Influence of Water on the Interfacial Behavior of Gallium Liquid Metal Alloys

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ⓢ *Supporting Information*

ABSTRACT: Eutectic gallium indium (EGaIn) is a promising liquid metal for a variety of electrical and optical applications that take advantage of its soft and fluid properties. The presence of a rapidly forming oxide skin on the surface of the metal causes it to stick to many surfaces, which limits the ability to easily reconfigure its shape on demand. This paper shows that water can provide an interfacial slip layer between EGaIn and other surfaces, which allows the metal to flow smoothly through capillaries and across surfaces without sticking. Rheological and surface characterization shows that the presence of water also changes the chemical composition of the oxide skin and weakens its mechanical strength, although not enough to allow the metal to flow freely in microchannels without the slip layer. The slip layer provides new opportunities to control and actuate liquid metal plugs in microchannels— including the use of continuous electrowetting—enabling new possibilities for shape reconfigurable electronics, sensors, actuators, and antennas.

KEYWORDS: *EGaIn, continuous electrowetting, rheology, wetting, slip layer, fluidic antenna*
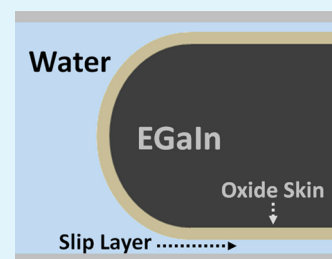
1. INTRODUCTION

The ability to manipulate the shape and control the motion of liquid metals in microchannels holds great promise for many microdevice applications, such as valves, switches, pumps, sensors, actuators, and electrodes.[1−8] Mercury has most commonly been used for these applications, despite the danger it poses to human and environmental health,[9] because of nontrivial technical challenges associated with other room-temperature liquid metals. Gallium is the leading alternative to mercury because of its low vapor pressure,[10,11] low viscosity, low toxicity, and metallic electrical conductivity.[12] However, gallium suffers from two challenges. The first challenge is that gallium is solid at room temperature (mp ∼29.7 °C). Alloying gallium with certain metals addresses this problem; in this study we use eutectic gallium−indium (EGaIn), which remains liquid at room temperature.[12]

The second challenge associated with the use of gallium and its alloys is the presence of a surface oxide composed primarily of oxides of gallium. This oxide is thin (1−3 nm),[13−17] effectively passivating, and forms spontaneously and nearly instantaneously upon exposure to atmospheric oxygen.[18] The oxide sticks to most surfaces[12,19−22] (with some notable exceptions[23,24]), preventing the metal from flowing freely. This unique feature can provide opportunities for new applications since the oxide mechanically stabilizes the liquid metal in nonequilibrium shapes,[25] which is useful for forming 2D[20] or 3D structures,[26] antennas,[27−29] micro pumps,[30] strain[31,32] and curvature sensors,[33,34] wires,[35] interconnects,[36] plasmonic structures,[37] and frequency selective surfaces.[38] The oxide, however, adheres to the walls of microchannels and thus excludes the use of gallium-based alloys in applications requiring the reversible control of microscale switches, pumps, optics, or shape reconfigurable electronics.[39]

Contact with vapor or liquid of a strong acid or base (e.g., HCl) removes the oxide and can address this problem.[12,40,41] However, the use of these harsh chemicals is undesirable for many practical implementations. It is also possible to modify the chemistry or roughness of the walls of microchannels to limit the wetting, but this approach limits the materials available for device construction, and it is not yet established how well it will work over many duty cycles.[19,23,42] Electrochemistry can remove the oxide, but this approach requires a constant supply of energy to keep the metal oxide-free.[43] For all of these reasons, most studies of liquid metal manipulation have used Hg.

