Next-Generation Liquid Metal Batteries Based on the Chemistry of Fusible Alloys

Yu Ding,‡ Xuelin Guo,‡ and Guihua Yu*

1. INTRODUCTION

Energy is regarded as one of the most essential ingredients in economies, and modern society calls for advanced energy systems to secure a sustainable future for human beings. Different from nonrenewable sources that cannot be readily replaced through natural processes to compensate for consumption, renewable energies represent a type of clean and inexhaustible energy source without emission of greenhouse gases or pollutants. Considering the intermittency of renewable sources, batteries are typically required to better regulate the electricity for peak load shifting. Since the first battery was invented by Volta two hundred years ago, batteries have witnessed great progress with diverse combinations of cathodes, anodes, and electrolytes. The 2019 Nobel Prize in Chemistry rewarded the development of Li ion batteries, which rely on the intercalation chemistry of anodes and cathodes. The highest theoretical capacity (3860 mAh g⁻¹) and lowest redox potential (−3.04 V versus the standard hydrogen electrode), is considered as the optimal anode to further boost the energy density of Li ion batteries. Nevertheless, the cycling performance of the Li metal anode during stripping–deposition is seriously plagued by its dendritic growth, in finite volume change, and continuous decomposition of the electrolyte. In fact, the first proof-of-concept Li ion battery was invented by Stanley Whittingham in the 1970s had employed metallic Li as the anode. However, the commercialized Li metal batteries were abandoned by the market due to serious safety concerns. In the past decade, research on alkali metal anodes was revived, and a variety of approaches have been taken to alleviate their issues. The adoption of liquid metal anodes could be a viable strategy to eliminate the intrinsic dendrite problem of alkali metals. A liquid metal battery is a cell containing liquid metal electrodes. In this Outlook, we comprehensively summarize the two types of cell designs: (1) batteries with only liquid metal anodes; and (2) batteries with both liquid metal anodes and cathodes. Figure 1 summarizes the appealing features of liquid metals for energy technologies. Liquid metals inherently possess a high concentration of electroactive materials compared to conventional electrode materials with high amounts of inert components, offering the potential to deliver a high capacity. In the meantime, liquid metal electrodes with self-healing capabilities are immune to structural cracks, and high power demand can be satisfied given the fast kinetics in liquids. The development of liquid metal batteries can be traced back to the 1960s, when scientists at General Motors designed a Na–Sn liquid metal cell with a NaCl–NaI molten salt electrolyte. The voltage of such a cell is greater than typical concentration cells considering the decrease in Na activity at high temperature.
Outlook, these advances made recently on the basis of fusible alloys have highlighted, and the development of high-temperature liquid metals will not be elaborated upon. The metallurgical properties and electrochemical characteristics of fusible alloys are also interpreted to gain more insights into the fundamentals of battery chemistry. Finally, a material perspective on the future opportunities of such emerging liquid metal batteries to achieve practical applications is provided.

2. METALLURGICAL FUNDAMENTALS OF FUSIBLE ALLOYS

2.1. The Family of Fusible Alloys. Metals, generally speaking, maintain high melting points because of the strong electrostatic attraction forces between metal ions and conduction electrons, and very few elemental metals exist in a liquid state at room-temperature. Mercury (Hg), with a melting point of ~39 °C, is one of the most known room-temperature liquid metals. From the point of view of quantum physics, all available subshells of Hg are filled up. Such a unique electron configuration, hindering removal of electrons from subshells, is akin to noble gases with fully occupied outer shells. Therefore, Hg also behaves like noble gases, which have weak interatomic forces and low melting points. Nevertheless, the application of Hg is restricted due to its high toxicity. Some other liquid metal alternatives include cesium (Cs) with a melting point of 28 °C, rubidium (Rb) with a melting point of 39 °C, francium (Fr) with an estimated melting point of 8 °C, and gallium (Ga) with a melting point of 30 °C. However, these elemental metals also have limitations, such as the high reactivity, radioactivity, and rarity in nature.

In addition to pure metals, the alloy systems provide more flexibility for wide selection and rational screening of fusible metallic electrodes to design liquid metal batteries. A fusible alloy is a metal alloy that can be easily fused at relatively low temperatures. Notably, many eutectic alloys are fusible alloys, but fusible alloys are not necessarily eutectic alloys. Several typical fusible alloys include Hg-based alloys, alkali metal-based alloys, Ga-based alloys, and bismuth (Bi)-based alloys, some of which have been utilized for die casting, rapid prototyping, cooling nuclear reactors, synthesis of nanomaterials, and energy devices.

