



Progress in solid electrolytes toward realizing solid-state lithium batteries

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HIGHLIGHTS

- Development of solid electrolytes is summarized.
- Sulfide electrolytes have become more conductive than non-aqueous electrolytes.
- Performance has become practical by the electrolytes and unique cathode interface.
- Reducing grain boundary resistance is still a big challenge in oxide systems.

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ABSTRACT

Solid-state lithium batteries have become more important than ever, because their high reliability as well as high energy density meet the requirements for energy storage in many aspects of the coming low carbon society. Solid electrolytes with high ionic conductivities are inevitable for realizing the solid-state lithium batteries, and the studies have been focused mainly on sulfide and oxide-based electrolytes. Sulfide-based solid electrolytes are advantageous to batteries owing to their high ionic conductivities and deformability. Although they show high resistance at the interface to cathode materials, interposing thin films of oxide-based solid electrolytes into the interface has successfully reduced the interfacial resistance. Combination of the highly-conductive sulfide electrolyte and the interface design have made performance of the sulfide-type solid-state batteries comparable or superior to current lithium-ion batteries. On the other hand, oxide-based electrolytes show higher chemical stability than sulfides, which is beneficial for manufacturing process. Although the highest conductivities have reached $10^{-3} \text{ S cm}^{-1}$ also in oxides, practical performance has not been achieved in the oxide system due to the high grain boundary resistance.

1. Introduction

Development of solid-state batteries began around 1950, which was initiated by discovery of fast ionic conduction around ambient temperature in α -AgI [1]. Although several solid-state batteries with silver halides were proposed on the basis of this finding [2], the first solid-state battery that was put into practical use was a lithium system. A battery for a cardiac pacemaker implanted to a patient in 1972 was not only the first commercialized solid-state battery but also the first lithium battery in practical use [3]. This battery is very specific. The developer said that it cannot start a car, run a cell phone, or even power a flashlight. However, it is so reliable that it is implantable to run a pacemaker. Almost half a century later, solid-state batteries have attained high performance [4].

2. Advantages of solid-state batteries

Advantages of solid-state batteries that initiated their research were (1) absence of electrolyte leakage from sealed batteries, (2) absence of problems relating to vaporization of liquid electrolytes, (3) absence of phase transitions at low temperature, and (4) ease of miniaturization and multiple shape factors [5]. On the other hand, different characteristics of solid-state batteries are energizing the research today [6].

2.1. Safety

The biggest topic that energized the research on solid-state batteries is emergence of lithium-ion batteries. Because they use organic-solvent electrolytes, they have never been free from safety issues. Moreover, the safety issues are more serious in large batteries, because the increasing

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battery size increases the amount of combustible electrolyte and lowers heat radiation. Although lithium-ion batteries have been used in portable electronics, such large batteries are strongly required today in order to install in vehicles, smart grids, etc. for realizing a low-carbon society. Therefore, non-flammability of solid electrolytes that provides a fundamental solution to the safety issues is attracting more attention than ever.

2.2. Durability

Durability of current lithium-ion batteries is not enough to meet the requirements for large batteries. For instance, durable life of several years may be enough for consumer use, while 10-year lifetime is necessary for the batteries in vehicles. One of the major factors governing the lifetime is side reactions, e.g. electrolyte decomposition. Lithium-ion batteries generate high cell voltage in order to store high energy by combining highly-oxidizing cathodes and highly-reducing anodes, which tend to decompose the electrolyte electrochemically. On the other hand, solid electrolytes provide high durability to the batteries by suppressing the side reactions. Only lithium ions are mobile in the solid electrolytes for solid-state lithium batteries at room temperature. Because there are no other species that diffuse to and undergo charge transfer at electrode surface, solid electrolytes effectively suppress side reactions to provide high durability to solid-state batteries. In fact, a thin-film battery exhibits very long cycle life [7], and extremely small self-discharge is reported for a bulk-type solid-state battery with a silver-ion conductive solid electrolyte [8].

2.3. Energy density

It may be strange that employment of solid electrolytes increases energy densities, because the materials storing energy are active materials. However, solid electrolytes have some possibilities to increase the energy densities, because they enable us to use electrode materials that increase the theoretical energy densities but do not work stably in liquids electrolytes, for instance. One example is transition-metal oxides, e.g. $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$, that generate high electrode potentials around 5 V vs. Li^+/Li [9]. Although they are expected to raise the cell voltage and thus energy densities, the high voltage cathodes do not work stably in organic solvent electrolytes, because the high potentials lead to oxidative decomposition of the electrolytes. On the other hand, electrolyte decomposition does not proceed continuously in solid electrolytes due to the absence of diffusive reactants, as mentioned above. That is, because solid electrolytes are kinetically stable in a wide potential range [10], high-voltage cathodes become available in solid electrolytes [11].