Here, we show that simply prefilling a channel with water prior to adding metal creates an interfacial slip layer between the surface of the metal plug and the walls of the microchannel that prevents the oxide from sticking to the walls. The presence of water also changes the composition of the oxide, decreases its modulus by nearly an order of magnitude, and makes it less passivating. The presence of water lowers the pressure required to inject the liquid metal into microchannels, even though water is ≈55 times more viscous than air. The aqueous slip layer allows continuous electrowetting (CEW) of the metal,[44,45] enabling the use of voltage to control the movement of the metal in microchannels. The slip layer also allows the use of pressure to inject and withdraw the metal from microchannels without it adhering to the channel walls.
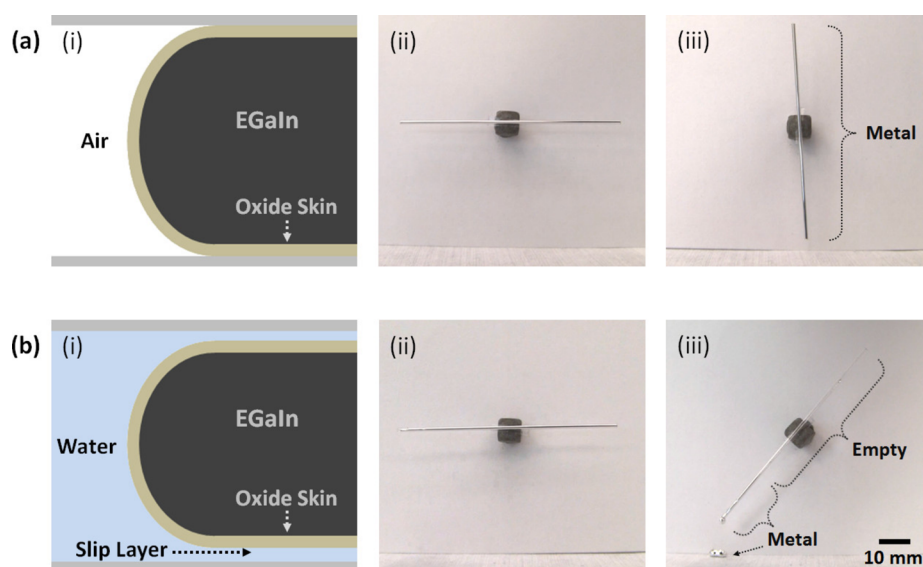
Figure 1. Contrasting the behavior of EGaIn in (a) a dry capillary, and (b) a capillary prefilled with water. The capillaries are mounted on a wall using adhesive attached to a rotating holder. (a) (i, ii) When EGaIn is injected into a dry capillary, the oxide skin forms spontaneously and adheres to 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.

The changes to the oxide in the presence of water are particularly important for applications that use the metal in aqueous environments, such as metal-hydrogel contacts.[46,47] This paper describes the use of water to provide new opportunities to modify and control the interfacial properties and microfluidic behavior of oxide-forming liquid metals.

2. EXPERIMENTAL SECTION

Eutectic gallium indium (EGaIn) was purchased from 5N Plus. Capillary tubes were obtained from Friedrich and Dimmock Incorporation. An AR-G2 rheometer (TA Instruments) was used for rheology of the EGaIn. Pristine laboratory glass slides (75 mm × 50 mm × 1 mm) were obtained from Fischer Scientific and Corning Corporation. These slides were cleaned by rinsing with isopropanol and water, unless otherwise noted. "Wet" substrates were prepared by submerging these slides into deionized water and removing excess water such that no water was visible. Polydimethylsiloxane (PDMS) microchannels, as shown in Figure 6, were fabricated by using soft lithography and replica molding techniques. Additional details are given in Supporting Information as well as explained throughout the main text.

