Structural evolution of plasma sprayed amorphous Li$_4$Ti$_5$O$_{12}$ electrode and ceramic/polymer composite electrolyte during electrochemical cycle of quasi-solid-state lithium battery

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Abstract: Solid-state batteries are one of the effective way to solve the safety of traditional power and energy storage batteries with flammable liquid electrolyte. This time, a quasi-solid-state lithium battery is assembled by plasma sprayed amorphous Li$_4$Ti$_5$O$_{12}$(LTO) electrode and ceramic/polymer composite electrolyte with a little liquid electrolyte (10 μl/cm$^2$) to provide the outstanding electrochemical stability and better than normal interface contact. SEM, STEM, TEM and EDS were used to analyze the structure evolution and performance of plasma sprayed amorphous LTO electrode and ceramic/polymer composite electrolyte before and after electrochemical experiments. By comparing the electrochemical performance of the amorphous LTO electrode and the traditional LTO electrode, the electrochemical behavior of different electrodes is studied. The results show that plasma spraying can prepare an amorphous Li$_4$Ti$_5$O$_{12}$ electrode coating of about 8 μm. After 200 electrochemical cycles, the structure of the electrode evolved, and the inside of the electrode fractured and cracks expanded, because of recrystallization at the interface between the rich fluorine compounds and the amorphous LTO electrode. Similarly, the ceramic/polymer composite electrolyte has undergone structural evolution after 200
cycles test. The electrochemical cycle results show that the cycle stability, capacity retention rate, coulomb efficiency, and internal impedance of amorphous LTO electrodes are better than traditional LTO electrode. This innovative and facile quasi-solid-state strategy is aimed to promote the intrinsic safety and stability of working lithium battery, shedding light on the development of next-generation high-performance solid-state lithium batteries.

**Keywords:** Plasma spraying; Li$_4$Ti$_5$O$_{12}$ electrode; Ceramic/polymer composite electrolyte; Electrochemical cycle; Quasi-solid-state lithium battery

1. Introduction

Compared with traditional rechargeable lithium batteries using liquid organic electrolyte, solid-state lithium batteries have become the first choice for the next-generation power and energy storage batteries due to their safety and potential high specific energy[1], are widely used in electric vehicles, consumer electronics, and other fields. The preparation methods of solid-state battery electrodes and electrolytes are mainly Radio Frequency Magnetron Sputtering Deposition (RFMSD)[2], Pulsed Laser Deposition (PLD)[3], Electron Beam Evaporation (EBE)[4], Chemical Vapor Deposition (CVD)[5], Molecular Beam Epitaxy (MBE)[6] and other methods[7]. However, these methods are not conducive to the high-efficiency preparation of macroscopic large-capacity lithium solid-state batteries used in electric vehicles. The plasma spraying process can realize the structural design and control of complex functional coatings, prepare functional coatings with good stress tolerance and high deposition efficiency, and then can prepare macroscopic large-capacity single battery.

Li$_4$Ti$_5$O$_{12}$(LTO) electrode for lithium-ion batteries is usually prepared by mechanically mixing highly viscous materials, coating and drying [8-10]. This traditional method has some inherent shortcomings: i) There are many process steps, a long process, low production efficiency and high cost. ii) It is inevitable to use volatile and toxic organic solvents, such as N-methylpyrrolidone (NMP). iii) The size
of the prepared pole piece is limited by the coating machine, and electrodes of any size cannot be customized. But the plasma spraying process can overcome the above shortcomings.

In recent years, the preparation of amorphous modified electrodes or electrolytes through processes can improve their electrochemical performance. Amorphous Li$_2$WO$_4$ protective layer helps to inhibit the degradation of LiCoO$_2$[11]. It can effectively improve the rate performance of the LiCoO$_2$ material. Amorphous modified silyl-terminated 3D polymer electrolyte enhances thermal stability and cycle performance for lithium metal battery[12]. The remarkable improvements of the amorphous Li$_3$PO$_4$-coated Li electrode is mainly attributed to high chemical stability and inhibit the growth of lithium dendrite[13].

In solid-state lithium batteries, ceramic electrolytes have received widespread attention, such as garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO)[14] and NASICON-type Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$(LATP)[15] or Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$(LAGP)[16]. Due to its excellent ion conductivity, chemical stability and wide electrochemical window relative to lithium metal, some of them have become a new class of solid-state electrolyte system (SSEs)[17]. However, when the ceramic solid electrolyte is in contact with the metal lithium negative electrode, electrochemical reactions are prone to occur, which reduces the battery performance. A feasible solution strategy is to use ceramic/polymer based composite electrolyte. The ceramic electrolyte channels provide continuous pathways, which help in maintaining a high ionic conductivity between the electrodes, while the polymer channels permit improvement of the mechanical properties compared to those of the ceramic alone, in particular, mitigation of the brittleness of ceramics.

