Surface Modification of Gallium-Based Liquid Metals: Mechanisms and Applications in Biomedical Sensors and Soft Actuators

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1. Introduction

This review focuses on surface modifications to gallium-based liquid metals (LMs), which are stretchable conductors with metallic conductivity and nearly unlimited extensibility due to their liquid nature. Despite the enormous surface tension of LM, it can be patterned into nonspherical shapes, such as wires, due to the presence of a native oxide shell. Incorporating inherently soft LM into elastomeric devices offers comfort, mechanical compliance, and stretchability. The thin oxide layer also enables the formation of stable liquid colloids and LM micro/nanosized droplets that do not coalesce easily. The oxide layer can also be exfoliated and chemically modified into semiconductor 2D materials to create and deposit atomically thin materials at room temperature. Thus, the interface and its manipulation are important. This review summarizes physical and chemical methods of modifying the surface of LM to tune its properties. The surface modification of LM provides unique applications, including use in soft biomedical sensors and actuators with mechanical properties similar to human tissue.

This review focuses on surface modifications of liquid metal (LM). Gallium (Ga) and Ga-based LMs show the promising ability to maintain metallic properties under large mechanical strains when encapsulated inside an elastomer matrix. This property is useful in a variety of applications, including wearable/deformable devices, sensors, and soft actuators—the focus of this special issue. There are several motives for creating soft and stretchable devices. For example, devices that are soft and flexible can make conformal contact to human skin for continuous and long-term monitoring. Likewise, devices assembled on or within soft robots can maintain function during actuation (bending or stretching) while sensing dynamic motion.

Conventional conductors in electronic systems are typically rigid (e.g., copper) and thus poorly suited for soft and stretchable devices. To address this issue, efforts have been taken to create stretchable and deformable conductors using thin metal films with special geometries (e.g., pop-up and serpentine electrodes) on a deformable substrate or polymer composites filled with conductive nanomaterials in a stretchable matrix. These approaches effectively render rigid materials stretchable through clever engineering of their geometry. However, due to the inherently nonstretchable nature of solid metal films or solid conductive particles, these components/inclusions would add to the overall rigidity of the composite and limit their deformability. LMs are interesting as stretchable conductors because they have metallic conductivity and deformability defined primarily by the encasing material (e.g., elastomer).
Ga-based LMs may be useful as flexible, stretchable conductors for additional reasons. Ga exhibits low toxicity\(^{17–19}\) and near-zero vapor pressure at room temperature.\(^{20,21}\) Ga has a melting point \(T_m\) of 30 °C\(^{22}\) but can be combined with other metals, such as indium (In) and tin (Sn) to create liquid alloys with lower melting points. For example, eutectic gallium-indium (EGaIn—75 wt% of Ga and 25 wt% of In) alloy\(^ {23}\) and eutectic alloys of Ga, In, and Sn (Galinstan—68 wt% of Ga, 22 wt% of In, and 10 wt% of Sn) have \(T_m\) values lower than room temperature.\(^{4,7}\) As liquids, these LMs are soft and stretchable conductive materials.\(^{4,23}\) Also, LMs have been shown to be used in a number of advanced fabrication technologies such as direct-write 3D printing,\(^ {24–25}\) microchannel injection,\(^ {26–28}\) and oxide printing.\(^ {29–32}\)

Although controlling the properties of the interface is a key parameter to utilize LM in a number of applications, most of the reviews have focused on only LM itself. Examples include reviews on composites, stretchable conductors, responsive materials, patterning, microfluidics, chemistry, and nanoparticles (NPs).\(^ {2,4,7,13–16}\) Herein, we critically review state-of-the-art techniques to physically and chemically modify the interface of Ga-based LM. We finish by discussing applications of modified Ga-based LM in advanced sensors and actuators.

## 2. Brief Summary of Notable Characteristics of Ga-Based LMs

Ga and Ga-based LMs have unique properties (Figure 1). Ga (Figure 1d) is safe to handle due to its low toxicity and negligible vapor pressure compared with other metallic elements with low melting points such as cesium, rubidium, and mercury.\(^{19}\) LM can be utilized as a soft and stretchable conductor at room temperature; it maintains metallic electrical and thermal properties even under extreme deformation (Figure 1a shows \(\approx 700%\) strain, although the strain at failure may be limited by the polymer itself), making it useful for a variety of stretchable electronics.

