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Oxide-Free Actuation of Gallium Liquid Metal Alloys Enabled by Novel Acidified Siloxane Oils

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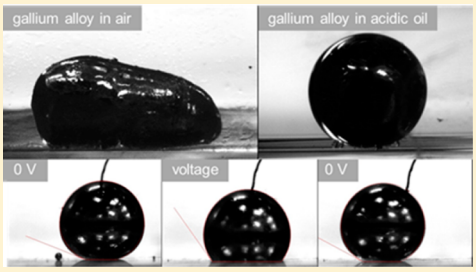
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Supporting Information

ABSTRACT: Electrowetting and electrocapillarity of liquid metals have a long history, and a recent explosion of renewed interest. Liquid metals have electromagnetic properties and surface tensions (>500 mN/m) that enable new forms of reconfigurable devices. However, the only nontoxic option, gallium alloys, suffer from immediate formation of a semirigid surface oxide. Although acids or electrochemical reduction can remove this oxide, these approaches surround the gallium alloy in a fluid that is also electrically conducting, diminishing electromagnetic effectiveness and precluding electrowetting actuation. Reported here are acidified siloxanes that remove and prevent oxide formation. Importantly, the siloxane oil associatively incorporates hydrochloric or hydrobromic acids, is electrically insulating, is chemically stable, removes etching byproducts (including water), and allows robust electrowetting. This work opens up new opportunities for liquid metal reconfiguration, and is of fundamental interest due to the unexpected chemical stability of the acidified siloxanes and their application to other materials and surfaces.



INTRODUCTION

Room-temperature liquid metals have seen an explosion of recent reports on self-healing,[1] reconfigurable,[2,3] and stretchable electromagnetic devices such as wires, switches, antennas, polarizers, light valves, diffraction gratings, and filters.[4−7] Fundamentally, liquid metals can provide a combination of electrical conductivity and analog reconfigurability far exceeding what can be achieved with semiconductor, MEMs, or other approaches. Mercury has been the material of choice historically, but because of its toxicity to neuronal cells,[8] is now avoided in recent liquid-metal device investigations.

The most promising alternatives to mercury are clearly gallium liquid metal alloys (GaLMAs), which can remain a liquid even down to −19 °C.[9−11] However, GaLMAs present a significant challenge because in only a matter of seconds an oxide skin rapidly forms even in environments with mere ppm levels of oxygen. This oxide then prevents reversible reshaping. To enable device demonstrations, researchers have removed this oxide by use of acidic vapor[12−14] or electrochemical reduction in electrolyte solution.[15,16] In these cases, the actuation of the GaLMA shape has been limited to predetermined geometries imparted by microfluidic confinement (channels). Also undesirable from an electronic or electromagnetic perspective, neither acid nor electrochemical approaches are ideal as the required acid or electrolyte solutions are inherently ionically conductive (electrically lossy). For example, consider a simple application of an all-electronic switch, where liquid metals can provide ON state conductivity superior to semiconductor switches, but where the OFF state current would be severely limited by the ionically conductive surrounding fluid. Furthermore, surrounding a GaLMA droplet with a conductive solution then makes it impossible to use some of the most reconfigurable electrostatic methods of control such as electrowetting.[18] There is hence a clear unmet need to find a materials system that can both eliminate the GaLMA surface oxide while simultaneously provide a geometrically open and electrically insulating environment. With such an advance, GaLMAs could achieve previously unseen levels of reconfigurability, enabling new and more sophisticated electromagnetic effects such as multiway switches, fast-switching optical effects such as diffraction or polarization, or even writeable/erasable meta-materials.

Other groups have shown removal of oxides from GaLMAs using "strong" acids, primarily hydrogen halides (X).[14] In general, $6HX + Ga_2O_3 \rightarrow 3H_2O + 2GaX_3$. In many cases, the water generated from this reaction causes problems for use in

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electronic devices since water itself is a conductive liquid.[17] In water and most other protic solvents the HX will primarily or completely dissociate, which substantially increases the ionic strength of the solution and thereby increases the effective conductivity.[18] As noted previously, surrounding a GaLMA with a conductive solution diminishes its possible electromagnetic device performance. Furthermore, even a miniscule amount of conductive solution can prevent actuation techniques such as electrowetting[19] because the conductive solution readily forms an annulus at the contact line which itself electrowets instead of the GaLMA.

Siloxanes are known to be good insulating fluids for electronics and electrowetting applications because they are electrochemically inert, chemically stable in water-free environments, and are highly electrically insulating.[20] However, with respect to GaLMA systems, they cannot prevent oxygen diffusion to the liquid metal surface nor can they remove an already formed oxide. Interestingly, siloxanes also naturally absorb water through hydrolysis[21] yet remain electrically insulating.[17] However, the challenge of removing the surface oxide from the GaLMA still remains.

