



Interfaces of Solid Electrolytes: Fundamentals and Applications

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Abstract | All solid-state batteries are candidates for the next-generation batteries owing to their potentially high safety, high reliability, and high energy density. In this review, first, the recent development of ASSBs is briefly summarised by showing both their advantages and shortcomings. Then, the interfaces of solid electrolytes, one of key factors of ASSBs, are discussed with some experimental results.

1 Introduction

1.1 Energy storage systems

“Energy” is one of the key global issues troubling the world this century, a widely shared concern. R. E. Smalley, a Nobel Laureate, considers the availability of cheap and clean energy as the number one constraint in the 21st century.¹ Although fossil fuels still dominate the world, the importance of renewable energies is increasing, not only because of the possible exhaustion of the fossil fuels but also due to their environmental impact, such as pollution of air, water and soil, and global warming. Solar and wind energies are two major renewable energies, but their instability limits their application to large-scale grid systems. To overcome their fluctuations, large-scale energy storage systems have been developed. Simultaneously, electric vehicles (EVs) are also being intensively developed all over the world to improve energy efficiency and to reduce emission gases, including CO₂ (if the electricity is generated from renewable energies). These systems require large-scale energy storage systems that exhibit high **energy density** (based on both weight and volume), high **power density** (based on both weight and volume), high reliability (or long life), high safety, and low cost. Lithium ion batteries (LIBs), which are widely used in portable electronic devices, are used in current electric vehicles. However, it is difficult to replace the internal-combustion engines with the current LIBs because of low energy density, low reliability, low safety and high cost.

1.2 Next-generation batteries

A LIB basically consists of a cathode, an anode and an electrolyte. Cathode-active materials are

transition metal oxides containing lithium ions, such as LiCoO₂, LiMn₂O₄, LiFePO₄, and so on. On the other hand, carbonaceous materials are widely used as anodes. Electrolyte is a solution of Li salts (LiPF₆, etc.) in organic solvents such as carbonates (ethylene carbonate, dimethylcarbonate), ethers (1,2-dimethoxyethane) and their mixtures. Energy density of LIBs is determined by the amount (i.e., capacity) of Li ion that can be extracted from the cathodes and inserted into the anodes, for which exploration of high-capacity materials is required. As for anode, Li metal may be an ultimate anode with highest capacity. When the Li anodes are charged, the deposited Li grows dendritically, which may cause internal short circuit in the cell. In addition, organic solvent-based electrolytes are flammable, with possible serious hazards of fire and explosion, especially in large-scale energy storage systems.

To overcome these constraints in LIBs, new types of batteries have been proposed with a different mechanism. For example, Li-sulfur batteries employ Li metal anodes and S cathodes, which exhibit very high capacity. Li-air batteries, which use oxygen as cathode, are likely to be useful as high-energy density batteries. Na ion batteries will reduce cost due to the abundance of sodium. On the other hand, **all solid-state batteries (ASSBs)** are based on a different concept. Ion-conducting solids, especially, nonflammable inorganic materials, are used as electrolytes. Researchers are studying various candidates of next-generation batteries using these solids. Other attractive features of ASSBs are their potential high reliability, long **cycle** and **shelf lives**. Liquid-based electrolyte-using batteries have the serious problem of leakage, which will deteriorate their performance and may also cause

Energy density: Amount of energy that can be stored per weight or volume of an energy storage device. In the case of EVs, energy storage devices with higher energy density enable longer driving distance per one charging.

Power density: Amount of energy that can be stored (charged) or emitted (discharged) per time per weight or volume. In the case of EVs, energy storage devices with higher power density enable faster driving and shorter charging.

All Solid-State Batteries (ASSBs): All of components of batteries (cathode, anode and electrolyte) are solid.

Cycle life: Capacity retention of a battery after repetition of charge/discharge cycles.

Shell life: Capacity retention of a charged battery after stored for a certain term without usage.

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damage to the devices. The environment where the next-generation batteries will be used would also be different from the one used by the present set of batteries. For example, the next-generation batteries in EVs will have to work at temperatures ranging from -20°C to $+60^{\circ}\text{C}$, at which liquid solvents may freeze or evaporate. So, it is imperative to mention not only the chemical stability but also the electrochemical stability of the solid electrolytes. Liquid electrolytes decompose solvents and solutes at both high and low potentials. In some cases, the oxidised or reduced materials of liquid electrolytes stabilise on further electrochemical reaction on the electrodes by forming a surface layer, the so-called solid electrolyte interphase, which are not reversible and also cause difference in the state of charge on cathodes and anodes. According to Wang *et al.*, a thin-film battery of $\text{Li} \mid \text{LiPON} \mid \text{LiCoO}_2$ had undergone 30,000 cycles,² and a charged cell of $\text{Ag} \mid \text{RbAg}_4\text{I}_5 \mid \text{Me}_4\text{NI}_9$ has exhibited ca. 90% capacity even after 20 years.³

LiPON:

Lithium phospho-oxy-nitride. One of solid electrolytes, which can be prepared in form of thin film by a sputtering process.

