Study of electrochemical properties of liquid gallium

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Study of electrochemical properties of liquid gallium

Yuchen Chen

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award of the Degree of
Master of Philosophy
of the
University of Wollongong"

March 2017
DECLARATION

I, Yuchen Chen, declare that this thesis, submitted in partial fulfilment of the requirements for the award of Master of philosophy, in the Institute for Superconducting and Electronic Materials (ISEM), Faculty of Engineering, University of Wollongong, NSW, Australia, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for a qualification at any other academic institution.

Yuchen Chen

March, 2017
ABSTRACT

Room temperature liquid metals have been widely studied because of their unique properties including large liquid range and excellent electrical conductivity. Recently, liquid metal gallium and its alloys have attracted huge interest, owing to the discovery of new phenomena based on them.

Inspired by these new phenomena, my master thesis focused on the electrochemical properties of liquid gallium and three related topics are presented as follows.

Spreading effects of liquid metal gallium have been demonstrated above the melting point of gallium. It was found that spreading of liquid metal can occur in alkaline and acid solution under an applied voltage and liquid metal can be transformed into its spherical shape when the external power supply is cut off. However, the deformations do not show up in pH neutral solution. The volumes of the liquid metal droplet, the externally applied voltage and the concentrations of the electrolyte have great influences in the spreading speed of liquid metal and the maximum top-view spreading area.

Spreading effects of liquid metal gallium in the supercooling state have been studied. The experiments were carried out in 0.5 mol/L NaOH and HCl solutions. The spreading and crystallization of liquid metal occurred simultaneously when an external voltage is applied. The crystallization rate is lower than the spreading rate at
22 °C. Our findings open new avenues for controlled liquid-solid shape reconfigurations and are of significant importance for potential applications of soft robotics and electronics.

A phenomenological study of the gallium beating heart system in both one wire electrode and one graphite ring electrode electrochemical cell configuration stimulated with a DC voltage is presented. The gallium drop is electrically connected to the graphite ring and acts as the working electrode. When a DC voltage is applied, the liquid metal droplet was jumping on the horizontal direction in the middle of graphite ring. The range of beating frequency from 2.3 to 6.1 Hz can be acquired in our experiments. As the voltage increases, the amplitudes of the oscillation of the liquid gallium droplets show dissimilar behaviors with different volumes of liquid gallium droplet.
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LIST OF ABBREVIATIONS

XPS = x-ray photoelectron spectroscopy
LEIS = low-energy ion-scattering spectroscopy
SEM = scanning electron microscopy
MCU = microcontroller unit
PDMS = patient data management system
RFID = radio frequency identification
PVC = polyvinyl chloride
IC = integrated circuit
ABS = acrylonitrile butadiene styrene
ECG = electrocardiography
EDL = electrical double layer
Gallium and its alloys represent a promising class of liquid metals that have been studied since its discovery in 1875. Recently, new phenomena have shown that the formation of the oxide layer on the liquid metal is very important. The unique properties of gallium and its oxide layer make it suitable for many new applications.

Figure 1.1 Crystallization of gallium from the melt.

1.1 Gallium and its properties

In 1936, Spells measured the viscosity of gallium at the melting point (approximately 30 °C) to be 0.0204 poise[1], which is approximate twice the value
of water at the same temperature. The low viscosity causes gallium to flow readily when it is driven by an external force.

Although the viscosity of liquid gallium is close to the value of water, the surface tension is larger than that of water. Hardy’s study in 1985 showed that the following relationship between the surface tension of gallium and the temperature could be yielded by linear regression analysis of the data of Figure 1.2[2]. The relationship can be expressed by equation 1.1,

\[ \gamma = 709 - 0.066(T - 29.8) \]  

(1.1)

where \( \gamma \) denotes the surface tension of gallium, and \( T \) denotes the temperature of gallium.
Figure 1.2 Hardy determined the temperature dependence of the surface tension of gallium in 1985, based on two gallium drops of different mass cleaned by argon ion sputtering[2].

According to Equation (1.1), the surface tension of gallium at its melting point is 709 mJ/m², which is approximately 10 times of the value of the surface tension of water at the same temperature. Because of the low viscosity and large surface tension, the shape of a liquid gallium droplet is usually spherical.

Evaporation is an important factor that has a great impact on the wettability. Gallium has no vapour pressure. This property not only means that gallium wetting experiments can be carried out in a high vacuum chamber, but also avoids the risk of inhaling gallium vapour in the experimental environment[3].

The electrical conductivity of gallium is lower than that of copper, but larger than for other liquids such as sodium chloride. Its electrical conductivity in the liquid state is larger than in the solid state[4].

In contrast to mercury, gallium salts have low toxicity. In Hart & Adamson’s study in 1971[5], gallium salts showed antitumor activity, and they discuss the potential of gallium salts as a tumour treatment.

The volume of gallium increases by ~3.2 vol % when it has been frozen[6].
Supercooling is the process of lowering the temperature of a liquid below its melting point without it becoming a solid. The melting point of gallium is approximately 29.8 °C, which is close to room temperature. As shown by Lyman & Briggs in 1957[7], small drops of gallium can still exist when the environmental temperature is -28 °C, which is approximately 57.8 °C below its melting temperature.

A thin oxide skin (approximately 5Å in thickness) is usually formed at the surface of gallium because of gallium’s high adhesion[8, 9]. Figure 1.3 shows a real-space model for a liquid gallium surface disclosed to 206 L of oxygen at room temperature[9].

![Figure 1.3 Real-space model for the liquid-Ga surface disclosed to 206 L of oxygen at room temperature. Top: the proposed atomic arrangement in the oxide layer, with atomic diameters of 2.64 Å for O²⁻, 1.24 Å for Ga³⁺, 2.44 Å for covalent (Cv) Ga, and 2.50 Å for metal (Me) Ga. Bottom: the corresponding electron density profile](image)
(thin solid line) with its separate components; the underlying liquid Ga (large dashed lines), the Gaussians representing the Ga$^{3+}$ (dash-dotted lines) and the O$^{2-}$ layers (short-dashed lines). The oxide adlayer contains three planes of oxygen atoms with Ga$^{3+}$ ions in locations suggested by the $\alpha$- and $\beta$-Ga$_2$O$_3$ structures.[9]

According to the study of Khan et al. in 2014[10], although the gallium oxide layer is thin (1-3 nm), it prevents the metal from flowing freely because it is quite unreactive. The research by Downs and John shows that the gallium oxide forms spontaneously when gallium is exposed to an oxygen environment[11].

1.2 Gallium and its oxide skin

Gallium oxide wets most surfaces and it prevents the liquid gallium from flowing smoothly[8, 12-14]. This property can improve the applications that depend on forming two- or three-dimensional (2D or 3D) structures[15], antennas[16], and wires[17], since the oxide surface sustains the unstable shape of the liquid metal[17]. On the other hand, it makes the gallium-based alloys too hard to use in shape-changing applications, such as microscale switches, pumps, or optics[18]. Significantly, the oxide layer holds the gallium in non-equilibrium shapes by mechanical means[12, 19]. Normally, a low viscosity liquid with extremely large surface tension should maintain a spherical shape. Gallium can be formed into non-spherical shapes, however, because of the oxide layer of gallium in ambient air, as shown in Figure 1.4a.
Figure 1.4 Gallium and its alloys can be physically manipulated into (a) non-equilibrium shapes resulting from an oxide skin on its surface. (b, c) Disclosure to acid etches the oxide skin and results in the metal (d) to bead up because of the high surface tension of the bare metal[3].

After acid treatment, the gallium droplet beads up (Figure 1.4d) because of the oxide skin erasure and the large surface tension of gallium and its alloys (>500 mN/m)[20]. The amphoteric oxide layer can be removed at pH <3 or pH > 10[21].
Figure 1.5 Schematic diagram of chemical reaction with HCl vapour. The phase of oxides (Ga$_2$O$_3$/Ga$_2$O), chlorides (GaCl$_3$/InCl$_3$), and water is solid, aqueous, and liquid, respectively. The contact angle of Galinstan droplets on (a, b) a bare glass slide, (c, d) Cytop-coated glass slide, and (e, f) Teflon-coated glass slide, before (panels a, c, and e) and after (panels b, d, and f) the HCl vapour treatment[22].

In 2013, Kim et al. reported a simple approach to erase the oxide layer on the surface of gallium alloy to restore its non-wetting characteristics by hydrochloric acid (HCl) vapour[22]. The non-wetting characteristics of the alloy were restored successfully by the HCl vapour treatment. The change in the surface chemistry before and after the HCl vapour treatment was analysed using X-ray photoelectron spectroscopy (XPS) and low-energy ion-scattering spectroscopy (LEIS). They found that InCl$_3$ and GaCl$_3$ replaced the oxidized surface of the gallium-based alloy Galinstan (Ga$_2$O$_3$ and Ga$_2$O) after the treatment. The surface tension of the HCl-vapour-treated Galinstan was measured to be 523.8 mN/m. The static contact angle
The wetting behaviours between droplets of gallium–indium alloys and thin metal films on tin and indium substrates were explored by Kramer et. al.[23]. Thin metal foils were wetted reactively by metallic droplets. The surface texture which produced by sputtering may affect and control the wettability of the foils. The droplet contact diameter and contact angle as a function of time were measured, which
showed that both the composition and the surface morphology of the substrate are two key elements of wetting behaviour. The sputtered and native substrates were studied by using the Cassie-Baxter model to understand the behaviour of liquid metals and the significance of the oxide formation during interfacial processes.