Presented here is the characterization and demonstration of a novel acidified siloxane that contains hydrochloric acid, which remains insulating due to the unique associative incorporation of the acids in the siloxane (i.e., HCl acting as a weak acid in the siloxane solvent system). Furthermore, we demonstrate that other acids, such as HBr produce similar results in our system. We present a straightforward and effective protocol to generate these acidic and anhydrous siloxanes, a protocol which can easily be reproduced in any laboratory setting without the need for specialized equipment. Demonstrations show that this novel siloxane is appropriate for even the most electrically challenging applications such as electrowetting (requiring high electric fields and therefore near perfect electrical insulation). The native oxide layer, which is nearly impossible to avoid when dealing with GaLMAs, is removed in a matter of seconds by the acidified siloxane. This is important because previous efforts requiring use of GaLMAs in extremely low oxygen or vacuum environments (e.g., a glovebox of <1 ppm oxygen and moisture, ultrahigh vacuum of 10^{-9} Torr)[11,22] often still fail due to oxide formation in matter of minutes if any trace oxygen is present. Instead, with this acidified siloxane, device assembly and rudimentary testing can be performed in a regular ambient environment. This greatly simplifies the complexity of constructing and operating GaLMA devices.

An additional and critical advantage of the acidic siloxane over an acidic vapor or aqueous solution is that the water produced by the reaction of the acid and oxide is hydrolyzed (consumed) by the siloxane, which produces silanol species.[21] Since there is only a small amount of oxide present to react, the siloxane degradation is minimal at the time of processing and is then rate-controlled by the diffusion of new oxygen into the system. Therefore, the better the system can be sealed after assembly, the better the stability and insulating properties of the siloxane will be maintained over time. Furthermore, our experiments suggest that the acidified siloxane interacts with the liquid metal to synthesize gallium and indium compounds or adducts. Synthesis and isolation of novel and unusual compounds involving Group 13 metals has been an area of strong research interest because of their implications in organometallic synthesis, in new materials development, and in biological, medical, and environmental systems.[23] To our knowledge, this is the first electrically insulating and chemically stable fluid capable of removing metal oxide and reaction byproducts even in the presence of atmospheric oxygen concentrations. We speculate this work is also more broadly relevant to anyone interested in acidic siloxanes for applications such as electrowetting, MEMs, coordination chemistry, electrochemistry, chemical vapor deposition (CVD) techniques, and charge transfer complexes.

EXPERIMENTAL SECTION

Synthesis of Acidic Siloxane. In order to make acidified siloxane, 12 N HCl or 12 N HBr was incubated with the siloxane (OS-20, Dow Corning) 1:1 (v/v) for 12 h, forming an immiscible mixture, with the top layer composed primarily of the siloxane and the bottom layer being the aqueous acid. This solution is allowed to equilibrate for 16−18 h. After 16−18 h, the water is initially removed by pipetting, and then further dried by addition of anhydrous magnesium sulfate until no clumping is observed. The subsequent solution is filtered by gravity through filter paper and stored in a sealed vial until it is used (caution, imperfect sealing can lead to 15% of HCl evaporating per week). The as-prepared siloxane contained 1.5 M HCl. More dilute samples were created as needed by adding additional OS-20 siloxane.

Chemical Characterization of Siloxane. ^{1}H NMR spectra were acquired on all OS-20 siloxanes containing both HCl and HBr at various concentrations, as well as virgin OS-20, HCl OS-20 doped with 5% DI water, OS-20 doped with 5% Silanol (Xiameter PMX-0156), and both OS-20, acidified and virgin, after exposure to the liquid metal. NMR spectra were acquired on a Bruker DMX-500 NMR spectrometer operating at proton frequency of 500.13 MHz and using a ^{1}H/^{13}C/^{15}N triple-resonance probe. All spectra were acquired on neat solutions, and were acquired in the same run in order to ensure the same referencing. Fresh OS-20 was acquired during all runs to act as a consistent reference point between runs. Spectra were processed and analyzed using Advanced Chemistry Development NMR Suite. Line broadening of 5 Hz was applied for all spectra reported.

ESI-MS was performed on all samples as follows: from each one, 2 μL of sample was further diluted in 100 μL of MeOH. Each sample solution was then analyzed using a Q-Tof 2TM mass spectrometer (Micromass/Waters) through direct infusion at 4 μL/min flow rate. The instrument was tuned and calibrated in positive ion mode with the source desolvation temperature set at 150 °C and the cone voltage at 10 V. Presented data are a summation of 1 min acquisition for each sample. Data acquisition and processing were done using MassLynx 4.0 software which is part of the Waters instruments.

