LiI-KI and LAGP electrolytes with a bismuth-tin positive electrode for the development of a liquid lithium battery

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**HIGHLIGHTS**

- Electrochemical behavior of the material was investigated for liquid lithium cells.
- Reduce operation temperature was achieved by the eutectic composition of LiI-KI.
- Reduce operation temperature was achieved by solid electrolyte LAGP.
- Li|[LiI-KI]|Bi–Sn and Li|[LiI-KI]|Bi–Sn cells showed high efficiency and high capability.

**ABSTRACT**

High-temperature liquid metal lithium batteries occupy a highly important position in the field of energy storage. Lithium batteries are long-lasting and have high energy storage efficiency. However, the development of new liquid metal lithium batteries are plagued by dangerous conditions and high operating temperatures. In this study, we report a new methodology for the creation of liquid metal batteries (LMBs) using either LiI-KI or LAGP as an electrolyte and Bi–Sn as a positive electrode to lower the operation temperature of Li-based LMBs and achieve long-term stability. We show that the assembled Li|[LiI-KI]||Bi–Sn and Li|[LAGP]||Bi–Sn cells stably cycle at an intermediate temperature less than 300 °C at current densities of 50 mA/cm² to 300 mA/cm², respectively, with almost no capacity decay and an average coulombic efficiency of 97–98%. Our design opens new avenues for the development of energy storage technologies.

1. Introduction

Energy storage systems are a promising technology that is important for sustainable future development. The liquid metal battery is an important piece of technology in the field of energy storage [1–4]. The development of this battery began in the 1960s as a low-cost, long-lasting, and highly efficient energy storage system. Among the liquid metals used in batteries, lithium is the most ideal anode material [5]. The density of lithium is the lowest among all metal anode materials, and lithium has the lowest electrode potential. Therefore, the development of a lithium-based liquid metal battery has the most application potential. Recently, Professor Sadoways of MIT proposed a new direction for the development of liquid metal batteries [3]. The metal is spontaneously divided into three layers by a liquid at a high temperature and a density: these layers consist of an upper metal negative electrode, a middle molten salt electrolyte, and a lower metal positive electrode. The articles published at the time of this report are mainly focused on positive electrode materials. Recently, reports on liquid metal lithium batteries have mainly been centered around positive electrode materials, and there have been few reports on special electrolyte materials. The operating temperature of batteries is mostly above 400 °C [6–13]. Such high operating temperatures greatly increase the requirements for sealing materials, and indirectly increase energy consumption. The cost of the battery contradicts the original intention behind the development of this energy storage system, and the high operating temperature is bound to reduce the safety of batteries. The determining factor in controlling the operating temperature of a liquid metal battery is the melting point and state of the electrolyte, and lithium molten salt has the highest melting point of any battery material. For molten salt electrolytes, lithium halides are currently the most widely used materials. The electrolytes of liquid metal lithium batteries include the following: LiCl–LiF (30:70 mol%), LiF–LiCl–LiBr (22:31:47 mol%), LiF–LiCl–Li (20:50:30 mol%), LiCl–Li (36:64%) [6–9, 11–13], and garnet solid electrolyte LLZTO [14]. The high melting point...
of the above molten salts requires batteries to operate at temperatures above 400 °C, which greatly increases the maintenance cost of the battery. Solid electrolytes have rarely been reported outside of the garnet-type solid electrolyte work performed at Tsinghua University [14]. Since the solid electrolyte [15,16] does not need to be melted into a liquid state, the operating temperature of the liquid lithium battery can be considerably reduced. However, the cost of the solid electrolyte is high relative to the molten salt electrolyte, and the formation and sintering of the solid electrolyte is difficult; therefore, it is necessary to find a more suitable sintering method and a lower cost solid electrolyte. For the positive electrode material, we chose Bi for its high electronegativity and alloyed it with metal Sn to lower the melting point [17–22].

