An On-Chip Liquid Metal Plug Generator

Sagar Bhagwat, Ciarán O’Brien, Ahmed Hamza, Shatakshi Sharma, Christof Rein, Mario Sanjaya, Dorothea Helmer, Frederik Kotz-Helmer, Pegah Pezeshkpour,* and Bastian E. Rapp

Department of Microsystems Engineering (IMTEK)
University of Freiburg
Georges-Köhler-Allee 103, 79110 Freiburg, Germany
E-mail: pegah.pezeshkpour@neptunlab.org

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Gallium-based liquid metal nonspherical droplets (plugs) have seen increasing demand recently mainly because their high aspect ratios make them beneficial for a wide range of applications, including microelectromechanical systems (MEMS), microfluidics, sensor technology, radio-frequency devices, actuators, and switches. However, reproducibility of the generation of such plugs, as well as precise control over their size, is yet challenging. In this work, a simple on-chip liquid metal plug generator using a commercially available 3D microprinter is presented and the plug generator in poly(dimethylsiloxane) is replicated via soft lithography. Liquid metal plugs are generated via a combination of electrochemical oxidation, design of well-defined constrictions based on Laplace pressure, and the application of modulated voltage control signals. It is shown that plugs of various aspect ratios can be generated reproducibly for channel widths of 0.5, 0.8, and 1.5 mm with constriction widths of 0.1 mm at 6 V. Laplace-pressure-controlled plugs in constricted channels are compared to modulated-voltage-generated plugs in straight channels showing that this technique provides significantly enhanced reproducibility and control over the size and spacing between the plugs. This work paves the way to sub-millimeter liquid metal plugs generated directly on-chip for on-demand MEMS and microfluidic applications.

1. Introduction

Francium (Fr), cesium (Cs), rubidium (Rb), mercury (Hg), and gallium (Ga) are classified as so-called liquid metals as their melting points are lower than or close to room temperature. Among these liquid metals, francium is extremely radioactive, cesium and rubidium are reactive, and mercury is toxic, thus gallium and its alloys gathered increased attention in recent years.[1,2] Although gallium has a melting point of 29.8 °C, it can be alloyed with other metals like indium (In) and tin (Sn) to further lower its melting point. In the last decade, particular focus has been on eutectic gallium indium (EGaIn; 75 wt% Ga, 25 wt% In; melting point: 14.2 °C) and Galinstan (68.5 wt% Ga, 21 wt% In, 10 wt% Sn; melting point: 13.2 °C).[3] These gallium-based liquid metal alloys have the properties of metals including high electrical conductivity (around $3.4 \times 10^6$ S m$^{-1}$, about 17 times lower than copper), low viscosity (about twice the viscosity of water), high surface tension (around 600–700 mN m$^{-1}$), negligible vapor pressures ($<10^{-6}$ Pa), and offer ease of bench-top processing without the need to work in a fume hood.[4] Galinstan and EGaIn have been of interest particularly in microelectromechanical systems and microfluidics, with applications including stretchable electronics,[5,6] reconfigurable antennas,[7,8] soft robotics and wearables,[9–11] microfluidic electrodes,[12,13] liquid-metal embedded elastomers,[14] and droplet generators.[15,16] Due to intrinsic challenges like injecting liquid metals inside microchannels owing to their high surface tension, a droplet generator allowing reproducible generation of droplet of configurable size is still challenging. Such a droplet generator would pave the way to nano- and microdroplets for applications like actuators,[17,18] pumps,[19,20] tactile devices,[21]
microswitches,\textsuperscript{[22,23]} controllable structures,\textsuperscript{[24]} and robots,\textsuperscript{[25,26]} Galinstan droplets are typically stable owing to a nanometer-thin oxide layer on the surface covering the liquid metal. While this oxide skin is useful in droplet formation, other applications like actuators and pumps call for the removal of this skin which can be ruptured chemically via acidic or basic solutions\textsuperscript{[27]} as well as mechanically\textsuperscript{[7,28]} Most of the liquid metal nano- and microdroplet generators reported in literature are based on flow-focusing,\textsuperscript{[15]} sonication,\textsuperscript{[29]} syringes,\textsuperscript{[30,31]} and molding.\textsuperscript{[32]} A review by Zhu et al. highlights the recent work in the field of liquid metal droplets and emphasizes the advantages and disadvantages of the oxide skin in terms of surface modification and droplet stability.\textsuperscript{[14]} While most of these droplet generators result in spherical nano-/microdroplets, Hutter et al. have demonstrated nonspherical liquid metal droplets generated via a flow-focusing device by implementing microchannels (80 and 160 µm) resulting in nonspherical or rod-shape droplets with an aspect ratio of two.\textsuperscript{[34]} These plugs are generated in aqueous solutions in the presence of a surfactant to retain their individuality or in acidified silicone oil, which restricts the actuation capability of these plugs. Nonspherical or plug-shape liquid metals are mostly used in radio frequency applications such as reconfigurable antennas\textsuperscript{[35–37]} and multifunctional antenna capable of wideband frequency tuning, dual band operations, and polarization reconfiguration.\textsuperscript{[18]} In these aforementioned applications, the nonspherical and rod-shape plugs have been generated via flow-focusing devices or by manually injecting the liquid metal into narrow channels, which retain the aspect ratio of the plug. A simple on-chip device which can directly generate multiple liquid metal plugs of any given size in an electrolyte would allow for the ease of plug generation along with the capability to actuate these plugs as and when necessary. However, for an on-chip plug generator to function optimally, it is necessary to find an effective technique to inject liquid metals into microchannels.

