

Glassy solid-state electrolytes

for all-solidstate batteries

By Jacob Wheaton, Madison Olson, Victor M. Torres III, and Steve W. Martin

Glassy solid-state electrolytes present several advantages over other classes of solid-state electrolytes, but some material and design challenges must be overcome prior to commercialization. The introduction of the lithiumion battery (LIB) to the market in 1991 revolutionized the energy storage field and enabled the development of portable electronic devices and electric vehicles that are widely available today. The improved energy density and cycle life compared to previous rechargeable batteries, such as leadacid or nickel-metal-hydride, allowed for their widespread adoption.

Though these batteries revolutionized energy storage, current LIBs present several issues, mainly due to their reliance on carbonaceous anodes and organic liquid electrolytes. Their use of carbon, typically low-cost graphite, decreases the energy density on the anode to values usually one-tenth that of a pure lithium metal anode.

Likewise, organic liquid electrolytes can accommodate the volume expansion of the intercalation and deintercalation processes of lithium during discharge and charge processes, plus allow for simple, low cost, and rapid assembly and processing.

However, their inherent flammability reduces their safety in small-scale applications, such as smartphones and laptop computers. Their use in larger scale applications, such as battery packs in electric vehicles, requires active cooling systems to prevent thermal runaway, which can lead to dangerous fires.

With demand for more energy dense, more reliable, and safer batteries sure to increase in the future, new energy storage materials, designs, and solutions must be developed.

Solid-state batteries (SSBs), which rely on solid-state rather than liquid electrolytes, are a favored solution to not only improve the safety of LIBs but also to enhance the gravimetric energy density by enabling the use of higher voltage cathodes and lithium metal anodes. SSBs with solid electrolyte separators and glassy solid-state electrolytes (GSEs) are one class of solid-state electrolytes (SSEs) that present several advantages over other classes of SSEs, such as polycrystalline ceramics or polymers. These advantages include lower processing temperatures, greater resistance to dendrite formation, and more tunable chemistries.

This brief overview summarizes the development and current status of GSEs, along with their challenges and future prospects.

Benefits of all-solid-state batteries

Commercially available LIBs contain a cathode, an organic liquid electrolyte, and an anode. Typical cathode materials include LiFePO₄, which is commonly used in some electric vehicles, or LiCoO₂. While LiCoO₂ possesses a higher capacity than LiFePO₄, cobalt remains expensive and difficult to ethically source.

The anode typically is graphitic carbon, which forms LiC₆ upon charging. Lithium metal anodes offer higher energy density than graphite anodes, but they are also prone to dendrite formation in liquid electrolyte cells, which in turn leads to short-circuiting. Short-circuiting can further cause the liquid electrolyte to increase in temperature, and eventually lead to fires and explosions. Graphitic carbon anodes help mitigate these safety hazards of the organic liquid, but they do

Graphite anode Liquid electrolyte Cathode

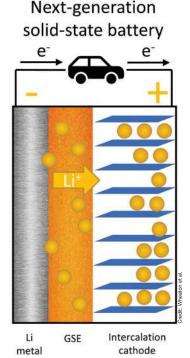


Figure 1. Schematic of a conventional lithium-ion battery (left) and a next-generation solid-state battery (right) with a glassy solid-state electrolyte (GSE). Solid-state batteries can achieve the same capacities as conventional batteries but with a more compact—and potentially safer—design.

so at the expense of reduced energy density relative to the lithium metal anode.

SSBs are seen as a potential solution to this performance compromise due to their less flammable nature, which would enable the use of lithium metal anodes possessing a gravimetric energy density more than an order of magnitude greater than graphite anodes (3,860 mAh/g vs. 330 mAh/g). This dramatic increase in energy density makes lithium metal anodes highly desired. Implementation, however, requires design of a compatible SSE.

Figure 1 shows a schematic illustrating the differences between conventional LIBs and newer SSBs. While the benefits of next-generation SSBs spur research, there are still many material and design challenges that must be overcome prior to commercialization.

Requirements for SSEs in SSBs

Prior to discussing the specific qualities of GSEs, it is important to define requirements that are necessary for SSEs to be used in SSBs.

