

# Progress and prospective of solid-state lithium batteries

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## Abstract

The development of lithium-ion batteries has energized studies of solid-state batteries, because the non-flammability of their solid electrolytes offers a fundamental solution to safety concerns. Since poor ionic conduction in solid electrolytes is a major drawback in solid-state batteries, such studies have been focused on the enhancement of ionic conductivity. The studies have identified some high performance solid electrolytes; however, some disadvantages have remained hidden until their use in batteries. This paper reviews the development of solid electrolytes and their application to solid-state lithium batteries.

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## 1. Introduction

The development of solid-state batteries started with the discovery of fast ionic conduction in solids. Solid-state batteries have the following potential advantages: absence of electrolyte leakage, absence of problems relating to vaporization of liquid electrolytes, absence of phase transitions at low temperatures improving low-temperature performance and ease of miniaturization [1,2]. In addition, studies revealed that solid-state batteries are highly reliable; that is, they usually show excellent storage stability and very long cycle life.

Battery life is often limited by side reactions, including decomposition of the electrolyte; however, these reactions rarely take place in solid electrolyte systems. Such side reactions are electrochemical, and thus involve the transport of reactants to the electrode surface, where charge transfer takes place, in order to proceed. However, only particular species are mobile in solid electrolytes. For example, only lithium ions diffuse in solid electrolytes that are used in solid-state lithium batteries. This means that there are no species that diffuse to the electrode surface and take part in the side reactions, and thus solid-state batteries generally tend to have a long life.

The study of solid-state batteries, which started in the middle of the 20th century, was prompted by the development of lithium-ion batteries. Lithium-ion batteries have rapidly become widespread since their development [3] because of the following advantages: high voltage, high volumetric and gravimetric energy density, low self-discharge rate, no memory effect, quick charge acceptance, excellent cycle life, and wide operating temperature range [4]. The high energy densities of lithium-ion batteries come from the high cell voltages. However, this is also a drawback, as high voltages do not allow us to use aqueous solutions as the electrolyte, because the cell voltage exceeds the decomposition voltage of water. Therefore, organic solvents are used to dissolve the supporting salts. Because the solvents are flammable substances, they cause safety concerns in lithium-ion batteries.

In addition, recent environmental concerns have increased the demand for large-sized batteries as shown in Fig. 1. Batteries are now expected to be able to power vehicles [5] for the efficient use of energy, and energy storage on a large scale is required to make renewable energy viable [6]. However, the increasing battery size increases the amount of combustible electrolyte. It also worsens the heat radiation, and the batteries tend to easily heat up toward thermal runaway. Therefore, the increasing battery size makes the safety issues more serious [7]. Use of solid electrolytes is expected to be a fundamental solution

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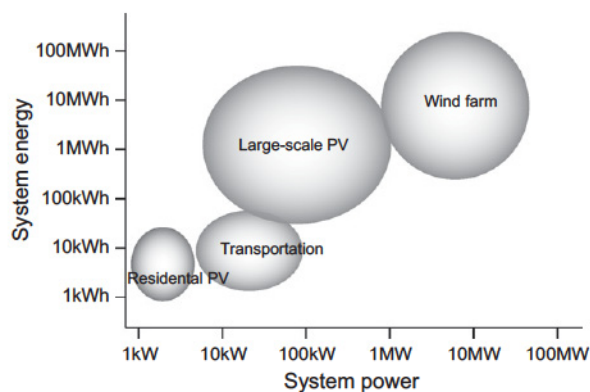


Fig. 1. Requirements of large-sized batteries for a sustainable society.

to the safety issue due to their non-flammability. Moreover, such batteries should have a much longer useful life than consumer ones, and solid-electrolyte systems will also meet these requirements.

On the other hand, disadvantages pointed out were volume changes, electrolyte impedance and discharge product impedance [8]. Because the electrode/electrolyte interface in solid-state batteries is between solid and solid, volume changes of electrode or formation of discharge product destroy the interface. The interface problem does not arise in intercalation electrodes. The use of intercalation chemistry [9] dramatically improved battery performance as demonstrated by lithium-ion batteries, where both electrodes are intercalation compounds. The benefit is significant, particularly in solid-state batteries, because intercalation reactions neither produce reaction products nor cause large volume changes.

The biggest disadvantage of solid-state batteries historically has been their low current drains, or their low power density – and this is still the case today. Since the disadvantage comes from the low ionic conductivity of the solid electrolytes, studies of solid-state batteries have been mainly focused on the development of highly conductive solid electrolytes. As will be described later, the studies have identified many solid electrolytes having high ionic conductivities; however, not all of them have led to high performance of solid-state lithium batteries.

## 2. History of solid electrolytes

Fast ionic conduction in solids around ambient temperature was found for the first time in  $\alpha$ -AgI [10].  $\beta$ - or  $\gamma$ -phase AgI at room temperature is transformed into the  $\alpha$ -phase with higher symmetry at 147 °C, in which  $\text{Ag}^+$  ions conduct as fast as ions in liquids. An attempt to stabilize the fast ion conducting phase has led to  $\text{RbAg}_4\text{I}_5$ , whose ionic conductivity at room temperature is  $0.21 \text{ S cm}^{-1}$  [11]. Analogous material design resulted in a  $\text{Cu}^+$ -ion superconductor,  $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$ , with an ionic conductivity at room temperature of  $0.34 \text{ S cm}^{-1}$  [12], which is the highest conductivity ever observed among solid electrolytes.

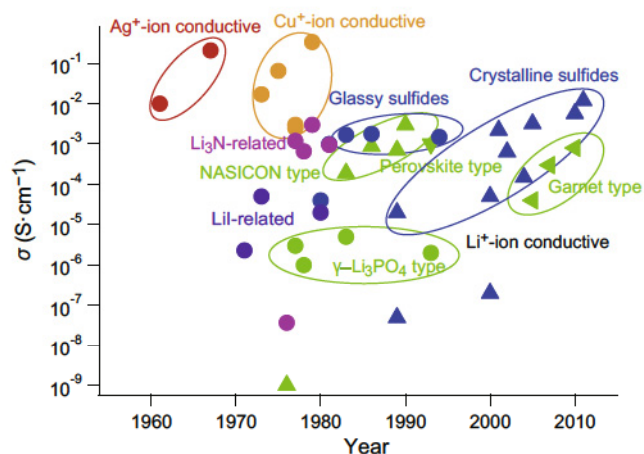


Fig. 2. Progress of solid electrolytes.

Solid-state batteries were also constructed with these fast ionic conductors. A solid-state battery with  $\text{RbAg}_4\text{I}_5$  showed very small self-discharge over 30 years [13], while  $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$  showed highly reversible charge–discharge operation [14] and high exchange current density [15] in combination with a three-dimensional (3-D) intercalation electrode,  $\text{Cu}_x\text{Mo}_6\text{S}_8$ .