3. RESULTS AND DISCUSSION

3.1. Plug Flow in Water and in Air. To investigate the difference in the behavior of the metal interfaced with air or water, we injected EGaIn into a dry capillary (borosilicate glass, 70 mm length, 0.9 mm inner diameter) and a capillary prefilled with deionized water. It is straightforward to inject the metal by syringe into microfluidic channels or capillary tubes. The capillaries were initially oriented horizontally and we observed whether the metal flows out of the capillaries under gravity as we rotated them vertically. Metal injected into a dry, empty capillary tube is stable since the oxide skin adheres to the capillary wall and provides mechanical stability to the liquid metal, as shown in Figure 1a (Supporting Video S1 shows the

entire process). Repeating the experiment with a capillary tube prefilled with water produces a different result (Figure 1b): in this case, tilting the tube beyond ∼50° relative to the horizon causes the metal to flow out of the capillary due to gravity (Figure 1b(iii); Supporting Video S2). The oxide also forms in water because of the presence of dissolved oxygen, yet it does not provide mechanical stability in the capillary. Similar behavior was also observed when prefilling the capillary with light mineral oil rather than water.

3.2. Rheology. There are two potential explanations of the behavior observed in Figure 1: (1) the presence of a slip layer between the metal plug and the walls of the capillary, and/or (2) the weakening of the oxide layer by water. We used rheological methods to determine the effect of water on the mechanical properties of the oxide that forms on EGaIn. With a rheometer (AR-G2, TA Instruments) configured with parallel plate geometry, we repeated previous rheological measurements[12,48] of the mechanical properties of the oxide in air. The top plate rotates with a controllable angular frequency while the bottom plate remains stationary; these parallel plates (40 mm diameter) sandwich ∼0.6−1 mL of EGaIn in a gap of ∼1.2−1.6 mm. Because the bulk viscosity of the liquid is so low, the measurements provide information solely on the mechanical properties of the thin solid oxide skin that spans the top and bottom plates around the circumference of the metal. Small amplitude oscillatory stress sweeps provide information about the surface modulus (10 N/m) and the surface yield stress (∼0.5 N/m) of the oxide in air as shown in Figure 2. The surface elastic modulus plateaus and dominates relative to the viscous modulus, as expected.

For the rheological measurements of the metal in water, we designed an acrylic reservoir which allows these measurements to also be made in a water environment. We filled the reservoir with deionized water, which brought water into direct contact with the oxide layer. After exposing the oxide to water for 10 min, we repeated the rheological measurements. The low
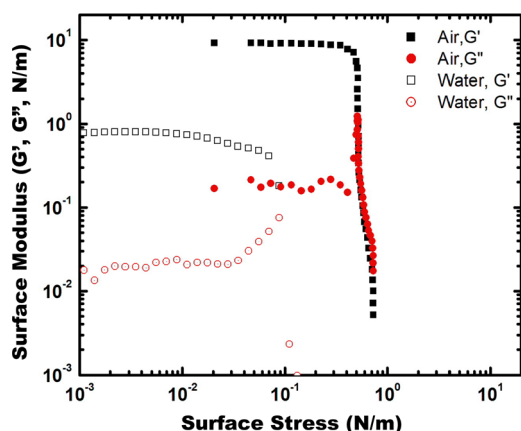
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Figure 2. Effect of water exposure on the mechanical properties of the oxide skin that forms on EGaIn. During a small amplitude oscillatory stress sweep in water, the surface elastic modulus G' plateaus near 1 N/m and yields at 0.1 N/m and dominates relative to the viscous modulus G''. The surface elastic modulus decreases by an order of magnitude in water relative to the modulus in air. The surface yield stress is also reduced by approximately a factor of 5.

viscosity of the surrounding water provides negligible resistance to the movement of the top plate and therefore any change in rheological properties are attributed to changes in the oxide itself.