Figure 1.7 (a) Illustration of the rough oxide–surface interface responsible for low adhesion, measured using the height variation method and scanning electron microscope (SEM) images showing (b) microscale and (c) nanoscale roughness of the old, air-formed, top surface of an oxidized GaInSn droplet formed at the tip of a syringe. (The drop was lightly sheared across a silicon wafer to make it adhere for imaging.) (d) Schematic illustration of the smooth oxide–surface interface formation around the perimeters of drops formed using the volume addition method[8]. (A composite interfacial area consisting of fractured pieces of old oxide, new oxide, and bare GaInSn is likely to be present underneath the droplet.)
Two modes of GaInSn adhesion were investigated by studying the dynamics of the formation and morphology of the liquid-metal–substrate interface[8]. In the first mode, the oxide shell is not cracked when it contacts with the substrate. Minimal adhesion between the liquid metal and numbers of solids was obtained in this mode, due to the nanoscale morphology of the oxide surface. The surface energy of the substrate or texture had almost no influence. The second mode applies when the oxide shell is cracked, in which the formation of the GaInSn–substrate interface involves two processes: 1) rupturing of the original oxide skin; 2) formation of a composite interface, including the contact between the substrate and old oxide, bare liquid metal, and new oxide. In the latter mode, the adhesion of GaInSn is dominated by the intimate contact between the new oxide and the substrate. The GaInSn adhesion can be either decreased or increased by altering the pinned contact line length via various degrees of surface texturing.

Figure 1.8 Comparing the behaviour of EGaIn in (a) a dry capillary, and (b) a capillary prefilled with water. The capillaries are mounted on a wall using adhesive
attached to a rotating holder. (a) (i, ii) When EGaIn is injected into a dry capillary, the oxide skin forms spontaneously and adheres to the capillary wall. (iii) When the capillary is rotated vertically (aligned with the force of gravity), the liquid metal does not flow out of the capillary. (b) (i) When a capillary tube prefilled with water is injected with EGaIn, the oxide skin does not adhere to the capillary wall because of the presence of a thin aqueous layer between the metal plug and the capillary wall. (ii) In this case, the metal is stable horizontally, but (iii) flows out of the capillary when tilted due to gravity[10].

Khan et al. studied the effects of water on the oxide skin of EGaIn and its application in liquid metal microsystems[10]. The metal can flow smoothly in capillaries and across surface with no sticking due to an interfacial slip water layer between EGaIn and other surfaces. The chemical composition of the oxide skin can be changed in the presence of water. The metal cannot flow freely in microchannels in the absence of the slip layer. The ability to actuate and subsequently control liquid metal plugs in microchannels via the slip layer may enhance the development of new devices, including shape-reconfigurable electronics, sensors, actuators, and antennas.
Figure 1.9 Instantaneous images of impact process, obtained with a GaIn droplet 4.1 mm in horizontal width during impact with a pool of the same liquid at impact velocity $v = 4.2$ m/s and room temperature[24].

Li et al. systematically studied the fluid dynamics of a liquid metal droplet dropped into a liquid metal pool[24]. A high-speed digital camera was employed to record the splashing process. Liquid metal droplet impingements with different droplet volumes, impact velocities, and pool temperatures were observed. The shape of the falling liquid metal droplet and the splashing structure for both a room temperature and a high-temperature liquid metal pool were hugely different from those for water. Both the liquid metal oxide layer and the pool temperature influence the height of the jet, which is also sensitive to the viscosity of the fluid.
1.3 Applications

Metals are useful in electronics; liquid metal has more advantages because it can be developed into soft, flexible, and stretchable electrical devices, such as stretchable electronics, artificial skin, and soft robotics[25-27]. The liquid metal also can form soft electrodes for measuring the electrical properties of thin films[28, 29], quantum dots[30, 31], and self-assembled monolayers[32, 33].

![Figure 1.10](image)

Figure 1.10 (a) SEM image of a dried microscopic electronic device consisting of one Ga droplet coated with a layer of Au nanoparticles. A schematic diagram of the measurement circuit is superimposed near the top of the image. (b) Schematic illustration showing a side view of the sample. The inset is an enlarged schematic illustration of a single nanoparticle layer[30].

The spontaneous assembly of ligand-stabilized gold nanoparticles on a gallium droplet surface has been demonstrated by Du et al[30]. In order to manipulate
electron transport, nanoscale controlled structure devices have been formed by deposition of liquid metal droplets on patterned electrodes. The surface of the gallium droplet is very smooth with roughness on the order of angstroms because capillary fluctuations. Sensitive electrical measurements were not influenced by the oxide skin of the gallium, because most of the samples were much more resistive than this oxide[34].

Figure 1.11 a) Schematic illustration of the disconnection and reconnection of a simple electronic circuit using a self-healing wire. A self-healing stretchable wire is pictured in the inset to (ii). The reconnected wires were misaligned on purpose to clearly identify the cut after self-healing in the inset to (iii) and show that only the EGaln channel has to be aligned to restore electrical conductivity. b) Variation of the resistance of the wire during connection/disconnection/reconnection experiments. The error bars indicate the variability across three sets of measurements. c)
Mechanical characterization of a self-healing stretchable wire before cutting (black line) and after self-healing (red squares)[35].

Self-healing wires recover mechanically and electrically after being cut, which enhances the durability of electronic components and is the key factor for stretchable electronics[36-39]. Palleau et al. fabricated stretchable wires with metallic conductivity that can self-heal both mechanically and electrically after being severed completely[35]. Liquid metal was injected into the self-healing microchannel polymer. The extraordinary properties of both liquid gallium and self-healing polymers have been integrated together.
Figure 1.12 Programmable flexible printed circuits fabricated by the dual-trans method. a) Top view of the transparent band with programmed lighting. b) SEM image of the connection between a resistor and the liquid metal circuit wire. Scale bar, 500 µm. c) The good performance of the band when rolled, twisted, and even formed into a wristband. d) Flexible temperature measurement circuit with a microcontroller unit (MCU), infrared temperature sensor, and Bluetooth module. e) Real-time and wireless temperature measurement system containing mobile phone and flexible liquid metal circuit, and (inset) temperature curve measured with the flexible wireless sensor module. f) Packaged and integrated flexible temperature measurement circuit which can properly adhere to the skin[40].

Wang et al. made flexible electronic devices for a Patient Data Management System (PDMS) using the liquid metal dual-trans printing technology[40]. In order to enhance the mechanical adhesion between the substrate and the liquid metal, the substrate surface temperature was controlled because of the unique property of the liquid metal. A programmed light-emitting band and wireless temperature-sensing modules were demonstrated.
Figure 1.13 Schematic illustration of the liquid metal printer and the printed electronics pattern. (A) 3D diagram of the low-cost computer-controlled printer to illustrate the tapping mode movement of the printing head and the composite fluid mechanics to deliver, transfer, and adhere the liquid metal ink to the substrate. (B) Photograph of the printing process of the machine. (C) Photograph of the radio frequency identification (RFID) structure printed with liquid metal ink on flexible polyvinyl chloride (PVC) film. (D) Printed circuit with integrated circuit (IC) chips incorporated. (E) Directly printed and packaged patterns as decorative drawings and building[40].

Although electronics printing technology has been in high demand recently, there are several restrictions, such as available printing technology and limitations of conductor ink and adhesive ink. Zheng et al. developed a low-cost automatic printing technology with a tapping-mode liquid metal ink delivery system[41]. Theoretical
explanations and experimental measurements were investigated to determine the mechanism for the adhesion of the liquid metal ink on the substrate. Complex configurations such as electronic circuits, electronic patterning, and electronic paintings were quickly and efficiently printed out.

Figure 1.14 Dynamic control over the size of EGaIn microdroplets. Production of EGaIn microdroplets using A) square wave signal with 5 V magnitude and 0 V offset at a frequency of 1 Hz, B) square wave signal with 5 V magnitude and 5 V DC offset at a frequency of 1 Hz, and C) sinusoidal wave signal with 10 V magnitude and a frequency of 1 Hz. Scale bars are 200 µm[42].
A novel method for controlling the size of liquid metal droplets in a microfluid system was presented by Tang et al [42]. The diameter of liquid metal microdroplets can be manipulated by the flow rate, the width of the orifice, and the magnitude of the voltage. Furthermore, the size of liquid metal droplets can be ~25% smaller than the width of the orifice. The surface tension of the liquid metal was controlled by voltage, and interfacial tension was modulated using electrocapillarity. The flow rate of liquid metal also has a dramatic effect on the size of droplets. This method can be utilised in microfluidic logic or optical instruments [43-45], ink materials [46], and small packages.

1.4 New phenomena

Figure 1.15 Snapshots of liquid metal transformation from the original flattened state in 1 to intermediate states in 2 and 3 and finally to a sphere in 4 [47].
Sheng et al. discovered how to achieve transformations of liquid metals between different morphologies and configurations using electric field[47]. Moreover, they observed the rotation of the liquid metal spheres along with water vortexes swirling nearby. Furthermore, planar locomotion of the liquid metal droplet was demonstrated because the electrical field induced a driving force on the liquid metal. With such merits of liquid metals under various electric fields, it offers great opportunities for potential applications, such as liquid metal recycling, locomotion-assisted devices and movable sensors.
Figure 1.16 (A) Oxidative spreading of a bead of liquid metal in 1 M NaOH solution. (Left) A needle serves as a top electrical contact to the droplet. (Right) A wire serves as a bottom electrical contact to the droplet. (A, i) The drop assumes a spherical shape initially due to its large surface tension; (A, ii) upon application of an oxidative potential, the metal assumes a new equilibrium shape; (A, iii) above a critical potential, the metal flattens and spreads without bound and ultimately forms finger-
like patterns that further increase its surface area and destabilize the metal. (B) The areal footprint of a drop of EGaIn as a function of time and potential identifies the critical potential above which spreading occurs without bound (solid circles) and below which the droplet adopts equilibrium shapes (hashed symbols). The inset photographs show the end states after 35 s of the indicated voltage[48].