On the other hand, lithium-ion-conductive solid electrolytes had been poor ionic conductors, as shown in Fig. 2. However, the discovery of fast lithium ion conduction in  $\text{Li}_3\text{N}$  [16], which had been previously suggested by  $^7\text{Li}$  NMR [17], and commercialization of cardiac pacemakers [18], in which  $\text{LiI}$  is used as the solid electrolyte, encouraged the development.

The maximum electric conductivities of organic-solvent electrolytes are of the order of  $10^{-2} \text{ S cm}^{-1}$ ; however, transport numbers of lithium ions are only less than 0.5. Since lithium-ion batteries are “shuttlecock” or “rocking chair” cells [19], in which lithium ions go back and forth between the cathode and the anode to operate the battery, the rate capability should be governed by the movement of lithium ions. When taking into account that the lithium transport number in solid electrolytes is unity, ionic conductivity of the order of  $10^{-3} \text{ S cm}^{-1}$  will be enough to make the power density of solid-state batteries comparable to that of commercial lithium-ion batteries with liquid electrolytes.

To date, such conductivities have been achieved in several oxides and sulfides; some have given solid-state lithium batteries, and some have not yet. Some solid electrolytes have been used in batteries in spite of their low ionic conductivity. Before overviewing them, it should be mentioned that fast lithium-ionic conduction was recently discovered in  $\text{LiBH}_4$  above 110 °C [20]. It was also reported that the addition of halides suppresses the phase transition to maintain the high conduction state down to room temperature [21], which has given a new class of super ionic conductor.

### 3. Solid electrolytes and solid-state lithium batteries

#### 3.1. Oxide electrolyte systems

##### 3.1.1. $\gamma$ - $\text{Li}_3\text{PO}_4$ -type oxysalts

Some oxysalts, including  $\text{Li}_2\text{SO}_4$ , show fast ionic conduction in their high-temperature phases [22], and many attempts have been made to stabilize the highly conducting phases down to ambient temperature [23]. A systematic study gave various kinds of oxysalts acting as solid electrolytes [24]. It revealed that ionic conduction is enhanced when two kinds of oxysalts are formed into solid solutions, and a fast ionic conductor called LISICON (Li superionic conductor),  $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ , was developed in 1978 [25] on the basis of this study. Studies motivated by the development of LISICON provided many lithium-ion-conducting oxysalts around 1980: one group comprises solid solutions based on  $\text{Li}_4\text{SiO}_4$ , and the other based on  $\gamma$ - $\text{Li}_3\text{PO}_4$ .

Another systematic study on  $x\text{Li}_4\text{M}^{\text{IV}}\text{O}_4-(1-x)\text{Li}_3\text{M}^{\text{V}}\text{O}_4$  systems ( $\text{M}^{\text{IV}} = \text{Ge}, \text{Ti}$  and  $\text{M}^{\text{V}} = \text{As}, \text{V}$ ) [26] also showed the consistent results that the conductivities of the solid solutions always showed maxima at  $x = 0.4$ – $0.6$ . In addition, the study revealed strong correlation between the unit cell volume and the ionic conductivity; conductivity increases and the activation energy for conduction decreases with increasing cell volume at constant  $x$  of 0.5, as demonstrated in Fig. 3. Because the constant  $x$  keeps the carrier concentration constant as supported by the constant pre-exponential factor, it can be concluded that the increasing cell volume increases the mobility of lithium ions. That is, the increasing cell volume will open the conduction channel for the lithium ions and make them more mobile, which lowered the activation energy and increased the conductivity.

##### 3.1.2. Thin-film batteries with $\gamma$ - $\text{Li}_3\text{PO}_4$ -type oxysalts

Since we had to wait for the development of highly conductive solid electrolytes, studies on solid-state lithium batteries began with the thin-film batteries. The thin-film fabrication of the electrolyte layer shortens the distance between the cathode and the anode to reduce the internal resistance to compensate for the low ionic conductivity of solid electrolytes.

The first thin-film battery [27] was constructed with Li and  $\text{TiS}_2$  as anode and cathode, respectively. The electrolyte layer was  $\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$  fabricated into the amorphous state by RF sputtering. Although the conductivity at 25 °C is only  $5 \times 10^{-6} \text{ S cm}^{-1}$ , the thin-film formation makes the battery operable at a current density of  $16 \mu\text{A cm}^{-2}$ .

Thermodynamic instability [28] with lithium metal in  $\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$  was improved in Lipon [29], which is currently the most popular thin-film solid electrolyte. The thin film is deposited by magnetron sputtering of  $\text{Li}_3\text{PO}_4$  under  $\text{N}_2$ -contained atmosphere, which introduces nitrogen into the  $\text{Li}_3\text{PO}_4$  and raises the conductivity from  $7 \times 10^{-8}$  to  $2 \times 10^{-6} \text{ S cm}^{-1}$ . Lipon itself is amorphous; however, it is

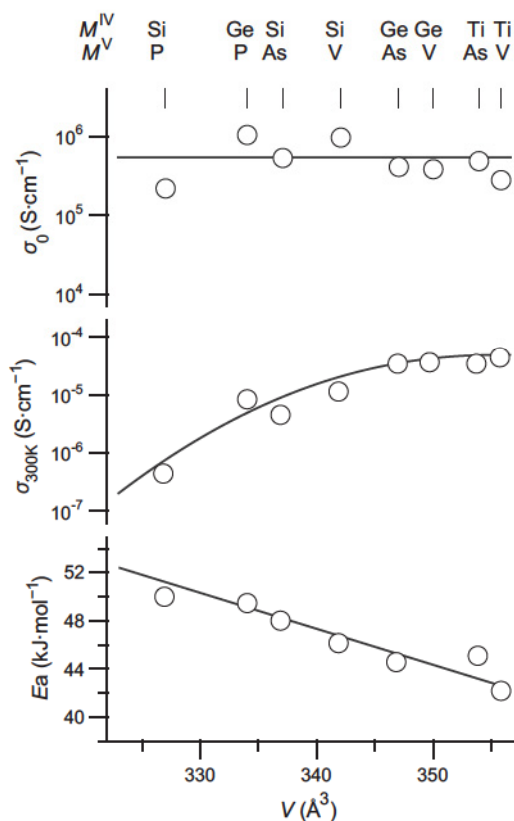


Fig. 3. Ionic conductivity at 300 K,  $\sigma_{300\text{K}}$ ; activation energy for conduction,  $E_a$ ; and pre-exponential factor,  $\sigma_0$ , as a function of unit cell volume for  $0.5\text{Li}_4\text{M}^{\text{IV}}\text{O}_4-0.5\text{Li}_3\text{M}^{\text{V}}\text{O}_4$  system [26].

regarded as a  $\gamma$ - $\text{Li}_3\text{PO}_4$ -type oxysalt from the structure of the crystalline counterpart [30]. Because it also has a wide electrochemical window from 0 to 5.5 V [31], many thin-film batteries have been constructed with this electrolyte so far. Various kinds of electrode materials have been used in the batteries:  $\text{V}_2\text{O}_5$  [29],  $\text{LiMn}_2\text{O}_4$  [32] and  $\text{LiCoO}_2$  [33] have all been used as the cathode, and lithium metal [29,32,33],  $\text{Si}_3\text{N}_4$  [34] and an amorphous Si–Sn oxynitride [35] have been used as the anode. Although the lithium metal anode promises high energy density of the battery, a battery design for a higher energy density was proposed. In “lithium-free batteries” [36], not even lithium metal is used. The anode is formed by in situ plating of metallic lithium on the anode current collector. That is, lithium metal in the anode is supplied from the  $\text{LiCoO}_2$  cathode during the charging process.

