

Editorial

Promising Superhalogen-Based Solid-State Electrolyte for the Next Generation of Batteries

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Editorial

In recent years, the development of lithium ions battery confronts some serious problems, such as stagnant capacity (150mAh/g), limited recycling life (<1000 times), potential security problem of self-combustion and explosion due to the combustible organic electrolyte [1,2]. In fact, mobile phone self-combustion and explosion have been reported frequently which poses potential threat to life and property safety. Furthermore, when working at high power and high temperature, the energy capacity declines persistently, and side reactions may occur in the electrolytes or at the interface between the electrodes and electrolytes. These factors mentioned above promote the demand of developing next generation of batteries that are safer, cheaper, more durable, more portable, and more efficient.

Solid-state electrolyte

Recently many corporations and institutions [3-5] (such as Samsung, Toyota, Panasonic, MIT, UMD, etc.) have paid extensive attention to the research and development of solid-state battery, where solid electrolyte is one of the key parts. Solid electrolyte can fit many different kinds of electrodes that cannot coexist with liquid electrolyte, and would maintain energy capacity after thousands of charging-discharging cycles. What is more, the battery is able to work without ignition even when the electrolyte is split or melt, which makes it much safer than traditional battery with liquid electrolyte. Compared with the traditional one, the simpler construction of solid-state battery would reduce the cost of encapsulation and elect-control system significantly. And it is convenient for solid-state battery to be processed into various shapes [6] (such as film, micro-particle, micro-cube, etc), which also makes it possible for smart wearable device with smaller volume and various configurations. For this purpose, the ionically conducting oxides for Li ions have been explored extensively including $\text{Li}_{14}\text{ZnGe}_4\text{O}_{16}$ [7], $\text{Li}_{1.5}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [8], $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ [9], $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [10]. However, their potential application was constrained for a long time by the low ionic conductivity (<1mS/cm²) at room temperature in comparison with liquid ones (>10mS/cm²), the situation was changed by the discovery of sulphide-based compounds [3] such as $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ (2.2 mS cm⁻¹), $\text{Li}_7\text{P}_3\text{S}_{11}$ (17 mS cm⁻¹), and $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (12 mS cm⁻¹). But the high cost and complex method in synthesis restrict their further development.

It is encouraging to note that scientists have successfully synthesized a new kind of superionic conductor with anti-perovskite structure such as Li_3OCl , Li_3OBr [11,12], where the ionic conductivity for the nearly perfect crystal is only about 0.12~0.85 mS cm⁻¹, which can be improved significantly when vacancies are introduced into these materials by doping other cations (Mg^{2+} , Ca^{2+} , etc) thus providing more migration positions for Li ions. In addition, rational mixing of halogens (Cl/Br/I) in anti-perovskite Li_3OX (X represents halogen) can also effectively tune the diffusion tunnel and lower the vacancy migration barriers, leading to the enhancement of ionic conductivity. Examples include $\text{Li}_{3-2x}\text{Ba}_x\text{ClO}$ ($x = 0.005$, 25 mS cm⁻¹ at 25°C, 38 mS cm⁻¹ at 75°C, 240 mS cm⁻¹ at 100°C), $\text{Li}_{3-2x}\text{Ba}_x\text{Cl}_{0.5}\text{I}_{0.5}\text{O}$ ($x = 0.005$, 121 mS cm⁻¹ at 50°C). The resources used to synthesize these materials are abundant and cheap, and the preparation technique is quite facile to be realized. For instance, by adding a few drops of deionized water in mixture of LiCl and Li_2O , a paste can be formed, and when heated in a reactor, the water can be evaporated. Finally, the Li_3OX can form through heating the reactor isolated from air at 220~240°C [11]. The enhanced ionic conductivity and the easier preparation method add the advantages for the anti-perovskite materials to be the next superstar as solid-electrolyte in the future energy storage.

The recent breakthrough

Halogen has been widely used in electrolyte. A breakthrough was made in 2014 by Puru Jena and his collaborators [13,14] at Virginia Commonwealth University, for the first time they theoretically proposed the application of Superhalogen instead of halogen in liquid electrolyte to mitigate the corrosion of electrodes. And the ionic conductivity also can be improved by use of superhalogens with appropriate binding energies with Li ions. Later on, Rana Mohtadi et al. [15] succeeded in synthesizing the first halogen-free, simple-type Mg salt with monocarborene Superhalogen $\text{CB}_{11}\text{H}_{12}^+$. The salt was compatible with Mg metal and it displayed an oxidative stability surpassing other solvents, which was a turning point in the research and development of Mg battery. The non-corrosive nature of Superhalogen can significantly expand the applicable range of electrodes.