Bare LMs (i.e., those lacking surface species, such as oxides) have enormous surface tension and therefore tend to form spherical shapes. The surface tension of bare Ga is \(>700\) mN m\(^{-1}\); in comparison, the surface tension of water is about 72 mN m\(^{-1}\).\(^ {17,18}\) Ga-based LM reacts spontaneously with oxygen to form a native oxide under the ambient atmospheres (Figure 1c).\(^ {39}\) This oxide “skin” acts as a solid-like shell that can retain the LM fluid in nonspherical shapes, such as wires.\(^ {11}\) The oxide layer also helps to adhere LM droplets on most smooth surfaces.\(^ {40–43}\) The oxide layer also helps stabilize small droplets or colloids

![Figure 1](https://www.advancedsciencenews.com/2000159/figure1.png)

**Figure 1.** Representative special characteristics of Ga-based LM. a) Soft and stretchable conductor with metallic conductivity and nearly unlimited deformability. b) Tunable surface demonstrated here by a redox reaction between Ga and a metal ion (M\(^{+}\) ions). c) The native oxide layer is only a few nm thick yet has profound impact on the behavior and utility of LM, such as EGaIn, at sub-mm length scales. d) The low toxicity and near-zero vapor pressure make handling safe (Note: Although we depict a bare hand, we recommend using gloves when handling as a precaution.).
of LM against coalescence. The oxide can also be stripped from the metal as a method to deposit oxide or semiconductor species at room temperature. Engineering this oxide layer also enables physical adhesion, chemical adsorption, electrochemical control of interfacial tension, and 2D material printing.  

2.1. Native and Non-Native Oxide Layer Properties  

Ga-based LM spontaneously and rapidly (nearly instantly) forms a self-passivating Ga oxide layer when exposed to ambient atmosphere. This oxide layer is composed of amorphous or poorly crystallized Ga oxide. Ga\textsuperscript{3+} is the most stable oxidation state in Ga oxide, and thus the expected stoichiometry should be Ga\textsubscript{2}O\textsubscript{3}; however, the oxide typically has substoichiometric ratios of Ga to O. \[ \beta\text{Ga}_{1-x}O_x \] For example, Auger spectroscopy shows a ratio of Ga and O (atomic % ratio Ga:O = 10:14). The oxide spontaneously forms even if the concentration of atmospheric oxygen is \( \approx 20 \text{ ppm} \). The most stable form of Ga oxide is \( \beta\text{Ga}_{1-x}O_x \), but like most native oxides, the skin is amorphous or poorly crystallized. The Cabrera–Mott oxidation mechanism is the most well-accepted theory to explain the growth of native oxides. When a metal without an oxide layer is exposed to an oxygen-containing environment, 1) metal and oxygen react to form a thin native oxide layer. 2) The native oxide layer acts as a barrier to prevent further direct contact between metal and oxygen. 3) However, electrons can tunnel through the oxide, creating negatively charged oxygen ions at the exterior of the oxide and leaving behind positively charged metal at the metal–oxide interface. These charged species create an electric field. 4) The electrical field can drive charged species through the thin oxide, causing the oxide to grow thicker. It continues until the electric field is no longer sufficient to drive the growth at appreciable time scales and the oxide effectively stops growing. Depending on various measurements and experimental conditions, the oxide thickness ranges from 0.5 to 5 nm (cf. the center of Figure 2). This range likely reflects the influence of both the chemical environment and time. The exact stoichiometry and composition depend on the surrounding environment and thermal history. For example, in water, the native oxide changes into GaOOH, which is a mechanically weaker and less passivating version of the oxide. The oxide layer has solid-like mechanical properties. It has a surface modulus of 13 N m\textsuperscript{-1} and breaks with a surface yield stress of 0.2–0.6 N m\textsuperscript{-1} according to interfacial rheological measurements. As a consequence, extruding the metal from a nozzle requires overcoming the surface stress in a manner that is similar to surface tension. The pressure required to expand a droplet of metal is equal to the surface stress multiplied by the curvature (in the case of a sphere, curvature is 2/R, where R is the droplet radius).  