LISICON:

Abbreviation of lithium super ionic conductor. A group of materials with formula Li_xXO_y , especially $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$. "Thio-LISICON" is sulfide-based materials with formula Li_xXS_y .

Transference number:

A ratio of charge carried by a specific charge carrier among several charge carriers.

1.3 All solid-state batteries

Among several candidates of next-generation batteries, ASSBs are discussed in this review. One of their most important advantages is safety, as they do not employ flammable organic solvent-based electrolytes. Another advantage is the possibility of employing Li metal anodes: dense ceramic layer of solid electrolytes would also play the role of separator and may prevent dendrite growth, which is a critical issue facing batteries using Li metal anode.

In the early stage of the development of ASSBs, thin-film batteries were studied, mainly because of the poor ionic conductivity of solid electrolytes. Although the thin-film ASSBs are still important to investigate the fundamental features of ASSBs, their low capacity limits their application to micro-electronic devices. On the other hand, as several important solid electrolytes with high Li-ion conductivity were reported, bulk-type ASSBs, especially lithium-based ASSBs, have attracted great interest. The basic structure of bulk-type ASSBs is similar to that of the conventional LIBs with liquid electrolytes: two composite electrodes for cathode and anode separated by a dense solid electrolyte layer. The composite electrodes consist of active materials, conducting additives and solid electrolytes. For bulk-type ASSBs, solid electrolytes with ionic conductivity of $10^{-3} \text{ S cm}^{-1}$ or higher are required for practical operation.

1.4 Solid electrolyte

Li-ion-conducting solid electrolytes can be classified into several groups: sulfides, oxides,

halogen, and complexes. Among them, sulfide-based Li-ion conductors are the most developed for practical application. Their most attractive feature is their high ionic conductivity, comparable to or even higher than that of organic solvent-based electrolytes. The properties required for solid electrolytes are chemical and electrochemical stability as well as high ionic conductivity.

Tatsumisago and his co-workers have developed glass and glass ceramics for $\text{Li}_2\text{S-P}_2\text{S}_5$ systems⁴⁻⁶ and applied them to ASSBs.^{7,8} The glass ceramic of $\text{Li}_7\text{P}_3\text{S}_{11}$ exhibits high Li-ion conductivity of $3.2 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. Kanno and his co-workers have studied crystalline sulfide-based solid electrolytes intensively in the system of Li-Ge-P-S, and found several epoch-making materials such as $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (known as thio-LISICON, ionic conductivity at room temperature: $2.2 \times 10^{-3} \text{ S cm}^{-1}$),⁹ $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ($1.2 \times 10^{-2} \text{ S cm}^{-1}$),¹⁰ $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ ($2.5 \times 10^{-2} \text{ S cm}^{-1}$).¹¹ Taking into account the transference number of Li-ion conduction of unity, the Li-ion conductivity of the latest material, $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$, exceeds that of organic solvent-based electrolytes. Another attractive feature of sulfide-based solid electrolytes is their mechanical property. These materials exhibit plastic deformation on mechanical pressure, and this softness makes it possible to prepare densely packed interface between active materials. On the other hand, their drawback is their chemical instability: these materials are sensitive to air and react with moisture to form toxic H_2S gas. In addition, their electrochemical stability is not sufficient. These materials react with metallic lithium, and hence, Li metal cannot be employed as anode of ASSBs.

Chemical stability is an advantage of oxide-based solid electrolytes, which would not produce toxic gases on exposure to air. However, their ionic conductivities are lower than those of sulfide-based ones. However, these materials are hard and hence require high-temperature heat treatment for sintering; otherwise, their grain-boundary resistance is very large but the total ionic conductivity is very low.

1.5 Surfaces and interfaces of solid electrolyte

In this context, surfaces and interfaces of solid electrolytes have been studied. Several important electrochemical processes in the ASSBs occur on solid–solid interfaces of active materials | solid electrolytes and solid electrolytes | solid electrolytes. As in other systems, surfaces and interfaces of solid electrolytes exhibit different properties from those

