Science Bulletin 68 (2023) 1598–1599

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Science Bulletin
www.scibull.com

Research Highlight

A new family of halide electrolytes for all-solid-state lithium batteries

Ning Zhao, Xiangxin Guo *

College of Physics, Qingdao University, Qingdao 266071, China

The worldwide research on all-solid-state lithium batteries (ASSLBs) flourished in the past decade due to the strong demand for high energy density and safe electrochemical energy storage. Deep understanding of the fundamental issues in ASSLBs is the foundation stone for achieving practical ASSLBs in industry [1–3]. Solid electrolytes (SEs), as the central parts of ASSLBs, are in priority worth exploring and investigating. So far, there is still a great task to obtain SEs that can satisfy the requirements of ASSLBS such as sufficiently high ionic conductivity as well as interfacial compatibility and deformability [4,5]. Sulfide electrolytes with high ionic conductivity and low mechanical moduli enable operation of ASSLBs at room-temperature (RT), while cathode coating and non-lithium-metal anodes are indispensable to overcome the poor interfacial stability [6]. Oxide electrolytes such as $Li_7La_3Zr_2O_{12}$ garnet can tolerate both the oxidation of high-voltage cathode and the reduction of lithium (Li) anode, but suffer from poor solid–solid contact with the electrode [7]. In recent years, the halide SEs have emerged with attractive properties such as RT ionic conductivity higher than 1 mS cm^{-1}, superior deformability, and excellent chemical stability against high-voltage cathode. Unfortunately, most of the halide SEs (e.g., Li_3YCl_6 [8], $Li_2In_xSc_{0.666-x}Cl_4$ [9] and Li_3InCl_6 [10,11]) generally exhibit poor interfacial stability against Li.

Recently in *Nature* [12], Yao and his colleagues, from the University of Science and Technology of China, reported a $LaCl_3$-based $Li_xTa_yLa_zCl_3$ ($x + 5y + 3z = 3$) with a high ionic conductivity of 3.02 mS cm^{-1} at 30 °C with respect to $Li_{0.388}Ta_{0.238}La_{0.475}Cl_3$, as well as an interfacial stability against Li. As demonstrated in Fig. 1a, the UCl_3-type $LaCl_3$ possesses a non-close-packed anion lattice with plenty of one-dimensional (1D) Li^+ channels. Each channel is enclosed by six columns of adjacent edge-sharing tricapped-trigonal prism [$LaCl_9$], providing Li^+ migration paths with the inner diameter of approximately 4.6 Å. The *ab initio* molecular dynamics simulations on the model system $Li_3La_5\square_1Cl_{18}$ revealed that Li^+ can move rapidly along 1D channels at closely spaced sites. Interestingly, the Li^+ migration between the adjacent channels can be connected by the La vacancies (Fig. 1b). On the basis of such idea, the authors sufficiently introduced La vacancies by doping of high-valence Ta^{5+} to constructing three-dimensional (3D) interconnected Li^+ migration pathways.

The interfacial stability of $Li_xTa_yLa_zCl_3$ against Li is also successfully achieved [12]. Without the addition of intermediate layer, the Li-Li symmetric cells with $Li_{0.388}Ta_{0.238}La_{0.475}Cl_3$ as SEs exhibit an ultra-long cycling over 5000 h at 1 mA cm^{-2} with a flat voltage plateau in all periods. Incorporation of $Li_{0.388}Ta_{0.238}La_{0.475}Cl_3$ with Li anodes and uncoated $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) cathodes, the cells run more than 100 cycles with 81.6% capacity retention. As interpreted by X-ray photoelectron spectroscopy (XPS), a small amount of Ta (13.4%) and La (8.4%) in $Li_{0.388}Ta_{0.238}La_{0.475}Cl_3$ is reduced at the interface in contact with Li, which is much lower than that of In in Li_3InCl_6 (>60%) [13], benefiting from the low electronegativity of La (i.e., 1.1) and Ta (i.e., 1.5). Furthermore, the formation of electrically insulated LiCl interphase shields SE from continuous reduction by Li (Fig. 1c), endowing $Li_{0.388}Ta_{0.238}La_{0.475}Cl_3$ with excellent anti-reduction capability. In addition, the dense nanocrystalline feature and the low electronic conductivity of $Li_{0.388}Ta_{0.238}La_{0.475}Cl_3$ pellet (1.74×10^{-10} S cm^{-1}) also play important role in improving the Li/SE interfacial stability. This discovery represents a breakthrough in the field of halide SE research.