2.2. Mechanism of Melting-Point Depression. The melting point of a metal, which can be roughly estimated via the bond strength, is governed by multiple factors, including the number of valent electrons, the ionization degree, and the crystal structure. Considering the increase of both enthalpy (ΔH > 0) and entropy (ΔS > 0) from solids to liquids, the melting point can be quantified as (ΔH/ΔS). When melting an impure solid, the enthalpy change is much less than the entropy change, corresponding to a lower melting temperature following the equation (ΔH/ΔS). Therefore, the melting point of a pure substance is typically higher than impure substances, which is called melting point depression. The eutectic system is a good example showing melting point depression. Many fusible alloys belong to eutectic systems, and the lowest possible melting point over the mixing ratios is the eutectic temperature (Figure 2a). From the perspective of quantum physics, the origin of the depressed melting point is attributed to the altered free-electron density around metal atoms in the presence of adjacent heteroatoms. To gain more insights into the mechanism, Kaviany et al. comprehensively studied the charge densities and crystal structure of a ternary eutectic Ga–In–Sn alloy by computational modeling. It is evident that the

Different from high-temperature liquid metal batteries invented at General Motors and Argonne National Laboratory 50 years ago, liquid metal batteries were revisited based on the chemistry of fusible alloys. Thanks to the remarkably reduced melting points of metallic alloy electrodes, the construction of intermediate-temperature or even room-temperature alkali-metal-ion batteries is possible. In addition to the merits mentioned above, the high deformability of room-temperature liquid metals is promising to design flexible devices beyond stationary storage. In light of the fundamental understanding of the interfacial chemistry of fusible alloys, a variety of novel liquid metal batteries were designed and demonstrated. In this Outlook, these advances made recently on the basis of fusible alloys are highlighted, and the development of high-temperature liquid metal batteries is possible melting point over the mixing ratios is the eutectic temperature (Figure 2a). From the perspective of quantum physics, the origin of the depressed melting point is attributed to the altered free-electron density around metal atoms in the presence of adjacent heteroatoms. To gain more insights into the mechanism, Kaviany et al. comprehensively studied the charge densities and crystal structure of a ternary eutectic Ga–In–Sn alloy by computational modeling. It is evident that the

Figure 1. Appealing features of liquid metals for energy technologies.
electrodes in batteries, the safety and availability are crucial. However, melting point is not the only parameter to consider in alloy and metal screening for a liquid metal battery including the melting temperatures of the metal electrodes, which determines the battery operating temperature. Accordingly, the melting temperature of eutectic Ga–In–Sn (−19 °C) is remarkably depressed in comparison with pure metals of Ga (30 °C), In (157 °C), and Sn (232 °C). Figure 2c presents the structure of the Ga–In–Sn eutectic alloy with contours of the constant charge density of 0.035 e Å⁻³. The isosurface electron distribution in Figure 2c matches the charge density is unevenly distributed in the Ga–In–Sn alloy, as shown in Figure 2b. The charge density is the highest around Ga atoms, indicating the valence electrons in the given atomic configuration. Additionally, it is noted that the electron distribution around In and Sn atoms is similar to that of Hg, where the electrons in subshells are strongly tied to the atoms. As introduced above, such an electron configuration resists removal of electrons, and the alloy behaves similarly to noble gases with weak interatomic forces and low melting points.

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### 2.3. Cost and Safety Analysis

Many important factors need to be considered in alloy and metal screening for a liquid metal battery including the melting temperatures of the metal electrodes, which determines the battery operating temperature. However, melting point is not the only parameter to evaluate a liquid metal electrode, because to really apply those electrodes in batteries, the safety and availability are crucial factors to be concerned about. Taking Hg as an example, although Hg has a low melting temperature, vaporized mercury is toxic and fatal after inhalation, which severely threatens human’s health, not only during production and use, but also by causing long-lasting damage to the environment. As another example, the alkali metals Rb and Cs are extremely active elements, but these chemicals are too costly to be used as major battery materials in electrodes. Therefore, the selection of a proper metal or alloy as a practical liquid electrode should take element availability and safety into consideration. Besides, the cost and abundance of an element determine the possibility of practical use of a designed battery, which should be considered in electrode screening as well. In Table 1, the low melting-temperature metals’ (MT < 300 °C) abundance, cost, safety notes, and possible elements in their common fusible alloys are listed.

