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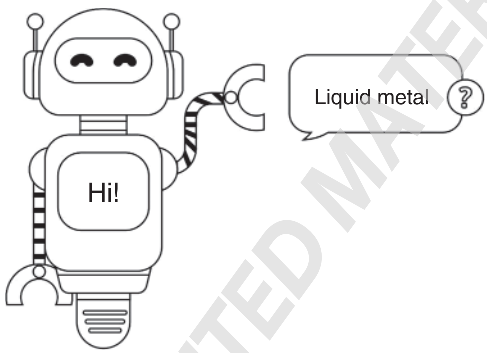
Introduction



The seeds of science are grown for the harvest of the people.
Source: Dmitri Mendeleev (1834–1907). Public Domain.

1.1 The Discovery and Development History of Liquid Metal

In the world of metals, the general “members” are solid. Generally, only when the metals are heated to a relatively high temperature, the metals will exhibit a reddish liquid state. In fact, even if there are no severe high-temperature conditions, we can observe the flowing liquid metal. The most common liquid metal is mercury, which is found in the thermometers we use every day. In ancient China, mercury was also endowed with mysterious colors. Emperor Qin Shi Huang, the first emperor of China, built a model of a river infused with mercury in his tomb, representing his ruling power over the land and his expectation of immortality [1]. In Europe, it is well-known that the philosophy of alchemy laid the foundation for the principles and rules of modern chemistry, and mercury is the core of alchemy research. European alchemists believed that mercury is the main component of all metals and can be combined with other metals to become gold [2]. Although not as expected by ancient alchemists, mercury can indeed dissolve almost all metals to form a soft alloy, that is, amalgam, which is regarded as a metal solvent and has a

Liquid Metals: Properties, Mechanisms, and Applications, First Edition. Lei Fu and Mengqi Zeng.

wide range of applications. Unlike mercury, which always appears in a liquid state in a general environment, the melting point of gallium is just around room temperature. We can easily switch the state of gallium between solid and liquid. For example, if we put gallium on the palm, we can observe its transition from solid to liquid (different from mercury). This may be the reason why people are fascinated by gallium.

As early as the nineteenth century, the special property of gallium became the subject of a classic prank among chemists. One popular trick is "a disappearing spoon." Since gallium looks like aluminum and molds easily, is to fashion gallium spoons and serve the unsuspecting guests with tea. Upon stirring the tea, the gallium spoon melts rapidly. And watch your guests' surprised looks when their tea "eats" their spoons [3]. More in practical, its low-melting point and high boiling point mean that gallium could exhibit metallic properties in the liquid phase across a range of useful, desirable, and accessible temperature.

Recently, scientists have played a new trick with gallium. They have written the smallest book in the world with the help of focused gallium ion beam. Teeny Ted from Turnip Town (2007), published by Robert Chaplin, is certified by Guinness World Records as the world's smallest reproduction of a printed book. The book, costing an enormous $15 000 (around £10 000), yet made is a 30 micro-tablet book carved on a pure crystalline silicon page by using a focused ion beam, is measured to be just 0.07 mm by 0.10 mm, according to Simon Fraser University. As we know, gallium is typically used as a liquid metal ion source for a focused ion beam. It is gallium as the liquid metal ion source used in the focused ion beam that created the smallest book in the world. The book even has its own ISBN reference, ISBN-978-1-894897-17-4, though the readers will require a scanning electron microscope to read the story of a turnip contest [4].

Liquid metals can bring us much more than that. In fact, they have become a part of our daily lives. Liquid metal may exist as a dental implant in our teeth, as fusible metal in automatic fire-fighting devices, or it could exist as a central processing unit (CPU) coolant in our computers. In the future, liquid metal could also be found in our foldable smartphones. Now, it's time to enter the world of liquid metals and learn more about this fascinating substance.

1.1.1 A Vindication for Mendeleev's Prediction

Gallium has only a short history. It was first discovered only a little over a 100 years ago. Particularly, gallium was the first chemical element in the history of chemistry that was predicted theoretically and then verified in nature in 1875.