Solid-state batteries are inherently highly reliable owing to the single-ionic conduction as described above, and the thin-film batteries also show high reliability. For example, cycling performance observed for a thin-film solid-state battery with a construction of  $\text{Li}/\text{LiCoO}_2$  was remarkable. Results from a cycling test over 30,000 cycles demonstrated excellent cycling performance with the capacity fading ranged from 0.0001% to 0.002% per cycle [37], as shown in Fig. 4.

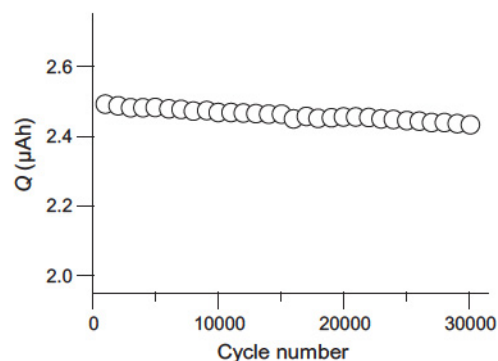


Fig. 4. Cycling properties of a Li/LiCoO<sub>2</sub> thin-film battery with Lipon [37].

### 3.1.3. Highly conductive oxide solid electrolytes

In the oxides and oxysalts, ionic conductivity of the order of  $10^{-3} \text{ S cm}^{-1}$  has been achieved in LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> [38] and Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub> [39].

The crystal structure of LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> is NASICON-type, named after a fast sodium ion conductor, Na<sub>1+x</sub>Zr<sub>2</sub>P<sub>3-x</sub>Si<sub>x</sub>O<sub>12</sub>, called NASICON (Na super ionic conductor) [40]. In NASICON, 3-D skeleton structure is made of ZrO<sub>6</sub> octahedra linked with PO<sub>4</sub> tetrahedra, through which sodium ions can be conducted. Since the open structure was considered to fit fast ionic conduction, many attempts have been made to obtain lithium ion-conducting counterparts. However, simple substitution of Na with Li did not give a good ionic conductor; ionic conductivity of LiZr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> is lower than  $10^{-9} \text{ S cm}^{-1}$ .

Ionic conduction is strongly correlated with the size of the skeleton network in NASICON [41] as well as  $\gamma$ -Li<sub>3</sub>PO<sub>4</sub>-type electrolytes; NaM<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> shows the highest conductivity at M = Zr. On the other hand, since lithium ions are smaller than sodium ions, the skeleton framework consisting of ZrO<sub>6</sub> octahedra is too large for high ionic conductivity. Fig. 5 shows the clear relationship between activation energies for conduction in the bulk and the cell volume of various kinds of NASICON-type phosphates. Conductivity measurements through different kinds of NASICON-type phosphates from LiGe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> to LiHf<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> revealed that activation energy for conduction is minimized at the cell volume of 1310 Å<sup>3</sup>; that is, the ionic conductivity of LiM<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> is the highest at M = Ti [42], which is a smaller tetravalent cation than Zr. Fine tuning of the lattice size and optimization of the carrier concentration in the skeleton framework by aliovalent cation substitution gave a bulk conductivity of  $3 \times 10^{-3} \text{ S cm}^{-1}$  in Li<sub>1.3</sub>Al<sub>0.3</sub>Ti<sub>1.7</sub>(PO<sub>4</sub>)<sub>3</sub> [43].

On the other hand, Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub> with a perovskite structure was found in the studies on dielectricity and ferroelectricity of perovskite-type alkaline-earth titanates (ATiO<sub>3</sub>, A = Ca, Sr, Ba). Cosubstituting of the alkaline earth ion with a trivalent rare earth (La) and a monovalent alkali ion (Li) gives Li<sub>1/2</sub>La<sub>1/2</sub>TiO<sub>3</sub> [44]. A dielectric anomaly [45], increasing capacitance upon the heating, large

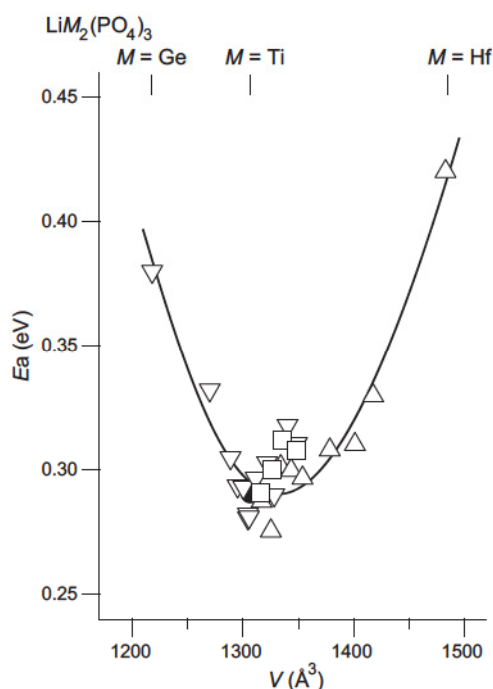


Fig. 5. Activation energy for conduction,  $E_a$ , of LiTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, LiGe<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, LiHf<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, and their derivatives plotted against the unit cell volume,  $V$  [42].

dielectric loss and dielectric relaxation were found in the material, which were attributed to ionic conduction, and the highest conductivity observed in the system was  $1 \times 10^{-3} \text{ S cm}^{-1}$  [39].

Li<sub>3x</sub>La<sub>2/3-x</sub>TiO<sub>3</sub> basically has a simple cubic perovskite structure, where Ti atoms octahedrally coordinated with oxygen atoms occupy the corner of the cube (B-site), and the center of the cube (A-site) is occupied by La<sup>3+</sup> ion, Li<sup>+</sup> ion or left vacant. Although when the La<sup>3+</sup>, the Li<sup>+</sup> ions and the vacancies are randomly distributed over the A-sites, the lattice belongs to cubic symmetry, the system shows many polymorphs [46]. When Li<sub>0.5</sub>La<sub>0.5</sub>TiO<sub>3</sub> is synthesized by heating at 1350 °C and then quenching, the lattice is cubic. On the other hand, when it is slowly cooled, Li<sup>+</sup> ions and La<sup>3+</sup> ions are somewhat ordered to form alternate Li-rich and La-rich planes. The ordering lowers the symmetry from cubic to tetragonal or orthorhombic. Tilting of the TiO<sub>6</sub> octahedra also distorts the cubic lattice to hexagonal symmetry. Conductivity among these polymorphs is mainly governed by two factors: one is bottleneck size, and the other is site percolation.