in bulk. The origins of interfacial phenomena can be classified into two groups: physical (mechanical) and chemical factors. The physical (mechanical) factor is point contact at the solid–solid interface. This issue is not very critical for thin-film batteries and sulfide-based ASSBs. Soft sulfide-based solid electrolytes will form densely packed interfaces just by applying pressure.⁷ The hardness in oxide-based solid electrolytes enables **point-contact interface** between solid electrolytes and active materials, and among solid electrolyte particles. The physical factor would be partly an issue of processes. To overcome point contact, Ohta *et al.* employed Li_3BO_3 as a solid electrolyte in cathode.¹² By heating a mixture of LiCoO_2 and Li_3BO_3 above 700°C , molten Li_3BO_3 forms continuous network as well as densely packed interface with LiCoO_2 . Tatsumisago *et al.*¹³ presented another approach to fabricate densely packed interface. They fabricated glass in Li_3BO_3 – Li_2SO_4 system, which was soft enough to prepare densely packed interfaces. In addition, after good interface was formed in cathode composite, the cell was annealed to crystallise the glass phase. The glass-ceramic phase in the system Li_3BO_3 – Li_2SO_4 exhibited higher ionic conductivity. Although they succeeded in preparing cathode composites with densely packed interface as well as well-connected network of solid electrolytes, the ionic conductivity of these materials is still lower than $10^{-4} \text{ S cm}^{-1}$.

On the other hand, the chemical factor is more general. Several mechanisms are proposed to explain the interfacial phenomena: (i) interfacial reaction, (ii) lattice distortion, and (iii) space charge layer. Interfacial reaction, i.e., formation of **interphases**, is derived from the interdiffusion of elements in active materials and solid electrolytes.^{7,14} Sakuda *et al.* confirmed the diffusion of Co from LiCoO_2 towards Li_2S – P_2S_5 solid electrolyte and increased the **charge transfer resistance** after the first charging. The Co diffusion was successfully suppressed by coating the surface of LiCoO_2 particles with Li_2SiO_3 thin layer. Ohta *et al.* also demonstrated that buffer layer of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ on LiCoO_2 suppresses the charge-transfer resistance at LiCoO_2 and thio-LISICON ($\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$) interface.¹⁵ They explained that the difference in the chemical potential of Li^+ in cathode and solid electrolyte results in the depletion of Li^+ in the region adjacent to the interface (i.e., space charge layer), and the coating of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ hinders Li^+ transfer from thio-LISICON to LiCoO_2 . Recently, Haruyama showed the formation of space charge layer by means of *ab-initio* calculation.¹⁶ Lattice distortion would be

mostly observed in thin-film systems.¹⁴ The lattice mismatch between active materials and solid electrolytes causes distorted lattice, which would exhibit different electrochemical properties.

2 Analysis of Interfaces of Solid Electrolyte

Although interfaces in ASSBs are one of the key factors, their details are still unclear. This is partly because of difficulty in analysing solid–solid interfaces. As for other interfaces, such as solid–liquid, liquid–liquid, liquid–gas, several techniques are available for analysis: microscopic techniques (including scanning probe microscope), spectroscopic analyses, diffraction, and so on. However, most of these techniques cannot be used for solid–solid interfaces.

2.1 Transmission electron microscope

A powerful tool to analyse solid–solid interfaces is transmission electron microscope (TEM). Sakuda *et al.* revealed the interdiffusion between a cathode and a solid electrolyte.⁷ Yamamoto *et al.* conducted an operando analysis on an interface between LiCoO_2 and a NASICON-type solid electrolyte (in the Li–Al–Ti–Ge–Si–P–O system) using **electron holography**.¹⁷ They clearly demonstrated the distribution of potential in the region adjacent to the interface, which ranged for ca. $1 \mu\text{m}$. It may be partly caused by the external electric field around the specimen and further investigation is needed. One of the advantages of TEM is that it provides images and changes in structure, composition and potential are shown visibly. But specimens for TEM observation need to be thin for electron beam to penetrate, and the thinning processes may cause damage to the specimens. In addition, TEM covers very tiny areas and provides only local information and observed images do not always show the typical structure of the specimens.

2.2 Electrochemical analyses

Electrochemical analyses consist of dc and ac methods, but the ac technique, i.e., **electrochemical impedance spectroscopy (EIS)**, is generally used to investigate interfaces. Although electrochemical systems generally have various processes, EIS can separate them depending on the characteristic frequencies or capacitance of each process. For example, **bulk resistance** and **grain-boundary resistance** of solid electrolytes exhibit characteristic capacitance of ca. $\sim 10^{-11} \text{ F}$ and $\sim 10^{-9} \text{ F}$, respectively. Information on resistance, capacitance and diffusion in electrochemical systems is obtained while they are in operation. These values are the average of the specimens. It is

Point-contact interfaces:

Interfaces where two rigid particles contact with very small area.

Electron holography:

A technique to investigate electric field in a material by analyzing phase difference of electron beams.

Interphases: Phases formed as a result of reaction among two contacting materials.

Charge transfer resistance:

Resistance of a charge transfer reaction on an electrode (oxidation on anode or reduction on cathode).

Electrochemical Impedance Spectroscopy (EIS):

A technique to investigate impedance of electrochemical devices. Ac voltage with frequency scan is applied and response current is recorded.

Bulk resistance: Resistance on electric conduction through inner grains.

Grain-boundary resistance:

Resistance on electric conduction across grain boundaries.

