CORE CONCEPTS

Liquid metal renaissance points to wearables, soft robots, and new materials

Marcus Woo, *Science Writer*

When chemical engineer Michael Dickey talks about his research on liquid metals, he knows what to expect. “People usually say mercury or the Terminator,” he says, alluding to the shape-shifting killer robot from the 1992 movie *Terminator 2: Judgment Day*. Even many researchers, he says, aren’t familiar with the unique properties and potential uses of these unusual materials, which conduct heat and electricity like any other metal yet are liquids near room temperature.

That unfamiliarity is changing. Over the last few years, he says, liquid metals have undergone a renaissance among researchers—thanks, in part, to growing interest in wearable devices and soft robotics. These

technologies demand new kinds of electronics that bend and stretch.

Liquid metals also hold enormous potential as routes to new materials and catalysts, which can kick-start useful chemical reactions for many industries and applications. The metals could even help trap and convert carbon dioxide, offering another technology to combat climate change. Less than a decade ago, only a handful of groups around the world were working with liquid metals, notes Kourosh Kalantar-Zadeh, a chemical engineer at the University of New South Wales in Sydney, Australia. “Now it’s exploding.”

A growing number of research groups are working with liquid metals, hoping to exploit their potential to create new materials, new catalysts, and possibly new ways to trap carbon dioxide. Republished with permission of Royal Society of Chemistry, from ref. 14; permission conveyed through Copyright Clearance Center, Inc.

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By encasing gallium alloys in flexible plastic, researchers have created a deformable and tunable antenna. Image credit: Michael Dickey (North Carolina State University, Raleigh, NC).

More than Mercury

Mechanical engineer Carmel Majidi, at Carnegie Mellon University in Pittsburgh, PA, says development of technology based on liquid metals has been held back by concerns about leaks and unreliability. But a push toward safer robots without heavy metal parts, and toward devices worn on clothing, skin, or even inside the body, make the flowing properties of a liquid a big asset.

Although mercury has been used for millennia in medicine, pigments, and, of course, thermometers, most research on liquid metals now focuses on gallium, which, unlike mercury, is nontoxic. Gallium also melts at just 30 °C; mixing in other elements such as tin or indium makes useful gallium alloys with even lower melting temperatures.

Liquid metals are also highly reactive, making them especially useful for chemical engineers. Gallium alloys have negligible vapor pressure, so they don't evaporate and can't be inhaled. And they have among the largest surface tensions of any liquid at room temperature, making them bead up into spheres.

To use liquid metal for soft and flexible electronics, researchers must control the fluid's shape and motion. Earlier this year, for example, a team from China demonstrated that magnetic fields could control a liquid-metal blob of gallium-indium-tin alloy—a phenomenon with an eerie resemblance to the T-1000 in *Terminator 2* (1).

And Dickey, who works at North Carolina State University in Raleigh, is exploiting one particular property to control these materials: a liquid metal's oxide skin. Like all metals, liquid metals oxidize when exposed to oxygen; this creates a nanometer-thick oxide skin around a fluid interior. "It allows you to manipulate the liquid in ways that are normally not possible with a conventional liquid like water," he says. Because the liquid is encased in this flexible skin, it doesn't spill or smear as an amorphous puddle. Instead, it holds its shape even while being stretched, bent, spread around like paint, injected through microfluidic channels (2), or printed with a three-dimensional printer (3).

That skin can lead to some curious behaviors. His lab has found that when a drop of gallium-indium alloy

sits in a strong alkali solution, applying voltage causes the skin to form around the drop. The skin acts as one of the world's most effective surfactants—chemicals that alter the drop's surface tension—by turning the drop's spherical shape into a snowflake-like fractal pattern (4).

The researchers still aren't exactly sure what causes this dramatic transformation. "I don't know if that work is as practical as others, but just in terms of the cool factor, I think it's pretty remarkable," Dickey says. "It's the kind of thing I show to people and their jaws hit the floor."

But he and his colleagues have demonstrated more practical applications as well. By encasing gallium alloys in flexible plastic, they've created a deformable and tunable antenna (5). And by forming thin tubes of liquid metal surrounded by the oxide skin, they have created wires that can stretch up to 10 times their original length (6). The wires are self-healing: When severed, they simply fuse back together.

By sandwiching gallium-indium nanoparticles—liquid encased in their oxide shells—between rubber sheets, Dickey's team has made a bendable circuit board (7). Pressing on the board pops the oxide shell around the nanoparticles, spilling out liquid metal that merges to form conductive wire. Using a pen to break the nanoparticles, researchers can then draw out a functioning circuit by hand.

The same principle can be used to draw or print on all kinds of surfaces. Similar to screen printing a T-shirt, Martin Thuo, a materials chemist at Iowa State University in Ames, has used nanoparticles of a bismuth, indium, and tin alloy, called Field's metal, to print circuits on rose petals and gelatin, a proxy for human tissue (8).

"It's the kind of thing I show to people and their jaws hit the floor."

