The Future of All Solid State Battery

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Abstract. All Solid State Battery, is a type of battery which uses no liquid electrolyte, instead, it uses solid electrolyte (alternative to lithium-ion battery). This type of battery still has not been commercially used, but will soon be used in electric vehicles. The demand for the production of solid state battery is due to the advantages that arise from the safety issue. Solid electrolytes are the solid that exhibits ionic conductivities about $10^{-3}$ S/cm, and it conducts ions between the cathode and anode in the lithium ion battery. Various solid electrolytes based on phosphate glasses have been developed. This article reviews the developments of solid electrolytes and its applications.

Keywords: Solid state battery, solid electrolyte, superionic conducting glass, ionic conductivity

1. Introduction
There are numerous types of rechargeable batteries, including rechargeable Li-ion batteries (LIBs). LIBs have several advantages, such as, long life cycle, high power density, low self-discharge property, high gravimetric, and volumetric energy. Currently, lithium-ion batteries (LIB) are widespread and promising candidates for future application, such as electric vehicles and energy storage [1]. Nonetheless, they suffer from raw materials availability, safety concerns, and limited energy storage capacity. State-of-the-art lithium-ion cells consist of two porous electrodes (anode and cathode) and a separator, as depicted in Fig. 1 current collector, which consist of the active material, conductive agents, and binder [2]. The ion transfer requires a liquid electrolyte which is mainly composed of aprotic organic solvents and a conductive salt.

Many of the issues that current LIBs are facing can be traced back to this liquid electrolyte. Safety concerns, in fact, arise from the flammability of the solvents. Side reactions of the solvents and the conductive salt lead to capacity fading and aging [2]. All solid-state batteries (ASSB), in contrast, are not only inherently safer due to the lack of flammable organic components, but also offer the potential for a dramatic improvement of energy density. Instead of a porous separator soaked with liquid electrolyte, ASSBs use a solid electrolyte, which acts as electrical insulator and ionic conductor at once (Fig. 1 (b)). The use of a compact solid electrolyte acting as a physical barrier for lithium dendrites also enables the use of lithium metal as the anode material [3]. All solid-state batteries (ASSB), in contrast, are not only inherently safer due to the lack of flammable organic components, but also offer the potential for a dramatic improvement of energy density. Instead of a porous separator...
soaked with liquid electrolyte, ASSBs use a solid electrolyte, which acts as electrical insulator and ionic conductor at once (Fig. 2).

![Figure 1. How the lithium-ion battery (LIB) works.](image1)

![Figure 2. Diagram of (a) Lithium ion Battery; (b) All Solid State Battery [1].](image2)

2. Advantages of Solid State Batteries

2.1 Advantages of Solid State Batteries over Lithium-Ion Batteries.

There are several advantages of all solid-state battery over lithium ion batteries. It is non-flammable. In Lithium Ion batteries, the ions that flow from the cathode to the anode may form dendrites on the surface of the cathode, which can pass through the liquid electrolyte and to the anode causing a short circuit [3]. When a short circuit is formed, the battery will get hotter and might explode. Solid State Batteries solved this case due to the use of solid electrolyte which prevents the formation of dendrites. It has a higher energy density, due to is attainable by direct-series-stacking of battery cells. It reduces battery size, especially when thin-film of solid electrolyte is used. It has longer lifespan and higher capacity: solid state battery enables use of lithium metal anode which increases cell voltage and capacity.

2.2 Challenges of using solid state batteries:

Finding a solid material that is conductive enough to be used in large batteries, e.g. polymer or ceramic (solid electrolyte has to have high ionic conductivity). To obtain material that has ionic conductivity,
superionic materials are used, which are materials suitable for creating solid electrolytes as they allow ions to move quickly and freely through their crystal structure.

Ionic conductivity is typically low, which prevents fast charge and discharge. Forming a stable conductive interface between solid electrolyte and electrode is difficult. Low power due to high solid electrolyte-electrode resistivity. The poor electronic conductivity can cause electron beam radiation damage.