Therefore, we report two electrolyte batteries, Li||LiI-KI||Bi–Sn and Li||LAGP||Bi–Sn batteries. The former battery uses a lower melting point LiI-KI (melting point 260 °C) eutectic molten salt, which can lower the operating temperature of the all-liquid metal lithium battery below 300 °C for the first time, and the battery remains stable after several weeks of cycling. This work greatly reduces the operating temperature of LMB and it is the big innovation point of this article. The discharge voltage is maintained at 0.5–0.6 V and has a high coulombic efficiency. The latter battery uses a LAGP solid electrolyte. This battery only needs positive and negative materials to be liquid at high temperature and can control the operating temperature of the battery below 250 °C. The battery is still stable after a long cycle with a coulombic efficiency of approximately 98%, and the discharge voltage platform is stable.

2. Experimental

2.1. Li||LiI-KI||Bi–Sn cell

2.1.1. Preparation of battery materials

High purity (>99%) ultra-dry grade LiI and KI were used as electrolytes in all the experiments. The salt mixture (LiI: KI = 58:42 mol%) was ground, mixed, and melted in an Alumina tube. The mixture was dried under vacuum (100 °C, 12 h) to remove residual water, and it was melted under vacuum at 400 °C for 10 h. After the mixture cooled, it was reground for use. A bismuth-tin alloy (53:47%) was used for the positive electrode. The negative electrode was prepared by soaking Ni foam in the liquid Li. The battery and the furnace body are shown in Fig. 1. The anode current collector is made of low carbon steel, and the graphite crucible is used as the battery casing and the positive current collector. The assembly process of the entire battery was carried out in a glove box in an argon atmosphere.

2.1.2. Electrochemical Measurement

The battery was placed in a high temperature furnace, heated to 290 °C at a rate of 5 °C/min under an argon atmosphere, and the battery was subjected to a cyclic charge and discharge test using a LAND test system. To prepare the battery for testing, it was placed into a high temperature test furnace (Fig. S1) and connected to the positive and negative poles before the chamber was sealed, vacuumed to ~0.08 MPa, filled with argon gas to 0.02 MPa, and then vacuumed again. This process was cycled three times. After the fourth cycle, the program was started, the temperature was raised to 100 °C at a heating rate of 5 °C/min, and the temperature was maintained for 3–4 h in order to completely remove the water; then, the temperature was raised to 290 °C at a heating rate of 5 °C/min, and the temperature was held steady. After 5–6 h of incubation at 290 °C, the positive and negative materials and the electrolyte were all melted into a liquid state, and the relevant electrochemical data were acquired.

The microstructure and elemental distribution of the battery cathode product were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The block sample is ground and polished, and the conductive adhesive is used in the Petri dish for use. Put it into the electron microscope room, vacuum process and scan test. The phase identification of the substance was carried out by X-ray diffraction (XRD). The voltage is generally set at 40 kV, the current is set to 40 mA, the scan rate is generally set to 10/ min by default, the step size is set to 0.02°, and the scan range is between 10 and 90°. For the electrolyte material, there are mainly powder and bulk materials. For powdery electrolyte materials, the powder is evenly spread, placed on a carrier glass slide, and then another slide is placed for XRD testing. For blocks, it is generally necessary to perform a flat polishing process. Firstly, the test surface is polished with sandpaper of different thicknesses, and then the block surface is subjected to XRD testing.

