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博士論文の要約

論文題目

Synthesis, structures and electrochemical properties of lithium ion conducting oxides with rock-salt, perovskite and anti-fluorite structures (岩塩・ペロブスカイト・逆蛍石型構造を有する酸化物系リチウムイオン導電体の合成、構造と電気化学特性)

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Chapter 1. Introduction

Solid-state lithium ion batteries offer a stable, reliable, and safer source for power storage with better power density as compared to that of Li ions batteries based on flammable organic liquid electrolytes.[1] Lithium ion conductive solid materials are expected to serve as solid electrolytes for all-solid-state batteries as they could replace the organic flammable liquid electrolytes. Therefore, recently battery researchers are focusing on solid-state lithium ion conductors with better performance. Among all such materials, sulfide- and oxide-based lithium ion conductors have attracted considerable attention recently. In particular, the lithium superionic conductor $Li_{10}GeP_2S_{12}$ exhibits a high conductivity of 1.2×10^{-2} S cm^{-1} at room temperature.[2] However, sulfide-based materials have serious problem of appearance of a high-resistance layer is easily formed in contact with the electrodes [3], and also sulfides based electrolytes are unstable in ambient air because of their high reactivity with moisture.[3]

On the other hand, oxide-based materials are relatively stable in air; thus, various synthesis methods can be applied and a facile fabrication processes are expected for all-solid-state batteries[4]. Among oxide-based solid electrolytes, perovskite-type $Li_{3x}La_{(2/3)-x}TiO_3$ is considered as one of the most promising candidates because of its high ionic conductivity (>10^{-3} S cm^{-1} at room temperature).[5] However, a reduction of Ti^{4+} to Ti^{3+} at the interface between the low-potential anodes during the electrochemical process gives rise to undesirable electronic conduction.[6] Hence, the practical use of $Li_{3x}La_{(2/3)-x}TiO_3$ in the batteries is still difficult. Therefore, it is necessary to investigate new oxide based solid lithium ion conductors; those satisfy all the strict requirements for using a solid electrolytes for all solid state battery applications (i.e., high ionic conductivity at room temperature, chemical stability, electrochemical stability, thermal stability, and low cost). Therefore, it is necessary to investigate new solid lithium ion conductors. In the present study, we focus on searching on oxide-type.

Chapter 2. Experimental

The materials were synthesized either solid-state reaction in air at 900−1350°C (Chapter 3, $LiScO_2$ system), 650−750°C (Chapter 5, Li_5FeO_4 anti-fluorite system) or by high-pressure solid-state reaction method at and 900−1250 °C with the pressure of 1GPa (Chapter 4, $LaScO_3$ perovskite system). Powder sample were subjected to X-ray, and synchrotron X-ray diffraction analyses for structure determination. Diffraction data was analyzed by Rietveld refinement method using Rietan-FP. Ionic conductivity was measured by the AC impedance method using frequency response analyzers (NF Corp. FRA5097 or Solartron 1260); the samples were placing under flowing Ar gas, and the measurements were performed over the temperature range from 25 to 450 °C and the frequency range from 0.1 Hz to 10 MHz. Gold pastes were used for the blocking electrodes and were painted onto both sides of each sample for the measurements.

Chapter 3. Synthesis, crystal structure and the ionic conductivity of new lithium ion conductors, *M*-doped $LiScO_2$ (*M* = Zr, Nb, Ta)

In Chapter 3, new lithium ion conductors in *M*-doped $LiScO_2$ (*M* = Zr, Nb, and Ta) system were obtained by a solid-state reaction method. The peak shifts in the X-ray diffraction patterns revealed the formation of new solid solutions with aliovalent cation doping. In addition, an increase in the ionic conductivity was observed because of *M* doping. The highest total conductivity of 7.94×10^{-6} S cm^{-1} with an activation energy of 88 ± 5 kJ mol^{-1} was observed at 350 °C for the Zr^{4+}-doped sample. The Zr^{4+}-doped system showed the highest solid solution limit in $Li_{1-x}Sc_{1-x}Zr_xO_2$ ($x \approx 0.1$) and a continuous increase in conductivity with increasing x. Structural analysis by Rietveld refinement indicated lattice expansion and the formation of lithium-ion vacancies in the structure because of Zr doping; these effects might contribute to the increase in ionic conductivity. Enhanced ionic conductivities of $LiScO_2$ which shows thermodynamic stability when placed in contact with lithium metal were achieved by the introduction of vacancies and amounts of Li with aliovalent cation doping.

Chapter 4. Synthesis, crystal structure and the ionic conductivity of new lithium ion conductors, doped $LiLaScO_3$ with perovskite structure

In chapter 4, new lithium ion conductors, $(Li_xLa_{1-x/3})ScO_3$, which show perovskite-structure, were obtained and their Li-ion conduction had been reported. The structure and the composition of the new lithium ion conductors have been tailored by cation doping, i.e., *A*-site with Ce^{4+} doped and *B*-site with M ($M = Zr^{4+}$, Nb^{5+}) respectively. The doped $(Li_xLa_{1-x/3})ScO_3$ solid solution have been further studied and the conductive properties were compared. In the $(Li_xLa_{1-x/3})ScO_3$ new lithium ion conductors, an optimal composition with $x \approx 0.45$ shows relatively high ionic conductivity of 4.22×10^{-5} S cm^{-1} at 350 °C as compared to other solid solution in the respective series. Further improvement of the ionic conductivity for $(Li_xLa_{1-x/3})ScO_3$ systems was observed by Ce^{4+} doping at *A*-site, an optimized Ce^{4+} doped composition $(Li_{0.4}Ce_{0.15}La_{0.67})ScO_3$ shows the highest ionic conductivity of 1.06×10^{-3} S cm^{-1} at 350 °C among all solid solutions. Structural analyses by Rietveld refinement also confirmed that the lattice expansion could contribute to the increase in the ionic conductivity.