Dielectric Characterization of Siloxane. Conventional cavity perturbation theory (as derived by ASTM D2520) was employed to determine the dielectric constant and loss of the pure and acidified siloxane samples at discrete frequencies ranging from approximately 2−20 GHz. The combined used of three standard rectangular waveguides, WR-284, WR-90, and WR-62 (S, X, and Ku band, respectively), allowed for such a discrete spectrum to be formed. A vector network analyzer (PNA model N5222A, Keysight [formerly Agilent]) was then utilized to detect the shift of resonant frequencies within the cavity upon insertion of a given sample. Finally, low frequency behavior was measured by a breakdown voltage test. A few drops of each oil sample were sandwiched between two slides of ITO coated glass separated by two thin strips of Kapton tape (76.2 μm thick). The slides were offset so that alligator clips could connect to them, and the ITO coated sides were placed facing each other. An AC voltage (100 Hz) was applied across the oil sample and the current was measured and recorded at 50 V increments. The test was concluded when the current spiked, indicating breakdown of the oil sample. The voltage recorded was converted into V/μm by dividing by the thickness of the oil sample, 76.2 μm.

Electrowetting of Liquid Metal. A borosilicate glass slide coated with a 180 nm thick layer of indium tin oxide was used as a substrate, on which 3 μm of Parylene C (Specialty Coating Systems, ε_r = 3.1) was deposited, and finally a 1−10 nm layer of fluoropolymer (Fluoropel, PFC 1601 V, Cytonix, 1 wt %) was deposited by dip

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coating. This substrate was submerged in the acidified oil and a droplet of liquid metal (eutectic gallium indium, Sigma-Aldrich) was deposited on the surface. The electrode which was probed into the liquid metal was a tungsten wire. A function generator (Tektronix AFG320), phase inverter (FLC Electronics model INV10) and amplifier (Trek model 603) were used to generate a 1 kHz square wave with a voltage differential of up to 330 V_{pp}. Images and analysis of the contact angle were taken and performed on a VCA Optima contact angle system.

RESULTS AND DISCUSSION

Rationale for Choice of Oil Preparation and Characterization Methods. Acidified solutions of anhydrous solvents can be produced by bubbling gaseous acid (including HCl) through the solvent. For example, 2.0 M hydrogen chloride in diethyl ether is produced and sold by Sigma-Aldrich. Previous work has demonstrated that the HCl behaves as a weak acid within a diethyl ether solvent.[24,25] In this work, we preferred an alternative protocol because vaporous acids are corrosive, highly toxic, and require special apparatus. Thus, we relied on equilibrium of the two liquid phases to generate the acidic siloxane from commercially available siloxane and aqueous acids. To prepare the acidified siloxane we combined octamethyltrisiloxane (Dow Corning, OS-20) with 12 M HCl (aq) overnight, approximately 16−18 h, and then dried the siloxane (see experimental section for details).

Siloxanes (Figure 1) have a dipole moment similar to but weaker than that of diethyl ether.[18] This suggests that HCl will hydrogen bond to the oxygen in the siloxane as it has been shown to for diethyl ether. However, the decreased polarity of siloxane means that we are less likely to observe dissociation of HCl into H^+ and Cl^-. While some of the hydrogen chloride still dissociates into the separate H+ and Cl- salts, the majority of it should remain covalently bound as a H−Cl molecular complex. We can therefore determine the concentration of the HCl complex versus the H^+ ion based on the proton chemical shift using ^{1}H NMR.

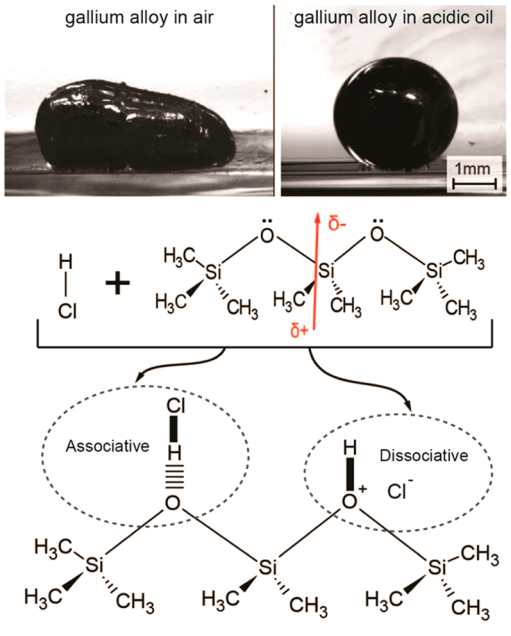


Figure 1. GaLMA droplet mechanically constrained by a surface oxide in deformed shape (left) and the resulting energetically favorable spherical shape of the GaLMA fluid when the oxide is removed (right) by HCl. HCl can be incorporated into siloxane, a polar, aprotic solvent. The now-acidified siloxane contains a combination of associated HCl that forms a hydrogen bonding complex with the oxygen, as well as a dissociative complex, whereupon the oxygen is protonated and the chloride acts as a counterion.

Acidic Siloxane Characterization by ^{1}H NMR. We acquired ^{1}H NMR to quantify the amount of acid taken up by the siloxane, identify impurities, and to identify any chemical changes that occurred upon acidification and/or mixing with the GaLMA.