Equivalent circuit:

A model circuit to be used to analyze EIS, in which electrochemical processes are replaced with resistors, capacitors, inductors, and so on.

important that a proper **equivalent circuit** should be used to analyse the EIS data, and wrong models yield improper result leading to misinterpretation of the phenomena.

2.3 Nanocomposite

As shown above, there are only a few methods to analyse solid–solid interfaces. Such limitation hinders an understanding of the interfacial phenomena and the development of ASSBs. We have so far proposed analyses using nanocomposites. Nano-sized solid-state materials exhibit large mixed interfacial area. By reducing the particle size, the ratio of the interfacial region to bulk is increased. Therefore, it is possible to obtain microscopic information by using macroscopic methods: crystalline structure (X-ray diffraction: XRD), local structure (X-ray absorption spectroscopy: XAS, Fourier-transform infrared: FT-IR, nuclear magnetic resonance: NMR, and so on), composition (energy dispersive X-ray spectroscopy: EDX, X-ray photoelectron spectroscopy: XPS), ionic conductivity (EIS), etc. In addition, this method can be applied to the interfaces of any material. The information obtained is an average of the interface region with a dimension of nanoparticles (nm ~ sub- μm). In the next section, some examples of interfaces generated by using nanocomposites are shown.

3 Surfaces and Interfaces of Solid Electrolyte**3.1 AgX/Al₂O₃**

“The nanosize effect” of ionic conductors is caused by exaggerating the surfaces and interfaces, which exhibit different physical properties from bulk materials due to differences in their environment. Enhanced ionic conduction at hetero-interfaces of solid electrolytes and insulators is the first nanosize effect reported on ionic conductors.¹⁸ The mechanisms are qualitatively explained with a space charge effect by Maier:¹⁹ mobile ions in solid electrolytes are attracted by surface of insulator, and resulting **vacancies** are accumulated near the interface to form a **space-charge layer**. Increased vacancies (mobile species) cause increase in ionic conductivity, but the activation energy of ionic conductivity does not change as the mechanism of ionic conduction is the same.

To maximise this effect, AgX (X = Br, I) is filled in **mesoporous alumina (MPA)** with average pore diameter of 5.8 nm.^{20,21} Mesoporous structure is beneficial not only to control the size of AgX, but also to control the percolation network of ionic conduction. For AgBr, ionic conductivity

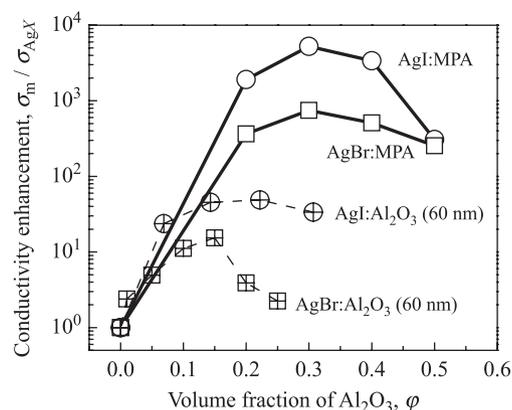


Figure 1: Conductivity enhancement in the systems of AgX (X = Br, I) and MPA at 25°C. Reproduced with permission from Ref.²¹ Copyright 2006, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

is enhanced by three orders of magnitude in comparison with pristine AgBr (Figure 1). The activation energy at lower temperature (related to migration enthalpy of silver vacancy in AgBr crystal) is not changed even when AgBr is in pores of Al₂O₃. The results on AgBr:MPA can be explained well by the space-charge layer model.

On the other hand, AgI:MPA composites exhibit enhancement by ca. 4 orders of magnitude, which is much higher than that expected from the space-charge layer model. In addition, AgI:MPA exhibits decreased activation energy. Differential scanning calorimetry suggests change in the thermal properties. Although AgI in pores was supposed to be different from bulk, the details are unclear. However, further investigation by ¹⁰⁹Ag NMR (Figure 2) and XAS at Ag K-edge (Figure 3) and I K-edge revealed that AgI in mesopores is amorphous with a local structure similar to α -AgI that exhibits very high ionic conductivity.²²

3.2 Cathode/Li⁺ conductors

The concept of the nanocomposite is also applied to interfaces between active materials and solid electrolytes in ASSBs.^{23,24} Here, two types of solid electrolytes were examined: Li₂SiO₃ (LSO) and Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP). These two solid electrolytes are different with respect to charge carrier: Li vacancy in LSO and Li ion in LATP. With these solid electrolytes, three active materials with different open circuit potential are mixed: TiO₂ (TO, ~3.3 V vs. Li/Li⁺), Li_{0.05}TiO₂ (LTO, ~2.7 V vs. Li/Li⁺), and FePO₄ (FPO, ~3.5 V vs. Li/Li⁺). In this case, nanocomposites were prepared by mixing nanoparticles of solid electrolytes and nanoparticles of active materials.

