Review article

Development of the cold sintering process and its application in solid-state lithium batteries

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HIGHLIGHTS

- Development of solid state batteries with advanced sintering technique.
- Report the development of cold sintering technique.
- Recent progress of cold sintering process applied in solid state battery.
- Give a perspective on the future development of cold sintering process.

ARTICLE INFO

ABSTRACT

Solid-state batteries (SSBs) are developed with the use of inflammable solid-state electrolytes to realize higher energy density and improved safety. However, the densification temperature of solid electrolytes via conventional sintering methods is usually high, especially for oxide-type electrolytes. Advanced sintering techniques such as spark plasma sintering have been developed to decrease the heat-treatment temperature and time. Recently, a novel cold sintering process (CSP) has been developed, which offers an alternative route to the densification of many solid-state electrolyte materials below 300 °C. Generally, the CSP involves multi-stage non-equilibrium processes such as dissolution-precipitation under external stress, viscous flow of saturated solutions and diffusion of species. Herein, the CSP application in different solid electrolytes and electrodes are summarized. It is expected that the CSP has great potential in preparing solid-state batteries and solid electrolytes in the future.

1. Introduction

1.1. History and development of solid-state batteries

Solid-state lithium ion batteries have been considered as one of the most promising next-generation battery systems with improved energy density and safety [1,2]. Among the reported classes of solid-state batteries, bulk-type inorganic solid-state lithium-ion batteries show great promise for future EV (electric vehicle) applications. For solid-state electrolytes and solid-state batteries, there has been impressive progress over the past decades [3–5]. Herein, we will only give a brief introduction to the development of solid-state electrolytes and batteries.

Generally, oxide electrolytes show good ionic conductivity, chemical stability, and wide electrochemical windows. Because of this, they have received significant attenions over past decadese. Garnet-type (e.g., $Li_7La_3Zr_2O_{12}$, LLZO) solid electrolyte is one of the most

popular oxide-type electrolytes due to its stability against Li metal [6]. Additionally, NASICON-type (e.g., $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, LATP) solid electrolytes have been widely investigated in previous studies due to the high conductivity and availability of raw materials [7]. However, the oxide electrolytes usually need high temperature processing, which makes them difficult to couple with other electrode materials because of side-reactions during the co-sintering process. Therefore, soft-electrolytes containing sulfide species have been widely developed. Over the past few years, different sulfide-based systems have been investigated systematically [8]. One type of promising sulfide-type electrolyte is the $Li_2S–P_2S_5$ glass-ceramic discovered by Tatsusmisago, which shows a highly conductivity close to that of commercial liquid electrolytes due to the precipitation of high conducive crystalline $Li_7P_3S_{11}$ in the matrix [9]. Crystalline sulfides, such as the super ionic $Li_{10}GeP_2S_{12}$ series [10], thio-lithium ion super ionic conductors (thio-LISICON) [11], and argyrodite (Li_6PS_5X, X = Cl, Br, I)-type sulfides were widely studied by different groups after 2010 [12]. Detailed

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information on inorganic lithium ion conductors can be found in the comprehensive reviews [13–18].

A monolithic all-solid-state oxide based battery of $Li_4Ti_5O_{12}$/LATP/$LiMn_2O_4$ was fabricated by Brike and coworkers, which demonstrated a limited capacity of 40 mAh g^{-1} due to the poor interfacial contact [19]. To reduce the physical mismatch between LATP and electrodes, solid-state batteries were fabricated based on the NASICON electrolytes through deposition of thin film electrodes on the surface of LATP sheets [20–23]. Compared to bulk-type solid-state batteries, the thin-film $LiCoO_2$ electrodes with LATP electrolyte showed an improved electrochemical performance of 120 mAh g^{-1} after annealing, which was attributed to the improved interface between LATP and $LiCoO_2$ electrode.

Ohta and coworkers fabricated a solid-state battery based on LLZO electrolyte, which showed a limited discharge capacity of 78 mAh g^{-1} due to the large interfacial resistance between $LiCoO_2$/LLZO [24]. Later on, the chemical information at interface between LLZO and $LiCoO_2$ after high temperature sintering was investigated by Park and coworkers, and they identified the cross-diffusion of Co to LLZO and La/Zr to $LiCoO_2$. In addition, a tetragonal LLZO phase was formed at the interface due to the leaching of Al at high temperature, which further decreased the ionic conductivity [25].

Furthermore, the moisture and carbon dioxide sensitivity of LLZO in the ambient environment has been proven to be problematic for bulk-type solid-state batteries with LLZO electrolyte, which may be unstable after assembly in air [26]. To reduce the influence of Li_2CO_3 and inhomogenous contact at the electrode-electrolyte interface, different strategies such as co-sintering and the insertion of buffer layers were adopted for garnet-type electrolyte interfaces. As an example, Li_3BO_3 has been used as a sintering additive to reduce the heating temperature for the fabrication of LLZO/LCO cells at a lower temperature of 700 °C [27]. With the addition of Li_3BO_3 and Al_2O_3, co-sintering of Al-doped LLZO/LCO was successfully prepared due to simultaneous inter-diffusion of Al between garnet oxide and additives, which delivered a charge-discharge capacities of 98 and 78 mAh g^{-1}, respectively [28].The formation of a stable and ionically conductive interface between solid electrolyte and electrode is critical to achieving functional solid-state batteries [29,30]. To alleviate the influence of Li_2CO_3, Li and coworkers proposed that the incorporation of a small amount LiF into the garnet LLZO electrolyte could effectively decrease the interface resistance from 1260 $\Omega \, cm^{-2}$ to 345 $\Omega \, cm^{-2}$ [29]. As an alternative strategy to form a stable interface, Han and coworkers utilized the Li_2CO_3 layer on LLZO by forming a highly conductive Li_2CO_3-Li_3BO_3 glass-ceramic buffer layer to reduce the interface resistance between LLZO and $LiCoO_2$. The full cell was capable of delivering a discharge capacity of 120 mAh g^{-1} at 100 °C and a long cycling life of over 100 cycle at room temperature [31].