2.3 Different types of solid electrolytes used in solid state batteries:

2.3.1 Glass-based electrolyte. There are several glass-based electrolytes: (i) Simplifies fabrication of the battery cell as it allows them to plate the alkali metals and strip them on both electrodes. Hence, preventing the formation of dendrites; (ii) Uses sodium instead of lithium. Sodium is cheaper as it can be easily extracted from seawater; (iii) More environmentally friendly and can operate in extreme temperatures unlike lithium; (iv) Absence of grain boundaries; (v) Flexibility of size and shape at fabrication of glass, (vi) Can be prepared over a wide range of composition. Glass-based electrolyte consist of glass former (i.e.P2O5), glass modifier (i.e.Ag2O, Li2O) and salt-doping (i.e. AgI, LiI). The most well known study superionic conducting glasses are the silver and lithium system, respectively, AgI-AgPO3, LiI-LiPO3, and the mixed AgI-Ag:S-AgPO3, AgI-LiI-LiPO3,etc.[4-8]. Usually, the superionic glass was prepared by mixing appropriate amounts of AgI, AgNO3, NH4H2PO4, heating up 100°C/h to 600°C within 6 hrs, casting and quenching into liquid-N2. It will resulted a clear yellowish glass, while the undoped AgPO3 is a clear transparent glass [4-11].

2.3.2 Lithium-based electrolyte. Lithium based electrolyte, has several advantageous, namely (i) Ultrafast charging; (ii) A superionic conductor, hence can allow ions to move quickly through it (high ionic conductivity); (iii) Very small internal resistance, hence can produce greater power; (iv) Cells can stack together without interference; (v) Can retain their charges for long period of time, hence has long lifespan. The lithium phosphate, Li3PO4 has been chosen as one good candidates for solid state battery [9-10]. Its application in the thin film battery has been well studied. However, the limitation of low ionic conductivities, made modification of this material by doping with LiI, AgI or mixed salts [12-13].

2.3.3 Sulfide electrolyte. It has been investigated that Li10GeP2S12 is one of the best solid ionic conductor (12mS/cm). However, it is expensive as Germanium is used. Germanium can be replaced with tin, but it will reduce the ionic conductivity of the substance, unstable, and toxic. The best solid ionic conductor is Li9.52Si1.73P1.44S11.7·Cl0.3 (25mS/cm). It is amendable to fast charging due to the very high ionic conductivity and can sustain high temperature [14].

2.3.4 Oxide electrolyte. Proven to be better than sulfide electrolyte as it is thermally and chemically stable, does not require a controlled environment for processing. More environmental friendly as it does not produce toxic gases, unlike sulfide electrolyte that produces hydrogen sulfide which can cause acid rain. The common one used is C-LLZO, for use in high-voltage batteries. It is because C-LLZO is electrochemically inert over wider voltage. The problem with C-LLZO is that it is not thin enough because to slot a solid electrolyte between anode and cathode requires dense thin films (less than 50μm thick).

3. Results and discussion

Figure 3(a) and 3(b) show examples of superionic conducting glass AgI-AgPO3 and the series of AgI-Ag:S-AgPO3, respectively. The ionic conductivity has been increased by three orders of magnitudes, for AgI-AgPO3≈10^{-13} S/cm from the AgPO3 ~10^{-7} S/cm. There are several Influence of factors governing behavior of solid electrolytes grain interior atomic configuration is on ionic conductivity. Impacts of grain boundaries Behavior of solid electrolyte-electrode interferences. The phenomena have
been described by Aniya et al, on the Bond fluctuation model shown in Fig. 4 [14]. In this model, it is assumed that the structure consist of two regions: the glass network and the doped salt. By the insertion of salt, the network fluctuates and the distance, d, increases, thus increase the ionic conductivity.

![Image](a) ![Image](b)

**Figure 3.** Superionic conducting glass AgI-AgPO₃ and the series of AgI-Ag₂S-AgPO₃ [4,6].

![Diagram]

**Figure 4.** Bond fluctuation model shown in Fig.4 [15].

### 4. Conclusion
It is concluded that the research and development of on LIB moving forward. This paper has summarized the early development of solid electrolyte for all solid state battery. The research on solid electrolyte is growing due to safety reason. The future of solid state battery will be replacing the current commercial lithium ion battery which based on liquid electrolyte. In the future, all solid state battery will be very safety and efficient battery. This is because of the solid electrolyte has high ionic conductivity, and also it has high melting point. The use of solid state battery in electric cars removes all the cooling elements, which makes the battery pack lighter. Hence, the car will have a longer range and smaller battery size. The application, though is still not commercially available, but its prospect is promising to replace the current lithium ion battery.

