

A Lithium Metal Anode Surviving Battery Cycling Above 200 °C

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Lithium (Li) metal electrode cannot endure elevated temperature (e.g., >200 °C) with the regular battery configuration due to its low melting point (180.5 °C) and high reactivity, which restricts its application in high-temperature Li metal batteries for energy storage and causes safety concerns for regular ambient-temperature Li metal batteries. Herein, this work reports a $\text{Li}_5\text{B}_4/\text{Li}$ composite featuring a 3D Li_5B_4 fibrillar framework filled with metallic Li, which maintains its initial structure at 325 °C in Ar atmosphere without leakage of the liquid Li. The capillary force caused by the porous structure of the Li_5B_4 fibrillar framework, together with its lithiophilic surface, restricts the leakage of liquid metallic Li and enables good thermal tolerance of the $\text{Li}_5\text{B}_4/\text{Li}$ composite. Thus, it can be facilely operated for rechargeable high-temperature Li metal batteries. $\text{Li}_5\text{B}_4/\text{Li}$ electrodes are coupled with a garnet-type ceramic electrolyte ($\text{Li}_{6.5}\text{La}_3\text{Zr}_{0.5}\text{Ta}_{1.5}\text{O}_{12}$) to fabricate symmetric cells, which exhibit stable Li stripping/plating behaviors with low overpotential of ≈ 6 mV at 200 °C using a regular sandwich-type cell configuration. This work affords new insights into realizing a stable Li metal anode for high-temperature Li metal batteries with a simple battery configuration and high safety, which is different from traditional molten-salt Li metal batteries using a pristine metallic Li anode.

Metallic lithium (Li) anode has the highest theoretical specific capacity (3860 mA h g^{-1}) and lowest electrochemical potential (-3.04 V vs standard hydrogen electrode), which make it ultimate anode choice for high-energy Li-based rechargeable batteries.^[1] However, Li metal anode suffers from inhomogeneous Li stripping/plating and low Coulombic efficiency rooted to its infinite relative volume change and high chemical reactivity for batteries operated at room temperature.^[2] Numerous efforts have been devoted to address the above issues and realize stable Li metal anode in the past decades.^[3] Despite the exciting progress achieved, few attention has been paid to realizing Li metal anode with good thermal tolerance, which can be coupled with solid ceramic/molten salt electrolyte and applied in high-temperature liquid metal batteries for grid energy storage, and improve the thermal safety of regular Li metal batteries.^[4] Successful example has been shown by special battery configuration using molten liquid Li salt electrolyte and pure liquid metallic Li for high-temperature liquid metal batteries.^[5]

However, the complex battery configuration and high reactivity of liquid metallic Li cause high costs and safety concerns.^[6,7] Therefore, it is of vital importance to explore Li metal electrode with good thermal tolerance which can simplify the battery configuration for high-temperature Li metal batteries and improve the thermal safety of regular Li metal batteries.

In this work, we propose the following three considerations that can potentially guide the search of an ideal Li metal electrode with good thermal tolerance: 1) The electrode should have 3D conductive framework with good mechanical and thermal stability. 2) The framework should have porous structure. 3) The surface of the framework should be lithiophilic. High conductivity of the framework can enable the charge transport within the entire electrode.^[8] The porous structure of the 3D framework provides void space for the storage of metallic Li, and the capillary force and lithiophilic property confine the metallic Li tightly within the framework even at elevated temperature. Based on these considerations, we thus target lithium–boron (Li–B) alloy/Li composite to be a promising candidate. Li–B alloy/Li composite can be synthesized by the reaction between excess molten metallic Li and B.^[9] Li–B alloy tends to form fibrillar structure that interconnects with each other,

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producing 3D conductive network, and the excessive free Li can be filled in the space of the framework in the Li–B alloy/Li composite.^[10,11] The 3D Li–B alloy framework is an excellent host for metallic Li for rechargeable high-temperature Li metal batteries. First, Li–B alloy possesses good thermal and mechanical stability, and it maintains its phase and structure till 400 °C or higher.^[12] Second, the Li in Li–B alloy would not be extracted during the plating/stripping cycling of metallic Li since there is reasonable potential gap between Li metal and Li–B alloy (>0.46 V vs Li^+/Li).^[11,13] Thus, stable 3D network of Li–B alloy will be maintained over cycling of metallic Li. Third, a porous interconnected structure of Li–B alloy can accommodate the volume changes during the stripping/plating process of metallic Li and improve the mechanical stability of the electrode.^[14,15] Fourth, high conductivity of Li–B alloy ($1.43 \times 10^3 \text{ S cm}^{-1}$) framework provides pathway for charge transport.^[13] The lithiophilic property of Li–B alloy enhances the interaction between the framework and metallic Li even at high temperature.^[14] Therefore, stable battery cycling for the Li–B alloy/Li electrode can be expected at high temperature above the melting temperature of metallic Li.

