

All-Solid-State Batteries and their Remaining Challenges

A potential route towards safer, higher performing batteries

Jitti Kasemchainan*, **Peter G. Bruce****

Department of Materials, University of Oxford,
Parks Road, Oxford OX1 3PH, UK

Email: *jitti.kasemchainan@materials.ox.ac.uk,
**peter.bruce@materials.ox.ac.uk

All-solid-state batteries, which utilise a solid electrolyte in place of liquid electrolytes, have the potential for higher energy densities and greater safety than current lithium-ion batteries. However they still face many challenges before the technology is ready to be commercialised. This short report summarises the current state of knowledge in all-solid-state batteries including the electrical, electrochemical and mechanical properties of the electrolytes, and the challenges that remain to be overcome in their development and processing.

Introduction

There is increasing worldwide motivation to research and develop all-solid-state batteries in order to achieve better safety, higher power and energy density, as well as wider operating temperature energy storage (1–3) as compared to conventional lithium-ion batteries. Liquid electrolytes used in Li-ion batteries are based on organic solvents, which are intrinsically volatile and highly flammable. In contrast, solid electrolytes are usually able to withstand high temperatures (>80°C). Several challenges related to solidifying batteries still remain to be addressed from fundamental understanding before the technology will be ready for widespread commercialisation.

State-of-the-Art in All-Solid-State Batteries

The main component of all-solid-state batteries is a solid electrolyte, which can be ceramic, glass, polymer or a mixture. The differences in the electrical, electrochemical and mechanical properties of a solid electrolyte compared to the more familiar liquid electrolytes are key to the challenges in all-solid-state batteries. At room temperature, the Li-ion conductivity of a solid electrolyte is usually at least two or three orders of magnitude lower than that of a liquid electrolyte, especially in the case of solid polymers (4). This can result from the solid electrolyte's intrinsic properties or from existing grain boundaries. However, the conductivities of some sulfide-based electrolytes like $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS), $\text{Li}_7\text{P}_3\text{S}_{11}$ and $\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br, I) are comparable to or even higher than those of liquid electrolytes (5–7).

It seems widely accepted and reported that the electrochemical oxidation potentials of solid electrolytes are superior to those of liquid electrolytes. Solid electrolytes may be stable above 5.0 V vs. Li^0/Li^+ . In the case of liquid electrolytes, it has been shown that decomposition occurs above 4.0 V vs. Li^0/Li^+ (8). In fact, recent results from density functional theory (DFT) computations (9–11) on the thermodynamic stability of various solid electrolytes hint that above 4.0 V vs. Li^0/Li^+ most solid electrolytes can be oxidised and decomposed into different phases. Even though there is little experimental evidence supporting such computational data, work by Auvergnon *et al.* (12) gives an idea of the possible decomposition of $\text{Li}_6\text{PS}_5\text{Cl}$ towards ordinary positive electrode materials of either LiCoO_2 (LCO), $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM)

or LiMn_2O_4 (LMO). With X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AEM) and scanning electron microscopy (SEM), it was possible to detect elemental sulfur, lithium polysulfides, P_2S_x ($x \geq 5$), phosphates and LiCl at the interface of $\text{Li}_6\text{PS}_5\text{Cl}$ with the positive electrodes. Similarly, Koerver *et al.* (13) used XPS and SEM to discover interphase formation between a $\beta\text{-Li}_3\text{PS}_4$ solid electrolyte and a NCM electrode material.

If the aim is for all-solid-state batteries that can achieve higher energy density than conventional Li-ion batteries containing liquid electrolytes, implementing Li metal as the negative electrode is crucial (2). Reactivity of solid electrolytes against Li metal has to be considered. The electrochemical reduction potential of solid electrolytes needs to be close to the redox reaction of Li metal, which is set as a reference at 0 V vs. Li^0/Li^+ . A Garnet-type ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO)) is the only stable solid electrolyte towards Li metal; up to now there is no real proof of its reactivity after exposure to Li metal. Other solid electrolytes will undergo reduction reactions by consuming Li-ions and electrons from Li metal to form an interphase layer, which is the so-called solid electrolyte interphase (SEI). The electrical properties of this SEI layer play a role in how the reaction between solid electrolytes and Li metal continues (14–16). If this layer is a mixed conductor of Li-ions and electrons, it will continue to grow as long as contact is maintained between the solid electrolyte and Li metal. Many solid electrolytes are in this category: for example, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (15, 16), $\text{Li}_{10}\text{SiP}_2\text{S}_{12}$ (15, 16), $\text{Li}_{10}\text{Si}_{0.3}\text{Sn}_{0.7}\text{P}_2\text{S}_{12}$ (15, 16) and $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (17). If the layer is a Li-ion conductor and minimally an electron conductor, the SEI acts as a protective layer to prevent further reactions between the solid electrolyte and Li metal. This behaviour is observed for lithium phosphorous oxynitride (LiPON) (18), $\text{Li}_7\text{P}_3\text{S}_{11}$ (19) and $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) (19).