First, SSEs should have a high ionic conductivity approaching that of liquid electrolytes, about 10⁻³ S/cm, coupled with a low electronic conductivity, below 10⁻⁹ S/cm.¹ The combination of high ionic conductivity and low electronic conductivity is necessary to sufficiently reduce the internal resistance of the electrolyte and allow for higher discharging and charging rates and to prevent premature failure of the cell. A large electrochemical stability window, from 0 V to more than 4 V vs. Li/Li⁺, is also important to prevent the electrolyte from decomposing in contact with either lithium metal or highvoltage cathodes.

An example of a cyclic voltammogram for a glass in the Li₂S-SiS₂-LiPO₃ compositional space is shown in Figure 2, where the GSE is stable up to 5 V vs. Li/Li⁺, as no reduction or oxidation peaks are present. The peaks centered around 0 V are attributed to lithium plating and stripping behavior. Electrolyte decomposition can lead to lower efficiency when charging and discharging. Typically, a stability window from 0 V

Glassy solid-state electrolytes for all-solid-state batteries

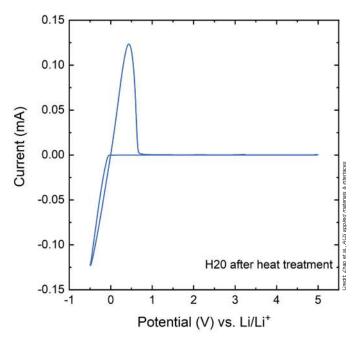


Figure 2. Cyclic voltammogram showing the electrochemical stability of a Li₂S-SiS₂-LiPO₃ glass. No redox peaks are seen above 0 V, indicating good stability of the GSE against lithium metal. This data was obtained using a stainless steel | GSE | Li asymmetric cell design. Adapted with permission from Ref. 3. Copyright 2021 American Chemical Society.

to 5 V against lithium metal is sufficient for usage of novel cathode materials.

SSEs should also be easy to process into films with thicknesses less than 100 μm to reduce internal resistance of the cell and be competitive with organic liquid electrolytes.²

There are many classes of GSEs. However, so far, none of them meet all the above requirements perfectly. The most wellstudied GSE types will now be discussed, beginning with the first ionically conductive glasses researched: alkali ion doped oxide glasses.

Oxide glasses

Oxide glasses were the first glasses developed for their ionic conduction properties. First studied in the late 19^{th} century, it was not until the 1930s that efforts were made to attempt to maximize the ionic conductivity of sodium silicate glasses by increasing the concentration of Na_2O in the glass forming melt, achieving a maximum room temperature conductivity of about 10^{-9} S/cm.⁴ Even with additional Na^+ added into the glass network through dopant salts such as NaCl, the conductivity only increased to about 10^{-6} S/cm.

The highest lithium ion conductivities reported in oxide glasses are typically about 10⁻⁵ S/cm, while sodium ion conductivities are normally even lower.⁵ These low ion conductivities remain one of the greatest issues with oxide GSEs: While they are easily processed and are very low cost, they possess intrinsically low ionic conductivities even at high alkali ion concentration due to the strong ion trapping behavior of oxide anions, which significantly limits their ionic conductivities.⁵

Researchers have conducted many studies on oxide glasses to determine the effect of different alkali ions and glass-forming systems on the ionic conductivity of glasses. The results of these studies indicate that larger alkali cations consistently exhibit lower conductivities while silicate glasses typically display higher conductivities than germanate, phosphate, or borate glasses.

Significantly, however, the ionic conductivities of AgI doped oxide glasses are some of the highest conductivities reported in glasses, approaching or often even surpassing 10⁻² S/cm.⁶ This high conductivity of the Ag⁺ cation is believed to be due to its high ionic polarizability. While this conductivity is well above the minimum desired conductivity of solid electrolytes, the voltage of silver batteries is limited, and the cost and density of silver limits its use.

Oxide glasses possess several desirable properties of SSEs, including a wide electrochemical stability window, relatively good atmospheric stability, high shear modulus (which is correlated with resistance to dendrite formation), and relative ease of processing. While the composition of oxide glasses can be optimized by using complex systems, such as multiple glass-forming cations and multiple ionic salt dopants, to increase conductivity, the low ionic conductivity of these glasses, at best 10⁻⁵ S/cm at 25°C, often makes them nonstarters for use in SSBs. A simpler method of increasing the conductivity of the glass is to replace the deep trapping energy of oxygen anions with a lower field strength, weaker trapping energy anion, such as sulfur.

