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

Xi WU^a, Xinghua LIANG^{a,b,*}, Xiaofeng ZHANG^{b,*},
Lingxiao LAN^{a,b}, Suo LI^a, Qixin GAI^a

^aGuangxi Key Laboratory of Automobile Components and Vehicle Technology, Guangxi University of Science & Technology, Liuzhou 545006, China

^bNational Engineering Laboratory for Modern Materials Surface Engineering Technology, Guangdong Institute of New Materials, Guangdong Academy of Sciences, Guangzhou 510650, China

Received: September 21, 2020; Revised: October 31, 2020; Accepted: December 15, 2020

© The Author(s) 2020.

Abstract: A quasi-solid-state lithium battery is assembled by plasma sprayed amorphous $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) electrode and ceramic/polymer composite electrolyte with a little liquid electrolyte ($10 \mu\text{L}/\text{cm}^2$) to provide the outstanding electrochemical stability and better normal interface contact. Scanning Electron Microscope (SEM), Scanning Transmission Electron Microscopy (STEM), Transmission Electron Microscopy (TEM), and Energy Dispersive Spectrometer (EDS) were used to analyze the structural 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 LTO electrode coating of about $8 \mu\text{m}$. 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 test cycles. The electrochemical cycle results show that the cycle stability, capacity retention rate, coulomb efficiency, and internal impedance of amorphous LTO electrode 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; $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) 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], and are widely used in electric vehicles, consumer electronics, and other fields. The preparation methods of solid-state battery electrodes and electrolytes are mainly Radio

* Corresponding authors.

E-mail: X. Liang, 309602373@qq.com;

X. Zhang, zxf200808@126.com

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.

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (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: (1) There are many process steps, a long process, low production efficiency, and high cost. (2) It is inevitable to use volatile and toxic organic solvents, such as N-methylpyrrolidone (NMP). (3) 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 [11–15]. Amorphous Li_2WO_4 protective layer helps to inhibit the degradation of LiCoO_2 [16]. 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 [17]. The remarkable improvements of the amorphous Li_3PO_4 -coated Li electrode are mainly attributed to high chemical stability and inhibiting the growth of lithium dendrite [18].

In solid-state lithium batteries, ceramic electrolytes have received widespread attention, such as garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) [19] and NASICON-type $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) [20] or $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) [21]. 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) [22]. However, when the ceramic solid electrolyte is in contact with the metal lithium negative electrode, electrochemical reactions are prone to occur, which reduce 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 methods were used to prepare the amorphous thin 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 [23]. The flexible electrolyte film with ceramic/polymer based composite was prepared by mechanical mixing and mold casting. And then, we attempted to construct a 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. The plasma sprayed method of preparing amorphous electrodes and applying them to quasi-solid batteries was adopted in this work to improve electrochemical stability. This innovative and quasi-solid-state lithium battery strategy aims to provide a new way to enhance electrochemical cycle performance of quasi-solid-state lithium battery.

2 Experimental

2.1 Preparation of amorphous and traditional LTO electrodes

Our previous work prepared spherical LTO powder material by spray granulation method [23]. The spherical LTO powder was shot 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 cm^2 was fixed on a copper plate (1 m^2) 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, and the plasma current varied between 400 and 500 A. The weight of active material load on the copper foil with holes was 1.1 mg. The schematic diagram of the LTO electrode preparation process is shown in Fig. 1. The traditional LTO electrode was prepared by the method of Ref. [24].

Fig. 1 Schematic image of preparing LTO electrode by plasma spraying.

2.2 Preparation of ceramic/polymer based composite electrolyte

Ceramic/polymer electrolyte film (CPCEF) was prepared by solution cast method. Before the experiment, the PVDF, LATP, and LiClO_4 powders were vacuum-dried for 24 h at 60 °C. The corresponding PVDF, LATP, LiClO_4 , and DMF at a mass ratio of 10:1:0.124:80 were weighed. 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, 0.5 g LATP and 0.062 g LiClO_4 were added to continue heating and stirring for 0.5 h to make the mixture even. Finally, the evenly stirred solution was casted into a polytetrafluoroethylene mold and placed under vacuum drying at 60 °C for 24–72 h. 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