### Table 1. Low Melting-Temperature (MT < 300 °C) Elements, Their Atomic Number in Periodic Table, Abundance in the Earth’s Crust, Estimated Market Price, Important Safety Notes, Standard Reduction Potential/Number of Charges at Room Temperature, and Some Commonly Contained Elements in Their Well-Recognized Fusible Alloys

| Element | Atomic Number | Abundance (Mg kg⁻¹) | Price (£ kg⁻¹) | MT (°C) | Safety Notes | RP (V/eq⁻¹) | Fusible Elements |
|---------|---------------|---------------------|----------------|--------|--------------|-------------|-----------------|
| sodium (Na) | 11 | 2.36 × 10⁴ | 2.33 | 97.8 | flammable, corrosive | −2.71/1 | Li, K, Rb, Cs |
| potassium (K) | 19 | 2.09 × 10⁴ | 9.99 | 63.71 | flammable, corrosive | −2.93/1 | Li, Na, Rb, Cs |
| rubidium (Rb) | 37 | 9.00 × 10⁴ | 11293 | 39.48 | flammable, corrosive | −2.98/1 | Li, Na, K, Cs |
| lithium (Li) | 3 | 2.00 × 10⁴ | 88.76 | 180.6 | flammable, corrosive | −3.04/1 | Na, K, Rb, Cs |
| gallium (Ga) | 31 | 1.90 × 10⁴ | 213 | 29.77 | warning, corrosive | −0.55/2 | Bi, In, Sn |
| cesium (Cs) | 55 | 3.00 | 56312 | 28.39 | flammable, corrosive, health hazardous | −3.03/1 | Li, Na, K, Rb, |
| tin (Sn) | 50 | 2.30 | 15.34 | 232 | warning | −0.14/2 | Bi, Pb, In, Cd, Ga, Zn |
| indium (In) | 49 | 2.50 × 10⁻⁴ | 262 | 156.6 | warning | −0.34/3 | Bi, Pb, Sn, Cd, Ga |
| mercury (Hg) | 80 | 8.50 × 10⁻³ | 29.49 | −38.84 | fatal, health hazardous, corrosive | 0.85/2 | TI |
| bismuth (Bi) | 83 | 8.50 × 10⁻³ | 7.93 | 271.4 | flammable | 0.31/3 | Pb, Sn, In, Cd, Ga |
| polonium (Po) | 84 | 2.00 × 10⁻¹⁰ | 254 | radiotoxic, health hazardous | 0.9/2 | |

From the above table, we could tell that there are mainly two types of metals that are easy to melt, according to the positions on the periodic table, which are recognized as the alkali metals and the post-transition metals. Among all the elements listed,
alkali metals are the most abundant elements in the Earth’s crust, especially Na and K elements, both of which are three orders of magnitude more abundant than lithium. However, the price of producing a metal depends not only on the abundance in the Earth’s crust. Some elements, such as Rb, is even more abundant than lithium, whereas the price of Rb metal is much higher. This is because the distribution of the element is very dispersed and not normally concentrated as minerals, so it increases the excavation and production difficulties. The technique applied to produce the metal also determines the cost, and highly reactive or dangerous metals need more critical preparation conditions. However, it is a signal for us that those abundant elements might be potentially viable alternatives for future applications, with the increasingly mature metallurgy technique and continuous exploration of the ocean and space. Besides, from the table, many of the low-melting-temperature elements are corrosive, owing to their relatively high chemical activity. Alkali metals are easy to be oxidized and are flammable in the air since they could emit hydrogen gas when in contact with water. Ga, In, and Sn are relatively stable in air and water, and barely have negative effects to human health unless from direct contact or swallowing. Moreover, from the table, it shows clearly that alkali metals tend to form fusible alloys with other alkali species, and the same situation is applicable for the post-transition metals. A similar electron distribution and affinity of the metal atoms are preferred to lower the free energy and form fusible alloys, which is observed and theoretically expected as well. With better understanding of the low MT metals and fusible alloys, we could evaluate the advantages and disadvantages of choosing one species as the electrode in the battery. Alkali metals are mostly abundant and reactive, and Ga-based alloys are safer and relatively less harmful, respectively. Therefore, many efforts have been dedicated to make these metals or alloys into electrodes.