We hypothesized that the surface elastic modulus and yield stress of the oxide skin in water would be similar to those in air because the oxide layer is considered passivating (in air). However, the surface elastic modulus decreases by an order of magnitude ($\sim$1 N/m) relative to that measured in air ($\sim$10 N/m). The surface yield stress of the oxide skin also shifts to a lower value in water compared to that in air from $\sim$0.5 N/m in air to $\sim$0.1 N/m in water. Thus, exposure to water represents a simple way to lower the elastic modulus and yield stress. These results suggest that when exposed to water, the oxide skin is either changing its composition or getting thinner. It is visually apparent that the oxide gets thicker after submerging the oxide-coated metal in water for a long time period (e.g., weeks) and preliminary ellipsometry measurements (not reported here) also suggest the oxide gets slightly thicker on the time scales of our experiments here. These results suggest that chemical changes are responsible for the weakening of the oxide.

3.3. XPS. Inspired by these surprising rheological results, we sought to understand why water changes the mechanical properties of the oxide. An X-ray photoelectron spectroscopy (XPS) study of the surface of gallium as a dental amalgam suggests that the oxide changes its composition in the presence of water to a gelatinous complex of gallium oxide monohydroxides (GaOOH).[49] This change in composition corresponds to a 0.5−0.7 eV shift in XPS data for the $Ga(2p_{3/2})$ and $O(1s)$ peaks relative to their dry state. We observe a similar 0.73 eV shift in the binding energies of Ga and O after exposing the oxide to water for 10 min. These results suggest further that the changes in the mechanical properties of the oxide are likely associated with chemical changes. Details of the XPS results are given in the Supporting Information.

We sought to understand whether the weakening of the oxide skin by exposure to water could explain the behavior in Figure 1b(iii). We filled a glass capillary with EGaIn (as shown in Figure 1a), oriented it vertically, and submerged it in water. If the weakened oxide was the only contributing factor to the

mechanical instability of the metal in Figure 1b, then the metal should flow out of the capillaries within minutes. Instead, the metal is stable in the capillary throughout the duration of our experiment (several hours), which suggests that the order of injection of the fluids (i.e., prefilled with water prior to injecting the metal) must be important and that the instability observed in Figure 1b is due to another mechanism.

3.4. Continuous Electrowetting. We hypothesized that a thin layer of water between the metal and the wall of a capillary explains the instability observed in Figure 1b. To test this hypothesis, we investigated whether a plug of the metal in a capillary prefilled with water moved under an electric field by the mechanism of CEW. CEW relies on a potential drop across the interface of a metal plug and a thin electrolyte layer between the metal plug and the capillary sidewall. This potential drop varies along the length of the plug. Because of electrocapillarity, this potential gradient translates into a difference in interfacial tension, driving plug movement, which has been used previously to move plugs of liquid metal.[50] Thus, movement of the metal plug in response to voltage provides evidence that there is a thin layer of water between the metal and the wall of the capillary.

To test the CEW effect, we injected aqueous electrolyte (0.01 M NaF) into a glass capillary and then subsequently injected a $\sim$1 mm long plug of EGaIn into the capillary. The electrolyte provides a polarizable interface with the metal like a capacitor (i.e., minimal charge transfer) in the range of applied voltage used here. The capillary bridged two electrolyte-filled reservoirs in a plastic holder, forming an electrically continuous path. Copper electrodes inserted into each reservoir applied a 1 V alternating current (ac) voltage while sweeping the frequency. Figure 3 shows several frames from a video demonstrating the CEW effect (Supporting Video S3). The metal moves smoothly through the tube without leaving any residue on the walls of the capillary. The plugs oscillate in
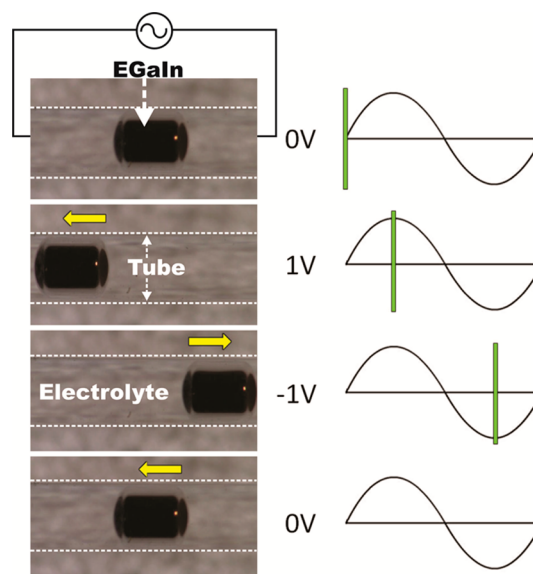

