Cryogenic-rolling ultrathin lithium metal driving the high- energy-density era

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The energy density of commercial lithium-ion batteries is nearing the theoretical limit with the swift advancement of the new energy sector. This poses challenges in meeting the higher practical demands of various applications. As a promising electrode material with an extremely high theoretical specific capacity (3860 mAh/g) and the lowest electrochemical potential (-3.04 V vs. the standard hydrogen electrode), lithium metal has once again garnered interest among the public. The increased utilization of thinner lithium metal is expected to expand the potential applications in various fields. Ultrathin lithium metal materials have the potential to serve as anodes in high-energy-density batteries and can also be utilized for prelithiation.[1] For the application of new high-energy electrode materials, the design of ultra-thin lithium metal with controllable thickness will greatly promote the development of energy storage devices (Figure 1A). The production of ultrathin lithium metal is significantly impeded by the low melting point and diffusion creep characteristics of Li.[2] It is essential to develop environmentally sustainable and efficient methods for large-scale processing of ultrathin lithium metal in order to advance the implementation of innovative energy storage technologies. Herein, we propose cryogenic rolling processing technology so that lithium metal can change its own characteristics at unconventional temperatures. Subsequently, we aim to design a phase-changeable machining interface for processing to enable large-scale practical ultrathin processing of lithium metal.

COMBINING PROCESSING PROGRESS UNDER CRYOGENIC TREATMENT

For the shaping and molding of solid metal materials, cryogenic treatment technology has excellent properties in regulating the performance of metal materials as an unconventional heat treatment. To ensure the accuracy of the processing equipment, the processing object is typically placed in a low-temperature environment. By adjusting parameters such as treatment temperature (T), treatment time (t), cooling rate (V), and the number of cycles from cold to hot (N), the microstructure properties of processed metals can be enhanced. For conventional metal materials, cryogenic rolling can significantly improve the processing properties of the metals. Due to the low temperature hindering the movement of dislocations and the recrystallization behavior of grains during plastic processing deformation, which enables the refinement of metal grains under cryogenic conditions. Therefore, cryogenic treatment enhances the strength and toughness of metal materials.[3] The main mechanical shortcomings of lithium metal in ultra-thin processing can be effectively compensated.

