

Solid Electrolyte: Strategies to Address the Safety of All Solid-State Batteries

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Lithium metal batteries (LMBs) are in the spotlight as a next-generation battery due to their high theoretical capacity. However, LMBs still suffer from inferior cycle stability owing to dendritic lithium (Li) growth during Li plating and stripping, leading to battery explosion. To solve this problem, solid electrolytes have emerged as a promising candidate by suppressing the dendritic Li growth. Despite numerous efforts, however, many challenges, such as low ionic conductivity, air stability, space charge layer, and contact loss issues, have been encountered. This review aims to provide the current challenges and new insights of solid electrolytes and then explore optimal solutions for next-generation solid electrolytes.

Lithium (Li)-ion batteries as a key technology are known to have the advantages of high stability and long lifespan for EVs.^[2] In general, Li-ion batteries use graphite as an anode, which is inexpensive and has high charge/discharge cycle stability. However, using graphite as an anode has led to the disadvantages of not only being able to travel a sufficient distance due to its low theoretical capacity (372 mAh g^{-1}) but also requiring a long time to charge.^[3] To overcome these drawbacks, lithium metal batteries (LMBs) using Li metal as an anode are getting significant attention. LMBs are considered to be the advanced technology that will ultimately be used in

1. Introduction


Electric vehicles (EVs) have become a key game changer that can replace internal and external combustion engines to curb climate change. Despite their high research and production costs, EVs are currently receiving a lot of attention from the viewpoints of long-term financial benefits and greener technology.^[1]

various fields. These advantages obtain high theoretical capacity ($3,840 \text{ mAh g}^{-1}$), low redox potential (-3.04 V vs SHE), and low density (0.534 g cm^{-3}).^[4] However, LMBs using liquid electrolytes suffer from serious stability issues. These issues usually arise from uncontrolled dendritic Li growth. The dendritic Li growth which is accumulated during the charging and discharging cycle accelerates the formation of a solid electrolyte interphase (SEI) which results in the decomposition of electrolyte.^[5] Furthermore, when the dendritic Li growth penetrates the separator, the dendritic Li growth causes an internal short circuit. These unintended short circuits instantaneously generate enormous heat, causing the liquid electrolyte to decompose, release toxic gases, and eventually the battery explosion.^[6] To inhibit this dendritic Li growth, researchers are making great efforts to develop solid electrolytes to inhibit dendritic Li growth and SEI formation. However, to ensure the practical application of solid electrolytes, they urgently address on the following challenges,^[7] as shown in **Figure 1**.

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1.1. Ionic Conductivity

The ionic conductivity of the solid electrolyte at room temperature ranges from 1×10^{-3} to $1 \times 10^{-7} \text{ S cm}^{-1}$, which is much lower than that of the liquid electrolyte. This low ionic conductivity seriously causes a lower number of ions passing through in a given time, thereby affecting the capacity of the battery.

1.2. Moisture Stability

When exposed to air moisture, solid electrolytes exhibit high reactivity, leading to decreased performance due to accompanying side reactions. In particular, the sulfide-based solid

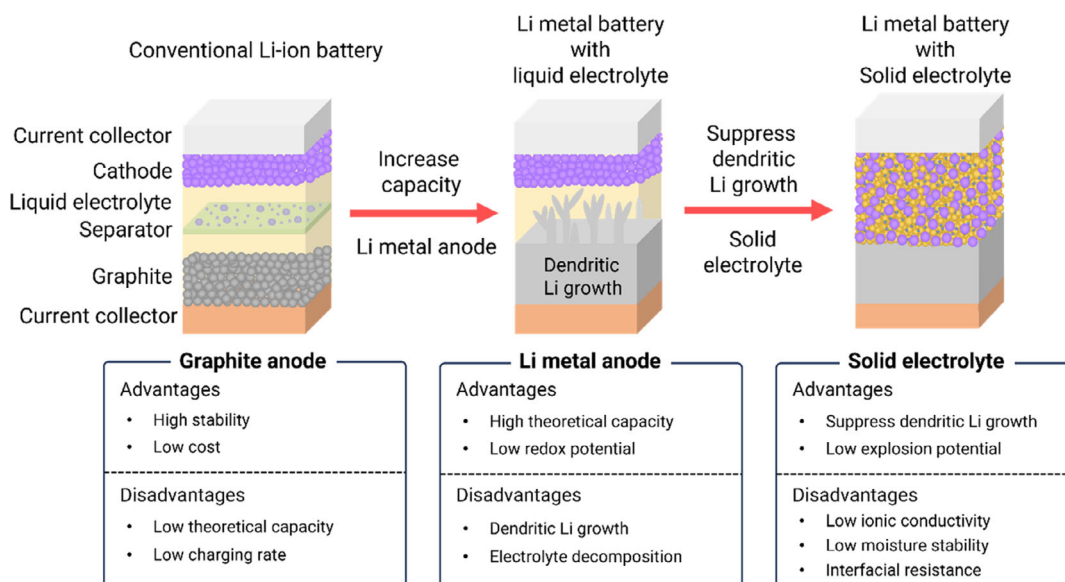


Figure 1. Schematic of the reason why solid electrolytes began to be studied and the requirements for ideal solid electrolytes.

electrolyte reacts with moisture in the air and generates hydrogen sulfide. Such gas causes various symptoms, such as headache, nausea, the throat and eyes irritation, and in severe cases, pulmonary edema and death.

1.3. Interfacial Resistance

Solid electrolytes have a smaller contact area with electrodes than liquid electrolytes due to their robust characteristics, and form empty spaces named as voids. Furthermore, there is a space charge layer (SCL) formed by the contact of materials with different chemical potential. These voids and SCL act as resistance and reduce the battery performance.

To address these major challenges, various studies such as atom substitution, electrode coating, and additive moisture absorbent are currently underway.^[8] The primary aim of this perspective is to provide a viewpoint on achieving the optimal solid electrolyte. This will be achieved by presenting an overview of ongoing research efforts that are specifically targeted at overcoming challenges related to solid electrolytes, including ionic conductivity, moisture stability, and interfacial resistance.