Rechargeable molten salt Li metal batteries using molten liquid Li salt electrolyte is the most popular high-temperature Li metal batteries.^[7,16] Very recently, a typical ceramic solid-state electrolyte ($\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$) with tube configuration has been explored as an alternative for high-temperature Li metal batteries due to its good chemical and thermal stability.^[17] Despite of the great success in electrolytes, the high flowability of liquid metallic Li at high temperature causes safety concerns and requires more specific battery design that involves complex fabrication process and increases the battery cost for practical applications. Stable Li stripping/plating cycling was

achieved for Li/granet composite structure fabricated by infiltrating metallic Li into 3D porous garnet framework on the dense garnet layer of at room temperature.^[18] Such unique electrode structure can restrict the leakage of liquid metallic Li and is promising for Li metal cycled at elevated temperature. However, the fabrication of such electrode is complex and the content of metallic Li in the composite is relatively low due to the high density of garnet materials.

Herein, we explored the possibility of using $\text{Li}_5\text{B}_4/\text{Li}$ composite as a stable anode for rechargeable Li metal batteries operated above the melting temperature of metallic Li. The unique 3D interconnected framework structure of Li_5B_4 improves the stability of the entire $\text{Li}_5\text{B}_4/\text{Li}$ composite above the melting pointing of metallic Li. Even at the temperature of 325 °C, the molten metallic Li is tightly trapped within the structure of $\text{Li}_5\text{B}_4/\text{Li}$ composite. In a regular cell configuration, stable cycling with low overpotential of ≈ 6 mV was achieved for a $\text{Li}_5\text{B}_4/\text{Li} \parallel \text{Li}_5\text{B}_4/\text{Li}$ symmetric cell using $\text{Li}_{6.5}\text{La}_3\text{Zr}_{0.5}\text{Ta}_{1.5}\text{O}_{12}$ (LLZTO) solid electrolyte operated at 200 °C, showing the promise of $\text{Li}_5\text{B}_4/\text{Li}$ composite in high-temperature Li metal batteries. Also, such anode can also improve the thermal safety for regular ambient-temperature Li metal batteries at room temperature.

The phase structure and composition information of $\text{Li}_5\text{B}_4/\text{Li}$ composite were investigated by X-ray diffraction (XRD, Figure 1a). The diffraction peaks were mainly ascribed to Li_5B_4 with cubic phase (JCPDS No. 73-0645) and three weak peaks for metallic Li (JCPDS No. 89-3940, Figure S1, Supporting Information) were observed at 36°, 52°, and 65°, suggesting the coexistence of Li_5B_4 (Li–B alloy) and metallic Li in the as-obtained $\text{Li}_5\text{B}_4/\text{Li}$ composite. Scanning electron microscopy (SEM) was performed to investigate the structure of the $\text{Li}_5\text{B}_4/\text{Li}$