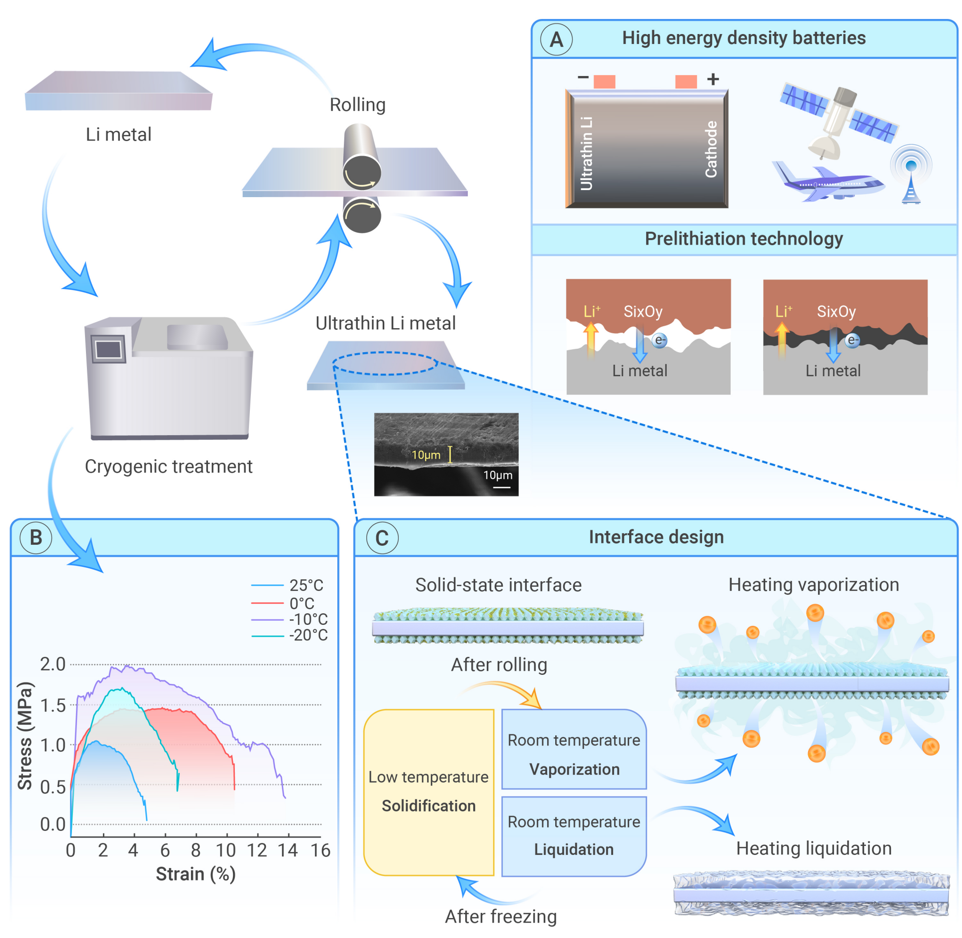

Figure 1. Schematic diagram of processing ultrathin lithium strips by cryogenic rolling (A) The application of ultrathin lithium metal. (B) Mechanical properties of lithium metal at low temperatures. (C) The new interface design concepts for machining at low temperature.

LOW TEMPERATURE TO REGULATE THE PROPERTIES OF LI

Due to the low melting point of lithium metal (~180.54°C), there is severe diffusion creep and very low tensile strength (~1.0 MPa) at room temperature.[4] Therefore, the preparation of lithium metal using conventional metal-working processes is not ideal. Based on *ex-situ* freezing technology, the pretreatment of lithium metal materials has shown a significant improvement in strength indicators in sub-zero environments (Figure 1B). A tensile test of 100-μm-thickness lithium metal is designed from room temperature to low temperature (25°C, 0°C, -10°C, -20°C). Due to the low strength and thin thickness of lithium, the specimen is designed to be 4 mm × 25 mm with a working distance of 10 mm. The result implies that the treatment of lithium metal at low temperatures is very different from that at room temperature. With temperatures ranging from 0 to -10°C, lithium metal is 1.8 times stronger than at 25°C. As the temperature decreases further, the intensity also decreases. This phenomenon may be caused by the brittleness characteristic of lithium metal materials, which is not conducive to the shaping process. Therefore, it is preliminarily inferred that the optimal low temperature to enhance the processing performance of lithium metal to a certain extent should not be lower than -20°C. Choosing a temperature range between 0°C and -10°C for processing could be suitable. Ensuring the ability for plastic deformation, the increased strength helps facilitate the processing of ultra-thin lithium metal.

THE CRYOGENIC ROLLING TO ACHIEVE LARGE-SCALE PREPARATION

According to the unique properties of lithium metal at room temperature, employing ultrathin processing at low temperatures would be innovative yet efficient. Comparing to the traditional rolling technology, cryogenic rolling is a revolutionary process. The key is to control the processing temperature to achieve plastic deformation of the Li metal at low temperatures. At present, cryogenic rolling has been greatly developed, especially in the application of aluminum alloys and titanium alloys. The application of this technology in metal materials is mainly to achieve higher yield strength, tensile strength, and elongation at break. In the processing of alkali metals, this process serves various purposes and produces different effects. Due to the highly evident viscoplastic property of lithium metal, significant shear deformation is introduced during the rolling process.[5] Under low temperatures, the strength of lithium metal is enhanced, which helps prevent thin lithium strips from tearing under high shear loads. On the other hand, it is expected to inhibit the contact adhesion of lithium metal and improve the interfacial processing properties.