Another important issue in all-solid-state batteries when using a Li metal electrode is Li dendrite growth, potentially causing short circuit. This is the case for solid electrolytes that do not react with Li metal or react and form a protective layer. Many studies that can be found elsewhere (20–23) point out the growth of Li dendrites in Garnet-type electrolytes, even when an electrolyte pellet was densified to obtain a relative density higher than 99.5%. Another interesting report about the sulfide electrolyte $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ illustrates locations in SEM micrographs that could be Li dendrites (24).

However, there is no fully developed mechanism to describe how Li dendrites start to grow at the interface of a solid electrolyte with a Li metal electrode and the properties of solid electrolytes responsible for Li dendrite growth are not yet well established. Newman and Monroe related dendrite growth to the shear modulus of polymer electrolytes (25, 26). Porz *et al.* (27) proposed that a surface crack or Griffith-like fracture in some glassy, polycrystalline and single crystalline solid electrolytes can invoke progressive crack opening for Li metal to plate and penetrate through.

Unlike liquid electrolytes, solid electrolytes are in general not readily deformable. Thus, preparation of ceramic or glassy electrolytes including assembly with electrodes and conductive carbonaceous materials is quite specific. For example, the process requires significant external pressure higher than 100 MPa for cell assembly (1, 12, 28–31). Note that the active negative electrodes used in the referenced literature were indium, graphite or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), possibly to avoid the problem of Li metal dendrites. During cycling of all-solid-state batteries, currently available electrode materials such as sulfur (32), NCM (13) or even LCO (28) experience a volumetric change when being lithiated and delithiated. This diminishes the physical contact between the electrode and solid electrolyte phases, subsequently impeding the batteries' cyclability or capacity retention.

Remaining Challenges

Thick composite positive electrode layers (high active mass loading) and thin solid electrolyte layers need to be considered for all-solid batteries so as to achieve favourable energy and power. Most all-solid-state batteries in the literature (1, 12, 13, 28) exhibit areal capacities less than 1.0 mAh cm^{-2} and operate at a C-rate around 0.1 C, particularly for charging. Commercial Li-ion battery electrodes (33) for cell assembly with liquid electrolytes can attain capacities over 2.0 mAh cm^{-2} and C-rates of 0.2 C. This implies that the performance of all-solid-state batteries is limited conceivably by kinetics or mass transfer. Moreover, there is a lack of feasible processes for assembly and scale-up for all-solid-state batteries (34, 35). It is also questionable whether available processing techniques from manufacturing standard Li-ion batteries can be directly exploited in all-solid-state battery systems.

Conclusion

Though all-solid-state batteries have extensively attracted attention in academia and industry, a number of known and unknown challenges make the technology immature. To accomplish comprehension and eventual commercialisation of the technology, long-term interdisciplinary research and development in science and engineering will be required.