Electrochemical deposition or removal of the oxide layer on the liquid gallium alloy surface was utilized to control the interfacial tension of a liquid metal by Khan et al[48]. As excellent surfactants for metals, surface oxides can be deposited or removed speedily and can control the interfacial tension of liquid metal from \( \sim 500 \) mJ/m\(^2\) to near zero by very low voltages, which is completely reversible. The dramatic change of the interfacial tension results in various electrohydrodynamic phenomena. The manipulatable ability of the interfacial properties of the metal offer multiple opportunities for potential applications in electronic devices.
Figure 1.17 (A) Inducing a flow of liquid metal into an upward-tilted capillary channel (~0.9 mm inner diameter (ID)) by application of a voltage in the presence of 1 M NaOH. (B) Controlling the shape and direction of a metal drop, causing it to flow into an open T-shaped Plexiglas channel submerged in 1 M NaOH solution using only voltage. Switching the position of the counter electrode at different points (B, ii-iv), guides the direction of the metal droplet. (C) Side view of a small droplet of EGaIn pumped out of a 0.5-mm ID polymer tube at 20 mL/h in 1 M NaOH. The metal forms droplets in the absence of potential. (D) Formation of an oxide-coated liquid metal fibre coming out of the tube at 5 V[48].
The spreading of EGaIn at oxidative potentials was employed for manipulating the morphology of the metal. For instance, the liquid metal can be induced to flow by oxidative potentials in the electrolyte, as shown in Figure 1.17A. Likewise, the locomotion of the metal in an open channel can be directed by the position of a counter electrode in the electrolyte, as shown in Figure 1.17B, as the spreading metal moves prone to the counter electrode. Metastable fibres can be formed by using oxidative potentials when the metal is extruded from a syringe, as shown in Figure 1.17D. Without the applied potential, metal flows out of the end of a capillary tube, forming beads that fall sequentially due to the effect of gravity, as shown in Figure 1.17C.
Figure 1.18 Working mechanism of the reversible liquid metal deformation. (A) Schematic illustration of the experimental setup without an external power supply when the gallium droplet is placed in the NaOH solution. (B) Schematic illustration of the gallium droplet surface charge redistribution when the direct power is applied. (C) The surface tension dominates the deformation of the liquid metal object with the accumulation and dissolution of the oxide layer[49].

The reversible shape transformation phenomenon in liquid metal was discovered by Zhang et al[49]. Both electrolytic oxidation and the dissolution effect are the main reasons for large scale material deformation. Further, to identify the major factors determining the deformation behaviour, a series of conditions have been investigated, such as the concentration of the solution, the acid-base property of the solution, the volume of the gallium object, etc.
Figure 1.19 Spatiotemporal evolution of a 160 µL EGaIn droplet in a circular open-top channel containing 0.25 mol/L NaOH solution. The inset shows a magnified image of the squeezed metal droplet, in which small bubbles are observed[50].

A self-fuelling motor based on liquid metal with aluminium fuel was developed by Zhang et al[50]. The milli-/centimeter size of liquid metal droplets can achieve a very high speed in aqueous solution and maintain its unidirectional motion for more than one hour without any extra energy. In order to go through a narrow channel which is smaller than the diameter of liquid metal, the motor can self-deform its shape. This extraordinary ability, which comes from the unique properties of liquid metal, makes the motor suitable for some special jobs. The mechanism has been studied theoretically and experimentally.

Figure 1.20 (a) Schematic diagram of an EGaIn drop in contact with an Ag/Au layered film on a glass slide, showing the electrons migrating from the liquid metal to the film, leading to proton reduction and the formation of hydrogen bubbles on both sides of the film. (b) Top-down and (c) bottom-up snapshots of an EGaIn drop in contact with a 90 nm silver/10 nm gold film and moving right to left in 2 M HCl solution. Dotted circles highlight the EGaIn drop[51].
A novel way to manipulate the motion of liquid metal droplets along prepared metallic film lines was demonstrated by Mohammed et al. [51]. The metallic thin films (~100nm thick and ~1 mm wide) were wetted and reacted with the liquid metal, which generated a force leading to the acceleration of the liquid metal droplet. The liquid gallium tends to wet and stay on the substrate because of its oxide skin and gravity. Unless an acidic medium is employed, the droplet can move quickly along the metallic paths and even go uphill at more than 20 degrees inclination angle.

1.5 Motivations

As overviewed in the literature review, room temperature liquid metals such as gallium and gallium alloys have attracted great attentions due to their interesting chemical, physical and mechanical properties at room temperature. Some fascinating phenomena have been discovered, including deformation, self-rotation, planar locomotion and spreading and so on. Giant deformation at room temperature in liquid metals such as gallium and gallium alloys is caused by the significant reduction of the surface tension of liquid metals due to the formation of oxide on the liquid metal surface under application of voltage. The giant deformation capability can lead to an enhanced capillary effect in thin tubes, migration of liquid metal droplets on a solid surface, and significant shrinkage of liquid metal. The liquid metals retain their liquid states for all these deformation phenomena at room temperature. The deformation from a liquid metal droplet can be reversible, i.e. the liquid metal can return to its initial spherical shape after the voltage is switched off. These phenomena make room temperature liquid metal potentially useful for soft robotics, microfluidic applications, and stretchable soft electronics.
Gallium is a rare near-room-temperature liquid metal with many unique properties. Liquid metal gallium possesses remarkable properties, such as high electrical conductivity, high thermal conductivity, high surface tension, extremely low vapour pressure, and low toxicity. The melting point of gallium is 29.8 °C.

Although liquid gallium has already been studied in some areas, there are still lots of opportunities for new phenomena that need to be explored, due to many intrinsic and easily neglected properties of the liquid gallium. For example, gallium has an extraordinary property that it can stay in the liquid state (supercooled state) when the temperature is reduced to a surprising degree (-28.2 °C). So, it is more convenient to manipulate gallium in its supercooled state at room temperature.

In this thesis, three effects: 1) spreading effect of liquid gallium, 2) spreading effect of supercooled liquid gallium; and 3) heartbeat effect of liquid gallium have been observed and studied systematically. Different conditions, such as voltage, types and concentrations of the electrolyte, electrode material and geometry, droplet size were investigated. The mechanisms at play for each effect are also studied. The present studies are expected to promote the exploration of liquid metal phenomena in their fundamental understanding as well as potential applications.

1.6 References


2 CONTROLLED REVERSIBLE DEFORMATION OF LIQUID GALLIUM

2.1 Introduction

Rigid materials, the components of most modern machines, have many limitations when the machines are required to change their shapes to make them suitable for different working environments, such as working in a narrow space or passing through a hole with a small diameter. In these situations, soft machines, especially those with controlled changeable shapes, are superior to the traditional rigid machines. Due to the unique special properties of the soft machines, many studies have been focused on the improvement of the control approach, such as pneumatic actuation[1, 2], electric field-induced[3, 4], magnetic force[5], biomimetic propulsion[6], light-driven rotation[7], materials-based actuation[8], temperature or pH actuation[9], and surface-tension-driven self-folding[10]. Comparing these methods, the electric field has significant advantages because it is simple to control its intensity, frequency, and phase.

In addition, many types of materials have been studied as components for soft mechanics, including hydrogels[9, 11], photo-crosslinked polymers[12], acrylonitrile butadiene styrene (ABS)[2], and various liquids[13]. Besides these materials, liquid metal, which is soft, stretchable, conductive, and can change its morphology, is an ideal choice for the soft machines[14-18]. Recently, many fascinating liquid metal phenomena are being exploited, such as liquid metal pumps[19], memristors, ion
sensing, antennas[4], printable electrocardiography (ECG) electrodes[20], etc. Due to its low melting point around room temperature, gallium (~30 °C melting point) can be in the liquid phase near room temperature. Furthermore, it has outstanding physical properties, such as super-compliance in the liquid phase, high surface tension[21], favorable electrical conductivity[21], extremely low vapour pressure, and low toxicity[22]. Due to its large surface-area-to-volume ratio and large surface tension, the liquid metal demonstrates remarkable performance in terms of changing its morphology, and the process of deformation can be driven by an external electric field[23]. This performance gives gallium and its alloys promise for fabrication into soft machines which require shape deformation rather than the traditional rigid materials.

A previous deformation experiment demonstrated that the liquid metal can be deformed from a spherical shape to a flat sheet[23]. This shape change results from the generation of gallium oxide, which reduces the surface tension of droplets of gallium or its alloys. Therefore, it is imaginable that if the oxide surface were removed, the droplet of gallium would recover its original spherical morphology because of the large surface tension of gallium and its alloys.

In this study, an electric field which generated by a DC voltage power supply and chemical solutions were utilized to control the production of the oxide layer surrounding a gallium droplet. Because the oxide layer reduces the surface tension of the droplet, reversible deformation between spherical state and unfolded state occurs. Furthermore, different voltages, electrolyte solution types, electrolyte concentrations
and volumes of gallium were used in order to clarify the factors which can affect the shape of the reversible deformation.

