Improvement in Electrochemical Properties of NASICON-type Electrode Active Materials for Li-ion Battery

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論 文 内 容 の 要 旨

Li-ion battery, which was commercialized 25 years ago in Japan, has been studied intensively and the improvement of the battery performance has been still continued year by year. The following advantages make current Li-ion batteries attractive; 1) Li-ion secondary battery show the high discharge voltage more than 3 V. LSI can be driven by a single Li-ion battery. 2) Li-ion secondary battery has the highest energy density among the secondary batteries in market. It play important rule to down sizing of the portable devices such as note PC and cellular phone. 3) Li-ion secondary battery does not show memory effect and detrimental self-discharging, while conventional Nickel-cadmium and Nickel-metal hydride batteries largely suffer from continuous capacity loss from these influences. On the other hand, the safety issue becomes more serious for the higher energy density battery. In addition, high manufacturing costs, high production costs, and limited amount of Li reserves are emerging as possible limitations as sustainable energy storage sources. In this paper, to ease these safety and cost problems in Li-ion battery, all-solid-state battery and aqueous Li-ion battery with NASICON-type electrode/electrolyte materials were investigated.

In chapter 1, the basic principles of secondary battery, and related methodologies including structural characterization techniques used in this researches are introduced.

In chapter 2, in order to improve the electric conductivity of NASICON-type $Li_3V_2(PO_4)_3$ cathode, substitutional Al- and Fe-doping was tried. The prepared doped samples were examined both in organic and all-solid-state configuration to investigate preliminary electrochemical characteristics. In this study, the increase of electrical conductivity when dopants (Al or Fe) were introduced was observed.

In chapter 3, in order to suppress the irreversible capacity and capacity fade on cycle, Li rich NASICON-type

$LiTi_2(PO_4)_3$ was tried as anode. In this study, modification from rhombohedral $LiTi_2(PO_4)_3$ to orthorhombic $Li_{1.5}Ti_2(PO_4)_3$ was induced by introducing mixed-valent titanium. The orthorhombic phase showed superionic property during charge and discharge with improved electrochemical performance compare to the conventional rhombohedral lithium titanium phosphate by the Li compensation.

In chapter 4, the conclusions of previous researches were treated with possible future research topics for improvement. This includes the use of thin-layer deposition technique to reduce interfacial resistance between solid-state electrolyte and electrode materials, and use of optimized particle size and aqueous electrolyte without oxygen gas for aqueous Li-ion battery.