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Thin-film electrode based droplet detection for microfluidic systems

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ABSTRACT

We report on a droplet-producing microfluidic system with electrical impedance-based detection. The microfluidic devices are made of polydimethylsiloxane (PDMS) and glass with thin film electrodes connected to an impedance-monitoring circuit. Immiscible fluids containing the hydrophobic and hydrophilic phases are injected with syringe pumps and spontaneously break into water-in-oil droplet trains. When a droplet passes between a pair of electrodes in a medium having different electrical conductivity, the resulting impedance change signals the presence of the particle for closed-loop feedback during processing. The circuit produces a digital pulse for input into a computer control system. The droplet detector allows estimation of a droplet's arrival time at the microfluidic chip outlet for dispensing applications. Droplet detection is required in applications that count, sort, and direct microfluidic droplets. Because of their low cost and simplicity, microelectrode-based droplet detection techniques should find applications in digital microfluidics and in three-dimensional printing technology for rapid prototyping and biotechnology.

1. Introduction

Droplet-based microfluidics has received increasing attention for applications that involve dispensing, isolating, and monitoring small amounts of reactants. Not only can the technology generate highly uniform droplets and particles using simple hardware [1], but it is also possible to perform chemical reactions and biosensing within the droplets [2,3]. The chief advantage of mixing liquids inside droplets is the lack of dispersion that occurs in continuous flow [4]. Because droplet diameter can depend on the presence of surfactants and the interfacial tension between immiscible fluids, droplet size measurement has been applied as an in-line interfacial tension sensor [5,6]. Properties like the droplet's shape, composition, volume, and location are also critical for applications in liquid dispensing and droplet-based printing. Solidified droplets are a possible route to "voxels" needed for three-dimensional (3D) printing of solid particles [7]. For printing applications, a real-time detection method is desired that offers feedback on droplet quality and arrival time so that a digital control system may coordinate movements of a stage for dispensing individual particles in registration with a substrate. Simple droplet detection systems that can be incorporated cheaply into a disposable print cartridge are likely to be commercially significant.

Detection methods originally developed for cells and particles are usually applicable to droplets. Sensing mechanisms include optical detection [8], capacitive detection [9], and impedance detection [10]. We use droplet-induced changes in electrical impedance at thin-film electrodes to detect the passage of droplets.

Optical droplet detection has been carried out in a microfluidic channel using laser light scattering and detection at a pair of optical fibers positioned across the channel [8]. This system requires a significantly more complex setup than the work here, but has advantages in performing other optics-based interrogation of the chemical environment within droplets carrying fluorescent dyes.

Because aqueous droplets generally have a different dielectric constant than the surrounding oil, capacitive detection has also been successfully demonstrated [9]. This involved building a liquid-filled capacitor from a pair of thick electrodes at the channel sidewalls, and monitoring the capacitance for changes as droplets entered and exited the electrode sandwich. While this sensitive device was able to detect changes in composition of the aqueous droplets, fabrication of the thick-film electrodes required many more steps than the method described here. The simpler thin-film electrodes are not as sensitive to droplet composition, but they are able to perform the basic droplet-counting function required by printing and dispensing applications.

2. Droplet formation and detection technique

Our system contains a T-junction microchannel system for spontaneous droplet formation in channels of 100–200 micron width and 100 micron height, and a series of three thin film electrodes located on the floor of the channel downstream from the T-junction,

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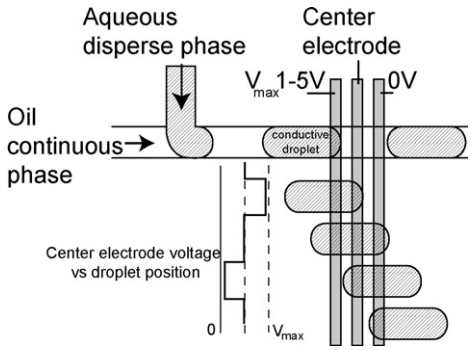

Fig. 1. Schematic of droplet formation at a T-junction and interaction of droplets with electrodes downstream. Voltages at the two outer electrodes are fixed, while voltage at the center electrode is monitored to detect droplets. The graph is a schematic of voltage at the center electrode as a droplet progresses across the three electrodes, as shown to the right of the plot.

schematically shown in Fig. 1. Electrode widths and spacings are 100 microns.

The two inlets to the T-junction are connected to syringe pumps, in which one is the oil or carrying liquid (continuous phase) and the other is the aqueous droplet liquid (dispersed phase). Droplet size and shape are determined by flow rates and channel geometry, so for printing applications it is important to understand the effect of these parameters. T-junction droplet formation spans two different regimes: the "dripping regime", which produces spherical droplets, or the "squeezing regime", which produces long plug-like droplets. This work was carried out in the plug-like "squeezing regime".