References

1. Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba and R. Kanno, *Nature Energy*, 2016, **1**, (4), 16030
2. J. Janek and W. G. Zeier, *Nature Energy*, 2016, **1**, (9), 16141
3. A. L. Robinson and J. Janek, *MRS Bull.*, 2014, **39**, (12), 1046
4. J. G. Kim, B. Son, S. Mukherjee, N. Schuppert, A. Bates, O. Kwon, M. J. Choi, H. Y. Chung and S. Park, *J. Power Sources*, 2015, **282**, 299
5. N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto and A. Mitsui, *Nature Mater.*, 2011, **10**, (9), 682
6. Y. Seino, T. Ota, K. Takada, A. Hayashi and M. Tatsumisago, *Energy Environ. Sci.*, 2014, **7**, (2), 627
7. M. A. Kraft, S. P. Culver, M. Calderon, F. Böcher, T. Krauskopf, A. Senyshyn, C. Dietrich, A. Zevalkink, J. Janek and W. G. Zeier, *J. Am. Chem. Soc.*, 2017, **139**, (31), 10909
8. Q. Li, J. Chen, L. Fan, X. Kong and Y. Lu, *Green Energy Environ.*, 2016, **1**, (1), 18
9. Y. Zhu, X. He and Y. Mo, *J. Mater. Chem. A*, 2016, **4**, (9), 3253
10. Y. Zhu, X. He and Y. Mo, *ACS Appl. Mater. Interfaces*, 2015, **7**, (42), 23685
11. W. D. Richards, L. J. Miara, Y. Wang, J. C. Kim and G. Ceder, *Chem. Mater.*, 2016, **28**, (1), 266
12. J. Auvergniot, A. Cassel, J.-B. Ledeuil, V. Viallet, V. Seznec and R. Dedryvère, *Chem. Mater.*, 2017, **29**, (9), 3883
13. R. Koerver, I. Aygün, T. Leichtweiß, C. Dietrich, W. Zhang, J. O. Binder, P. Hartmann, W. G. Zeier and J. Janek, *Chem. Mater.*, 2017, **29**, (13), 5574
14. S. Wenzel, T. Leichtweiss, D. Krüger, J. Sann and J. Janek, *Solid State Ionics*, 2015, **278**, 98
15. P. Bron, B. Roling and S. Dehnen, *J. Power Sources*, 2017, **352**, 127
16. S. Wenzel, S. Randau, T. Leichtweiß, D. A. Weber, J. Sann, W. G. Zeier and J. Janek, *Chem. Mater.*, 2016, **28**, (7), 2400
17. M. Zhang, K. Takahashi, N. Imanishi, Y. Takeda, O. Yamamoto, B. Chi, J. Pu and J. Li, *J. Electrochem. Soc.*, 2012, **159**, (7), A1114
18. A. Schwöbel, R. Hausbrand and W. Jaegermann, *Solid State Ionics*, 2015, **273**, 51
19. S. Wenzel, S. J. Sedlmaier, C. Dietrich, W. G. Zeier and J. Janek, *Solid State Ionics*, 2017, *In Press*, *Corrected Proof*
20. E. J. Cheng, A. Sharafi and J. Sakamoto, *Electrochim. Acta*, 2017, **223**, 85
21. F. Aguesse, W. Manalastas, L. Buannic, J. M. Lopez del Amo, G. Singh, A. Llordés and J. Kilner, *ACS Appl. Mater. Interfaces*, 2017, **9**, (4), 3808
22. R. H. Basappa, T. Ito, T. Morimura, R. Bekarevich, K. Mitsuishi and H. Yamada, *J. Power Sources*, 2017, **363**, 145
23. A. Sharafi, H. M. Meyer, J. Nanda, J. Wolfenstine and J. Sakamoto, *J. Power Sources*, 2016, **302**, 135
24. M. Nagao, A. Hayashi, M. Tatsumisago, T. Kanetsuku, T. Tsuda and S. Kuwabata, *Phys. Chem. Chem. Phys.*, 2013, **15**, (42), 18600
25. C. Monroe and J. Newman, *J. Electrochem. Soc.*, 2004, **151**, (6), A880
26. C. Monroe and J. Newman, *J. Electrochem. Soc.*, 2005, **152**, (2), A396
27. L. Porz, T. Swamy, B. W. Sheldon, D. Rettenwander, T. Frömling, H. L. Thaman, S. Berendts, R. Uecker, W. C. Carter and Y.-M. Chiang, *Adv. Energy Mater.*, 2017, **7**, (20), 1701003
28. W. Zhang, D. A. Weber, H. Weigand, T. Arlt, I. Manke, D. Schröder, R. Koerver, T. Leichtweiss, P. Hartmann, W. G. Zeier and J. Janek, *ACS Appl. Mater. Interfaces*, 2017, **9**, (21), 17835
29. Y. Ito, Y. Sakurai, S. Yubuchi, A. Sakuda, A. Hayashi and M. Tatsumisago, *J. Electrochem. Soc.*, 2015, **162**, (8), A1610
30. T. Ohtomo, A. Hayashi, M. Tatsumisago, Y. Tsuchida, S. Hama and K. Kawamoto, *J. Power Sources*, 2013, **233**, 231
31. D. H. Kim, D. Y. Oh, K. H. Park, Y. E. Choi, Y. J. Nam, H. A. Lee, S.-M. Lee and Y. S. Jung, *Nano Lett.*, 2017, **17**, (5), 3013
32. M. Nagao, A. Hayashi, M. Tatsumisago, T. Ichinose, T. Ozaki, Y. Togawa and S. Mori, *J. Power Sources*, 2015, **274**, 471
33. 'Li-ion Battery Electrode/Li Chips', MTI Corp: <http://www.mtixtl.com/li-ionbatteryelectrodelichips.aspx> (Accessed on 30th January 2017)
34. K. Kerman, A. Luntz, V. Viswanathan, Y.-M. Chiang and Z. Chen, *J. Electrochem. Soc.*, 2017, **164**, (7), A1731
35. Y.-S. Hu, *Nature Energy*, 2016, **1**, (4), 16042

The Authors



Jitti Kasemchainan is a postdoctoral researcher with Peter G. Bruce's group at the Department of Materials, University of Oxford, UK. He completed an Erasmus Mundus Master Course of Materials for Energy Storage and Conversion (MESOC) in 2011. He carried out a doctoral thesis at Robert Bosch GmbH in Gerlingen, Germany, and received his PhD in Mechanical Engineering from Karlsruhe Institute of Technology (KIT), Germany, in 2015. His current research is focused on solid electrolytes and the electrode-electrolyte interfaces for rechargeable batteries.



Peter Bruce's research interests embrace materials chemistry and electrochemistry, especially lithium and sodium batteries. Recent efforts have focused on the synthesis and understanding of new materials for lithium-ion batteries, on understanding anomalous oxygen redox processes in high capacity Li-ion cathodes, the challenges of the lithium-air battery and the influence of order on the ionic conductivity of polymer electrolytes. His research has been recognised by a number of awards and fellowships, including from the Royal Society, the Royal Society of Chemistry, the German Chemical Society and The Electrochemical Society. He was elected to the Royal Society in 2007 and the Royal Society of Edinburgh in 1994. As well as directing the UK Energy Storage Hub, SUSTAINABLE POWER GENERATION and supply (Supergen), Peter is Chief Scientist in the Faraday Institution, the UK centre for research on electrochemical energy storage.