Research Progress of Thin Film Structures of All-Solid-State Lithium-Ion Battery

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Abstract. The need for portable power sources has increased quickly with the advent of the electronic information era. Due to the significant benefits of lithium-ion batteries' high voltage, high capacity, and extended cycle life, these batteries have a wide range of potential applications in a variety of industries, including portable electronic gadgets, electric vehicles, and space technology. Lithium-ion batteries may cause safety issues such as thermal runaway under harsh conditions. By employing solid electrolytes in the thin layer of all-solid-state lithium batteries (TFLIBs) instead of organic liquid electrolytes, the safety issues with current commercial lithium-ion batteries may be effectively remedied. They outperform bulk solid-state lithium batteries, which has made the industry pay close attention to them. Because they directly affect the charge-discharge rate, cycle life, self-discharge, safety, and high and low-temperature performance of thin film batteries, electrolyte thin films play a crucial role in TFLIBs. This paper reviews three innovative thin film structures, their different benefits and drawbacks, the most current research on them, and projections for their future development to serve as a reference for future research on lithium-ion batteries.

Keywords: Lithium-ion battery, all-solid-sate, thin film structure.

1. Introduction

Nowadays, we are facing a global energy crisis because of supply chain disruption, bad weather, insufficient investment, and many other reasons. And the global energy crisis has become increasingly serious. Therefore, it is urgent to solve the energy crisis. The field of energy storage has greatly benefited from the advancements achieved by lithium-ion batteries in recent years, which are employed in many portable electronic gadgets, new energy vehicles, and other applications. Thus, the solution to today's energy dilemma lies in lithium-ion batteries. However, accidents brought on by lithium-ion batteries have been happening more frequently lately, which is a reflection of how unsafe they are. Making a separator for lithium-ion batteries is an excellent way to address the problem since it will immediately improve the batteries' safety and electrochemical performance [1]. TFLIBs have been widely used due to their good safety performance, small size, and portability [2]. TFLIBs are not yet commercially available because of a number of problems, including an unstable interface, low volume energy density, and expensive production costs. The innovative thin film structural design can boost the stability and energy density of TFLIBs [3]. This review will outline some innovative structural designs of TFLIBs thin films, examine their benefits and drawbacks, and assess their level of industrialization, all of which will contribute to future TFLIBs advancements.

2. TFLIBs

2.1. Characteristics of TFLIBs

TFLIBs have replaced conventional lithium-ion batteries. By using solid conductive materials rather than organic liquid electrolytes, a suitable thin film production technique, easy miniaturization, and flexible size control, the performance of the battery may be significantly improved, including safety, energy density, and environmental friendliness [4]. Since the very thick film electrode material used in TFLIBs and the atomic/molecular level deposition of the electrolyte and electrode, there are fewer interface issues since discrete microscopic flaws at the solid-solid interface may be avoided [3]. The basic components of TFLIBs are the cathode, anode, electrolyte, and current collector [2].

TFLIBs are deposited utilizing thin film deposition techniques. Typically, they are made using solid substrates like glass, ceramics, or even polymers. The specific structure is shown in Figure 1 [3].

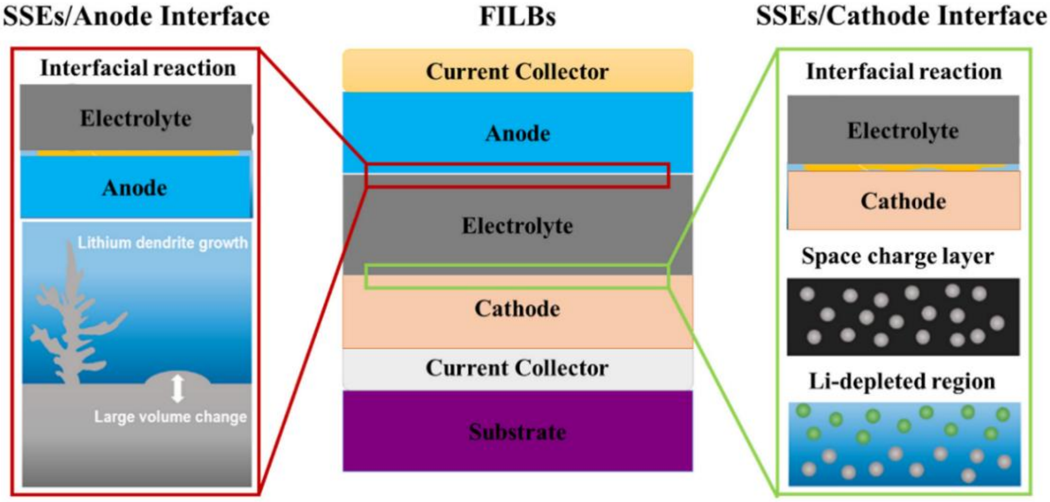

Figure 1. The structure of TFLIBs and interface issues [3].