Figure 3. Presence of a thin slip layer of aqueous electrolyte between the capillary wall and a plug of liquid metal enables continuous electrowetting of the plug. Application of low-frequency ac bias (1 V) causes plug movement inside the capillary. As the potential oscillates from positive to negative, the plug displacement oscillates left and right. The diameter if the tube is 0.9 mm.

response to voltage and frequency using 1 V over frequencies spanning from direct current (dc) to ~70 Hz. The observation of the movement of the metal plug by CEW confirms that there is a layer of water between the metal and the capillary wall.

We speculated that hydrophobic channels might prevent the slip layer from forming. While the system is seemingly more responsive in hydrophilic channels such as glass capillaries, CEW actuation occurred in hydrophobic channels, such as perfluoroalkoxy tubing (Omegaflex TYTP-116132). This result suggests that the electrolyte solution wets the oxide skin during injection of the metal, forming a sheath over the metal plug. This sheath functions as a slip layer between the plug and the channel wall.

Notably, plugs of metal do not move under these same conditions if the metal plug is injected before the water. When there is a slip layer of water between the metal plug and the walls of the channel, ions can travel freely from end-to-end of the capillary and CEW occurs. However, in the absence of the slip layer, the ions in the electrolyte have to convert to electrons via electrochemical reactions at the interface to travel from the electrodes placed at each end of the capillary. In this case, application of higher voltage ac bias causes the electrolyte solution to slowly infiltrate from the ends of the plug toward the center of the plug, enabling plug oscillation only to the point at which water has maximally infiltrated. When the infiltration fronts from each end of the plug meet, the entire plug begins to move in a manner identical to that seen during CEW of a metal plug injected into a water-filled capillary. The infiltration of water is therefore likely due to the electrochemical reduction of the surface oxide that coats the metal and adheres to the walls of the capillary (cf., Figure 1a).

3.5. Slip Layer. The presence of a slip layer also has implications outside of microchannels. We observed the behavior of droplets of metal placed on dry substrates and compared them to the same substrates exposed to water. As a control sample, we placed a drop of EGaIn on a pristine glass substrate cleaned by oxygen plasma (Figure 4a). We refer to these substrates as "dry", although we made no additional efforts to remove surface-bound water to represent normal

laboratory conditions. The drop stayed on the surface even after tilting the substrate to 90° (Figure 4b), as expected since the oxide skin adheres to the substrate.[19] In contrast, after pre-exposing the glass surface to water (dipped in deionized water), the drop of EGaIn slid off, as shown in Figure 4d. This result further supports the hypothesis that water acts as a slip layer. Notably, water was not visible on the surface of the glass when we placed the EGaIn drop onto it, which suggests that the water layer is thin. We repeated these experiments multiple times and observed the same result each time.

We speculated that substrates dipped in water would start to behave like a dry substrate as the trace amount of water on the surface evaporates. We brought droplets of the liquid metal hanging at the end of a needle into contact with glass slides. The droplets stick to dry substrates and break away from the needle as it is pulled away from the substrate. However, the droplets did not stick to glass slides presubmerged in a deionized water bath (Figure 5a), which further illustrates the importance of water as a nonstick layer. After ~8−9 min of drying (Figure 5b), the drop begins to stick to the substrate. After ~10−12 min (Figure 5c), the droplets fully adhere to the substrate. These results suggest that dipping substrates in water represents a temporary way to prevent adhesion of the oxide to the substrate. This may inspire new approaches for designing substrates that do not adhere to the metal, approaches such as liquid-infused surfaces,[51−53] which mimic lubricating structures found in *Nepenthes* pitcher plants.