Sulfide glasses

In the 1980s, several sulfide-based glass systems were found to have conductivities approaching that of organic liquid electrolytes. The higher polarizability and lower charge density and field strength of sulfide anions reduces the Coulombic attraction between the mobile cations and the sulfur anion, which in turn allows for the alkali ion conductivity to increase relative to oxygen analogues.

While sulfide glasses often present high conductivities, they also typically have several disadvantages, including their hygroscopic nature, lower resistance to crystallization, and lower electrochemical stability compared to oxide glasses. However, many of these issues can be overcome through use of controlled atmospheres and processing.

Binary alkali thiophosphates were some of the first sulfide glasses studied, particularly glasses based on Li₄P₂S₇ or Na₄P₂S₇. While melt-quenched samples typically have had issues with volatilization of P₂S₅ during melting, large additions of modifying sulfides, such as Li₂S or Na₂S, can help to prevent sublimation of P₂S₅ during melting due to the increased ionic nature of the glass system. These binary alkali thiophosphates typically present ionic conductivities 2–4 orders of magnitude higher than their oxide counterparts, with lithium ion conductivities often approaching 10⁻³ S/cm. Figure 3 is an Arrhenius plot showing typical ranges of conductivities for oxide, sulfide, and mixed oxysulfide glasses.

In addition to phosphate glasses, alkali thiosilicate glasses (Li₂S-SiS₂) have also been extensively studied because these glasses have fewer issues with sublimation of starting materi-

als during melting, and therefore can be easily synthesized in open crucibles without significant mass loss. Still, these glasses are typically only moderately glass forming and as such they often require fast quenching rates to prevent crystallization and reach the glassy state. For example, Pradel and Ribes used twin-roller quenching to rapidly cool glass melts and extended the glass-forming region of the $\text{Li}_2\text{S-SiS}_2$ system to produce glasses with conductivities approaching 10^{-3} S/cm.⁸

Further, it is often advantageous to combine desirable properties from multiple glass-forming systems. As such, mixing of the glass-forming cations silicon, phosphorous, and boron can be a valuable tool to improve the properties of a glass.

Mixed glass former glasses

Mixing glass-forming cations can add to the disorder of the system, leading to both positive and negative effects on the glass properties. For instance, substitution of $\rm B_2O_3$ for $\rm P_2O_5$ in sodium systems shows an increase in the ionic conductivity over that of binary phosphate and borate glasses, with the conductivity three orders of magnitude higher than the phosphate glass and one order of magnitude higher than the borate glass. This phenomenon is often referred to as a positive mixed glass former effect. 5

Negative mixed glass former effects also are encountered in certain glass systems, such as in the $0.5\text{Na}_2\text{S} + 0.5[x\text{GeS}_2 + (1-x)\text{PS}_{5/2}]$ system, where the conductivity decreases with addition of a second glass forming cation.⁹

Mixing glass-forming cations can be a valuable technique to improve the glass-forming nature, stability, and conductivity of glass systems with minimal detrimental effects. Along the same lines, mixing anions in glass can also lead to similar desired property changes.

Mixed anion glasses

Mixed anion glasses have been studied in recent years by a few different groups, primarily at Osaka Prefecture University (Sakai, Japan) and Iowa State University (Ames, Iowa), with the goal of merging the high ionic conductivity of sulfide glasses with the good chemical stability of oxide glasses. These mixed oxysulfide glasses were studied with the expectation of finding an optimized compromise between chemical, electrochemical, and thermal stabilities and conductivity, but frequently, these glasses are also found to exhibit a mixed anion effect.

Small introductions of oxygen in a primarily sulfide glass system, typically less than 10 to 20 at%, will actually increase the conductivity above that of the parent pure sulfide glass. Tatsumisago et al. discovered this phenomenon in several glass systems, including in $\text{Li}_2\text{S} + \text{SiS}_2 + \text{Li}_4\text{SiO}_4$ and in $\text{Li}_2\text{S} + \text{P}_2\text{S}_5 + \text{P}_2\text{O}_5$ systems. Often, the addition of oxygen helps retain the high conductivity of the sulfide glass while greatly improving the chemical durability and the electrochemical stability. Martin and Kim also demonstrated this effect with glasses in the $0.5\text{Li}_2\text{S} + 0.5(x\text{GeO}_2 + (1-x)\text{GeS}_2)$ system that exhibit a conductivity nearly a full order of magnitude higher at the x = 0.05 composition compared to that of the pure sulfide x = 0 glass. 11