To further reduce the solid-state diffusion length between electrode and electrolyte, 3D porous scaffold solid electrolytes were invented. The electrode materials were filled into the pores using a wet chemical method followed by heat treatment, which resulted in lower sintering temperatures and good electrolyte/electrode contact, as illustrated by Kotobuki and coworkers [32,33]. Until now, the oxide-based solid-state electrolytes have faced significant challenges in interfacial contact and conductivity, and further efforts in both materials design and novel fabrication processes are required to make further advancements.

Unlike the rigid mechanical properties of oxide-based electrolytes, the sulfide glass-type electrolytes are soft and have higher ionic conductivities. Therefore, the interfacial problems can be easily addressed through high-pressure pressing at room temperature through room-temperature sintering mechanism. For example, Li_3PO_4-Li_2S-SiS_2 glass electrolyte was pressed with spherical graphite and TiS_2 in a full battery. The overall resistance of the fabricated cell was close to the resistance of the pure solid electrolyte layer, which indicated that the interfacial contact resistance was negligible. Another example was the Li_2S–P_2S_5 glass-ceramic electrolyte, it was used in the fabrication of solid-state batteries with $LiCoO_2$ cathodes by Ohta and coworkers

[34,35]. A capacity of 102 mAh g^{-1} at room temperature was delivered, which was 73% of theoretical capacity of $LiCoO_2$ [36]. To increase the performance, a highly conductive Li_2S–P_2S_5–GeS_2 (thio-LISICON) sulfide electrolyte was prepared by Kanno and coworkers, where the discharge capacity was only 80 mAh g^{-1} due to reduction of Ge species [37]. In order to stabilize the interface and reduce the side reactions, argyrodite-type sulfide Li_6PS_5X(X = Cl, Br, F, I) electrolyte was recently developed and applied in solid-state batteries due to its high electrochemical stability. Yubuchi and coworkers synthesized argyrodite sulfide electrolytes using a solution method followed by the fabrication of cells with a Li-In alloy anode and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) layered cathode, showing a capacity of 140 mAh g^{-1} at room temperature [38]. Discovered in 2011, a superionic conducting $Li_{10}GeP_2S_{12}$ demonstrated an extremely high ionic conductivity of 1×10^{-2} S cm^{-1} [10]. In 2016, the same group fabricated batteries using this new superionic conductor with higher chemical stability, which showed a stable cycling performance for 1000 cycles [39]. Compared to oxide based solid-state batteries, sulfide based solid-state batteries shows better electrochemical performance due to the low interfacial resistance.

Bulk inorganic solid-state batteries have achieved remarkable progress in recent years. Nevertheless, there are still several major challenges that need to be addressed in order to realize their practical application. The problems that need to be overcome include the synthesis of a robust solid electrolyte with high ionic conductivity, poor interfacial compatibility and stability, and low-cost cell fabrication processes. Among the prominent interfacial problems, the severe side reactions between solid-state electrolyte and electrode during high-temperature sintering has largely impeded the progress of solid-state lithium-ion batteries. Formation of an ion-blocking interface will increase the interface resistance and slow down the transport of lithium ions. Therefore, the next section will address this issue with the development of advanced sintering techniques.

1.2. Development of sintering techniques for solid-state batteries

Solid electrolyte particles need to be bonded together by sintering before use in batteries. A sintering process usually involves two major steps: densification and grain growth. Both steps require a thermodynamic driving force, that is, the reduction of the total Gibbs free energy of the system, rendering them thermodynamic favorable. Therefore, the process of sintering is intrinsically driven by the Gibbs free energy.

During the sintering process, two popular mechanisms are often mentioned in literature: solid-state sintering and liquid phase sintering [40]. The latter is preferred during solid electrolyte preparation because of the simplicity and effectiveness in reducing the sintering temperature. The so-called liquid phase sintering is a process where liquid-phases emerge during the sintering process, which is beneficial for mass transport and particle compaction. The typical process of liquid phase sintering is divided into multiple stages. The initial stage is similar to solid-state sintering, wherein the particles are bonded together with the help of a liquid-phase formed at high temperature. The second stage involves the crystallization of dissolved species after the liquid-solution is over-saturated. The final stage is the mass transport process, which result in the exchange of atoms between different particles and finally grain growth [41].

Conventionally, the sintering of materials only involves the application of heat upon a green body with 40–60% density, which can facilitate the mass transport/diffusion. Thus, some advanced sintering techniques are developed by utilizing other factors such as external pressure and/or electric field in combination with external heating to facilitate the mass transport. Caused by pressure or an applied electric field, the mass transport in materials can be largely enhanced, and lower sintering temperatures can be realized. Several advanced sintering techniques that are widely reported in the densification of solid electrolytes include hot pressing, field-assisted sintering, flash sintering,