Prior work suggests that droplets of EGaIn only adhere to glass surfaces when the droplet volume increases while in direct contact with the glass.[19] Figure 5c suggests that droplets adhere to the glass without expanding or significantly distorting the droplet. We repeated the experiments depicted in Figure 5 ten times. We also measured the adhesion of droplets to nominally dry glass slides (i.e., those without exposure to water immediately before measuring) after cleaning them separately with (1) water followed by a rinse with isopropanol, (2) water followed by a rinse with acetone, (3) acetone followed by a rinse with water, (4) isopropanol only, (5) acetone only, (6) oxygen plasma, and (7) heating at 70 °C for an hour to drive off water. In all cases—which were each repeated at least ten times—the EGaIn droplets adhered to the glass in a manner similar to that shown in Figure 5c. However, the drops did not adhere to the glass after washing with soap and rinsing with isopropanol and acetone, which suggests that the method of preparation affects wetting. Nevertheless, the increased adhesion with time shown in Figure 5 suggests that the surface dries over time.

3.6. Implications of Slip Layer and a Demonstrative Device. The presence of water has implications for injecting the metal into microchannels because (1) water weakens the oxide and (2) the slip layer prevents the oxide from sticking to the walls of the channel. We measured the pressure required to inject the metal into dry versus water-filled microchannels composed of PDMS (length 65 mm, width 1 mm, height 0.05 mm) fabricated using standard replica molding techniques. We placed a drop of metal at the inlet to these channels and measured the pneumatic pressure required to inject the metal. The average pressure required to partially fill a microchannel prefilled with water was ~40% lower than that needed to fill a dry microfluidic channel. We repeated these measurements more than 20 times and always found the pressure to be lower in wet channels. We are currently working to understand the competing influences of water during injection including the
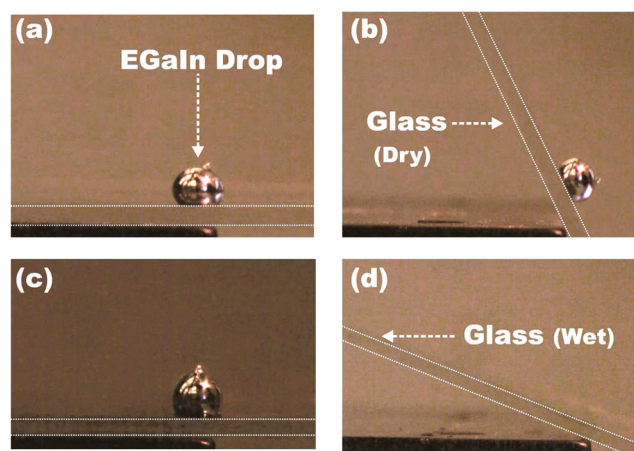