The Dickey group reported a vacuum filling and sonication technique to inject liquid metals into microchannels.\textsuperscript{[19]} Vacuum filling involves adding a drop of EGaln at the inlet of a microchannel made from a gas-permeable material like polydimethylsiloxane (PDMS) while placing the setup into a vacuum chamber. The liquid metal will then fill the channel even if the channel geometry is complex. Unfortunately, this technique is only applicable for closed channels and is not suitable for the generation of liquid metal plugs in a continuous fashion, i.e., a plug generator.\textsuperscript{[19]} A second method proposed by the same group uses sonication of liquid metal and a solvent (e.g., ethanol), resulting in a saturated suspension which can be injected into microchannels.\textsuperscript{[7]} However, the used solvent evaporates and leaves behind liquid metal particles whose oxide skin must be reduced with an electrolyte. In general, direct injection of liquid metal into microchannels of a few micrometers diameter is challenging as the pressure required increases substantially with decreasing channel widths (40 kPa for 100 µm, ~89 kPa for 20 µm).\textsuperscript{[10]} Hence, an alternative technique which enables pristine liquid metal injection inside microchannels which overcomes the previously mentioned challenges was sought for.

Gough et al. reported such a technique demonstrating that by imposing a quasi-planar geometry, the liquid metal is forced to be in a state of high surface tension, which makes it sensitive to a modest change under applied voltage.\textsuperscript{[14]} This planar design enables the liquid metal to easily fill microchannels via electrocapillary or electrochemical actuation, which makes this setup very convenient for an on-chip plug generator. In general, electrochemical oxidation is a very potent technique to drive liquid metal movement. It is based on the application of an oxidative potential on the liquid metal, resulting in a sharp decrease in its surface tension owing to the formation of an oxide skin allowing it to rapidly fill microchannels.\textsuperscript{[42–44]} While electrochemical oxidation enables the liquid metal to rapidly fill microchannels, it would be necessary to trap the liquid metal by designing constrictions since on switching off the oxidative potential, the liquid metal will retract back to its source without generating any plugs. These constrictions could be compared to Laplace barriers, as liquid metal plugs will coalesce owing to inherent Laplace pressure imbalance inside the microchannels.\textsuperscript{[45]} Cumby et al. showed that by designing trenches which exerted a lower Laplace pressure than the channels, the liquid metal selectively de-wets inside the trenches on release of vacuum.\textsuperscript{[46]}

In this work, we show a simple way for generating Galinstan plugs of various aspect ratios on a fabricated plug generator by tuning the channel dimensions at the fabrication stage (Figure 1). For this, we adapted a quasi-planar design in conjunction with an electrochemical oxidation technique to generate Galinstan plugs of defined sizes in constricted and straight microchannels. We explore the concept of electrochemical oxidation to locally “switch” Galinstan into a wetting state by applying an oxidative potential across a channel.

![Figure 1](image-url)
prefilled with 1 m NaOH. In the case of a straight channel, Galinstan would initially wet the entire channel length, but de-wet/retract on switching off the potential (see Figure 1a). We study the effect of modulated voltages for generating Galinstan plugs in straight channels, which can coalesce to form larger plugs (Figure 1b). We show that the generated Galinstan plugs can retain their individuality due to the presence of carefully designed constrictions (Figure 1c). We investigate the importance of having accurate constriction dimensions, which define the coalescing or noncoalescing of the generated plugs. We finally compare the effect of direct oxidation in constricted channels and modulated voltage in straight channels and show that the former leads to reproducible plugs defined by the geometry, whereas the latter results in nonreproducible Galinstan plugs of varying dimensions.