Lithium ions conduct from an A-site to the neighboring A-site in the perovskite structure through a bottleneck surrounded by four oxygen atoms. Because the oxide ions attract the lithium ions to act as a potential barrier for the conduction, perovskite-type oxides also show clear correlation between the ionic conductivity and the bottleneck size, or the lattice size, as  $\gamma$ -Li<sub>3</sub>PO<sub>4</sub> or NASICON-type electrolytes. That is, the larger the lattice parameter, the higher is the conductivity and the lower is the activation

energy for conduction [47]. Therefore, divalent  $\text{Sr}^{2+}$  ions, which are larger than trivalent cations including  $\text{La}^{3+}$  should give higher conductivity as A-site cation. In fact, Sr-substituted  $[(\text{Li}_{1/2}\text{La}_{1/2})_{1-x}\text{Sr}_x]\text{TiO}_3$  showed a conductivity of  $1.5 \times 10^{-3} \text{ S cm}^{-1}$  [48], which was slightly higher than that in  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ .

Composition influences the conductivity of the perovskite oxides, not only in respect of the carrier concentration. A-sites on the conduction paths are partially occupied by  $\text{La}^{3+}$  ions, which block the migration of lithium ions; therefore, site percolation plays an important role in the ionic conduction [49]. That is, the La content should be low enough to make a group of neighboring lithium ions and vacancies percolate through the system. Sr is preferable to La as the A-site cation in terms of the lattice dimensions as described above; however, the divalent state increases the Sr content to increase the percolation threshold.

As described above, ionic conductivity of oxides has become  $10^{-3} \text{ S cm}^{-1}$ ; however, high conductivity alone is not enough for battery application. These solid electrolytes have two major disadvantages for the application to solid-state batteries. The first one originates from the presence of Ti. Ti in these solid electrolytes is tetravalent, or  $3d^0$  state; that is, the solid electrolytes do not have conducting electrons. However, they are easily reduced;  $\text{Ti}^{4+}$  ions in  $\text{LiTi}_2(\text{PO}_4)_3$  and  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  are reduced to  $\text{Ti}^{3+}$  below 2.5 V [50] and 1.5 V [51], respectively. Therefore, when they come into contact with low-potential anodes including Li metal or  $\text{C}_6\text{Li}$ , the reduction injects electrons to the electrolytes.

The second disadvantage is that the grain boundary resistance in these solid electrolytes is generally very high [52,39]; that is, although the intragrain diffusion of lithium ions is fast, movement between the grains limits the current drain. Of course, heat treatment at high temperatures reduces the grain boundary resistance to some extent; however, another serious problem arises at the electrode/electrolyte interface. The solid electrolytes have to be in contact to active materials in batteries, and thus the high-temperature treatment to promote the sintering also induces the interdiffusion between the materials. Such reactions between the active material and the solid electrolyte take place to form impurity phases at the interface to increase the electrode resistance [53].

Because the solid electrolyte alone can be sintered at high temperatures, low-temperature formation of the electrodes will solve the problem. One example is the formation of electrode layers by evaporation process [54], and another is in situ formation of electrodes [55,56], in which parts of the electrolyte in contact with the current collectors are electrochemically converted to electroactive materials at room temperature.

### 3.1.4. Garnet-type solid electrolytes

The most-recently developed oxide electrolytes have garnet-type structure [57]. The conductivity observed for

$\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) was of the order of  $10^{-6} \text{ S cm}^{-1}$ ; it increased to  $4 \times 10^{-5}$  in  $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$  [58],  $5 \times 10^{-4}$  in  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  [59] and finally  $8 \times 10^{-4} \text{ S cm}^{-1}$  in  $\text{Li}_{6.75}\text{La}_3(\text{Zr}_{1.75}\text{Nb}_{0.25})\text{O}_{12}$  [60]. The conductivities of the garnet-type oxides are still lower than that of NASICON-type phosphates and perovskite-type oxides, while they show the following advantages: one is a small grain boundary resistance, and the other is stability against lithium metal.

In NASICON-type phosphates and perovskite-type oxides, contribution of grain boundaries to the resistance is much larger than that of the bulks, even at sintering temperatures higher than  $1200^\circ\text{C}$ . On the other hand, the contribution of the grain boundaries is in the same order of or less than that of the bulk in garnet-type  $\text{Li}_6\text{A}\text{La}_2\text{Ta}_2\text{O}_{12}$  ( $\text{A} = \text{Sr}, \text{Ba}$ ), even when the samples were sintered at  $900^\circ\text{C}$  [58].

The second advantage of garnet-type oxides is compatibility with lithium anode. Although NASICON-type phosphates and perovskite-type oxides are unstable to electrochemical reduction,  $\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$  was reported to be stable against lithium metal. No reaction was observed, even when it was immersed in molten lithium [58]. Moreover, the electrochemical window of  $\text{Li}_{6.75}\text{La}_3(\text{Zr}_{1.75}\text{Nb}_{0.25})\text{O}_{12}$  was demonstrated to be very wide: it is stable from 0 to 9 V vs.  $\text{Li}^+/\text{Li}$  [60].

## 3.2. Sulfide electrolyte systems

### 3.2.1. Sulfide solid electrolytes

Studies on ionic conduction in sulfides started in glasses [61]. Because the high polarizability of sulfide ions weakens the interaction between the anions and the lithium ions, sulfides inherently tend to show fast ionic conduction. In fact, the highest conductivities observed among sulfide glasses, e.g.  $\text{LiI-Li}_2\text{S-P}_2\text{S}_5$  [62] and  $\text{LiI-Li}_2\text{S-B}_2\text{S}_3$  [63], were already of the order of  $10^{-3} \text{ S cm}^{-1}$  in the early 1980s, as listed in Table 1. Besides the high ionic conductivity, sulfide electrolytes have the following advantages. The first advantage is that they show high ionic conductivity without presence of transition metal elements that narrow the electrochemical window. Another advantage is the low grain-boundary resistance.

Contrary to oxide or oxysalt solid electrolytes, sulfide solid electrolytes show small grain boundary resistance even in a cold-pressed pellet [64]. That is, the sintering process is not necessary to connect ionic path between the particles. This feature is convenient for constructing bulk-type batteries, because the batteries can be assembled by pressing powders of batteries materials into a three-layered structure of anode/electrolyte/cathode.