In Figure 2a, we observe that there is minimal change in the line width, the position, and the intensity of the peaks upon subsequent dilutions of the acidified siloxane with virgin OS-20. The only difference between the spectra is the presence and intensity of the peak at 1.02 ppm, which decreases proportionally with dilution. No other peaks were observed above 1.02 ppm. In contrast, Supporting Information Figure S1 presents an acid peak was observed in diethyl ether + 2 M HCl (Sigma-Aldrich) at 2 ppm as well as at 5 ppm. We quantified the concentration of the acid by integration of the peak areas of both the siloxane and the HCl, determining that overnight combination of the siloxane and the acid results in 1.5 M HCl.

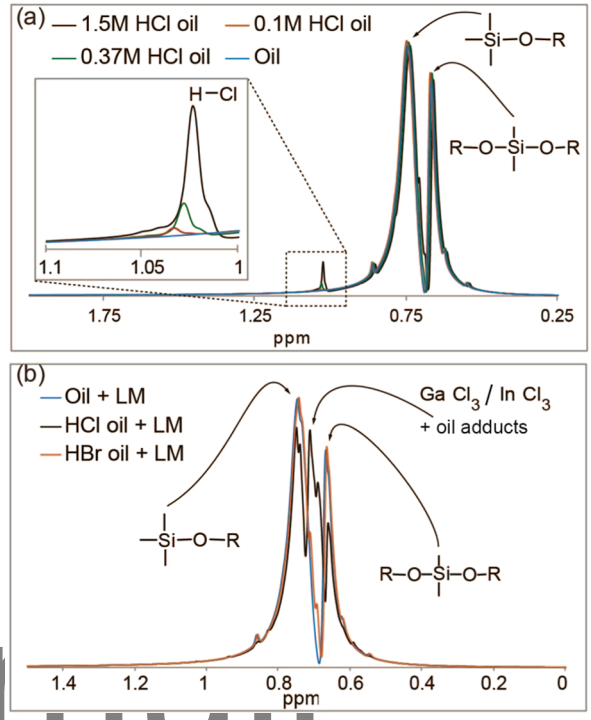


Figure 2. (a) ^{1}H NMR of the siloxane, the siloxane after combination with HCl overnight and after several dilutions with virgin siloxane. No changes are observed for peaks corresponding to methyl protons (0.6 and 0.8 ppm). However, a peak appears after incubation with HCl at 1.02 ppm. This peak reduces in intensity upon dilution with virgin siloxane. Integration of the acid peak area enabled us to determine the concentration of HCl. (b) Comparison of the oil and acidic oils after exposure to the GaLMA demonstrates the generation of a third, unique peak that we attribute to $GaCl_3$/$InCl_3$ siloxane adducts only after exposure to the GaLMA.

After verifying the chemical composition and integrity of the acidified siloxanes and the absence of potential impurities and degradation products (Figures S2 and S3 in the Supporting Information), we looked for any changes in the siloxane after exposure to GaLMAs. Figure 2b shows the ^{1}H NMR spectra of