2. Solid Electrolyte

As shown in **Figure 2a**, researches related to solid electrolytes gained momentum in the 20th century.^[9] The development of solid electrolytes has a long history, with the discovery of solid ionic conductors in Ag₂S by Michael Faraday in 1833.^[10] In the 1950s, researches related to all-solid-state batteries led to the emergence of two types: silver salt-based (Ag/AgI/V₂O₅, Ag/AgBr/CuBr₂, Ag/AgCl/KICl₄) and Li salt-based (Li/LiI/AgI, and Li/LiI/I₂).^[11] The batteries with silver salt-based electrolytes and silver metal anode suffer low cell voltages and energy density due to their high redox potential (0.8 V vs SHE).^[12] Later, in 1976, inorganic type sodium superionic conductor (NASICON) with

chemical formula Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ (0 < x ≤ 3) were reported by Goodenough et al.^[13] NASICON structure is synthesized by adding additional Na atoms to balance the negative charge when substituting the Si atom for P atom in the NaZr₂(PO₄)₃ structure. Additionally, to act NASICON as a Li-ion conductor, the Na-ion was replaced by Li⁺.^[14] This NASICON structure shows impressive high ionic conductivity up to 1 mS cm⁻¹, even comparable to conventionally available liquid electrolytes.^[15] Two years later, in 1978, The lithium super ionic conductor (LISICON) type solid electrolytes with the chemical formula Li₁₄Zn(GeO₄)₄ was proposed by Hong et al. The LISICON-type solid electrolyte also had high ionic conductivity of 1.25 × 10⁻¹ S cm⁻¹ at 300 °C.^[16] This high ionic conductivity could be explained by the size of bottlenecks between neighboring Li⁺ and bonding energy between Li⁺ and O²⁻ in the structure.^[17] Later, LISICON and NASICON which have higher ionic conductivity than other conventional solid electrolytes provide insights to the new solid electrolytes such as Li_{1+x}Al_xGe_{2-x}(PO₄)₃ (LAGP) and Li_{1+x}Al_xTi_{2-x}(PO₄)₃ (LATP).^[18] In the 1990s, the perovskite-type Li_{0.34}La_{0.51}Ti_{0.29} (LLTO) with high ionic conductivity of ≈10⁻³ S cm⁻¹ was reported by Inaguma et al. (1993).^[19] However, there is a barrier to adopting LLTO as a solid electrolyte due to the low electrochemical stability caused by Ti⁴⁺. This drawback could be overcome by substituting Ti⁴⁺ with other transition metals such as Sn⁴⁺, Zr⁴⁺, Mn⁴⁺, and Ge⁴⁺. Note that these various atom substitutions could be available by its high tolerance factor (0.75 < t < 1.0).^[20] Even in the 21st century, research on solid electrolytes continues to be actively conducted. In 2003, Thangadurai et al. reported garnet type Li₅La₃M₂O₁₂ (M = Ta, Nb). This garnet-type solid electrolyte shows outstanding stability than other solid electrolytes in terms of wide chemical window (>6 V vs Li/Li⁺) and stability with Li metal anode.^[21] In 2008, Deiseroth et al. proposed the argyrodite-type Li₆PS₅X (X = Cl, Br, I), which has extraordinary ionic conductivity

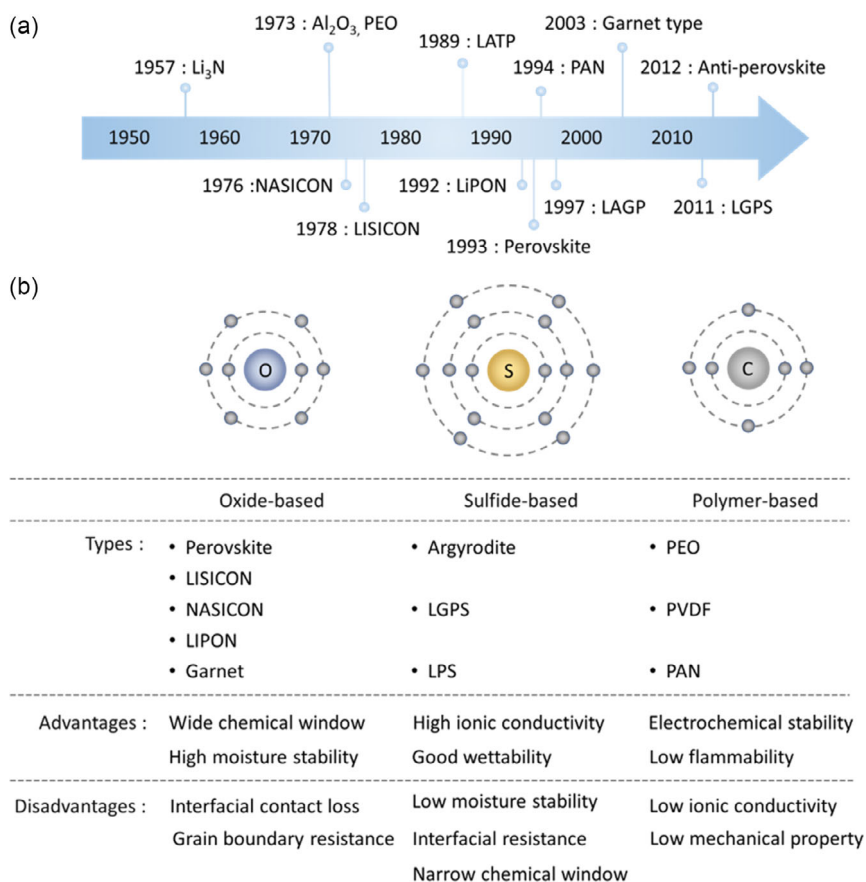


Figure 2. a) Schematic of solid electrolyte development. b) Types, advantages and disadvantages of solid electrolyte according to categorized into the three classes: oxide, sulfide, and polymer solid electrolyte.