CR2025 button battery in a glove box filled with argon was assembled. The plasma sprayed LTO electrode

was to cut out the pole piece as the cathode, the Li metal as the anode, and the CPCEF as the solid electrolyte. Then, a given volume ($10 \mu\text{L}/\text{cm}^2$) of liquid electrolyte with 1 M LiPF_6 EC/EMC/DEC was injected into flexible electrolyte film to get the quasi-solid-state composite electrolyte. 1–2 spacers were added and assembled 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 micromorphology of the plasma sprayed LTO electrode before and after the charge–discharge cycle test. Auxiliary focused ion beam (FIB; 450S, FEI) was used to etch the sample surface for characterizing 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 by electrochemical impedance spectroscopy (EIS) in the frequency range of 10^5 – 10^{-3} Hz with electrochemical workstation (CHI660E).

Fig. 2 Illustration of the preparation process of flexible electrolyte film with ceramic/polymer composite.

Fig. 3 Schematic image of LTO/ceramic/polymer composite electrolyte/Li quasi-solid battery assembly.

3 Results and discussion

3.1 Electrochemical performance of amorphous and traditional LTO electrodes

As can be seen from Fig. 4(a), 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 test cycles, 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 improves the cycle stability of the battery, which is consistent with the conclusion of Ref. [25]. Figure 4(b) shows the cycle performance of amorphous and traditional LTO electrodes at a charge–discharge rate from 0.1 to 0.5 C. The capacity retention rate is the discharge capacity of each cycle relative to the first cycle. Under 0.1 C 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 0.2 C, dropped to 0% when the rate exceeded 0.3 C, and finally returned to 13% at a rate of 0.1 C. In contrast, the amorphous LTO electrode still maintained a high capacity retention rate of 41% at 0.5 C. After 30 cycles, the capacity retention rate of the amorphous LTO electrode recovered to 78% at 0.1 C. The results indicated that the amorphous LTO electrode shows excellent rate performance in terms of high-power durability.

Fig. 4 Comparison of electrochemical performance between amorphous and traditional LTO electrodes: (a) discharge performance and coulomb efficiency under 200 test cycles, (b) capacity retention, (c) EIS, (d) partial enlarged view of EIS.

Figures 4(c) and 4(d) are the EIS between amorphous and traditional LTO electrodes, and the illustration is its equivalent circuit. R_{Ω} is the internal resistance of the solid electrolyte and electrodes in the circuit, R_{ct} is the charge transfer resistance in the solid electrolyte, and the total resistance R is the sum of R_{Ω} and R_{ct} . Figure shows that the interface impedance of the amorphous LTO electrode|ceramic/polymer composite electrolyte (525 Ω) is smaller than that of the traditional LTO electrode|ceramic/polymer composite electrolyte (3600 Ω), indicating that the amorphous structure interface has excellent electrical conductivity and facilitates the migration of lithium ions to obtain better electrochemical performance, thereby improving the electrochemical performance of the amorphous LTO electrode. This is consistent with the conclusion of Ref. [26].

3.2 Structural evolution of amorphous LTO electrode

Structural evolution of plasma sprayed amorphous LTO electrode before and after the cycle test is analysed by SEM, STEM, TEM, and EDS to explore the root cause of the difference in electrochemical performance. Amorphous LTO electrode surface micromorphology was investigated using SEM, as shown in Figs. 5(a)–5(d). Spherical LTO powder was sprayed on the perforated copper foil to form a full coverage layer (Fig. 5(a)). After partial magnification, the typical stack forming method of thermal spray coating was found [27] (Fig. 5(b)), and the unmelted spherical LTO particles could also be observed in the figure. When further zoomed into the nanoscale (Fig. 5(c)), local nano-structured tiny particle protrusions were discovered. These protrusions combined with the flexible CPCEF could increase the interface contact between the electrode and the electrolyte film, thereby promoting the electrochemical reaction at the interface. Figure 5(d) is the surface of the amorphous LTO pole piece after the cycle 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.