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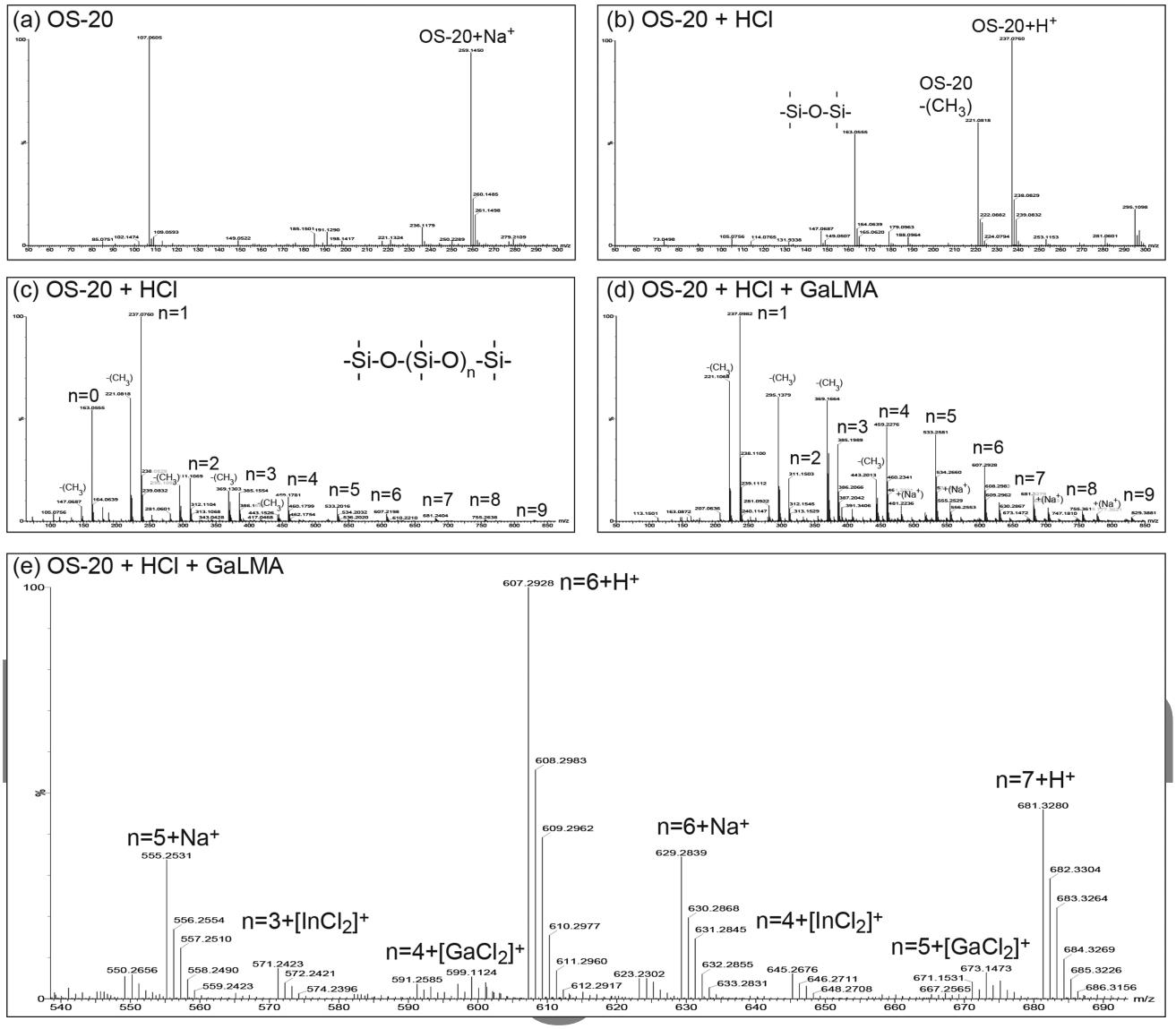


Figure 3. (a) ESI-MS of the OS-20 oil shows it is of high purity and of a singular species (n = 1), where n is the number of dimethylsiloxane groups. (b) Upon addition of HCl, we now observe a peak at n = 0 and (c) polymerization of the siloxane where n = 2, n = 3... (d) Addition and incubation of the GaLMA in the acidified siloxane oil maintained the same patterns of polymerization, but now (e) we also observe gallium and indium complexes and/or adducts, demonstrating the solubility of $GaCl_3$ and $InCl_3$ into the siloxane oil.

the regular siloxane, HCl siloxane, and HBr siloxane after exposure to the GaLMA for 1 week (~50 μL of GaLMA immersed in ~10 mL of the oil). It should be noted that the oxide is visually observed (as in Figure 1a) to be removed in the HCl and HBr siloxane samples, but not in the regular siloxane. Interestingly, even in an environment with minimal oxygen (glovebox with 0.5 ppm oxygen), the HCl peak disappears and we observe a change in the number of distinct peaks corresponding to methyl protons from two to three. The central peak that appears after exposure of the GaLMA with the acidified siloxane is believed to be either solubilized gallium chloride and indium chloride adducts interfacing with the siloxane, or the byproduct (silanol) generated from the degradation of the siloxane by water hydrolysis. In the latter case, water is generated upon the oxide being etched away, thus breaking down siloxane into silanols. Supporting Information Figure S4 presents these reactions.

The NMR clearly shows that the HCl siloxane reacts with the GaLMA and reveals a limitation of this acidic siloxane approach: it works initially to remove and prevent the oxide, but the acid will continue to be consumed afterward as it etches the metal and metal oxide (In + 3HCl → $InCl_3$ + 1.5H_2 (g)). This is not unexpected, as most etching agents have limited selectivity for the oxide over the metal, especially hydrogen halides. While this limits the effective potlife of the mixture to days for building and sealing a device (i.e., upon addition of the GaLMA, the acid will be depleted both by oxide removal as well as metal etching), there is still sufficient time to fabricate the device and to consume residual oxygen remaining within the device. We have found that a concentration as low as 0.1 M HCl oil could remove the oxide in an ambient environment (similar to what is seen in water[26]), but using a higher concentration allowed for a larger window of time to carry out experiments before the acid was depleted. However, we do not believe that continuous acid depletion is a major limitation. There are at least two options which could allow long-term stability in a sealed device. (1) Oxygen barriers and/or scavengers should be effective in minimizing oxide formation

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upon depletion of the acid. The application advantage of this acidified siloxane is that a device can be fabricated in the presence of oxygen and assembled in a 1 step process (e.g., not chemically treated in one solution then transferred to another). 2) A device could also be sealed with a small amount of HCl or HBr that is placed in a sealing subassembly inside the outer sealing. The only requirement would be that the release of HCl or HBr into the oil over time would be at a greater rate than that of oxygen entering the sealed system. Since hermetic sealing can reduce oxygen entry down to extremely low levels, the required acid release rate could also be extremely low as well. Any resulting continual loss of GaLMA mass would be negligible for any application that we can currently envision.