Vacancy:

A place at which ions should be but don't exist in a crystal.

Space charge layer:

A layer in which electric charge is not neutral.

Mesoporous alumina:

Porous alumina with pore diameters in the range from 2 to 50 nm.

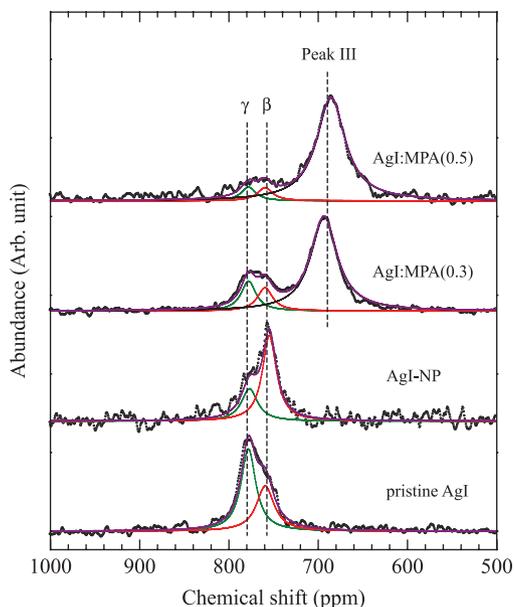


Figure 2: ^{109}Ag NMR spectra of pristine AgI and AgI:MPA ($\phi = 0.5$) composites. Numbers in the brackets denote volume fractions of alumina in the composites. Open circles and solid lines are experimental and fitted data, respectively. Reproduced with permission from Ref.²² Copyright 2014, American Chemical Society.

For LSO system,²³ the changes in ionic conduction depend on cathode materials (Figure 4). LSO:TO exhibits enhanced ionic conductivity, while mixing LTO causes suppressed ionic conductivity. Activation energy is not changed for both the composites. These results can be explained by the space charge layer model by taking into consideration the potential of the active materials. The potential of active materials is proportional to the gain of free energy by the insertion of small amount of Li ion into the lattice. In other words, materials with high-electrode potential (TiO_2) tend to attract or accept Li ions from solid electrolytes, and low-potential materials ($\text{Li}_{0.05}\text{TiO}_2$) donate or expel Li ions. The decrease in the activation energy and expansion of LSO lattice are confirmed for materials with higher electrode potential (FPO). Nevertheless, FT-IR and NMR indicate no change in the local structure of the composites. XPS suggests the partial oxidation of LSO and partial reduction of FPO. These results suggest that Li ions are attracted from LSO to FPO surfaces at the interfaces of LSO | FPO, as in the space-charge layer model. Due to the strong attraction force of FPO, the concentration of vacancy in LSO is so high that the lattice gets expanded. The accumulated Li on the surface of FPO may be partly inserted into the surface of FPO, i.e., reduction of FPO and

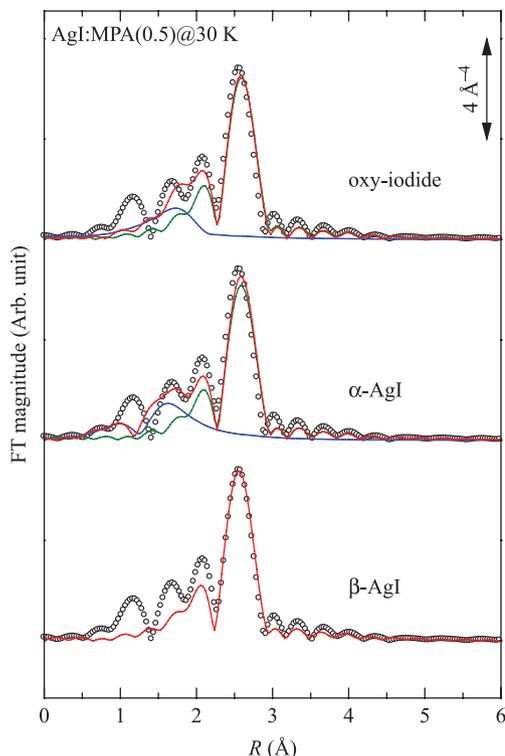


Figure 3: Fourier transforms of EXAFS of Ag K-edge at 30 K fitted with three structural models, β -AgI, α -AgI, and oxy-iodide. Open circles and red lines are experimental and calculated data, respectively. Blue and green lines represent the contribution of each coordinate. Reproduced with permission from Ref.²² Copyright 2014, American Chemical Society.