($\approx 10^{-2} \text{ S cm}^{-1}$) as a next-generation solid electrolyte.^[22] However, argyrodite-type solid electrolytes react violently with moisture and this reaction results in degradation of ionic conductivity.^[23]

The invented solid electrolyte can be classified into an oxide-based, sulfide-based, and polymer-based electrolyte, as shown in Figure 2b.^[24] The oxide-based solid electrolyte, such as perovskite-type, LISICON, NASICON, lithium phosphorus oxynitride (LiPON), and garnet type has the advantages of stability especially wide chemical window and excellent moisture stability.^[25] Additionally, the oxide-type solid electrolytes can suppress the dendritic Li growth, which is a critical issue of all solid-state batteries, by its high Young's modulus.^[26] However, the oxide-based solid electrolytes suffer from some limitations, such as insufficient contact area between the electrolyte and electrode due to its high stiffness, low ionic conductivity compared to sulfide-type solid electrolyte, and non-contact area, named as void, which is known to reduce the performance of the battery as the voids act as internal resistance ($\approx 10^3 \Omega$) at the interface with the electrode.^[27] These contact losses are partially caused by Li_2CO_3 and LiOH components, which act as an insulator of ionic and electronic movement, at the interfacial between solid electrolyte and Li metal.^[28] To solve this contact loss, Li et al. proposed a lithium fluoride (LiF) additive as a solution. They add 2 wt% LiF to the $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ (LLZTO) and LiF covers the surface

of the LLZTO particles. The LiF additive on LLZTO reduces Li_2CO_3 on the surface of Li metal anode by reducing unintended side reaction between LLZTO and moisture.^[29] This problem occurs not only at the interface with the Li metal anode but also between the interface between the two crystallites of solid electrolyte, which is called the grain boundary.^[30] It is to be noted that grain boundaries have 10–100 times lower ionic conductivity compared to the bulk, which is a major hurdle to battery application.^[31] The size of the grain boundary is mainly decided by temperature and time. Shin et al. reported that Li_3BO_3 (LBO) additives, which enhances the lithium lanthanum zirconate (LLZO) densification at low temperature. Liquid phase LBO, formed under 1000°C during the LLZO sintering process, caused increased LLZO densification by liquid-phase sintering. Additionally, LBO covers the LLZO grain and reduces the grain boundary resistance.^[32]

Sulfide-based solid electrolytes, which have a brilliant ionic conductivity of $1 \times 10^{-2} \text{ S cm}^{-1}$ and good wettability, have been explored.^[33] This high ionic conductivity comes from S^{2-} , which has a larger ionic radius and polarizability than O^{2-} .^[34] The representative sulfide-based solid electrolytes include $\text{Li}_6\text{PS}_5\text{X}$ (Argyrodite), $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS), and Li_3PS_4 (LPS).^[35] Despite these advantages, however, sulfide-based solid electrolytes have crucial problems, such as poor moisture stability, the high interfacial resistance caused by the presence of a space charge layer,

and a narrower electrochemical window than the oxide-based solid electrolytes.^[23,36] The electrochemical window has emerged as a crucial factor in addressing sustainable solid electrolytes. The electrochemical windows indicate the range of voltage where the solid electrolyte is neither oxidized nor reduced during the charging and discharging process. The reduction potential is determined by the lowest unoccupied molecular orbital (LUMO), while the oxidation potential is determined by the highest occupied molecular orbital (HOMO).^[37] For solid electrolytes to exhibit sustainable and stable behavior with conventional cathode materials such as lithium cobalt oxide (LCO) and nickel manganese cobalt oxide (NMC), the desired range of electrochemical window is upper 4.2–4.5 V.^[38] However, solid electrolyte with a narrow electrochemical window is utilized, it can lead to the decomposition of the solid electrolyte through side reactions and the generation of by-products, which subsequently increases resistance at the interface and causes a rapid decline in performance. For instance, LGPS which has extremely narrow electrochemical stability in the range of 1.7–2.1 V decomposed into Li₂S, Li₁₅Ge₄, and Li₃P. To prevent side reactions of LGPS, additional technology such as artificial solid electrolyte interphase must be adopted.^[39] Recently, not only electrochemical window but also interfacial reactivity between cathode materials and sulfide-type solid electrolyte is on the chopping block. Komatsu et al. reported that the nickel content of the cathode material is an important factor in the interfacial reactivity between cathode materials and LPSCI. In detail, among manganese, cobalt, and nickel, which are the components of NMC, manganese exhibits the highest interfacial stability with LPSCI, while nickel has the lowest interfacial stability. This result means that to decrease the interfacial resistance, the content of nickel in cathode material must be considered.^[40] Another critical issue of sulfide-based solid electrolyte is the hydrogen sulfide gas generation (H₂S). H₂S gas comes from an unavoidable side reaction between sulfide-type solid electrolyte and moisture during the sintering process and this side reaction cause the cell performance. To adopt the sulfide-based solid electrolyte, the generation of H₂S must be suppressed.^[41]

Polymer-based electrolytes are a type of macromolecular polymer system capable of transporting Li⁺ between cathode and anode.^[42] In 1973, Fenton et al. discovered that polyethylene oxide (PEO) and alkali metal salts could act as Li⁺ transporters, which was the first discovery of polymer electrolytes.^[43] Since then, other polymer electrolytes, such as polyvinylidene fluoride (PVDF) or polyacrylonitrile (PAN), have also been developed.^[44] Polymer electrolytes have not been considered a major key technology due to their low ionic conductivity (<10⁻⁶ S cm⁻¹) and mechanical properties.^[45] However, with active research on lithium metal batteries, polymer electrolyte has been actively revived and gained attention with the advantages of low flammability and electrochemical stability.^[46] For example, pure PEO has a relatively high thermal decomposition of 400 °C, thus it does not decompose at normal operating temperatures and does not cause thermal runaway.^[47] Also, polymer-type solid electrolyte has a wide electrochemical window. In particular, polyacrylonitrile (PAN) has the highest oxidation potential (4.46 V vs SHE), while the reduction potential (−3.65 vs SHE) is similar to the electrochemical potential of Li metal anode (−3.04 vs SHE).^[48] Such polymer electrolytes with high thermal and electrochemical

stability are well suited to the current battery research that emphasizes the stability of batteries.

Unfortunately, Among the three types of solid electrolytes mentioned above, there is no perfect solid electrolyte that has only advantages. The three types of solid electrolytes are engaged in competition, each presenting its unique set of advantages and disadvantages. The oxide-based solid electrolytes show superior sustainability and stable behavior due to wide electrochemical window and moisture stability, while it shows poor battery performance due to the low ionic conductivity.^[25–27] In contrast, the sulfide-based solid electrolyte shows outstanding battery performance similar to liquid electrolyte. However, H₂S generation due to the reaction with moisture and dramatic decrease in ionic conductivity resulted from side reaction with the electrode are the chronic drawbacks.^[33–36] The polymer-based solid electrolytes have the advantage of wide electrochemical window and low flammability, however, low ionic conductivity remains a barrier to overcome.^[44–47]

