論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	In-situ scanning electron microscope observation of microstructural changes in all-solid-state lithium batteries
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出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第12519号, 授与年月日:2023年9月22日, 学位の種別:課程博士, 審査員:平山 雅章,鈴木 耕太,荒井 創,谷口 泉,和田 裕之
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第12519号, Conferred date:2023/9/22, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

Summary of doctoral dissertation

Dissertation title:

In-situ scanning electron microscope observation of microstructural changes in all-solid-state lithium batteries

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Chapter 1. General introduction

All-solid-state batteries (ASSBs) are attracting great attention as next-generation energy storage systems based on their high thermal stability. In the electrode of an all-solid-state battery, lithium ions mainly move along the solid electrolyte. Therefore, if the solid electrolyte has a good mixing state with the active material, unlike the liquid electrolyte, it does not experience a problem of infiltration or diffusion. Therefore, it is possible to make the loading level of the cathode layer thicker than that of conventional electrodes of conventional lithium-ion batteries (LIBs). In addition, if a lithium metal or alloy electrode is successfully applied, the energy density of an ASSB is expected to rise more drastically than that of a LIBs. However, ASSBs are still far from practical use due to chemical and physical degradation occurring at the solid-solid interface. Expected chemical degradation is mainly known as interdiffusion of elements or decomposition due to composition and potential differences. Thanks to many prior studies on chemical degradation, electrochemically stable materials and evaluation methods are reported.

On the other hand, very small amount of information about physical degradation is known. Due to the high deformability of sulfide electrolytes, a good solid-solid interface is formed with a simple press. Because of this advantage, many researchers are less interested in physical degradation. However, this interface is also physically destroyed as the active material will experience a volume change during subsequent charge/discharge process. Loss of solid-solid contact blocks the transfer path of lithium ions or electrons, so it will be a direct reason of cell performance reduction. Therefore, it is necessary to conduct in-situ cell observations to understand physical degradation. If the mechanism of physical degradation occurring inside the ASSB is known, the required properties of the material can also be identified and improved.

Chapter 2. Experimental

In order to observe the physical problems occurring in the operating cell, a scanning electron microscope (SEM) was employed. SEM has high spatial/temporal resolution. Therefore, it is possible to quickly observe problems arising from the entire cell to small interfaces. In order to control the particle size of the electrolyte used in cell fabrication, a wet milling (WM) process was applied. The WM process is

applied that uses solvents and balls to grind (**Fig. 1**). Also, in this study, an indentation test was performed to find out the difference in mechanical properties according to the particle size distribution of LGPS. A schematic diagram of the indentation test is shown in **Fig. 2**. The formed pellets were evaluated through universal material testing equipment. A load was applied to the sample at a constant speed through a steel ball intender, and removed immediately (loading-unloading). By repeating this, the cycle data of P-h curves were obtained.

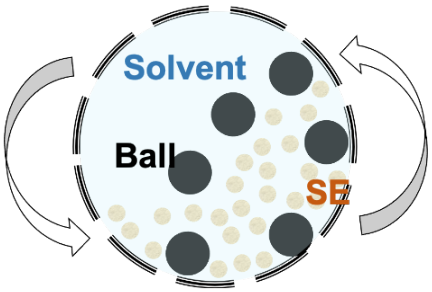

Fig. 1 Physical degradation of the NCM811 and β-Li_3PS_4 interface after cycle test.

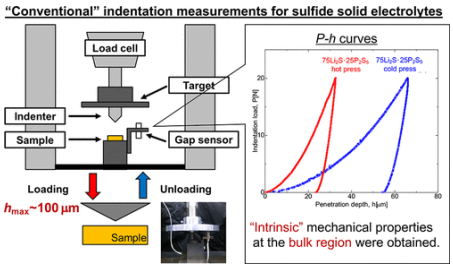

Fig. 2 Schematic of the indentation testing instrument and the P-h curves.[1]

[1] HIKIMA, *ACS Applied Energy Materials*, **2022**, 5.2: 2349-2355.