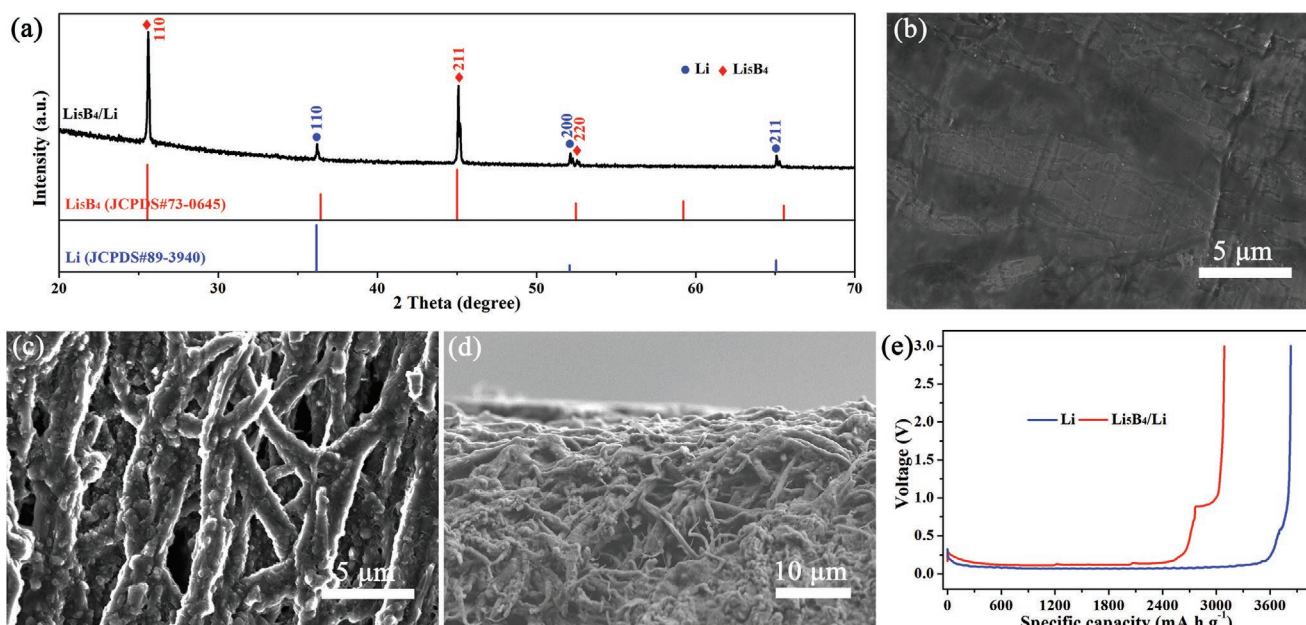


Figure 1. a) XRD pattern of a $\text{Li}_5\text{B}_4/\text{Li}$ composite. b) Top-view SEM image of a $\text{Li}_5\text{B}_4/\text{Li}$ composite. c) Top-view and d) cross-section SEM images of a $\text{Li}_5\text{B}_4/\text{Li}$ composite after Li stripping at a current density of 10 mA cm^{-2} . e) Electrochemical Li stripping curves of a thin $\text{Li}_5\text{B}_4/\text{Li}$ composite foil electrode ($\approx 50 \mu\text{m}$) and a pure Li foil electrode at a current density of 1 mA cm^{-2} . To investigate the structure of the Li_5B_4 in the $\text{Li}_5\text{B}_4/\text{Li}$ composite, metallic Li was electrochemically stripped in a symmetric cell using a liquid carbonate electrolyte.

Li composite before and after the electrochemical stripping of metallic Li. The initial $\text{Li}_5\text{B}_4/\text{Li}$ composite foil showed a dense structure with a smooth surface (Figure 1b, Figure S2, Supporting Information). Interestingly, fibrils with the diameter of hundreds of nanometers were observed for the product after stripping of metallic Li. They interconnected with each other and formed a stable 3D framework with porous structure (Figure 1c,d; Figure S3, Supporting Information). Such network structure of Li_5B_4 can work as a stable host and provide abundant of interspersed void space for the physical confinement of metallic Li, providing high capacity. Note that there exists a reasonable potential gap with hundreds of millivolts (>0.46 V) between Li–B alloy and metallic Li,^[11] and thus the metallic Li in the $\text{Li}_5\text{B}_4/\text{Li}$ composite can cycle stably while maintaining the 3D framework structure and phase of Li_5B_4 unchanged. Also, stable plating and stripping behavior of metallic Li can be achieved within the Li_5B_4 framework by providing conductive path ways for charge and buffering volume change during electrochemical cycling. The content of metallic Li in the $\text{Li}_5\text{B}_4/\text{Li}$ composite can be measured by the electrochemical galvanostatic charge/discharge measurement. A $\text{Li}_5\text{B}_4/\text{Li}||\text{Li}$ cell was assembled and the Li in the $\text{Li}_5\text{B}_4/\text{Li}$ electrode was electrochemically extracted by galvanostatic charge test at a current density of 1 mA cm^{-2} (Figure 1e). A long potential plateau with potential slightly higher than the stripping of pure metallic Li (≈ 0.05 V) was first observed in a carbonate electrolyte, corresponding to the stripping of metallic Li in the $\text{Li}_5\text{B}_4/\text{Li}$ composite. After the

fully stripping of Li, the potential quickly increased and then a potential plateau was shown around 0.88 V, which arises from the extraction of Li from Li_5B_4 .^[11,13] The content of metallic Li in the $\text{Li}_5\text{B}_4/\text{Li}$ was calculated as high as 72%, corresponding to a capacity of $\approx 2778 \text{ mA h g}^{-1}$ for the metallic Li in the $\text{Li}_5\text{B}_4/\text{Li}$ composite. The extraction of Li from Li_5B_4 only takes place after the exhaustion of metallic Li due to the large voltage gap. During the practical application of the $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode, only stripping/plating reaction of metallic Li takes place due to the existence of excess metallic Li.