Identification of Chemical Species Generated Using Electrospray Ionization Mass Spectrometry (ESI-MS). ^{1}H NMR clearly identified the methyl protons in the siloxanes as well as the proton in the HCl complex. ^{1}H NMR also enabled us to observe significant changes in chemical composition as a function of how the acidic siloxane was prepared. However, we were unable to observe coordinate covalent complexes and/or polymers we believed were being generated through our process due to sensitivity limitations. We used ESI-MS to answer the following questions: (1) Were gallium/indium chloride species being produced; (2) were these species associating with the siloxane in some manner; (3) was chemical rearrangement occurring upon adding acid to the siloxane, causing both longer chain and shorter siloxanes to be produced; and (4) could we identify any additional chemical species that may be produced through the process?

The ESI-MS in Figure 3a shows the spectrum of virgin OS-20, where only the sodium adduct of OS-20 is observed. The peak at 107 mass units was observed in a background spectra as a contaminant. Upon acidification of the siloxane by HCl (Figure 3b, c) we observed rearrangement and polymerization. Instead of solely observing n = 1, where n is the number of repeat units of the dimethylsiloxane group, there is now $n = 2$, $n = 3$, $n = 4$..., where the intensity of the observed peak decreases as chain length increases. We clearly observe the protonated siloxane (M+1), as well as the peak (M-15) corresponding to loss of a methyl group. This is unsurprising, considering how acid is known to catalyze hydrolysis and/or rearrangement of siloxanes.[21]

ESI-MS of the acidic siloxane after exposure to the liquid metal showed additional species (Figure 3d, e). We were able to identify these unknown peaks as gallium chloride/siloxane adducts due to the unique 40% M, 60% M+2 isotope pattern observed (Figure S5 in the Supporting Information). Further analysis identified the corresponding indium chloride/siloxane adducts. Interestingly, there is an absence of literature identifying or characterizing these adducts. It is likely that $GaCl_3$ and $InCl_3$ exist in a coordinate covalent complex analogous to diethyl ether adducts previously identified and observed.[27,28] It is apparent that the gallium and indium chloride produced on the shell of the liquid metal are being solubilized by the siloxane solution and exist stably in solution. It is interesting to note that adducts are observed only when $n = 3$ or greater. The reason for this is unknown, but we believe it is worth calling attention to.

Dielectric Characterization of the Acidic Siloxane. As electrical insulation is one of the stated advantages of our acidified siloxane, the dielectric properties of the 1.5 M HCl acidic siloxane were characterized and compared to the behavior of the regular siloxane. Because the regular siloxane is proven to be effective as the insulating fluid for electronics applications, including electrowetting,[29] the acidic siloxane should ideally show similar electrically insulating properties to be useful in this manner. It is also important to quantify these properties such that various electronic devices can at least be conceptually designed and theoretically modeled.

The high frequency complex permittivity was calculated using a resonant cavity perturbation method[30,31] (details in experimental section) at frequencies ranging from about 2−20 GHz, shown in Figure 4a. The real and imaginary parts of the permittivity are calculated by measuring the slight shift in the resonant frequency and peak Q before and after the sample is placed in the cavity, using the equations below.