2.2. The Utility of the Native Oxide Layer of Ga-Based LM  

Figure 2 shows several approaches to engineer the interface of LM for a number of applications. For example, as shown in Figure 2a, the oxide forms a stabilizing shell around the metal to enable patterning of nonspherical structures, such as wires or 3D structures. Electrochemical reactions can remove or deposit oxide species, thereby making it easy to tune the interfacial tension (Figure 2b). The oxide layer provides anchor points to covalently bond molecules to the surface or for adhering particles (Figure 2c,d). The oxide compositions can be tuned and stripped from the surface to form unique 2D materials (Figure 2e). Section 3 will discuss the details of these methods to use, modify, and manipulate the surface.  

3. Surface Modification Methods  

Among the various surface modifications (cf. marble, ligand, oxides control, surface reduction, electrical control, magnetic control, etc.), the representative methods are described in Figure 3 and 4. We divide these methods into two categories: 1) depositing and removing the oxide layer in Section 3.1, and 2) modifying the interface in Section 3.2 and 3.3.  

3.1. Depositing or Removing the Oxide Layer  

Figure 3 shows examples for removing, disrupting, or depositing the oxide layer. The state of the interface of the metal can be
Figure 3. Examples for controlling, removing, and depositing the oxide layer. a) Scheme for fracturing the oxide by mechanical deformation of LM. b) Schematic illustration of a LM droplet (left) breaking into smaller droplets (right) formed by stirring.\textsuperscript{[76]} c) Scanning electron microscope (SEM) image of AgNP (top) sintering with LM (bottom). Reproduced with permission.\textsuperscript{[78]} Copyright 2018, Wiley-VCH. d) Enhanced stretchability (blue) and conductivity (green) of AgNP-LM (right) relative to AgNP (left). Reproduced with permission.\textsuperscript{[78]} Copyright 2018, Wiley-VCH. e) The oxide surface can be dissolved by acidic or basic solutions. f) Contact angle changes over time by removing the oxide in HCl or NaOH solution. Reproduced with permission.\textsuperscript{[75]} Copyright 2017, Wiley-VCH. g) Photographs of a droplet of metal adhering to a surface in air (upper). Reproduced with permission.\textsuperscript{[75]} Copyright 2017, Wiley-VCH. NaOH solution removes the oxide and the metal slides down an inclined surface (bottom). Reproduced with permission.\textsuperscript{[75]} Copyright 2017, Wiley-VCH. h) Oxide layer deposition and removal by electrochemistry. i) At $-1.5 \, \text{V}$ (left), the metal is effectively free of oxide in NaOH solution and therefore at high tension. Increasing the potential to a more positive value, $-0.5 \, \text{V}$ (right), deposits the oxide and lowers the tension significantly. Reproduced with permission.\textsuperscript{[51]} Copyright 2014, National Academy of Sciences. j) The effective interfacial tension changes as a function of potential. The green shaded region indicates the portion of the plot in which the metal is free of oxide. Reproduced with permission.\textsuperscript{[51]} Copyright 2014, National Academy of Sciences.

Figure 4. Examples of surface modifications of LM. a) Schematic illustration of LM marbles. b) A LM marble covered with PTFE particles, which eliminates the adhesion of LM to surfaces. Reproduced with permission.\textsuperscript{[100]} Copyright 2019, Wiley-VCH. c) Schematic illustration of the change in surface adhesion caused by particles at the interface. d) Schematic illustration (top), photograph (bottom left), and SEM image (bottom right) of PTFE- and Fe-coated marbles. Reproduced with permission.\textsuperscript{[100]} Copyright 2019, Wiley-VCH. e) Schematic illustration of magnetically responsive LM marble (top) and nonwetting properties of a marble (bottom). Reproduced with permission.\textsuperscript{[100]} Copyright 2019, Wiley-VCH. f) Schematic illustration of modifying LM with ligands. g) Core–shell structure of EGaIn encased in a polymer. The polymer, POMA, has both hydrophilic and hydrophobic functional groups, which forms a micelle structure that keeps the metal stable even in water. Reproduced with permission.\textsuperscript{[101]} Copyright 2018, Royal Society of Chemistry. The use of a POMA-toluene emulsion in water facilitates the coating process. h) Schematic diagrams showing deformable NPs with core (LM nanodroplets) and shell (thiolated cyclodextrin) loaded with drugs for delivery into the cellular cytoplasm. Reproduced with permission.\textsuperscript{[102]} Copyright 2015, Nature Publishing Group.
altered by mechanical deformation of the oxide, chemical dissolution of the oxide, and electrochemical reduction and oxidation.\textsuperscript{[72–76]} Whereas chemical methods dissolve the oxide (e.g., acidic or basic pH solutions), physical methods break the oxide layer by applying external force. Figure 3a shows that a physical force (cf. stirring or vibration) can break the native oxide and expose fresh metal. One protocol called SLICE (shearing liquids into complex particles)\textsuperscript{[76]} breaks LM into particles to mix it with other materials, such as elastomers. Although few materials (other than metals) can disperse in the LM due to the high cohesion forces, the oxide layer can help encase particles and enable them to be mixed in.\textsuperscript{[50,77]}