Here we emphasize the important role of capillary force between metallic Li and the 3D porous Li_5B_4 framework with lithiophilic surface in confining the liquid metallic Li. Li_5B_4 has a high melting point temperature (above 1000°C),^[19] which makes the Li_5B_4 framework of the $\text{Li}_5\text{B}_4/\text{Li}$ composite good structural and mechanical stability even at a temperature far above the room temperature. Moreover, the physical confinement of metallic Li within the void space of the Li_5B_4 framework and the chemical interaction between metallic Li and Li_5B_4 can enable metallic Li trapped firmly within the Li_5B_4 framework even at elevated temperature above the melting point of metallic Li, which make it possible to operate cells with $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode at high temperature. To verify the chemical interaction between metallic Li and Li_5B_4 , density functional theory (DFT) calculations were performed (Figure 2). The strongest diffraction peak (110) of Li_5B_4 according to the XRD result (Figure 1a) was used to calculate the corresponding

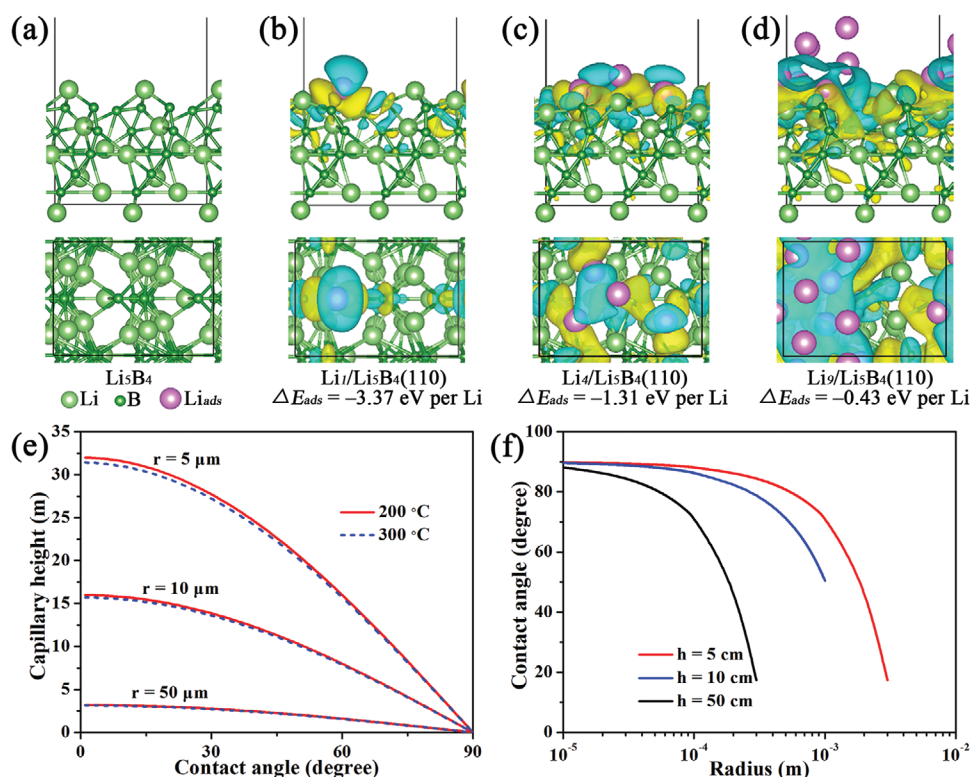


Figure 2. a) Crystal structure of Li_5B_4 . b–d) Simulations for the local charge density difference iso-surfaces of Li adsorption of 1 (b), 4 (c), and 9 (d) Li clusters. $0.001 e$ per $\text{\AA}^3$ iso-surfaces, cyan: $-$, yellow: $+$, purple: adsorbed Li. The top and bottom sections of (a–d) show the side-view and top-view structures, respectively. e) Capillary height of liquid metallic Li at various temperatures and capillary radius. f) The relationship between contact angle and capillary radius at various capillary height at 300°C .

ΔE_{ads} with three Li cluster states. The values of ΔE_{ads} reached to -3.37 , -1.31 , and -0.43 eV per Li atom when n (number of Li cluster) was equal to 1, 4, and 9 (Figure 2a–d), respectively, demonstrating the strong interaction between Li_5B_4 and Li atoms, and thus the excellent lithiophilic property of the Li_5B_4 framework. As such, the high porosity (with average pore size of ≈ 5 μm) and good lithiophilicity of the Li_5B_4 framework, and low density of molten Li would lead to strong interaction between metallic Li and Li_5B_4 framework and could immobilize liquid metallic Li within the framework (Figure S5, Supporting Information). To verify the confinement effect of the Li_5B_4 framework for liquid metallic Li, the capillarity height of a $\text{Li}_5\text{B}_4/\text{Li}$ composite foil was measured. Here, the capillarity height was evaluated according to

$$h = 2\gamma \cos \theta / (\rho g r) \quad (1)$$

where h , γ , θ , ρ , g , and r are the capillarity height, surface tension, contact angle, density, gravitational acceleration, and capillary radius, respectively. The experimental results showed that the capillarity height reached centimeter scale at 300 $^\circ\text{C}$ (Figure 2e,f), indicating the good confinement of liquid metallic Li within the composite electrode. Note that the interaction between metallic Li and Li_5B_4 would decrease with the increase of metallic Li content. As such, there is a tradeoff between the capacity and high temperature tolerance of the