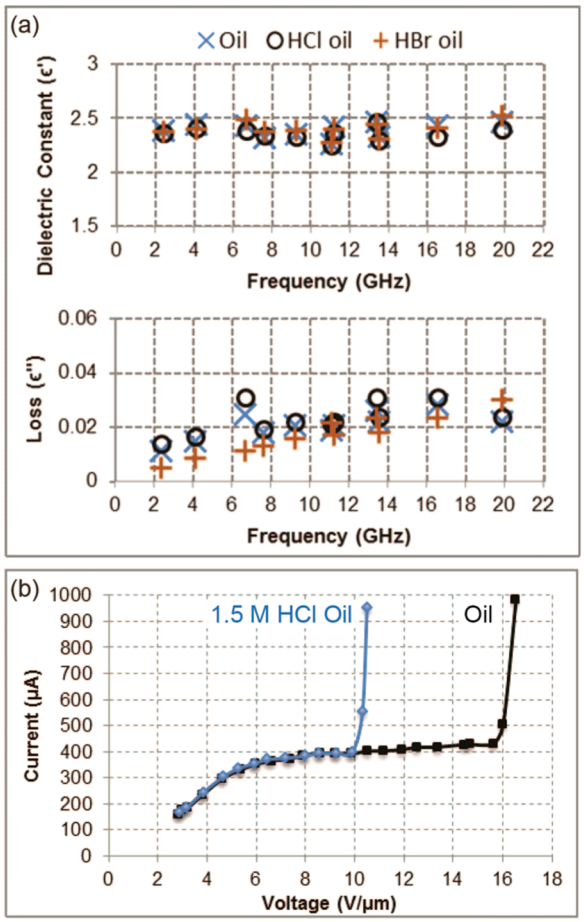


Figure 4. (a) Waveguide perturbation analysis showed minimal difference in the dielectric properties of the oil versus the acidic oils, all were found to be highly insulating. The one sigma of the measurements at each frequency was typically equal to or less than the size of the data points shown in the figure. (b) Breakdown voltage test showed that the I−V response of the oil versus acidic oil is similar until the breakdown voltage is reached.

$$Q = \frac{f_0}{\Delta f(-3\ \mathrm{dB})} \quad (1)$$

$$\varepsilon'_r = \frac{V_c(f_c - f_s)}{2V_s f_s} + 1 \quad (2)$$

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$$\varepsilon''_r = \frac{V_c}{4V_s}\left(\frac{1}{Q_s} - \frac{1}{Q_c}\right) \quad (3)$$

where f_0 is the frequency at the maximum resonant signal, $\Delta f(-3\ \mathrm{dB})$ is the frequency width of the peak at 3 dB below the peak maximum, V is volume, and the subscripts c and s refer to the values of no sample and with a sample, respectively. The dielectric behavior of both HCl and HBr acidic siloxanes is shown to be essentially the same as that of the regular siloxane. This is quite encouraging and exciting considering that the tested HCl acidic siloxane is at 1.5 M HCl, and in sealed devices far less HCl content would be needed.

The low frequency current−voltage response of the HCl and regular siloxane oils were measured by an electrical breakdown test (see Experimental Section for details). Figure 4b shows that the HCl siloxane behaves identically to the regular siloxane at lower voltages up until the breakdown voltage is reached. The experiment was repeated 3 times with similar results for each oil type. We observed breakdown at approximately 10 V/μm for the 1.5 M HCl siloxane compared to 16 V/μm for the regular siloxane. We hypothesize that this is due to the Wein effect (also known as the dissociation field effect). In this effect the electric field induces greater alignment of the siloxane and the acid molecules along the electric field. By orienting the molecules according to their dipole moments, greater proton conduction occurs. This results in a shift in the pK_a which frees up more ions, and thus increases current flow.[32]

Electrowetting Demonstrations of GaLMA. The ability to control and manipulate the GaLMA through electrowetting is a potential breakthrough for reconfigurable electronic device design and applications. Historically, liquid metal electrowetting has relied on mercury, or, as noted in the Introduction, alternative approaches to electrowetting are used which bring additional challenges if used in electronics applications. Furthermore, electrowetting is an excellent validation of the acidic siloxane, as electrowetting requires nearly perfect electrical insulation around the electrowetting phase, and is very sensitive to changes in interfaces between any of the three phases in a siloxane/liquid metal/solid system. For example, our own experiments have shown that simply trying to use HCl vapor does not work for electrowetting because, upon reacting with the gallium oxide, water forms on the surface of the GaLMA along with dissociated metal chloride ionic byproducts. When water is present it will preferentially electrowet and the GaLMA contact angle does not change.

Electrowetting[19] requires having a conducting fluid, surrounded by an insulating fluid, which is separated from an electrode by a solid dielectric layer. A low interfacial surface tension between the insulating fluid and the solid dielectric layer surface is used to achieve a high zero-voltage contact angle (up to 180°). When a voltage is applied between the electrode and the conducting fluid, charges build up at the interface of the liquid metal and the electrode beneath the dielectric, creating an electromechanical force that alters the force-balance of interfacial surface tensions. The result is a decrease in the observable contact angle. However, the actual microscopic contact angle, governed by the surface energies of the three phases involved, is unchanged.[33]

Figure 5 shows the contact angle vs applied voltage for the GaLMA in the HCl siloxane of approximately 0.135 M HCl (see methods for fabrication details). The contact angle was measured at increasing voltages over a time period of about 5