The periodic table is undoubtedly the most commonly used tool in chemistry. In fact, it greatly facilitates scientific research and the memory and analysis of elements. Before Dmitri Mendeleev arranged the elements as the periodic tables that we are familiar with now in 1869, there were various periodic tables. However, in contrast to the previous scientists, Mendeleev's method of dividing the elements is more concise and beautiful, which is widely recognized and has been used ever since. He reasoned that there should be an as-yet-undiscovered element. Based on the position of the element in the table, he predicted some of their characteristics and properties. The main reason that Mendeleev's periodic table is so convincing may come from the fact that he initially left gaps in it to predict the existence of elements and then to be confirmed later.

As early as 1875, the French chemist Lecoq de Boisbaudran discovered gallium and successfully extracted and purified this new metal. The measured properties of this new element were surprisingly in agreement with Mendeleev's prediction and confirmed his placement of the eka-elements in the periodic table. At present, the industry of gallium production and purification technology has been highly mature, and the purity of gallium can reach 99.9999% [3, 5].

1.1.2 Gallium's Applications in the Semiconductor Industry

With the discovery of gallium arsenide (GaAs) compounds as semiconductor materials, in the early 1960s, gallium alloy began to attract the attention of various researchers. Perhaps alloying with various metals easily is the most crucial characteristic of gallium. And the low-melting point property of gallium can be conferred to the final gallium alloy, making the resulting material more easily workable, stable, and cost-effective. In the semiconductor industry, its alloying with other elements and phase transition properties are highly valuable. Thus, a lot of gallium applications are concentrated in the semiconductor industry. GaAs, as gallium's most common alloy and a new type of high-quality semiconductor, has launched a research boom, which is widely used in preamplifiers and high-speed logic chips in mobile phones, while AlGaAs and InGaAs are often applied as the light-emitting materials. Blue light-emitting diodes (LEDs) were successfully developed in the early 1990s, and the development of white LEDs also followed. Since then, a "lighting revolution" have begun. With gallium consumption soaring, coupled by commercial speculation, the price of gallium rose substantially. After nearly 20 years of development, white LED lighting technology has made great achievements. Compared with the traditional lighting technology, LED lighting technology has the advantages of high-efficiency, energy-saving, long life, green environmental protection, and high light efficiency, which has been supported by governments all over the world. At present, the research and production of GaAs have been mostly turned to the LED industry [3].

1.1.3 Tackling Fundamental Problems in Fuel in Energy Science

In addition to its contribution to the semiconductor field, gallium chemistry has also addressed many fundamental questions in energy science. Early studies have shown that the zeolite doped with gallium can effectively catalyze methylcyclohexane [6]. The ring is opened and broken to form short alkanes, which is used to recover gasoline pyrolysis products. Moreover, gallium zeolites can also catalyze the aromatization of *n*-decane [7]. Emerging studies have shown that GaN nanowires can even catalyze the formation of benzene from methane [8]. Breaking the C—H bond of methane is not easy, which will contribute to these processes mentioned above.

The relative inactive methane exhalations and undesired by-products of gasoline production can be converted into useful petrochemicals. These reactions are crucial for the conversion, which are of great significance for fine chemical production and fuel storage.

1.2 Liquid Metal Family

It is common knowledge that the existing form (solid, liquid, and gas) of all elements and chemical compounds rely on conditions of temperature and pressure. But when it comes to metal, the first thing we think about is bulky objects and high melting point. It is hard to believe that some metals exist in liquid form at room temperature. One of the most intriguing properties of gallium is its liquid state at room temperature. When you cut off a piece of solid gallium with a knife and put it in your hand for a closer look, an interesting thing happens: It melts and turns into a silvery drop that rolls around in your hand like a drop of water on a lotus leaf. The reason for this curious phenomenon is that the melting point of gallium is only 29.8 °C, below the human body temperature, so it will melt in the hand. In addition, although gallium's melting point is low, the boiling point can be as high as 2200 °C. In other words, from about 30 °C to about 2000 °C, gallium would remain in liquid state, while mercury would boil at 360 °C. Therefore, gallium can be used to make high-temperature thermometers that can measure temperatures below 1500 °C [3].