$\text{Li}_5\text{B}_4/\text{Li}$ composite, which can be realized by adjusting the content of metallic Li in the $\text{Li}_5\text{B}_4/\text{Li}$ composite. Additionally, the continuous 3D structure with high accessible area to metallic Li of the as-used Li_5B_4 framework due to its fibrillary morphology is beneficial for the enhancing interaction between metallic Li and the Li_5B_4 framework. Therefore, the high porosity of the Li_5B_4 framework and strong interconnection between the Li_5B_4 framework and metallic Li stabilize the metallic Li firmly within the Li_5B_4 framework make it possible a solid feature of the overall $\text{Li}_5\text{B}_4/\text{Li}$ composite at elevated temperature above the melting point of metallic Li.

We investigated the stability of the $\text{Li}_5\text{B}_4/\text{Li}$ composite foil under various temperature conditions in an argon-filled glove box. Digital images showed that the $\text{Li}_5\text{B}_4/\text{Li}$ composite foil maintained its structure and morphology, and showed overall solid feature even at 300 $^\circ\text{C}$, 120 $^\circ\text{C}$ higher than the melting point of metallic Li (Figure 3a; Movie S1, Supporting Information). In contrast, the bare Li metal foil started to melt above 180 $^\circ\text{C}$ and the flow of liquid metallic Li was observed above 200 $^\circ\text{C}$, which made the pure metallic Li electrode not suitable for high-temperature operation in regular battery configuration (Figure 3b; Movie S1, Supporting Information). Meanwhile, significant color change from metal white to light blue was observed for the bare Li metal, and a thick and wrinkled structure was formed on the surface of bare Li metal due to the reaction between active metallic Li and the trace amount