While germanium-based glasses often exhibit high conductivities, especially when paired with another glass-forming cat-

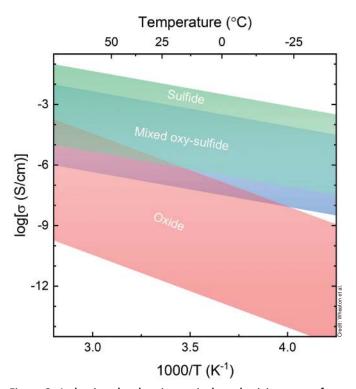


Figure 3. Arrhenius plot showing typical conductivity ranges for three composition families of glasses. The green shaded region corresponds to sulfide, the blue to mixed oxysulfides, and the red to oxides.

ion, the high cost of germanium often limits their viability in practical applications.

Mixed anion glasses in the $\text{Li}_2\text{S} + \text{SiS}_2 + \text{Li}_x\text{MO}_y$ system also show promise for improving the chemical and electrochemical stability of the GSE against lithium metal. A Nyquist complex impedance plot (Figure 4A) of a symmetric cell of a typical pure sulfide GSE sandwiched between two pure lithium metal electrodes shows that the interfacial impedance grows strongly over time. This growth in the resistance of the cell arises from the persistent reaction of the pure sulfide glass with the lithium metal anodes. Because the resistance continues to grow with time, no passivation layer (i.e., stable solid electrolyte interphase) forms to stabilize the interface. 12

Figure 4B, on the other hand, shows a Nyquist plot of a mixed oxysulfide GSE that was doped with oxygen to stabilize the interface between the GSE and lithium metal. The interfacial impedance decreases over time after fabrication of the cell until it stabilizes. This decrease is believed to be due to creep of the lithium metal filling voids at the interface while under moderate pressure in the coin cell.¹³

Perhaps one of the most successful and well-studied mixed anion GSE materials is LiPON, first studied at Oak Ridge National Laboratory in the early 1990s. ¹⁴ Nitrogen was studied as a dopant in lithium orthophosphate ($\rm Li_3PO_4$) with the hope of increasing the electrochemical potential stability window and conductivity of the base oxide.

LiPON was successfully developed and used in thin film microbatteries. Thin film LiPON is synthesized through radio-

Glassy solid-state electrolytes for all-solid-state batteries

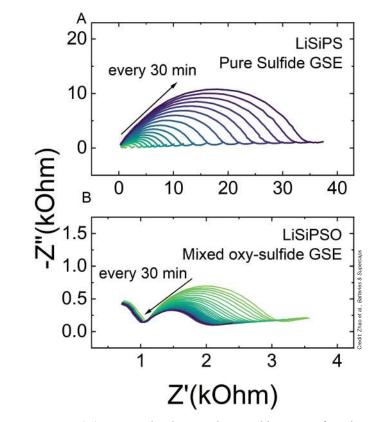


Figure 4. (A) Nyquist plot showing the unstable nature of a sulfide GSE against lithium metal. (B) Nyquist plots showing the stable behavior of mixed oxysulfide GSE against lithium metal. Top plot reproduced with permission from Ref. 12.

frequency magnetron sputtering of a crystalline $\mathrm{Li_3PO_4}$ target in a vacuum lightly backfilled with nitrogen gas. The sputtering process promotes replacement of oxygen with nitrogen up to a few atomic percent into the short-range structure of the material, altering the properties of the glass. The resulting film is typically amorphous, no thicker than a few microns, and exhibits a conductivity that is often more than an order of magnitude higher than the base $\mathrm{Li_3PO_4}$, even at low concentrations of nitrogen (N/O ratio less than 0.1).

The conductivity of LiPON is nevertheless rather low, at best about 10⁻⁶ S/cm. This low conductivity is typically not a major issue in solid-state microbatteries, however, as 1-µm-thick radiofrequency magnetron sputtered films are durable enough to prevent short circuiting.

