

ELUCIDATION OF DEGRADATION MECHANISM OF LAGP SOLID ELECTROLYTE

Akihiro Kawasaki¹, Kenta Watarai², Linchun He³, Masato Morita¹, Tetsuo Sakamoto^{1,2,#}

¹*Department of Applied physics, School of Advanced Engineering, Kogakuin University*

²*Graduate School of Electric Engineering and Electrics, Kogakuin University*

2665-1 Nakano-machi, Hachioji, Tokyo 192-0015 Japan

³*Department of Mechanical Engineering, National University of Singapore 117574*

Abstract

All solid state lithium ion battery (ASS-LIB) is attributed much attentions as a next generation's power source because of its safety and high energy density. Making clear the solid state electrolyte (SSE) failure mechanism is undoubtedly important for developing and spreading ASS-LIB. In this study, SSEs were analyzed to reveal the process of degradation of SSE by Time of Flight Secondary ion Mass Spectrometry (TOF-SIMS). We successfully observed morphological and elemental differences before and after charge and discharge cycle test.

Introduction

The demand for all solid state lithium ion batteries (ASS-LIBs) is increasing in today's society because of its safety and high energy density. Designing superior solid state electrolyte (SSE) is necessary in order to spread ASS-LIBs to market. A lot of SSEs have been designed so far [1], $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) which has sodium super ion conductor (NASICON) crystal structure is one of the most famous SSE material due to its high ion conductivity ($\times 10^{-3}$ - 10^{-4} S/cm) at room temperature and stability in atmosphere[2]. However, some cracks and amorphous region which a few micrometers length were observed on an LAGP cross section after charge and discharge cycle test, and these phenomenon were considered as cause of LAGP's degradation [3].

The degradation mechanisms should be revealed because it is undoubtedly important for developing superior SSE material. LAGP's amorphization was investigated by Electrochemical Strain Microscopy technique, and it indicates that origin of LAGP particle is fabrication Li compounds in the interface of each particle [3]. Nevertheless, since other

E-mail:ct13087@ns.kogakuin.ac.jp

elements distribution have not studied, such amorphization process is still unknown.

Focused ion Beam (FIB) attached Time of Flight Secondary ion Mass Spectrometry (TOF-SIMS) which was constructed by our laboratory [4] is suit for studying LAGP's amorphization because it has extremely high lateral resolution (40 nm) and TOF-SIMS can easily detect Li ion. Therefore, in this study, TOF-SIMS measurement was conducted in order to reveal the LAGP amorphization and cracking process. After preparing of the smooth cross section of charge and discharge cycle degraded LAGP and no-degraded one, these samples was compared by elemental distribution imaging.

Experiment

LAGP pellets were synthesized by a modified solid-state reaction method [3]. In a typical process, stoichiometric amounts of Li_2CO_3 (99%, Sigma-aldrich) (10% excess), Al_2O_3 (99.98%, Alfa Aesar), GeO_2 (99.999%, Alfa Aesar) and $\text{NH}_4\text{H}_2\text{PO}_4$ (98%, Sigma-aldrich) were mixed at 150 rpm for 4 h in a zirconia jar filled with ethanol. The mixture was dried at 80°C for 10 h followed by calcination at 380°C for 4 h. After dry-milling at 100 rpm for 30 min, the powder was then melted at 1350°C for 2 h with heating rate of 10°Cmin^{-1} . The molten powder was immediately poured into a pre-heated (of 500°C) stainless steel container to obtain a dense glass pellet. This glass pellet was maintained at 500°C for 2 h to release internal stress. It was then dry ball-milled again to obtain small glass particles and further crystallized at 800°C for 8 h with heating rate of 5°Cmin^{-1} . The obtained LAGP powders were pelletized and sintered at 900°C for 8 h with the same heating rate as before.