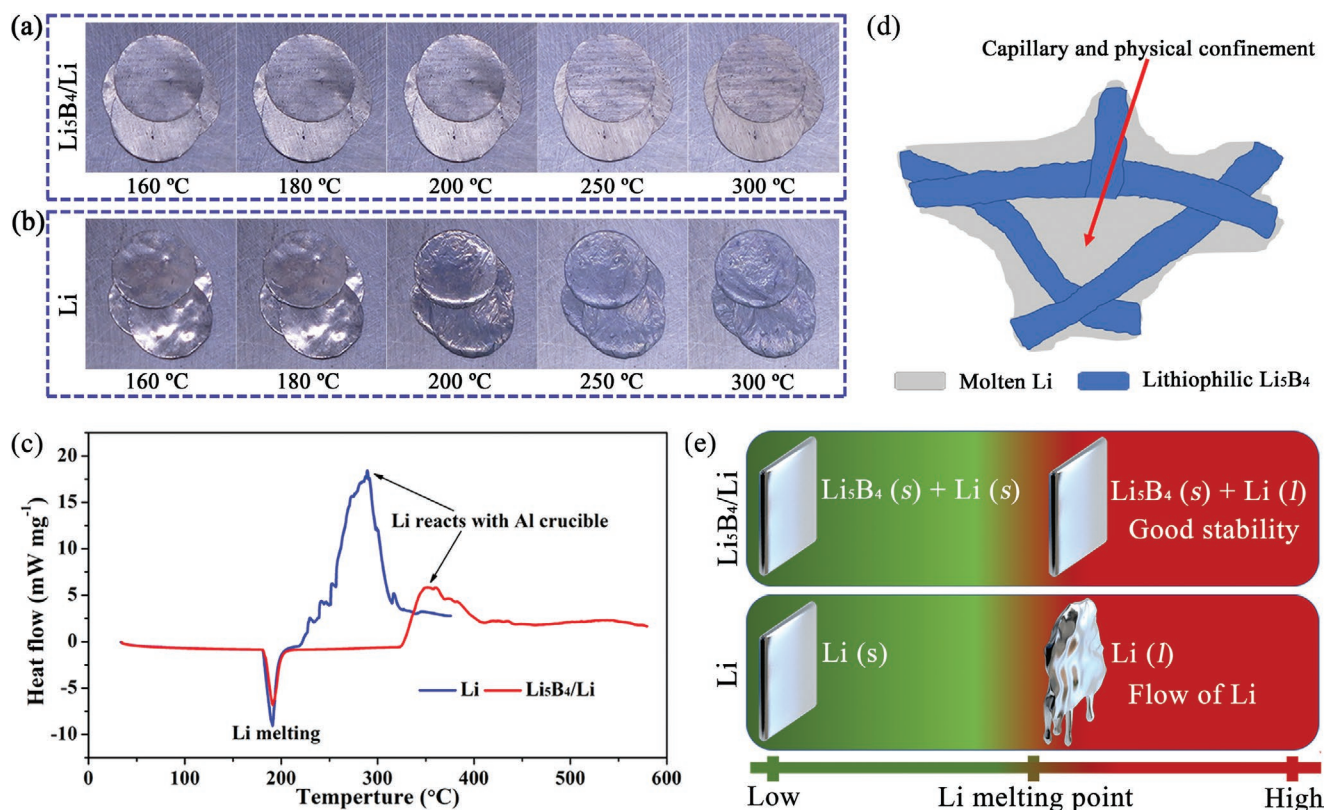


Figure 3. a,b) Digital photos of the $\text{Li}_5\text{B}_4/\text{Li}$ (a) and pure Li (b) disks at 160, 180, 200, 250, and 300 $^\circ\text{C}$, respectively. c) DSC curves of the $\text{Li}_5\text{B}_4/\text{Li}$ composite and pure metallic Li. d) Schematics for the trappment of liquid metallic Li in the Li_5B_4 framework for the $\text{Li}_5\text{B}_4/\text{Li}$ composite at a temperature above the melting point of metallic Li. e) Schematics of the behaviors of the $\text{Li}_5\text{B}_4/\text{Li}$ composite and pure Li electrodes at the temperature above the melting point of metallic Li.

of oxygen in the glove box. In contrast, the $\text{Li}_5\text{B}_4/\text{Li}$ composite did not show such surface layer and maintained its initial morphology and structure, suggesting the reduced reaction activity due to the existence of Li_5B_4 . Therefore, $\text{Li}_5\text{B}_4/\text{Li}$ composite anode is promising for high-temperature Li metal batteries. Differential scanning calorimetry (DSC) measurement was carried out using an Al crucible in Ar atmosphere to investigate the thermal stability of the $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode (Figure 3c). For the pure metallic Li, a sharp endothermic peak originated from 181 °C, which could be ascribed to the melting of metallic Li. Subsequently, molten Li reacted rapidly with Al to form Li–Al alloy and release heat (Figure S7, Supporting Information). The DSC curve of the $\text{Li}_5\text{B}_4/\text{Li}$ composite exhibited an endothermic peak at the same temperature (181 °C) to pure metallic Li, corresponding to the melting of metallic Li in the $\text{Li}_5\text{B}_4/\text{Li}$ composite. Interestingly, the reaction between metallic Li in the $\text{Li}_5\text{B}_4/\text{Li}$ composite and Al to form Li–Al alloy occurred above 325 °C, 105 °C higher than the temperature for the reaction between pure Li foil and Al. This result indicated that the Li_5B_4 fibrillar framework firmly trapped the metallic Li and inhibited its leakage and the $\text{Li}_5\text{B}_4/\text{Li}$ composite showed reduced reaction activity in comparison to pure metallic Li. It is noteworthy that the liquid Li metal finally leaked out of the framework at the temperature that was ≈ 140 °C higher than its melting point, since the viscosity of liquid metallic

Li decreased with the increase of temperature.^[20] Thus, the metallic Li was successfully trapped in the 3D Li_5B_4 framework above the melting point of metallic Li due to the capillary force between liquid metallic Li and the 3D porous framework with lithiophilic surface (Figure 3d). These results suggest the possibility of the operation of the $\text{Li}_5\text{B}_4/\text{Li}$ composite anode above the melting temperature of metallic Li using regular cell configuration (Figure 3e). In contrast, bare Li metal anode cannot be operated above 181 °C using conventionally packaged battery system owing to the mobility of molten Li.

$\text{Li}_5\text{B}_4/\text{Li}||\text{Li}_5\text{B}_4/\text{Li}$ swagelok-type symmetric cells were fabricated using garnet-type LLZTO (Figure S8, Supporting Information) solid electrolyte and their electrochemical performance was investigated at 200 °C (Figure 4a). As shown in Figure S9 in the Supporting Information, the diffraction peaks for Li_5B_4 are well maintained after stripping of metallic Li, indicating the good phase stability of Li_5B_4 . The ionic conductivity of LLZTO was measured using EIS (Figure 4b; Figure S10, Supporting Information). LLZTO solid electrolyte maintained stable solid structure and its ionic conductivity at 200 °C reached as high as 13.1 mS cm^{-1} (much higher than 0.8 mS cm^{-1} at 25 °C), which ensured fast Li-ion transport across the electrolyte layer during cell cycling. During the fabrication of symmetric cells, a homogeneous ultrathin nanolayer of Au was sputtered onto the surface of LLZTO (namely Au-LLZTO) to