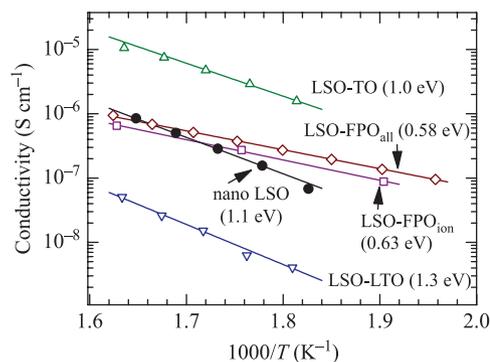


Figure 4: Li^+ conductivities and their activation energy of nano-LSO, nanocomposites of LSO-TO, LSO-LTO and LSO-FPO with a volume fraction of active materials of 0.4. Reproduced with permission from Ref.²³ Copyright 2012, The Electrochemical Society.

oxidation of LSO. The surface layer on FPO also exhibits Li-ion conductivity. This is in consistence with the fact that activation energy is close to that for LiFePO_4 .

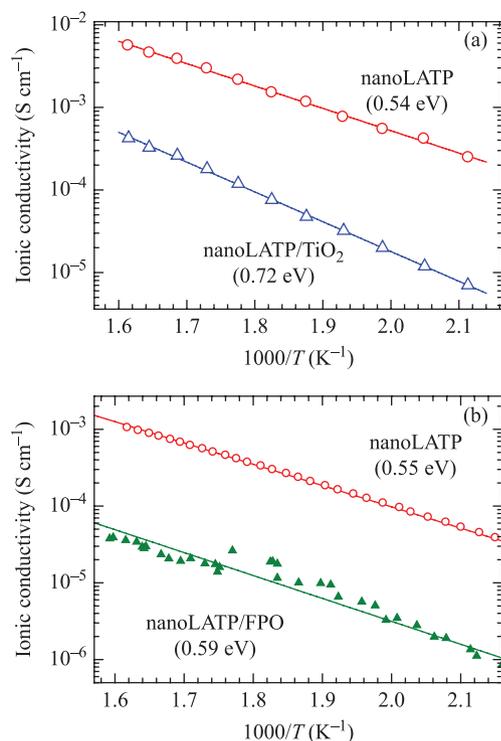


Figure 5: Li⁺ conductivities and activation energies of Li⁺ conduction of nano LTP, (a) nanocomposite of LTP–TO, and (b) LTP–FPO with a volume fraction of active materials of 0.4. Reproduced with permission from Ref.²⁴ Copyright 2013, Elsevier B.V.

For LSO, in which vacancy is a major charge carrier, ionic conductivity is enhanced at interfaces with active materials at high electrode potential due to increased vacancy. But, in the high ionic conductors, such as LTP, Li ions are carriers. Therefore, at the interface between cathodes and solid electrolytes, Li ions are depleted and ionic conductivity is decreased. This was demonstrated by LTP | TO nanocomposites and LTP | FPO nanocomposites (Figure 5).²⁴

3.3 Surface of LTP

The surface of solid electrolytes (i.e., interfaces between solid electrolytes and gas phase) is of importance. The surface of commercial NASICON-type solid electrolyte (LICGC, Ohara, Inc.) was investigated by grazing incidence X-ray diffraction (GIXD) and XPS.²⁵ Change in lattice parameters along depth was confirmed by GIXD recorded with various incidence angles (Figure 6). XPS also demonstrated the distribution of ions along the depth, and Li ions were accumulated at the surfaces of the solid electrolyte (Figure 7). The accumulation of Li ions is caused by the attraction of adsorbed water and/or carbon dioxide.

NASICON:

Abbreviation of sodium super ionic conductor. A group of materials with formula Na_xM₂(XO₄)₃.

Grazing Incidence X-ray Diffraction (GIXD):

One of techniques of X-ray diffraction. By reducing incidence angle of X-ray, X-ray is diffracted mostly by surface region.

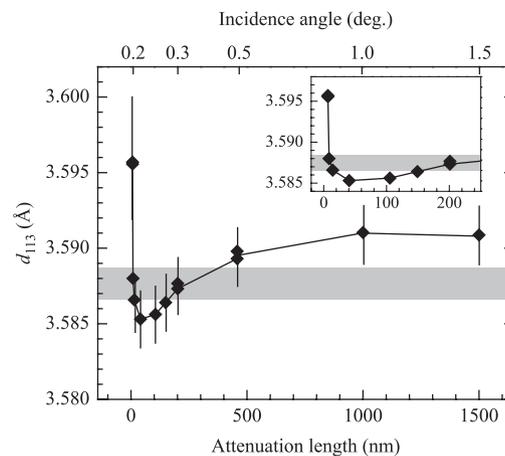


Figure 6: d -value of (113) plane of LICGC as a function of attenuation depth. A horizontal grey band shows a d -value for bulk LICGC (3.588(1) Å). Inset shows an enlarged plot for shallow range. Reproduced with permission from Ref.²⁵ Copyright 2015, Elsevier B.V.