Chapter 3. Particle size control of sulfide electrolyte using dry and wet milling process

Through SEM observations, it has been shown that problems occurring in in-situ cells mainly originate from disproportionately large electrolyte particles. Therefore, a process for pulverizing the electrolyte into small and uniform particles are required. The wet-milling (WM) process is applied that uses solvents and balls to grind. When pulverizing crystalline electrolytes, it is necessary to minimize degradation of crystallinity (= decrease of ionic conductivity) due to excessive milling energy. For this reason, studies on milling of crystalline electrolytes have been extremely rare so far. However, in this study, it was succeeded in exploring the appropriate milling conditions for LGPS (WM LGPS). The pulverized LGPS still exhibits high crystallinity and ionic conductivity. The average size was 0.51 μm, which is much smaller and more uniform than hand-milled (in a mortar) LGPS (HM LGPS) (**Fig. 3**).

By low-temperature impedance analysis at 175 K, bulk and grain boundary resistance components were separated. If the solid electrolyte is pulverized without degradation of crystallinity, it is expected that there is no difference in bulk resistivity before and after milling. However, it is expected that only the grain boundary resistance has grown due to the small grain size. The bulk resistance of the WM LGPS was 1.2 x 10^4 ohms, which was not much different from that of the HM LGPS (1.1 x 10^4 ohms). On the other hand, the grain boundary resistance component in the WM LPGS greatly increased from 3.3 x 10^4 ohms to 10.2 x 10^4 ohms. In conclusion, if the crystalline electrolyte is pulverized under appropriate conditions, a small electrolyte can be obtained without reducing the ionic conductivity in the bulk (**Fig. 4**).

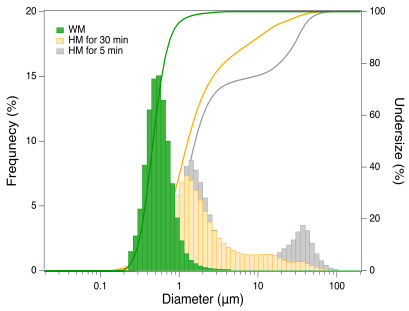

Fig. 3 Dispersed particle size distributions of HM/WM LGPS.

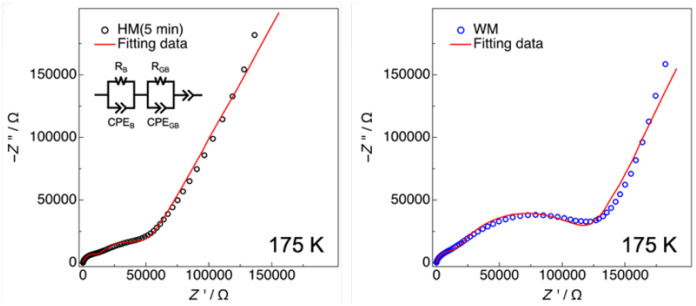

Fig. 4 Nyquist plots of EIS measurements of HM/WM LGPS at 175 K.

Chapter 4. In-situ scanning microscopy observation of $Li_{10.35}Ge_{1.35}P_{1.65}S_{12}$ and $LiNbO_3$-coated $LiCoO_2$ cathode electrode microstructure

By applying WM LGPS to the solid electrolyte layer (SE layer), we were able to solve problems that occur in in-situ cell manufacturing (**Fig. 5**).