In this contribution, the plasma spraying and fast cooling method were used to prepare the amorphous thin Li$_4$Ti$_5$O$_{12}$(LTO) electrode on the perforated copper foil. Our previous works showed that LTO electrode with excellent electrochemical performance can be prepared by suspension plasma spraying[18]. The flexible electrolyte film with ceramic/polymer based composite was prepared by mechanical mixing and mold casting. And then, we attempted to construct an quasi-solid-state
lithium ion battery by adopting flexible film as the solid electrolyte, LTO electrode as cathode and Li metal as anode. Structural evolution of plasma sprayed amorphous LTO electrode after 200 cycles and cyclic characteristics were investigated for quasi-solid-state lithium ion battery. In order to compare the electrochemical behavior of the two electrodes, traditional LTO electrode was prepared by method of coating slurry on current collector and drying.

2. Experimental

2.1. Preparation of amorphous and traditional LTO electrodes

Our previous work prepared spherical LTO powders material by spray granulation method[18]. The spherical LTO powders were shotted at high speed onto the perforated copper foil by plasma spraying. The perforated copper foil with a thickness of 45 μm and an area of 20 cm² is fixed on a copper plate(1 m²) with good heat dissipation. The main gas in the plasma was argon, and hydrogen was used as auxiliary gas. The effective spraying distance was 110 mm, the plasma current varied between 400 and 500 A. The schematic diagram of the LTO electrode preparation process is shown in Fig. 1. The traditional LTO electrode was prepared by the method of literature[19].

2.2 Preparation of ceramic/polymer based composite electrolyte

Preparation of ceramic/polymer electrolyte film by solution cast method. Before the experiment, the PVDF, LATP and LiClO₄ powders were vacuum-dried for 24 h at 60°C. Weigh the corresponding PVDF, LATP, LiClO₄ and DMF at a mass ratio of 10 : 1 : 0.124 : 80. Firstly, 0.5 g PVDF was dissolved in 40 mL DMF with stirring at 65°C for 0.5 h. After forming a transparent viscous solution, added 0.5 g LATP and 0.062 g LiClO₄ continue heating and stirring for 0.5 h to make the mixture even. Finally, casted the evenly stirred solution into a polytetrafluoroethylene mold and placed it under vacuum drying at 60°C for 24-72h. Flexible electrolyte film with ceramic/polymer composite could be obtained after the solvent was evaporated. The specific illustration is shown in Fig. 2.
2.3 LTO|ceramic/polymer composite electrolyte |Li quasi-solid battery assembly

Assembled CR2025 button battery in a glove box filled with argon. The plasma sprayed LTO electrode was to cut out the pole piece as the cathode, the Li metal as the anode and the ceramic/polymer composite electrolyte film as the solid electrolyte. Then, a given volume (10 μl/cm²) of liquid electrolyte with 1 M LiPF₆ EC/EMC/DEC was injected into flexible electrolyte film to get the quasi-solid-state composite electrolyte.

Added 1-2 spacers and assembled them with all materials to form a quasi-solid battery(Fig. 3).

2.4 Characterization and electrochemical measurements

The scanning electron microscope (SEM, GeminiSEM 500, ZEISS) was applied to observe the micro morphology of the plasma sprayed LTO electrode before and after the charge/discharge cycle test. Using auxiliary focused ion beam (FIB, 450S, FEI) to etch the sample surface for characterize the microstructure of the sample by transmission electron microscope (TEM, Titan Themis 200, FEI). The prepared quasi-solid battery samples were subjected to charge and discharge test by NEWARE battery test system(CT-4008). At room temperature, the samples were tested for electrochemical impedance spectroscopy (EIS) in the frequency range of 10⁵-10⁻³ Hz by electrochemical workstation(CHI660E).

3. Results and discussion

3.1. Electrochemical performance of amorphous and traditional LTO electrodes

As can be seen from Fig. 4a, the initial capacity of traditional LTO electrode is about 95 mAh/g, while the capacity of amorphous LTO electrode is slightly smaller, about 73 mAh/g. However, after 200 cycles test, the coulombic efficiency of amorphous LTO electrode (about 99.8%) is better than that of traditional LTO electrode (about 88%), and the capacity attenuation rate of amorphous LTO electrode (about 68%) is better than that of traditional LTO electrode (about 82%). This shows that the amorphous structure improve the cycle stability of the battery, which is
consistent with the conclusion of the literature [20]. Fig. 4b shows the cycle performance of amorphous and traditional LTO electrodes at a charge-discharge rate from 0.1 C to 0.5 C. The capacity retention rate is the discharge capacity of each cycle relative to the first cycle. Under 0.1C charge and discharge cycles, the capacity retention rate of amorphous electrode decreased slowly, but that of traditional electrode decreased rapidly, clear differences are observed between these two electrodes. The capacity retention rate of the traditional LTO electrode dropped to 9% at a rate of 0.2C, dropped to 0% when the rate exceeded 0.3C, and finally returned to 13% at a rate of 0.1C. In contrast, the amorphous LTO electrode still maintained a high capacity retention rate of 41% at 0.5C. After 30 cycles, the capacity retention rate of the amorphous LTO electrode recovered to 78% at 0.1C. The results indicated that the amorphous LTO electrode shows excellent rate performance in terms of high power durability.