Herein, we define metals and alloys with melting point between room temperature and 300 °C as liquid metals. Single-component liquid metals are predominantly composed of post-transition metals (Ga, In, Tl, Sn, Pb, Al, and Bi), zinc-group metals (Zn, Cd, and Hg), and alkali metals (Li and Na). We note that alloys possess much lower melting point than the pure metal. For example, the melting point of eutectic gallium and indium alloy (EGaIn) is only 16 °C [9]. So there are much more liquid metal alloys. Tables 1.1 and 1.2 list the melting point of several liquid metals and alloys. To enrich the content of this book, we will also introduce some molten metals (such as copper, gold, etc.), which have similar properties compared to liquid metals [10] (Figure 1.1).

In recent decades, low-melting point liquid metals have been used in many different fields. Gallium base liquid metal at room temperature has unique surface properties and physicochemical properties. It can achieve a variety of morphological changes such as deformation, movement, separation, and fusion through a variety of energy fields such as electric, magnetic, and concentration gradient fields or surface modification. Liquid metals show a promising application in microfluidics, biomedicine, and robotics, and other fields.

At present, numerous studies devoted to liquid metals are dispersed and need to be unified. All the emerging applications in the fields of catalysis, synthesis, microfluidics, soft electronics, sensor, and therapy exploit the same phenomena that occur in liquids and at metal interfaces. Integrating these seemingly unrelated research directions into a single field of liquid metal is quite challenging. But it will facilitate the development of innovative applications that take full advantage of the unique properties of liquid metals and its alloys [10].

Table 1.1 Atomic number and melting point of liquid metals.

Elements	Atomic number	Name (abb.)	Melting point (°C)
Lithium	3	Li	180.5
Sodium	11	Na	97.8
Aluminum	13	Al	660.3
Cadmium	48	Cd	321.1
Mercury	80	Hg	−38.8
Zinc	30	Zn	419.5
Gallium	31	Ga	29.8
Indium	49	In	156.6
Thallium	81	Tl	304.0
Tin (white)	50	Sn	231.9
Lead	82	Pb	327.5
Bismuth	83	Bi	271.4

Table 1.2 The composition and melting point of several eutectic binary alloys, ternary alloys, quaternary alloys, and quinary alloys.

Alloyed elements	Element A (at%)	Element B (at%)	Element C (at%)	Element D (at%)	Element E (at%)	Melting point (°C)
Ga/In(EGaIn)	85.8	14.2	0	0	0	15.4
Ga/Sn	91.7	8.3	0	0	0	21.0
Ga/Bi	38.3	61.7	0	0	0	222.0
In/Sn	52.7	47.3	0	0	0	116.9
In/Bi	79.2	20.8	0	0	0	72.5
Pb/Au	84.6	15.4	0	0	0	215.0
Sn/Tl	56.6	43.4	0	0	0	170.2
Ga/In/Sn (Galinstan)	78.3	14.9	6.8	0	0	13.2
In/Sn/Bi (Field's alloy)	60.1	18.8	21.1	0	0	62.0
Bi/Pb/Sn (Rose's alloy)	43.1	23.5	33.4	0	0	95.0
Bi/Pb/Sn/Cd (Wood's alloy)	41.5	20.9	18.3	19.3	0	70.0
Bi/Pb/Sn/Cd/In (French's alloy)	31.5	17.1	14.4	11.7	25.3	46.9

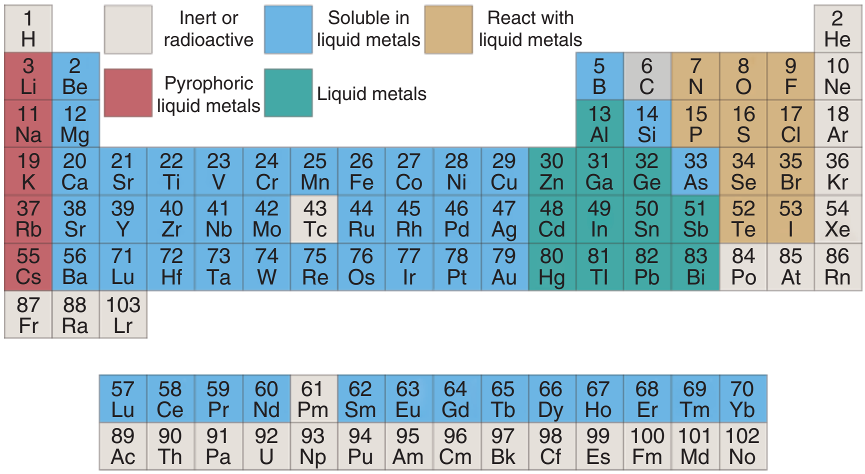


Figure 1.1 Liquid metal base elements. [10]. Source: Daeneke et al. [10]. Reproduced with permission of Royal Society of Chemistry.