3. INTERMEDIATE-TEMPERATURE LIQUID METAL BATTERIES

3.1. Chalcogen-Based Liquid Metal Batteries. The Na-sulfur (Na−S) battery is a typical molten-salt battery consisting of a liquid Na anode, a sulfur cathode, and a β-Al2O3 solid electrolyte (BASE). The first Na−S battery was invented at Ford in 1967. Because of their advantageous features, including high energy density (~760 Wh kg⁻¹), high efficiency, long cycle life, and inexpensive electrode materials, Na−S batteries have been commercialized for stationary energy storage. To maintain the high ionic conductivity of the ceramic tube solid electrolyte and good wetting with molten Na, Na−S batteries need to be operated at above 300 °C. The highly corrosive nature of the sodium polysulfides may cause degradation of cell components especially in a harsh environment. More seriously, the violent reaction between molten Na and fluidic S may give rise to major safety risks. To alleviate the high cost and safety concerns related to the high operating temperature of Na−S batteries, researchers at Pacific Northwest National Laboratory (PNNL) proposed an intermediate-temperature Na−S battery (150 °C). Tetraglyme, which can dissolve high-concentration polysulfides, was adopted as the cathode solvent, and the ceramic membrane prohibited the self-discharge reaction. The Na anode is still in a molten state at such a working temperature, and the dendrite growth can be suppressed. The proof-of-concept Na−S battery exhibits 70% capacity retention after 60 cycles at a current density of 2.33 mA cm⁻². The poor wetting of Na on the ceramic membrane is one of the grand challenges for intermediate-temperature Na−S batteries. The Na−K liquid metal alloy can wet the ceramic membrane well, but the ion exchange between Na−K and BASEs will cause cracks of the ceramic membranes (Figure 3a). To decrease the operating temperature and maintain a good compatibility between alkali metals and BASEs in the meantime, Lu et al. designed a novel K−S battery composed of a K anode, K⁺-conducting BASE, and a sulfur cathode. Such a K-BASE, consisting of 91 wt % K-β”-Al2O3, 8.4 wt % K-β-Al2O3, and 0.6 wt % ZrO2, not only can be well wetted by molten K at 150 °C, but also is compatible with K without cracking. On the basis of a similar tetraglyme-based catholyte containing polysulfides and K salts, the intermediate-temperature K−S battery shows negligible capacity decay for more than 1000 cycles at 150 °C. The battery chemistry of such a novel K−S battery was elucidated via an in situ Raman study, showing a sequence of reactions from K2S2 to K2S3 and finally to K2S4 during discharge. Although the delivered capacity is not comparable to Na−S batteries, the demonstrated energy density is similar given the higher discharge voltage.

Solid electrolytes play a critical role in regulating the performance of chalcogen-based liquid metal batteries. A stable electrolyte-electrode interface is the prerequisite to achieve a reversible electrochemical reaction during battery cycling. In 2020, researchers at Stanford reported intermediate-temperature liquid Li−S and Li−Se batteries enabled by a garnet type Li4ZnLa2Zr14Ta2O42 (LLZTO) solid electrolyte. The battery configuration consists of a liquid Li anode, a molten S or Se cathode with carbon black to improve the contact, and an LLZTO ceramic tube electrolyte just like BASE. In the proof-of-concept test, the Li−S and Li−Se battery was evaluated at 240 and 300 °C, respectively, with the charge/discharge schemes shown in Figure 3b. The Coulombic efficiency can be stabilized at 99.99%, with outstanding power density (180 mW cm⁻²) and high energy efficiency (>80%). A good stability over 50 cycles was demonstrated in the Li−S cell, and further
improvement on the cycling stability can be expected by better sealing to suppress escape of S vapor. Taking advantage of the high capacity of both the Li anode and S or Se cathode, the theoretical energy density can reach \( \sim 1850 \text{ Wh kg}^{-1} \) and \( \sim 920 \text{ Wh kg}^{-1} \) for Li–S and Li–Se batteries, exceeding most grid-scale energy storage systems.\(^{38-40}\)