Figure 4. Evidence of a water slip layer in an open system. (a) An EGaIn drop is placed on a dry glass slide. (b) The glass slide is tilted to 90° yet the droplet does not slide off the surface. (c) An EGaIn drop placed on a glass slide dipped briefly in water. (d) When tilted, the drop slides off at a small angle (30°−40°). For scale, the glass slides are 1 mm thick.
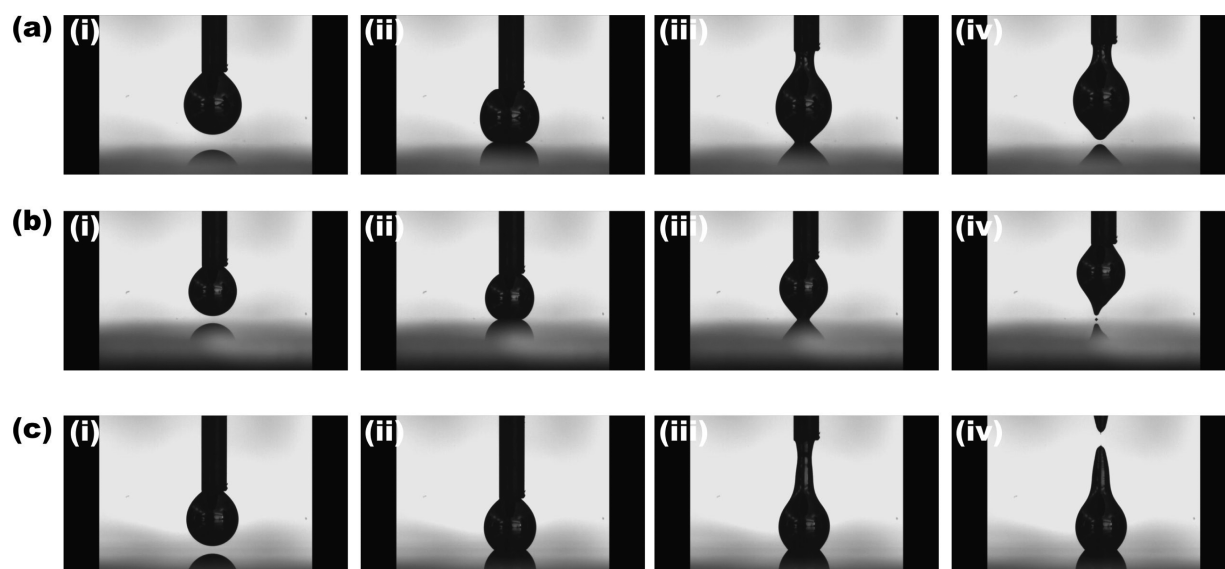
Figure 5. "Wet" to "dry" transition of a glass substrate. In each row, the metal is brought into contact with a substrate (i, ii) and then removed (iii, iv). (a) On a glass slide exposed to moisture (immediately after dipping in a water bath), the metal does not stick to the surface. (b) After the substrate has dried in air for 8−9 min, the metal begins to stick and leaves some residue on the substrate. (c) After ~10 min, the metal sticks to the surface in a manner identical to adhesion on a dry glass substrate. The diameter of the needles is 1 mm.
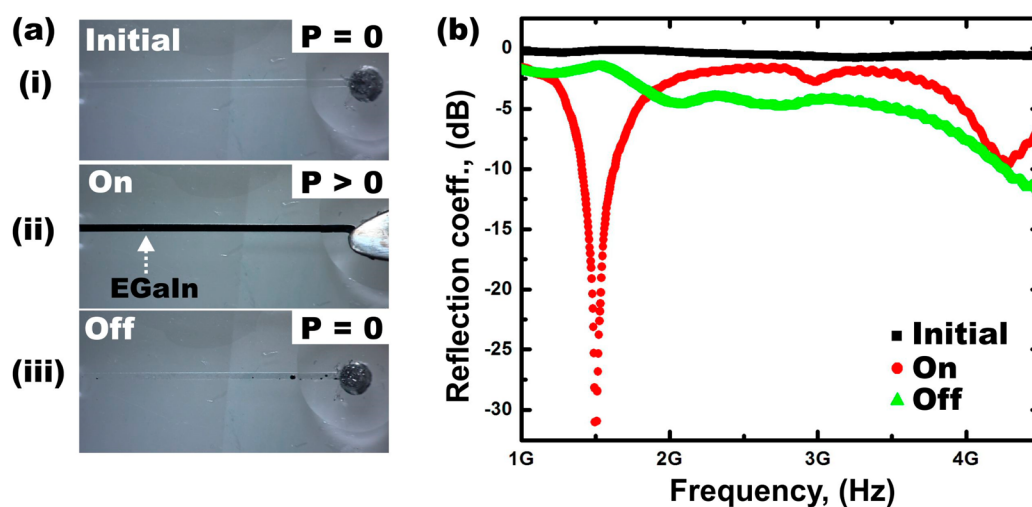