2.1. Ionic Conductivity

The ionic conductivity of solid electrolytes is a major challenge for replacing conventional liquid electrolytes with solid electrolytes.^[49] However, there are many hurdles due to the intrinsic characteristics of solid electrolytes.^[50] To achieve a certain level of ionic conductivity comparable to liquid electrolytes, understanding the Li⁺ transport mechanisms is essential in the solid electrolyte. The ionic conductivity of the solid electrolyte is mainly determined by defects, such as point defects, line defects, planar defects, volume defects, and electron defects of crystal structures.^[51] The most significant factor in determining ionic conductivity is the presence of point defects in the crystal structure.^[52] In particular, the two representative types of point defects are the Frenkel defects (the vacancies accompanied by an interstitial ion) and Schottky defects (the anion vacancies accompanied by a cation). The transport of Li⁺ is the movement along the energy landscape by point defects, the transport of Li⁺ does not occur in a perfect crystal structure without defects.^[53]

Sulfide-based solid electrolytes are being considered as a promising candidate for next-generation solid electrolytes, as they exhibit the highest ionic conductivity among solid electrolytes with a value as high as 10⁻² S cm⁻¹, as shown in **Figure 3**.^[54] Among the sulfide-based solid electrolytes, research related to the new material derived from the LGPS type are reported ardently due to its high ionic conductivity.^[55] In 2016, Kato et al. reported the chlorine-doped silicon-based superionic conductors (Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}), which demonstrated an untouchable high ionic conductivity of 25 mS cm⁻¹ at room temperature.^[56] This high ionic conductivity was achieved by the three-dimensional (3D) lithium transport pathways (1D along the c axis and 2D in the ab plane).^[57]

Argyrodite-type solid electrolytes, such as Li₆PS₅X (X = Cl, Br, I), are another promising candidate for next-generation solid electrolytes due to their high ionic conductivity.^[58] In 2022, Lee et al. reported Ge-substituted thioantimonate argyrodite (Li_{6.5}Sb_{0.5}Ge_{0.5}S₅I) which showed the highest value (16.1 mS cm⁻¹) among the reported cold-pressed solid electrolyte pellets. They conducted the ab initio molecular dynamics (AIMD)

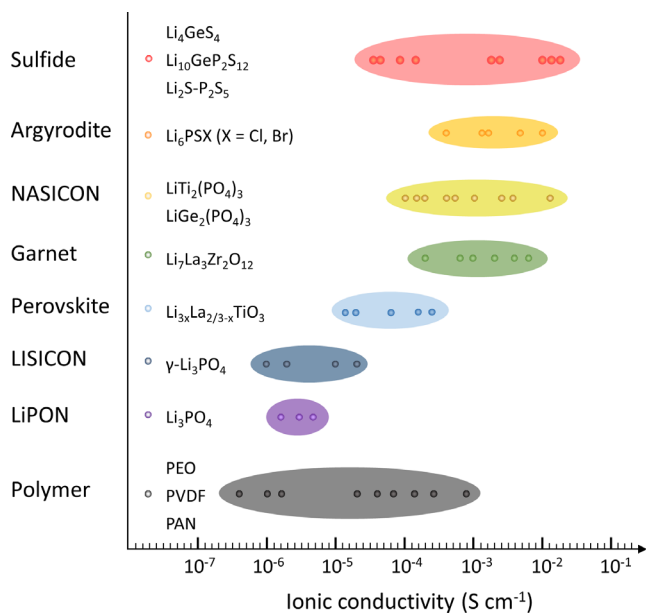


Figure 3. Ionic conductivity of various types of solid electrolytes, classified into sulfide, oxide, and polymer based. Reproduced with permission.^[54b] Copyright 2018, Elsevier.

to confirm the effect of Ge-substitution. The iso-surfaces were more connected in $\text{Li}_{6.5}\text{Sb}_{0.5}\text{Ge}_{0.5}\text{S}_5\text{I}$ than in conventional $\text{Li}_6\text{SbS}_5\text{I}$. This result indicates that a high Li^+ diffusivity is derived from the inter-cage jump.^[59]

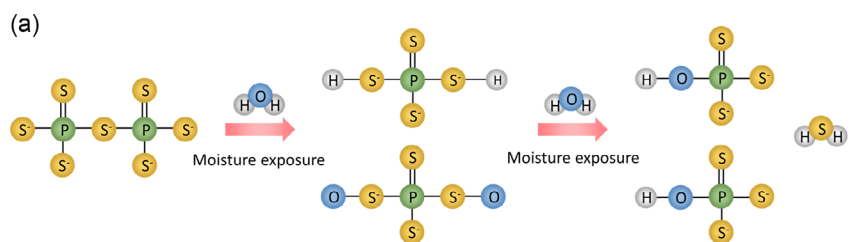
The ionic conductivity of oxide-based solid electrolytes, such as NASICON-type, perovskite-type, and garnet-type is approximately one order of magnitude lower than that of sulfide-based solid electrolytes.^[60] In 2007, Murugan et al. reported the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, which is predominantly an ionic conductor with high ionic conductivity ($10^{-4} \text{ S cm}^{-1}$ at room temperature).^[61] In 2011, Awaka et al. reported that only cubic phase LLZO structures have an ionic conductivity approximately two orders of magnitude higher than the tetragonal phase LLZO structure.^[62] To increase the ionic conductivity, atom substitution strategies such as Al, Ga, Y, Si, Ge, Nb, Ta, and W into the LLZO structure have been reported.^[63] In 2014, Bernuy-Lopez et al. reported a Ga-doped LLZO structure, which has one of the highest ionic conductivity (1.3 mS cm^{-1}). In this structure, Ga substitutes the 24 d sites of the Li^+ to form vacancies and Li^+ is located at the 96 h sites. The transportation of Li^+ is increased by charge repulsion between Ga^{3+} and Li^+ .^[64]

Polymer-based electrolytes such as PEO, PVDF, and PAN suffer from the critical issue of low ionic conductivity.^[65] The general ionic conductivity of the polymer-based electrolytes is 10 to 1000 times lower than that of other solid electrolytes. The Li^+ is mainly transported by segmental motion and ion hopping of the polymer. To increase the ionic conductivity of polymer-based electrolytes, the construction of fast ion pathways and the concentration and mobility of charge carriers must be increased.^[66] In 2020, Lin et al. reported poly(vinyl ethylene carbonate) (PVEC) based polymer electrolytes. The PVEC showed superior ionic conductivity ($2.1 \times 10^{-3} \text{ S cm}^{-1}$), which was comparable to other solid electrolytes, and high thermal stability. The

high ionic conductivity of PVEC is derived from the coupling and decoupling process between the Li^+ and O atoms in $\text{C}=\text{O}$ groups.^[67] In 2021, Liu et al. reported a gel polymer electrolyte consisting of cellulose acetate (CA), poly (ethylene glycol) diacrylate (PEGDA), and layered boron nitride (BN), which showed superior ionic conductivity ($8.9 \times 10^{-3} \text{ S cm}^{-1}$). In detail, the CA provided high electrolyte affinity due to its spinnable structure and functional groups such as ether and ester. Moreover, the BN filler facilitated the transport of Li^+ through interactions with the electrolyte as well as the polymer matrix.^[68]