2.2. Thin film structures of TFLIBs

The thin films of TFLIBs include anode films, cathode films, and electrolyte films.

In the early days, lithium metal was commonly used as the anode for TFLIBs. However, it has a drawback because it has a low melting point but high chemical activity, making it difficult to maintain stability at higher operating temperatures. For Si-based anodes, the design of novel thin film structures is a good way to improve battery performance. The most commonly mentioned 3D thin film anode currently is TiO_2. Létiche et al. combined Si microtubule arrays with nanoscale TiO_2 and then covered them with Li_3PO_4 solid electrolyte (SSE) sheets to maximize the footprint of 3D TiO_2 films. At a rate of 16 C, it can reach 370 Ah cm^2.

There are two main deposition processes for cathode thin films, including physical and chemical processes. Physical methods include magnetron sputtering, electron beam evaporation deposition, pulse laser deposition, and other methods. The chemical method is mainly the sol-gel method. It determines the performance of TFLIBs, therefore, research on cathode films is also a popular direction. Su et al. used bias sputtering technology to improve the structural integrity of LNMO thin film cathodes in high-voltage TFLIBs [2].

The electrolyte layer acts as an electrical insulator between the anode and cathode and permits lithium-ion mobility. By using the PLD technique, Z. Lee et al. created an amorphous $Li_{0.5}La_{0.5}TiO_3$(LLTO) layer. The consistent and well-grown LLTO sheet (1.2 m) regulates the temperature and pressure of the surrounding air to provide an ionic conductivity of $3*10^4$ S/cm^2 [2]. Thermal ALD was used by Nisula et al. to create high-quality, 3D microstructured LiPON sheets on a Si substrate. At room temperature, the LiPON electrolyte was found to have an ionic conductivity of $6.6*10^7$ S/cm^2 [3].

3. Some novel structural designs of TFLIBs thin films

3.1. A TiO2 thin film (AC-TO)

Due to its excellent structural stability, excellent chemical stability, and tolerance to high temperatures, the anode material for thin film batteries that shows the most promise is TiO_2. TiO_2 thin films have a low specific capacity and poor rate capability. However, the problem may be resolved by thin films formed of amorphous TiO_2 [5].

According to research, altering TiO_2's crystal structure can significantly enhance the safety of batteries during rapid charging. The pertinent processes, nevertheless, remain unclear. In response, scientists studied thin films made of TiO_2 in-depth. According to the study's findings, the diffusion rate of Li^+ in amorphous films has increased by a factor of two compared to films with regular crystal structures. Additionally, scientists carried out simulation studies from various angles in order to better grasp the fundamental characteristics like diffusion rate and energy distribution. It was discovered that amorphous TiO_2 thin films have a special structure that boosts their diffusion rate, lowers their energy barriers, and produces the effect of high-speed energy storage [6].

Another publication used the magnetron sputtering technique to create thin layers of TiO_2. The film has a distinctive amorphous crystalline heterostructure and is generated at ambient temperature. The structural design was thoroughly studied by the researchers. The findings show that this special structure allows Li^+ in the battery to transfer quickly in the amorphous phase of TiO_2 thin films. Additionally, the crystalline phase's uniform structure gives it good conductivity for the battery. The resulting TFLIBs combines the advantages of both, and is currently under development. The battery created by AC-TO has a high reversible specific capacity and a decent rate capacity, according to relevant performance tests that were conducted on it. The thin film battery continues to work well after 400 experimental cycles, proving that it has high cycling performance. These pieces offer some suggestions for next film design [5].