1.3 Overview of Liquid Metal

What is well-known is that mercury can dissolve almost all metals to form an amalgam and is regarded as a metal solvent with considerable application. Similarly, liquid metals can also dissolve some metallic elements and nonmetallic elements. And unlike conventional molecular liquid and ionic liquid, liquid metals possess some unique properties (high electrical conductivity, etc.). So liquid metals can serve as a new reaction medium to synthesis different dimensions, compositions, and morphology materials. Liquid metals can spontaneously form smooth, soft, defect-free, stress-free interfaces, which provide an ideal substrate for crystal growth. There are also self-limiting metal oxide films on the liquid metal surface, which are naturally available high-quality two-dimensional films and can serve as precursors to synthesis other two-dimensional materials. Moreover, many two-dimensional atomic crystals have been predicted to grow on liquid metals [11] (Figure 1.2).

In the Terminator series of science fiction movies, the fact that the T-1000 is the most amazing terminator is indisputable. He can transform into anyone and anything, and can heal wounds back to their original state as quickly as a fluid when attacked. It was the presence of liquid metal that endow the killer magical ability to transform and repair himself, making him an unbreakable killer. Thanks to this cool sci-fi fantasy about liquid metal robots, it brought liquid metals into the public eye and aroused the interest of scientists in the study of liquid metals. Compared to conventional rigid robotics, liquid metals hold huge merits, such as low-melting point, high electrical conductivity and thermal conductivity, and liquidity, which broaden their utilization in stretchable and wearable electronics, such as flexible pressure sensors, a stretchable electromagnetic actuator, stretchable wireless power transfer, and stretchable loudspeaker. Recently, a series of magical phenomena have been discovered successively, such as the movement and deformation of liquid metal through

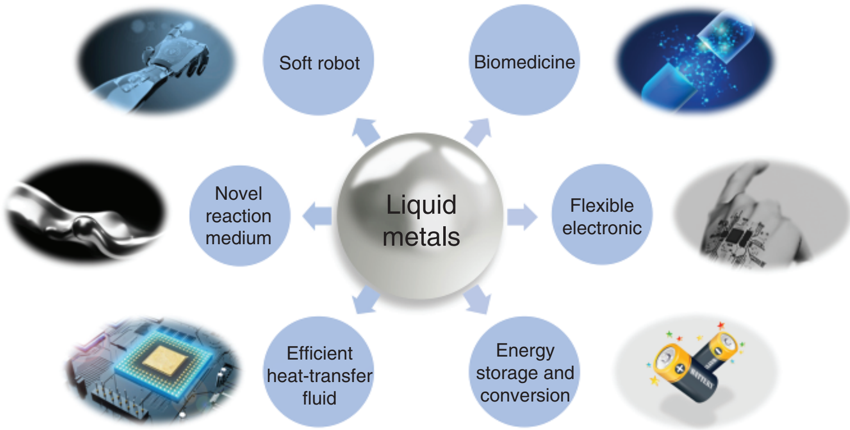


Figure 1.2 The application of liquid metals [11]. Source: Zavabeti et al. [11].

electric field control or magnetic field, the repair of biological fractured nerve with liquid metal, and the autonomous movement of liquid metal without external power after swallowing a small number of substances [12–14]. Liquid metals can also be applied to manufacture a new artificial bioinspired optoelectronic sensorimotor system, which is similar to the neuron system [15]. Besides, the color of liquid metals, which is generally shiny silver-white, can be changed by applying an electrical field, such as pink, purple, and blue. This provides a new route to create kaleidoscopic and colorful liquid metals and will expand their applications in biomimetic intelligent soft robots. These findings lay the theoretical and technical foundation for complex liquid metal robots in the future. So, will robots like Terminator become a reality in the future? Let's wait and see!