Fig. 4c-d shows that the interface impedance of the amorphous LTO electrode | ceramic/polymer composite electrolyte is smaller than that of the traditional LTO electrode | ceramic/polymer composite electrolyte, indicated that the amorphous structure interface facilitated the migration of lithium ions to obtain better electrochemical performance, this is consistent with the conclusion of the literature [21].

3.2. Structural evolution of amorphous LTO electrode

Structural evolution of plasma sprayed amorphous LTO electrode before and after the cycles test are analyzed by SEM, STEM, TEM and EDS to explore the root cause of the difference in electrochemical performance (Figs. 4). Amorphous LTO electrode surface micromorphology was investigated using SEM, as shown in Fig. 5a-d. Spherical LTO powders were sprayed on the perforated copper foil to form a full coverage layer (Fig. 5a). After partial magnification, the typical stack forming method of thermal spray coating was found [22] (Fig. 5b), and the unmelted spherical LTO particles could also be observed in the figure. When further zoomed in to the nanometer scale (Fig. 5c), local nano-structured tiny particles protrusions were
discovered. These protrusions combined with the flexible ceramic/polymer electrolyte film could increase the interface contact between the electrode and the electrolyte film, thereby promoting the electrochemical reaction at the interface. Fig. 5d is the surface of the amorphous LTO pole piece after the cycles test. It could be seen that the surface protrusions were reduced, and cracks were found in the coating. The appearance of these cracks caused the electrochemical reaction to penetrate deep into the coating.

In order to obtain the structure evolution information inside the amorphous LTO electrode after the electrochemical cycle test, the FIB was used to cut the samples before and after the cycles test, as shown in Fig. 6. It can be known from the figure that the thickness of the thin coating after spraying is about 5-8 μm.

From Fig. 7a-c, it could be seen that the main elements of the original LTO electrode are Ti and O. Because Li cannot be distinguished in EDS, which can confirm that the coating is Li₄Ti₅O₁₂(LTO). The magnified TEM image of Fig. 7a are Fig. 7d-e, only the amorphous diffraction ring were observed, indicating that the coating had an amorphous structure. The electrode coating with amorphous structure had good electrochemical stability, high coulomb efficiency and good rate performance [11,23], which explained the good cycle stability and low interface impedance of the above sprayed LTO electrode.

After 200 cycles of test, microcracks (Fig. 8a) appeared in the coating. Since the quasi-solid electrolyte film contains about 10ml/cm² of the liquid electrolyte which main inorganic salt is LiPF₆. These electrolytes penetrate into the amorphous LTO electrode through surface cracks (Fig. 5c-d) and react with the internal electrode (Fig. 8b-d). In order to explore the reaction inside the coating, the magnified partially coating electrode (Fig. 9) showed that the crystalline phase of LTO was formed at the interface between rich fluorine compounds and amorphous LTO electrode, which indicated that LTO recrystallization occurred under the action of electrochemical reaction. The crystallization behavior caused the fracture and cracks propagation inside the amorphous LTO electrode coating, increased the active sites of the electrochemical reaction and improved the overall cycle performance.
3.3. Structural evolution of ceramic/polymer composite electrolyte

The initial state of the ceramic/polymer composite electrolyte film had a smooth surface an irregular holes(Fig.10a). These holes provided channels for the liquid electrolyte to penetrate, and its surface state was consistent with that reported[19,24]. After 200 cycles, as shown in Fig. 10b, the number of holes on the surface of the ceramic/polymer based composite electrolyte film increased, showed a worm-like connection, which indicated that the structure of the film had changed after the electrochemical reaction.

4. Conclusion

In this paper, the plasma spraying method was used to prepare amorphous LTO electrodes for the study of structural evolution during electrochemical cycle of quasi-solid-state lithium battery. The flexible electrolyte film with ceramic/polymer based composite was prepared by mechanical mixing and mold casting. The electrochemical behavior of amorphous and traditional LTO electrodes has been studied, and the conclusions are as follows:

i) The plasma spraying process conditions can prepare the coating of amorphous LTO electrode about 8μm, with internal dense. Mechanical mixing and mold casting method can prepare ceramic/polymer composite electrolyte with good flexibility.

ii) Compared with the traditional LTO electrode, the capacity attenuation rate of the amorphous LTO electrode battery after 0.1C 200 cycles is about 68%, coulomb efficiency is about 99.8%, better than traditional LTO electrode.

iii) The rate test shows that the amorphous LTO electrode battery can withstand a rate of 0.5C charge-discharge, while the traditional LTO electrode can only withstand at 0.2C. The capacity retention and rate performance of the amorphous LTO electrode is better than that of the traditional LTO electrode.

iv) The structure of the amorphous LTO electrode and ceramic/polymer composite electrolyte has evolved after 200 cycles, fracture and cracks have occurred inside the electrodes, and the electrolyte film has changed from an irregular porous state to an ordered hole.
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