2.2. Moisture Stability

Addressing the moisture stability of solid electrolytes is very important for their practical applications. On a lab scale, it is possible to minimize exposure to moisture in the air when synthesizing materials or constructing a battery, but when scaling up for commercialization, it is not easy to prevent contact between solid electrolytes and moisture.^[69] Polymer-based electrolytes which has outstanding moisture stability due to their hydrophobic characteristic.^[70] Many studies have been reported on making a protective layer from moisture by coating a hydrophobic polymer electrolyte on an electrode or a solid electrolyte, while oxide-based solid electrolytes such as $\text{Li}_{0.3}\text{La}_{0.57}\text{TiO}_3$ and $\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$ have a problem that Li^+/H^+ exchange which results in degradation of battery performance.^[71] However, one of the challenges is the H_2S gas generation of sulfide-type solid electrolytes.^[72] Conventional sulfide-type solid electrolyte contains PS_4^{3-} units and $\text{P}_2\text{S}_7^{4-}$ as their crystal structures. When the $\text{P}_2\text{S}_7^{4-}$ ion interacts with moisture, hydroxide (OH) and hydrosulfide (SH) are formed. This reaction generates H_2S gas when SH reacts with moisture in the air, as shown in Figure 4a.^[73] To suppress the H_2S gas generation, the control of moisture is a prior step. However, it is unavoidable in large scale processes. Additionally, this side reaction can negatively impact the ionic conductivity of the solid electrolyte.^[74] To suppress this, various strategies such as atom substitution, moisture absorbent, and protective layer have been reported. Zhao et al. reported $\text{Li}_{6.24}\text{P}_{0.823}\text{Sn}_{0.177}\text{S}_{4.58}\text{I}_{0.9}$ which P was replaced by Sn in the conventional $\text{Li}_6\text{PS}_5\text{I}$ (LPSI). It was confirmed that the ionic conductivity ($3.5 \times 10^{-4} \text{ S cm}^{-1}$) increased approximately 125 times when Sn was substituted by 20% for the P atom. Additionally, Sn-substituted LPSI has enhanced moisture stability. The moisture reactivity between electrolytes and pure O_2 (99.999%) was investigated by monitoring the weight change of the electrolyte in a microbalance of a thermogravimetric analysis (TGA) instrument. The mass change percentage of Sn substituted LPSI was 0.28% after exposure to pure O_2 for 10 h and only 0.35% after 20 h, while pristine LPSI was over about 1.2% after 10 h. This result means that the Sn-substituted LPSI maintains its structure after pure O_2 exposure, as shown in Figure 4b.^[75] It was confirmed that not only Sn but also Ge substitution increased ionic conductivity and moisture stability. Lee et al. reported $\text{Li}_{6.5}\text{Sb}_{0.5}\text{Ge}_{0.5}\text{S}_5\text{I}$ (LSGSI) which is Ge substituted thioantimonate argyrodite. LSGSI achieved outstanding ionic conductivity of 16.1 mS cm^{-1} compared to reported cold-pressed solid electrolyte pellets. The optimum temperature to achieve high ionic conductivity and high crystallinity was 450°C . Ge substitution



Strategies to increase moisture stability

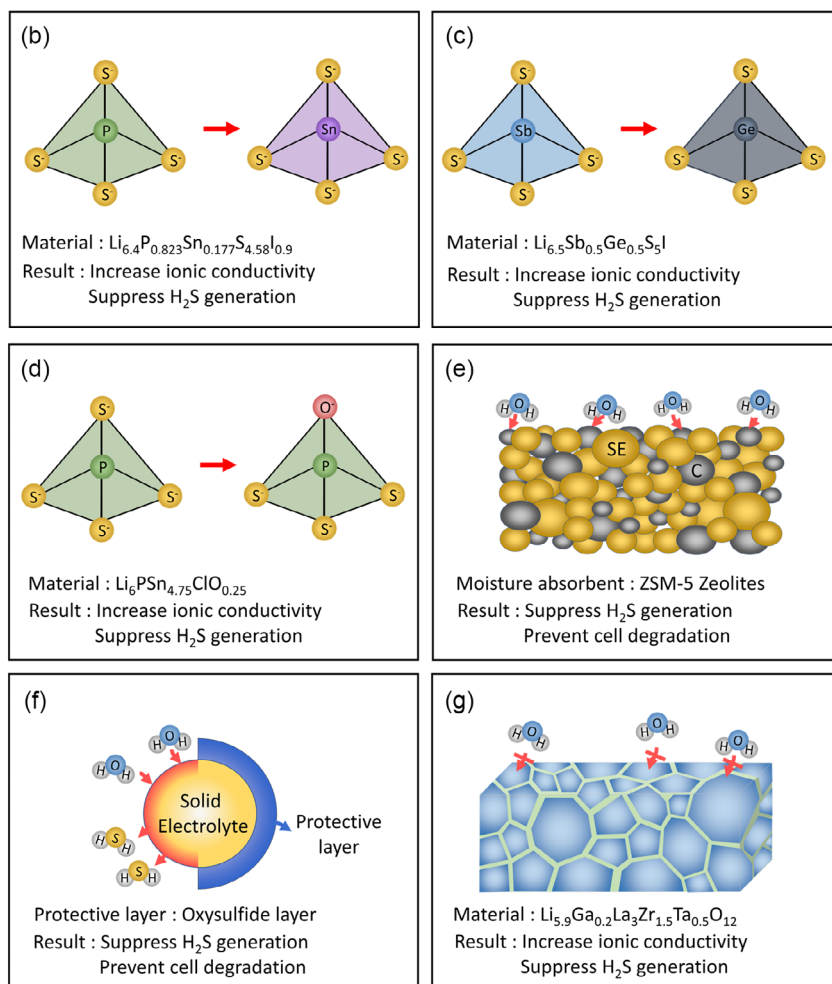


Figure 4. Schematic of a) H_2S generation process. Strategies to increase moisture stability. b) Sn substitution. Reproduced with permission.^[75] Copyright 2020, Wiley. c) Ge substitution. Reproduced with permission.^[59] Copyright 2022, ACS. d) O substitution. Reproduced with permission.^[76] Copyright 2022, AIP Publishing. e) Zeolite moisture absorbent. Reproduced with permission.^[77] Copyright 2021, Royal Society of Chemistry. f) Oxysulfide nano protective layer. Reproduced with permission.^[78] Copyright 2020, ACS. g) Ga substitution. Reproduced with permission.^[79] Copyright 2023, Elsevier.