Liquid nitrogen or liquid argon is commonly utilized as the refrigeration source in the cryogenic process to regulate the temperature of the lithium metal. During the rolling process, the heat generated by plastic deformation and the heat conduction of the rollers will cause the temperature to rise. In the actual process, the dynamic low-temperature range should be selected. Meanwhile, it is necessary to apply cryogenic treatment repeatedly during processing. In contrast to the entire process system operating at low temperatures, cryogenic processing involves only maintaining the lithium metal within a low temperature range. This approach minimizes energy consumption during processing and prevents damage to the rolling devices caused by harsh environmental conditions. This method is more efficient and safer than vacuum evaporation or using molten lithium. The process shows promise for the large-scale production of ultra-thin lithium metal and will facilitate the utilization of ultra-thin lithium metal in energy storage devices. So far, cryogenic rolling is still immature in terms of temperature selection and interface design between lithium metal and the machine. Some preliminary research and design are provided below, aiming to foster the rapid development of this field.

NEW INTERFACE DESIGN CONCEPT FOR CRYOGENIC PROCESSING

Engaging in the cold temperature operational setting, the lubrication system employed in the rolling procedure may exhibit variability. Liquid-phase friction systems, which are used to improve surface hardness and provide lubrication, will solidify at low temperatures (Figure 1C). Lithium metal with a solid-phase friction system at the interface will exhibit improved mechanical processing performance. As the process generates heat, the frictional interface that was initially solidified at low temperatures will gradually change into a liquid state. The study of dynamic changes in interface states is highly valuable for preparing ultra-thin lithium metals. A more aggressive approach to the friction interface design involves using a lubricant system that turns solid at low temperatures and evaporates at room temperature. In this case, the base liquid phase of lubricant components can be shifted from mineral oils, silicone oils, ionic liquids, etc., to the volatile liquid electrolytes that are closer to electrochemical applications. It will create a direct connection between the production of ultrathin lithium metal and the electrochemical application, eliminating barriers in the process. Under the unconventional processing environment, the design of the interface will also make a significant impact. This study is valuable for promoting the large-scale preparation of ultra-thin lithium metals.

OUTLOOK

With the increasing demand for high-energy-density batteries, significant changes in electrode materials are expected. At present, the high-capacity electrode materials such as silicon/carbon heavily rely on the pre-lithiation assistance provided by ultra-thin lithium metal. Ultra-thin lithium metal will enable more diverse application scenarios and facilitate the evolution of battery technology. Herein, we propose a viable cryogenic rolling technology to enhance the controlled processing and preparation of ultra-thin lithium metal. Cryogenic rolling technology is on the rise and is at the forefront of processing and preparation technology in recent years. The unconventional low-temperature environment can alter the properties of metal materials. Meanwhile, under high load stress conditions causing deformation, the interface design becomes more flexible and adaptable. In light of the utilization of ultra-thin lithium metal in various applications, it is possible to design more distinctive lithium metal interfaces. These processes can also be expanded to the ultrathin preparation of alkali metals like sodium metal, which owns great practicality and promise. This paper also initiates the study of the low-temperature material properties of lithium metal for designing batteries intended for low-temperature applications. Furthermore, a new concept is proposed to investigate the interplay between low-temperature processing technology and the electrochemical properties of lithium metal.

There are still major challenges to address in realizing cryogenic processing for preparing lithium metal.

(1) A lack of a scientific research system on the properties, and processing mechanism of the deformation, brittleness, and strength of alkali metal materials especially lithium still represents a scientific gap at low temperatures.

(2) It is still necessary to study how temperature changes affect the phase transformation process of the interfacial lubrication system. Subsequently, designing a multifunctional interface can aid in processing efficiency and enhance the performance of electrochemical applications.

(3) The equipment system for continuous cryogenic processing of lithium metal needs further development, which the process control is achieved by utilizing the low-temperature characteristics.

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DECLARATION OF INTERESTS

The authors declare no competing interests.