Although the pure liquid gallium has no biological activity, gallium ions can influence the reaction in our body, similar to iron ions. Several gallium salts have been used in pharmaceutical and radiopharmaceutical industries. For example, gallium nitrate has been used to treat hypercalcemia associated with tumor metastasis to bones. Besides, owing to the nontoxic and extraordinary flexibility, liquid metals can also be applied in biomedical applications, such as drug delivery, molecular, cancer therapy, and biomedical devices. The nanomachines prepared by liquid metals can be injected into cells to treat some cell diseases [16]. Due to its self-driven ability, the liquid metals robot containing medicine can be automatically delivered into targeted tissues to release medicines to cure diseases [17]. As for the biocompatibility problem of theses liquid metal microrobots, it can be solved by the functionalization of liquid metal (Figure 1.3).

Recently, various technology giants have started the launch boom of foldable smartphones. The emergence of foldable phones (mobile phones with folding screen) has provided a new application opportunity for liquid metals and attracts people's attention to liquid metals again. Going back to the problem of screens, folding screens is not as easy as it seems. How to solve this technical problem? The liquid metal gives the answer. The liquid metal itself has excellent shaping

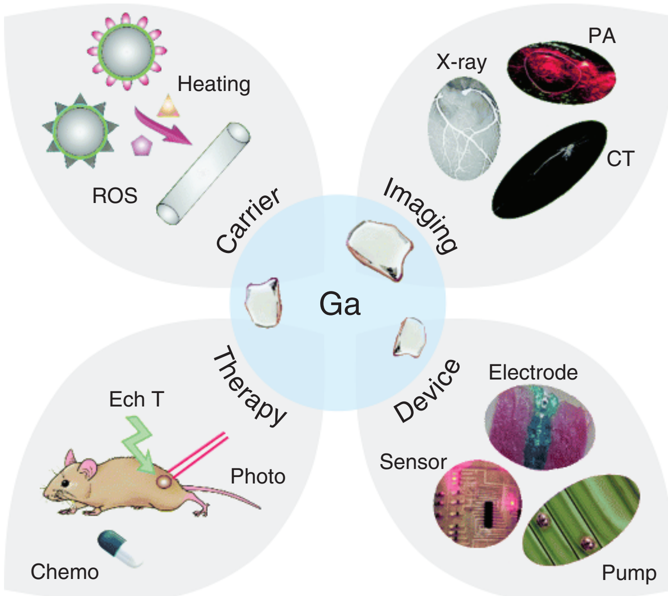


Figure 1.3 Schematic of liquid metals (or alloys) and gallium-based LMs for biomedical applications [18]. Source: Yan et al. [18]. Reproduced with permission of Royal Society of Chemistry.

ability and excellent dimensional stability. Therefore, it can meet the requirements of thickness, strength, and precision of hinge support parts, which makes liquid metal one of the main solutions for support. In this case, the prospects for liquid metals with outstanding performance advantages are clearly limitless. In addition, liquid metals combine the advantages of traditional metal conductivity with the flexibility of nonmetallic materials. At present, liquid metals have been widely used to make flexible electrons, such as stretchable wire, interconnects, and antennas. Liquid metals can also be applied in memory devices, diodes, electrodes, and capacitors. In principle, the deformation ability of liquid metals is not limited. In addition, liquid metals can form self-healing and shape-reconfigurable circuits, and it can be utilized in soft sensors, such as strain sensing, pressure sensor, and touch sensing, because their resistance or capacitance will correspondingly change when deformed. Liquid metals can also be utilized as electronics to sense the change of relative humidity, oxygen, and temperature. Compared with the traditional rigid electron, the flexible electron has great bendability and stretchability, leading to promising applications in the fields of information, energy, medical treatment, and national defense (Figure 1.4).

