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Investigation of Fabrication Process for Realizing of All Solid State Lithium Battery using Garnet Oxide Type Solid Electrolyte

(ガーネット型酸化物系固体電解質を用いた全固体リチウム二次電池の実現に向けた作製プロセスの検討)

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Chapter 1

General Introduction

In Chapter 1, background and motivation of this thesis was described. The energy density of lithium ion batteries is theoretically limited. In order to develop higher energy density, new battery systems have been studied as next generation batteries. Among many kinds of next generation batteries, all solid state battery is one of the attractive battery systems. In the case of battery using liquid electrolytes, battery has a risk which is an explosion due to flammable of organic solvent. On the other hand, all solid state battery is expected as highly safe battery due to more stable of solid electrolyte compared with organic electrolyte. In this thesis, aluminum doped LLZ (Al-LLZ) with composition of $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ was used for solid electrolyte. Then, the fabrication process for realizing all solid state lithium battery by using garnet oxide type solid electrolyte has been studied.

Chapter 2

Improvement of $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ Sintering Process by Using Pre-heat Treatment

In order to fabricate all solid state lithium using $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (Al-LLZ), sintered Al-LLZ pellet is required. In chapter 2, synthesis of Al-LLZ type solid electrolyte by solid state reaction was investigated. We have focused on the phase transformation of Al-LLZ precursor. Based on this information, sintering process was optimized by obtained knowledge. The ball milled fine Al-LLZ precursor consisted of Al-LLZ with low temperature cubic garnet structure and Li_2CO_3 as an impurity. The crystal structure of the ball milled Al-LLZ precursor was changed during the heating process. After the heat treatment at 900 °C, Al-LLZ precursor was converted to garnet structure without any impurity. A grain boundary of Al-LLZ pellet sintered at 1150 °C with the heat treatment process at 900 °C for 3 hours was reduced, compared with that prepared without pre-heat treatment at 900 °C. In this way, the sintering of Al-LLZ pellet was improved by using the pre-heat treatment due to low content of carbonate species and low temperature garnet structure formation.

Chapter 3

Effect of Gold Layer on Interface Resistance between Lithium Metal Anode and $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ Solid Electrolyte

In Chapter 3, an improvement of interfacial contact between lithium metal anode and $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (Al-LLZ) pellet was investigated by an introduction of gold interlayer to decrease the interfacial resistance. The interfacial resistance was decreased to 150 ohm from 1200 ohm by the introduction of gold interlayer with heat treatment at 150 °C, in which Li-Au alloy was formed. The interfacial resistance decreases with increasing the thickness of gold interlayer until 50 nm. Li/Au/Al-LLZ/Au/Li symmetric cell with the heat treatment showed smaller overpotential for dissolution and deposition of lithium than Li/Al-LLZ/Li symmetric cell, due to difference in the interfacial resistance. From this result, it can be concluded that the gold interlayer is effective to decrease the interfacial resistance.

Chapter 4

Thermal Stability of Various Cathode Materials against $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ Electrolyte

The formation process of cathode layer, for example sputtering and pulse laser deposition, includes heat treatment processes. Therefore, it is very important to understand compatibility between solid electrolytes and cathodes at high temperatures. In Chapter 4, thermal stability of $LiCoO_2$, $LiMn_2O_4$ and $LiFePO_4$ with Al-LLZ solid electrolyte was investigated at different temperature. In the case of $LiCoO_2$/Al-LLZ mixture, the XRD patterns and charge-discharge behavior did not change after the heat treatment at 800 °C. In contrast, the formation of impurities and degradation of cathode performance were observed for $LiMn_2O_4$/Al-LLZ mixture and $LiFePO_4$/Al-LLZ mixture. The decomposition of Al-LLZ and the formation of some impurities were observed from 600 °C for $LiMn_2O_4$/Al-LLZ mixture, leading to decrease in the discharge capacity. In the case of $LiFePO_4$/Al-LLZ mixture, the decomposition of both materials was started at 400 °C. These results indicate that the limit of heat treatment temperature for the formation of electrode/solid electrolyte system strongly depends on the kind of electrode material.

Chapter 5

General Conclusion

In this thesis, the fabrication process for realizing all solid state lithium battery using garnet oxide type solid electrolyte has been studied. The results obtained in this study were summarized in Chapter 5.