2.2 Experiment

2.2.1 Chemical properties

Gallium with 99.99% purity was purchased from Qinghe Jiarun Metal Materials CO., LTD, China, as shown in Figure 2.1. Three kinds of solutions, including acid solution (HCl), salt solution (NaCl), and alkali solution (NaOH), with different concentrations, were injected into a Petri dish to immerse the gallium droplet. 0.1 mol/L, 0.2 mol/L, and 0.5 mol/L HCl solution were prepared by mixing 37% HCl solution and deionized water. 0.5 mol/L NaOH solution was formed by mixing a solid 99% NaOH capsule and deionized water. 0.5mol/L NaCl solution was prepared by mixing 99% NaCl crystal and deionized water. All the deionized water was prepared by Purelab Ultra Elga.
Figure 2.1 Liquid metal gallium with 99.99% purity at room temperature. Solid gallium, which had been sealed in a plastic bottle, was placed in a Petri dish and heated to 34 °C, so that it melted to the liquid phase.

2.2.2 Spreading of gallium droplet

Gallium was heated up to 30 °C to be melted into liquid state then extracted by a syringe. The syringe was mounted onto a Goniometer system (Dataphysics OCA15, Germany) that can drip out liquid with the precision of 1 µL. We use this system to accurately measure the volume of gallium droplets discussed in this thesis.

50 µL, 100 µL, and 150 µL gallium droplets were gathered in glass Petri dishes respectively with different solutions. Each one was placed on a heater (BANTE MS400) which kept the temperature of the solution at 34 °C. A thermocouple was placed in the solution and touched the bottom of the Petri dish to monitor its temperature. A piece of blue reference paper with 10 mm*10 mm grids is placed under the Petri dish. A copper wire anode was connected to the liquid gallium droplet, and a copper wire cathode was placed in the solution, in which the distance between the two electrodes was 6 centimetres. The applied DC voltages were supplied from 0 to 20 V by a GW laboratory DC power supply GPS-1850. A camera was placed over the Petri dish and recorded the whole progress of the experiment by 1080p, 30fps video.

2.2.3 Area Measurements

The camera started to film the droplet when the power supply was switched on. The power supply was switched off after each droplet reached its maximum area or after it separated from the copper wire due to excessive spreading. The images were then analysed in ImageJ to determine the areal footprint.
2.3 Results

Figure 2.2 Mechanism behind the reversible deformation of the liquid gallium droplet. (A) Diagram of the experimental set-up before applying the DC voltage. (B) Diagram of the deformation of the gallium droplet after DC voltage was applied.

Figure 2.2A is a schematic illustration giving a cross-sectional view of the experimental set-up. The liquid gallium droplet and electrolytes were placed in the glass Petri dish, which is insulated and transparent. Two copper wires, each with a diameter of 0.5 mm, acted as the two electrodes, one in contact with the liquid gallium, while the other is put into the electrolyte solution. The distance between the two electrodes was kept constant at 6 centimetres. In order to investigate the effects
of electrolytes on spreading and reversibility, three electrolytes, sodium hydroxide, sodium chloride, and hydrogen chloride solutions, were studied.

When a liquid gallium droplet is put into the NaOH solution without applying any external DC voltage, the droplet takes on a spheroidal shape, as shown in Figure 2.2A, due to the large surface tension of gallium. Meanwhile, the alkaline hydroxide solution reacts with the gallium and forms gallate salt, which contains $[\text{Ga(OH)}_4]^-$ [24]. Therefore, negative charges are accumulated on the surface of the gallium droplet, and the negatively-charged surface induces a positive charge layer generated nearby the droplet. The positive and negative charge layers form a diffuse electrical double layer (EDL), which can be considered as a capacitor.

This model is known as electrocapillarity, According to the study of Grahame in 1947 [25], the surface tension of a gallium droplet can be described by the following equation.

$$\gamma = \gamma_0 - \frac{1}{2} c V^2 \quad (2.1)$$

where $\gamma_0$ is the initial surface tension of the gallium droplet, $c$ is the capacitance of the electrical double layer (EDL) per unit area, and $V$ is the potential difference across the electrical double layer.

When no external voltage is applied to the electrodes, the electrical double layer causes a potential difference $V$ in Equation (2.1) which has a nonzero value, and this implies that the surface tension $\gamma$ is less than the maximum value $\gamma_0$. In addition to the effect of the gravity of the droplet, the droplet tends to be slightly flat as shown in Figure 2.2B.
After an external voltage is supplied between the two electrodes, the distribution of the negative charge on the droplet surface and the positive charge accumulated nearby the droplet surface are changed. When the voltage across the EDL is not high enough to induce an electrochemical reaction, positive charge is injected into the gallium droplet via the anode, which neutralizes the negative charge on the gallium surface. The potential difference across the EDL is reduced until all the negative charge on the surface is neutralized by the injected positive charge supplied by the external power supply. At that time, \( V \) is equal to zero, and \( \gamma \) achieves its maximum value \( \gamma_0 \).

Under the continuous effect of the external voltage, the potential difference across the surface of the droplet increases after it reaches zero. Conversely, positive charge accumulates on the surface of the droplet and negative charge is induced surrounding the droplet. According to Equation (3.1), the surface tension \( \gamma \) decreases due to the increased potential difference, which reduces the height of the droplet compared to the value when the charge on the droplet surface is zero.

A redox reaction proceeds when the applied voltage is high enough. Hydrogen is produced at the cathode, while two reactions occur on the anode: The oxidation reaction in the solution generates oxygen on the anode and gallium droplet. Furthermore, the oxygen oxidizes the gallium surface, which produces Ga\(_2\)O\(_3\) on the surface of the liquid gallium droplet[26].

The oxide layer plays a significant role in the droplet spreading performance. On the one hand, according to a study of the Khan et al. in 2014[27], an oxide layer
forms between the solution and the liquid metal. The original metal-solution interface, which has large interfacial tension, is replaced by new metal-oxide and oxide-solution interfaces, which lower the surface tension of the liquid metal. On the other hand, the study of Ladd et al. in 2013 [28] indicated that the rapidly formed oxide could stabilize the structure of the droplet, which would restrict the liquid metal deformation. The deformation performance is determined by the combined effects of the oxide.

2.3.1 Acid solution

2.3.1.1 Effect of the volume of liquid gallium on the deformation performance.

Figure 2.3 Investigation of the time-dependence of the reversible deformation of liquid gallium droplets in the acid solution (0.1 mol/L HCl aq.). The vertical coordinate is the relative change in the top-view area, where $A$ denotes the initial top-view areal footprint and $\Delta A$ denotes the difference in the top-view areal footprint from the initial areal footprint. The volumes of the gallium droplets are 50 $\mu$L, 100
µL, and 150 µL, respectively. The external voltage is 1.5 V, and the distance between the two electrodes is 6 centimetres.

Figure 2.3 demonstrates the effect of the volume of liquid gallium on the reversible deformation. The horizontal coordinate refers to the time from when the external power supply was turned on. The vertical coordinate refers to the relative change in the area of a top-view of the droplet, where \( \Delta A \) denotes the value of the top-view area minus the initial top-view area when the external power supply is off, and \( A \) denotes the value of the initial top-view area. To inspect the influence of the liquid gallium volume on the deformation performance, three droplet volumes, 50 µL, 100 µL, and 150 µL, were studied. As shown in Figure 2.3, the relative changes in shape for all three increased sharply after a 1.5 V DC voltage was applied. At around 34 seconds, the relative changes in the three volumes gallium achieved their maximum values. The maximum value of the relative change in the top-view area of the 50 µL droplet is half those of the values of the 100 µL and 150 µL droplets, respectively. The maximum top-view areas of the 100 µL and 150 µL droplets are approximately equal. On removing the DC voltage, all of the top-view areas decreased. The rate of decrease was smaller than the rate of increase. At the end, the top-view areas were stable and were larger than the initial values.
Figure 2.4 Snapshots of top-view of droplets, showing reversible deformation variation with time of the liquid gallium droplets with volumes of (A) 50 µL, (B) 100 µL, and (C) 150 µL.

The changes in the relative top-view area of the 100 µL gallium droplet are similar to those of the 150 µL gallium droplet, while the rate of increase of the relative changes of the top-view area of the 50 µL gallium droplet is smaller than that for the other two volumes. Although the maximum values of the three volumes of gallium were achieved at the same time, the value for the 50 µL gallium droplet is smaller than the values for the 100 µL and 150 µL gallium droplets. Similar to the increasing process, the decrease rate for the 50 µL gallium droplet is smaller than the rate for the other two volumes. The 150 µL gallium droplet has the largest rate of decrease and spends the least time on decreasing to a stable state. In the end, all of the three top-view areas of the equilibrium shapes of the three droplets are a little
larger than their respective initial values because of the oxide residues on the surfaces of the droplets.

2.3.1.2 Effect of the concentration of acid solution on the liquid gallium deformation.

Figure 2.5 Investigation of time-dependence of the reversible deformation of liquid gallium droplets in the acid solution with different concentration. The vertical coordinate is the relative change in the top-view area, where $\Delta A$ denotes the difference between the top-view area and the initial top-view area and $A$ denotes the initial top-view area, respectively. The experiments were implemented in 0.1 mol/L, 0.2 mol/L, and 0.5 mol/L HCl solutions, respectively. The volume of the gallium droplet is 100 $\mu$L, the external voltage is 1.5 V, and the distance between two electrodes is 6 centimetre.