Energy is the basis of human survival and development. How to use energy efficiently has been extensively studied? Considering the intermittent and nonuniformity of energy, energy storage and conversion is very important. At present, batteries, capacitors, and inductors have been widely used in energy storage and conversion. The battery is widely used in people's life because of high efficiency and

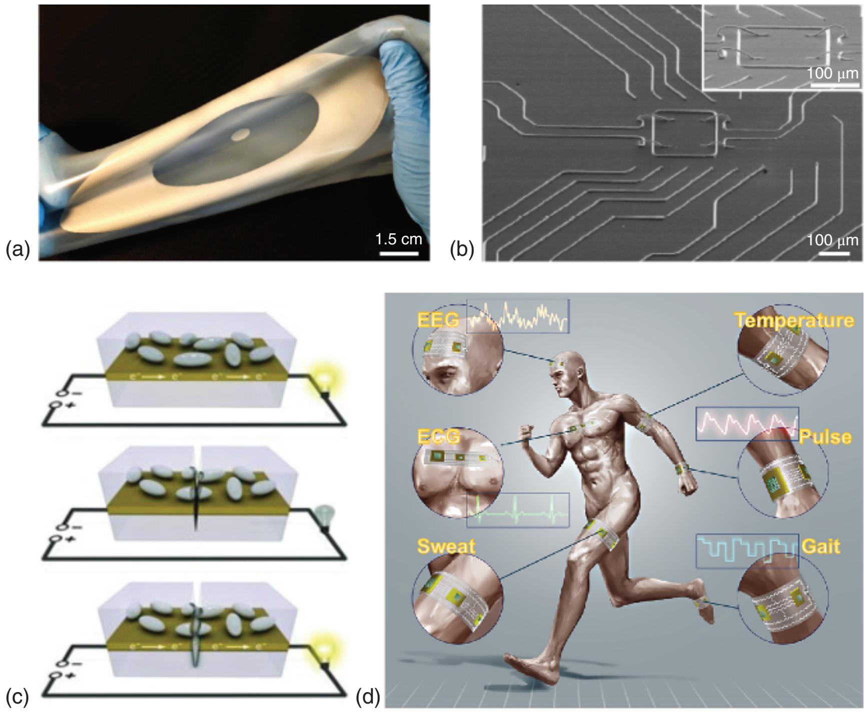


Figure 1.4 (a) Stretchable materials based on liquid metals [19]. Source: Pan et al.[19]. (b) The shape-reconfigurable circuits [20]. Source: Park et al. [20]. (c) The self-healing circuits [21]. Source: Blaiszik et al. [21]. Reproduced with permission of John Wiley and Sons. (d) The sensor based on liquid metals [22]. Source: Rui et al. [22]. Reproduced with permission of Springer Nature.

convenience. But the major challenges of traditional lithium batteries lie in dendrite growth. Liquid metals and alloys, which possess inherent deformability, high electronic conductivity, self-healing, and excellent electrochemical properties, have attracted considerable attention. Utilizing liquid metals can realize dendrite-free, self-healing, low reduction potential, high capacity and energy density, and fast mass/charge transport [23] (Figure 1.5).

Liquid metals usually exhibit outstanding thermal conductivity. For example, the thermal conductivity of water is 0.6 $W\,(m\,K)^{-1}$, which is seriously lower than those of gallium (29.6 $W\,m^{-1}\,K^{-1}$) at 50 °C [24]. So it is a good coolant. In fact, the application of gallium is particularly prominent in the field of heat dissipation [25]. As a liquid metal, it is inherently more conductive than air, water, and many nonmetallic media. Sapphire Technology, a famous video card manufacturer, displayed a graphics card with liquid metals at the E3 game show and Taipei International Computer Show in 2005. The data showed liquid metal cooled the working temperature of the strongest video card at that time, the Radeon X850 XT PE, to 12 °C, and its heat conduction efficiency was 65 times or faster than that of water at that time. At the beginning of 2019, liquid metals cooling systems appeared in high-end gaming laptops, such