3.2. Transition Metal-Based Liquid Metal Batteries.

Besides the chalcogen-based cathodes, transition metal alloys and metal halides can also be employed to build liquid metal batteries. In the 1980s, a new class of molten-salt batteries was developed by the Zeolite Battery Research Africa Project (ZEBRA) group. Such a Na-NiCl\(_2\) battery works at 245 °C with a BASE membrane separating a molten Na anode and the NaAlCl\(_4\) (melting point of 170 °C) electrolyte. Compared with highly corrosive polysulfides, the solid-state cathode of Ni/\(\text{NiCl}_2\) is less corrosive and much safer. Even if the BASE is punctured, the molten salt of NaAlCl\(_4\) will react with Na to produce solid NaCl and Al. Such a reaction is much less violent than Na–S cells, and the reaction products can seal the punctured sites spontaneously. The cell is generally constructed in a discharge state with a NaCl-based anode, circumventing the direct handling of highly reactive Na metals. Therefore, ZEBRA cells possess high safety and reduced cost associated with thermal management and cell component degradation. However, the energy density of ZEBRA cells is not comparable with that of Na–S cells, and the cathode materials cost is higher. In 2015, Li et al. designed a Na-FeCl\(_2\)-based molten salt cell with low-cost cathode chemistry, and the schematic of the cell structure with the overall reaction is provided in Figure 4a.\(^{41}\) According to the London Metal Exchange price, the cost of Fe ($0.48 \text{ kg}^{-1}$) is over 1 order of magnitude lower than that of Ni ($14.5 \text{ kg}^{-1}$). It was further estimated that 61% reduction in all materials cost can be achieved by replacing Ni with Fe in the novel ZEBRA cell. Moreover, by lowering the operating temperature, more cost-effective manufacturing/operating process can be implemented with inexpensive cell components and sealing materials. In this work, the authors also found that S-based additives in the Fe cathode can remove the passivation layers with in situ formation of polysulfide species. The charge–discharge voltage profiles in Figure 4b prove the stable cycling performance of the Na-FeCl\(_2\) cell at 190 °C.

The rapid progress of solid electrolytes in the past decade also enables the revival of novel all-liquid-metal batteries. By employing the same LLZTO ceramic electrolyte tube for Li–S batteries (Figure 4c), researchers at Stanford assembled the Li|\(\text{Sn–Pb}\) and Li|\(\text{Bi–Pb}\) cells that can stably cycle at an intermediate temperature of 240 °C.\(^{42}\) The deep discharge voltage profiles are presented in Figure 4d, and a volumetric capacity of 896 mAh cm\(^{-3}\) can be delivered with negligible decay after 30 cycles. A puncturing experiment was further conducted, and the surface temperature only increased by 80 °C when mixing the molten Li with the molten Sn–Pb alloy, demonstrating a high safety margin for practical applications. Owing to the high density of the molten alloys, the theoretical volumetric energy density can reach 570 Wh L\(^{-1}\) and 940 Wh L\(^{-1}\) for Li|\(\text{Sn–Pb}\) and Li|\(\text{Bi–Pb}\) cells, respectively. Finally, the cells were evaluated in terms of materials cost. The intermediate-temperature liquid metal batteries with low cost and high performance are promising for grid-scale energy storage.\(^{43}\)

4. ROOM-TEMPERATURE LIQUID METAL BATTERIES

4.1. Na–K Alloy Based LMBs. Alkali metals have relatively low melting temperatures compared with other metals in general, and some of them have been applied in high-
temperature liquid metal batteries as well. A high operating temperature is crucial to those batteries because the molten salt or ceramic electrolytes require much higher temperatures to melt or keep high conductivity than alkali metals. However, at high temperatures, the fluidity and heat exhaustion of alkali metals could be boosted, which therefore could increase the possibility of ignition and corrosion. Therefore, the alkali metals would be more practical choices as anodes at moderate temperatures. Among the fusible alloys, the Na–K alloy, due to the low melting point and low reduction potential (−2.71 V for Na and −2.92 V for K vs standard hydrogen electrode), is one of the most competitive alternatives for the lithium anode that eliminate the dendrite growth issue. It has been reported by Goodenough et al. that the high surface tension liquid Na–K alloy could be a dendrite-free potassium-ion anode at room temperature by being absorbed into a carbon porous substrate (Figure 5a). Limited by the liquidus line in the phase diagram, the specific capacity of Na–K can reach 629 mAh g⁻¹ as a Na anode and 579 mAh g⁻¹ as a K anode. Although the Na–K alloy was undoubtably in the liquid phase at room temperature, the requirement of high temperature in that work to prepare the Na–K absorbed substrate could bring safety concerns and consume excess energy. In the following work, they established the vacuum infiltration method and systematically studied the liquid metal wettability in different substrates and the compatibility with different electrolytes. Notably, the ether-based electrolytes in their experiments showed poor compatibility with Na–K extracted out of the substrate, whereas the carbonate electrolytes could wet the Na–K in the substrate very well. Meanwhile, Yu et al. reported the preparation of liquid metal anode with fibrous carbon that could be achieved by immersion of the substrate in alloy, possibly induced by the capillary force and chemical induce-ment of the K–C compound (Figure 5b). With this method to confine the position of liquid metal, stable cycling with various cathodes could be achieved. Although metals’ surface tension could be largely depending on temperature, it is not hard to tell from these studies that the wetting of an alkali liquid metal needs to be taken much care of compared to other metals, for they have high corrosivity. Na-/K+ alunina solid electrolyte (Na-BASE) as a highly conductive Na-ion solid electrolyte has been used for molten sodium at elevated temperature, whereas the Na–K alloy on Na-/K+ alunina could cause the pulverization of electrolyte by ion exchange. Not only Na–K alloy, the Na–Rb alloy is also unstable with Na-BASE at elevated temperature because of the slightly larger size of K and Rb ions allowing the exchange with Na ions in BASE could cause the collapse of the crystal structure. Whereas a K-BASE that has a lower free-energy than Na-BASE is stable in contact with both molten K and Na–K alloy, which is more suitable for the Na–K system.