It was recently suggested the highly modified structure of LiPON and other weakly networked, ionic glasses can allow for enough ductility to prevent cracking of the GSE during cycling, preventing the growth of lithium metal dendrites. ¹⁵ The uses of LiPON as a thin film GSE are limited in smart sensors, RFID cards, and similar applications. ¹⁶ Typically, these thin film batteries are only 10–15 µm thick with capacities ranging from 0.1–5 mAh. LiPON thin film batteries are also limited by high processing costs, low deposition rates, and high processing temperatures.

Further mixing of anions was attempted based on the promising results of nitrogen doping in stabilizing and increasing

the conductivity of oxide glasses, such as LiPON. Our group at Iowa State developed several compositions that combine some of the above strategies to optimize GSEs that show promising behaviors for use as SSEs. For example, the mixed glass former mixed oxysulfide-nitride GSE 0.95(0.67Li₂S + 0.264SiS₂ + 0.066P₂O₅) + 0.05(LiPO_{2.2}N_{0.54}), while possessing a lower conductivity than the base pure sulfide GSE, achieved a critical current density of 1.76 mA/cm² at 100°C (i.e., the current density below which the SSE does not short due to lithium dendrites). This achievement indicates that the GSE inhibits the growth of lithium dendrites up to this current density. Cyclic voltammetry of the GSE also shows that the glass is stable against lithium metal up to at least 5 V, allowing for the use of novel high-voltage cathodes without electrolyte oxidation. 12

Even with such progress, mixed anion glasses for use as SSEs are still an understudied area of glass research, with more work needed to fully understand the property changes associated with addition of other anions to the glass network.

Mechanochemically milled glasses

While melt-quenched samples can be preferable for eliminating grain-boundary impedance, high-energy mechanochemically milled (MCM) samples also present several advantages.

MCM is an interesting technique that is used to produce glasses without material loss due to volatilization and is easily scalable. The resultant powders are easily processible using common ceramic processing techniques already used in battery manufacturing, such as tape casting.

MCM glasses are typically milled at high speeds, often more than 400 rpm, for more than 20 hours, with X-ray diffraction patterns showing an amorphous halo, indicating the loss of crystalline order in the material. These materials exhibit similar thermal behavior to glasses, going through a glass transition in differential scanning calorimetry experiments. Also, recent work showed that MCM samples and melt-quenched samples with similar compositions are often structurally equivalent when compared using techniques such as Raman and magicangle-spinning nuclear magnetic resonance spectroscopies.⁵

Recently, our group and collaborators showed a MCM Na₃PS_{3.4}O_{0.6} glass can be formed into a fully dense material free of pores through simple cold uniaxial pressing.¹⁷ This GSE showed excellent rate capabilities for sodium systems, demonstrating stable cycling for hundreds of hours at 0.5 mA/cm² at 60°C. The sodium-sulfur full cell produced with this pressed electrolyte also exhibited excellent behavior with a specific capacity of 1,116 mAh/g at 0.1 mA/cm² with the cell cycling for 150 cycles consistently.

While this study is the first report of a fully dense pressed glass, many MCM GSE materials present excellent processing behavior, and future work may reveal more glass systems that can exhibit similar behavior.

Glass-ceramic solid-state electrolytes

Glass-ceramic solid-state electrolytes (GCSEs) are a relatively new type of GSE with several advantageous properties. These GCSEs are synthesized by partial crystallization of a GSE and often exhibit ionic conductivities higher than that of the parent glass.

This phenomenon was discovered when a thiophosphate GSE was overheated during temperature-dependent conductivity measurements, where the resulting GCSE exhibited a significantly higher ionic conductivity after cooling to room temperature compared to the asprepared GSE at the same temperature. In lithium thiophosphate GCSEs, the increase in conductivity is nearly a full order of magnitude. Lithium thiosilicate GSEs exhibit the opposite behavior, where the ionic conductivity decreases by more than two orders of magnitude on partial crystallization.

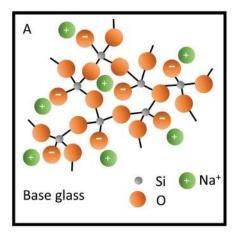
Many of the studied GCSEs are synthesized from a parent glass formed through MCM. To our knowledge, the studied GCSEs in the literature are primarily lithium-ion conductors; very few studies on other alkali ion conductors, such as Na⁺ GCSEs, have been performed. Even among the lithium SSEs, GCSEs are not widely studied nor is the mechanism behind their occasionally higher conductivity fully understood.