2. Effect of Laplace Pressure on Plug Generation in Constricted Channels

We fabricated a plug generator with constricted channels and chambers as shown in Figure 2a,b. The inlet consists of an inner reservoir of (R1) 0.2 mm height and outer reservoir (R2) of 0.1 mm height but much larger circumferences (see Drawing S1 and S2 in the Supporting information). This planar design forces Galinstan to be in a state of high surface-tension which makes it easier to wet channels and generate plugs inside the chambers. R1 is specifically used to inject and store Galinstan whereas 1 m NaOH injected in R2 ensures that the Galinstan in R1 is free of oxide skin. An oxidative potential (+6 V) is applied directly to an electrode inserted into R1, which electrochemically wets Galinstan and forces it to spread inside the channels and chambers owing to a decrease in surface tension of Galinstan. We refer to the overall component from inlet to outlet as “channel,” whereas a “chamber” is specifically designed to generate plugs. The height of the channels ($H_{CH}$) and chambers ($H_{CT}$) is identical (i.e., 0.2 mm). The speed of wetting depends on the applied voltage. The higher the voltage, the faster the generation of the oxide skin which hinders further flow. In our case, we found that 6 V DC allows optimal wetting without any mechanical hindrances across the length of the channel. We believe that the electrochemical force is the dominant mechanism driving the flow of Galinstan inside the channels by reducing the interfacial tension. Khan et al. hypothesized that the electrochemically generated oxide competes with the continuous etching of the oxide by NaOH, which imparts fluidic properties to the liquid metal.$^{[47]}$ Potentials greater than 6 V DC also result in hydrolysis, at which point the hydrogen bubbles block the channel. Voltages below 6 V DC are insufficient to wet the channels and lead to slow oxidation. We designed the chambers and constrictions by calculating the Laplace pressure exerted on Galinstan (Equations (2)–(3)) by optimizing their respective widths (see Figure 2b). Correctly choosing $W_{CT}$ with respect to $W_{CH}$ is critical to obtain segregated Galinstan plugs. We observe that for a $W_{CH}$ of 0.8 mm and a $W_{CT}$ of 0.2 mm, the difference in the Laplace pressure of $\Delta p_{CT}$ (constriction Laplace pressure) and $\Delta p_{CH}$ (chamber Laplace pressure) is 37.5 mbar (Table 1), which leads to the generation of a connected Galinstan plug (Figure 2c). On the contrary, for the same $W_{CH}$, reducing the $W_{CT}$ to 0.1 mm resulted in well-defined segregated

![Figure 2. Design overview and exemplary images of Galinstan plugs generated via electrochemical oxidation in constricted channels. a) Top-view schematic of the liquid metal plug generator with inlet reservoirs R1 of 0.2 mm height (Galinstan injection) and R2 of 0.1 mm height (1 m NaOH for oxide removal), outlet, and constrictions. b) The denotations for chamber ($W_{CH}$) and constriction ($W_{CT}$) widths. c) Captured image for a connected Galinstan plug for a $W_{CT}$ of 0.2 mm and $W_{CH}$ of 0.8 mm. d–f) Exemplary segregated Galinstan plugs of 1 mm (d) and 2.5 mm (g) in length generated in $W_{CT}$ of 0.1 mm and $W_{CH}$ of 0.8 mm, respectively, and plugs of 1 mm (e) and 2.8 mm (f) in length generated in $W_{CT}$ of 0.1 mm and $W_{CH}$ of 0.5 mm, respectively. Channel outlines (in black) are manually drawn over channels and chambers for ease of visualization.](image-url)
Galinstan plugs. This suggests that a critical limit of Laplace pressure difference exists, which will define if the plugs are connected or segregated. In this study, with \( W_{\text{CH}} \) of 0.5 and 0.8 mm and \( W_{\text{CT}} \) of 0.1 and 0.2 mm, a pressure difference of constrictions to channels (\( \Delta p_{\text{CT}} - \Delta p_{\text{CH}} \)) greater than 37.5 mbar resulted in segregated Galinstan plugs. This implies that on switching to oxidative potential, Galinstan wets the entire length of the channel (including the chambers) and constrictions, and will preferentially de-wet the constrictions (which exert a higher Laplace pressure than the chambers) and fill the chambers when switching off the potential. Surpassing the critical Laplace pressure difference will allow preferential de-wetting to form plugs inside the chambers, whereas differences below the critical Laplace pressure difference will fill the entire channel (including chambers) and constrictions, to form a connected plug (see Figure 2c). This also holds true for a \( W_{\text{CH}} \) of 1.5 mm and \( W_{\text{CT}} \) of 0.1 and 0.4 mm, where segregated plugs are generated for \( W_{\text{CT}} \) of 0.1 mm (Laplace pressure difference 93.4 mbar) whereas connected plugs are generated for 0.4 mm (Laplace pressure difference: 18.4 mbar; Figure S2, Supporting Information). We generated Galinstan plugs of 1 and 2.5 mm length for \( W_{\text{CH}} \) of 0.5 mm and plugs of 1 and 2.5 mm for \( W_{\text{CH}} \) of 0.8 mm with a constant \( W_{\text{CT}} \) of 0.1 mm, where the Laplace pressure difference is greater than 37.5 mbar (Figure 2d–g). The generated plugs remain inside the chambers unless intentionally moved via application of potential or electrolyte injection (see Video S3, Supporting Information). Continuous electrowetting would possibly enable the extraction of liquid metal plugs without disturbing their aspect ratio. However, this would require electrodes at each constriction to avoid cross-talk and coalescing of plugs. A possible option to extract the plugs could be a concept as shown by Gol et al. We also observed that the length of constriction does not affect the Laplace pressure, as segregated Galinstan plugs were generated for \( W_{\text{CH}} \) of 0.5 and 0.8 mm with \( W_{\text{CT}} \) of 0.1 mm for constriction length of 0.4 mm (Figure 2d,e) and 0.2 mm (Figure 2f,g), respectively. We further observe that having rounded corners is pertinent to obtaining Galinstan plugs that can completely seal the chambers, as in most cases sharp rectangular corners allowed entrapment of air bubbles formed due to the hydrolysis at the electrodes and were moved along with Galinstan to the chambers, which affected the Laplace pressure and resulted in failure of the on-chip generator (Figure S2 and Video S3, Supporting Information). Application of a cathodic potential of ~6 V on the liquid metal also resulted in the generation of plugs in the well-defined chambers, wherein Galinstan droplets were shot from the first constriction end until the entire channel was filled, followed by de-wetting of the constrictions to form segregated plugs (see Video S3, Supporting Information).