Figure 2.5 demonstrates the effect of the concentration of the acid solution on the reversible deformation. Taking the solution concentration into account, three different concentrations, 0.1 mol/L, 0.2 mol/L, and 0.5 mol/L HCl, have been studied.
As shown in Figure 2.5, after external 1.5 V DC voltage was applied, all of the top-view areas of droplets increased sharply. The largest rate of increase for the relative change of in the top-view area is for the droplet which was immersed in 0.2 mol/L HCl solution, and the smallest one is for the droplet in the 0.1 mol/L solution. Although the rate of increase in 0.5 mol/L solution is the median value, the droplet in the solution with this concentration achieved its maximum top-view area in the least amount of time, and its maximum top-view area is the smallest compared to the maximum values of the top-view areas of the other two droplets in lower concentration solutions. The droplet in the 0.2 mol/L solution spent 33 seconds on reaching its maximum top-view area, which is shorter than the 35 seconds for the 0.1 mol/L solution. In addition, the maximum value of the relative change in the top-view area in the 0.2 mol/L acid solution, 5.54, is larger than the value for the droplet in the 0.1 mol/L acid solution, which is 5.30.
Figure 2.6 Snapshots of top-views of reversible deformation of 100 μL liquid gallium droplets with time in solutions with concentrations of (A) 0.1 mol/L HCl, (B) 0.2 mol/L HCl, and (C) 0.5 mol/L HCl.

When the external power supply is turned off, all of the three extended droplets can recover their original spheroidal shape. The fastest time (1 second after power off) occurs in the 0.5 mol/L acid solution, and the slowest time (more than 70 seconds after power off) occurs in the 0.1 mol/L solution. The reason is that the higher concentration of the solution dissolves the gallium oxide layer faster, which causes a shorter time of recovery.

In other words, at the spreading stage of the experiments, the higher concentrations of acid in the solution result in a shorter time from their original state to the maximum top-view area. The largest maximum relative change in the top-view area is for the droplet spreading in 0.2 mol/L acid solution. When the external power supply is turned off, the recovery time of the droplet is inversely proportional to the concentration of the acid solution.

2.3.2 Alkali solution

2.3.2.1 Effect of the volume of the liquid gallium droplet on the deformation performance.
Figure 2.7 Investigation of the time-dependence of the reversible deformation of liquid gallium metal in the alkaline solution (0.5 mol/L NaOH aq.). The vertical coordinate refers to the relative change in the top-view area, where $\Delta A$ denotes the difference between the top-view area and the initial top-view area and $A$ denotes the initial top-view area, respectively. The volumes of the gallium droplets are 50 µL, 100 µL and 150 µL, respectively. The external voltage is 15 V, and the distance between the two electrodes is 6 centimetre.

Figure 2.7 demonstrates the effect of volume of the liquid gallium droplet on the reversible deformation in alkaline solution. To investigate the influence of the liquid gallium droplet volume on the deformation performance, 3 typical volumes of the droplets, 50 µL, 100 µL, and 150 µL, were studied. As shown in Figure 2.7, for all of the three, the relative change in the morphology increased sharply after the external DC voltage was applied. The 50 µL liquid gallium droplet spread faster than the other two droplets, and it achieved its maximum top-view area first. The 100 µL liquid gallium droplet spent more time on extending than the 50 µL gallium droplet. The 150 µL droplet spent the most time on extending, with the largest relative
change in its top-view area among all of the three droplets, while the 100 µL liquid gallium droplet had the smallest relative change value.

Figure 2.8 Snapshots of top-views of reversible deformation variation with time of the liquid gallium droplets with volumes of (A) 50 µL, (B) 100 µL, and (C) 150 µL in alkali solution (0.5 mol/L NaOH aq.).

After their top-view areas achieved their maximum values, the morphology did not change while the external voltage was applied. When the external power supplied was turned off, all of the three extended droplets recovered their original spheroidal shape as a result of the dissolution of the oxide layer. The three recovery times are approximately equal to each other, around 3 s. The extension time, which is taken from their original state to the maximum top-view area, is proportional to the volume of the liquid gallium droplet. The largest maximum relative change in top-view area is for the 150 µL droplet, which has the largest volume in three comparative experiments. In the recovery stage, the four recovery times are close to each other.
This indicates that the external voltage is unrelated to the recovery time in the reversible transformation performance of the liquid gallium droplets.

2.3.2.2 Effects of the applied voltage on the liquid gallium deformation.

Figure 2.9 Investigation of the time-dependence of the reversible deformation in an alkali solution for different applied voltages. The vertical coordinate refers to the relative change in the top-view area, where $\Delta A$ denotes the difference between the top-view area and the initial top-view area and $A$ denotes the initial top-view area, respectively. The experiments were implemented in 0.5 mol/L NaOH solution. The volume of the gallium droplets is 50 µL, and the distance between the two electrodes is 6 centimetre. The external voltage was varied from 5 V to 20 V.

Figure 2.9 demonstrates the effect of applied voltage on the reversible transformation in alkaline solution. To investigate the influence of the applied voltage on the deformation performance, 5 V, 10 V, 15 V, and 20 V external applied
voltages were studied, respectively. As shown in Figure 2.9, in three of the four, the relative change in the morphology increased sharply after the external DC voltage was applied, although the spreading rate at the applied voltage of 5 V was much lower than the rates at the other voltages in the experiment. The liquid gallium droplet at 20 V applied voltage achieves its maximum top-view area by spending the shortest time to reach its maximum deformation, which is a little faster than for the droplet under 15 V external voltage.

Figure 2.10 Snapshots of top-views of reversible deformation with time dependent of liquid gallium droplets with applied external voltage of (A) 5 V, (B) 10 V, (C) 15 V, and (D) 20 V in alkali solution.

Although the droplet under applied voltage of 5 V had the slowest extension rate, the value of the relative change in its top-view area is larger than for the other
voltages. The value recorded under 10 V external voltage is smaller than the value for the 5 V external voltages but larger than the values under higher external voltage. The smallest value was recorded when the external voltage was 20 V. After their top-view areas achieved their maximum value, respectively, the morphology did not change while the external voltage was applied. When the external power supplied was turned off, all three extended droplets recovered to their original spheroidal shape as a result of the dissolution of the oxide layer. The three recovery times are approximately equal to each other and around 4 s. Therefore, the increased external voltage results in a decreased extension time from power on to the maximum top-view area, resulting in an increased value of the relative change of the top-view area. In the recovery stage, the four recovery times are close to each other. This indicates that the external voltage is unrelated to the recovery time in the reversible deformation performance of the liquid gallium.

2.3.2.3 Special case
Figure 2.11 Snapshots of top-view of the liquid gallium droplet as it jumps from anode to cathode.

Very interestingly, we found that the liquid gallium droplet could escape from the anode and jumps to the cathode electrode. As shown in Figure 2.11, a 100 µL liquid gallium droplet was first placed in 0.5 mol/L NaOH solution at 34 °C. After a 5 V was applied to the electrodes, the droplet spread quickly and asymmetrically. As the cathode attracted the liquid gallium droplet, after 10 seconds, the majority of the metal stretched in the direction of the cathode and formed a two-winged shape.
Finally, the liquid gallium leaves the anode and jumps to the cathode. Normally, the liquid gallium droplet will not disconnect from the anode, because the adhesion of the liquid gallium to the anode is much larger than the attractive force from the cathode. We believe that when a voltage is applied, some vortices are created in the electrolyte. There are two vortices on each side of the liquid gallium, and these vortices help the liquid gallium to escape from the anode.

2.3.3 Salt solution

![Graph](image)

Figure 2.12 Investigation of change in morphology change in the pH neutral solution. The vertical coordinate refers to the relative change in the top-view area, where $\Delta A$ denotes the difference between the top-view area and the initial top-view area and $A$ denotes the initial top-view area, respectively. The experiments were implemented in 0.5 mol/L NaCl solution. The volume of the gallium droplet is 100 $\mu$L, and the distance between the two electrodes is 6 centimetre. The external voltage is 10 V.
The insets are snapshots of top-views of the droplet, showing the progress of the deformation of the liquid gallium.

Figure 2.12 illustrates the performance in a pH neutral solution. 0.5 mol/L NaCl solution was studied. As shown in Figure 2.12, compared to the performance in acid or alkaline solution, the relative change in the top-view area of the liquid gallium droplet is small (less than 1), and then the shape is fixed. After withdrawing the external voltage, the morphology of the liquid gallium droplet fails to recover to its original state. This indicates that reversible deformation cannot occur in a pH neutral solution. Because there is no hydrogen or hydroxyl in the pH neutral solution, the oxide that is produced cannot be dissolved, which stops the recovery process from happening. The relative changes in deformation in alkaline or acid solution are much larger than the relative change in the salt solution. After power off, the droplet of gallium in the alkaline solution or the acid solution can change back to the original morphology. Nevertheless, the droplet of gallium cannot return all the way back to its original state. The deformation in the salt solution is not reversible.

2.4 Conclusions

In summary, the experiments have demonstrated that spreading can occur in alkaline or acid solution under an applied voltage, and the morphology can be restored when the external power supply is turned off, which means that the deformation is reversible. In the pH neutral solution (NaCl solution), however, the top-view area of the liquid gallium is only extended a little, and then it is fixed in this shape, while the morphology cannot be restored to its original state by the
withdrawal of the voltage. The experiments indicate the important role of oxide in the reversible transformation of the liquid gallium. In acid or alkaline solution, gallium oxide is produced by the oxidative reaction on the anode when there is an external applied voltage. It is dissolved due to the reaction with the hydrogen or hydroxyl ions. Under the combined effects of production and dissolution, oxide lowers the interfacial tension of the liquid gallium surface, but the amount of oxide is not enough to stabilize the unbalanced shape. This results in the spreading performance. Furthermore, when the external power supply is turned off, there is no power to drive the oxidation reaction, but the dissolution reaction is continuous. The decreased oxide results in the recovery of interfacial tension, which drives the morphology back to its spherical shape. In contrast, no dissolution of oxide occurs when the solution is the pH neutral solution. After the external power supply is connected, the increased oxide lowers the interfacial tension of liquid gallium first, which result in the extension of the footprint area in the beginning. Due to the oxide progressively accumulated on the surface, the shape is stable, as it is restricted by the oxide. When the voltage is turned off, the oxide still exists on the surface of the gallium, which prevents the morphology from returning to its initial spheroid.