2.1.3. Results and Discussion

To lower the operating temperature of the battery, a LiI-KI eutectic molten salt is used as the electrolyte. When the LiI-KI molar ratio is 58%/42%, the eutectic point of the molten salt is 260 °C. In this study, we performed a cyclic charge-discharge test on the battery at 290 °C and conducted voltage tests at different current densities and different cycle stages, as well as an analysis of coulombic efficiency and energy density. Fig. 2a shows that the open circuit voltage of the battery is stable at approximately 0.76 V. The battery has a stable discharge and charging voltage platform. The discharge voltage is stable at approximately 0.5–0.6 V, and the charging voltage is maintained at approximately 0.8–0.9 V. The battery was operated at a low temperature of 290 °C, and still had good charge and discharge stability. Moreover, at temperatures less than 300 °C, the corrosiveness and sealing performance of the battery can be greatly improved, and there are more options for sealing materials and the insulating materials available; at the same time, lowering the operating temperature can effectively reduce the need to maintain the operating temperature of the battery. Saving energy by not requiring temperature maintenance indirectly reduces the cost of the battery and is conducive to high-power storage. Fig. 2b shows that as the current density increases, the charging platform increases, as well, while the discharge platform of the battery decreases. These patterns align with battery functions. Overall, the current density increases by 100 mAh/cm². As the current density increases, the discharge platform of the battery drops by approximately 0.09 V. As the current density increases, and internal voltage of battery increase, and the discharge platform decreases. Fig. 2c shows that the charge and discharge curves of the battery coincide across different cycle times. The discharge platform is essentially stable between 0.5 and 0.6 V over different cycles, indicating good stability between the electrolyte and the positive electrode.
material. These results indicate good cycle stability. After approximately 10 cycles, the battery was de-energized, cooled to room temperature, and then raised to the operating temperature; the performance of the battery was not affected. Fig. 2d shows that the coulombic efficiency of the battery is stable at 97%, and the energy attenuation is small. This efficiency is a common feature of liquid batteries. The charge and discharge capacity of the battery shows almost no attenuation and is maintained between 6.7 and 7.1 Ah; the energy density of the battery is calculated to be 100 Wh/kg. After more than 100 cycles, the battery still has good charge and discharge performance, indicating stability. The liquid high-temperature battery has a long lifespan because the electrodes and the electrolyte are all in a liquid state under high temperature conditions. A liquid state limits the formation of lithium dendrites, which commonly cause short circuits in ordinary lithium batteries; this improvement gives liquid lithium batteries a remarkable advantage in the field of energy storage.

The battery consists of a metal lithium negative electrode as the upper layer, an intermediate molten salt electrolyte layer, and a lower layer of bismuth tin alloy. The positive and negative electrodes do not react with molten salt electrolyte, therefore, they can stay stable. And the densities of the materials naturally divide the battery into three layers. When discharging, the metal lithium ions pass through the molten salt. The internal structure of the battery after discharge is shown in Fig. S3. Also, Fig. 3 is a schematic showing a vertical section and a horizontal section of the positive electrode. Component analysis of alloy phase and intermetallic compound is shown in Figs. S4–S5. According to the XRD (Fig. 4) analyses of the positive electrode material, the electrolyte layer preferentially combines with the bismuth in the alloy layer to form LiBi and Li₂Bi intermetallic compounds. The discharge product of the positive electrode mainly takes the form of a Li₅Bi intermetallic compound phase and an alloy phase. It can be observed from Fig. 4 that the positive electrode mainly consists of two phases. It can be seen from the comparison of the XRD analysis with the standard card that the positive electrode intermetallic compound is mainly LiBi and Li₂Bi, the alloy phase is the Bi–Sn alloy, and the negative electrode metal lithium is mainly passed through the electrolyte. There, the lithium combines with bismuth to form an intermetallic compound which is distributed in the positive electrode, and the metal Sn mainly serves to reduce the melting point and the eutectic temperature of the Bi positive electrode. The alloy phase is mainly a bismuth-tin alloy with a high percentage of tin. The discharge process of the battery was also verified. When charging, the lithium ions in the Li₅Bi become metal lithium and deposit on the surface of the negative metal lithium by moving through the electrolyte to complete the charging process.