2.1. Dripping regime

When the dispersed-phase inlet channel is narrow, or when flow rates are high, small spherical droplets result. In this "dripping regime", the shear forces generated by the continuous phase, and the applied pressure from the pumps, make the head of the dispersed phase protrude into the main channel until the neck of the dispersed phase becomes thin and breaks the stream into a droplet. By altering the fluid flow rates, the channel geometry, or by changing the relative viscosity between the two phases, the frequency and size of the droplets can be varied. The diameter of the droplets in the dripping regime is determined mainly by the interfacial tension and the flow rate [8].

2.2. Squeezing regime

In contrast, when shear forces are relatively small, as seen in this work, the T-junction produces long "plugs" instead of small spherical droplets, and the droplet size is no longer determined by the interfacial tension.

The capillary number (Ca) is useful in predicting what type of droplets (if any) will be produced by a given system. It is the ratio of viscous drag forces to interfacial tension forces:

$$\mathrm{Ca} = \frac{\mu U}{\sigma} \quad (1)$$

where μ is the viscosity, U is the droplet velocity, and σ is the interfacial or surface tension between the droplet and the continuous phase. When liquids of different viscosity are used, the higher-viscosity liquid dominates the behavior of the system, and should be used in calculating Ca. A T-junction with equal inlet widths and a square channel cross section will form long plug-like droplets at Ca less than ~0.01, entering the "squeezing regime" [11]. At higher Ca, the aforementioned "dripping regime" starts: shear forces increase in importance and produce small spherical droplets (diameter smaller than the channel dimensions). For $\mathrm{Ca} \gg 1$, shear forces dominate and droplets are no longer produced; instead there are co-flowing laminar streams.

In this work, using an interfacial tension of 52 mN/m for water/hexadecane, a viscosity of 3.3 mPa s [12] (for the hexadecane continuous phase) and a flow velocity of 25 mm/s (for the fastest-moving droplets in the experiments), the maximum capillary number is 0.0016, well into the $\mathrm{Ca} < 0.01$ "squeezing" regime. Hence the droplets are plug-like and are able to span a pair of electrodes on the floor of the channel.

2.3. Droplet detection

After the plug-like droplets are formed and steady, they flow over detection electrodes approximately 5 mm downstream from the T-junction. The electrodes are monitored for changes in inter-electrode resistance due to contact with a conductive droplet. A three-electrode design allows comparison of the signal between adjacent electrode pairs; this differential mode removes background conductivity drift that occurs from temperature changes and enables amplification of the conductivity signal using a comparator circuit.

3. Device fabrication and experimental setup

3.1. Microfluidic chip fabrication

Droplet microreactors shown in Fig. 2 were fabricated in PDMS elastomer (Sylgard 184, Dow Corning) using standard soft lithography [13] on a 100 micron thick mold of SU-8 negative photoresist (MicroChem Inc).

A PDMS mold was prepared by mixing PDMS prepolymer and curing agent in a 10:1 ratio and then degassing in vacuum to remove bubbles. The degassed PDMS mixture was then distributed onto the silicon master and cured at 60 °C in an oven. After curing and demolding, holes were punched in the PDMS replica to add the fluid inlet lines.

Thin film electrodes, with widths and spacings of 100 μm, were patterned on a glass slide using photolithography. A 25–50 nm thick titanium adhesion layer was applied in a sputter deposition system followed by a 100–150 nm thick layer of platinum. Next, a perfluorodecyltrichlorosilane (FDTS) hydrophobic coating was deposited on the electrode slide using liquid precursors in a MVD100 vapor deposition system (Applied Micro Structures). The Molecular Vapor Deposition (MVD) method used has been described elsewhere [14]. The FDTS monolayer selectively adheres to the glass, producing a hydrophobic surface without significantly blocking electrical contact between electrodes and the solution. Surface cleaning and hydroxylation of the replica and a FDTS coated glass substrate were performed in an air atmosphere using a RF plasma cleaner (Harrick Plasma, 30 W, 100 mTorr) for 20 s. Substrates were then brought into contact to irreversibly bond to each other, forming a microchannel with all four walls being hydrophobic, which is necessary for maintaining aqueous droplets in an oil-based continuous phase. Wires were attached to the electrode bond pads using

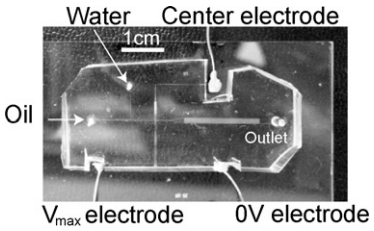

Fig. 2. Photograph of a device with T-junction and triple electrodes. Flow is from left to right.