

学 位 論 文 の 要 旨

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| 学位論文題目 | Development of solid electrolyte materials for solid-state lithium batteries (全固体型リチウム二次電池用電解質材料の開発) | | |

学位論文要旨

Solid-state lithium batteries (SSLBs) with solid electrolytes (SEs) have attracted great attention for the replacement of traditional lithium batteries with liquid electrolytes due to their advantages such as high safety, excellent electrochemical cycling property and long-term stability. To date, the strategies to improve electrochemical performance especially ionic conductivity and stability of SEs have been widely studied. However, nowadays, SSLBs are still not commercialized and used in our daily life. The main purpose of this research is to develop high-performance SEs for SSLBs. In this study, the effects of various doping materials for solid sulfide electrolytes and solid polymer electrolytes on the performances were investigated, which focused on ionic conductivity, ion transference number, electrochemically stable, lithium stability, thermal stability, and charge-discharge stability. It is found that when loading material type and material support were adjusted, the electrochemical performances of SEs were changed significantly. The mechanisms and structures of SEs were proposed and discussed. It is expected to provide a guidance for the development of novel SEs with higher ionic conductivity and environmental stability for SSLBs. The main conclusions in this dissertation are summarized as follows:

Firstly, $\text{Li}_2\text{S-P}_2\text{S}_5$ (LPS) based glass-ceramic electrolytes doped with SeS_2 were prepared by a facile high-energy ball milling combined annealing way. The structures, ionic conductivities and electrochemical stabilities of the $70\text{Li}_2\text{S} \cdot (30-x)\text{P}_2\text{S}_5 \cdot x\text{SeS}_2$ ($x=0, 0.3, 0.5, 1, 3, 5$) glass-ceramic electrolytes were investigated. By combining X-ray powder diffraction (XRD) analysis-refinement and first-principle calculations, it is confirmed that a little amount of SeS_2 ($x \leq 1$) was successfully doped into the framework of LPS composite, and as such, the ionic conductivity was greatly enhanced by the substitution of a part of P_2S_5 with SeS_2 . In particular, the $70\text{Li}_2\text{S} \cdot 29\text{P}_2\text{S}_5 \cdot 1\text{SeS}_2$ glass-ceramic exhibited the highest conductivity of $5.28 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 20°C with a low activation energy of $24.7 \text{ kJ} \cdot \text{mol}^{-1}$, and higher electrochemical stability than the original $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ glass-ceramic. Furthermore, SSLBs assembled based on $70\text{Li}_2\text{S} \cdot 29\text{P}_2\text{S}_5 \cdot 1\text{SeS}_2$ electrolyte and sulfur-reduced graphene oxide (S-rGO) composite electrode showed excellent rate capability and cycling stability at low temperatures. Furthermore, electrochemical impedance spectroscopy (EIS) analyses and the cross-section observation by scanning electron microscope (SEM) of SSLBs revealed that addition of SeS_2 into the $\text{Li}_2\text{S-P}_2\text{S}_5$ electrolyte substrate decreased the interfacial resistance between the electrodes and solid electrolyte and reduced the production of lithium dendrites. These results indicated that $70\text{Li}_2\text{S} \cdot 29\text{P}_2\text{S}_5 \cdot 1\text{SeS}_2$ electrolyte can be served as an effective solid electrolyte for the construction of high performance SSLBs.

Air and electrochemical stability, high interfacial resistance, and complex preparation process are significant problems which should be solved in sulfide-type solid electrolyte development. In air atmosphere, these sulfide solid electrolytes were easily decomposed in the reaction with the atmospheric water/hydrogen, resulting in the generation of H_2S . Recently, many researchers concentrated to develop polymer electrolytes with relatively reliable stability, low interfacial resistance, high flexibility, stretchable property, and low fabricating cost. In this

study, a novel polyethylene oxide (PEO)-Lithium bis(trifluoromethylsulphonyl)imide (LiTFSI)-nanocomposite-based polymer electrolyte was also prepared by using nickel phosphate (VSB-5) nanorods as the filler. The ionic conductivity of the obtained PEO-LiTFSI-3%VSB-5 solid polymer electrolyte was found to be as high as $4.83 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ at 30 °C and electrochemically stable up to about 4.13 V versus Li/Li⁺. The enhanced ionic conductivity was attributed to the reduced crystallinity of the PEO and the interaction between VSB-5 and PEO-LiTFSI. In addition, the solid polymer electrolyte exhibited improved compatibility to the lithium metal anode with excellent suppression of lithium dendrites. The assembled LiFePO₄/Li battery with the PEO-LiTFSI-3%VSB-5 solid polymer electrolyte showed better rate performance and higher cyclic stability than the PEO-LiTFSI electrolyte. It is demonstrated that this new solid polymer hybrid should be a promising electrolyte applied in SSLBs with lithium metal electrode.

To elevate the conductivity of SPE, restrain lithium dendrite growth and increase the thermal stability, a flame-retardant filler, Zn₂(OH)BO₃ with rod-like structure and relatively high dehydration temperature (about 415 °C), was also used for the improvement of the performance of SPE. In this work, a novel solid polymer composite electrolyte based on poly (ethylene oxide) (PEO) with rod-like Zn₂(OH)BO₃ particles was prepared by a grinding process followed with a heating treatment process and a cold pressing process. The effect of the incorporation amount of rod-like Zn₂(OH)BO₃ particles on the ionic conductivity was investigated systemically. It is found that 10 mol% of rod-like Zn₂(OH)BO₃ particles addition resulted in the highest ionic conductivity of 2.78×10^{-5} at 30 °C and the improved ionic conductivity was considered to be caused by the reducing of PEO crystallinity and the increasing of Li ion migrating pathway on the interface between the Zn₂(OH)BO₃ and PEO. In addition, the optimum composite electrolyte exhibited a high electrochemical stability window of 4.51 V (vs. Li/Li⁺), good lithium stability and excellent thermal stability.

注) 和文 2,000 字以内又は英文 800 語以内

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