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PRESS RELEASE

Source: Toyohashi University of Technology, Japan, Committee for Public Relations

Release Title: Building a new mechanical property evaluation method for atmospherically unstable sulfide solid electrolyte

Release Subtitle: Towards all solid-state batteries based on the mechanical properties of their components

Overview

Prof. Matsuda research group at Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, revealed that an indentation test can effectively evaluate the mechanical properties of a sulfide solid electrolyte for all-solid-state lithium-ion secondary batteries. Since the sulfide solid electrolyte must be handled in an inert atmosphere due to its atmospheric instability, research on mechanical properties is limited. Against this background, the research group found that mechanical properties of a sulfide solid electrolyte can be evaluated by using indentation tests with glove bags filled Ar gas to maintain an inert atmosphere. This result is expected to be applied in battery design based on the mechanical properties of the battery components.

Details

Due to the target of achieving carbon neutrality[1] by 2050 and the recent increase of awareness of the SDGs[2], there is increased demand for the continued development of power generation technologies using green energy sources and electricity storage devices. A prime candidate electricity storage device is the lithium-ion secondary battery, which can handle high voltage and have high energy density. Though they are widely used in smartphones, electrical vehicles, and other applications, it is necessary to increase the energy density, lifespan, safety and lower the cost. All-solid-state lithium-ion secondary batteries (all-solid-state batteries) are drawing attention as a potential next-generation electricity storage device. The all-solid-state batteries replace the organic electrolyte used in lithium-ion secondary batteries with an inorganic solid electrolyte that has the following advantages: excellent stability and reliability, excellent energy density, excellent output properties, and ability to operate in a wide range of operating temperatures.

The all-solid-state batteries are constructed by stacking an anode composite, a solid electrolyte that acts as a separator, onto a cathode composite, which mixes the cathode active materials with a solid electrolyte and a conductive carbon. A main issue of the all-solid-state battery is the construction of a good solid-solid interface between the solid electrolyte and the electrode active material on the cathode composite. During the charge/discharge reaction, the electrode active material expands/contracts. Contact between the solid electrolyte and the electrode active material must be maintained to transport lithium ions. To solve the issue of the interface between the electrode active material and the solid electrolyte, it is important to quantitatively understand the Meyer hardness[3], elastic modulus[4], and other mechanical properties of the electrode active material and the solid electrolyte before determining the combination of materials and their ratio of each material. However, it is difficult to evaluate mechanical properties, because a typical solid electrolyte, sulfide solid electrolyte, easily reacts with atmosphere. Though some research has used the ultrasonic pulse method[5] and the nanoindentation technique[6], there were problems accurately evaluating the mechanical properties because of a strong dependency on a void within a pellet, and the surface roughness.

Therefore, this research focused on the indentation method for evaluating mechanical properties. This method does not require the complicated process for sample preparation and can obtain information about significant mechanical properties such as Meyer hardness and elastic modulus by loading and unloading the indenter into a sample and analyze the data based on theoretical formulas. In contrast to the nanoindentation test (1 mm or less), the indentation depth is several dozens of mm. Therefore, it is expected to enable an evaluation of intrinsic mechanical properties independent from the surface state. The research team evaluated the mechanical properties of the Li_2S-P_2S_5 sulfide solid electrolyte (75Li_2S-25P_2S_5) and an oxide solid electrolyte ($Li_{0.33}La_{0.57}TiO_3$, $Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O_{12}$) using the indentation test. In addition, glove bags filled with Ar gas were used to maintain an inert atmosphere. The Meyer hardness (H_M =0.66 GPa) and elastic modulus (E =21 GPa) of the sulfide solid electrolyte were calculated, which were lower than those of the oxide solid electrolyte (H_M = ~7.5 GPa, E = ~200 GPa). This result confirmed that sulfide-type solid electrolytes have superior mechanical properties for fabricating all-solid-state batteries.

Future Outlook

The research team revealed that an indentation test in an inert atmosphere can evaluate the mechanical properties of a sulfide solid electrolyte. This method does not require complicated process for sample preparation but can obtain significant mechanical properties such as Meyer hardness and elastic modulus by loading and unloading the indenter into a sample and analyze the data based on theoretical formulas. By evaluating the mechanical properties of various solid electrolytes materials using the indentation method, a database of mechanical properties will be created. It is expected that the database can be applied in the design of all-solid-state batteries based on their mechanical properties.

Glossary

[1] Carbon neutrality is the balance of greenhouse gas emissions and absorption. In October 2020, the Government of Japan declared it would achieve net zero greenhouse gas emissions by 2050.