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### References
[1] B. Scrosati and J. Garche, “Lithium batteries: Status, prospects and future,” *J. Power Sources*, vol. 195, pp. 2419–2430, 2010.
[2] Joscha Schnell, Till Günther, Thomas Knoche et al., All-solid-state lithium-ion and lithium metal batteries – paving the way to large-scale production, *Journal of Power Sources* 382, pp. 160–175, 2018

[3] Sveinbjörnsson, D. P., Vegge, T., Norby, P., & Mogensen, M. B. 2014. Design and Characterisation of Solid Electrolytes for All-Solid-State Lithium Batteries. Department of Energy Conversion and Storage, Technical University of Denmark.

[4] E. Kartini, S.J. Kennedy, K. Itoh, T. Kamiyama, M.F. Collins, S. Suminta, “Anion effect on the structure of Ag3S–AgPO3 superionic glasses”, *Solid State Ionics* 167 (1–2), pp. 65–71, 2004

[5] E. Kartini, M.F. Collins, “Neutron scattering and thermal measurements on the superionic-conducting Ag3S–AgPO3 glass system”, *Solid State Ionics* 314, pp.633–636, 2002.

[6] E. Kartini, M. Arai, F. Mezei, M. Nakamura, M. Russina, “Structure and dynamics on superionic conducting phosphate glasses by neutron scattering”, *Phys. B Condens. Matter.* 385–386, pp. 236–239 (2006).

[7] E. Kartini, S.J. Kennedy, K. Itoh, T. Fukunaga, S. Suminta, T. Kamiyama, “Characterization of the intermediate-range order in new superionic conducting AgI–Ag3S–AgPO3 glasses by neutron diffraction”, *Appl. Phys. A,* 1238 (1–3), pp. 1236–1238, 2002.

[8] E. Kartini, M. Manawan, M. F. Collins, M. Avdeev, 2017, “Neutron diffraction study on Li3PO4 solid electrolyte for lithium ion battery”, *Physica B: Condensed Matter* 551, pp. 320–326, 2018.

[9] N.I.P. Ayu, E. Kartini, L.D. Prayogi, M. Faisal, Supardi, “Crystal structure analysis of Li5PO4 powder prepared by wet chemical reaction and solid-state reaction by using X-ray diffraction (XRD)”, *Ionics* (Kiel) 353, pp. 1–7, 2016.

[10] E. Kartini, T.Y.S. Panca Putra, I. Kuntoro, T. Sakuma, K. Basar, O. Kamishima, J. Kawamura, “Recent studies on lithium solid electrolytes (LiI)0.3(LiPO3)0.7 for secondary battery”, *J. Phys. Soc. Jpn.* 79, pp. 54–58, 2010.

[11] E. Kartini, M. Nakamura, M. Arai, Y. Inamura, K. Nakajima, T. Maksum, W. Honggowiranto, T.Y.S.P. Putra, “Structure and dynamics of solid electrolyte (LiI)0.3(LiPO3)0.7”, *Solid State Ionics* 262, pp. 833–836, 2014.

[12] Evvy Kartini, Valentia Yapriadi, Heri Jodi, Maykel Manawan, Cipta Panghegar, Wahyudianingsih, Solid electrolyte composite Li4P2O7–Li3PO4 for lithium ion battery, Progress in Natural Science: Materials International, https://doi.org/10.1016/j.pnsc.2020.01.020

[13] D.P. Singh, K. Shahi, K.K. Kar, “Scaling behavior and nearly constant loss effect in AgI–LiPO3 composite glasses”, *Solid State Ionics* 231, pp. 102–108, 2013.

[14] M. Tatsumisago, M. Nagao, A. Hayashi, “Recent development of sulfide solid electrolytes and interfacial modification for all-solid-state rechargeable lithium batteries”, *J. Asian Ceram. Soc.* 1 (1)17–25, 2013.

[15] M. Aniya, J. Kawamura, “Medium range structure and activation energy of ion transport in glasses” *Solid State Ionics* 154, pp. 343, 2002.