Briefly, designing and fabricating channels with well-defined constrictions result in the generation of Galinstan plugs whose size is dependent on the aspect ratio of the channel. Since this method can generate reproducible Galinstan plugs of a given size in constricted channels, it is limited in terms of generating plugs of different sizes and interspacing. Thus, we further compared the method of implementing constricted channels with straight channels under applied modulated voltages to generate reproducible Galinstan plugs of different sizes.

### Table 1. Comparison of the calculated Laplace pressure for different widths but similar heights of chambers and constrictions and the resulting ratio of their respective Laplace pressures.

| \( \frac{W_{\text{CH}}}{\text{[mm]}} \) | \( \frac{W_{\text{CT}}}{\text{[mm]}} \) | \( \frac{H_{\text{CH}}}{\text{[mm]}} \) | \( \frac{H_{\text{CT}}}{\text{[mm]}} \) | \( \Delta p_{\text{CH}} \) | \( \Delta p_{\text{CT}} \) | \( \Delta p_{\text{CT}} - \Delta p_{\text{CH}} \) |
|---|---|---|---|---|---|---|
| 0.8 | 0.1 | 0.2 | 0.2 | 62.5 | 150 | 87.5 |
| 0.5 | 0.1 | 0.2 | 0.2 | 70 | 150 | 80 |
| 0.8 | 0.2 | 0.2 | 0.2 | 62.5 | 100 | 37.5 |
| 0.5 | 0.2 | 0.2 | 0.2 | 70 | 100 | 30 |
| 1.5 | 0.1 | 0.2 | 0.2 | 56.6 | 150 | 93.4 |
| 1.5 | 0.4 | 0.2 | 0.2 | 56.6 | 75 | 18.4 |