The forces necessary to break the oxide layer are similar conceptually to surface tension because the oxide is confined to a thin surface layer. Rheological measurements show that the surface yield stress (i.e., the force per length necessary to break the oxide) is \( \approx 0.2–0.6 \) N m\(^{-1}\).\textsuperscript{[1,64–66]} Thus, it is straightforward to mechanically rupture the oxide layer by applying mechanical force such as scraping, mixing, vibrating/sonicating, swelling (of a surrounding medium), and stirring. When the oxide breaks, the underlying metal gets exposed temporarily to the ambient. In the presence of oxygen, the exposed metal oxidizes rapidly (in a fraction of a second). Rupturing the oxide provides an opportunity to react the underlying metal with other functional groups, for example, thiol.\textsuperscript{[59]} Likewise, the exposed metal can initiate free radical polymerization from the surface (notably, without the need for classic molecular initiators).\textsuperscript{[79]} The exposed metal can also facilitate partial merging of adjacent particles to form a percolated, conductive networks.\textsuperscript{[5,48]} This process is called “mechanical sintering” to highlight the ability to make conductive pathways using force rather than other thermal or chemical sintering processes.\textsuperscript{[54,73,74,80,81]} Mechanical deformation of the oxide layer can help facilitate metal–metal contact between LM particles and diverse metals (Au, Mg, Ag, Cu, and Fe).\textsuperscript{[54,82–86]} Figure 3b shows an example of LM particles contacting silver nanoparticles (AgNPs). Stirring LM and AgNPs provides shear forces on the oxide layer that allows metal–metal contact. The exposed LM and AgNP percolate and form a Ag-based ink (Figure 3c) that exhibits excellent electrical conductivity because the LM bridges the gap between Ag particles (Figure 3d).\textsuperscript{[78,82]}

Chemically, as shown in Figure 3e, acidic or basic solutions can remove the native oxide layer. The native oxide is amphoteric and can therefore be removed by acid (typically HCl) or base (typically NaOH). The removal of the oxide occurs more rapidly in the basic solution (1 M NaOH) than in the acidic solution (1 M HCl) (Figure 3f), although both can remove the oxide quite rapidly.\textsuperscript{[29]} A practical video on how to remove the oxide using acid and base is provided in this reference.\textsuperscript{[87]} According to the Pourbaix diagram, the oxide layer is unstable in aqueous solutions with low pH (<3) or high pH (>10).\textsuperscript{[88]} One study suggests the following reactions occur:\textsuperscript{[89]}

\[
\begin{align*}
\text{Ga}_2\text{O}_3(s) + 2\text{NaOH(aq)} + 3\text{H}_2\text{O(l)} & \rightarrow 2\text{NaGa(OH)}_4(aq) \\
\text{Ga}_2\text{O}_3(s) + 6\text{HCl(aq)} & \rightarrow 2\text{GaCl}_3(aq) + 3\text{H}_2\text{O(l)} \\
2\text{Ga(s)} + 2\text{OH}^-\text{(aq)} + \text{O}_2\text{(g)} & \rightarrow 2\text{GaO(OH)(s)} \\
\end{align*}
\]

(4)

Equation (3) and (4) show mechanisms by which oxide can form, whereas Equations (1) and (2) show reactions by which it can be removed. Although all reactions are reversible, these reactions are so heavily favored in the direction depicted that we show only a single arrow. Extreme pH solutions provide a way to remove or “clean” LM from surfaces. In our lab (based on a helpful suggestion from the Majidi group), we use a product called “Simple Green” (Industrial Cleaner & Degreaser, Sunshine Makers) to clean surfaces contaminated with LM. This formulation of “Simple Green” contains mixtures of citric acid, citrate salts and nonionic surfactant (C9-11 alcohols ethoxylated), which is much less corrosive than HCl or NaOH. Whereas oxide-coated metals adhere to surfaces, removing the oxide can cause them to withdraw from a microfluidic channel or detach from a surface (Figure 3g).\textsuperscript{[25,34,90]}