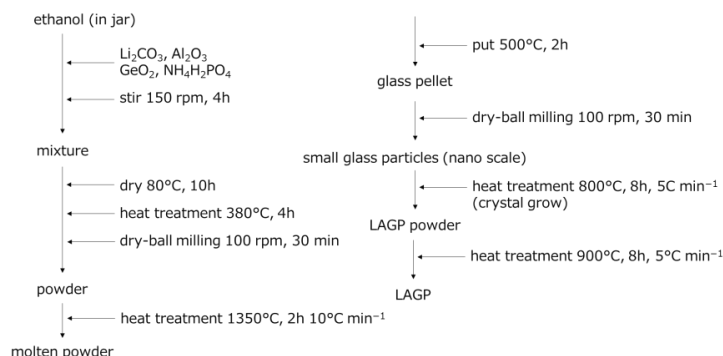


Fig.1. Follow chart of LAGP pellet preparation

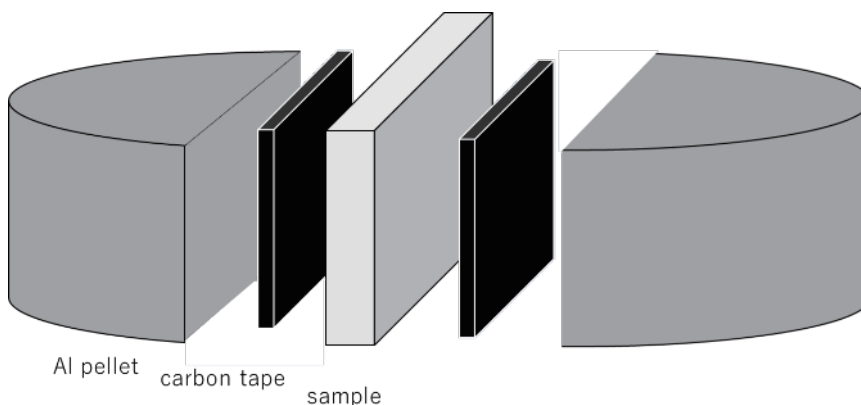


Fig. 2. Sample preparation image

Using this LAGP material as solid electrolyte, ASS-LIB was fabricated by coating with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) as cathode and MnO_2 as anode. Assembled ASS-LIB was tested by charge and discharge cycle using a commercial battery tester (MACCOR SERIES-4000, USA) in the voltage range of 0.8–4.1 V with a current rate of 0.15 C, 80 cycles at room temperature.

The LAGP smooth cross sections were obtained by Ar^+ ion beam milling at 8 kV acceleration voltage, 4h and finishing at 4 kV for 1 h using commercial cross section polisher (JEOL, IB-19530CP). In the case of pristine LAGP, finishing was done 2.5 h because difference in sputter ratio from cycled one. After milling, the sample was sandwiched by Al pellets half-moon shape and carbon tape to set the sample holder.

TOF-SIMS measurements were performed for both pristine and cycled LAGP to clarify the degradation process.

Result and Discussion

Figure 3 and 4 show TOF-SIMS images of each element. All element was uniformly distributed on the pristine cross section's particles. However, in the case of cycled LAGP, Li and PO_2 (fragment ions of PO_4) were distributed in the interfaces of the large particles. This result coincided with the previous work [3]. Since distribution of Li and PO_2 was difference from pristine LAGP, it is possibility of LAGP was changed by charge and discharge cycle. AlPO_4 , $\text{Li}_4\text{P}_2\text{O}_7$, and GeO_2 are detected from cycles LAGP [3], the formation of secondary phases include such materials is assigned to the loss of Li ions in the NASICON framework, reflecting by the decreased conductivity [5].

Further, the small size and Li rich particles were newly observed in this study. Figure 5 shows an overlay image of Li in green and Al in blue. The morphologically changed particles are highlighted near the amorphous region. This image indicates that the LAGP particles were degraded with morphologically and elementally changing. These degraded particles were considered that they have intact NASICON structure, and are not able Li ions to migrate. Such increasing the unmovable Li ions is also assign to decreasing conductivity and capacity. It is also considered that degraded particles finally change to amorphous. In fact, Li was clearly detected stronger than other materials.