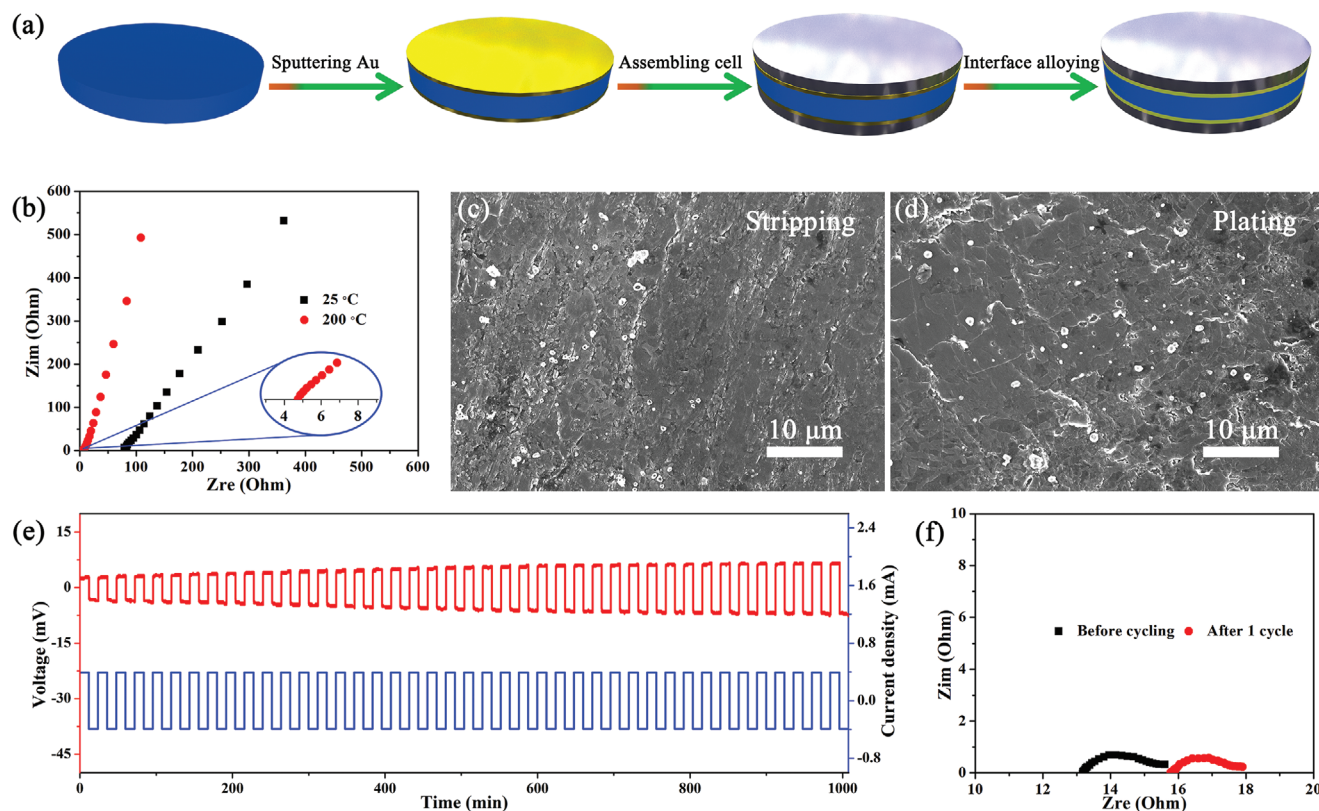


Figure 4. a) Schematics for the fabrication of a $\text{Li}_5\text{B}_4/\text{Li}||\text{Li}_5\text{B}_4/\text{Li}$ symmetric cell with LLZTO solid state electrolyte pellet. For reducing the interfacial impedance between the electrode and the electrolyte, an ultrathin film was sputtered on the LLZTO surface. b) EIS spectra of LLZTO solid electrolyte at 25 °C and 200 °C. c,d) SEM images of the $\text{Li}_5\text{B}_4/\text{Li}$ electrode after the 1st Li stripping process (c) and the 1st full stripping/plating cycle (d). e) Voltage profiles of the $\text{Li}_5\text{B}_4/\text{Li}||\text{Li}_5\text{B}_4/\text{Li}$ symmetrical cell during cycling at 200 °C. f) EIS spectra of the $\text{Li}_5\text{B}_4/\text{Li}||\text{Li}_5\text{B}_4/\text{Li}$ symmetric cell before cycling and after 1 cycle at 200 °C. The current density and areal capacity for cycling were fixed at 0.5 mA cm^{-2} and 0.1 mA h cm^{-2} .