2.5 References


3 SUPERCOOLED GALLIUM

3.1 Introduction

Recently, room-temperature liquid metal has been gaining extensive interest because of the discovery of new liquid-metal phenomena,[1-5] which have great potential applications for soft robotics, microfluid applications, and stretchable soft electronics.

The supercooling effect is the process by which the temperature of a liquid falls below the freezing point, but there is no transition to its solid state. The various properties of liquids can be changed sharply in the supercooling state, such as the isobaric heat capacity[6] and isothermal compressibility[7] of liquid water.

Gallium is a rare near room temperature liquid metal with many unique properties. The melting point of gallium is 29.8 °C[8], and it can stay in the liquid state when the temperature drops down to an extraordinary degree (-28.2 °C).

This chapter describes a method to pattern materials which change from liquid to solid into certain shapes without a printer or mould at room temperature. The ability to mould a solid into certain shapes is usually limited to making a mould. Here, we show that it is possible to form a supercooled liquid metal at room temperature into a variety of shapes by combined liquid metal deformation and the supercooling property.
3.2 Experiment

3.2.1 Chemical properties

Gallium with 99.99% purity was purchased from Qinghe Jiarun Metal Materials Co., LTD, China. An acid solution (HCl) and an alkali solution (NaOH) were injected into a Petri dish to immerse a gallium droplet. 0.5 mol/L HCl solution was prepared by mixing 37% HCl solution and deionized water. 0.5 mol/L NaOH solution was formed by mixing a solid 99% NaOH capsule and deionized water. All the deionized water was prepared by Purelab Ultra Elga.

3.2.2 Crystallization of supercooled liquid gallium

Gallium was heated above 35 °C and melted to the liquid state, and then was placed in a 90 mm diameter glass Petri dish which was insulated and transparent.

3.2.3 Spreading of supercooled gallium droplets

Gallium was heated above 35 °C and melted to the liquid state, and then 150 µL gallium droplets were placed in glass Petri dishes with different solutions. A piece of blue reference paper with 10 mm × 10 mm grids was placed under the Petri dish. A copper wire anode was connected to the liquid metal droplet, and another copper wire cathode was placed in the solution, so that the distance between the two electrodes was 6 centimetres. A 1.5 V DC voltage was supplied by a GW laboratory DC power supply, model GPS-1850. A camera was placed over the vessel and recorded the whole progress of the experiment via 1080p, 30fps video.
3.2.4 Area Measurements

The camera started to film the drop when the power supply was switched on. The power supply was switched off after each droplet reached its maximum area, or after it separated from the copper wire due to excessive spreading. The images were then analysed in ImageJ to determine the areal footprint.

3.3 Results

3.3.1 Crystallization of supercooled liquid gallium

3.3.1.1 Shaking the supercooled liquid gallium

Supercooled water can be crystalized to ice when it are impacted by an external force. This study shows, however, that an external force cannot solidify supercooled liquid gallium.

Figure 3.1 Snapshots of top-view of supercooled liquid metal gallium pool in a glass vessel a) before shaking, b) during shaking, and c) after shaking.

Solid gallium was heated above 35 °C to melt it to the liquid state. Then, the liquid gallium was tilted in a glass vessel 90 mm in diameter. The vessel was
insulated and transparent, and was placed at room temperature to allow its temperature to cool down to 22 °C, as shown in Figure 3.1a. The glass vessel was shaken sharply for 15 seconds, so that a liquid metal wave can be seen in Figure 3.1b. Nevertheless, liquid metal crystallization was not observed in this experiment. The liquid metal gallium remained in its liquid state.

3.3.1.2 Placing a silicon crystal in the supercooled liquid gallium

Figure 3.2 Snapshots of top-view of supercooled liquid metal gallium pool in a glass vessel. a) A small piece of silicon crystal was placed on the surface of the liquid metal gallium. b) Shaking the glass vessel, and c) after shaking

The effect of putting a silicon crystal into the supercooled liquid metal gallium was studied. After the same preparation as for the previous experiment, a piece of silicon crystal with dimensions of about 1×2.5×2.5 mm³ was placed on the surface of the supercooled liquid gallium (Figure 3.2a). The glass vessel was shaken sharply for 15 seconds (Figure 3.2b). Also, the silicon crystal was kept in full contact with the liquid metal by using tweezers. Nevertheless, liquid metal crystallization was not observed in this experiment. The liquid metal gallium remained in its liquid state.
3.3.1.3 Placing a piece of solid gallium on supercooled liquid gallium

The effect of placing a solid gallium seed on the surface of supercooled liquid metal gallium was obtained. A piece of solid gallium $0.5 \times 1 \times 3$ mm$^3$ in dimensions was placed on the surface of the supercooled liquid gallium to act as a seed. Solid gallium started forming around the gallium seed. After 10 seconds, the liquid metal gallium was crystallized to more than five times the top area of the gallium seed (Figure 3.3b). As the solid gallium formed, the heat of freezing was absorbed.
3.3.2 Crystallization with spreading under certain DC voltages

3.3.2.1 The crystallizing process occurs along with the spreading process

Figure 3.4 Investigation of time-dependence of the spreading and crystallization of 150 µL supercooled liquid metal droplet in 0.5 mol/L NaOH solution at 22 °C. The vertical coordinate is a relative change in the top-view area, where $A$ denotes the top-view areal footprint, and $A_0$ denotes the initial top-view areal footprint. The external voltage was 1.5 V, and the distance between the two electrodes was 6 centimetres.

Spreading and crystallization of supercooled liquid metal gallium droplets have been observed synchronously. Figure 3.4 indicates that the change in droplet area due to the spreading of the droplet and the change in the crystallization area depend on time. The top-view footprint area of the droplet increased sharply after the external DC voltage was applied for 2 seconds, so that it was nearly three times larger than the initial top-view footprint area. Then, the relative change in the footprint area for droplet spreading decreased to 2.45 in about 2 seconds. After that, the relative change in the footprint area increased steadily. The trend in the spreading
process is the same as what we described in chapter 3 Controlling large scale reversible deformation of liquid metal objects. The change in the crystallization area is different from the change in the spreading area. There is no obvious solid gallium formation before 8 seconds. Then, the relative size of the footprint of the crystallization area increased gradually.
Figure 3.5 Snapshots of top-view of spreading and crystallization of 150 µL supercooled gallium droplet in 0.5 mol/L NaOH solution at 22 °C.

Figure 3.5 shows that the supercooled gallium droplet deforms and crystallizes simultaneously in 0.5 mol/L NaOH solution at 22 °C. Firstly, the gallium droplet remains in a spherical shape. After 1.5 V voltage is applied, the droplet extends into a pancake shape immediately, as shown in Figure 3.5b. From the top-view, the area expands to more than 2 times the initial area. The crystallization of liquid gallium has only just started and isn’t observed clearly at this time. Then, the surface tension of the liquid gallium is broken, so that the droplet extends into a tree structure towards the cathode direction (Figure 3.5c-l). Crystallization of the gallium appears on one side of the gallium droplet and grows slowly through the spreading footprint. In the end, the entire liquid metal droplet is crystallized (Figure 3.5l).

3.3.2.2 The crystallizing process occurs after the spreading process

Figure 3.6 Investigation of the time-dependence of the spreading and crystallization of a 150 µL supercooled liquid metal droplet in 0.5 mol/L HCl solution at 20 °C. The
vertical coordinate is the relative change in the top-view area, where $A$ denotes the top-view areal footprint, and $A_0$ denotes the initial top-view areal footprint. The external voltage is 1.5 V, and the distance between the two electrodes is 6 centimetres.

Deformation and crystallization of a supercooled liquid metal gallium droplet have been observed simultaneously. Figure 3.6 shows the time dependence of the changes in the droplet spreading area and the crystallization area. The top-view footprint area increased sharply as the external DC voltage was applied over the first 2 seconds, so that it was nearly 1.5 times larger than the initial top-view footprint area. Then, the relative change of the footprint area for droplet spreading increased steadily to about 3 times the initial footprint area by 25 seconds after the voltage was applied. After that, the relative change in the footprint area starts to level off. The trend for the spreading process is the same as what was described in Chapter 3 Controlling large scale reversible deformation of liquid metal objects. The change in the crystallization area is different from the change of spreading area. There is no obvious solid gallium formation before 20 seconds from the application of voltage. Then, the relative footprint of the droplet spreading area increased gradually.
Figure 3.7 Snapshots of top-view of spreading and crystallization of 150 μL supercooled liquid metal droplet in 0.5 mol/L HCl solution at 22 °C.

Figure 3.7 shows how a supercooled gallium droplet deforms and crystallizes simultaneously in 0.5 mol/L HCl solution at 22 °C. Firstly, the gallium droplet remains in a spherical shape with a reflective surface. After 1.5 V voltage is applied, it extends to a pancake shape immediately, as shown in Figure 3.7b. From the top-view, the area expands to more than 1.5 times the initial area, and the top surface of the gallium turns black. The crystallization of liquid gallium has only just started at this stage and isn’t observed clearly at this time. After 20 seconds, crystallization appears on one side of the gallium droplet, which is observed as a non-reflective area. In the end, the whole liquid metal droplet is crystallized (Figure 3.7h).