Another important finding of this work is the high tolerance of the UCl_3-type structure with dopant ions. The $LaCl_3$ lattice can accommodate various ions with valance state ranging from +1 to +6, which makes the UCl_3-type electrolytes a large family (Fig. 1d). As proved experimentally, the dopant ions including Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Y^{3+}, In^{3+}, Sc^{3+}, Zr^{4+}, Hf^{4+}, Ta^{5+}, Nb^{5+} and W^{6+} can be introduced into the $LaCl_3$ lattice without changing the UCl_3-type structure. Such features empower the $LaCl_3$-based SEs the potential to further improve their electrochemical properties, including the ionic conductivity, interface and air stability, economic viability and so on. As a proof of principle, the authors selected earth-abundance metal elements such as Ca^{2+} and Zr^{4+} to substitute the Ta. It was found that the $Li_{0.495}Zr_{0.259}Ca_{0.086}La_{0.432}Cl_3$ maintained the $LaCl_3$ structure without impurity and exhibited an ionic conductivity of 1.61 mS cm^{-1} at room temperature, which indeed achieved a trade-off between performance and cost.

Yao and his colleagues [12] undoubtedly have proposed a new type of SEs for ASSLBs, while many issues are worth further studying concerning the industry application. Scaling-up fabrication of $LaCl_3$-based SEs should be taken into account. Besides the milling method used in this work, the sintering or solution route that is well-established in industry is also worth exploring. The air/humidity tolerance of $LaCl_3$-based SEs requires careful and critical evaluation, which lies as an obstacle for scalable fabrication.

* Corresponding author.
E-mail address: xxguo@qdu.edu.cn (X. Guo).