Chapter 5. Synthesis, crystal structure and the ionic conductivity of new lithium ion conductors, *M*-doped Li_5FeO_4 (M = Zn) with anti-fluorite type structure

In Chapter 5, Lithium iron oxides (Li_5FeO_4) are attractive as lithium ion conductor used for lithium secondary battery from the viewpoint of low cost and nontoxicity. Li_5FeO_4 was found showing high temperature phase (β-phase) and low temperature phase (α-phase). Both phases belong to the anti-fluorite type structure with high lithium intrinsic vacancies (25%), which is quite useful for further improving ionic conductivity. In order to improve the ionic conductivity, $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ were synthesized by quenching method from high temperature (1000 °C) and formed single phases in $0 \leq x \leq 0.1$ and $0.1 < x \leq 1$, for α− and β−phases, respectively and show relative high ionic conductivity[7]. However, since the founding, less in-depth investigation about the ion conductivity has been reported. Thus, in an attempt to investigate: (1) same composition but different phase-type (α or β), which is dominant for higher ionic conductivity, phase-type or composition? (2) The reason, why there has an ionic conductivity jump at 430 °C in the anti-fluorite that have not well understood [7]. In this study, $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ were synthesized by solid state method with a slow cooling process. Single phases formed in range $0 \leq x \leq$

0.3 and 0.5 ≤ x ≤ 1, for α− and β−phases, respectively. Thus α−phase anti-fluorite structure, $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ (x = 0.2, 0.3) were obtained. Comparing with same composition with different phase-type, the reported β-phase $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ ($x = 0.3$) shows higher ionic conductivity than that of the obtained α-phase, which indicates phase-type is dominant for higher ionic conductivity than composition. The formation of LiOH in both the α− and β−phase anti-fluorite Li_5FeO_4 system as the samples decomposed with water in a moist atmosphere were detected and confirmed by high-temperature Synchrotron XRD in this work, which provide direct evidences to explain why the abnormally abrupt increase of conductivity at the temperature around 430 °C in this system. β-phase in anti-fluorite system could be a good candidate as solid electrolyte. Controlling the atmosphere is required for this material.

Chapter 6. Summary

In this chapter, following results have been briefly concluded.

1. Series new lithium ion conductors are obtained in M-doped $LiScO_2$ (Zr^{4+}, Nb^{5+}, and Ta^{5+}) with rock-salt structure. In which, an optimal composition $Li_{1-x}(Sc_{1-x}Zr_x)O_2$ ($x \approx 0.1$) exhibit a highest ionic conductivity of 7.94×10^{-6} S cm^{-1} at 350°C, which was improved by two orders of magnitude than pure $LiScO_2$. Enhanced ionic conductivities were achieved by the introduction of vacancies in the structure by doping with higher aliovalent cations at Sc-site.
2. Series new lithium ion conductors are developed in $(Li_xLa_{1-x/3})ScO_3$ and the Ce^{4+}, M ($M = Zr^{4+}$, Nb^{5+}) doped-$(Li_xLa_{1-x/3})ScO_3$ system with perovskite structure. New lithium ion conductor, $(Li_{0.45}La_{0.85})ScO_3$ (x=0.45), shows the highest ionic conductivity in $(Li_xLa_{1-x/3})ScO_3$ system. A-site Ce^{4+} doped system, $(Li_xCe_yLa_{1-x/3-4y/3})ScO_3$ improved the conductivity of $(Li_xLa_{1-x/3})ScO_3$, while the presence of M at B-site did not contribute the improvement. An optimal compound $(Li_{0.4}Ce_{0.15}La_{0.733})ScO_3$ (x=0.4, y=0.15) shows the maximum ionic conductivity of 1.06×10^{-3} S cm^{-1} at 350 °C, which is nearly two orders of magnitude improved comparing to that of the optimal composition $(Li_{0.45}La_{0.85})ScO_3$ (x=0.45) in $(Li_xLa_{1-x/3})ScO_3$. The crystal structure analyses and ionic conductivity measurements show the ionic conductivities of $(Li_xLa_{1-x/3})ScO_3$ are further improved might be because of the introduction of lithium-ion and lithium-ion interstitials in the structure by doping with higher-aliovalent cation (Ce^{4+}) at A^{3+}-site.

3. In anti-fluorite $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ system, α-phase, $Li_{5+x}(Fe_{1-x}Zn_x)O_4$ ($x = 0.2$, 0.3), were obtained by solid state method with a slow cooling process. Lattice parameters expand might contribute to the increase of ionic conductivity. Phase-type is dominant for higher ionic conductivity. The ionic conductivity jumps at about 430 °C was confirmed due to the presence of LiOH. β-phase in anti-fluorite system could be a good candidate as solid electrolyte. Controlling the atmosphere is required for this material.

The results reveals the ionic conductivities of the well selected materials with rock-salt, perovskite and anti-fluorite structures could be improved by cations doping when the structures and compositions are well designed for higher ionic conduction.

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