—Michael Dickey

He's now trying to print circuits on neurons—a step toward better electrodes implanted in the brain to treat disorders including Parkinson's disease and obsessive-compulsive disorder. Liquid metal electrodes could better conform to the shape of the brain, creating a more reliable contact. They would also be easier and safer to implant, Thuo says. With a minimally invasive procedure, the liquid metal could be delivered and removed through a small incision.

Metal Muscles

Liquid metals could even bestow a soft robot with a sense of touch. Most recently, Dickey embedded liquid-metal circuitry inside a stretchable silicone material that changes color with heat. Pushing on the material deforms the wire and changes its electrical resistance; the current will then heat the material and change its color. Pressing harder can, depending on how the circuit is designed, change it again. "If you touch it one way, it does one thing," Dickey says. "If you touch it in a different way, it does something else."

When voltage is applied to a liquid gallium alloy in an alkaline solution, the liquid forms a fractal pattern. Image credit: Minyung Song (North Carolina State University, Raleigh, NC).

This, he says, demonstrates rudimentary logic on a soft material without a computer chip to tell the material what to do—similar to how an octopus's nerve-packed skin morphs and camouflages in response to its environment without any direct commands from its brain. This technique could enable a soft robot to touch or grab an object and respond according to its hardness or shape (9).

But in addition to sensors, soft robots need actuators and, perhaps, even some sort of artificial muscle. This presents a problem: Most stretchable, rubbery materials don't conduct heat or electricity.

Adding tiny droplets of liquid metals, Majidi has shown, offers a solution. Using a blender, he stirs in a gallium-indium alloy with the chosen polymer in liquid form, which then cools and sets, creating metal droplets (analogous to neurons) suspended in a rubbery material. Pressing hard on the rubber then ruptures the droplets so they merge into a dense metallic network, which essentially mimics nervous tissue. "These pathways would be so dense they would be almost like nervous tissue where the whole material would suddenly become conductive," Majidi says. The liquid metal network can spontaneously reform around any cracks or holes in the rubber to maintain conductivity.

Majidi recently used the technique to build an artificial muscle from a liquid-crystal elastomer, a rubbery material that can spontaneously warp and hold its shape but returns to its original form when heated. By infusing the elastomer with liquid metal, the researchers could use electricity to make the material morph on demand (10).

Liquid metals' heat conduction could prove useful as well. By blending liquid metals into rubber, Majidi has produced a heat-dissipating material that can squeeze into the nooks and crannies of electronics and machines to keep them cool (11). Majidi has already found commercial interest in the technology in the electronics, semiconductor, automotive, and

healthcare industries. Last year, his lab received a NASA grant to develop a version of the material suitable for use in space.

New Paradigm

Perhaps the biggest impact of liquid metals will be as a medium for chemical reactions. Unlike solids, liquids can facilitate reactions below the surface, where a sea of ions and electrons—many more than in a standard aqueous solution—can be exploited.

Researchers, for example, can engineer a liquid metal to break down organic molecules or create new compounds and metals—all at room temperature, making the process cheap and easy. For example, when researchers supersaturate a metal in a liquid metal, the two will react and crystallize into a new material, similar to the way sugar crystallizes in syrup. "It's basically a new paradigm for chemical reactions for the chemical engineering industry," says Kalantar-Zadeh.

Last year, he and his colleagues demonstrated an inexpensive way to make a water filter by adding aluminum to a gallium-indium alloy. The aluminum rises to the surface, where it oxidizes into a smooth sheet of aluminum oxide. This oxide sheet is porous and lets water molecules flow through, while any dissolved ions of lead or other heavy metals adsorb onto the oxide (12).

The approach could even offer a low-energy way to reduce atmospheric carbon and help mitigate climate change. Earlier this year, Kalantar-Zadeh, Dickey, and others published details of a technique that uses liquid metal technology to break down carbon dioxide. Adding cerium to a liquid gallium-indium alloy, they created a catalyst that converts carbon dioxide into solid carbon products that can be used or stored away (13). The process works at room temperature and requires less energy than any current method, Kalantar-Zadeh says. Some other methods can also be inexpensive, but the way carbon dioxide is stored can be impractical and costly.

In unpublished work, the researchers have shown that by creating tiny droplets of the liquid-metal catalyst, they can increase the surface area available and use the process to efficiently convert larger amounts of carbon dioxide. This, in effect, scales up the technique for real-world use, and yields useful materials as byproducts including graphene oxide, which has many applications in electronics.

They envisage such catalysts incorporated in the exhaust systems of cars or factories. Once industries recognize that this method could be cheap and easy, Kalantar-Zadeh says, its use should hopefully become commonplace.

Regardless of the application, liquid metal technologies are generally at least a few years from entering the market—and there are more than just technical issues to address. Although basic research is flourishing, industry hasn't fully embraced liquid metals—and Dickey is still trying to spread the word that these materials are not only fascinating but potentially useful. "Some of the challenge," he says, "is just awareness and perception."

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