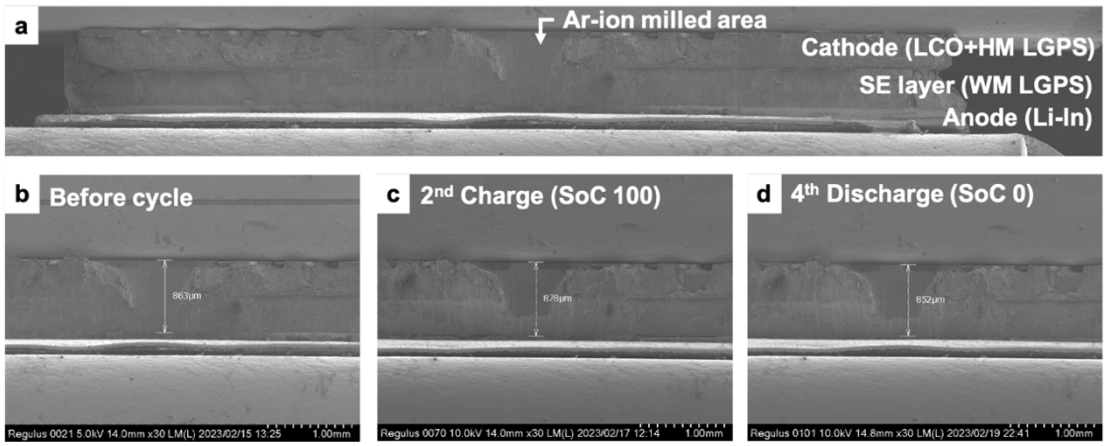

Fig. 5 Cross-section SEM images In-Li/WM LGPS/LNO-coated LCO+HM LGPS pellets. (a) Whole complete in-situ cell without defects, (b) before cell test, (c) after 2nd charge, and (d) after 4th dischge.

First, degradation occurring in the cathode composite (HM LGPS+$LiCoO_2$) was observed during electrochemical evaluation. After a successful initial charge (118 mAh g^{-1}), a large capacity decrease occurred in the initial discharge (77 mAh g^{-1}). It is expected that the transfer path of lithium ions, which was maintained in the first charge, was destroyed and could not return to the cathode active material. In the in-situ SEM images, it is observed that the well-formed initial interface undergoes physical degradation after completion of the first charge (**Fig. 6**). This physical degradation includes loss of contact and the development of massive cracks. These physical issues are expected to play a direct role in lowering the

initial Coulombic efficiency. In subsequent cycles, no additional physical degradation has occurred and the cycle performance remains relatively stable. In other words, the main degradation factor of the cathode (composite) is the volume change experienced by each electrode material during the initial charge process. Until now, the low initial coulombic efficiency of all-solid-state batteries has been known due to the formation of an electrochemically stable interface (i.e., SEI layer). However, as a result of elemental mapping through SEM/EDX, no aspect of chemical change was observed (**Fig. 7**).

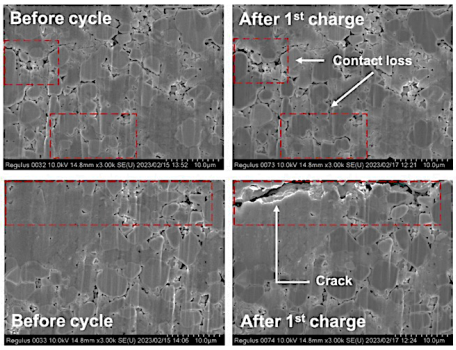

Fig. 6 Observed physical degradations (contact loss and crack) during 1st charge.

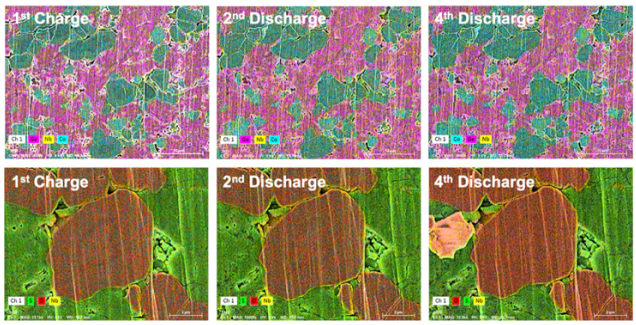

Fig. 7 Observation of chemical degradation at LGPS-LCO interface through SEM/EDX.

