Study for Thermodynamic Properties of Fluoride Ion Battery Cathode Materials

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論 文 名　：Study for Thermodynamic Properties of Fluoride Ion Battery Cathode Materials
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論 文 内 容 の 要 旨
Thesis Summary

High-energy density storage devices are urgently required to meet the increasing demand for battery-operated electric vehicles, electric trains, and airplanes, which may become the future of mobility. Hence, the demand for efficient and sustainable systems is increasing drastically. Therefore, fluoride-ion batteries (FIBs), which works through a chemical reaction that shunts F-ions between anode and cathode, have been studied. FIBs show higher ion mobility and energy density than most multivalent ion batteries because monovalent F^- ions have a small ion radius, and the theoretical energy density of FIBs are eight times that of current lithium-ion batteries owing to the movement of several charged anions per reaction step. Numerous combinations of cathode and anode materials have been explored for FIBs based on monovalent anions and multivalent cations. Several active materials, such as Bi, Cu, and Sn, have been used for the development of FIBs. CuF_2 exhibits unique capacity and a high theoretical conversion potential as a cathode material. However, most CuF_2 cathodes cannot reach their theoretical capacity values because of the low F^- ion diffusion rate in CuF_2.

In terms of utilization rate for active material Cu of FIBs, the cathode material $CuPb_2F_6$ was reported and demonstrated a capacity exceeding that of the conventional CuF_2 cathode in previous studies, in which dispersion of nano Cu and super ion conductor PbF_2 improved the utilization of Cu. However, the deterioration of cathode material was occurred during charge/discharge process, because of the coarsening of Cu grains during discharging process. In this study, we focus on thermodynamics properties of Cu-Pb-F ternary system, which is helpful to understand the chemical reaction during discharge process of $CuPb_2F_6$. The thermodynamical properties were investigated by CALPHAD (Calculation of Phase Diagrams) method, in which the binary, ternary compounds were assessed by first principal calculation and the optimization of calculated phase diagram was

implemented using experimental data. Especially, the discrepancy of stability between calculated phase diagram and experimental data was discussed by experimental methods, including atomic pair distribution function (PDF) analysis of neutron powder diffraction (ND), in which the analysis of discrepancy is helpful to improve the accuracy of calculated phase diagram and the understanding of thermodynamics properties.

To investigate the deterioration of cathode and reaction during the discharging process, the Multi-Phase-Field (MPF) method coupling with CALPHAD database we calculated above was implemented to simulate the decomposition and discharge reaction of $CuPb_2F_6$ cathode material. Because of the conservation restriction for all elements during simulation, it is difficult to simulate discharging process, in which the amounts of F element keep decreasing along with every time step. Novel model, which splits discharging process into some simulation with small time step, was used to evaluate microstructure evolution during discharging process by different parameters of simulation. The grain growth of Cu nanoparticles is considered to be an important cause of deterioration, and simulations are performed among parameters such as discharge rate, nucleation ratio and diffusion coefficient.

For the viewpoint of Cu-La-F ternary system, since the ternary compounds does not exist, we focused on the microstructure of Cu-La alloy in which La can form the fluoride ion conductor LaF_3. Owing to thin-film (2.3 nm) Cu almost accomplished the theoretical capacity in previous studies, rapid solidification method was used to synthesize Cu-La alloys with fine lamella microstructure, in which Cu-enrich phases and La-enriched phases were dispersed and expected to be fluorinated as reported $LaNi_5$ cathode material. Besides, we evaluated the microstructures processed by different compositions and cooling speed to obtain finest lamella structure. After fluorination, the finest lamella structure was expected that the dispersed finer Cu and ion conductor LaF_3 could shorten the diffusion path of F^- ions.

For investigating the unknown ternary compounds of Cu-La-F and Cu-Pb-F ternary systems, which is possible to be promising cathode materials as $CuPb_2F_6$. the phase stability among these compounds of Cu-La-F and Cu-Pb-F ternary systems was calculated by Density Functional Theory (DFT) calculation method and the existence of ternary compounds was predicted by evolutionary algorithm. Furthermore, the predicted energy curve of Cu-La-F and Cu-Pb-F ternary systems were evaluated by comparing with reported crystal structure.

Chapter 1 introduced the general information of fluoride ion batteries, fluoride ion conductors, research methods about thermodynamics properties and the objectives of this study.

Chapter 2 discussed the thermodynamic assessment of Cu-Pb-F system, in which the compounds in the Cu-Pb-F system were assessed by first principal calculation. The Cu-Pb-F ternary phase diagram was calculated by CALPHAD method. Moreover, the crystal structure of $CuPb_2F_6$ was refined by ND method and PDF analysis.

Chapter 3 discussed microstructure evolution simulation of promising cathode material $CuPb_2F_6$ by Multi-Phase-Field (MPF) method coupling with the database calculated in the Chapter 2. The decomposition of $CuPb_2F_6$ was simulated at high temperature. Moreover, to evaluate discharging process of $CuPb_2F_6$ cathode material, novel model was stablished to investigate the effects of different parameters, which was helpful to analyze the deterioration of cathode material $CuPb_2F_6$.

Chapter 4 discussed the synthesis of Cu-La alloys, as an alternative cathode material in FIBs. Based on Cu-La phase diagram, the formation of the lamellar structure and Cu-La alloys near eutectic point were investigated by rapid solidification method. To investigate the effect of cooling rate, composition of Cu-La alloys was fixed at 24.5 at% La and synthesized at different cooling speed. Besides, for the detailed observations of microstructure, the alloys, with composition fixed at 24.5 at% La and cooling speed of 500 and 1000 rpm, were observed by Electron Backscatter Diffraction (EBSD) and Transmission Electron Microscope (TEM).

Chapter 5 discussed the phase stability of compounds in Cu-La-F and Cu-Pb-F ternary systems. In order to search for a wider range of stable structures, we used both an evolutionary algorithm and first-principles calculations to search for stable structures without any restrictions on crystal structures.

Chapter 6 summarized the general results of thermodynamic properties for Cu-La-F, Cu-Pb-F systems.

In general, according to study the thermodynamical properties of Cu-La-F, Cu-Pb-F systems, the approaches, which could improve the utilization of Cu in the cathode materials of FIBs, were investigated.