3.4 Conclusions

In summary, reversible and irreversible deformations, as well as the simultaneous solidification of liquid gallium, were achieved in the supercooled liquid state of gallium at room temperature. The irreversible deformation and
transformation from liquid to solid can be triggered by using a gallium-coated electrode under electric field. These phenomena of supercooled liquid gallium have significant potential applications such as in soft artificial robots, tunable electronics, microfluids, microelectromechanical systems, and rheology. Importantly, our study reveals that room temperature liquid metals and supercooled liquid metals have fascinating properties, and more exciting phenomena are expected to be discovered in the future for various applications.

3.5 References


4 GALLIUM BEATING HEART

4.1 Introduction

In the previous chapter, the topic was the spreading of liquid gallium. This chapter reports on observations of new phenomena related to oscillation of liquid gallium in acid and base solutions; I call this oscillation the “beating gallium heart”.

Beating mercury is one of the well-known and interesting oscillations in electrochemical systems[1-10]. Kühne first observed liquid metal oscillation induced by chemical reactions. Lippmann reported the mercury heartbeat in 1873[1]. It has been generally understood that an electrocapillary effect was involved in the oscillation. After nearly a century, Keizer et al. in 1979 provided a detailed analysis of the mercury beating heart[2, 3].

In this chapter, we report the beating gallium heart in a circular graphite electrode in acid and base solutions without any strong oxidizing agent.
4.2 Experiment

4.2.1 Chemicals

Gallium with 99.99% purity was purchased from Qinghe Jiarun Metal Materials. Three kinds of solutions, including acid solution (HCl), salt solution (NaCl), and alkaline solution (NaOH), with different concentrations, were injected into the vessel so as to immerse a gallium droplet. 1 mol/L HCl solution was prepared by mixing 37% HCl solution and deionized water. 1 mol/L NaOH solution was adjusted with a solid 99% NaOH capsule and deionized water. A 0.5 mol/L NaCl solution was adjusted with 99% NaCl crystal and deionized water. All the deionized water was prepared by Purelab Ultra Elga.

4.2.2 Beating of Gallium heart

Gallium was heated to above 30 °C and melted to then liquid state, and then 50, 100 and 150 µL gallium droplets were placed in a glass vessel (diameter of 9 cm) with different solutions. The vessel was the placed on a heater (BANTE MS400), which kept the temperature of the solution at 34 °C. A thermocouple was placed in the solution and touched the bottom of the vessel to monitor its temperature. A piece of blue reference paper was placed under the vessel. A copper wire anode was connected to a graphite ring, which had an inner diameter of 10 mm and an outer diameter is 30 mm. The gallium droplet was placed in the graphite ring and touched its inner wall. A copper wire cathode was placed in the solution. The applied DC voltages were supplied from 0 to 20 V by a GW laboratory DC power supply, model GPS-1850. A camera was placed over the vessel and recorded the whole process of the experiment via 1080p, 30fps video.
4.2.3 Distance and Area Measurements

A camera started to film the droplet when the power supply was switched on and recorded the process of droplet oscillation. The images were then analyzed in ImageJ to determine the areal footprint. Meanwhile, the distances were measured in ImageJ, in which the distance was defined as the distance between the geometric center of the gallium droplet and the nearest point on the inner wall of the graphite ring electrode.

4.3 Results

Figure 4.1 Experimental setup and mechanism of the heart-beating phenomenon of the liquid metal droplet. (A) Diagram of the experimental setup before the external
DC voltage was applied. (B) Schematic illustration of top-view of one heartbeat cycle.

In Figure 4.1A, the top-view of the experimental set-up is sketched. A graphite ring and the electrolyte were placed in an insulated and transparent glass Petri dish, and a droplet of liquid gallium was put in the middle of the graphite ring. Two copper wires, each with a diameter of 0.5 mm, acted as the two electrodes. The cathode was inserted into the electrolyte, while the anode was in contact with the surface of a graphite ring electrode. In order to investigate the effects of electrolytes on the spreading and reversibility, three electrolytes were studied: sodium hydroxide, sodium chloride, and hydrogen chloride solutions. The applied voltage and the amount of gallium were altered to control the heartbeat performance of the liquid metal droplet.

Figure 4.1B shows the mechanism of the heartbeat experiment. As shown in Figure 4.1B(i), a liquid metal droplet is placed in the graphite ring electrode so that it touches the inner wall of the ring. The anode is in contact with the surface of the graphite electrode. As mentioned in Chapter 3, when the external voltage is applied, positive charge is injected into the liquid metal via the anode and the graphite ring electrode, which result in extension of the droplet. The extended droplet extrudes towards the inner wall of the graphite ring. The reaction from the inner wall of the ring on the liquid metal droplet pushes the droplet away from the inner wall, as shown in Figure 4.1B(ii). Under the effect of the reaction force, the droplet is detached from the ring, which cuts the connection between the droplet and the external power supply. In acid or alkaline solution, hydrogen or hydroxyl ions can
dissolve the oxide layer surrounding the liquid metal surface, which causes the top-view area to shrink. Under the effect of the partial force of gravity in parallel with the bottom of the Petri dish of the droplet (Figure 4.1B(iii)), the shrunken droplet returns back to its initial position to touch the inner wall of the graphite ring again (Figure 4.1B(iv)), which causes the next ‘heartbeat’ cycle.

Figure 4.2 Illustration of heartbeat phenomenon. The top graphs show the changes in the top-view area and the distance between the geometric centre of the top-view of the liquid metal and the closest point on the inner edge of the graphite ring, respectively, while the lower sequence of snapshots shows images of the “beating heart” in the liquid metal droplet over one heartbeat cycle.
Figure 4.2 (top) shows the changes in the top-view area of the droplet and the distance between the geometric centre of the top-view of the droplet and the inner wall of the graphite ring electrode. The horizontal coordinate refers to the time from when the voltage was switched on. The vertical coordinate for the upper graph represents the top-view area of the droplet, and the vertical coordinate for the lower graph represents the distance between the geometric centre of the top-view of the droplet and the inner wall of the ring. Both of these two curves are periodic and share the same frequency. The distance curve can be fitted by a sine wave function, which is shown in Figure 4.3.

![Distance changes over time fitted by a sine wave function](image)

Figure 4.3 Distance changes over time fitted by a sine wave function, as expressed by Equation (4.1).

\[ y = 3.56 + 0.87 \times \sin[\pi(x - 0.044) \div 0.175] \]  (4.1)

Figure 4.3 (bottom) contains images of the beating heart phenomenon over one period from 0.297 s to 0.66 s in the upper diagram. At 0.297 s, the distance and the top-view area achieve their minimum value, respectively. As top-view area expands in the photographs, the distance and the top-view area increase sharply. At 0.396 s, the reaction force on the liquid metal pushes the droplet away from the inner wall of
the ring electrode, while the top-view area achieves its maximum value in the period and then decreases to the value that it had before the external voltage was applied. The distance continues to increase until its rate of change is equal to zero, which is observed in the image at 0.495 s. Thereafter, the droplet moves towards the inner wall under the component of the gravitational force that is parallel to the bottom of the Petri dish. The distance decreases until the droplet touches the inner wall of the ring electrode again (at 0.66 s), and then the next cycle of the heart beating phenomenon occurs.

4.3.1 Effects of the applied voltage and the volume of the droplet on the beating heart phenomenon in alkaline solution (1 mol/L NaOH solution)

We analyzed the footprint areas and amplitudes of the gallium droplets as a function of the applied voltage and the volume of the gallium droplets. These experiments were carried out for gallium droplets with three different volumes and four different applied voltages. The tabulated results for three such volumes (50, 100, and 150 µL) and four such potentials (5, 10, 15, and 20 V) are presented later. For each gallium droplet volume and potential of applied voltage, the experiments were carried out for more than 5 minutes to evaluate the reproducibility. For the purpose of consistency, the footprint areas and amplitudes of the gallium droplets are shown with the same volumes of gallium droplets first.
Figure 4.4 Distance versus time curves for 50 µL liquid metal droplets showing the heartbeat phenomenon in the alkaline solution (1 mol/L NaOH aq.), when DC voltages of 5, 10, 15, and 20 V are applied at 34 °C. The vertical coordinate Distance denotes the distance between the geometric centre of the top-view of the liquid metal to the closest point on the inner edge of the graphite electrode.

Figures 4.4 – 4.9 show the top-view footprint areas and amplitudes of the oscillations of gallium droplets with the same volume for different applied voltages. Figures 4.10 – 4.11 show the top-view footprint areas and amplitudes of gallium droplets for the same potential of applied voltage with different liquid gallium volume.
Figure 4.5 Area versus time curves for the heartbeat phenomenon acting on 50 µL liquid metal droplets in the alkaline solution (1 mol/L NaOH aq.), when DC voltages of 5, 10, 15, and 20 V are applied at 34 °C. The vertical coordinate Area denotes the top view footprint area of the liquid metal droplet.
Figure 4.6 Distance versus time curves for the heartbeat acting on 100 μL liquid metal droplets in the alkaline solution (1 mol/L NaOH aq.) when DC voltages of 5, 10, 15, and 20 V are applied at 34 °C. The vertical coordinate Distance denotes the distance between the geometric centre of the top-view of the liquid metal droplet and the nearest point on the inner edge of the graphite electrode.