reduce the interfacial impedance between the $\text{Li}_5\text{B}_4/\text{Li}$ electrode and the LLZTO solid electrolyte by forming Li-Au alloy interfacial layer (Figure 4a; Figure S11, Supporting Information).^[21] The morphology and structure of the $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode before and after cycling were investigated. As expected, the electrode maintained its initial structure and a smooth surface was shown for the $\text{Li}_5\text{B}_4/\text{Li}$ electrodes after Li stripping and plating cycling (Figure 4c,d) without formation of Li dendrites. The homogeneous stripping/plating of metallic Li, together with good thermal and mechanical stability, can ensure the security of operation for the $\text{Li}_5\text{B}_4/\text{Li}$ electrode above the melting temperature of metallic Li. Furthermore, the phase structure of the $\text{Li}_5\text{B}_4/\text{Li}$ electrode remains unchanged after 1 stripping/plating cycle of metallic Li at 200 °C (Figure S12, Supporting Information), indicating good stability of the electrode. Then, electrochemical Li stripping/plating behavior of the $\text{Li}_5\text{B}_4/\text{Li}$ electrode was then evaluated. A $\text{Li}_5\text{B}_4/\text{Li}||\text{Li}_5\text{B}_4/\text{Li}$ symmetric cell with Au-LLZTO displayed stable and flat potential plateaus during the Li stripping/plating cycling at 200 °C under a current density of 0.5 mA cm⁻² with a fixed area capacity of 0.1 mA h cm⁻², suggesting the stable electrochemical performance of the $\text{Li}_5\text{B}_4/\text{Li}$ composite at such high temperature. The initial overpotential of the cell was only ≈ 3 mV, which gradually increased to ≈ 6 mV within 25 cycles and remained stable in the subsequent cycles (Figure 4e). This value was comparable to previous results using pure liquid Li metal electrode in complex tubular cell configurations.^[17] To detect the impedance of the cell during cycling, electrochemical impedance spectroscopy (EIS) of a $\text{Li}_5\text{B}_4/\text{Li}||\text{Li}_5\text{B}_4/\text{Li}$ symmetric cell was performed (Figure 4f; Figure S13b, Supporting Information). The EIS curves showed a semicircle at the high frequency region and a tail at the low frequency part, which corresponded to the total resistance from the electrolyte and its interface between the electrodes.^[22] The intercept of semicircles with real axis (Z_{re}) at the high frequency represented the bulk resistance of electrolyte and the electrical resistance of electrode.^[23] The increased impedance could be ascribed the degradation of LLZTO (Figure S8, Supporting Information) and the electrode/electrolyte interface^[24] (Figure S14 in the Supporting Information, detailed explanation in Supporting Information), which caused the increase of overpotential in the initial 25 cycles. Thus, the composite structure of the $\text{Li}_5\text{B}_4/\text{Li}$ composite did not cause additional impedance. Finally, good full-battery performance at high temperature can be expected by pairing the $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode with advanced cathode materials with excellent high-temperature stability. $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$ ($x \leq 0.4$, e.g., $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.4}\text{Co}_{0.3}\text{Mn}_{0.3}\text{O}_2$) cathodes possess good thermal stability at charge and discharge states above 300 °C and can be potential cathode candidates.^[25] Based on the above results and discussion, we believe that the $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode will advance the development of high-temperature Li metal batteries. Besides, the $\text{Li}_5\text{B}_4/\text{Li}$ electrode also showed advancement in rechargeable Li metal batteries operated at room temperature with regular battery configuration (Figures S16 and S17, Supporting Information).

In summary, $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode was explored as a stable battery anode for the potential application in rechargeable high-temperature Li metal batteries for energy

storage and improve the thermal safety for rechargeable ambient-temperature Li metal batteries. The $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode possessed 3D Li_5B_4 fibrillar framework with metallic Li filled in. The 3D Li_5B_4 framework with high thermal tolerance and mechanical stability played an important role in maintaining the overall structure of the $\text{Li}_5\text{B}_4/\text{Li}$ electrode at elevated temperature. The metallic Li was tightly trapped by capillary force in the 3D Li_5B_4 framework with good lithiophilicity even at a high temperature above the melting point of metallic Li (e.g., >200 °C), evidenced by our experiment and simulation. With a high metallic Li content of 72%, the liquid metallic Li would not leak out of the composite electrode at 325 °C. As a demonstration of the $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode applied in high-temperature Li metal batteries, we fabricated a $\text{Li}_5\text{B}_4/\text{Li}||\text{Li}_5\text{B}_4/\text{Li}$ symmetric cell using garnet-type LLZTO solid electrolyte in a simple cell configuration and achieved stable electrochemical Li plating/stripping cycling with low overpotential and stable cycling at 200 °C. The use of the $\text{Li}_5\text{B}_4/\text{Li}$ composite electrode can avoid complex battery configuration that pure Li metal anode need, reduce the safety concerns caused by the flow of liquid metallic Li at high temperature, and thus show potentially practical application value.

Experimental Section

All experimental details are included in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

capillary and physical confinement, Li metal batteries, $\text{Li}_5\text{B}_4/\text{Li}$ composites, high-temperature operation, thermal stability

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