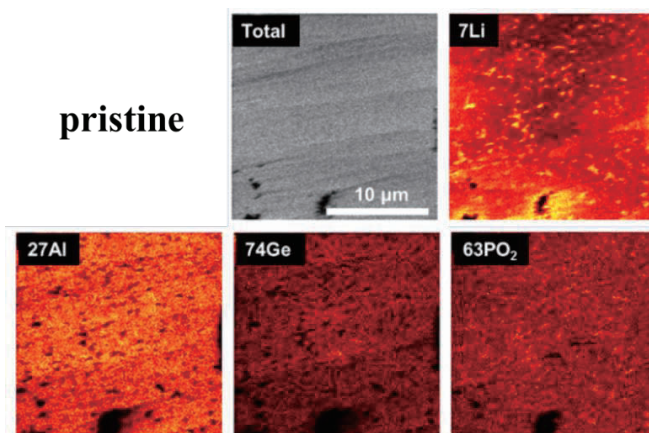


Fig. 3. TOF-SIMS image of pristine LAGP

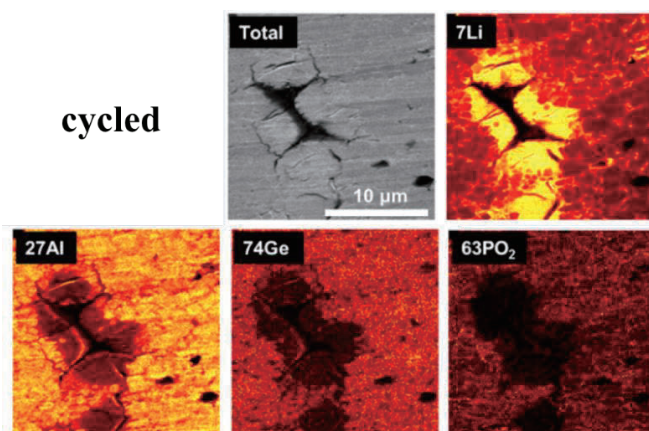


Fig. 4. TOF-SIMS image of cycled LAGP

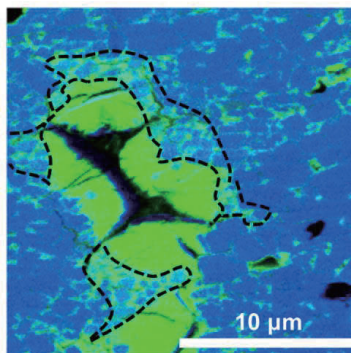


Fig. 5. TOF-SIMS image of cycled LAGP overlay Li (green) and Al (blue): The dotted areas indicate small size and Li rich particles near the amorphous

Conclusion

We measured amorphous region of the LAGP smooth cross section using FIB-TOF-SIMS to make clear the LAGP electrolyte degradation process. We successfully observed morphological and elemental differences before and after charge and discharge cycle test. Particularly, Li ion is distributed in the particle interfaces and amorphous region. Such Li was predicted to be not able to migrate, and it was considered that loss moveable Li ion is one of causes of the degradation.

Acknowledgement

This study was supported by "Development of System and Technology for Advanced Measurement and Analysis" SENTAN, JST.

References

1. F. Zheng *et al.*, *J. Power Sources*, **389** (2018) 198-213.
2. K. Arbi *et al.*, *J. EUR. CERAM. SOC.*, **35**, (2015) 1477-1484.
3. Q. Sun *et al.*, *J. Power Sources*, **471** (2020) 228468
4. T. Sakamoto *et al.*, *Appl. Surf. Sci.*, **255** (2008) 1617-1620.
5. Y. Meeasala *et al.*, *J. Phys. Chem. C*, **122** (2018) 14383-14389.