3.2. High-quality epitaxial LNMO thin films

Numerous techniques, including as electrostatic spraying, electrophoretic deposition, pulsed laser deposition, sol-gel, and radio frequency (RF) magnetron sputtering, can be used to create LNMO films. The latter method is best suited for large industrial output because to its reputation for offering layers of consistently excellent quality and precisely controlled thicknesses. However, if the oxygen content is either too low or too high, the LNMO cubic spinel structure will lose crystallinity. High-performance electrochemical oxygen content may be changed to create LNMO thin films. The rate performance of LMNO thin films produced by this technology is noticeably superior to LNMO thin films produced by other techniques [7].

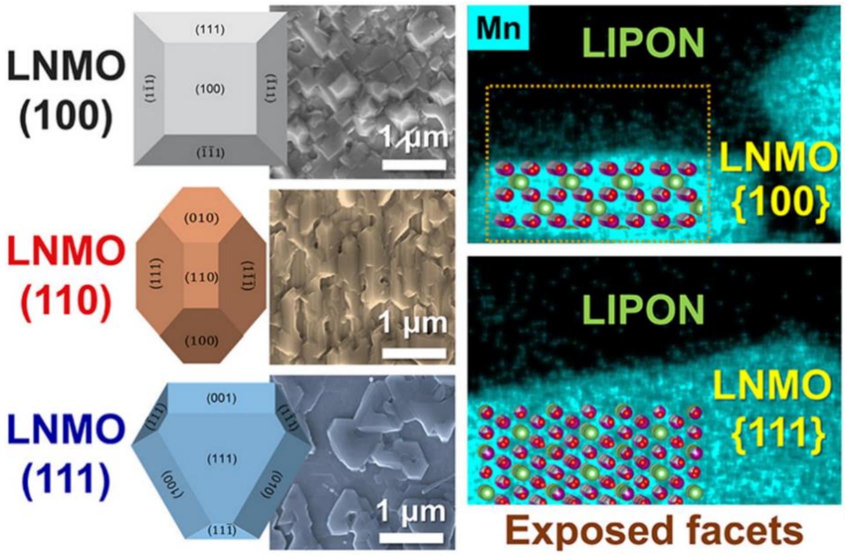

Figure 2. The structure and microscopic diagram of LNMO {100} (110) {111} [8].

The high interface resistance between the solid electrolyte and cathode, which is also the major cause of why it is challenging to commercialize, is the key issue with all solid-state thin film lithium batteries. Because there are no atoms of the same material around the atoms at the interface, which are extremely likely to form alternative atomic configurations, unusual physical events will take place on the contact surface of two different substances. This process alters the configuration of atoms in TFLIBs and restricts the transmission of charges. Researchers initially identified the crystal structure of the substance affecting the solid contact in order to overcome this issue. Then, a thin film is produced along the direction established by the substrate crystal using epitaxial film technique. As illustrated in Figure 2, cathode films with various exposed crystal planes were produced under various growing circumstances. The influence of exposed crystal faces on the contact between the solid electrolyte and cathode material was then thoroughly examined by the researchers. According to the findings, all solid-state batteries will be more stable because of the closely packed structure of the exposed crystal surfaces, which can prevent transition metal leakage from the cathode material to the electrolyte. Additionally, the passage of ions and electrons along the crystal is unhindered when the interface is positioned parallel to the direction of electron motion, lowering resistance and raising output power. This indicates that the cathode material may be enhanced, assuring the high performance and stability of the battery by increasing the density of crystal planes and changing the orientation of crystal interfaces [8].

3.3. PEO-based blend solid electrolyte thin films

PEO-based electrolytes have received a lot of attention and have been employed as substantial parts of solid polymer electrolytes due to their remarkable thermal, mechanical, and interfacial stability when paired with lithium metal. It is simpler for the polymeric chain to travel in segments because of the structure of PEO, which comprises ether-oxygen bonds at an advantageous interatomic distance, which in turn facilitates simple ionic conduction. The microstructure of PEO includes both crystalline and amorphous phases, which have a substantial impact on the material's ability to transport ions [9].