Because sulfide systems have advantages for fabricating bulk-type solid-state batteries, the development of lithium-ion batteries triggered many studies on sulfide electrolytes in 1990s. Various kinds of sulfide glasses doped with oxysalts were developed [65,66], and in the 21st century, con-

Table 1  
Conductivities at room temperature of sulfide solid electrolytes.

| Solid electrolyte                                                               | Conductivity (S cm <sup>-1</sup> ) | Preparation method              | Reference |
|---------------------------------------------------------------------------------|------------------------------------|---------------------------------|-----------|
| <i>Glassy materials</i>                                                         |                                    |                                 |           |
| 0.5Li <sub>2</sub> S–0.5 GeS <sub>2</sub>                                       | 4.0 × 10 <sup>-5</sup>             | Water quenching                 | [61]      |
| 0.66Li <sub>2</sub> S–0.33P <sub>2</sub> S <sub>5</sub>                         | 10 <sup>-4</sup>                   | Water quenching                 | [62]      |
| 0.45LiI–0.37Li <sub>2</sub> S–0.18P <sub>2</sub> S <sub>5</sub>                 | 1.7 × 10 <sup>-3</sup>             | Water quenching                 | [62]      |
| Li <sub>2</sub> S–B <sub>2</sub> S <sub>3</sub>                                 | 10 <sup>-4</sup>                   | Water quenching                 | [63]      |
| 0.44LiI–0.30Li <sub>2</sub> S–0.26B <sub>2</sub> S <sub>3</sub>                 | 1.7 × 10 <sup>-3</sup>             | Water quenching                 | [63]      |
| 0.5Li <sub>2</sub> S–0.5SiS <sub>2</sub>                                        | 1.2 × 10 <sup>-4</sup>             | Water quenching                 | [76]      |
| 0.3LiCl–0.35Li <sub>2</sub> S–0.35SiS <sub>2</sub>                              | 2.7 × 10 <sup>-4</sup>             | Water quenching                 | [76]      |
| 0.40LiI–0.36Li <sub>2</sub> S–0.24SiS <sub>2</sub>                              | 1.8 × 10 <sup>-3</sup>             | Liquid N <sub>2</sub> quenching | [73]      |
| 0.6Li <sub>2</sub> S–0.4SiS <sub>2</sub>                                        | 5.0 × 10 <sup>-4</sup>             | Twin-roller quenching           | [74]      |
| 0.3LiI–0.42Li <sub>2</sub> S–0.28SiS <sub>2</sub>                               | 8.2 × 10 <sup>-4</sup>             | Twin-roller quenching           | [74]      |
| 0.01Li <sub>3</sub> PO <sub>4</sub> –0.63Li <sub>2</sub> S–0.36SiS <sub>2</sub> | 1.5 × 10 <sup>-3</sup>             | Twin-roller quenching           | [65]      |
| 0.6Li <sub>2</sub> S–0.4SiS <sub>2</sub>                                        | 1.5 × 10 <sup>-4</sup>             | Mechanical milling              | [75]      |
| <i>Crystalline materials</i>                                                    |                                    |                                 |           |
| Li <sub>3.25</sub> Ge <sub>0.25</sub> P <sub>0.75</sub> S <sub>4</sub>          | 2.2 × 10 <sup>-3</sup>             | Solid-state reaction            | [69]      |
| 70Li <sub>2</sub> S–30P <sub>2</sub> S <sub>5</sub>                             | 3.2 × 10 <sup>-3</sup>             | Glass–ceramic                   | [71]      |
| Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub>                               | 1.2 × 10 <sup>-2</sup>             | Solid-state reaction            | [72]      |

ductivities of the order of 10<sup>-3</sup> S cm<sup>-1</sup> have been achieved also in crystalline sulfides.

Li<sub>4</sub>GeS<sub>4</sub> was found to be a solid electrolyte in 2000 [67]. Although the conductivity is only 2.0 × 10<sup>-7</sup> S cm<sup>-1</sup>, cation substitution in this material has given a lot of solid solutions. They are categorized into thio-LISICON family, because they have γ-Li<sub>3</sub>PO<sub>4</sub>-type structure oxysalts typified by LISICON. Aliovalent substitution introducing lithium-ion vacancies or interstitial lithium ions increased the conductivity [68], and the conductivity has reached 2.2 × 10<sup>-3</sup> S cm<sup>-1</sup> at a composition of Li<sub>3.25</sub>Ge<sub>0.25</sub>P<sub>0.75</sub>S<sub>4</sub> [69].

Another high conductivity was found in glass ceramic. Fast ion-conducting phase is precipitated as a primary crystal in the crystallization process of a supercooled Ag<sup>+</sup>-ion-conducting glass [70]. A lithium-ion-conducting sulfide glass also showed a similar phenomenon, although the mechanism may be different. Precipitation of a metastable crystalline phase increases the conductivity from 5.4 × 10<sup>-5</sup> S cm<sup>-1</sup> in 70Li<sub>2</sub>S–30P<sub>2</sub>S<sub>5</sub> glass to 3.2 × 10<sup>-3</sup> S cm<sup>-1</sup> with a very low activation energy of conduction of 12 kJ mol<sup>-1</sup> in the glass–ceramic phase [71].

Very recently, the highest ionic conductivity among lithium-ion conductive solid electrolytes of 1.2 × 10<sup>-2</sup> S cm<sup>-1</sup> was observed in Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> [72]. Although the paper tells that electric conductivity is comparable to that of organic-solvent liquid electrolyte, lithium-ionic conductivity is much higher, when taking into account that the transport number of lithium ion is unity.

Improvements have been made not only to the conductivity; synthesis methods have also been improved during the development. The materials should be heated in a sealed container for the synthesis because of the high vapor pressure of P<sub>2</sub>S<sub>5</sub> or B<sub>2</sub>S<sub>3</sub> at high temperatures. Syntheses under ambient pressure had become possible in LiI–Li<sub>2</sub>S–SiS<sub>2</sub> glasses [73] owing to low vapor pressure of SiS<sub>2</sub>. Since the starting materials do not need to be sealed, a twin-roller

method is available for the quenching [74]. The fast cooling rate in the twin-roller method allows glass-formation at high lithium contents, which is promising for high ionic conductivity due to the high carrier concentration. Moreover, preparation of the glasses was reported to be possible by mechanical milling [75]. That is, even heating process is not necessary, which is beneficial in mass-production of the solid electrolytes.

### 3.2.2. Solid-state lithium batteries with sulfide electrolytes

One of the main objectives on the development of solid electrolytes other than increasing conductivity is to use electrode materials giving high energy densities. The first sulfide solid electrolytes that showed high ionic conductivities are glasses made from P<sub>2</sub>S<sub>5</sub>, B<sub>2</sub>S<sub>3</sub>, or SiS<sub>2</sub> as a glass network former and Li<sub>2</sub>S as a glass modifier to provide ionic conduction to the glass networks. Although the ionic conductivities of the quasi-binary glasses are of the order of 10<sup>-4</sup> S cm<sup>-1</sup>, doping of lithium halides enhances the conductivity [76]; especially LiI increases the conductivity to the order of 10<sup>-3</sup> S cm<sup>-1</sup> [62,63,73]. However, the iodide ions limit the oxidation potential of the glasses below 3 V vs. Li<sup>+</sup>/Li [62]. This problem became critical in the 1990s, because 4 V cathodes [77–79] became mainstream in lithium batteries. In the mid-1990s, the addition of oxysalts was found to allow elimination of LiI while keeping the conductivity of the order of 10<sup>-3</sup> S cm<sup>-1</sup> [65], which enabled the use of 4 V cathodes in sulfide solid electrolyte systems [80,81].

