zdeněk Slouka[a,b], Jiří Lindner[a], Michal Přibyl[a,b,*]

[a] Department of Chemical Engineering, University of Chemistry and Technology, Prague, Technická 5, 166 28, Praha 6, Czech Republic
[b] New Technologies - Research Centre, University of West Bohemia, Univerzitní 8, 306 14 Plzeň, Czech Republic

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ABSTRACT

We adopted a method of electrochemical impedance spectroscopy (EIS) for the characterization of slug flow of two immiscible aqueous phases in a flow channel. The impedance response (both magnitude and phase shift) of the two-phase system is measured as a function of time at selected frequencies. The presence of slugs or a continuous phase at a pair of parallel facing electrodes can be determined under various signal frequencies mainly due to a significant difference in the electrolytic conductivities of both phases. We found that EIS data are sensitive to the total flowrate at low signal frequencies. Further, we suggested an equivalent electric circuit that takes into account all capacitances and resistances emerging between the two sensing electrodes. We determined the values of these elements by fitting a theoretical model to the experimental data. The obtained values of resistances were used to estimate the thicknesses of the wall film of the continuous phase that is present between a slug of the dispersed fluid and a channel wall. The estimates given by the EIS method were successfully verified by microscopic observation and an available hydrodynamic correlation. The developed EIS method represents an original approach to the estimation of wall film thickness applicable to the efficient control of various droplet-based microfluidic devices such as microreactors and microextractors working with aqueous two-phase systems.

1. Introduction

We report on the development of an electrochemical impedance method for the characterization of two-phase slug-flow formed by two immiscible aqueous phases in small fluidic channels.

Slug flow microfluidics utilizes the advantages of enhanced mixing, reduced transport resistances, suppressed Taylor dispersion as well as large interfacial area to substantially increase the performance of reaction and separation processes in microreactors and microseparators [1,2]. Slug flow is typically formed by two immiscible liquids when droplets of one of the liquids move in series within the other liquid through a capillary or microchannel. The first liquid creates a dispersed phase and the other one wetting the channel walls the continuous phase. There is a thin film of the continuous phase between a droplet and wall. Recent applications of microfluidic systems with slug flow or other type of multiphase flow include nanoparticle and microparticle synthesis [3,4], heterogeneous catalysis, point-of-care diagnostics or biochemical synthesis of fine chemicals [5]. Many publications address the chemical engineering aspects of reactions and separations performed in slug flow and microflow extraction [4,6–9].

Types of slug flows can be differentiated according to the phase arrangement. Slug flows formed in systems of gas-liquid, liquid-liquid, gas-(liquid-liquid) etc. are recognized [10]. One type of the two-phase systems relies on the use of two immiscible aqueous liquids. These systems are referred to as aqueous two phase systems abbreviated as ATPSs. Aqueous solutions, in general, provide mild environment for biochemical and biological compounds and therefore ATPSs have become a powerful tool for the separation of biomaterials, including plant and animal cells, microorganisms, fungi, viruses, chloroplasts, mitochondria, membrane vesicles, proteins or nucleic acids [11]. ATPSs consist of two phases formed by dissolving either two incompatible polymers, such as polyethylene glycol (PEG) and dextran, or one polymer and an inorganic salt [11]. One phase (top phase) is predominantly rich of one component (typically PEG) and the second phase (bottom phase) is enriched by either dextran or the inorganic salt. If properly chosen, ATPSs can be used for selective extraction of biochemical products [12].

To effectively employ the advantageous characteristics of two-phase slug flow for extraction of biochemical products in using ATPSs, we need some tools for the flow diagnostics and characterization. For example, the detection of the presence of one or the other phase or analysis of certain phase composition are typically required in slug-flow

* Corresponding author at: Department of Chemical Engineering, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic.
E-mail addresses: petr.polezhaev@vscht.cz (P. Polezhaev), Zdenek.Slouka@vscht.cz (Z. Slouka), Jiri.Lindner@vscht.cz (J. Lindner), pribylm@vscht.cz (M. Přibyl).

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microreactors. There are numerous characterization methods available for the droplet microfluidics. These methods include imaging-based droplet analysis (bright field and fluorescence microscopy, FTIR and electron microscopy), laser based molecular spectroscopy, MS, NMR and some electrochemical methods [13]. Electrochemical methods, in most cases, rely on either measurement of the impedance characteristics of two-phase flow by electrochemical impedance spectroscopy (EIS) [14,15] or on chronamperometric analysis of an electroactive compound in a carrier (continuous) phase [13]. The electrochemical characterization represents a suitable choice for microfluidic systems because of low cost, small size, high sensitivity, high speed, and the possibility of simple integration of electronic structures into a chip.

Electric impedance methods are particularly suitable for the characterization of single and multiphase flows as they can sense different resistance and capacitance elements distributed in a flow channels under different signal frequencies. For example, Seleghim and Hervieu [16] used electrodes regularly disposed around the circumference of a pipe (i.d. 60 mm) for the impedance characterization of air-water flow. They were able to visualize stratified, intermittent and bubbly flows. Wang et al. [17] developed a ring sensor for electric impedance tomography to visualize oil/gas/water multiphase systems and foams. Instead of a set of electrodes placed inside a pipe, they suggested single conductive ring with electric contacts on the outer surface of the ring. Ji et al. [18] developed a contactless impedance sensor for the measurement of the void fraction in liquid-gas two-phase flow. The sensor exploits a pair of concave electrodes placed on the outer diameter of an insulating pipe. Influences of coupling capacitances (insulating pipe) were overcome by the impedance elimination principle. An electrode impedance sensor [19] was used for flow rate measurement in a pipe (i.d. 60 mm). The changes of impedance caused by flow variations were significant especially at low flow rates.

