Favorable composite electrodes for all-solid-state batteries

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All-solid-state batteries show great promise as next-generation batteries with high safety, high power, and long life. In addition to high-performance active electrode materials and solid electrolytes, the properties of the electrode–electrolyte interface and the morphology of the electrode layer are important for the development of high-performance batteries. In this review, current research and future prospects for the design of composite electrodes for all-solid-state batteries are outlined. In order to achieve high-performance all-solid-state batteries, composite electrodes must satisfy a number of requirements. The resistance at the electrode–electrolyte interface must be minimal, the contact area between the electrode and solid electrolyte must be maximized, favorable lithium-ion and electron conducting pathways must be formed in the electrode layer. Maintenance of the formed interface is important to enhance cyclability. In this review, some effective approaches to construct better composite electrodes are demonstrated.

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1. Introduction

1.1 Advantages of all-solid-state batteries

As the energy density of lithium batteries has increased, their safety problems have become obvious. Moreover, the demand for small or light secondary batteries for high-power applications such as electric vehicles and electric power tools continues to increase. The development of safe and high-power secondary batteries is strongly required.

Lithium-ion batteries have been widely used as secondary batteries with large energy densities. However, the use of flammable organic liquid electrolytes in these batteries presents fire and explosion risks. The replacement of the organic liquid electrolytes with nonflammable inorganic solid electrolytes could eliminate the safety hazards from leakage and flammability. Thus, all-solid-state lithium secondary batteries based on inorganic solid electrolytes have attracted great attention.

The most important component of all-solid-state batteries is the solid electrolyte. Inorganic solid electrolytes have several advantages over organic-solvent-based liquid electrolytes, such as their non-fluidity, non-flammability, single-ion conducting nature, and high-temperature stability. Some solid electrolytes have demonstrated lithium-ion conductivities of over 10⁻² S cm⁻¹, which is greater than in conventional liquid electrolytes. These advantages of solid electrolytes enable the development of high-performance secondary batteries. Table 1 summarized the expected advantages of all-solid-state batteries. The high safety and long lifetimes of all-solid-state batteries have long been known, and their high-rate operation of all-solid-state batteries has been achieved through high-temperature operation and the development of highly conducting solid electrolytes.¹,² Furthermore, these solid electrolytes have an ideal transference number (τ = σLi⁺/σtotal) of almost 1.³ It should be noted that the five advantages listed in Table 1 are closely inter-related and highly synergistic.

1.2 Recent interest in all-solid-state batteries

Figure 1 shows the number of papers published in the fields of solid electrolytes and all-solid-state batteries over the last 20 years. The annual number of papers has increased rapidly since 2010, and the number of researchers working in the field of all-solid-state batteries continues to increase. The number of patent applications has also increased rapidly since 2010.

1.3 Configuration of bulk-type all-solid-state batteries

All-solid-state batteries are roughly classified into two categories: thin film batteries⁵–⁷ and bulk-type batteries.⁸–¹⁰ Thin-film batteries consist of a positive electrode, a negative electrode, and solid electrolyte films. The composite electrodes used in bulk-type batteries consist of an active material and solid electrolyte particles, with a...
solid electrolyte separator layer sandwiched between the positive and negative composite electrodes as shown in Fig. 2. Solid electrolyte particles are blended into the electrode layer to form lithium-ion conducting pathways and increase the contact area between the electrode and electrolyte. The incorporation of particles of the active electrode material particles in the electrode layer can increase the battery capacity. Thus, bulk-type batteries are more suitable for large-scale batteries.

2. Mechanical properties of sulfide solid electrolytes

Understanding the mechanical properties of solid electrolytes is important to battery manufacturing and for long-term reliability. Sulfide-based solid electrolytes are known to be “soft” and “ductile”, put details of their mechanical properties have not been clarified yet. In this section, the “soft” nature of sulfide-based solid electrolyte is discussed.

2.1 Plastic properties (formability of powders)

Sulfide-based solid electrolytes have a “soft” nature, and can be densified to produce favorable interface contact simply by pressing at low temperatures, such as 25°C. As a result, the boundary resistances at the electrolyte/electrolyte and electrolyte/electrode interfaces are effectively decreased. Figure 3 shows the scanning electron microscope (SEM) image of a smooth cross-section of a 70Li2S·30P2S5 glass-ceramic pellet prepared by pressing at 370 MPa at room temperature (≈25°C). The cross-section was polished using an Ar-ion beam. The pressed pellet cross-section shows a sintered body, indicating that pressure sintering proceeds at room temperature in the sulfide-based solid electrolytes.