In addition, even if such high-voltage cathodes are not employed, there is a room for increasing energy density. For example, the theoretical capacity of LiCoO_2 is 274 mAh g^{-1} , when all the lithium ions are available in the electrode reaction. However, practical capacity is limited to half of this value, because extraction of such an amount of lithium ions makes the electrode potential higher than the decomposition potential of the electrolyte as well as destabilize the crystal structure. Solid-state batteries are expected to be free from this limitation.

Another advantage for the high energy density is that solid electrolytes simplify the battery system. Since organic-solvent electrolytes are combustible, lithium-ion batteries should be equipped with competent safeguards. First of all, non-flammability of solid electrolytes will reduce the number of safeguards. Especially, the increase in energy density by simplifying the safeguards will be remarkable in large batteries, because safety issues are serious there. Increasing battery size means increasing amount of combustible substance, which is the electrolyte, and lowers heat radiation.

In addition, solid electrolytes are expected to simplify module structure in large battery systems. For example, battery modules for vehicles should generate high voltage. When the electrolytes are liquid,

tens of cells should be connected in series to generate the high voltage, where corresponding number of battery cases is also necessary. On the other hand, serial connection is achievable in solid systems only by stacking bipolar electrodes and electrolyte layers alternately in a single battery case, which reduces the weight and volume of battery cases to increase the gravimetric and volumetric energy density [12]. Moreover, cooling system is necessary to protect the batteries from overheating. Although it occupies a large volume in the battery module to decrease the volumetric energy density, the cooling system may be eliminated or reduced in volume in solid-state systems.

2.4. Power density

It may be more astonishing that high power density has been expected for solid-state system, because the most serious shortcoming of solid-state batteries has been regarded as their low power density. Because anions as well as lithium ions are mobile in liquid electrolytes, battery operation at high current density brings about severe concentration gradient in the electrolyte, leading to diffusion limitation [13,14]. In contrast, solid-state batteries are unlikely to reach such a situation, because negative charge in solid electrolytes is immobilized on their framework.

In addition, lithium ions are solvated in liquid electrolytes. They should be desolvated before intercalating into the interlayer galleries of active materials; however, the desolvation step needs high activation energy and thus limits the kinetics in electrode reactions [15,16]. Of course, lithium ions intercalate to electrodes without such desolvation steps in solid systems. Because solid-state batteries are free from these limiting processes, they have potential capability in generating higher current drains than liquid systems.

Of course, the potential will not be fulfilled without solid electrolytes that exhibit comparable ionic conductivities to liquid systems. Electric conductivities of non-aqueous electrolytes are of the order of $10^{-2} \text{ S cm}^{-1}$; however, their transport number for lithium ion is less than 0.5 at the highest [17]. Therefore, it can be concluded that the solid electrolytes must have conductivities higher than $10^{-3} \text{ S cm}^{-1}$ to generate power densities comparable to current lithium-ion batteries. Achieving this value in solid electrolytes is the first task for developing solid-state batteries [18]. Various kinds of solid electrolytes have been proposed [19–21], and the ionic conductivity has been increasing gradually, as shown in Fig. 1.

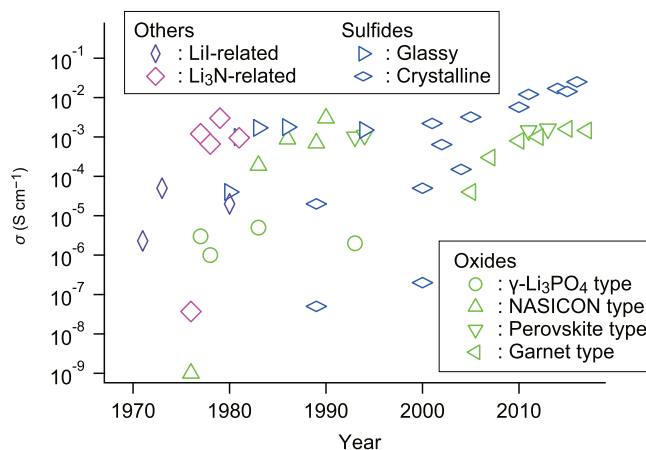


Fig. 1. Ionic conductivities of typical lithium-ion conductive solid electrolytes. The horizontal axis indicate the publication year, when the solid electrolytes were reported.

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