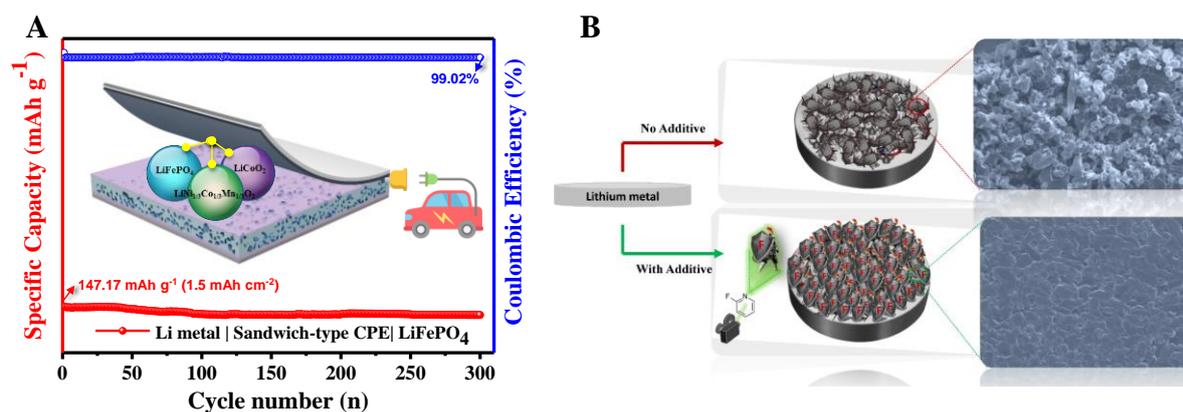


## 学 位 論 文 の 要 旨

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| 学位論文題目   | Novel electrolyte formulations for lithium metal batteries<br>(リチウム金属電池用新規電解質の開発) |             |                          |
| <p>学位論文要旨</p> <p>Rechargeable lithium-metal batteries (LMBs) have been recognized as one of attractive energy storage devices since Li metal has an ultrahigh specific capacity as well as an ultralow standard negative electrochemical potential. However, due to the high reactivity of Li metal, Li dendrites are always generated to shorten the cycle life of LMBs, which impedes the widespread deployment of high-energy density LMBs. Recently, tremendous efforts including the applications of artificial current collector, anode coating layers, host matrix, solid-state electrolytes, concentrated electrolytes, electrolyte additives, and so on, have been devoted to the protection of Li metal anode to extend the cycle life of LMBs. Among all of those strategies, owing to the low cost and easy processing, the novel electrolyte formulations are considered as the most promising way to simply but effectively improve the performance of LMBs. In this dissertation, some novel electrolyte formulations, i.e., quasi-solid-state electrolyte, solid-state electrolyte, practical liquid electrolyte were developed for the high-energy density LMBs. The effects of various electrolytes on inducing a robust electrode/electrolyte interface, decreasing the parasitic reactions between metallic Li and electrolytes, suppressing the growth of Li dendrites, and prolonging the cycle life of LMBs were elucidated. These electrolyte formulations with broad compatibility could be considered as the candidates for the next-generation LMBs designs. The main progress can be briefly summarized as follows:</p> <p>Firstly, a flexible poly-(ethylene oxide) (PEO)-lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) polymer electrolyte assisted with a bifunctional ionic liquid (IL) of tetrabutylphosphonium 2-hydroxypyridine (TBPHP) as well as a fast-ion conducting ceramic of <math>\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}</math> (LLZTO) was fabricated and applied for the LMBs. It is found that the <math>\text{TBP}^+</math> cation and <math>\text{HP}^-</math> anion of IL effectively tuned the crystallinity of PEO and enhanced lithium ion transference, respectively, and the TBPHP and LLZTO played a synergistic role in improving the performance of electrolyte. Meanwhile, the density functional theory (DFT) study was performed to understand the interaction between TBPHP and LiTFSI. As a result, the obtained electrolyte possessed a high ionic conductivity of <math>9.39 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}</math> at <math>50^\circ\text{C}</math> and a wide electrochemical stability window (more than 5 V) with significantly promoted uniform Li plating/stripping properties. The LMBs assembled with this quasi-solid-state electrolyte and <math>\text{LiFePO}_4</math> cathode rendered excellent cycling stability with a high discharge capacity above <math>150 \text{ mAh}\cdot\text{g}^{-1}</math> even after 100 cycles at 0.2 C and <math>50^\circ\text{C}</math>. Besides, the fabricated flexible pouch cell showed excellent performance. Such a polymer composite could be a promising electrolyte for the next generation of LMBs.</p> |   |             |                          |



**Figure 1** (A) Schematic diagram of solid-state and (B) liquid electrolyte formulations for LMBs.

Secondly, in order to develop a solid-state electrolyte with lower operating temperature and faster ion conductivity for LMBs, a flexible and stable composite polymer electrolyte (CPE) composed of poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP)-LLZTO sandwiched by PEO-LiTFSI polymer skin layers in two sides (denoted as sandwich-type CPE) was fabricated and displayed in Figure 1A. In such a CPE membrane, the PEO-LiTFSI layers not only ameliorated the ion conductivity of PVDF-HFP-LLZTO, but also improved the intimate contact with the electrodes. Meanwhile, the crystallinity of PEO and PVDF-HFP polymer was significantly reduced owing to the cross-linking of them so that the obtained CPE membrane had faster  $\text{Li}^+$  ions transportation ability. Assembled with this sandwich-type CPE, the all-solid-state  $\text{LiFePO}_4|\text{Li-metal}$  battery exhibited excellent rate performance and cycle stability with a discharge capacity of  $120.01 \text{ mAh g}^{-1}$  even after 300 cycles at  $40^\circ\text{C}$ , also, other two all-solid-state  $\text{LiCoO}_2|\text{Li-metal}$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2|\text{Li-metal}$  batteries showed high voltage stability along with the satisfied energy density as well as excellent cycle performance. Moreover, the fabricated flexible pouch cell also exhibited outstanding performance, indicating its feasibility for the next generation of flexible LMBs.

Thirdly, to achieve good compatibility in the practical applications of LMBs, a novel electrolyte additive, 2-Fluoropyridine (2-FP), was applied to enhance the stability of commercial liquid electrolytes and effectively improve the performance of LMBs. The 2-FP additive was found to play a critical role in the decrease of Li nucleation/deposition overpotential, and finally suppressing the Li-dendrites (Figure 1B). As a result, the  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  cathode ( $1.5 \text{ mAh cm}^{-2}$ )|Li metal cell using the  $\text{LiPF}_6$  electrolyte with 2% of 2-FP additive exhibited a stable capacity retention of 67.6% even after 300-cycle test with a coulombic efficiency as high as 99.89 % at  $0.75 \text{ mA cm}^{-2}$ . Meanwhile, in the case using another LiTFSI electrolyte with it, the  $\text{LiFePO}_4$  cathode ( $1.5 \text{ mAh cm}^{-2}$ )|Li cell also maintained long-term stability even at  $1.5 \text{ mA cm}^{-2}$ . The surface analysis and DFT calculations verified that the stabilization effect by introduction of this additive was resulted from the formation of a robust and stable solid electrolyte interphase (SEI), in which the LiF and  $\text{Li}_3\text{N}$  components could play a synergistic role in the improvement of SEI layer performance. Such a fluoropyridine molecule with good compatibility in the LMBs is expected to be a promising electrolyte additive for the next generation of LMBs.