Beside the physical properties, the electrochemical properties of the liquid alkali alloys are also complicated. In the initial study by Goodenough et al., they found that although the stripping–deposition process was stable for K ions, if the Na ions are desired to be the charge carrier in the Na-based electrolytes, Na ions in the electrolyte would be gradually replaced by the K ions for the potential difference. They attributed this phenomenon to the potential difference between two species. In their following work, they found that the cathode materials could select Na or K ions to be the charge carrier, by cathode crystal structure (kinetic control) or full cell reaction potential (thermodynamic control) (Figure 5d). On the basis of their study, for a crystal that has a
relatively smaller layer space to intercalate, i.e., the Na$_{2/3}$Li$_{1/3}$Mn$_{2/3}$O$_2$ the sodium ions will be selected from the anode to be the charge carrier. For a cathode that operates at a higher voltage with K ions intercalation rather than Na ions and when the size of crystal cites are large enough, like K/Na$_2$MnFe(CN)$_6$, K ions will be selected in this case. On the other hand, Yu et al. designed an organic cathode-based cell that could be functional with both Na ions and K ions as charge carriers (Figure 5e).\textsuperscript{52} On the basis of the computational modeling, the organic molecule sodium rhodizonate (SR), which has been reported as a potentially high energy density sodium cathode material, showed comparable affinity toward Na and K ions with their carbonyl groups.\textsuperscript{53} In this case, the potential difference between Na and K became the only difference between two charge carriers, which, according to the experimental result, could be dominated by the species in the electrolyte. They inferred that the electrolyte could control charge selection by forming the Na-rich or K-rich electrolyte-electrolyte interface, i.e., the normally mentioned solid-electrolyte interphase (SEI) on the surface of the anode, which became the pathway for one species and a barrier for another.

Inspired by the charge selection mechanism studies, Guo and co-workers designed a ternary hybrid-cation battery (Figure 5e).\textsuperscript{52} The commercialized lithium-ion cathode Li$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ was paired with a Na–K anode in the Li/K ions hybrid electrolyte, while only Li ions could intercalate into the cathode side, which was controlled by size, and only K ions could stably strip-deposit on the anode in the Na-free electrolyte. By inspecting the anode surface chemical distribution and analyzing the cyclic voltammograms, they confirmed that the ion distribution in the SEI layer was the reason for this charge selection behavior. The SEI contained same ratio of cations with the anode materials near the interface in contact with the anode surface, which gradually changed, with the increasing thickness, by the change of cation concentration in electrolyte. Therefore, the two types of SEI, the contact SEI and cycling SEI, would dominate the ionic pathway by their ratio differences, which could be controlled by the cycling rate. The study also helped to confirm the SEI growing process experimentally, which has been debated for years. In another work of Yu et al., they achieved the in situ formation of liquid Na–K on electrode, and the anion effect in the SEI layer was also studied (Figure 5f).\textsuperscript{52} By adopting a proper electrolyte system, the in situ formation of the liquid metal with extended chemistry of galvanic replacement reaction on the electrode surface could be achieved, which could successfully protect the alkali metal electrode in a facile method. They found that the -F group in the SEI component largely affects the transport of cations. Some salts, such as sodium bis(ﬂuorosulfonyl)imide (NaFSI), compared with the SEI formed by perchlorate (-ClO$_4$) or hexafluoroarsenate (-PF$_6$) salts, could form a stable NaF layer which allows Na ion to be transported. Also, the transport of Na ions showed a smaller energy barrier along the NaF crystal than in the KF crystal through the same pathway, which further explains the mechanism of the SEI’s dominating role in the diffusion of charge carriers and the controlling the kinetics of interfacial reaction for this in situ liquid metal formation interface. Furthermore, the researchers adopted Na$_2$C$_2$O$_4$ and Na$_3$V$_2$(PO$_4$)$_3$ cathodes as examples to demonstrate the stable full cell performance. Along with the study of the insertion-based materials for alkali ions beyond Li, more combinations will possibly be achieved to boost the total battery energy density, and it should be one of the future study directions to design more practical liquid Na–K anode batteries.\textsuperscript{55}