The 4 V cathodes enhanced the energy density of the solid-state battery to practical level, and many studies on similar bulk-type batteries followed [82,83]. These batteries showed excellent performance besides the high energy densities. Self-discharge is negligible, even at a storage temperature 60 °C [84], and cycling performance is also excellent, as shown in Fig. 6 [85]. These features should be attributed to single-ion conduction suppressing side reaction.

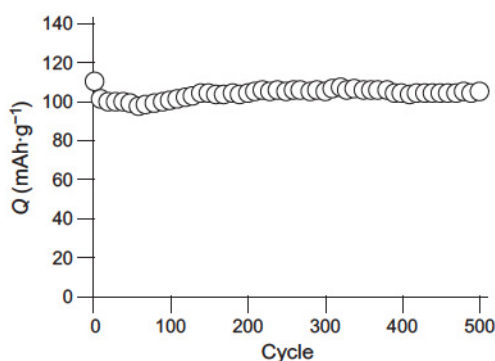


Fig. 6. Change in the discharge capacity of a solid-state lithium battery on cycling [85].

These batteries use lithium alloys as the anode, although they lower the cell voltage compared with graphite. Detailed investigation on the compatibility of different solid electrolytes with graphite anode [86] gave the first solid-state “lithium-ion” battery in 2003, i.e. a solid-state lithium battery with a graphite anode and a  $\text{LiCoO}_2$  cathode, where energy density of solid-state batteries has become comparable to that of commercial lithium-ion batteries [87].

Two kinds of solid electrolytes were used in the solid-state batteries, because there were no sulfide solid electrolytes having stability against both a 4 V cathode and a graphite anode, as well as conductivity of the order of  $10^{-3} \text{ S cm}^{-1}$ . However, the two-tiered electrolyte layer separating the cathode and anode increases the volumetric fraction of the electrolyte and thus decreases the energy density. Development of a solid electrolyte having stability against both of the electrodes in addition to a high conductivity was the remaining problem. The problem was also solved by  $\text{Li}_2\text{S}$ – $\text{P}_2\text{S}_5$  glass ceramics [71], which allows us to construct lithium-ion-type solid-state batteries without using two kinds of solid electrolytes [88].

The successful construction of solid-state lithium-ion batteries made us feel that the development of sulfide solid electrolytes was almost finished, even though higher conductivity is preferable. However, a drawback had still been hidden, which was that the power densities of solid-state lithium batteries were not comparable with that of organic-solvent liquid electrolytes in spite of the high ionic conductivities.

### 3.2.3. Nanoionics in sulfide solid electrolyte systems

High polarizability of sulfide ions is beneficial for high ionic conductivity in sulfide solid electrolytes; however, the weak attraction to lithium ions is turned into a disadvantage, when the sulfide electrolytes are combined with high-voltage cathodes, including  $\text{Li}_{1-x}\text{CoO}_2$ .

When graphite anode and  $\text{LiCoO}_2$  cathode are employed in a solid-state lithium battery with a sulfide electrolyte with a conductivity of  $10^{-3} \text{ S cm}^{-1}$ , the rate-determining step is no longer in the electrolyte; high resis-

tance is found at the  $\text{LiCoO}_2$ /sulfide electrolyte interface [89]. In other words, because the resistance is rate-determining, the power density is low, no matter how high the conductivity of the sulfide solid electrolyte is [86,88]. Ionic conductors often show anomalous ionic conduction at the interface to different kinds of ionic conductor or at the surface; such phenomena are called “nanoionics” [90]. The stage of nanoionics is a space-charge layer formed at the interface between the two kinds of ionic conductors, which is generated by the difference in the electrochemical potential of the mobile ion between the ionic conductors. Because lithium batteries generate high cell voltage by combinations of anodes and cathodes with quite different electrochemical potentials, nanoionics tends to be prominent there.

When a sulfide solid electrolyte is in contact with a high-voltage cathode including  $\text{Li}_{1-x}\text{CoO}_2$ , lithium-ion concentration on the electrolyte side at the interface should be lowered in order to make the interface reach equilibrium, because the sulfide ions in the solid electrolyte attract lithium ions weakly. That is, the high potential of the cathode forms a lithium-depleted layer on the electrolyte side of the interface, which is highly resistive because of the absence of the charge carrier, and is thus rate-determining. Therefore, in order to increase the power densities of the solid-state

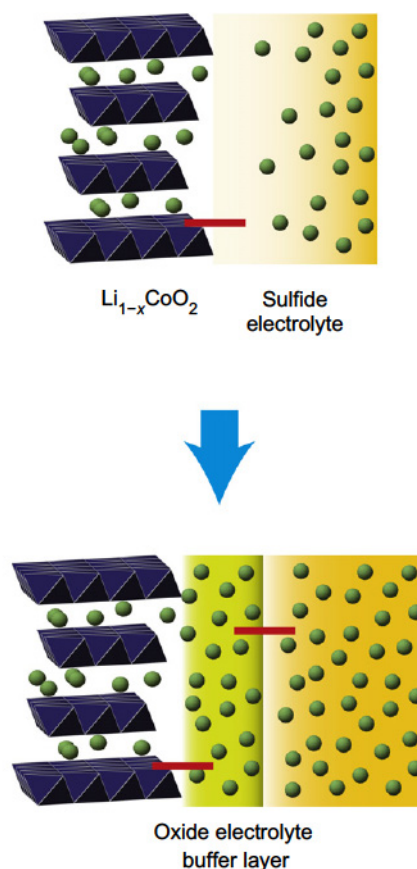


Fig. 7. Schematic representation for the reduction mechanism of electrode resistance at a 4 V cathode/sulfide electrolyte interface.

lithium batteries, the formation of the lithium-depleted layer should be suppressed.

Because the high voltage of the cathode causes the lithium depletion, the sulfide electrolytes must be electronically shielded from the high-voltage cathode for the suppression. That is, when an electronically insulating layer is interposed at the interface, it acts as a buffer layer against the lithium depletion. Moreover, the buffer layer should have ionic conduction. Finally, anions in the buffer layer should strongly attract lithium ions, or the high potential of the cathode depletes the lithium ions in the buffer layer; that is, the buffer layer should be, for instance, an oxide. Consequently, when the surface of the cathode material is covered with an oxide solid electrolyte, it will suppress the lithium depletion at the interface, as schematically illustrated in Fig. 7, and reduce the electrode resistance to enhance the power density of the solid-state battery [91]. In fact, when the surface of the  $\text{LiCoO}_2$ -cathode particle is coated with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  as the oxide electrolyte buffer layer, it dramatically increases the power density to be comparable to that of commercial lithium-ion batteries with organic-solvent liquid electrolytes [92], as shown in Fig. 8b.