Chapter 5. Changes in mechanical properties according to the particle size of solid electrolyte and effect on all-solid-state battery performance

In the WM LGPS SE layer in-situ cell, a stable structure was maintained while HM LGPS SE layer experience crack. Solid electrolytes with the same composition but smaller size appear to have changed mechanical properties compared to larger electrolytes. To investigate the size effect of the electrolyte, an in-situ cell with WM LGPS applied to the cathode composite was made and electrochemically evaluated. The cathode composite with WM LGPS also experienced contact loss during the initial charging process but showed a tendency to recover contact again during subsequent discharging. Also, cracks did not occur inside the electrolyte particles. Thanks to the improved physical degradation, it exhibits higher efficiency (92%) and discharge capacity (123 mAh g^{-1}) than the previous in-situ cell (65%, 77 mAh g^{-1}). In order to investigate the changed mechanical properties of the small electrolyte, an indentation evaluation was conducted. As a result of the indentation test, WM LGPS showed higher plastic deformation than HM LGPS in both electrolyte and cathode composite pellets (**Fig. 8**). Plastic deformability means a property that is good for deformation with stress applied from the outside. Therefore, it is advantageous to change well without contact loss for compression and tensile stress during volume change of the cathode composite. The high plastic deformability of small grains is a widely known fact in the field of materials. Also, the same effect can applied to sulfide electrolytes.

Also, no electrolyte fracture (cracking) was observed within the WM LGPS cathode composite. This

phenomenon is known to be related to grain size also, in many materials engineering fields. The larger the grain size, the more likely the fracture mode is to occur as a transgranular mode in which cracks penetrate the grain. Conversely, in small grains, fracture tends to occur in an intergranular mode in which cracks propagate through the boundary. Therefore, direct destruction of the electrolyte is suppressed in WM LGPS. Destruction of a large electrolyte means that many ion transport paths within the electrode are lost, thus adversely affecting cell performance. Since the intergranular mode fracture that occurs in WM LGPS composite has a high probability of recovering at the next discharge process, it is very advantageous to maintain the cell performance.

In-Li/HM- or WM-LGPS/In-Li symmetry cells were evaluated to analyze the correlation between the particle size of the electrolyte and mechanical durability. Since the In-Li alloy anode experiences volume change, it is expected that there will be a difference in durability depending on the mechanical properties. As a result of symmetry cell evaluation, the WM LGPS SE layer showed an improved overvoltage suppression effect at a higher current density than the HM LGPS SE layer (**Fig. 9**). Also, the WM LGPS symmetric cell was shown to operate more stably for a longer time than the HM LGPS symmetric cell. Since the In-Li anode is electrochemically stable against LGPS, the occurrence of overvoltage was expected to be due to the restriction of the lithium-ion transfer path due to physical degradation. To confirm this fact, postmortem SEM/EDX observations were conducted on symmetric cell. As a result of cross-sectional observation of the symmetric cell, cracks were observed in the adjacent of the anode interface after 5 cycles in the HM LGPS SE layer. Since these cracks restrict the movement of lithium, they become a major cause of overvoltage growth. In addition, this crack gradually grew and caused complete separation of the anode-electrolyte layer in 43 cycles. On the other hand, in the WM LGPS SE layer, cracks were not observed even after 5 cycles. As a result, it was confirmed that it could operate for 71 cycles thanks to the effect of suppressing crack generation (**Fig. 10**).