3. **Effect of Modulated Voltages on Plug Generation in Straight Channels**

Actuating liquid metals by applying modulated voltages has been studied for applications like electrical switches and artificial muscles. Direct application of an oxidative potential results in local oxidation of the liquid metal which is countered by the reducing effect of NaOH. We reasoned that the application of modulated voltages should tune the interfacial tension of the liquid metal resulting in localized expansion and contraction to achieve plugs of tuneable size. We studied the effect of an inverted sinusoidal wave and a square wave on the generation of Galinstan plugs inside straight channels (Figure 3). We reasoned that by implementing modulated voltages, a liquid metal can be shocked locally, resulting in stretching and relaxation in an oscillating pattern, thus breaking the liquid metal and resulting in the formation of plugs. The forward and backward pulses are concurrent, which means that Galinstan is subjected to repeated oscillations. The idea is to locally create a forward bias by intentionally implementing a higher pulse duration and pulse duration range for the forward voltage compared to the backward voltage. For an inverted sinusoidal waveform (see Figure 3a), we set a forward pulse duration (FPD) of 20 ms (50 Hz) with a range of 45–65 ms and a backward pulse duration (BPD) of 3 ms (333.3 Hz) in a range of 38–41 ms. Additionally, the applied voltage level for FPD and BPD was set to 255/255 and 125/255 (analogWrite()), respectively. analogWrite() is a function on Arduino UNO which allows to control the voltage output, with 255 being the highest at 100% duty cycle and 0 being the lowest at 0% duty cycle. We set the external applied voltage to +6 V, resulting in FPD and BPD voltages of 6 V (255) and ~3 V (125), respectively. The set modulations were applied to Galinstan in R1 (Figure 2a), resulting in oscillation of Galinstan followed by generation of plugs inside straight channels. The images in Figure 3b1–7 are snapshots of a slow-motion video (see Video S1 in Supporting Information). Once the potential is applied, Galinstan initially stretches to a point where the leading oxide edge is reduced by NaOH, but the applied oscillations and electrochemical oxidation result in pinching of Galinstan (see Figure 3b1). A plug of Galinstan breaks out at the pinching point (Figure 3b2–4) and undergoes oscillatory motion as an individual entity but continues to move forward (toward the outlet) due to the set forward bias. The potential was temporarily switched off to record the size of...
generated Galinstan plug (1.2 mm in length, see Table 2 and Figure 3b3). Similar stretching of Galinstan is observed for the generation of the second plug (Figure 3b5–7), which is of a similar dimension (1.4 mm) as the first plug. The interplug distance was 5 mm (±0.5 mm) and was consistent over a period of three iterations. Electrochemical oxidation of Galinstan is only effective until the anode is in contact with Galinstan, otherwise electrocapillarity dominates over the actuation mechanism. This implies that the limited volume of Galinstan owing to limitations in fabrication is a bottleneck for on-chip plug generators. To reduce the interplug spacing, we tested a reduced FPD range to minimize the forward bias. We kept the pulse duration at 20 ms, and reduced the range of FPD and BPD to 25–45 and 18–21 ms, respectively, which resulted in an interplug distance of 2 mm. The smallest generated plug based on modulated voltage in a straight channel was 0.5 mm for an inverted sinusoidal waveform with an FPD range of 40 ms (25–65 ms) and backward pulse duration of 3 ms (38–41 ms) at applied oxidative potential of 6 V (a) with the corresponding snapshots of plug generation (1–7) (b). c,d) Representative sketched plots for a square waveform with forward voltage level of 255/255 (=6 V) and backward voltage level of 50/255 (=1 V) for a delay of 50 ms at applied oxidative potential of 6 V (c) with the corresponding snapshots of plug generation (1–7) (d). Channel outlines (in black) are manually drawn over channels and chambers for ease of visualization.

Figure 3. Effect of programmed waveforms and the resulting generated Galinstan plugs. a,b) Representative sketched plots for an inverted sinusoidal wave with forward voltage level of 255/255 (=6 V) and backward voltage level of 125/255 (=3 V) for forward pulse duration range of 20 ms (45–65 ms) and backward pulse duration of 3 ms (38–41 ms) at applied oxidative potential of 6 V (a) with the corresponding snapshots of plug generation (1–7) (b). c,d) Representative sketched plots for a square waveform with forward voltage level of 255/255 (=6 V) and backward voltage level of 50/255 (=1 V) for a delay of 50 ms at applied oxidative potential of 6 V (c) with the corresponding snapshots of plug generation (1–7) (d). Channel outlines (in black) are manually drawn over channels and chambers for ease of visualization.
Table 2. Overview of all the graphical representation of the iterations of modulated waveforms tested in this work with the resulting Galinstan plug size statistics (mean, SD for \( n = 11 \)), plug size range, and interplug distance in comparison to +6 V direct oxidative potential, along with the corresponding snapshots of generated plugs (guiding lines in black are manually drawn over the channel and chamber boundary for ease of visualization; scale bar: 1 mm).