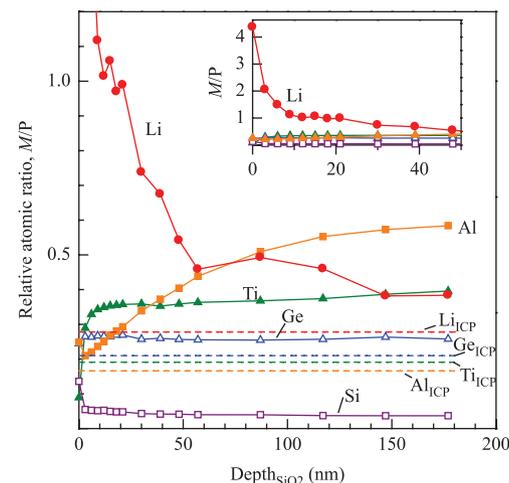


Figure 7: Depth profiles of elements of LICGC. Vertical axes show a relative atomic ratio to phosphorus. Depth is estimated from a standard SiO₂ film. Dashed lines show bulk composition estimated from ICP-OES. Reproduced with permission from Ref.²⁵ Copyright 2015, Elsevier B.V.

3.4 Interface modification of solid electrolytes

As shown above, the surface and interfaces of solid electrolytes are different from bulk in terms of structure, composition, and ionic conductivity. Therefore, it is important to design the interfaces so that desirable properties are obtained.

For ASSBs, it is important to prepare composite electrodes consisting of active materials and solid electrolytes with densely packed interface. In addition, it is also important to establish a network

of ionic conduction in the composite electrodes. However, it is difficult to prepare highly conducting network using solid electrolytes. When dense solid electrolytes are prepared, high-temperature sintering is usually employed to decrease the grain-boundary resistance. But, in the case of composite electrodes, high-temperature sintering would result in thermal reaction between active materials and solid electrolytes to deteriorate electrochemical properties of the materials. Therefore, low-temperature processes are needed

to prepare composite electrodes. As discussed in Section 3.3, the concentration of Li ions in solid electrolytes is not constant, and the distribution of Li-ion at the surface would be one of the reasons for grain-boundary resistance. Hence, to control ion distribution in solid electrolyte, the surface of solid electrolyte particles was modified with other solid electrolytes. In solid electrolytes with high Li-ionic conductivity, the major carrier is Li ion, and depletion of Li^+ at the surface results in large interfacial resistance. On the other hand,