Our experimental observations can be summarized as follows:

1. As the voltage increases, the amplitude of the oscillation of the liquid gallium droplets (in the top view) shows almost no change for the 150 μL Ga droplets (Fig. 4.8) and decreases slightly for 100 μL droplets (Fig. 4.6). For the 50 μL gallium droplets, the amplitudes of the oscillations of the liquid metal
droplets at 15 and 20 V are less than one-third of those at 5 and 10 V, as shown in Figure 4.4.

Figure 4.7 Area versus time curves for the 100 µL liquid metal droplets for the “beating heart” in the alkaline solution (1 mol/L NaOH aq.), when DC voltages of 5, 10, 15, and 20 V are applied at 34 °C. The vertical coordinate Area denotes the top-view footprint area of the liquid metal droplet.

2. As the voltage increase, the footprint areas of the liquid metal gallium increase from about 35 to 45 mm² for the 150 µL droplets of Ga, as shown in Fig. 4.9. The footprint areas of the liquid metal gallium droplets are also inversely proportional to the voltage for the 50 and 100 µL gallium droplets.
(Fig. 4.5 and 4.7). For the 50 μL gallium droplets, the top-view footprint areas of the liquid metal droplets at 15 and 20 V are less than half of those at 5 and 10 V.

Figure 4.8 Distance versus time curves for the liquid metal heartbeat in the alkaline solution (1 mol/L NaOH aq.) for 150 μL droplets, when DC voltages of 5, 10, 15, and 20 V are applied at 34 °C. The vertical coordinate Distance denotes the distance between the geometric centre of the top-view of the liquid metal droplet and the nearest point on the inner edge of the graphite electrode.
Figure 4.9 Area versus time curves for the liquid metal heartbeat acting on 50 µL droplets in the alkaline solution (1 mol/L NaOH aq.), when DC voltages of 5, 10, 15, and 20 V are applied at 34 °C. The vertical coordinate Area denotes the top-view footprint area of the liquid metal droplet.
Figure 4.10 The relative change in distance as a function of time for liquid metal droplets with different volumes (50, 100, and 150 µL) in the alkaline solution (1 mol/L NaOH aq.) when 5 V DC is applied at 34 °C. Distance denotes the distance between the geometric centre of the top view of the liquid metal droplet the closest point on the inner edge of the graphite electrode. The symbols $\Delta D$ and $D$ denote the change in distance and the original distance before voltage was applied, respectively.

3. When the potential of the applied voltage is fixed, and the relative changes of footprint area are compared for liquid metal droplets with different volumes: The relative changes in footprint area are inversely proportional to the volume of liquid metal gallium in the droplet, and this holds for all the different voltages (Fig. 4.10).

4. The largest frequencies are achieved when the volume of the liquid gallium droplet is 50 µL with 15 and 20 V applied voltages, and these frequencies are 6.17 and 5.41 Hz, respectively. For the rest of the experiments, the frequencies of the heartbeat are from about 2.5 to 3.5 Hz.
Figure 4.11 The relative change of top-view footprint area with the time for different volumes (50, 100 and 150 µL) of liquid metal droplets in the alkaline solution (1 mol/L NaOH aq.) when 5 V DC is applied at 34 °C. The left vertical coordinate refers to the relative change in the top-view footprint area, where the symbols $\Delta A$ and $A$ denote the change in the top-view footprint area and the original top-view footprint area, respectively.

5. The relative changes in the amplitude of the oscillation are inversely proportional to the volume of the liquid metal gallium droplet at 5 V (Fig. 4.11). The relative changes in amplitude for the 100 and 150 µL droplets are about 3 and 2 times larger, respectively, than those for the 50 µL droplets at 15 and 20 V.
Figure 4.12 Effects of voltage and liquid metal volume on the frequency of the “heartbeat”.

Figure 4.12 shows the beating frequencies for liquid metal droplets with different volumes and applied voltages. The frequency achieves its maximum value when the applied voltage is 15 V in all of the three individual experiments. For the 50 µL droplets, the frequency increased when the voltage was turned up until the voltage reached 15 V. The frequency under 20 V is slightly less than the frequency at 15 V, which is almost twice the voltage under 5 V and 10 V. For the 100 µL and 150 µL gallium droplets, although the maximum values are achieved under 15 V DC, the frequencies fluctuate from 2.5 to 3.5 Hz for the 100 µL droplets and from 2.0 to 2.5 Hz for the 150 µL droplets.

Generally, under the same test voltage, the frequency is inversely proportional to the volume of the droplets. The difference between the maximum and the minimum values increases as the voltage is increased up to 15 V. The difference
between the maximum and minimum values under 20 V is less than the difference under 15 V.

4.3.2 Effects of the applied voltage and the volume of the droplet on heart beating in acid solution (1 mol/L HCl solution)

In this section, all experiments used 1 mol/L HCl aqueous solution. 100 µL gallium droplets were studied under three different DC voltages: 1, 2, and 3 V. The following figures show the distance measured between the geometric centre of the top-view area of the droplet and the nearest point on the inner wall of the graphite ring electrode, and the area, which is the area of the top-view footprint of the gallium droplet over five oscillation periods.
Figure 4.13 Area versus time curve for the liquid metal heartbeat acting on 100 µL droplets in the acid solution (1 mol/L HCl aq.) when DC voltages of 1, 2, and 3 V are applied at 34 °C. The vertical coordinate Area denotes the top-view footprint area of the liquid metal droplet.

Figure 4.13 indicates the relationship between the top-view footprint area of the 100 µL liquid metal droplet and the oscillation period. The largest oscillation was clearly observed when the 3 V was applied. There is almost no change in the 1 V experiment, because the reduction reaction is dominant under these conditions, which means the ability of HCl to remove oxide skin is stronger than the production of oxide skin.
Figure 4.14 Distance versus time curve for the liquid metal heartbeat acting on 100 µL droplets in the alkaline solution (1 mol/L HCl aq.) when DC voltages of 1, 2, and 3 V are applied at 34 °C. The vertical coordinate Distance denotes the distance between the geometric centre of the top-view of the liquid metal droplet the nearest point on the inner edge of the graphite electrode.

Figure 4.14 shows the relationship between the distance from the geometric centre of the top view of the gallium droplet to the nearest point on the inner wall of the ring electrode and the oscillation period under three different applied DC voltages. When the applied voltage is 1 V, the time for five oscillation periods is longer than the times under the other two applied voltages. Therefore, the frequency of oscillation under the 1 V DC is lower than the frequencies under 2 and 3 V. In addition, the peak value for the distance under 3 V DC is larger than the peak values for the other two voltages.

4.3.3 Effects of the applied voltage and the volume of the droplet on the “beating heart” in pH neutral solution (1 mol/L NaCl solution)
Figure 4.15 After 5 V DC is applied, no change occurs in the morphology of the gallium droplet in NaCl solution.

Figure 4.15 shows that the liquid metal droplet has non-equilibrium shape after 5 V DC is applied. This can be explained by considering only the effect of the electrochemistry because sodium chloride cannot react with oxide skin of gallium. So, the shape of the gallium droplet only slightly changes.

4.4 Conclusions

A new heart beating phenomenon has been discovered by using non-toxic gallium droplet. This gallium droplet put into a graphite ring in electrolytes which were kept at 34 °C. When applied a DC voltage, the liquid metal droplet was jumping on the horizontal direction. The range of beating frequency from 2.3 to 6.1 Hz can be acquired in our experiments.
4.5 References


5 CONCLUSIONS

In this thesis, gallium heartbeat phenomenon, spreading effects of liquid metal gallium in liquid state and supercooled state have been presented. Their electrochemical, morphology properties are studied in details.

For spreading effects of liquid metal gallium in liquid state, solutions (NaOH, HCl and NaCl) and their concentrations, the external applied voltages, the volumes of the liquid metal droplet, are found to play important roles in the spreading performance. The deformation of liquid gallium droplet is well explained by the combination of the electrochemical reaction and the dissolution of the oxide skin of gallium droplet. The reversible transformations of liquid gallium have been obtained in alkaline and acid solutions. However, the deformations do not show up in pH neutral solution. Under the same applied voltage, electrolyte and distance of electrodes, the maximum of the relative change of the top-view area increases as the increase of the volumes of the liquid gallium. Interestingly, the maximum of the relative change of the top-view area was not obtained in the highest and lowest concentrations of electrolyte. The highest concentration of the acid solution results in the shortest time, which takes from the maximum top-view area to original spherical shape.

Compared with the spreading effects of liquid metal gallium in the liquid state, the spreading effects of liquid metal gallium in the supercooling states were demonstrated irreversible deformation. The spreading and crystallization of liquid
metal gallium in 0.5 mol/L NaOH presented a tree structure. It showed pancake shape in 0.5 mol/L HCl solution. The crystallization rate is lower than the spreading rate at 22 °C. The spreading direction is from the anode to the cathode. Controlled liquid-solid shape reconfigurations were achieved in supercooled liquid gallium spreading.

For gallium heart beating phenomenon, the electrochemical cell configuration was set up with both one wire electrode and one graphite ring electrode in the electrolyte. The gallium droplet was put in the graphite ring and electrically connected to graphite ring. When a DC voltage is applied, the gallium droplet oscillated in the middle of graphite ring, which is induced by the spreading effect of liquid metal gallium. The amplitudes and the top-view areas of the oscillation of liquid gallium droplet have been systematically studied. The range of beating frequency from 2.3 to 6.1 Hz can be acquired in our experiments.