https://doi.org/10.1016/j.scib.2023.06.034

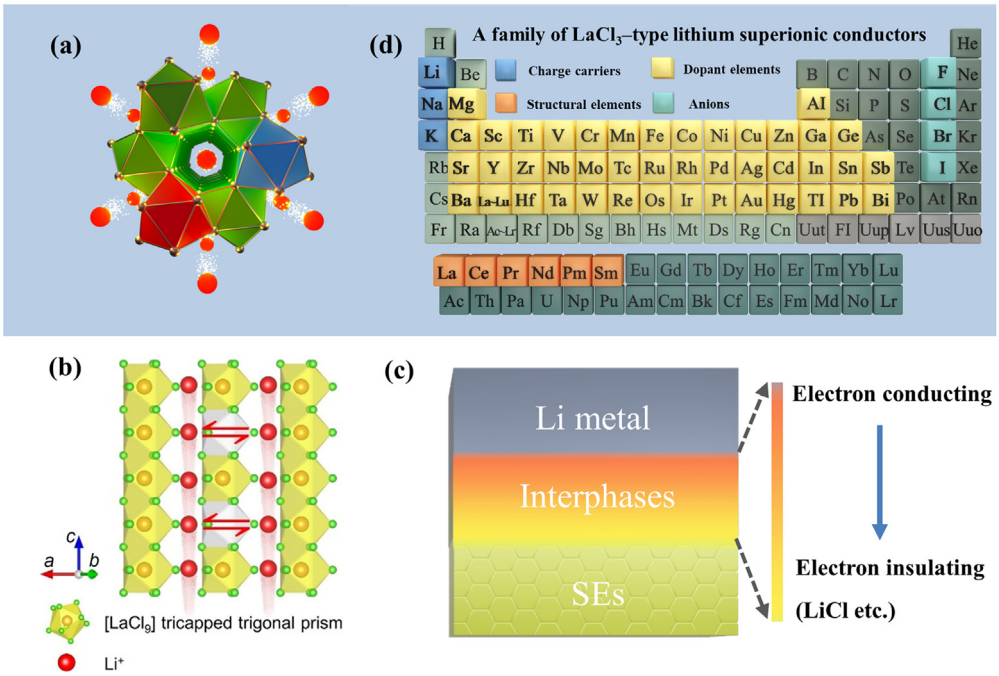

Fig. 1. (a) An illustration of a $LaCl_3$-type Li^+ superionic conductor with three-dimensional (3D) Li^+ migration pathways. (b) The one-dimensional (1D) channel for Li^+ migration (red spheres) in the $LaCl_3$ lattice and the Li^+ migration between adjacent channels enabled by La-vacancy. Reproduced from Ref. [12] with the permission of Springer Nature. (c) Schematic of the gradient passivation interphase layer formed at the interface between Li metal and $LaCl_3$-type solid electrolytes. (d) Schematic of the periodic table showing the great potential of $LaCl_3$ lattice to generate a new family of SEs.

To construct ASSLBs with realistically high energy density, the approaches of battery assembly, not just SEs, deserve equal attention. Both thick cathodes with the low SE fraction and the low stack-pressure during battery operation should be considered. Although there still needs a lot of work to achieve the practical use of $LaCl_3$-based SEs in industry, the strategy of material design demonstrated in this Nature article provides a novel idea for finding new and high-performance SEs for ASSLBs.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] Janek J, Zeier WG. Challenges in speeding up solid-state battery development. Nat Energy 2023;8:230–40.
[2] Sang JW, Tang B, Pan KC, et al. Current status and enhancement strategies for all-solid-state lithium batteries. Acc Mater Res 2023;4:472–83.
[3] Chang Z, Yang H, Zhu X, et al. A stable quasi-solid electrolyte improves the safe operation of highly efficient lithium-metal pouch cells in harsh environments. Nat Commun 2022;13:1510.
[4] Manthiram A, Yu X, Wang SF. Lithium battery chemistries enabled by solid-state electrolytes. Nat Rev Mater 2017;2:16103.
[5] Tufail MK, Zhai P, Jia M, et al. Design of solid electrolytes with fast ion transport: computation-driven and practical approaches. Energy Mater Adv 2023;4:15.
[6] Kato Y, Hori S, Saito T, et al. High-power all-solid-state batteries using sulfide superionic conductors. Nat Energy 2016;1:16030.
[7] Zhao N, Khokhar W, Bi ZJ, et al. Solid garnet batteries. Joule 2019;3:1190–9.
[8] Asano T, Sakai A, Ouchi S, et al. Solid halide electrolytes with high lithium-ion conductivity for application in 4 V class bulk-type all-solid-state batteries. Adv Matter 2018;30:1803075.
[9] Zhou L, Zuo TT, Kwok CY, et al. High areal capacity, long cycle life 4 V ceramic all-solid-state Li-ion batteries enabled by chloride solid electrolytes. Nat Energy 2022;7:83–93.
[10] Li XN, Liang JW, Chen N, et al. Water-mediated synthesis of a superionic halide solid electrolyte. Angew Chem Int Ed 2019;58:16427–32.
[11] Chen X, Jia ZQ, Lv HM, et al. Improved stability against moisture and lithium metal by doping F into Li_3InCl_6. J Power Sources 2022;545:231939.
[12] Yin YC, Yang JT, Luo JD, et al. A $LaCl_3$-based lithium superionic conductor compatible with lithium metal. Nature 2023;616:77–83.
[13] Riegger LM, Schlem R, Sann J, et al. Lithium-metal anode instability of the superionic halide solid electrolytes and the implications for solid-state batteries. Angew Chem Int Ed 2021;60:6718–23.

Ning Zhao received his Ph.D. degree in Material Physics and Chemistry from Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS) in 2016. He is currently an associate professor at College of Physics, Qingdao University. His current research focuses on solid-state electrolytes, solid-state batteries and Li/Na-O_2 batteries.

Xiangxin Guo received his Ph.D. degree from Institute of Physics, Chinese Academy of Sciences (CAS) in 2000. As a postdoctoral scientist, he continued research at the Max Planck Institute for Solid State Research, at the Paul Drude Institute for Solid State Electronics, and at the European Synchrotron Radiation Facility. He then worked as a staff scientist at the Max Planck Institute, before joining the Shanghai Institute of Ceramics. He is currently a full professor at College of Physics, Qingdao University. His research focuses on solid garnet batteries, metal-air batteries, and heterostructure-based solid-state ionic devices.