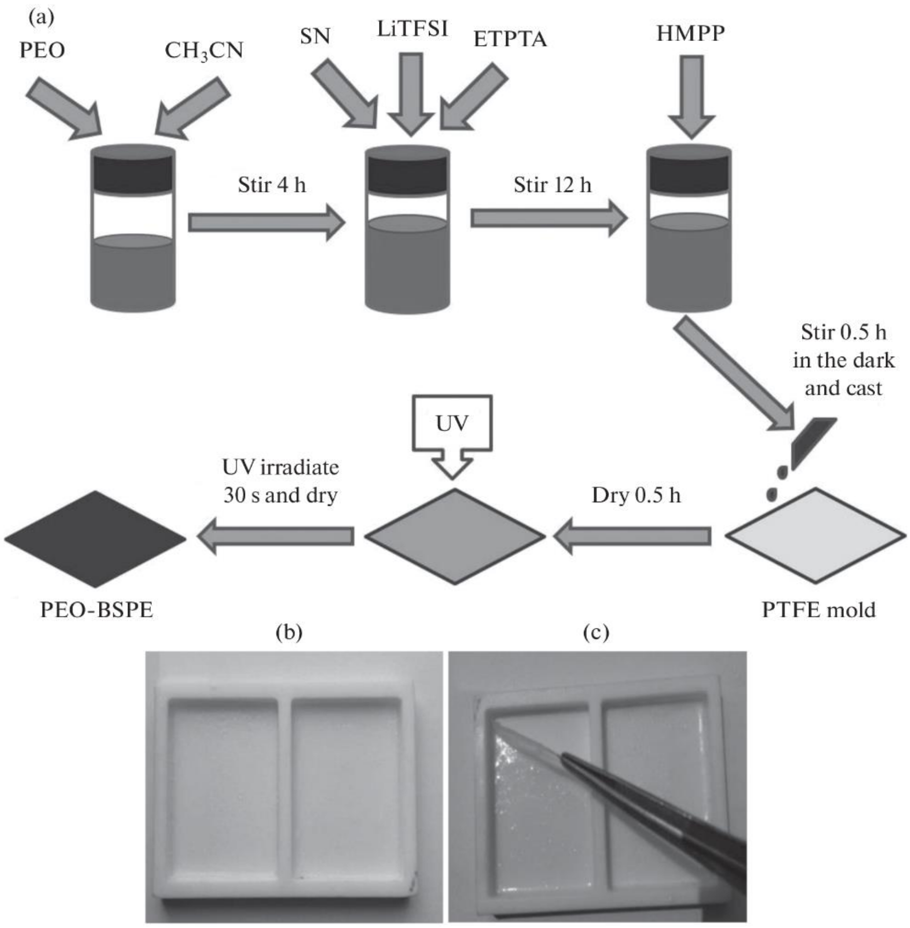

Figure 3. Preparation process and actual diagram of PEO-BSPE film [10].

A study reported a solid polymer electrolyte (SPE) sheet containing a mixture of PEO and poly (vinyl pyrrolidone) (PVP), as well as $LiNO_3$ as a salt. SPE membranes have a smooth surface and are porous, exhibiting good thermal stability and electrochemical performance above 400 °C [9]. In addition, self-reinforcing polyethylene oxide-based solid electrolyte (PEO BSPE) thin films were prepared in a PEO electrolyte matrix under UV irradiation [10]. The preparation process and actual diagram of the PEO-BSPE film are shown in Figure 3. The thin film is characterized by a tight three-dimensional cross-linking network inside. Therefore, its performance is superior to that of SPE thin films. PEO-BSPE film is smooth, amorphous, and bendable, with a tensile strength 20 times that of PEO-SPE film. The solid-state battery constructed with it exhibits strong cycling stability, low interface impedance, and high Coulomb efficiency at 55 ° C, which can meet high-temperature usage conditions [10]. It is necessary to conduct more research on it to determine whether other defects in PEO-BSPE have a greater adverse impact on battery performance.

4. Summary

Due to its major benefits in terms of safety, mobility, and integration, all-solid-state thin-film batteries have attracted a lot of attention among the several types of lithium-ion batteries. Additionally, wearable flexible devices powered by TFLIBs have a lot of potential to boost device mobility. There are still several issues with TFLIBs, such as an unstable interface, low volume energy density, and high production costs. The thin film structure can be improved as a means of improving battery performance. This review uncovered three novel structural designs for TFLIB thin films that would improve battery performance. However, the research on these three thin films has only stayed in the laboratory stage and has not been applied to practical life. In addition, solid-state lithium batteries based on these three thin films also require testing in different actual environments, such as different temperatures and longer operating times. I believe that with the deepening of research, researchers can develop thin film structures with better performance and apply them to solid-state lithium batteries.

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