Figure 6 shows the XRD of the LTO coating. The LTO powder has a very strong diffraction characteristic peak, while the coating cannot detect the sharp characteristic peak, indicating that the coating has been transformed into amorphous state. Studies in Refs. [13,16,17] show that the sharp characteristic peaks of amorphous materials cannot be measured accurately.

Fig. 5 SEM images of amorphous LTO electrode surface: (a) original spray state image, (b) magnified image of (a), (c) partial magnified image of (b), (d) surface structure image after 200 test cycles.

Fig. 6 XRD of the amorphous LTO coating and LTO powder.

In order to obtain the structural evolution information inside the amorphous LTO electrode after the electrochemical cycle test, the FIB was used to cut the samples before and after the cycle test, as shown in Fig. 7. It can be known from the figure that the thickness of the thin coating after spraying is about 5–8 μm .

From Figs. 8(a)–8(c), it could be seen that the main elements of the original LTO electrode are Ti and O. Although Li cannot be distinguished in EDS, after the quantitative EDS test, the composition of sample are Ti (53.8 wt%) and O (46.2 wt%) roughly, which can confirm that the coating is LTO. The magnified TEM images of Fig. 8(a) are Figs. 8(d) and 8(e); only the amorphous diffraction ring was 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 [16,28], which explained the good cycle stability and low interface impedance of the above sprayed LTO electrode.

Fig. 7 FIB-SEM of amorphous LTO electrode before (a) and after (b) 200 test cycles.

Fig. 8 Cross section (a) and corresponding elemental mappings (b, c) of the original amorphous LTO electrode; TEM image of the corresponding marked area (d), and amorphous diffraction ring (e).

After 200 cycles of test, microcracks (Fig. 9(a)) appeared in the coating. Since the quasi-solid electrolyte film contains about 10 mL/cm² of the liquid electrolyte whose main inorganic salt is LiPF₆, these electrolytes penetrate into the amorphous LTO electrode through surface cracks (Figs. 5(c) and 5(d)) and react with the internal electrode (Figs. 9(b)–9(d)). In order to explore the reaction inside the coating, the magnified partially coating electrode (Fig. 10) 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 crack propagation inside the amorphous LTO electrode coating, increased the active sites of the electrochemical reaction, and improved the overall cycle performance.

Fig. 9 Cross-sectional view of amorphous LTO electrode after 200 test cycles and corresponding elemental mappings: (a) cross section, (b) O elemental mapping, (c) Ti elemental mapping, (d) F elemental mapping.

Fig. 10 Cross section (a), internal state (b), and phase analysis (c) of amorphous LTO electrode coating through TEM after 200 test cycles.

3.3 Structural evolution of ceramic/polymer composite electrolyte

The initial state of the CPCEF had a smooth surface with irregular holes (Fig. 11(a)). These holes provided channels for the liquid electrolyte to penetrate, and its surface state was consistent with that reported [24,29]. After 200 cycles, as shown in Fig. 11(b), the number of holes on the surface of the CPCEF increased showing a worm-like connection, which indicated that the structure of the film had changed after the electrochemical reaction.

The solid electrolyte composed of polymer and ceramic can give full play to the good mechanical properties of polymer and high ionic conductivity of ceramic, and overcome their respective shortcomings [30,31]. Figure 12 shows the XRD of the CPCEF, which implies the characteristic diffraction peaks of ceramic LATP and PVDF are both obvious before the cycle test, indicating that CPCEF is a mechanical mixture. The CPCEF material retains the respective characteristics of polymer and ceramic, but the crystallinity of the polymer matrix and the conduction of lithium ions will be reduced through the active ceramic filler [32]. The diffraction peak of the ceramic material (LATP) was reduced to a very low level, and the polymer matrix (PVDF) is further amorphized after 200 cycles. The results show that the viscoelastic film of CPCEF has changed after 200 cycles, and the

Fig. 11 SEM images of the structural evolution of ceramic/polymer composite electrolyte before (a) and after (b) 200 test cycles.

Fig. 12 XRD of the structural evolution of ceramic/polymer composite electrolyte before and after 200 test cycles.

physical and chemical properties have transformed as well. It indicates that the transformation of physical and chemical properties of the composite electrolyte is one of the reasons for the capacity degradation of the quasi-solid-state battery, but the exact mechanism needs rigorous improvements further.

