

学 位 論 文 の 要 旨

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学位論文題目	Development of solid polymer electrolyte with excellent lithium dendrite suppression ability for all solid-state lithium metal batteries (デンドライト成長の抑制機能を有する全固体リチウム金属電池用高分子固体電解質の開発)		
学位論文要旨			
<p>With the development of renewable energy and electric vehicles, high energy density power sources have received more and more attentions. All solid-state lithium (Li) metal batteries (ASSLMBs) with the advantages of low flammability, non-volatile, and high energy density have become one of the most promising directions. However, the industrial application of ASSLMBs with long lifespan, excellent cycling stability, and low cost is still hindered by several issues, such as the uncontrolled growth of Li dendrite, degradation of interface contact, and low ion conductivity of electrolytes. In particular, Li dendrite growth is thought as the cause of continuous formation of solid-electrolyte interphase (SEI) and “dead Li”, which directly lead to a decrease of coulombic efficiency (CE). Therefore, high capacity retention and long cycle life are both based on excellent Li dendrite suppression ability of solid-state electrolyte (SSE). In this view, development of new SSEs, which possess an acceptable ion conductivity, a wide electrochemical stability window (ESW), high mechanical strength and a good Li dendrite suppression ability even combined with the high-loading cathode is of great importance.</p> <p>In this study, a poly(ether block amide) (PEBA) based solid-state polymer electrolyte (SPE) with lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) as the Li salt is developed. It is found that the PEBA 2533-20% LiTFSI electrolyte possesses an ion conductivity of 3.0×10^{-5} S cm⁻¹ at 25 °C. Especially, the Li dendrite suppression ability of SEI is greatly enhanced since it provides abundant amide groups to activate TFSI- anions and further enriches lithium fluoride (LiF) content in the SEI layer, which endows the full-cell with enhanced cyclability. As a result, the fabricated solid-state Li/PEBA 2533-20% LiTFSI/LiFePO₄ (areal capacity: 0.15 mAh cm⁻²) battery remains 94% of its maximum capacity (127.5 mAh g⁻¹) at a rate of 0.5 C and 60 °C after 200 cycles. In particular, the full cell can cycle for almost 1000 cycles without short circuit. Therefore, the PEBA based electrolyte could promote the LiF enriched SEI layer into a platform to suppress the growth of Li dendrite toward ASSLMBs with a long lifespan.</p> <p>In order to further enhance the Li dendrite suppression ability of PEBA 2533 based SPE, aluminum oxide (Al₂O₃) nanoparticles are used as the solid plasticizer. In the case of addition of 3wt% Al₂O₃ nanoparticles, ion conductivity of the obtained PEBA 2533-20wt% LiTFSI-3wt%</p>			

Al_2O_3 SPE was $3.57 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C . Furthermore, the Li symmetrical battery assembled with it shows excellent cycling stability (1000 h) at 0.1 mA cm^{-2} . While, the assembled all-solid-state Li/PEBA 2533-20% LiTFSI-3wt% Al_2O_3 /LiFePO₄ (areal capacity: 0.15 mAh cm^{-2}) battery maintains 94.9% of the maximal capacity (133.9 mAh g^{-1} @ 0.1 mA cm^{-2}) at 60°C even after 650 cycles with a superior average CE of 99.84%. By using X-ray photoelectron spectroscopy (XPS), self-aggregation layer (SAL) of polyamide 12 (PA12) of PEBA 2533 is discovered, which should contribute to promoting the robustness of LiF enriched SEI layer. In addition, it is considered that the state of interface between SPE and cathode should be the cause of voltage polarization of the full cell.

Commonly, the larger the amount of Li deposited is, the more obvious the volume effect will be, and the more difficulty of it is to suppress Li dendrites. The excellent Li dendrite suppression ability of PEBA based SPE has been demonstrated with PEBA 2533 as the polymer matrix. However, the excellent performance of the batteries is based on low-loading cathode (0.15 mAh cm^{-2}). In the last work, PEBA 4033 based SPEs with LiTFSI as the Li salt are prepared and the ion conductivity of PEBA 4033-40wt% LiTFSI SPE achieves $3.49 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C . Besides, the SPEs with Al_2O_3 nanofillers are also prepared and used to assemble the ASSLMBs combining with the high-loading LiFePO₄ cathode (1.5 mAh cm^{-2}). Thereafter, the effects of solvent evaporation temperature on battery performance are investigated and as a result, a higher CE is realized at higher solvent evaporation temperature.