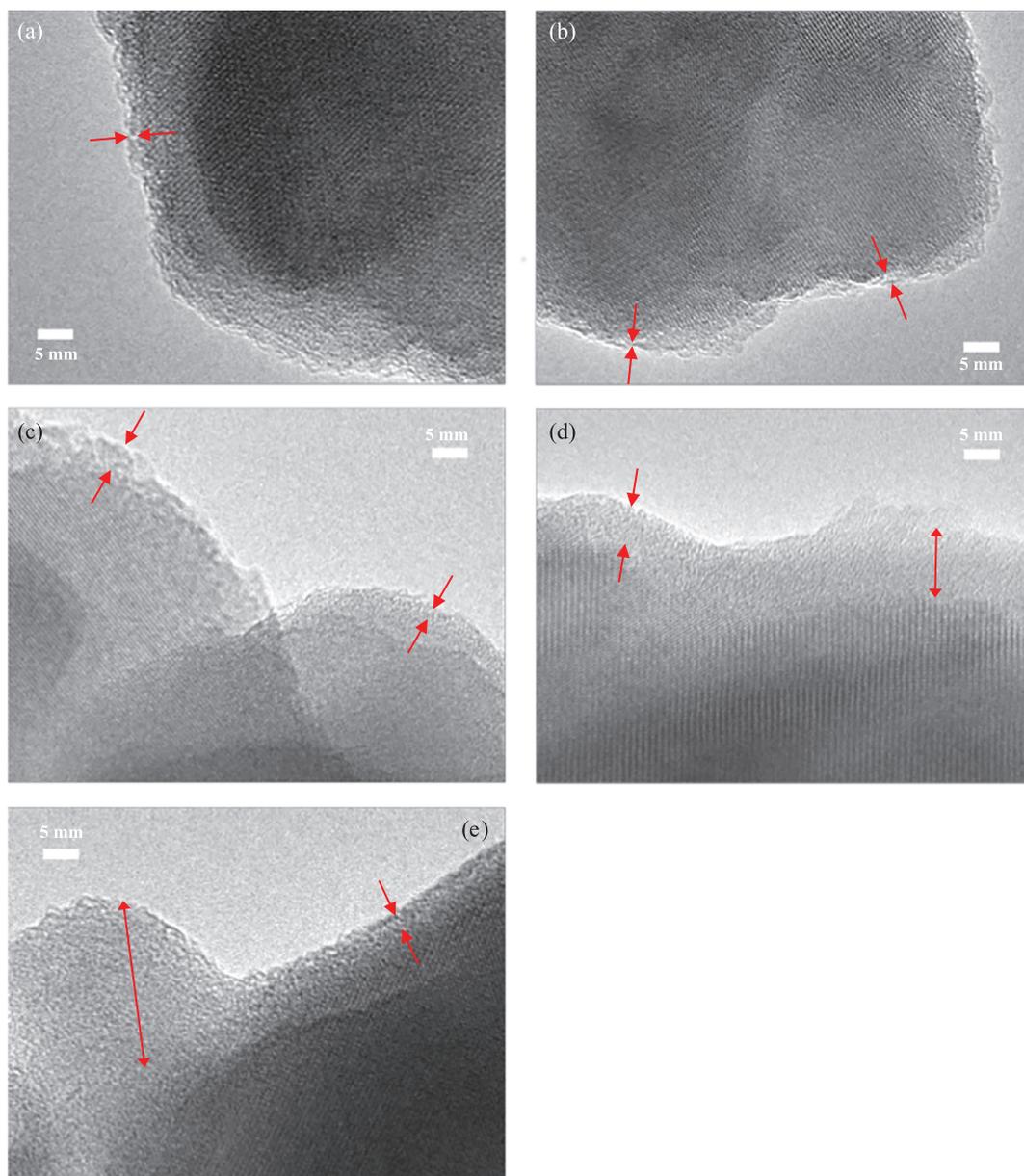


Figure 8: HR-TEM images of surface-modified solid electrolytes of LATP@LSO. Estimated LSO thickness by the volume fraction of LSO is (a) 0 (bare LATP), (b) 0.5, (c) 2, (d) 6, and (e) 10 nm. Scale bars show 5 nm. Arrows indicate the amorphous layers on crystalline particles. Reproduced with permission from Ref.²⁶ Copyright 2015, American Chemical Society.

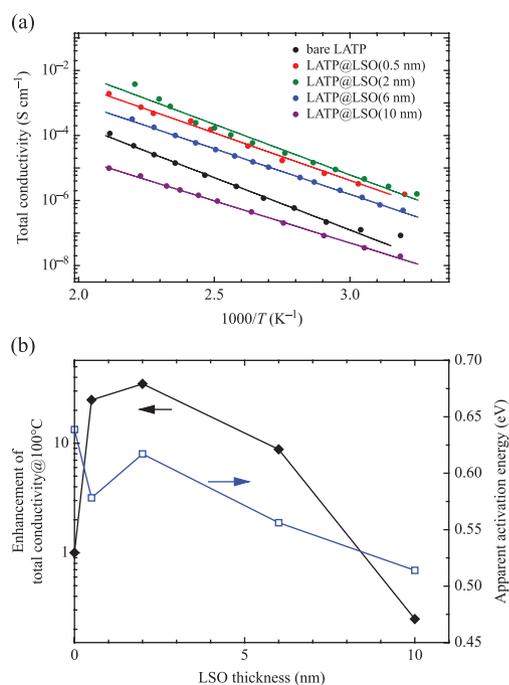


Figure 9: (a) Arrhenius plot of total conductivity. (b) LSO-thickness dependence of enhancement factor of total conductivity and apparent activation energy. Reproduced with permission from Ref.²⁶ Copyright 2015, American Chemical Society.

in some solid electrolytes, major carrier is Li vacancy. Although these solid electrolytes exhibit rather low ionic conductivity, depletion of Li ions around interfaces would increase carrier density and thus ionic conductivity. In this context, LSO thin layer (major carrier: Li vacancy) was coated on the surface of the LTP particles (major carrier: Li ion) (Figure 8).²⁶ LSO-coated LTP (LTP@LSO) exhibited ca. 30 times higher ionic conductivity in comparison to bare LTP, and the total ionic conductivity reached 10⁻⁶ S cm⁻¹ without the sintering processes (see Figure 9). This is mainly due to the reduction in the grain-boundary resistance. Further enhancement is possible through proper designing of the particle size, shape and materials of the core, and the shell.

4 Summary

In this review, the interfaces of solid electrolytes are discussed in the context of application to ASSBs. It shows that the structure, ion distribution, and ionic conductivity at the interfaces of solid electrolytes are different from those in bulk materials. In addition, these changes are also dependent on the electrode potential and type of main charge carriers (interstitial ions or vacancies). Therefore, it is important to design and control interfaces

between solid electrolytes and active materials, or interfaces among solid electrolytes on the basis of the concept of defect chemistry.

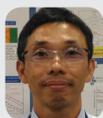
The phenomena shown in this review describe only a part of the solid electrolyte interface. There should be plenty of important things still unravelled, which may be difficult to study employing the available technologies. It is important not only to fabricate densely packed interfaces for the development of ASSBs, but also to develop new tools to study solid–solid interfaces.

Received 1 September 2016.

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