The terms “room-temperature pressure sintering” and “cold sintering” have been used to describe this phenomena or process. “Cold” is a technical term in sintering, which indicates a temperature lower than the normal
sintering temperature but usually much higher than room temperature, i.e., 200 to 300°C. Thus, the term “room-temperature” is used to emphasize particularly low temperatures. Recently, Randall and coworkers defined the cold sintering process as a process in which an inorganic powder is densified in the presence of a transient liquid phase at a phase fraction typically between 1 and 10 vol%.

However, pressure sintering is observed in many sulfide electrode and electrolyte materials even without a transient liquid phase, that is, they can be densified at 25°C as a pure electrolyte. The formation of a glass or glass-containing material is important for smooth connection of particle boundaries.

2.2 Elastic properties
The elastic moduli of several solid electrolytes have been reported. The elastic modulus of a solid electrolyte can be obtained by various methods, including the ultrasonic pulse echo method, compression tests, and indentation. The ultrasonic pulse echo method is particularly useful because it does not require a large-scale apparatus, and even small samples (10 mm diameter, ~2 mm thickness) can be measured with relatively high accuracy. Figure 4 shows the relationship between mean atomic volume and Young’s modulus; in general, these quantities are strongly correlated. Oxide glasses have higher Young’s moduli and smaller mean atomic volumes. Chalcogenide glasses without alkaline ions have lower Young’s moduli and larger mean atomic volumes. The properties of sulfide solid electrolytes are intermediate between the oxide and other chalcogenide glasses. Further details have been summarized in previous papers.

3. Design of composite electrodes
3.1 Requirements and challenges for composite electrodes
The major challenge in all-solid-state batteries is the formation of a favorable solid-solid interface. In conventional liquid-electrolyte lithium-ion batteries, the interface between the electrode active materials and the electrolyte solution is a solid–liquid interface, whereas all-solid-state batteries have a solid–solid interface. The construction and maintenance of solid–solid interfaces has limited the performance of all-solid-state batteries and thus has been extensively researched. In particular, the performance of this solid-solid interface greatly depends on the electrode design. Table 2 summarizes the requirements for designing high performance composite electrodes; all of these requirements should be fulfilled to construct high performance all-solid-state batteries. An overview of each requirement is given in this section.

3.2 Suppression of interfacial resistance between the electrode and electrolyte
Designing a low-resistance electrode–electrolyte interface is important. The resistance is greatest at the interface between the high-voltage positive electrode and the sulfide solid electrolyte particles. In particular, Takada and coworkers at the National Institute of Materials Science reported a large resistance component at the interface between lithium transition metal oxides used as positive electrode active materials and sulfide-based solid electro-
Table 2. Requirements for designing high performance composite electrodes

| Requirement                      | Remarks                                      |
|----------------------------------|----------------------------------------------|
| High performance materials       | High performance active electrode materials and solid electrolytes, as well as suitable additives and current collectors, are essential. |
| Low-resistance interface between electrode and electrolyte for high power | Large interfacial resistance usually occurs between the high-voltage electrode and the sulfide-based solid electrolyte rather than at negative electrode side interface. This resistance can be reduced by interfacial modifications such as coatings. A large contact area between the electrodes and electrolyte is essential. |
| Dense electrode with a large volume ratio of active electrode materials for high power and energy density | A large volume ratio of the active electrode material in the composite electrode is required for high energy density. However, there is a trade-off between the volume ratio and ionic conductivity. Furthermore, the formation of effective lithium-ion and electron conducting pathways by incorporating a small amount of solid electrolyte and conducting additives is essential. |
| Suppression of mechanical damage to the electrodes for long cycle life | Stress concentration in brittle materials should be avoided. Highly reversible electrode structure during charging and discharging leads to high performance. |
| Development of a versatile manufacturing process for commercialization | Development of a process to produce highly designed electrode layers is essential for practical application of all-solid-state batteries. The slurry coating process is one promising approach. |

The introduction of a oxide solid electrolyte such as LiNbO₃ can considerably decrease this interfacial resistance, as first reported by Takada and Ohta et al. Similar results have been observed in all-solid-state batteries using polymer electrolytes. Many coating materials have been reported to effectively decrease interfacial resistance, demonstrating that modification of the electrode–electrolyte interface is critical in all-solid-state batteries, and that coating can improve the interface properties.

The high-resistance component has been proposed to originate from mutual diffusion due to chemical reactions between the electrode material and the solid electrolyte and from lithium-ion deficiency due to the difference in their electrochemical potentials, which is explained by the space charge layer model.