not only increases the ionic conductivity but also increase the moisture stability. Based on the hard and soft acids and bases (HSAB), soft acids tend to form stronger bonds with soft bases, while hard acids react and form with hard bases. Sb and Ge based as central cations, solid electrolytes generate significantly smaller amounts of H_2S gas than other electrolytes. The amount of H_2S gas generation of LSGSI decreased up to 96%, compared to pristine LPSCl after 15% humidity air exposure. This result means that Ge substitution is one of a solution to suppress the H_2S gas generation, as shown in Figure 4c.^[59] To suppress the H_2S

generation, anion substitution is considered, as shown in Figure 4d.^[76] Wu et al. reported oxygen doping argyrodite $\text{Li}_{6.05}\text{PS}_{4.9}\text{O}_{0.1}\text{Cl}_{1.05}$. The ratio of Cl^- and S^{2-} is increased by oxygen doping, as a result, the ionic conductivity reached 7.49 mS cm^{-1} . Additionally, $\text{Li}_{6.05}\text{PS}_{4.9}\text{O}_{0.1}\text{Cl}_{1.05}$ exhibits outstanding H_2S suppression. Amount of H_2S gas after moisture exposure (35% humidity at 30°C) for 15 min was 49.2 ppm, while pristine LPSCl was 92.9 ppm. In other words, $\text{Li}_{6.05}\text{PS}_{4.9}\text{O}_{0.1}\text{Cl}_{1.05}$ can resist ionic conductivity degradation by reducing unintended side reaction. The ionic conductivity

of $\text{Li}_{6.05}\text{PS}_{4.9}\text{O}_{0.1}\text{Cl}_{1.05}$ and LPSCL was 1.3×10^{-4} and $1.8 \times 10^{-6} \text{ S cm}^{-1}$, respectively.

To suppress the unintended side reaction between the solid electrolytes, research on moisture absorbents is widely underway, as shown in Figure 4e.^[77] In 2021, Lee et al. proposed incorporating a zeolite socony mobil-5 (ZSM-5) zeolite as a functional additive, which plays the role of inhibitor of H_2S gas generation. Furthermore, the ZSM-5 zeolite nanoparticles prevent the decrease of performance of solid electrolytes, prolonging the cycle stability of the battery. To confirm the role of ZSM-5 zeolite nanoparticles in $\text{Li}_6\text{PS}_5\text{Cl}$, the pristine $\text{Li}_6\text{PS}_5\text{Cl}$, and ZSM-5 zeolites incorporated $\text{Li}_6\text{PS}_5\text{Cl}$ were exposed to humid air (relative humidity (RH) 50%) for 1 h. The concentration of H_2S in pristine $\text{Li}_6\text{PS}_5\text{Cl}$ (≈ 120 ppm) was approximately three times higher than ZSM-5 zeolites incorporated $\text{Li}_6\text{PS}_5\text{Cl}$ (≈ 40 ppm). This phenomenon was similarly observed in terms of the degradation of ionic conductivity. After exposure to humid air (RH 50%) for 1 h, the ionic conductivity of ZSM-5 zeolites incorporated $\text{Li}_6\text{PS}_5\text{Cl}$ ($0.39 \times 10^{-3} \text{ S cm}^{-1}$) was about 50% higher than pristine $\text{Li}_6\text{PS}_5\text{Cl}$ (0.23×10^{-3}), even though their initial ionic conductivity was 1.27×10^{-3} and $1.31 \times 10^{-3} \text{ S cm}^{-1}$.

To prevent the deterioration of solid electrolyte performance, core-shell structure solid electrolyte was also suggested, as shown in Figure 4f.^[78] In 2020, Jung et al. proposed to cover the solid electrolyte with an oxysulfide nanolayer. Using environmental mechanical alloying and precise control of oxygen partial pressure, a novel core-shell structure sulfide-type solid electrolyte (argyrodite) was fabricated. This new sulfide-type solid electrolyte with oxysulfide nano layer showed a superb degradation rate of ionic conductivity. Both the pristine argyrodite and the argyrodite with oxysulfide layer were exposed to air (RH 35%) for 15 min to confirm the effect of the oxysulfide layer. The degradation rate of ionic conductivity was estimated to be $-58.0 \mu\text{S cm}^{-1} \text{ min}^{-1}$ for pure argyrodite, while for the oxysulfide-coated argyrodite, it was reduced to $-21.4 \mu\text{S cm}^{-1} \text{ min}^{-1}$. Despite the initial ionic conductivity of the argyrodite with oxysulfide layer (3.02 mS cm^{-1}) being 10.4% lower than the pure argyrodite (3.37 mS cm^{-1}), it demonstrated a significantly lower degradation rate.

LLZO-type solid electrolytes are known to have excellent stability, but they encounter some performance fading when exposed to moisture. In particular, during the synthesis of conventional polycrystalline LLZO, lithiophobic Li_2CO_3 is formed at the grain boundaries. The Li_2CO_3 species block the Li^+ transportation between bulk grains, as a result, the interfacial resistance is increased. In 2023, Jeong et al. reported the Ga-substituted into Ta-doped LLZO, which significantly increased resistance to H_2O and CO_2 gases. They conducted ADT analysis combined with compositional analyses and microstructural analyses and confirmed that Ga substitution into LLZTO plays a significant role in reducing the grain boundary density and suppressing the degradation of Li^+ by migrating the formation and growth of Li_2CO_3 , as shown in Figure 4g.^[79]