Figure 6. (a) Photographs of a reconfigurable antenna that can be injected and withdrawn from microchannels due to a water slip layer. (a) Initially (i), water fills the channel and a drop of metal rests in a reservoir at one end of the channel, capped by a hemisphere of PDMS. Pressing the reservoir with the tip of a spatula (ii) pushes the metal into the channel. (iii) Removing the pressure causes the metal to spontaneously withdraw back into the reservoir. (b) The spectral response of the device in all three states. For scale, the width of the microchannel is 1 mm wide.

need to displace the fluid in the capillary (pressure increases due to the larger viscosity of water relative to air), rupture the oxide (pressure decreases due to water weakening the oxide), slip along the walls (only possible with water), and overcome any effects of interfacial tension. Nevertheless, the presence of water provides a simple and nonintuitive way to lower the pressure required for injection of gallium alloys into microchannels.

The presence of the slip layer offers an opportunity to push metal in and out of microchannels without adhesion to the channel walls. This capability is particularly compelling for antennas since the frequency of an antenna depends on its shape. We utilized the slip layer to fabricate and characterize a reconfigurable antenna that can be activated or deactivated by hand. This antenna, depicted in Figure 6, is comprised of a reservoir of EGaIn connected to a water-filled PDMS

microchannel. When confined to the reservoir, as shown in Figure 6a(i), the liquid metal has no resonant frequency because of its negligible length—it is therefore in the "off" state. To activate the antenna, we pressed the reservoir manually, forcing the metal into the microchannel, as shown in Figure 6a(ii). In this "on" state, the antenna has a resonant frequency corresponding to the length of the microchannel, as expected. After releasing the applied pressure, the metal withdraws back into the reservoir, transitioning the antenna back to the "off" state, as shown in Figure 6a(iii). A thin, dome-shaped membrane of PDMS caps the reservoir and deforms when depressed. Upon releasing the applied pressure, the dome returns back to a hemispherical shape and helps pull the metal back into the reservoir. The spectral responses of these three different states are shown in Figure 6b. The "off" and "initial"

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states are slightly different due to challenges connecting the antenna to the network analyzer in this prototype device.

4. CONCLUSION

This paper describes the effects of water on the oxide skin of EGaIn and discusses the implications of these effects in the context of liquid metal microsystems. Water changes the chemical composition of the oxide and weakens its critical yield stress by a factor of 5. Water can also create a slip layer between plugs of metal and the walls of microchannels by placing water in the microchannels prior to injecting the metal. We focus on water and aqueous solutions in this paper, but other fluids appear to create slip layers too, including mineral oil. In the future it may be possible to use functional slip layers for active control over the metal.[54] An aqueous slip layer enables controlled actuation of liquid metal plugs inside microchannels via continuous electrowetting and prevents the metal from sticking to wet surfaces, addressing one of the major practical issues in the use of gallium alloys. We utilize the slip layer to demonstrate a shape reconfigurable antenna based on EGaIn that reversibly changes its spectral properties by pushing metal in and out of microchannels. The presence of a slip layer thus provides a route to avoid Hg in devices and experiments that depend on liquid metals, but does have the drawback of requiring the presence of an additional fluid (and, notably, water appears to cause the oxide to get thicker over long time scales). Remarkably, the presence of water also reduces the pressure necessary to inject the metal into microchannels relative to dry microchannels, which warrants further investigation.

This work is a step toward enabling the actuation of low toxicity liquid metals that have surface oxides. Although we focus on EGaIn, other alloys of gallium support a surface oxide of similar composition and, thus, the conclusions can likely be extended to these metals. The ability to reversibly actuate liquid metal plugs by CEW or pneumatics may help facilitate the development of shape-shifting devices and reconfigurable antennas, sensors, actuators, meta-materials, circuits, and passive elements.

◼ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental information about the rheology and XPS measurements as well as descriptions of the supporting videos. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

◼ ACKNOWLEDGMENTS

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