Salt doping strategies

GSE conductivity can be improved through dissolution of dopant salts into the glassy network, much like salt doping aqueous and nonaqueous solvents. However, while dopant halide salts help improve the conductivity, they can degrade other desired properties of a GSE, such as resistance to crystallization and electrochemical stability.

Typically, the salt contains the desired conductive cation and a large, low field strength anion. For example, alkali halides, especially LiI, are used due to the low mobility of the large halide anion in the glassy network.

Often, high concentrations up to 30 or 40 mol% of halide salts can be doped into a glass without precipitation of the dopant salt on cooling to the glassy state. Typically, the dopant salt is chosen such that the field strength of the counter anion (for example, Cl⁻, Br⁻, or I⁻) is low enough to not change the fraction of bridging/nonbridging anions, i.e., it does not react with the host glass network structure. Rather, the dopant salt anion



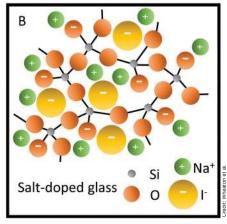


Figure 5. (A) Schematic showing a base glass with no salt doping and cations such as sodium, lithium, or potassium loosely bonded to nonbridging sulfur or oxygen. (B) Schematic showing a salt-doped glass with the same network but more spread out due to the salt dopant.

introduces more free volume into the glass by increasing the space between the tetrahedral units of the glass structure, effectively acting as a plasticizer, weakening the glass forming ability and network connectivity, as shown in Figure 5.

This change in the glass structure can significantly impact the properties of the glass, including a reduction in the glass transition temperature, reduced resistance to crystallization, and a significant increase in the conductivity. For example, the 0.3LiI + 0.7LiPO, glass has a room temperature ionic conductivity more than two orders of magnitude higher than that of the base LiPO₃.5 The change in conductivity is more pronounced in oxide glasses than in the already higher conducting sulfides. Salt doping can be problematic, however, as many of the salts used can be electrochemically unstable when in contact with lithium metal.5

Recent developments in glassforming techniques for GSEs

While the electrochemical properties of a glass are important to its success as a GSE, the formability of the glass into thin separators is also crucial in moving from lab-scale to large-scale synthesis.

As mentioned earlier, films of 100 µm in thickness or less are necessary to be competitive with current LIBs; however, processing glasses into durable thin films can be a challenging task. General Motors developed a process of hot pressing thiosilicophosphate glasses into a low-density fiberglass mesh achieving relative densities

of around 93% with films around 150 µm thick, while still preserving a conductivity of 7×10⁻⁴ S/cm.¹⁸ While the film thickness still needs to be further reduced, this technique is an interesting approach to processing glass powders into a thin film.

Our group recently reported the drawing of thin-film monolithic lithium metaphosphate (LiPO₃) glass down to about 50 µm in thickness, as shown in Figure 6.¹⁹ LiPO₃, as an oxide glass, has a conductivity of only 10⁻⁹ S/cm at room temperature, which is too low for use in SSBs. However, thin film drawing can be used with other much higher conductivity GSEs, such as mixed oxysulfide glasses, with reports being prepared on highly conducting sodium and lithium glasses being drawn into thin films through this process.

Performance of solid-state batteries using glassy electrolytes

In the past decade or so, several groups started testing their GSEs in full cell batteries. As described previously, LiPON full cells can perform well, at high currents; however, their energy densities typically only reach 2–3 mWh/cm² with cycling efficiencies typically between 80–99% ¹⁴

Recently, General Motors tested a Li–S hybrid full cell with their previously described GSE. In use for 300 cycles, their cell demonstrated a Coulombic efficiency of more than 98%, using a small amount of liquid electrolyte to improve surface contact between the electrolyte and the electrodes. While