Studies based on computational chemistry have clearly shown that the calculated electrochemical windows of sulfide-based solid electrolytes are narrow, that is, sulfide-based electrolytes are easily oxidized and reduced at interfaces with high- or low-voltage electrode materials. However, these oxidation and reduction reactions can be effectively suppressed by introducing a buffer layer consisting of more electrochemically stable solid electrolytes.

From a physical view point, the origin of the high resistance at the interface and the effect of the coatings has not yet been fully clarified, apart from the above-mentioned discussion of the space charge layer model and some computational studies. Further studies to elucidate the nature of these phenomena are currently being conducted.

3.3 Formation of lithium-ion and electron conducting pathways

In addition to minimization of the interfacial resistance between the electrode and electrolyte, the formation of both lithium-ion and electron conducting pathways and close contact between the electrode and the electrolyte are essential in composite electrodes. Furthermore, the volume ratio of the active materials should be high in order to construct a high-energy battery. There is generally a trade-off between these requirements, and therefore the development of electrodes that can achieve both of these goals is important. The use of solid-electrolyte-coated electrode particles is an effective approach to enable both good electrode–electrolyte contact and the formation of effective conducting pathways. The first proof of this concept was demonstrated using solid electrolytes prepared via a vapor-phase process; LiCoO₂ particles were coated with Li₂S–P₅S₅ solid electrolyte using pulse laser deposition (PLD). A schematic of the solid electrolyte coating apparatus is shown in Fig. 5(a). In the PLD vacuum chamber, a target holder was attached above a vibrating sample holder to deposit the solid electrolyte on the electrode particles. Recently, research into the production of solid-electrolyte-coated electrode active materials has turned to more practical liquid-phase process studies.

Figure 5(b) shows a schematic of the construction of a dense electrode layer. A composite electrode with solid-electrolyte-coated electrode particles is densified by room temperature pressure sintering. In addition, the relatively hard active oxide materials of the positive electrode can also be brought into partial contact by pushing out the solid electrolyte. Simple mixing of the fine solid electrolyte particles and coating with solid electrolyte are both useful, as they both produce a dense electrode layer after room temperature pressure sintering.

Solid electrolyte coating is advantageous for forming ion conduction pathways, but disadvantageous for the formation of electron conduction paths. When solid electrolyte coating is effective in improving cell performance, the electron conductivity is thought to be higher than the ion conductivity, that is, the lithium-ion conductivity and conduction path limit the cell performance. Solid electrolyte coating is generally effective in improving performance, indicating that improvement of the ionic conductivity of the electrode layer is important. In order to design effective conducting pathways, conductivity measurements of the composite electrode are important. Traditionally, measuring electronic and ionic conductivities separately has been challenging; however, novel techniques have recently been reported. Siroma et al. reported an AC impedance technique based on the transmission line model for measurement of the ionic and electronic conductivities of composite electrodes. In this technique, the electronic and
Ionic conductivities are measured using only a simple ion-blocking cell. However, the conductivities often change dramatically depending on the state of charge and the magnitude of deterioration. For example, electronic conductivity can drastically increase (LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$; NCM) after charging. Thus, the investigation of conductivity changes during charging and discharging is important to determine the ideal electrode morphology with effective conducting pathways. The ideal electrode morphology varies according to the properties to be prioritized, i.e., power density, energy density, or cyclability. Quantitative evaluation of the conductivities of the composite electrodes is important in order to determine the optimal cell configurations.

### 3.4 Suppression of mechanical damage

Mechanical damage, such as cracking, fracturing, and densification, must also be controlled to achieve high performance. To prevent cracking and fracturing, stress concentration on brittle materials should be avoided. The active electrode material can be crushed by high local stresses generated during the molding and charge–discharge processes. When coarse electrode particles are used, the electrode active material (NCM) and the solid electrolyte [75Li$_2$S·25P$_2$S$_5$ (mol %) glass] particles are disproportionately located in the electrode layer. In contrast, the NCM particles are dispersed throughout the solid electrolyte matrix when fine solid electrolyte particles are used. The particle volume is roughly proportional to the cube of the particle diameter; thus, the average volume of a solid electrolyte 16 μm in diameter is roughly 64 times larger than that of a 4 μm electrolyte. That is, approximately 64 times more fine particles will be present in the same volume compared to coarse particles, which should yield a more homogeneous distribution of the solid electrolyte particles. Fine solid electrolyte particles also yield dense composite electrodes, which are advantageous to lithium-ion conduction and smooth electrode reactions. Furthermore, the homogeneous distribution of a solid electrolyte with a low elastic modulus suppresses damage to the active electrode material. Lithium insertion and extraction inflict additional stresses on the electrode materials, causing cracking and fracturing of the electrodes. Thus, the suppression of the initial damage to the brittle materials is important to prevent further deterioration.

