別紙５－１（論文博士（英文））

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Abstract（Doctor）

Title of Thesis	Building up all-solid-state lithium batteries using sulfide solid electrolytes via liquid phase process

Approx. 800 words

Sulfide solid electrolytes (SSE) for all-solid-state lithium batteries (ASSLB) have been fabricated via liquid phase process, and their characteristics and the performance of batteries have also been evaluated in our research group of the department of electrical and electronic information engineering in Toyohashi University of Technology. SSEs in the $Li_2S-P_2S_5$ system were fabricated via liquid phase shaking process (LS). In this study, the LS method was applied to synthesize Li_3PS_4 directly on the cathode active materials, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) to maintain good contact between the active material particles and SSE via liquid phased process, which was named SEED process.

Spherical Graphite (SG) particles used as anodes for ASSLB were coated with the sulfide solid electrolyte $Li_7P_2S_8I$ (LPSI) using the SEED process, and ASSLBs were assembled using the obtained SG composites and sulfide solid electrolytes such as LPSI and Li_6PS_5Cl (argyrodite). Cross-sectional observation using SEM confirmed that the LPSI coating was not only on the surface of the SG particles but also inside them. When the weight ratio SG to LPSI was 87:13, the interfacial contact area increased, resulting in good output performance for the ASSLB. To further enhance the charge–discharge performance, a hetero-SE coating was applied. In this approach, SG particles were first coated with an ultra-thin LPSI layer and then hand-mixed in a mortar with an argyrodite SE. When the thin-coated SG (SG: LPSI = 97:3) was mixed with the argyrodite SE (SG:total SE =70:30), the ASSLB exhibited excellent cycle performance in a half-cell, maintaining a capacity of 251 mAh g^{-1} after 100 cycles with a 95% capacity retention rate, owing to the improved interface contact between the SG particles and SEs. Boundary control between active materials and SEs is one of the most critical issues for fabricating ASSLBs. This LPSI coating via SEED process is a promising method to improve the problem.

Phosphorous-containing SSE reacts with H_2O and generates toxic H_2S gas. To synthesize non-phosphorus SSE, Li_4SnS_4 and Li_3SbS_4, I offered ion-exchange (IE) process with aqueous solution in ambient air. In IE process, Na_2S was used for starting material, which is stable against H_2O. The obtained Na_4SnS_4 was ion-exchanged to Li-ion using positive ion-exchange resins. Na ions in the Na_4SnS_4 were

almost exchanged to Li ions. The amounts of H_2S gas generation of these SSE were very low in 50 % relative humidity (RH) ambient air at room temperature. The ionic conductivity of Li_4SnS_4 obtained by a twice-repeated ion-exchange and heat-treated at 240 ℃ showed 1.0×10^{-4} S cm^{-1} at 25 ℃. The XRD pattern of the Li_4SnS_4 after exposure to ambient air and re-heat-treatment at 240 ℃ was essentially the same as before. Because of its stability in both the atmosphere and water, it was suggested that the Li_4SnS_4 obtained via this process could be recycled as an electrolyte for all solid lithium batteries. Li_3SbS_4 electrolyte was synthesized from an Na_3SbS_4 aqueous solution by ion-exchange, freeze-drying, and subsequent heat treatment. The temperature dependence of the ionic conductivities of $(100 - x)$ $Li_3SbS_4{\cdot}xLiI$ obtained via the IE process showed a unique behavior, in which the ionic conductivity of $60Li_3SbS_4{\cdot}40LiI$ sharply increased from 10^{-7} S cm^{-1} at 25 °C to 8.4×10^{-3} S cm^{-1} at 65 °C. Further, the ion conductivity reached 1.3×10^{-4} S cm^{-1} at 25 °C by homogenizing the surface of the particles using mechanical milling and annealing. Some XRD measurements and investigation using TEM showed LiI thin layers on the surface of Li_3SbS_4 –LiI primary particles. This is crucial in maintaining the high ion conductivity from around 70 °C to room temperature. The Li_3SbS_4–LiI SEs were stable in ambient air and the cathode composite containing $60Li_3SbS_4{\cdot}40LiI$ showed good charge−discharge performance. Therefore, from the industrial and safety viewpoints, the electrolyte obtained via the IE process is an excellent candidate for all-solid-state lithium batteries.

To increase the energy density of ASSLB, the higher the weight ratio of active material in the cell, the better, which leads to a thinner separator. To decrease the weight ratio of SSE for the separators, self-standing SSE sheets were fabricated with SiO_2 fiber as a reinforcing filler using liquid phase process. Argyrodite-type $Li_{6-x}PS_{5-x}Cl_{1+x}$ and Li_4SnS_4 SSE were dispersed in the mixed solvents with SiO_2 fiber. These slurries were poured into the polytetrafluoroethylene (PTFE) dishes and dried under low pressure. The LS method was applied to directly fabricate the LPSI-sheets with SiO_2 fiber. The thickness of these sheets was approximately 50 μm. Using obtained LPSI-sheets and active materials sheets, thinner ASSLBs were built up and successfully operated.

Silicon (Si) is a promising an anode active material for next generation ASSLB due to its large capacity. However, the volume change during charge-discharge cycles is more than 300 %, which decreases batteries capacity. Studying Si behavior as an anode active material is an especially important issue. Using LPSI obtained by the LS method as SE, several Si anode composites were fabricated using different sizes of Si particles and evaluated the size effect for ASSLB performances. Further, the charge-discharge performances of the Si composites with different SSEs were evaluated by scanning electron microscope (SEM) observation and Auger electron spectroscopy analysis. As a result, optimum microstructures to achieve good performance were clarified.