Electrochemical reactions are an appealing way to control the interfacial behavior of LMs through the use of applied voltage (Figure 3h). The electrochemical deposition of the oxide lowers the surface tension of Ga-based LM.\textsuperscript{[51]} As shown in Figure 3j, reducing the oxide electrochemically in electrolyte puts the bare metal in a state of high surface tension in which modest changes to surface tension are achieved by electrocapillary effects (i.e., modifying the amount of ions in the electrical double layer at the surface of the oxide-free metal).\textsuperscript{[51,91]} However, applying an oxidative potential deposits oxide electrochemically (so-called anodization) and causes a large drop in surface tension. The change from high to low surface tension is apparent in the shape of the metal, going from a droplet (Figure 3i, left) to a pancake shape (Figure 3i, right). The corresponding changes in surface tension are captured in Figure 3j in which the background color depicts the transition from oxide-free (green region) to oxide-coated (white region). These values were measured by evaluating the shape of a droplet of metal versus potential. The significant decrease in effective tension (“effective” because the surface has oxide species on it) is not well understood but thought to be due to a combination of the oxide behaving like a surfactant as well as compressive stresses (opposed to tension) arising from oxidation. An important detail in these experiments is the use of 1 M NaOH as the electrolyte. While oxide deposits electrochemically on the surface, the basic conditions dissolve the deposited oxide such that the surface is dynamic; as such, it can effectively flow despite the deposition of solid-like species on the surface. Electrochemical oxidation in neutral electrolytes forms a thick oxide that prevents the metal from flowing freely (yet, in neutral electrolyte, the metal can still generate protrusions that expand laterally, consistent with the notion that anodization generates stress at the interface).\textsuperscript{[51]}

A key takeaway from Figure 3j is that the oxide layer can be controlled electrochemically, which is distinct from the well-established phenomenon of electrocapillarity. Electrocapillarity does not involve Faradaic reactions and instead utilizes charge at interfaces to lower the interfacial tension. The resulting electrical double layer resembles a capacitor at the interface of the metal and electrolyte. Increasing the charge at the interface by applied potential lowers the tension relative to the so-called “point of zero charge” (i.e., the potential at which minimal charge exists at the metal–electrolyte interface). Because this concept
holds true for positive or negative charges (i.e., it does not matter which side of the “capacitor” is positive), the so-called “electrocapillary” curve (surface tension vs potential) is typically a downward facing parabola centered at the point of zero charge. This classic theory assumes only charge at the interface and does not account for surface reactions that produce oxide or other species. Notably, Ga-based LMs only follow electrocapillary behavior at potentials at which the surface is effectively free from oxide (below $-1.4 \text{ V vs } \text{Ag/AgCl}$ in 1 M NaOH). However, at potentials where the oxide forms (above $-1.4 \text{ V vs } \text{Ag/AgCl}$), the tension drops dramatically. This result suggests the oxide helps to lower the tension of the metal. For a more nuanced and detailed explanation, please see a recent review.[3] These approaches (Figure 3a,e,h) can modulate the surface tension over a huge range to form reconfigurable antennas,[92–94] actuators,[91,95–97] and a soft “transistor” (switch).[98]

### 3.2. Surface Modification via Marbles

A “marble” is a method of uniformly coating the surface of a droplet by rolling it on a bed of powder. Figure 4a shows the method of interfacial modification through the marble method. Marbles form when microparticles or NPs attach to the surface of a LM droplet. Such nano/microparticles can attach to the oxide or fresh metal (native oxide layer removed) coated surface of LM particles. Figure 4b shows a LM marble formed by rolling LM droplets in inert polytetrafluoroethylene (PTFE) particles (35 μm diameter). Similar to flour coated on dough, particles on the LM modify the tendency of the oxide-coated metal to adhere to surfaces, as shown in Figure 4c. These particle coatings prevent the LM from adhering to surfaces due to the roughness of the coating, which can be explained by the Cassie-Baxter model. Preventing adhesion of LM to surfaces is useful in sensors and devices that require droplet fluidity, such as lab-on-a-chip devices. Marble coatings can help avoid LM from amalgamating with certain other metal particles (Figure 4d, bottom). Droplets of LM can also form marbles with Fe particles or a mixture of ferronickel (FN) and polyethylene (PE) microparticles.[99,100] In Figure 4e, marbles of EGaIn with a mixture of FN and PE microparticles can have magnetic properties (Figure 4e, top) and nonwetting properties (Figure 4e, bottom).[100]