| Graphical representation of used waveforms with the program name | Plug size mean ± SD [mm] | Galinstan plug size range [mm], interplug distance [mm] | Snapshot of generated plugs |
|-----------------------------------------------------------------|--------------------------|----------------------------------------------------------|-----------------------------|
| Direct oxidative                                                | –                        | –                                                        | –                           |
| Inverted sinusoidal                                             | 1.2 ± 0.19               | 1.1–2.4, 2.3–3.7                                         | ![Image](image1) |
| Inverted sinusoidal                                             | 1.5 ± 0.49               | 0.8–0.9, 5.7                                            | ![Image](image2) |
| Inverted sinusoidal                                             | 1.06 ± 0.16              | 0.5–1.5, 1.5                                            | ![Image](image3) |
| Inverted sinusoidal                                             | 1.18 ± 0.43              | 1.5–1.6, 2.2                                            | ![Image](image4) |
| Graphical representation of used waveforms with the program name | Plug size mean ± SD [mm] | Galinstan plug size range [mm], interplug distance [mm] | Snapshot of generated plugs |
|---------------------------------------------------------------|--------------------------|---------------------------------------------------------|----------------------------|
| Inverted sinusoidal                                            | 0.99 ± 0.39              | 1.2–1.4, 5.6                                            | ![Inverted Sinusoidal Plug](image) |
| Sinusoidal                                                     | 1.09 ± 0.45              | 0.8–1.2, 1                                              | ![Sinusoidal Plug](image) |
| Sinusoidal                                                     | 1.19 ± 0.73              | 0.9–2.3, 1.1–1.5                                       | ![Sinusoidal Plug](image) |
| Square wave                                                    | 1.31 ± 0.42              | 0.7–0.8, 3.5                                            | ![Square Wave Plug](image) |
| Square wave                                                    | 1.36 ± 0.72              | 2.3–4.2, 1.4–1.7                                       | ![Square Wave Plug](image) |
and backward voltage level to 125/255 (≈3 V) and delays of 50 ms (Figure 4e) and 35 ms resulted in larger plugs in the range of 0.7–2.5 mm with varying interplug distance of 2–6 mm (Table 2), which implies that no reproducibility in terms of plug size and interplug distance is observed for the square wave pattern. We also tested a sinusoidal wave (not inverted) to study the generated plugs. In this case, we set the FPD range as 0–120 ms and BPD as 0–24 ms, denoting that both the forward and backward pulse originated from 0 and overlapped each other for each cycle. As seen in Figure 4b,c, changing the backward voltage level from 50/255 to 125/255 significantly affects the size and distance between the generated plugs. Ideally, in the case of a backward voltage level of 50/255 (≈1 V), a stronger forward bias should result in longer Galinstan plugs. However, we did not notice any repeatable or predictable pattern for a sinusoidal waveform, while for inverted sinusoidal waveforms we obtained reproducible plugs in the same dimension range for different modulated voltages (Table 2). For the inverted sinusoidal waveform, we had the forward and backward pulse in symmetry and synchronization with each other, but not overlapping. Similar plug generation is observed for the different iterations of the square wave, which has the forward and backward pulse overlap as well. This suggests that in order to achieve reproducible plug generation, the forward and backward pulses should be in symmetry, but not overlap. Adding a constriction at the center of the straight channel did not improve plug size reproducibility. It resulted in plug generation via stretching and breaking off at the constriction, followed by shooting of smaller liquid metal droplets from the constriction toward the cathode at the outlet (see Video S4, Supporting Information). The constriction behaves as a Laplace barrier and traps the generated plugs, which coalesce together and undergo continuous pulsation motion resulting in bubble formation and possible oxide residue at the bottom of the channel due to frictional forces. Table 2 provides an overview of all the waveforms tested in this work along with the measured plug size mean, standard deviation, and plug size range for a plug sample size of $n = 11$. A graphical overview of the plug size mean and standard deviation indicates that the inverted sinusoidal waveforms with a pulse duration of 20 ms (FPD 45–65 ms and FPD

Table 2. Continued.

| Graphical representation of used waveforms with the program name | Plug size mean ± SD [mm] | Galinstan plug size range [mm], interplug distance [mm] | Snapshot of generated plugs |
|---------------------------------------------------------------|--------------------------|----------------------------------------------------------|----------------------------|
| Square wave                                                   | 1.0 ± 0.22               | 1.1–3.0, 4.7                                             | ![Square wave plug generation](image1.png) |
| ![Square wave waveform](image2.png)                          |                          |                                                          |                            |
| Square wave                                                   | 1.28 ± 0.49              | 2.2–3.3, 2                                              | ![Square wave plug generation](image3.png) |
| ![Square wave waveform](image4.png)                          |                          |                                                          |                            |
| Square wave                                                   | 1.31 ± 0.6               | 0.7–1.0, 2–4                                            | ![Square wave plug generation](image5.png) |
| ![Square wave waveform](image6.png)                          |                          |                                                          |                            |
25–45 ms) for a forward voltage level of 255/255 and backward voltage level of 125/255 showed the least deviation of ± 0.19 and ± 0.16 mm, respectively (Figure 5). These results suggest that plug generation based on voltage modulation is sensitive to the applied parameters and in most cases results in plugs of different dimensions and interplug distance.