Such improved power density has been observed also in various systems with different kinds of buffer layer materials [89,93–97] or different kinds of high-voltage oxide cathodes [91,98–100] as summarized in Table 2. For example,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -coated  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  showed excellent rate capability, which delivered a high capacity of  $110 \text{ mAh g}^{-1}$  at a high-rate discharge of  $10 \text{ mA cm}^{-2}$  [100].

The buffer layers in these studies were formed by the sol-gel or evaporation method. It should be as thin as possible, or resistance of the buffer layer determines the rate capability due to poor ionic conduction in oxide solid electrolytes. However, the formation of a very thin and uniform layer on the cathode particles needs careful control, which does not fit mass production. In order to avoid the difficulty, i.e. in order to cover the surface without increasing the thickness, it is better to wrap the  $\text{LiCoO}_2$  particles with a sheet-like oxide solid electrolyte. An example of the sheet-like electrolyte is  $\text{TaO}_3$  nanosheet [101]. A study revealed that the nanosheet plays a role of the buffer layer at the interface as a self-standing oxide solid electrolyte layer with a thickness of 1 nm [102].

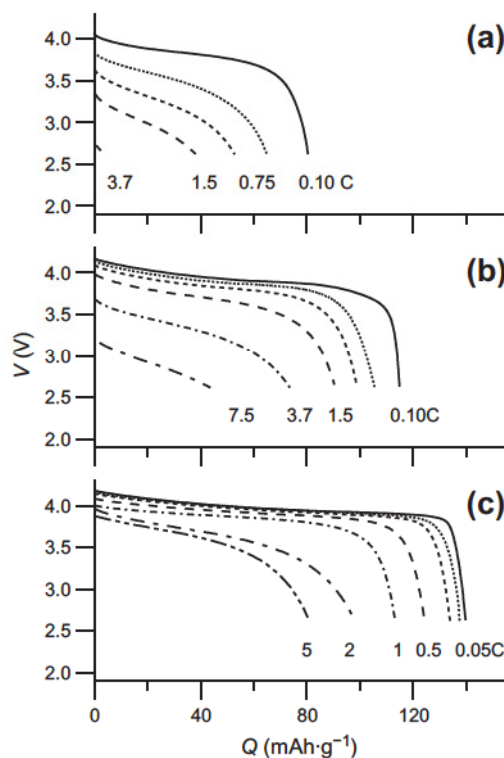


Fig. 8. Comparison between the rate capability of  $\text{LiCoO}_2$  electrodes in a  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$  solid electrolyte. Rate capability of  $\text{LiCoO}_2$  without modification,  $\text{LiCoO}_2$  coated with  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  buffer layer [92], and  $\text{LiAl}_{0.08}\text{Co}_{0.92}\text{O}_2$  with self-organized core-shell structure [103] is shown in (a), (b) and (c), respectively.

On the other hand, a simple and low-cost way to construct the high-power interface was proposed. In Al-substituted  $\text{LiCoO}_2$ , the Al-enriched layer is automatically formed on the particle surface. Because the  $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$  is basically an electron-lithium-ion mixed conductor, the increasing Al content lowers the electronic conductivity to make the Al-enriched surface layer an oxide solid electrolyte. That is, the surface layer acts as a self-formed buffer layer, and thus the  $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$  shows high rate capability without any surface modifications [103], as compared in Fig. 8c.

Surface coating in solid-state lithium batteries has been reported to have other advantages as well. A coating layer was reported to suppress the interdiffusion of the elements

Table 2  
Surface-coating enhancing the rate-capability of oxide cathodes in sulfide solid electrolytes.

| Buffer layer                                     | Oxide cathode                                                 | Sulfide solid electrolyte                                            | Current density ( $\text{mA cm}^{-2}$ ) | Electrode resistance ( $\Omega$ ) | Reference |
|--------------------------------------------------|---------------------------------------------------------------|----------------------------------------------------------------------|-----------------------------------------|-----------------------------------|-----------|
| $\text{Li}_4\text{Ti}_5\text{O}_{12}$            | $\text{LiCoO}_2$                                              | $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$          | 10                                      | 44                                | [92]      |
| $\text{LiNbO}_3$                                 | $\text{LiCoO}_2$                                              | $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$          | 10                                      | <20                               | [93]      |
| $\text{Li}_2\text{O}-\text{SiO}_2$               | $\text{LiCoO}_2$                                              | $80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$                       | 6.4                                     | 160                               | [94]      |
| $\text{LiTaO}_3$                                 | $\text{LiCoO}_2$                                              | $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$          | Not shown                               | <20                               | [89]      |
| $\text{Li}_2\text{Ti}_2\text{O}_5$               | $\text{LiCoO}_2$                                              | $80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$                       | 6.4                                     | 100                               | [96]      |
| $\text{Li}_4\text{SiO}_4-\text{Li}_3\text{PO}_4$ | $\text{LiCoO}_2$                                              | $80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$                       | 6.4                                     | 48                                | [97]      |
| $\text{Li}_4\text{Ti}_5\text{O}_{12}$            | $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$   | $80\text{Li}_2\text{S}-19\text{P}_2\text{S}_5-1\text{P}_2\text{O}_5$ | 3.8                                     | 100                               | [98]      |
| $\text{Li}_4\text{Ti}_5\text{O}_{12}$            | $\text{LiMn}_2\text{O}_4$                                     | $80\text{Li}_2\text{S}-20\text{P}_2\text{S}_5$                       | 2.6                                     | 100                               | [99]      |
| $\text{Li}_4\text{Ti}_5\text{O}_{12}$            | $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ | $70\text{Li}_2\text{S}-30\text{P}_2\text{S}_5$                       | 10                                      | 48                                | [100]     |

between the cathode and solid electrolyte materials that increases the electrode resistance [95]. In addition, it was demonstrated that coating of a sulfide solid electrolyte onto the cathode particles enlarges the electrode/electrolyte interface area to enhance the electrode performance [104].

#### 4. Conclusions and future perspectives

Studies on solid-state lithium batteries have been focused on achieving a battery performance comparable to that of liquid systems and produce fruitful results, as described above. On the other hand, much higher energy densities are required for batteries, for example, to realize electric vehicles without internal combustion engines, which have never been achieved even in liquid electrolyte systems. Interestingly, although energy densities of rechargeable batteries are mainly governed by the electrode materials, solid electrolytes are expected to play an important role in developing high-energy batteries. One reason for the expectation is that solid electrolytes are nonflammable and thus solve the safety concern of lithium-ion batteries. They will simplify the safety mechanism and decrease the number of the safeguards that have been lowering the energy density. A second reason is the possibility of simplified battery structure, especially in the case of constructing a cell stack. When the electrolyte is liquid, we have to use individual containers for each cell and connect them to construct a stack. On the other hand, all the cells can be set in a container, which reduces the weight of the battery case. The third reason is the possibility of new electrode materials.