### 3.3. Surface Modification Using Ligand Binding

The LM surface also can be modified through interaction of ligands to the LM (or more commonly, oxide-coated LM) (Figure 4f). Ligand binding involves chemical or physical binding of small molecules, polymers, or polymer precursors to the oxide-coated LM. Applying mechanical mixing or sonication to the LM in a liquid media (cf. ethanol) can generate LM particles. However, LM particles produced in water (and certain solvents) often settle over time. Water can also react with liquid metal particles, causing them to form GaOOH rods,[63] which have proven useful for destroying cancer cells[103] (in response to NIR light) and bacteria[104] (in response to magnetic fields). However, in other conditions, it would be preferable to keep liquid metal particles suspended stably in water. As shown in Figure 4g, poly(1-octadecene-alt-maleic anhydride) (POMA) can stabilize the LM particle suspensions in water.[101] To achieve such a coating, POMA in toluene, deionized water, and LM are sonicated to form a toluene-POMA emulsion. As the toluene evaporates, it leaves behind a POMA coating on the LM particles. The suspensions are stable for 60 days in biological buffer.

Modifying LM surfaces via covalent or hydrogen bonds with polymer or other macromolecules also helps increase the stability of LM suspensions.[76,79,105–108] For example, thiol groups (e.g., 1-dodecanethiol) can form thiol–metal bonds directly on the LM surface, although this coating does not fully prevent oxidation.[51,56] In addition, various chemical ligands (cf. dodecylphosphonic acid, 11-phosphonoundecanoic acid, silanes) chemically and/or physically bond with the native oxide layer of LM.[109,110] Such surface modifications can tune the thickness of the oxide from 1.28 to 4.46 nm.[109] Due to the increase in oxide skin thickness, elastic modulus increases from 0.37 to 1.38 GPa and also stiffness increases from 0.05 ± 0.03 to $2.90 \pm 0.51 \text{ N m}^{-1}$. The presence of ligands can narrow the size distribution of particles formed by sonication relative to LM particles formed without ligands.[59,80,111] Recently, initiators have been grafted to liquid metal particles to grow polymer from the surface of liquid metal particles via atom transfer radical polymerization (ATRP), thereby providing a versatile tool to control the interfacial chemistry and thereby suspending particles in a variety of media.[108] In addition to suspending particles, surface modification can also provide function, such as for drug delivery (Figure 4h); in this example, drugs loaded on the surface of NPs get released inside cancer cells due to changes in the pH inside the cell.[103] Surface functionalization can also be used for biorecognition events.[112]

### 4. Sensors and Actuators Applications of LM

The electrical properties of LM circuits—such as resistance, capacitance, or inductance—can be altered by changing the geometry of devices under mechanical deformations such as stretching, bending, and twisting. Taking advantage of this peculiar characteristic, LM and its composites can be integrated into devices such as soft sensors and actuators, as shown in Figure 5. Although there are many examples of sensing applications of LM in the literature, we focus here on those that demonstrate the importance of interfaces.

#### 4.1. Surface Modification of LM for Soft Sensors

LM can be utilized as a stand-alone sensor in which resistance, capacitance, or inductance can be manipulated in response to a stimulus (e.g., touch or deformation).[2–4,113] Figure 5a,b shows a soft composite consisting of LM droplets suspended in an elastomer matrix. In this composite, the thin elastomer walls between the LM droplets can rupture under damaging mechanical impact (e.g., compression, fracture, or puncture), leading to the formation of conductive pathways (Figure 5b).[97] The resulting change in local conductivity can be actively sensed in a way to identify damage spatially and temporally. For example, the composite was placed on the surface of a soft, humanoid-like inflatable structure (Figure 5c,d). The electrical response by damage of liquid
metal embedded elastomers (LMEE) sensor and microcontroller is monitored with a closed-loop system, which triggers a pump to compensate for the loss of gas. Such a sensing system allows the soft robot mimic to continuously detect and respond to local damage that would otherwise cause deflation.