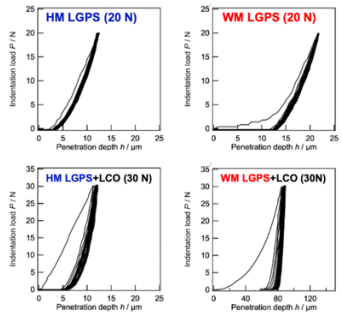

Fig. 8 Indentation cycle test on HM/WM LGPS pellets and LGPS+LCO composite

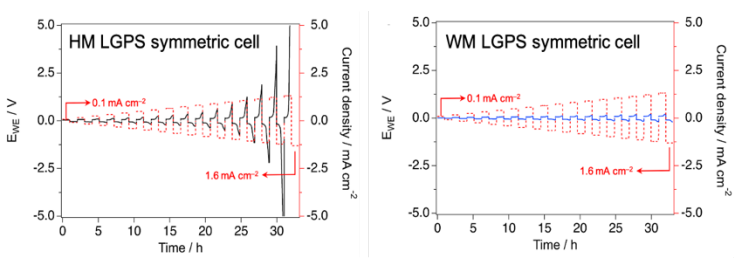

Fig. 9 The symmetric cell evaluation of (a) In-Li/HM LGPS/In-Li, (b) In-Li/WM LGPS/In-Li, respectively.

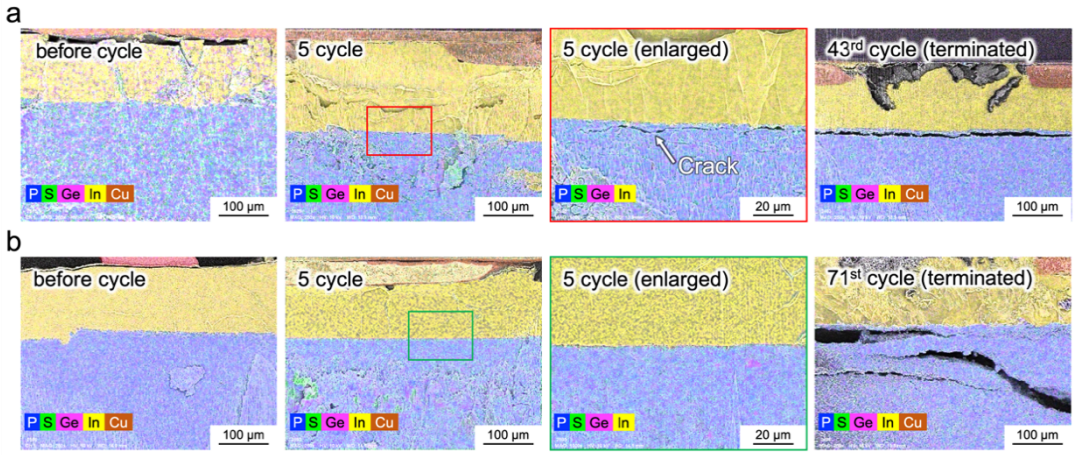

Fig. 5.11 Postmortem SEM/EDX cross-sectional images of the before, during, and after cycles of symmetric cells (a) In-Li/HM LGPS/In-Li and (b) In-Li/WM LGPS/In-Li, respectively.

Crack suppression means that the yield strength against normal stress caused by contraction-expansion of In-Li metal was improved. The phenomenon that increases of yield-strength at small grains is also a well-known in materials engineering widely. Since dislocations are difficult to accumulate at the boundaries of small grains, more stress is required for dislocations to move to the next grain (= yield). This relationship is known as grain boundary strengthening or Hall-Petch strengthening. Therefore, it is expected that the WM LGPS could better withstand the stress caused by the anode and maintain the lithium-ion transfer path well.

Chapter 6. General conclusion

Through in-situ cell observation through SEM/EDX, the physical degradation mechanism occurring in ASSBs were confirmed. In addition, thanks to the size effect through electrolyte pulverization, it was possible to understand the physical properties required for battery materials to suppress physical issue. High plastic deformation and small size are required in the cathode composite, and high yield strength is required at the anode metal interface.

Although the size effect of small grains is widely known throughout materials engineering. However, it is an unfamiliar concept in sulfide electrolytes. Perhaps, many researchers have not paid attention to this because small electrolytes have a reduced ionic conductivity due to increased grain boundary resistance. However, since this study revealed the need to suppress the physical degradation of ASSBs, a strategy for improving mechanical properties is essential. It is expected that size effects are not the only way to obtain improved mechanical properties. Research on all-solid-state batteries can be further expanded by developing materials that can satisfy the mechanical properties learned through this research or by designing cells that suppress the physical degradation mechanism.