### 4.2. Ga-Based Liquid Metal Batteries

Beside alkali metals, Ga metal and Ga-based alloys, such as Ga–In alloy, also have a relatively low melting point. They have been applied in the electronic field for special electronic and thermal properties, as cooling agents or flexible components in the devices.\textsuperscript{56,57} As a good base material for alloying reactions with various alkali ions, the electrochemical properties of them are also attractive. On the basis of the thermodynamic principle, the alloying capacity of an electrode could be predicted by the stable phases of the product in the phase diagram, which is normally much larger than insertion-based electrodes. Si-based anodes, for example, have a theoretical capacity of 4200 mAh g$^{-1}$, whereas the large volume expansion is as much as 400%, which could cause severe cycling degradation and sustainability issues.\textsuperscript{58} The Mg–Li battery using a Mg–Li alloy or Mg anode possesses a dendrite-free property, while the stripping–deposition of Mg ions requires rigorous chemical condition. In addition, the high energy density Mg-ion cathodes are rare.\textsuperscript{59} Ga-based liquid alloys, inheriting the fluidity of liquid metals, could avoid the potential damages caused by the dendrites or volume expansion while maintaining high specific capacity as an alloy electrode. In some early explorations, the electrode property of the Ga metal was studied as a Li-ion anode, but due to the slightly higher than room temperature melting point of Ga metal (29.8 °C), the extra energy input was still necessary.\textsuperscript{60,61} Besides, since the transport and reaction kinetics of the solidified electrode is more sluggish than in the liquid phase, the bulk Ga electrode shows relatively low cyclability.\textsuperscript{62}

These results are valued references for understanding the surface and interface chemistry, which could guide future designs of more practical liquid metal batteries.

Ga–In alloy, on the contrary, has a melting point of 15.3 °C at the eutectic concentration, while the ternary alloy of Ga–In–Li has a melting point above room temperature throughout the entire concentration range. However, since the battery reaction is reversible, the alloy electrode will return to the liquid phase and recover any possible defect because of the high surface tension of liquid metals, and therefore it is considered as a “self-healing” material. Eutectic Ga–In (EGaIn) has been used directly as the liquid metal-air battery as a conceptual prototype. It could be made into a wire-shaped flexible battery to sufficiently utilize the flexibility feature, although stable cycling could be challenging to achieve.\textsuperscript{63} With a carbon framework, the Ga–Sn alloy (melting point 10.7 °C) has a superior cyclability up to 4000 cycles by slightly sacrificing the capacity.\textsuperscript{64} Yu et al. reported a Ga–In liquid metal battery that could achieve high cyclability without complicated frameworks in the electrodes.\textsuperscript{65} The bulk liquid metal was dispersed into liquid metal nanoparticles (LMNPs) by ultrasonication, and LMNPs were simply mixed with conductive carbon and binder to cast on the current collector in the same method as preparing a solid electrode material.
It was observed with scanning electron microscopy (SEM) that the liquid metal droplets were initially in the liquid state in the spherical shape, while the absorption of Li ions could turn the droplets into nonspherical solid state, and the delithiation process would bring the alloy back to spherical. Compared with bulk liquid metal, the LMNPs would not pulverize or delaminate from the substrate, which therefore confirmed the stable long cyclability. It is worth noticing that the LMNPs showed different behavior during sodiation, not only on the capacity difference, but also on the phenomenon that the sodiation would not bring the LMNPs into the solid state. The result was observed by SEM, and confirmed by X-ray diffraction (XRD) and thermogravimetry/differential scanning calorimetry (TGA/DSC) measurements. It was inferred that the Ga−In−Na ternary alloy might remain in the liquid state, possibly owing to the melting-point depression of the nanoparticles. It inspires people that, beside the thermodynamic property, some physical properties such as the quantum confinement might assist the application of liquid metal electrodes to achieve more possibilities. In contrast to the Na−K alloy that prefers to "give" the ions away from itself, Ga-based alloys prefer to "receive" ions from others, due to the reduction potential differences. In Ding and co-workers’ work, a room-temperature all-liquid metal battery was designed with these two types of liquid metals (Figure 6b). In such an all-liquid metal battery configuration, the negative electrode, electrolyte, and positive electrode will self-segregate into three layers due to immiscibility and density difference. The natural self-segregation of the three liquid components with high manufacturing scalability is beneficial for practical applications. To maximize the volumetric density, the wetting behavior of liquid metals was crucial to understand. Among Al, Au, and stainless-steel surfaces, the Ga−In alloy would wet the Au surface very well while showing large contact angles on other two surfaces. The density-functional theory (DFT) calculation result showed that the adsorption energy between Ga−In alloy and Au was around six times larger than the other two substrates, which revealed the origin of this wettability difference. The electrostatic potential maps (Figure 6b) also demonstrate more binding sites of Au-coated substrates toward liquid metal atoms with the strongest interaction strength and anchoring effect. Also, in this work, the Na−K anode was mapped spatially with time-of-flight secondary ion mass spectroscopy (TOF-SIMS) analysis technology from the top SEI down to the electrode, and the result clearly showed the chemical component distribution in a Na−K SEI. Some components such as the fluorides and organic components were concentrated at the surface, while some components such as the chlorate could diffuse and disperse into the bulk Na−K. These results are valued references for understanding the surface and interface chemistry, which could guide future designs of more practical liquid metal batteries. Because of the special physical and chemical properties of the liquid metals, they may help to solve more fatal issues in current designs, such as the contact issue between battery components and pulverization of dead electrode materials.