4. Conclusion

We have shown the generation of Galinstan plugs via electrochemical oxidation in the sub-millimeter range by fabricating a plug generator with constricted and straight channels fabricated via soft lithography from a 3D microprinted template. We investigated the effect of Laplace pressure of the fabricated channels with constrictions for generating Galinstan plugs of any given aspect ratio inside chambers of any given length in a reproducible manner. We applied 6 V oxidative potential directly on Galinstan injected inside a reservoir, which was initially pre-filled with 1 m NaOH. For channel widths of 0.5 and 0.8 mm, having constriction widths of 0.1 mm, Galinstan preferentially fills the chambers on switching off the potential. Constriction widths of 0.2 mm allow Galinstan to form a connected plug for 0.5 and 0.8 mm width, highlighting the importance of having a significant difference in Laplace pressures between the constrictions and chambers. We performed experiments on structure with \( W_{CH} \) of 0.5 and 0.8 mm and \( W_{CT} \) of 0.1 mm. We were able to reproducibly generate plugs of size 1, 2.5, and 2.8 mm. As an alternative technology, we investigated electrochemical potentials applied via pulse width modulation (PWM) for their suitability in generating Galinstan plugs in straight channels of width 0.5 and 0.8 mm and length of 15 mm without any constrictions. We studied the effect of inverted sinusoidal and square waveforms, by intentionally setting a forward bias to generate plugs by stretching and snapping oxidized Galinstan. For both inverted sinusoidal and square waveforms, the reproducibility and plug dimensions of Galinstan plugs were inconsistent. While inverted sinusoidal waveforms generated consistent plug dimensions, the interspacing between the plugs varied as the forward bias was reduced. For square waveform, Galinstan plug dimensions ranged from 0.7 to 4.2 mm and the plug generation was inconsistent. For reproducible, scalable, and plug dimensions of a certain size, generating liquid metal plugs by fabricating constricted channels based on Laplace pressure is favorable compared to PWM-based generation in straight channels. We believe that the methods developed in our work will find broad use in various microfluidic applications like microactuators, valves, switches, and pumps, where the properties of gallium-based liquid metals are highly desirable.

5. Experimental Section

Materials: Elastosil RT 601 A/B was purchased from Wacker (Germany) and was used as received. Galinstan was purchased and used as received from Strategic Elements (Germany). Sodium hydroxide pellets (>98%), 37% hydrochloric acid, 2-propanol, acetone, and methanol were purchased from Carl Roth (Germany) and were
Polyethylene glycol diacrylate (PEGDA 250) with an average molar mass of 250 g mol\(^{-1}\), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, hydroxyquinone monomethylether, and toluene were purchased from Sigma Aldrich (Germany) and were used as received. 3-methacyryloxypropyl-dimethylchlorosilane (MACS) was purchased from abcr (Germany). Tinned copper wires of 0.2 mm diameter were purchased from RS Components (Germany) and were cut to 5 cm before using as electrodes. A biopsy punch of 0.5 mm inner diameter (ID) was used as received to punch inlets from World Precision Instruments (Germany). Proxxon Micromot FBS 240A multifunction tool with a 1.2 mm OD drill head was used to drill outlets and was purchased from Conrad Electronic (Germany). Microscope slides (76 × 52 × 1 mm) made of soda lime glass were used as substrates and were provided by Paul Marienfeld (Germany). 1 mL Injekt-F single use syringes were purchased from B. Braun (Germany) and were used as received. 0.5 in. dispensing tips with 0.25 mm interior diameter (Product ID F560015) were purchased from Vieweg (Germany) and used as received. Transparent silicon rubber sheet of 4 mm thickness was purchased from Technikplaza (Germany) and was cut accordingly to be used as molds for replication. Galinstan plug size analysis and plug generation videos were captured on a VHX-6000 digital microscope purchased from Keyence Deutschland (Germany). The plug generation videos were converted to slow-motion videos on a One Plus Nord CE smart phone (Germany).

**Template 3D Microprinting:** The microchannel templates were printed on a commercial high-resolution 3D microprinter of type Dilase 3D (Klöd, France). The photoresin was prepared by mixing PEGDA, 0.2 wt% phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide as the photoinitiator, and 0.4 wt% hydroxyquinone monomethylether as an inhibitor. A 40 μm laser line width and a slicing thickness of 10 μm were applied, and the structures were printed on a MACS functionalized silicon wafer at a laser intensity of 28% modulation (14 mW) at 50 mm s\(^{-1}\) writing speed. The MAS-functionization protocol was previously described. Printed structures were rinsed with distilled water to wash off the uncured resin, post-cured for 5 min at 189.9 W m\(^{-2}\) in a UV curing chamber (XYZ Printing, New Taipei City, Taiwan) and further rinsed in distilled water and 2-propanol and dried with a compressed N2 gun.

**Replication in PDMS:** Elastosil RT 601 A/B was mixed in a ratio of 9:1 (A to B, by weight), according to the manufacturer’s instructions. Entrapped air bubbles were removed using a vacuum desiccator. The mixture was carefully poured inside a 4 mm-thick silicon mold surrounding the fabricated template, and was cured at 65 °C for 2 h. The cured mold was allowed to cool to room temperature and carefully peeled off. Inlets were punched with a 0.5 mm ID biopsy punch and the outlet was drilled with a 1.2 mm drill.