4 Conclusions

In this paper, the plasma spraying method was used to prepare amorphous LTO electrode 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:

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

(2) Compared with the traditional LTO electrode,

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

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

(4) 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. The transformation of physical and chemical properties of the composite electrolyte is one of the reasons for the capacity degradation of the quasi-solid-state lithium battery.

Acknowledgements

This work was supported by the Fund Project of the GDAS Special Project of Science and Technology Development, Guangdong Academy of Sciences Program (No. 2020GDASYL-20200104030); the Innovation Project of Guangxi University of Science and Technology Graduate Education (No. YCSW2020217); Guangxi Innovation Driven Development Project (No. AA18242036-2); Innovation Team Project of Guangxi University of Science and Technology (No. 3); and the Fund Project of the Key Lab of Guangdong for Modern Surface Engineering Technology (No. 2018KFKT01).

References

- [1] Chen Y, Wen KH, Chen TH, *et al.* Recent progress in all-solid-state lithium batteries: The emerging strategies for advanced electrolytes and their interfaces. *Energy Storage Mater* 2020, **31**: 401–433.
- [2] Pat S, Özen S, Yudar HH, *et al.* The transparent all-solid-state rechargeable micro-battery manufacturing by RF magnetron sputtering. *J Alloys Compd* 2017, **713**: 64–68.
- [3] Matsuda Y, Kuwata N, Kawamura J. Thin-film lithium batteries with 0.3–30 μm thick LiCoO_2 films fabricated by high-rate pulsed laser deposition. *Solid State Ionics* 2018, **320**: 38–44.
- [4] Choi M, Lee SH, Jung YI, *et al.* The high capacity and cycle stability of NiFe_2O_4 thin film prepared by E-beam evaporation method for lithium ion batteries. *J Alloys Compd* 2017, **729**: 802–808.