5. OUTLOOK

The development of liquid metal batteries, in the history of the energy research field, has been promoted toward various possibilities based on different battery chemistries, cost and safety evaluations, operation temperatures, and battery working performance. In Figure 7, the operating temperature and
Voltage of representative liquid metal batteries are summarized and presented. Recent research achievements on liquid metal batteries are summarized and introduced in this article focusing on the chemistry of fusible alloys. The liquid metals with low reduction potentials and high theoretical capacities are ideal alternatives for high-energy, metal-based or alloy-based anodes in energy storage applications. On the basis of the standard reduction potential (Table 1) and the summarized voltage (Figure 7), by coupling the anodes that have a lower reduction potential with the cathode materials that have higher alloying potentials toward the anode species, the battery voltage could be further increased. Because of the superior physical and thermodynamic properties, liquid metal batteries based on fusible alloys, which alleviate the severe safety issues of solid metal electrodes, can inherit the merits of fusible alloys that no extra heat input is required. By controlling the working temperature, extra cost and safety concerns, brought by sealing and corrosion, could be controlled as well. However, because of the nature of strong metallic bonds, the available fusible alloy systems are limited. The lower the working temperature is applied, the less utilization of the fusible alloys should be limited to, so the system may not exceed a confined concentration ratio to affect the battery capacity severely. Besides, for fusible alloys, the transport kinetics could be sluggish when solidified, which should be considered in the battery design stage as well.

Different from the high-temperature liquid metal batteries, studies based on fusible alloys are not as well developed, and thus more efforts should be dedicated to strengthen the understanding of physical or electrochemical properties, and the battery designs should be more refined based on those special properties. The studies on next-generation liquid metal batteries should pay attention to some important aspects, as shown in Figure 8. First, electrolytes allowing stable electrochemical cycling of the highly reactive liquid metal species need to be better designed. The electrolytes designed for low temperature liquid metals should have not only the capability of fast charge transport, but also good wettability and chemical stability toward the electrode alloys.76 Besides, in some complicated alloys containing more than one type of potential charge carrier, the charge transport plays an important role in selecting the carrier by the existing ionic pathways in the interfacial layer. Therefore, deeper understanding and rational design of the interfacial layers are crucial to improve battery performance as well.77 What is more, to better utilize the active species in the liquid alloys to boost energy density while maintaining superior safety and fast kinetics, the methods of uniform stripping–deposition of the alloy components with controlled ratios and rates should be explored. Metallurgical techniques, such as alloy codeposition, could be taken as references, and exploring the suitable chelation agents or additives to control the activities of the active species may be a promising approach.78 Finally, with more advanced simulations benefiting from the increasingly powerful computational technologies, including simulations, artificial intelligence, and data mining, more possible eutectic and fusible systems could be explored, and the physiochemical properties, molecular interactions, as well as performance predictions would be modeled more accurately.

Figure 7. Development of all-liquid-metal batteries after 1960s, showing the operating temperature and voltage of those representative designs.42,46,75

Figure 8. Perspective for future scalable liquid metal batteries.
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