**Fig. 2.** (a) Charge and discharge curves of the Li/LiI-Kl/Bi–Sn battery at a current density of 100 mA/cm²; (b) Charging and discharging curve test of Li/LiI-Kl/Bi–Sn batteries at different current densities; (c) Charge and discharge curves of Li/LiI-Kl/Bi–Sn batteries in different cycles; (d) Curve of Coulomb efficiency and charge-discharge capacity of Li/LiI-Kl/Bi–Sn battery versus cycle number.
Compared with the previously reported liquid metal batteries, the working temperature of our battery is below 300°C for the first time, and the battery still has good electrochemical performance. The discharge voltage of battery stabilizes at 0.6 V at a large current density and coulombic efficiency of the battery is almost 100%. The discharge voltage of the battery and coulombic efficiency are at a higher level than the similar battery. The operating temperature and voltage parameters of this battery and those previously reported are shown in Table S1.

2.2. Li || LAGP || Bi–Sn cell

2.2.1. Preparation of battery materials

LiCO₃, Al₂O₃, GeO₂, In₂O₃ and NH₄H₂PO₄ powders were weighed to obtain the following composition ratio: 4.5:4.0:26.0:2.0:53.5 mol%. The mixed powder was added to a ball mill and ground for 1–2 h. Then, the uniformly ground powder was poured into a platinum crucible, placed in a muffle furnace, and raised from 25°C to 700°C at a rate of 5–6°C/min, and the temperature was maintained for 1–2 h. The powder was further heated to 1500°C at a rate of 5–6°C/min, and the temperature was maintained for 2–3 h. The platinum crucible was then removed from the muffle furnace, and the powder was mixed with distilled water to form a glassy substance. This substance was placed in a tube furnace and heated to 850°C at a rate of 1°C/min and maintained at that temperature for 10–12 h. After cooling, the obtained glass ceramics were removed and ball milled into the final product, an LAGP powder. The milled powder was placed in an alumina mortar, and a 5–8% mass fraction of 5% PVA solution was added as a binder. An additional 1% of LiOH was added as a reaction inhibitor. The product was then ground again, and the ground powder was passed through a 40-mesh sieve. After repeated grinding and sieving, the micron-sized particles are agglomerated and particles of varying sizes are evenly distributed, leading to denser packing and facilitating better molding. The prepared powder was placed into a cold isostatic pressing rubber mold and sealed. The powder was pressed at 200–210 MPa for 30–40 s. The pressed product was placed in a high-temperature electric furnace, heated from room temperature to 300°C at a rate of 1°C/min, and kept for 1–2 h in order to facilitate the removal of the binder; next, the temperature was raised to 850°C at a rate of 1°C/min, and the product was heat-treated for 3 h, which is beneficial to the recrystallization of the green body. Finally, the product is slowly lowered to room temperature. The sintered electrolyte tube is shown in Fig. S2. In addition, the bismuth-tin alloy described above (53:47%) was used for the positive electrode. The negative electrode was prepared by soaking Ni foam in liquid Li. The battery and the furnace body are shown in Fig. 5. The anode current collector is made of low carbon steel, and the graphite crucible is used as the battery casing and the battery positive current collector. The assembly process of the entire battery was carried out in a glove box in an argon atmosphere.

2.2.2. Electrochemical Measurement

The battery was placed in a high temperature furnace, heated to 245°C at a rate of 5°C/min under an argon atmosphere, and subjected to a cyclic charge and discharge test using a LAND test system. To prepare the battery for testing, it was placed into a high temperature test furnace.
and connected to the positive and negative poles before the chamber was sealed, vacuumed to \(-0.08\) MPa, filled with argon gas to \(0.02\) MPa, and then vacuumed again. This cycle was repeated three times. After the fourth vacuuming, the program was started, and the temperature was raised to \(100\) °C at a heating rate of \(5\) °C/min and maintained for \(3\)–\(4\) h in order to completely remove the water; then, the temperature was raised to \(245\) °C at a heating rate of \(5\) °C/min after \(5\)–\(6\) h of incubation at \(245\) °C, the positive and negative materials were melted into a liquid state, and the relevant electrochemical data were obtained.

The microstructure and elemental distribution of the battery cathode product were investigated by scanning electron microscopy (SEM). The phase identification of the substance was carried out by X-ray diffraction (XRD). The experimental conditions are the same as Li/LiI-KI/Bi-Sn battery.