[2] The Sustainable Development Goals (SDGs) are international goals that aim to build a sustainable world by 2030, as stated in the 2030 Agenda for Sustainable Development.

[3] Meyer hardness is an index of the hardness of materials. It is one of the ways of measuring indentation hardness and is defined as the ratio of the peak load to the projected area of the residual indentation impression. The larger value means the harder material.

[4] Elastic modulus is a physical property, which represents the difficulty of deformation. It is a proportional constant of the stress and strain curve in the elastic deformation area. The larger value means the harder deformation.

[5] The ultrasonic pulse method uses an oscillator to create longitudinal or lateral waves to propagate ultrasonic pulses in a test piece. The Young's modulus is calculated based on the longitudinal or lateral waves propagated in the test piece.

[6] The nanoindentation technique evaluates mechanical properties are calculated based on the relationship between the load and indentation depth. Generally, the nanoindentation is used a minute indentation depth of approximately several nm to several hundred nm.

Reference

Kazuhiro Hikima, Mitsuhiro Totani, Satoshi Obokata, Hiroyuki Muto, Atsunori Matsuda, Mechanical Properties of Sulfide-Type Solid Electrolytes Analyzed by Indentation Methods. *ACS Applied Energy Materials* **2022,** *5* (2), 2349-2355, DOI: 10.1021/acsaem.1c03829.

Acknowledgments

This research was performed with the support of the Japan Science and Technology Agency (JST)'s Advanced Low Carbon Technology Research and Development Program in the special focus technology area of Next-generation Batteries (ALCA-SPRING, JPMJAL1301).

Further information

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Toyohashi University of Technology founded in 1976 as a National University of Japan is a research institute in the fields of mechanical engineering, advanced electronics, information sciences, life sciences, and architecture.

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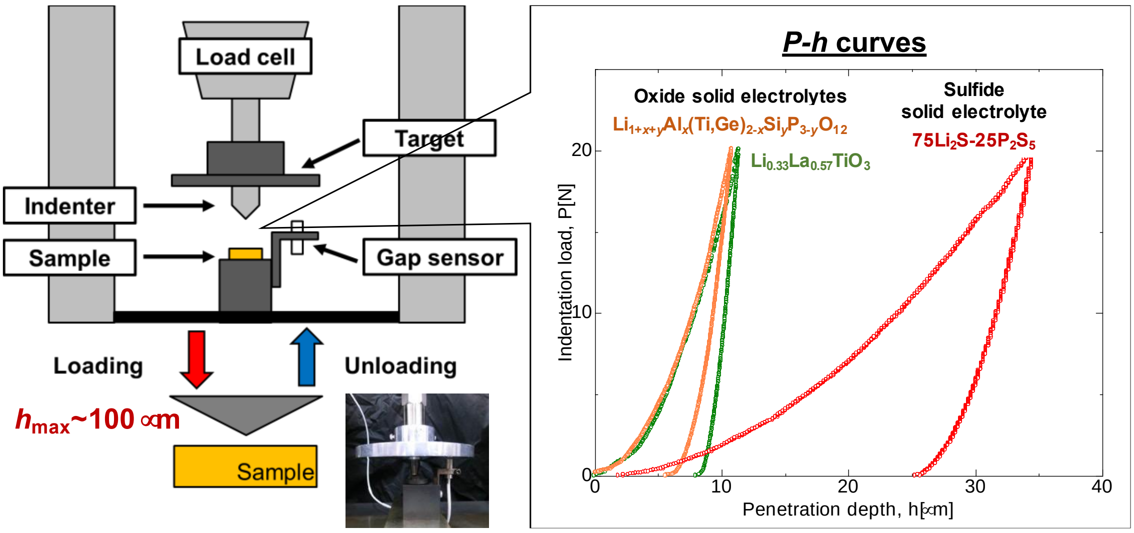
Figure:



Title: Schematic image of indentation apparatus and obtained raw data.

Caption: Schematic image of indentation apparatus (left), and the obtained *P*-*h* curve (right), *P* indicates a load, and *h* indicates an indentation depth. The red line indicates the *P* -*h* curve of the $75Li_2S$-$25P_2S_5$ sulfide-type solid electrolyte. The brown and green lines indicate the *P* -*h* curves of the oxide-type solid electrolytes such as $Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O_{12}$ and $Li_{0.33}La_{0.57}TiO_3$, respectively.

Keywords: Solid electrolytes, Batteries, Composite materials, Materials science, Solid state physics, Lithium ion batteries