- [5] Shi HB, Zhang H, Li XX, *et al.* In situ fabrication of dual coating structured SiO/1D-C/a-C composite as high-performance lithium ion battery anode by fluidized bed chemical vapor deposition. *Carbon* 2020, **168**: 113–124.
- [6] Chen T, Meng FB, Zhang ZW, *et al.* Stabilizing lithium metal anode by molecular beam epitaxy grown uniform and ultrathin bismuth film. *Nano Energy* 2020, **76**: 105068.
- [7] Choi Y, Kim JI, Moon J, *et al.* Electron beam induced strong organic/inorganic grafting for thermally stable lithium-ion battery separators. *Appl Surf Sci* 2018, **444**: 339–344.
- [8] Nuroniah I, Priyono S, Subhan A, *et al.* Synthesis and characterization of Al-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with sol gel method for anode material lithium ion battery. *Mater Today: Proc* 2019, **13**: 65–70.
- [9] Xue B, Wang K, Tan Y, *et al.* Studies on performance of SiO addition to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode material for lithium-ion batteries. *Chem Phys Lett* 2019, **730**: 623–629.
- [10] Wang Y, Zhu WJ. Micro/nano-structured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as high rate anode material for lithium ion batteries. *Solid State Ionics* 2020, **349**: 115297.
- [11] Matsuyama T, Sakuda A, Hayashi A, *et al.* Electrochemical properties of all-solid-state lithium batteries with amorphous titanium sulfide electrodes prepared by mechanical milling. *J Solid State Electrochem* 2013, **17**: 2697–2701.
- [12] Matsuyama T, Sakuda A, Hayashi A, *et al.* Preparation of amorphous TiS_x thin film electrodes by the PLD method and their application to all-solid-state lithium secondary batteries. *J Mater Sci* 2012, **47**: 6601–6606.
- [13] Hayashi A, Konishi T, Tadanaga K, *et al.* All-solid-state rechargeable lithium batteries using $\text{SnX-P}_2\text{X}_5$ (X = S and O) amorphous negative electrodes. *Res Chem Intermed* 2006, **32**: 497–506.
- [14] Chen LB, Xie JY, Yu HC, *et al.* An amorphous Si thin film anode with high capacity and long cycling life for lithium ion batteries. *J Appl Electrochem* 2009, **39**: 1157–1162.
- [15] Meng RJ, Hou HY, Liu XX, *et al.* Binder-free combination of amorphous TiO_2 nanotube arrays with highly conductive Cu bridges for lithium ion battery anode. *Ionics* 2016, **22**: 1527–1532.
- [16] Hayashi T, Matsuda Y, Kuwata N, *et al.* High-power durability of LiCoO_2 thin film electrode modified with amorphous lithium tungsten oxide. *J Power Sources* 2017, **354**: 41–47.
- [17] Lin ZY, Guo XW, Yu HJ. Amorphous modified silyl-terminated 3D polymer electrolyte for high-performance lithium metal battery. *Nano Energy* 2017, **41**: 646–653.
- [18] Wang LP, Wang QJ, Jia WS, *et al.* Li metal coated with amorphous Li_3PO_4 via magnetron sputtering for stable and long-cycle life lithium metal batteries. *J Power Sources* 2017, **342**: 175–182.
- [19] Zhao Y, Yan JH, Cai WP, *et al.* Elastic and well-aligned ceramic LLZO nanofiber based electrolytes for solid-state lithium batteries. *Energy Storage Mater* 2019, **23**: 306–313.
- [20] Yang ZL, Yuan HY, Zhou CJ, *et al.* Facile interfacial adhesion enabled LATP-based solid-state lithium metal battery. *Chem Eng J* 2020, **392**: 123650.
- [21] Cheng J, Hou GM, Sun Q, *et al.* Cold-pressing PEO/LAGP composite electrolyte for integrated all-solid-state lithium metal battery. *Solid State Ionics* 2020, **345**: 115156.
- [22] Zhang BH, Liu YL, Liu J, *et al.* “Polymer-in-ceramic” based poly(ϵ -caprolactone)/ceramic composite electrolyte for all-solid-state batteries. *J Energy Chem* 2021, **52**: 318–325.
- [23] Liang XH, Wang YT, Zhang XF, *et al.* Performance study of a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode for lithium batteries prepared by atmospheric plasma spraying. *Ceram Int* 2019, **45**: 23750–23755.
- [24] Umirov N, Yamada Y, Munakata H, *et al.* Analysis of intrinsic properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ using single-particle technique. *J Electroanal Chem* 2019, **855**: 113514.
- [25] Sun RB, Gao JY, Wu G, *et al.* Amorphous metal oxide nanosheets featuring reversible structure transformations as sodium-ion battery anodes. *Cell Rep Phys Sci* 2020, **1**: 100118.
- [26] Yun YS, Jin HJ. Electrochemical performance of heteroatom-enriched amorphous carbon with hierarchical porous structure as anode for lithium-ion batteries. *Mater Lett* 2013, **108**: 311–315.
- [27] Zhang BY, Yang GJ, Li CX, *et al.* Non-parabolic isothermal oxidation kinetics of low pressure plasma sprayed MCrAlY bond coat. *Appl Surf Sci* 2017, **406**: 99–109.
- [28] Hayashi T, Miyazaki T, Matsuda Y, *et al.* Effect of lithium-ion diffusibility on interfacial resistance of LiCoO_2 thin film electrode modified with lithium tungsten oxides. *J Power Sources* 2016, **305**: 46–53.
- [29] Bhat MY, Yadav N, Hashmi SA. A high performance flexible gel polymer electrolyte incorporated with suberionitrile as additive for quasi-solid carbon supercapacitor. *Mat Sci Eng B* 2020, **262**: 114721.
- [30] Guo QP, Han Y, Wang H, *et al.* New class of LAGP-based solid polymer composite electrolyte for efficient and safe solid-state lithium batteries. *ACS Appl Mater Interfaces* 2017, **9**: 41837–41844.
- [31] Li A, Liao X, Zhang H, *et al.* Nacre-inspired composite electrolytes for load-bearing solid-state lithium-metal batteries. *Adv Mater* 2019, **32**: 1905517.
- [32] Yu XW, Manthiram A. A review of composite polymer-ceramic electrolytes for lithium batteries. *Energy Storage Mater* 2021, **34**: 282–300.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.