Electric impedance and related techniques gradually found their use in slug-flow microfluidics. They can not only discriminate the presence of the discrete or continuous phase on the impedance electrochemical sensor, but theoretically they also allow for the determination of the individual resistance and capacitance elements representing the contributions of bulk of the phases and their interfaces to the overall impedance signal. A combination of infrared light sensors and simple impedance sensors was used for velocity and slug length measurement in a capillary with water-organic solvent-gas three-phase flow [20]. Impedance measurement of the void fraction was carried out in a microchannel with a square cross-section [21,22]. A pair of facing stainless steel microelectrodes was used. Temporal analysis of impedance signal allowed for the determination of flow regime and void fraction [22]. A microfluidic chip with integrated capacitive sensors was designed for the detection of aqueous droplets in a water-oil two phase system [23] and the estimation of droplet size and speed [24]. Single droplet characterization based on the monitoring of electrolyte resistance was carried out in a microfluidic device with coplanar microelectrodes [25]. Two-phase system consisting of an aqueous phase and a phase of vegetable oil was used in this case. Velocities and dimensions of oil droplets were estimated with the accuracy of a few percent for droplets with the size ranging from 60 to 100 μm. An electrochemical impedance sensor incorporated in a microfluidic device was also used for the detection of aqueous droplets in a water-in-oil two phase system [26]. Impedance spectroscopy allowed for an efficient and contactless determination of the electric conductivity of aqueous droplets dispersed in an oil phase [27]. Mavrogiannis et al. [28] developed an EIS sensor incorporated into a microfluidic device and successfully monitored position of the interface in a two-phase system with parallel flow. They used a set of coplanar interdigitated electrodes.

To our best knowledge, we test, for the first time, the use of EIS and the equivalent circuit approach for the characterization of slug flow formed in an ATPS. Similar to the methodology reported in Ref. [21], we fabricated a pair of contact facing electrodes to measure corresponding impedance spectra of the two-phase flow. Our EIS measurement allows not only for droplet counting and characterization (size and velocity) [24,25], but also for the efficient determination of the film thickness δ formed by the continuous phase between the droplets and microchannel walls. For that reason, we have developed an original equivalent circuit model that contains ideal capacitor and resistor elements representing electric resistances of both conductive phases, resistances and capacitances of all interfaces, and takes into account the resistance of the wall film that behaves as a shortcut for electric current. Finally, we show that the estimates of the film thickness given by EIS are in good agreement with the results of optical measurement and the predictions calculated from a chemical engineering correlation.

2. Experimental

2.1. Materials and chemicals

Materials listed below were used for the microchip fabrication and EIS characterization: 500 μm copper plates (Metal Sheets, UK), 2 mm transparent plexiglass (PMMA) plates (Zenit, CZ), sodium hydroxide p.a., potassium chloride p.a., sodium sulphate p.a., hydrogen peroxide 30%, hydrochloric acid 35%, isopropyl alcohol, acetone (PENTA, CZ), PEG-4000 liquid form, Congo red (Sigma Aldrich), Acrifix 192 (UV curable acrylic glue, Evonik), photoresist developer ma-D 331, positive photoresist ma-P 1275 (Microresist Technology), bath for electroplating (Auruna 553 (Umicore Galvanotechnik), potassium peroxodisulphate (Carl Roth).

The following devices were used: CNC micromilling machine GV21 (Gravos), Reference 600+ Potentiostat (Gamry), camera PL-D775CU (PixeLINK), microscope BX51WI (Olympus), dual syringe pump Gemini 88 (KD Scientific), ultrasonic cleaner U3STH (Ecoson), spin coater (Laurell), drying oven (Heraeus), hydraulic 20 tons Press (OMCN, Italy), UV exposure unit and electroplating bath.

2.2. Microchip fabrication

A PMMA chip (Fig. 1) contains a single fluidic channel with the length and cross-section of 5 cm and 1 × 1 mm^2, respectively, and a set of microelectrode pairs. The microelectrodes of each pair are oriented parallel face to face.

In the first step, the microelectrode array was fabricated using the method of sacrificed substrate that combines photolithography, galvanic deposition of gold and wet etching [29]. A set of parallel facing gold microelectrodes with the cross-section of 100 μm × 8 μm was produced. The sacrificed substrate method provides microelectrodes fully embedded into the UV cured Acrifix 192 (PMMA) substrate.

The obtained plate containing a gold microelectrode array was covered with a 500 μm thick layer of Acrifix and cured by UV light. This layer provides fixation of the array, which is necessary for the next step. The fluidic channel (50 mm × 1 mm × 1 mm) was milled in the center of the PMMA plate with the embedded and covered microelectrodes. It resulted in the formation of a set of parallel facing microelectrodes located in the middle of height of the fluidic channel. The interfacial area 100 μm × 8 μm between a microelectrode and electrolyte is thus well defined. Parallel facing microelectrodes allow for the efficient EIS characterization because the applied electric field has more homogeneous character than in the case of common coplanar arrangements [30]. Thus, the measured electrochemical characteristics are more sensitive to the presence of a slug of a dispersed phase.

Finally, the plate with the microchannel was sealed with a PMMA counter plate by the solvent assisted thermal bonding [29]. Microchannel inlets and outlets were then equipped with Tygon tubing. We note that the used fabrication technique [29] allows for the fabrication of even smaller microelectrodes (10 μm × 8 μm). Dimensions of the fluidic channel are limited only by the resolution of a used CNC machine.