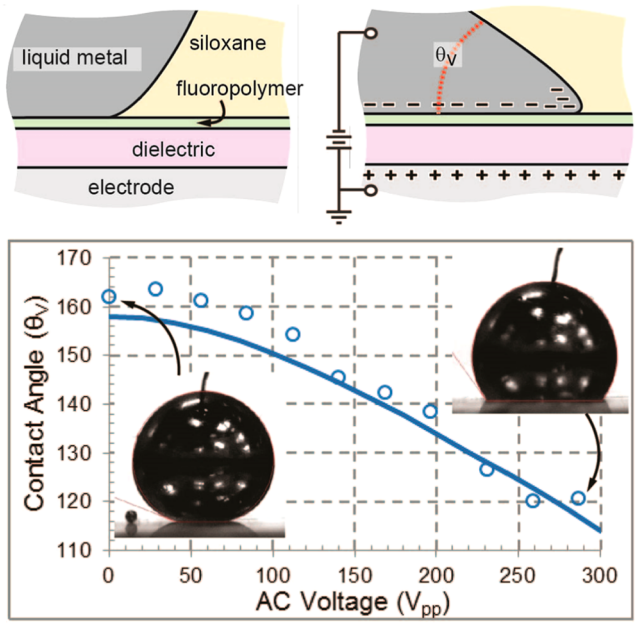


Figure 5. Schematic showing the process of electrowetting: a conducting fluid (liquid metal) surrounded by an insulating fluid (oil) on an electrode but separated by a dielectric layer. The equilibrium state of the liquid metal droplet is a high contact angle (~180°) due to the interfacial energy balance. When a voltage is applied between the liquid metal and electrode, the droplet is forced out of equilibrium by the applied electric field, lowering its contact angle. The plot shows the experimental GaLMA relationship of the applied voltage to the contact angle (dots) as well as the theoretical relationship based on the interfacial energies (solid line).

min in an open container; therefore the exact concentration of acid in the siloxane at each measurement cannot be guaranteed as some HCl leaves the system as vapor. The zero voltage contact angle (Young's angle) of the LM is expected to be 180° but due to gravity and the limit of using images for measurement, it appears as 160°. Using electrowetting, the contact angle can be reduced to approximately 120° with 300 V. In electrowetting, there is a saturation limit where the decrease in contact angle plateaus as voltage is increased.[34] We do not see such behavior because our system's maximum peak to peak voltage was 330 V, which might not be enough to reach the saturation limit. The experimental data also shows good agreement with the theoretical curve, which was calculated using the electrowetting equation:

$$\cos\theta_V = \frac{\gamma_{id} - \gamma_{cd}}{\gamma_{ci}} + \frac{\varepsilon_o\varepsilon_r}{2z\gamma_{ci}}V^2 \quad (4)$$

where θ_V is the apparent contact angle when voltage is applied, γ is the interfacial energy between any two of the conducting liquid (c), insulating liquid (i), and dielectric (d) phases, ε is the dielectric constant, z is the thickness of the dielectric, and V is the applied voltage. Even this relatively small change in contact angle can be levied in useful device applications.[35] We also present a simple demonstration of GaLMA reconfiguration (shape-change) by electrowetting. Figure 6 shows zoom-in photo demonstration of a switchable wire-grid polarizer device using electrowetting to actuate the GaLMA. When no voltage is applied the liquid metal splits into droplets but when a voltage is applied the liquid metal is pulled to follow the electrode lines. Details on the device design and testing were performed.[35]

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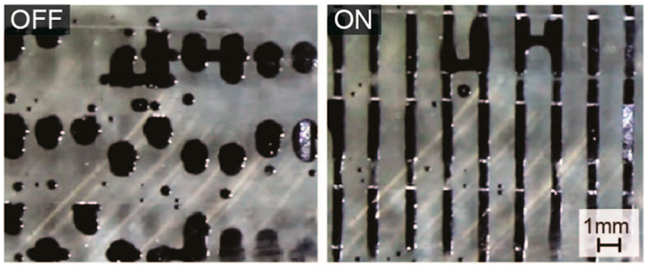


Figure 6. Photos of a portion of wire-grid polarizer device in both on and off states where the dark areas are the GaLMA and the light areas are the substrate. In the off state, the liquid metal is split into droplets by shallow channels patterned on the top plate.[35] In the on state, the liquid metal takes the line shape of the electrodes patterned on the bottom plate.

CONCLUSION

We have demonstrated herein a new material enabling a breakthrough in nontoxic (GaLMA) liquid metal reconfigurable devices. The acidified siloxane has numerous advantages over other methods being explored to remove/prevent oxide without interfering with device functionality. Laboratories and fabrication lines can now use GaLMAs to fabricate devices without resorting to use of cumbersome ultralow oxygen environments. Furthermore, this work now represents a first solution to make long-lasting functional devices, because even sealed devices will allow some minute oxygen entry over time which will cause GaLMA oxidation. As a result, GaLMA is now more practical for a wide variety of applications. We believe our novel acidified siloxane can also be used in a variety of broader applications requiring the presence of acid in an insulating aprotic environment. The siloxane itself has been shown to eliminate oxides as well as solubilize and incorporate the metal ions into the liquid with minimal impact on the insulating properties. In our case, we have used this novel solvent in order to enable electrowetting of GaLMAs.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b03501.

NMR spectra; effects of varying aqueous acid exposure time and acid composition; FTIR spectra; proposed chemical reactions; isotope pattern used to identify gallium chloride and indium chloride adducts (PDF)

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Notes

The authors declare no competing financial interest.

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