Glassy solid-state electrolytes for all-solid-state batteries

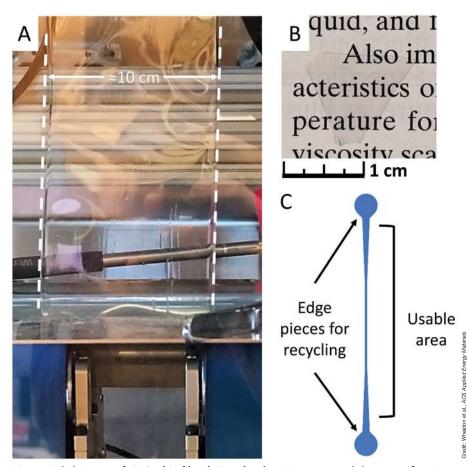


Figure 6. (A) Image of LiPO, thin film during the drawing process. (B) Image of a 45 µm thin film for use in testing. (C) Diagram of a cross-section of the drawn thin film showing the usable area. Reprinted with permission from Ref. 19. Copyright 2021 American Chemical Society.

lithium batteries are the most studied, in the past few years, our group collaborated to produce highly energy dense Na-S full cell batteries that offer specific capacities of greater than 1,100 mAh/g at 0.1 mA/cm² for more than 150 cycles.¹⁷

While there has been some progress in using these GSEs in full cell configurations to create solid-state batteries in the past couple decades, much work is still required prior to moving beyond the laboratory setting.

Challenges and perspectives

GSEs have several unique characteristics that make them desirable materials to replace flammable organic liquid electrolytes. While oxide-based GSEs and sulfide-based GSEs each have desirable properties, they both present drawbacks-low conductivity and high reactivity, respectively-that reduce the likelihood of their use in this application.

The cost of sulfide materials and their processing is also a challenge to their use, as they require atmospheres of less than 5 ppm O, and H,O to prevent degradation. The synthesis costs of some sulfide materials are higher than \$10 per gram.

While still in the early stages of development, it seems that mixed anion glasses, such as the mixed oxysulfide and mixed oxysulfide-nitride GSEs, may be able to offset material costs while reconciling the low conductivity of oxides and the high reactivity of sulfides to form glasses that are highly conductive and stable against alkali metals, such as sodium or lithium.

Prior to commercialization of GSEs, several challenges need to be addressed and solved. Along with many other ceramic materials, glasses remain brittle materials and are typically mechanically fragile when reduced to the thicknesses required for use as an SSE. Small

defects, such as bubbles or surface flaws, can lead to fracture of the GSE during use, leading to a potentially dangerous short circuit. Many engineering controls must be developed to eliminate flaws and reduce the risk of fracture. Additionally, as with all classes of solidstate electrolytes, large interfacial impedances between the electrodes and the GSE remain a critical issue. Researchers are working to reduce these impedances to less than 10Ω -cm².

Currently, GSEs are being studied on the laboratory scale, with very few materials in commercial production. Other electrolyte materials, such as lithium lanthanum zirconium oxide, receive more attention in literature, but glassy materials are quickly gaining attention with their improved processability relative to hard and brittle ceramic powders, such as the garnet-structured electrolytes.

Acknowledgements

This work was supported by DOE EERE VTO DE-EE0008852, NASA EPSCoR 80NNSSC20M0219, NSF DMR 1936913, and Iowa Energy Center Grant 307352.

About the authors

Jacob Wheaton, Madison Olson, and Victor M. Torres III are Ph.D. students and Steve W. Martin is an Anson Marston Distinguished Professor in Engineering in the Department of Materials Science and Engineering at Iowa State University. Contact Martin at swmartin@iastate.edu.

References

¹Han, F.; Westover, A. S.; Yue, J.; Fan, X.; Wang, F.; Chi, M.; Leonard, D. N.; Dudney, N. J.; Wang, H.; Wang, C., "High electronic conductivity as the origin of lithium dendrite formation within solid electrolytes," Nature Energy 2019, 4 (3), 187-196.

²Kerman, K.; Luntz, A.; Viswanathan, V.; Chiang, Y.-M.; Chen, Z., "Review-Practical challenges hindering the development of solid state Li ion batteries," Journal of The Electrochemical Society 2017, 164, A1731-A1744.

3Zhao, R.: Hu, G.: Kmiec, S.: Gebhardt, R.: Whale, A.; Wheaton, J.; Martin, S. W., "New amorphous oxy-sulfide solid electrolyte material: Anion exchange, electrochemical properties, and lithium dendrite suppression via in situ

interfacial modification," ACS applied materials & interfaces 2021, 13 (23), 26841–26852.

⁴Ravaine, D., "Glasses as solid electrolytes," *J. Non-Cryst. Solids* **1980**, 38–39, 353–358.