Based on the experimental and theoretical studies as discussed above, it is quite logic and reasonable to propose a new model of solid-state electrolyte for the future research direction in this field, namely, replacing the halogen elements in anti-perovskite Li_3OX (X represents halogen) with superhalogens, where the size of channel for Li ions migration can be effectively tuned by the incorporation of superhalogens with different size and shape. It should be noticed that too large channels would disorder the migration, while small ones would cause higher energy barriers, leading to less conductivity. Besides, the Li^+ binding energy to Superhalogen also needs to be carefully tuned. If the binding is too strong, Li ions would become less mobile; on the other hand, if the binding is too weak, the crystal

structure might not be stable during the operation. Guided by a combination of first principles calculations with thermodynamic theory a rational incorporation of Superhalogen clusters could be applied to maximize the Li⁺ conductivity in the lithium-rich anti-perovskites. Recently, Y. Zhao et al. [16] have synthesized Li₃OBr materials with defective anti-spinel structure at 1.84 GPa/326°C, which provided another promising candidate for designing Li⁺ solid-state electrolyte. It is known that Li ion migration will be more likely to occur when vacancies exist, but more research attention should be paid to the dynamics and stability of ion transportation in materials with high defect concentration. When superhalogens are introduced to these systems, more exciting progresses can be expected in this field, and synergetic efforts combined high-throughput simulations and experiments would speed up the process.

In summary, the new-type electrolyte would bring excitement to battery industry. Among all the possible electrolyte candidates, solid-state electrolyte is promising due to the fact that it not only simplifies the cell structure but also avoids inflammability, and it is easier to be integrated in various electronic devices. Especially the derivatives of anti-perovskite Li₃OX solid-state electrolyte have high Li ionic conductivity and simple synthetic routes; we thus can expect a new design of Li ion solid electrolyte by introducing Superhalogen clusters in anti-perovskite Li₃OX materials, where the transportation tunnels of Li ions can be tuned effectively by appropriate superhalogens with different compositions, different size and shape. However, there are still a lot of work to be done for better understanding the kinetics and dynamics of ion transportation in materials with high concentrations of defects and porosities. In short, the Superhalogen-based solid electrolyte not only can stand for a new research direction of the next generation of Li ion battery but also can act as a good example of nano-assembled materials for energy applications.

References

- Gallagher, S. Boeing's Dreamliner batteries 'inherently unsafe'-and yours may be too. *Ars Technica*. 2013.
- Meier F, Woodyard C. Feds review third Tesla fire as shares fall again. *USA Today*. 2013.
- Wang Y, Richards WD, Ong SP, Miara LJ, Kim JC. Design principles for solid-state lithium superionic conductors. *Nat Mater*. 2015; 14: 1026-1031.
- Knauth P. Inorganic solid Li ion conductors: An overview. *Solid State Ion*. 2009; 180: 911-916.
- Li J, Ma C, Chi M, Liang C, Dudney NJ. Solid electrolyte: The key for high-voltage lithium batteries. *Adv Energy Mater*. 2015; 5: 1401408.
- Kuwata N, Kawamura J, Toribami K, Hattori T, Sata N. Thin-film lithium-ion battery with amorphous solid electrolyte fabricated by pulsed laser deposition. *J Electrochemistry Communications*. 2004; 6: 417-420.
- Bruce PG. The A-C conductivity of polycrystalline LISICON, Li_{1-2x}Zn_{1-x}GeO₄, and a model for intergranular constriction resistances. *J Electrochem Soc*. 1983; 130: 662-669.
- Aono H. Ionic conductivity of solid electrolytes based on lithium titanium phosphate. *J Electrochem Soc*. 1990; 137: 1023-1027.
- Inaguma Y. High ionic conductivity in lithium lanthanum titanate. *Solid State Commun*. 1993; 86: 689-693.
- Murugan R, Thangadurai V, Weppner W. Fast lithium ion conduction in garnet-type Li₇La₃Zr₂O₁₂. *Angew Chem Int Ed Engl*. 2007; 46: 7778-7781.
- Braga MH, Ferreira JA, Stockhausen V, Oliveirad JE, El-Azab A. Novel Li₃ClO based glasses with superionic properties for lithium batteries. *J Mater Chem A*. 2014; 2: 5470-5480.
- Yi Zhang, Yusheng Zhao, Changfeng Chen. Ab initio study of the stabilities of and mechanism of superionic transport in lithium-rich antiperovskites. *Phys Rev B*. 2013; 87: 134303.
- Giri S, Behera S, Jena P. Superhalogens as building blocks of halogen-free electrolytes in lithium-ion batteries. *Angew Chem Int Ed Engl*. 2014; 53: 13916-13919.
- Jena P. Superhalogens: A Bridge between Complex Metal Hydrides and Li Ion Batteries. *J Phys Chem Lett*. 2015; 6: 1119-1125.
- Tutusaus O, Mohtadi R, Arthur TS, Mizuno F, Nelson EG. An Efficient Halogen-Free Electrolyte for Use in Rechargeable Magnesium Batteries. *Angew Chem Int Ed Engl*. 2015; 54: 7900-7904.
- Zhang J, Zhu J, Wang L, Zhao Y. A new lithium-rich anti-spinel in Li-O-Br system. *Chem Commun (Camb)*. 2015; 51: 9666-9669.