It is easy to find the combinations of the cathode and anode giving a high energy density, because the capacity and cell voltage for calculating the energy density are easily derived from Faraday's law and the Nernst equation, respectively. In other words, the combinations are already known; however, they have not been put into practical use. Solid electrolytes are anticipated to make these electrode materials available.

A noteworthy feature of solid electrolytes is their single-ion conduction. It has a beneficial effect for suppressing

side reactions to realize long battery life, as described above. In addition, continuous decomposition of the electrolyte hardly takes place in solid systems, because reactants are not supplied to the electrode surface. It allows us to use high-voltage cathodes including  $\text{LiCoPO}_4$  [105] and  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  ( $M = \text{Co}$  or  $\text{Fe}$ ) [106]. Even  $\text{LiCoO}_2$  delivers a high capacity in solid electrolytes. Because the electrode potential of  $\text{Li}_{1-x}\text{CoO}_2$  is very close to oxidative decomposition potentials of organic-solvent liquid electrolytes [107], it is difficult to charge it up to a high potential. On the other hand, solid electrolytes permit it:  $\text{LiCoO}_2$  delivers [108] a high capacity of  $170 \text{ mAh g}^{-1}$  without capacity fading in Lipon, when it is charged up to 4.4 V, and a similar capacity was also observed in a sulfide solid electrolyte [109].

Contrary to the use of the high-voltage cathodes, high-capacity electrode materials are considered to be available in solid electrolytes. Electrode reactions of the high-capacity electrodes are not based on intercalation chemistry, because the host structure delimits the capacity in intercalation compounds. However, the absence of rigid host structure results in morphology changes in the electrode on cycling, which cause rapid capacity fading and must be overcome for the practical use of the high capacity materials. On the other hand, single-ion conduction in solid electrolytes means the absence of mass transfer causing the morphology changes, and thus solid electrolytes may improve the capacity fading and pave the way to the use of the high capacity materials. Typical examples are summarized in Table 3.

High packing density of lithium in alloys is a significant advantage to the energy density. However, volume changes related with alloying/dealloying reactions in liquid electrolytes cause morphology changes, including pulverization and rapid failure of lithium-alloy anodes [110]. Such morphology changes seem suppressed in solid electrolytes, because capacity fading for alloy anodes is very small in solid electrolytes [81,111].

Lithium alloy anodes formed from convertible oxides [112] were also proposed to overcome the disadvantages of alloy anodes in liquid electrolytes. Reduction of particle

Table 3  
High capacity anodes in solid electrolytes.

| Anode material                                 | Solid electrolyte                                               | Capacity ( $\text{mAh g}^{-1}$ ) | Potential (V vs. $\text{Li}^+/\text{Li}$ ) | Reference |
|------------------------------------------------|-----------------------------------------------------------------|----------------------------------|--------------------------------------------|-----------|
| <i>Alloy anodes</i>                            |                                                                 |                                  |                                            |           |
| In                                             | $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$ glass | 180                              | 0.6                                        | [81]      |
| $\text{Ge}_x\text{Si}_{1-x}$                   | $\text{Li}_2\text{S}-\text{SiS}_2$ glass                        | 190                              | 0.5                                        | [111]     |
| <i>Alloy anodes from convertible compounds</i> |                                                                 |                                  |                                            |           |
| $\text{SnO}-\text{B}_2\text{O}_3$              | $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{BO}_3$ glass | 650                              | 0.5                                        | [115]     |
| $\text{SnS}-\text{P}_2\text{S}_5$              | $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass ceramics       | 600                              | 0.5                                        | [116]     |
| <i>Conversion anodes</i>                       |                                                                 |                                  |                                            |           |
| $\text{Li}_2\text{FeS}_2$                      | $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$ glass | 400                              | 1.6                                        | [119]     |
| FeS                                            | $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$     | 450                              | 1.6                                        | [120]     |
| $\text{NiP}_2$                                 | $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass ceramic        | 600                              | 0.5                                        | [121]     |
| $\text{Li}_2\text{SiS}_3$                      | $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ glass ceramic        | 1200                             | 1.5                                        | [122]     |

size is known to improve the cyclability of alloy electrodes. In the case of amorphous tin-based composite oxide [113], SnO in the composite oxide is converted to Sn by in situ reduction in the electrode reaction, which is finely distributed within the B–P–Al oxide matrix and shows the alloying reaction. Since the glassy matrix acts as a network to stabilize the composite microstructure, reversibility of the alloying reaction is improved in the composite oxide [114]. Similar convertible systems have been tested in solid electrolytes [115,116].

Another high capacity anode suffering from rapid capacity fading is the conversion electrode, which utilizes the redox reactions between the transition metal and the corresponding transition metal oxide [117]. Although the particles should be kept to a nanosize, charge–discharge cycling aggregates them into large particles to cause the capacity fading [118]. Solid electrolytes do not allow the aggregation to make the conversion reactions stable [119–121]. Moreover, because both alloying and conversion reactions are stable in solid electrolytes, much higher capacity can be expected in an electrode, where the two reactions successively take place [122].

Single-ion conduction in solid electrolytes also opens doors for other high-capacity electrode materials. For example, Li/O<sub>2</sub> and Li/S batteries are believed to be options going beyond the horizon of Li-ion batteries to meet the long-term needs of society [123]. Single-ion conduction is beneficial for realizing these battery systems.

The theoretical capacity of sulfur cathode is 1670 mAh g<sup>−1</sup>, which is ten times larger than the effective value of LiCoO<sub>2</sub>. When the batteries start to be operated, the sulfur is reduced to form polysulfides as intermediates. Because the polysulfides are soluble in organic-solvent liquid electrolytes [124], performance of Li/S batteries is poor; for instance, they show rapid capacity fading. The single-ion conduction means that active materials are never dissolved into the electrolyte. Preliminary studies have shown that the use of solid electrolytes improves the cyclability of sulfur cathodes [125–127], and a full cell with a construction of Li/S was also constructed with Li<sub>2</sub>S–P<sub>2</sub>S<sub>5</sub> as the solid electrolyte [128]. In addition, the insulating nature of sulfur limits the rate capability. Formation of nano-composites with carbon materials [129,130] and employment of spark-plasma-sintering [131] have been proposed in order to improve the poor kinetics.

Lithium–air batteries also require solid electrolytes. Needless to say, the lithium anode must be sealed from ambient atmosphere, while the air cathode must be in contact with it. When the electrolyte is liquid, water molecules taken into the batteries through the cathode from humid atmosphere diffuse to and react with the lithium anode. Solid electrolytes are expected to overcome the problem as lithium-ion-conducting membranes in lithium–air batteries, which allow lithium ions to diffuse but block water molecules [132–134].

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