![Fig. 6](image-url)
Maintaining good solid–solid contact is one of the greatest challenges in all-solid-state batteries. The loss of contact is believed to result from the large volume change in the active electrode materials during charging and discharging. Thus, the use of materials which undergo only small volume changes, such as NCM\textsuperscript{60,61} and Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} (LTO),\textsuperscript{62} is favorable.\textsuperscript{55,63} Otherwise, to maintain contact between the electrode active material and the solid electrolyte, the solid electrolyte must have an appropriate elastic modulus.\textsuperscript{12,17,22}

Keeping good contact can also be maintained by the use of “soft” electrode materials, which maintain contact with the electrolyte despite large volume changes during charging and discharging. Transition metal sulfides with sulfur-rich compositions are model soft electrode materials, and have a high capacity. Figure 7(a) shows cross-sectional SEM images of the electrode layers of all-solid-state cells with Li\textsubscript{3}NbS\textsubscript{4} as the active electrode material after charge and discharge measurements.\textsuperscript{15} Schematics of the healing phenomenon are also shown in the figure. Li\textsubscript{3}NbS\textsubscript{4} is capable of room-temperature pressure sintering. This material undergoes a volume change of \approx 25\% during the transition from Li\textsubscript{3}NbS\textsubscript{4} to Li\textsubscript{4}NbS\textsubscript{4} during charging and discharging. During charging, the electrode becomes “gappy”, that is, the void volume increases. During discharging, the electrode becomes dense due to the volume expansion of the active material. Contact between the particles improves during the discharging process. The electrode is believed to become dense due to pressure sintering as a result of the volume changes, increasing the contact between the particles. The electrode shows “healing” of the contact between particles, where the “room temperature pressure-sintering” assisting the “healing”. As a result of its ability to maintain good contact, the all-solid-state cell showed excellent cyclability and retained 90\% of its initial capacity for 200 cycles despite the large volume changes, as shown in Fig. 7(b).

The stress concentration at a point in ductile solid electrolyte and electrode materials results in densification. This has both positive and negative influences on the cell performance.\textsuperscript{15,63} Further research into the relationship between mechanical damage and electrode performance is needed to understand and control the dynamic changes in the electrode morphology, and for the development of ultra-long cycle life in all-solid-state batteries.

3.5 Development of electrode sheets
Development of new processes suitable for industrial production is essential to the wide use of all-solid-state batteries. In this section, a slurry coating process for the construction of all-solid-state batteries is briefly discussed. The construction of sheet-type all-solid-state batteries is laborious, not only from a fundamental science point of
view, but also in terms of processing technology, which requires step-by-step development. Figures 8(a) and 8(b) show optical images of a solid electrolyte slurry and the resulting electrode and electrolyte sheets. The most important requirement in this process is determining a good combination of solid electrolyte, binder, and solvent to enable slurry coating. The binder should have a low resistance, and fine solid electrolyte particles should be used in order to obtain homogeneous solid electrolyte and electrode sheets. At maximum, the size of the largest solid electrolyte particles should be less than half the target thickness of the solid electrolyte and electrode films.

Figure 8(c) shows a cross-sectional SEM image of a sheet-type all-solid-state fuel cell after 10 cycles.64)

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4. Summary and perspective

A comprehensive review of composite electrodes for all-solid-state lithium secondary batteries has been provided. All-solid-state batteries have the strong advantages of high safety, high power, long cycle life, and wide temperature operation. Thus, all-solid-state batteries have received increasing attention, and the number of the papers published in this field has increased ten-fold over the past decade.

Composite electrodes must fulfill a number of criteria, including the minimization of interfacial resistance, the maintenance of good contact between the electrolyte and electrodes, the formation of favorable conducting pathways, and the suppression of mechanical damage. In this review, several effective strategies for producing better electrodes have been demonstrated, mainly using results from our group. The insertion of a buffer layer at the interface between the high-voltage electrode and solid sulfide electrolyte effectively reduces the interfacial resistance. The importance of understanding the mechanical properties of sulfide-based solid electrolyte has also been emphasized. Sulfide-based solid electrolytes such as lithium thiophosphates are easily sintered by simple room temperature pressing. This enables both good contact between the electrode and electrolyte and the formation of effective conducting pathways to be achieved through room-temperature processing.

Further investigation of the influence of the dynamic changes in the electronic and ionic conductivity of the composite electrode, as well as in the electrode performance, is important. The formation of effective contacts between solids has been a major challenge in last decade. In addition to constructing such contacts, the development of new strategies for maintaining such contacts will become much more important.

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