2.3. Interfacial Resistance

Solid electrolytes aim to prevent dendritic Li growth through their unique mechanical properties.^[80] Compared to the liquid

electrolyte, however, these can lead to other issues such as space charge layer (SCL) and contact loss at the interface with the active material, as shown in Figure 5a.^[81] The SCL is a resistance layer that exists on a nanometer scale at the interface between cathode particle and solid electrolyte. It is commonly found in sulfide-type electrolytes and oxide-type electrolytes. However, it is a great challenge to experimentally prove its existence.^[82] With the advancement of observation and analysis equipment, the existence of the space charge layer has been confirmed. In 2015, Haruta et al. reported the resistance of the space charge layer ($8.6 \Omega \text{ cm}^2$) at the interface between $\text{Li}_3\text{PO}_{4-x}\text{N}_x$ and LiCoO_2 . This report highlighted the importance of research direction to overcome the obstacles associated with the space charge layer.^[83]

In 2022, Park et al. studied the effect of paraelectric materials such as BaTiO_3 and SrTiO_3 , which can effectively suppress the formation of the space charge layer. The direction of the permanent dipole moment of BTO nanoparticles is determined in the synthesis process, making it difficult to alter without an external electric field. Furthermore, the tetragonal structure (BTO-T) shows a random polarization direction, making the impact of BTO-T unclear. In contrast, the cubic structure of BTO (BTO-C) allows for easy alternation of the dipole moment direction in response to the electric field in the battery. As a result, the BTO-C has the potential to suppress the formation of SCL and enhance Li^+ transportation. The effect of the magnitude of the dielectric constant can be validated by electrochemical impedance spectroscopy (EIS) analysis with STO nanoparticles. This forms a dipole moment with a significantly higher dielectric constant than BTO nanoparticles. The interfacial resistances between the cathode and solid electrolyte of bare LCO, LCO@BTO-C, and LCO@STO-C were estimated to be 524.8, 262.1, and $175.4 \Omega \text{ cm}^2$, respectively. This result reveals that paraelectric nanoparticles are effective to suppress the SCL, as shown in Figure 5b.^[84]

Owing to the robust nature of solid electrolyte, a non-contact region named a void is generated at the interface between the anode and the solid electrolyte. Despite efforts to reduce the non-contact area by applying high pressure, voids persist, resulting in interfacial resistance. In 2021, Parejiya et al. suggested a new solution to solve this issue with high-voltage pulses technology, leading to reduced contact impedance. When the short time pulse (0.1–0.5 s) is applied to the cell at nominal pressure ($\approx 1 \text{ kPa}$), the interfacial resistance was improved up to 58%. In particular, after 20 pulses were applied, the interfacial resistance was decreased from 2.58 to $1.90 \text{ k}\Omega \text{ cm}^2$, as shown in Figure 5c.^[85]

The non-contact region called void that leads to an increase in interfacial resistance is also observed in polymer solid electrolytes due to their non-liquid behavior. The poor contacts between polymer electrolyte and Li metal anode are accelerated by the periodic vast volume change of Li anode during the cycle and result in dendritic Li metal growth. The dendritic Li growth caused by persistent interfacial contact problems leads to the deterioration of battery performance.^[86] To solve this problem, Porcarelli et al. reported a super soft polymer electrolyte network derived from regulating the mobility of classic –EO– based backbones. The polymer electrolytes are synthesized by ultraviolet (UV)-induced (co)polymerization which results in an effective

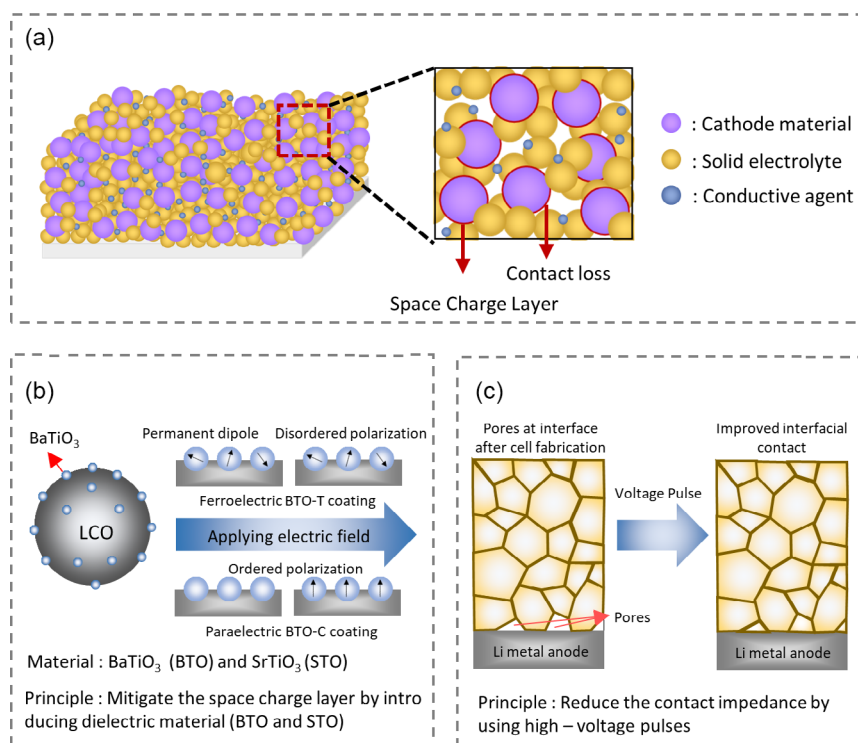


Figure 5. Schematic of a) interfacial resistance, b) solution for space charge layer. Reproduced with permission.^[84] Copyright 2022, Wiley-VCH and c) solution for contact loss. Reproduced with permission.^[85] Copyright 2021, ACS.

interlinking between the PEO chains. The EIS analysis demonstrates that the lithium symmetric cell, utilizing this polymer electrolyte, maintains stable resistance even after several days of testing. In detail, during the early period of storage, the resistance increases due to the formation of SEI at the surface of the Li metal anode. After, the appropriate formation of a thin SEI layer, the resistance swiftly decreases and stabilizes at $700 \Omega \text{ cm}^{-2}$. This result means that the improved contact is achieved at the interface between the polymer electrolyte and lithium metal anode.^[87]