### 2.2.3. Results and discussion

The sintered SEM image (Fig. 6) shows that the electrolyte contains a large number of glass-ceramic continuous phases, and the crystal grains are covered by the bonded phase without obvious grain boundaries and allow good lithium ion migration. The XRD image (Fig. 7) before and after sintering shows that LiGe\(_2\)(PO\(_4\))\(_3\) constitutes the main skeleton structure of the LAGP battery. And Li ions participate in the creation of the entire skeleton as a balanced charge.

Fig. 8a shows that the open circuit voltage of the battery is stable at approximately \(0.73\) V. The battery has a stable discharge and charging voltage platform. The discharge voltage is stable at approximately \(0.6\)–\(0.7\) V, and the charging voltage is maintained at approximately \(0.8\)–\(0.9\) V. The battery was shown to operate at a low temperature of \(245\) °C and still had good charge and discharge stability. Fig. 8b shows
that as the current density increases, the discharge platform of the battery decreases and the charging platform rises. After increasing the current density to 75 mA/cm², the discharge platform of the battery drops by approximately 0.08–0.1 V. As current density increases, the internal resistance of the battery does not change and the internal voltage increases, and the discharge platform is reduced. Since the positive and negative electrodes are in a liquid state and in close contact with the electrolyte, the charge transfer resistance is small, and the voltage loss mainly comes from the ohmic resistance. Fig. 8c shows that the charge and discharge curves of the battery essentially coincide under different cycle times. The discharge platform is stable between 0.6 and 0.7 V under different cycles, indicating the electrolyte and the positive electrode material are stable. The cycle stability is good. Fig. 8d shows that the coulombic efficiency of the battery is stable at 97–98%, and the energy attenuation is very small. This is a common feature of the liquid battery. The charge and discharge capacity of the battery is stable and almost unattenuated, as it is maintained between 0.36 and 0.37Ah. After more than 30 cycles, the battery maintains good charge and discharge performance. After the battery goes through 10 cycles, the temperature is lowered to room temperature to examine the power-off performance of the battery. After the battery is re-heated to the required temperature, the cycle performance and discharge performance of the battery are not affected, and the battery is found to have good stability and safety. The operating temperature of the battery is 245 °C, and it is the lowest value among lithium-based liquid metal batteries. At the same time, the battery still has good electrochemical performance. For battery temperature and voltage parameters, the comparison of this work with previously reported batteries are shown in Table S1.

3. Conclusion

We investigated two liquid metal lithium batteries that drastically reduced the operating temperature of the battery to 300 °C and below 250 °C, respectively, which reduced energy consumption and improved battery safety. At lower operating temperatures, the corrosion rate of the material can be reduced, and the life of the battery can be increased. At the same time, lowering the operating temperature can also reduce the sealing cost and improve the cost performance of the battery. Li || LII-KI || Bi–Sn and Li || LAGP || Bi–Sn both have high coulombic efficiency (>98%) and high energy density (>80 Wh/kg). In addition, both have good cycle stability, as indicated by the fact that even if the battery temperature is lowered to room temperature and then returned to operating temperature, the performance of the battery is largely unaffected. Both batteries also have good anti-interference performances. A Bi–Sn alloy was selected as the positive electrode material. Metal Bi acts as an effective material for the positive electrode, as it is able to share electrons readily. Metal Sn acts to reduce the melting point and wettability of the positive electrode and improves the stability. Additionally,
the Bi–Sn alloy is environmentally safe, as it is not a pollutant. These two batteries offer high performance, cycle stability, and safety, making them a very competitive option in the field of grid energy storage. These two battery structures greatly reduce the operating temperature of the LMB, which is in line with expectations. These two electrolyte materials are also expected to become one of the material choices in the field of high temperature liquid lithium energy storage batteries.

Declaration of competing interest

The authors declared that they have no conflicts of interest to this work. We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Appendix A. Supplementary data

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References