⁵Martin, S. W., "Glass and glass-ceramic sulfide and oxy-sulfide solid electrolytes." In *Handbook* of Solid State Batteries, 2nd Edition, Dudney, N.; West, W.; Nanda, J., Eds. World Scientific: New Jersey, 2015; pp. 433–501.

⁶Martin, S. W.; Schiraldi, A., "Glass formation and high conductivity in the ternary system silver iodide + silver arsenate (Ag₃AsO₄) + silver metaphosphate (AgPO₃): host to glassy .alpha.silver iodide?" *J. Phys. Chem.* **1985**, 89 (10), 2070–2076.

⁷Robert, G.; Malugani, J. P.; Saida, A., "Fast ionic silver and lithium conduction in glasses," *Solid State Ionics* **1981**, 3/4, 311–315.

⁸Pradel, A.; Ribes, M., "Electrical properties of lithium conductive silicon sulfide glasses prepared by twin roller quenching," *Solid State Ionics* **1986**, 18–19, 351–5.

⁹Martin, S. W.; Bischoff, C.; Schuller, K., "Composition dependence of the Na⁺ ion conductivity in 0.5Na₂S + 0.5[xGeS₂ + (1 − x)PS_{5/2}] mixed glass former glasses: A structural interpretation of a negative mixed glass former effect," *J. Phys. Chem. B* **2015**, 119 (51), 15738–15751. ¹⁰Tatsumisago, M.; Hirai, K.; Minami, T.; Takada, K.; Kondo, S., "Superionic conduction in rapidly quenched lithium sulfide-silicon disulfide-lithium phosphate, tribasic glasses," *J. Ceram. Soc. Jpn.* **1993**, 101 (Nov.), 1315–1317.

¹¹Kim, Y.; Saienga, J.; Martin, S. W., "Anomalous ionic conductivity increase in Li₂S + GeS₂ + GeO₂ glasses," *Journal of Physical* Chemistry B **2006**, 110 (33), 16318–16325.

¹²Zhao, R.; Hu, G. T.; Kmiec, S.; Wheaton, J.; Torres, V. M.; Martin, S. W., "Grain-boundary-free glassy solid electrolytes based on sulfide materials: Effects of oxygen and nitrogen doping on electrochemical performance," *Batteries & Supercaps* **2022**, 5 (11), e202100356.

¹³LePage, W. S.; Chen, Y.; Kazyak, E.; Chen, K.-H.; Sanchez, A. J.; Poli, A.; Arruda, E. M.; Thouless, M. D.; Dasgupta, N. P., "Lithium mechanics: Roles of strain rate and temperature and implications for lithium metal batteries," *Journal of The Electrochemical Society* **2019**, 166 (2), A89–A97.

¹⁴Dudney, N. J., "Thin film micro-batteries," *The Electrochemical Society Interface* **2008**, 17 (3), 44.

¹⁵Kalnaus, S.; Westover, A. S.; Kornbluth, M.; Herbert, E.; Dudney, N. J., "Resistance to fracture in the glassy solid electrolyte LiPON," *Journal of Materials Research* **2021**, 36 (4), 787–796.

¹⁶LaCoste, J. D.; Zakutayev, A.; Fei, L., "A review on lithium phosphorus oxynitride," *The Journal of Physical Chemistry C* 2021, 125 (7), 3651–3667.

¹⁷Chi, X.; Zhang, Y.; Hao, F.; Kmiec, S.; Dong, H.; Xu, R.; Zhao, K.; Ai, Q.; Terlier, T.; Wang, L.; Zhao, L.; Guo, L.; Lou, J.; Xin, H. L.; Martin, S. W.; Yao, Y., "An electrochemically stable homogeneous glassy electrolyte formed at room temperature for all-solid-state sodium batteries," *Nature communications* **2022**, 13 (1), 2854.

¹⁸Yersak, T.; Salvador, J. R.; Schmidt, R. D.; Cai, M., Hybrid Li-S pouch cell with a reinforced sulfide glass solid-state electrolyte film separator. *International Journal of Applied Glass Science* **2021**, 12 (1), 124–134.

¹⁹Wheaton, J.; Kmiec, S.; Schuler, D.; Sorensen, C.; Martin, S. W., "Electrochemical behavior of drawn thin-film vitreous lithium metaphosphate," ACS Applied Energy Materials 2021. ■