3. Perspective and Outlooks

Lithium-ion batteries have proven to be a key technology in our lives as they are used in various fields such as transportation, mobile devices, drones, satellites, and energy storage systems. In particular, it is expected that lithium-ion batteries, which are used in electric vehicles, will have a greater demand compared to other industries. By 2030, it is projected that the lithium-ion batteries used in electric vehicles will reach approximately 8.1 TWh, accounting for about 77% of the total demand of 10.5 TWh. This result means that electric vehicles are receiving greater preference from customers compared to those powered by internal or external combustion engines. These consumer's preferences for electric vehicles can contribute significantly to reducing the emission of carbon dioxide (CO_2) and the cost of tens of trillions of dollars used to combat climate change. However, the drawbacks of electric vehicles, including their short

driving range and long charging time, are being brought to attention. Conventional Li-ion batteries using graphite as a negative electrode have drawbacks of low theoretical capacity, despite their superior stability. To achieve a high-capacity battery, a Li metal anode is required. However, conventional electrolytes can cause some problems such as dendritic Li growth and formation of SEI due to active side reactions at the interface between Li metal and electrolyte. To overcome these problems, numerous research on solid electrolytes is intensively conducted. In particular, the studies of ionic conductivity, moisture stability, and interfacial problem, which are considered drawbacks of solid electrolytes, are receiving significant attention, as shown in **Figure 6**. Still, ionic conductivity, a chronic problem of conventional solid electrolytes, obtains poor ionic conductivity compared to liquid electrolyte. To increase the ionic conductivity of solid electrolytes, new technologies employing various materials are reported. Interestingly, among solid electrolytes, sulfide-type solid electrolytes such as LGPS and argyrodite have shown a promising approach because of their superior ionic conductivity up to $10^{-2} \text{ S cm}^{-2}$. However, the sulfide-type solid electrolyte has a technical issue that it generates H_2S gas in a cell assembling process. These problems not only cause critical harm to the health of workers but also have a great impact on the performance of the electrolyte, so they must be resolved. To suppress H_2S gas, the solid electrolytes must be redesigned through atom substitution, moisture absorbent, and protective layer. We mentioned only Sn, Ge, and O substitution, However, there are many candidates which can suppress the H_2S generation and increase the ionic conductivity of solid electrolytes. Thus, it is essential to explore

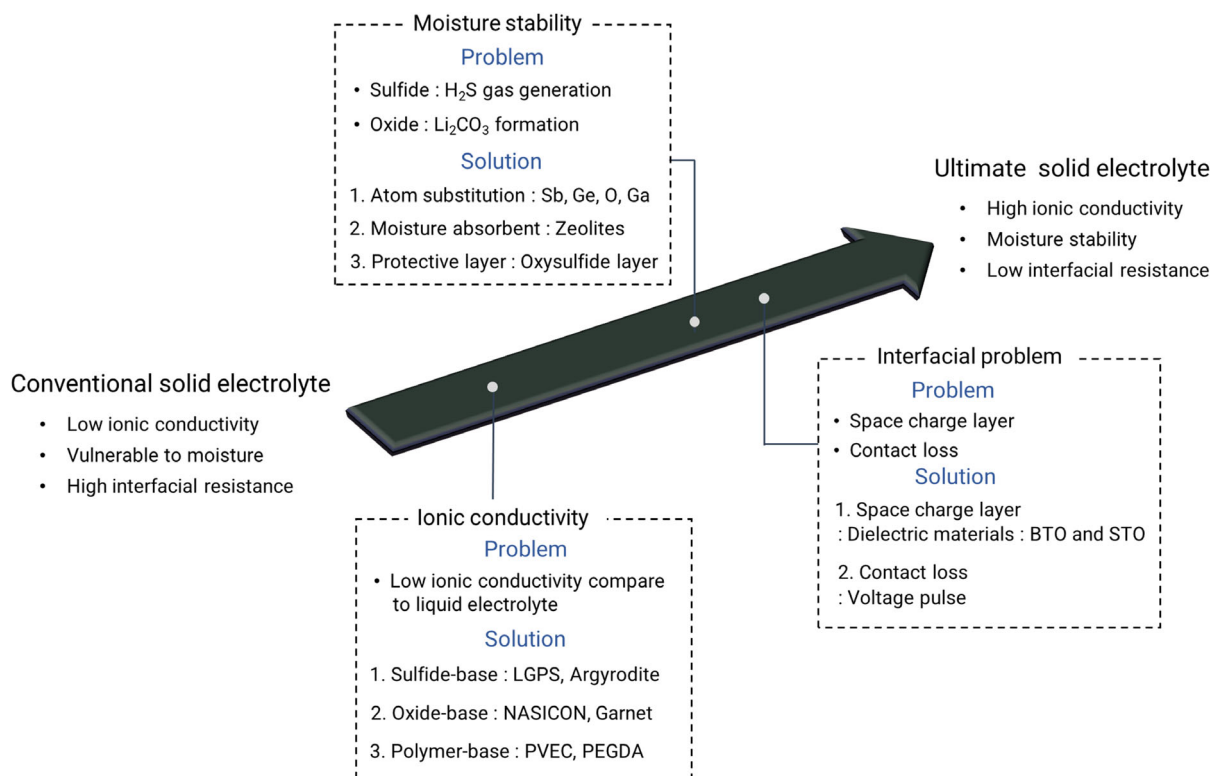


Figure 6. Challenges and solutions focused on the moisture stability, ionic conductivity, and interfacial problem to address ultimate solid electrolyte.

atom substitution and methods to synthesize stable crystal structure. Furthermore, the interfacial issue between the active material and solid electrolyte must also be addressed. These interfacial problems act as a resistance at the interface and deteriorate cell performance. The interfacial problems such as SCLs and voids, could be resolved through the dielectric nanoparticles and voltage pulse. In this perspective, a recent solution was introduced, focusing on ionic conductivity, interface resistance, and moisture stability, which are the prior hurdles of solid electrolytes. By addressing these issues of solid electrolytes from different viewpoints, Li metal batteries can become a reality and be a significant step toward addressing the challenge of climate change.

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Conflict of Interest

The authors declare no conflict of interest.

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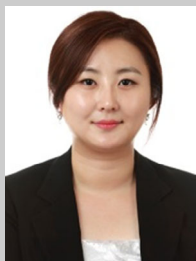
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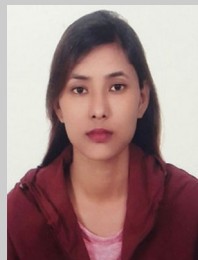
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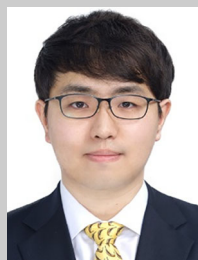
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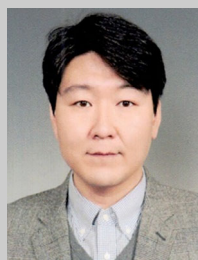
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