LM dispersed in elastomer can sense a stimulus via the capacitance change, leading to the change in dielectric constant.\[114,115\] For example, EGaIn micro- or nanodroplets can be suspended in elastomers such as polydimethylsiloxane by high shearing forces; the mixture can be further utilized in strain sensors.\[114,116\] Fibers filled with liquid metal can sense changes in capacitance in response to touch.\[117\] In addition, LM can be incorporated into microfluidic channels and used as a capacitive sensor to detect the difference in distances from two electrodes.\[118–121\]

**4.2. Surface Modification of LM for Soft Actuators**

LM can also be used for actuators. Under external input such as pH and voltage, the oxide layer of LM can be deposited or removed for the generation of actuation force.\[75\] For example, a field-programmable device can coalesce or separate LM droplets using pulsed voltage (1–10 V) to make or break electrical connections.\[98\] On–off switch of LM can be controlled by pH of the surrounding solution, which can remove the native oxide.\[75\] Working principle of photo-chemically induced actuator using WO$_3$-coated LM droplet. Reproduced with permission.\[46\] Copyright 2013, AIP Publishing Group. SEM image of the surface of LM marble droplet. WO$_3$ (80 nm) acts as a catalyst to generate oxygen bubbles to actuate LM in H$_2$O$_2$ solution. Reproduced with permission.\[46\] Copyright 2013, AIP Publishing Group.
removed, leading to a significant change in surface tension, as shown in Figure 3. As a result, adjacent LM droplets can coalesce or separate driven by interfacial forces. In Figure 5e, an example shows the layout and mechanism of a LM transistor (switch), in which a pair of EGaIn droplets wet underlying copper pads.\textsuperscript{[98]} In the basic solution, two droplets of EGaIn can undergo coalescence and separation depending on the applied potential from adjacent electrodes. This LM switch has similarities to conventional field-effect transistors (on-to-off when droplets separate, off-to-on when droplets coalesce), yet it is built entirely from soft materials. Alternatively, a LM switch can sense and respond to pH changes.\textsuperscript{[75]} A Galinstan droplet was placed in contact with two conductive tungsten electrodes in a special environmental chamber (Figure 5f). The fluid in the environmental chamber was exchanged with the following sequence: air $\rightarrow$ 1 M NaOH $\rightarrow$ distilled water $\rightarrow$ air. Figure 5f is the illustration of the sequence, showing a morphological view of the Galinstan droplet and how the droplet contacts the electrodes to power a light-emitting diode (LED).

As a final example, LM droplets can sense and respond to UV light. Galinstan droplets coated with 80 nm WO$_3$ NPs are known to be photocatalytic (Figure 5g,h).\textsuperscript{[46]} Exposure to UV light (320–380 nm) produces hydrogen peroxide (H$_2$O$_2$), which decomposes to produce oxygen gas bubbles according to the following reaction: 2H$_2$O$_2$ $\rightarrow$ 2H$_2$O + O$_2$. These bubbles can actuate the Galinstan droplet. LM droplets can also sense and respond when contacted with, for example, AI, which generates reactions that propel the droplets.\textsuperscript{[122]}

### 5. Conclusion

Ga-based LM has an interesting combination of characteristics such as low toxicity, extremely high surface tension, high thermal and electrical conductivity, and high deformability. These properties are well suited for soft devices. The spontaneously formed oxide layer facilitates LM patterning into interesting shapes such as stretchable wires, interconnects, electrodes, and antennas. The interfacial properties enable most applications of these LMs. In this review, we focused on recent advances in such surface modifications such as the deposition/removal of the oxide, chemical functionalization of the interface, and electrochemical reactions. Surface modifications can affect wetting properties, the interfacial tension of the LM, the mechanical strength of the interface, the chemical activity, and the ability to suspend LM particles in liquids. These tools empower new applications and inspire continued interest in liquid metals.

### Acknowledgements

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2019M3C1B807746). M.D.D. gratefully acknowledges support from the National Science Foundation CBET-1510772 and ASSIST, EEC-1160483. K.Y.K. was supported by the Ministry of Trade, Industry, and Energy (MOTIE) in Korea, under the Fostering Global Talents for Innovative Growth Program (PO008746) supervised by the Korea Institute for Advancement of Technology (KIAT).

### Conflict of Interest

The authors declare no conflict of interest.

### Keywords

actuators, EGaIn, Galinstan, gallium, soft sensors, surface modification

Received: July 10, 2020
Revised: August 18, 2020
Published online: November 20, 2020

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