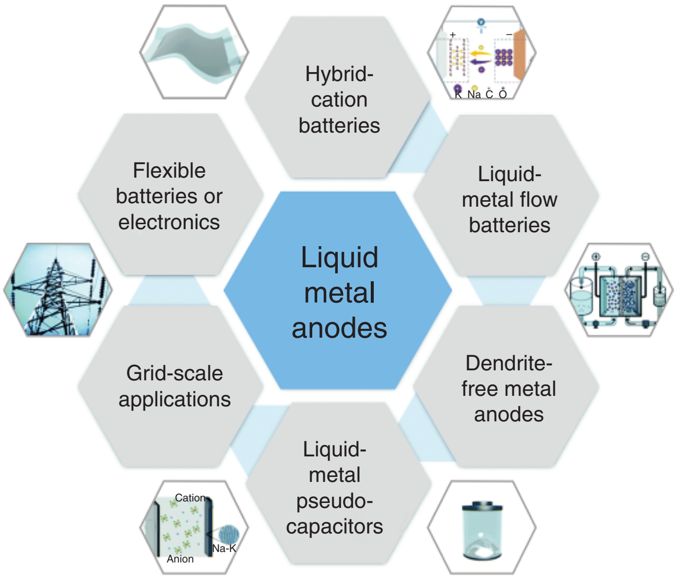


Figure 1.5 Prospective designs and applications of the liquid-metal-based electrodes in various energy storage strategies [23]. Source: Guo et al. [23]. Reproduced with permission of Royal Society of Chemistry.

as ASUS, HP, and MACHENIKE. There is no doubt that the price will increase, but it can give you a very enjoyable experience. Making good use of liquid metals as a radiator of laptops would bring rapid advances in technology.

In recent years, people focus on exploring, developing, and utilizing the universe, so new space materials with a strong performance is essential to overcome the evil environment, such as zero gravity, vacuum, larger temperature, and strong radiation. Up till now, space materials mainly include carbon-based materials, porous metals, polyimide, and fiber. Compared to the above materials, liquid metals possess a lot of distinguished properties, such as high electric conductivity, high thermal conductivity, fluidity, and low volatility, which make them a good choice for utilization in space science and technology. It has also been introduced that liquid metal has very good heat dissipation capacity. For space exploration, a liquid metal cooling system has been proved to be the most effective space nuclear electric heating management method [26]. In addition, liquid metal can be used as a thermal interface material for heat conduction. Solar energy is the only energy source in spacecraft operation, so how to store solar energy is very important. Usually, solar energy is converted into heat energy, and then heat energy is converted into electrical energy for storage. Compared with the common thermal storage materials (fluorine), liquid metal has high thermal conductivity, high latent heat of phase change, and low thermal expansion rate, which can be used as a new type for energy storage material. Three-dimensional printing technology of liquid metals provides a very simple method for rapid manufacturing and maintaining electronic circuits. More importantly, there is a large amount of electromagnetic radiation in the universe, which is

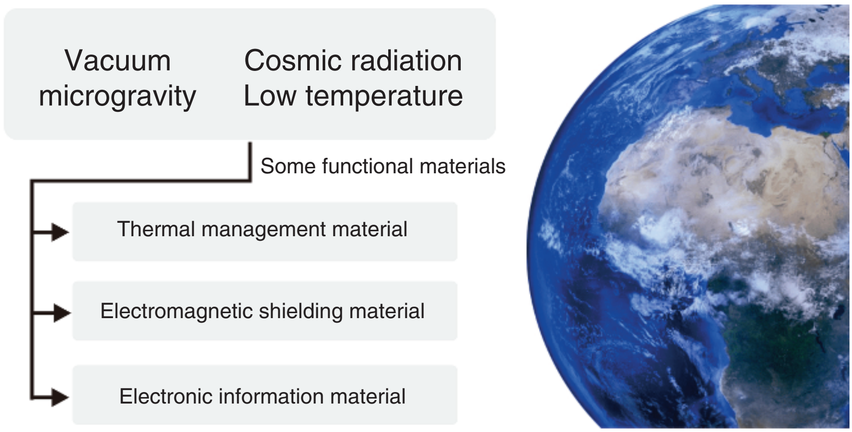


Figure 1.6 Candidate materials needed to satisfy the space physical environment [27]. Source: Zhang and Liu [27]. Reproduced with permission of Springer Nature.

not conducive to the operation of devices. The flexible liquid metal electromagnetic shielding material has good wettability and plasticity, which can meet the requirements of complex shape and effectively protect the equipment from radiation. Moreover, the liquid metals usage in science and technology is still in its infancy and we need to keep exploring and look forward to your joining (Figure 1.6).

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