**Bonding of the PDMS Replica on Soda Lime Glass Slide:** PDMS microchannels were closed by bonding against a soda lime glass slide using a bonding method based on corona discharge activation. A corona discharger (BD-20V, 230 V, 50/60 Hz, Electro-Technic Products Inc., USA) was used as a handheld source for generating the corona. The PDMS replica was rinsed in 2-propanol, dried in compressed nitrogen before being subjected to corona discharge for 30 s. A 76 × 52 × 1 mm\(^3\) soda lime glass slide was immersed in a solution of acidic methanol (HCl:methanol, 1:1, by volume) for 1 min to remove contaminants, rinsed in 2-propanol, dried in compressed nitrogen, and subjected to corona discharge for 30 s. The corona-discharged PDMS replica was then placed on top and the setup was placed inside an air circulating oven at 65 °C for 2 h to allow complete bonding.

**Galinstan Injection and Plug Generation:** The reservoir for injecting was fabricated by adapting the work of Gough et al. by utilizing a quasi-planar geometry to allow Galinstan to be in a state of high surface tension. The nanometer-thick oxide skin formed on the surface of the Galinstan...
is the reason for the liquid metal’s sticking to the substrate hampering the generation of segregated segments in microchannels. The presence of an electrolyte not only helps removing the oxide skin but also helps to form a slip layer surrounding Galinstan which allows it to fill the channels smoothly.[53] Sodium hydroxide pellets were used to prepare 1 m NaOH solution. The channels and both reservoirs (R1 and R2, Figure 2a) were prefilled with 1 m NaOH followed by injecting Galinstan in the inner reservoir (R1). 1 mL Injekt-F single use syringes and 0.5 in. dispensing tips with 0.25 mm interior diameter were used to inject 1 m NaOH and Galinstan. Excess NaOH was wiped off with Kimtech precision wipes. Tinned copper wires of 0.2 mm diameter were used as electrodes and were inserted inside the inner reservoir and the outlet as indicated in Figure 1. A 6 V DC oxidative potential provided by a power supply (Triple output DC, E3631A, HP, Korea) was applied at the reservoir end relative to ground at the outlet end. The electrochemically oxidized Galinstan was allowed to fill the entire length of the channel after which the power source was switched off.

Voltage Modulation Setup: The iterated waveforms were programmed on a customized PCB (Beta Layout, Germany). Arduino Uno R3 (Reichelt Electronic, Germany) system consisting of a L293B H-Bridge module (Reichelt Electronic, Germany) which was consisted of four transistors (see Figure S1, Supporting Information). These transistors were controlled by PWM. The used programs are provided in the Supporting Information. Briefly, the waveforms were broken down into three components: pulse duration, range of pulse durations, and applied voltage level. The pulse duration denoted the duration in milliseconds for a forward or backward pulse and depended on the preset pulse duration parameter \(d\) (in ms). The range of pulse durations influenced the bias, i.e., forward or backward bias. The applied voltage level was 8-bit modulated (i.e., from 0 to 255 where 0 corresponds to 0 V and 255 to 6 V) but directly depended on the supplied external potential. These parameters were set in the programs to switch between “on” and “off” states, and were run to test the resulting Galinstan plug generation.

Laplace Pressure Calculation: The chambers and constrictions were designed by considering the Laplace pressure exerted on Galinstan by optimizing the chamber dimensions respective widths. The required pressure to inject Galinstan in the microchannels was given by

\[
\Delta p = 2\gamma \left( \frac{1}{H} + \frac{1}{W} \right)
\]

(1)

where \(\Delta p\) is the difference between the pressure inside the liquid metal plug (\(p_{\text{plug}}\)) and the pressure exerted by the electrolyte (\(p_{\text{electrolyte}}\)), \(\gamma\) is the interfacial tension between the Galinstan and the electrolyte, \(H\) and \(W\) are the chamber or constriction height and width, respectively.[54] The exerted Laplace pressure \(\Delta p_{\text{CH}}\) (for the chamber) and \(\Delta p_{\text{CT}}\) (for the constriction) was inversely proportional to the width of chamber \(W_{\text{CH}}\) and constriction \(W_{\text{CT}}\) and height of chamber \(H_{\text{CH}}\) and constriction \(H_{\text{CT}}\), respectively. For both cases, Equation (1) was thus simplified to

\[
\Delta p_{\text{CH}} = 2\gamma \left( \frac{1}{W_{\text{CH}}} + \frac{1}{H_{\text{CH}}} \right)
\]

(2)

\[
\Delta p_{\text{CT}} = 2\gamma \left( \frac{1}{W_{\text{CT}}} + \frac{1}{H_{\text{CT}}} \right)
\]

(3)

The interfacial surface tension of Galinstan in 1 m NaOH was assumed to be 500 mN m\(^{-1}\).[55]

Statistical Analysis: Snapshots of the generated plugs from the recorded slow-motion videos were captured and the size was measured via CorelDRAW software. Plug size measurement was done along the centerline length for calculating the mean and standard deviation. For each set of modulated waveforms, the plug sample size was 11 (n).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

3D microprinting, electrochemical oxidation, liquid metals, nonspherical droplets
