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Study of inorganic solid lithium ion conductor with mixed degrees of sintering

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ABSTRACT

A series of $Li_{1+x}Al_xZr_{2-x}(PO_4)_3$ samples with varied amount of Al doping have been prepared using a solid state reaction method and the optimum doping amount of aluminum is determined as 0.6. All the doped samples showed an increased conductivity, which is attributed to the transformation of the triclinic phase to the rhombohedral phase and the density increasement upon doping of Al. By mixing powders calcined at two different temperatures (700 °C and 1100 °C), samples $Li_{1.6}Al_{0.6}Zr_{1.4}(PO_4)_3$ with the optimum doping amount of Al have been made to study the effect of the mixed degrees of sintering. The overall conductivities of samples with mixed degrees of sintering are all improved and peaked at 20–30% of powders calcined at 700 °C. This improvement is thought to relate to the role of powders calcained at 700 °C, which acted as "bridges" to connect all the other well-defined grains together.

1. Introduction

Limitations of the flammable organic liquid electrolytes of the Li-ion batteries, such as safety concerns, leakage, corrosion and miniaturization difficulty, have stimulated intensive researches on inorganic solid lithium ion conductors, including perovskite type, NASICON type, LISION type and garnet type [1]. However none of these materials studied so far exhibits a satisfactory conductivity which is comparable to that of organic electrolytes. The reason accounting for an overall low conductivity of crystalline materials is the small grain boundary conductivity, which is normally one order of magnitude lower than grain conductivity. Thus intensive researches have been focused on how to reduce the grain boundary resistance of crystalline materials thus to improve the overall conductivity of lithium ion conductors. Measures, including doping Si, Li_2O, mechanical attrition and etc., have been taken by various groups, no significant improvements have been achieved so far.

Current researches show that crystalline materials with a NASICON structure, especially $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) and $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP), exhibiting conductivities in the range of 10^{-3}-10^{-4} S cm^{-1} [2–4], are promising candidates to replace organic liquid electrolytes. Apart from low grain boundary conductivity, main drawbacks related to LAGP and LATP like expensive raw material of germanium and unstable Ti^{4+} under reducing atmosphere have prevented them from being a real practical interest. Zirconium, having the same valence as Ti^{4+} and Ge^{4+} and even bigger ionic radius, are stable and relatively cheap, which makes it a possibly suitable candidate to replace Ti^{4+} and Ge^{4+}. Therefore, $Li_{1+x}Al_xZr_{2-x}(PO_4)_3$ system has been chosen to be the study object. Since polycrystalline lithium ion conductors are limited by the high grain boundary resistance, the doping of some homogenous components like amorphous counterpart into $Li_{1+x}Al_xZr_{2-x}(PO_4)_3$ system could help to reduce the grain boundary resistance. Thus, a series of $Li_{1+x}Al_xZr_{2-x}(PO_4)_3$ materials with varied x has been prepared and efforts have been attempted to improve the overall conductivity by creating a microstructure with a mixed degree of sintering.

2. Experimental

A series of $Li_{1+x}Al_xZr_{2-x}(PO_4)_3$ (x = 0, 0.2, 0.4, 0.5, 0.6 and 0.8) materials with a mixed degree of sintering has been prepared by solid state reaction method in this study. Start materials used are Li_2CO_3 (≥99%), $Al(OH)_3$ (≥99%), ZrO_2 (≥99%) and $NH_4H_2PO_4$ (≥99%). For each composition, stoichiometric starting materials were weighed and mixed thoroughly in a pestle mortar. Then all the mixtures were calcined at 700 °C for 2 h to remove volatile components and the resulting mixtures were named as powder A. Powder A were then ground again and half of them were thermally treated in a furnace at 1100 °C for 2 h to achieve powder C with a higher degree of sintering. Powder C were then ground thoroughly and mixed with powder A in a 50%:50% weight percentage. The mixed powders were then pressed into pellets and sintered at 800 °C and 900 °C for 2 h to study effect of the doping amount of aluminum. Once the optimum doping amount of aluminum (x = n) has been obtained, a series of $Li_{1+n}Al_nZr_{2-n}(PO_4)_3$ powders with varied weight percentage of powder A (10%, 20%, 30%, 40% and 50%) were also prepared, pressed into pellets and subsequently sintered at 900 °C for 2 h in order to study the effect of the mixed degree of

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sintering. The density of the samples was determined by the Archimedes method using water as the immersion fluid.

All the sintered pellets were polished and painted with silver paste on both sides for electrochemical impedance spectra (EIS) analysis. The EIS measurements were carried out using a PARSTAT2273 station by applying a stimulus amplitude of 10 mV over the frequency range of 0.1 Hz- $2x10^6$ Hz at room temperature.

The microstructures were examined by using a field emission scanning electron microscope (JSM-7800F). Crystallographic phases analysis was carried out by X-ray diffraction with a D/max-2500 J/pc diffractometer using a Cu K-radiation source ($\lambda = 0.15418$ nm). The obtained XRD patterns were analyzed using the MDI jade 6 software program. The crystal lattice parameters are calculated by using the Jade cell refinement program.

3. Results and discussions

3.1. Microstructures examinations

The microstructures of samples $Li_{1+x}Al_xZr_{2-x}(PO_4)_3$ ($x = 0, 0.5, 0.6$) with the same ratio of powder A and powder C sintered at 900 °C were examined by SEM and SEM photographs are shown in Fig. 1. It was found that all these samples are showing a mixed morphology of well-defined grains and less well-defined grains. The well-defined grains observed are thought to originate from powders C which have been thermally treated at 1100 °C and powders A which were calcined at 700 °C were the root of those less well-defined grains. Powders A seem to act as binders to fuse powders C together upon annealing. The morphologies of these samples suggest that a mixed degree of sintering have been successfully introduced as expected.

Furthermore, it can be seen that the well-defined grains observed in the sample without Al doping tend to grow in a spherical shape and the grain size is in the range of 200 nm ~ 1000 nm, while the well-defined grains in the samples with Al doping tend to evolve into a rod-like shape. The doping of aluminum has altered the shape of grains as reported by other researchers [5]. As reported by Wang et al. [6], the doping of aluminum also helped to improve the sinterability and the relative density has increased from 70% to 74% for $x = 0.5$ and 76% for $x = 0.6$. The increased relative density is thought to be beneficial to the ionic conduction of $Li_{1+x}Al_xZr_{2-x}(PO_4)_3$.

Fig. 2 is the fractured surface of samples with varied weight percentage (10%, 20%, 30%, 40% and 50%) of powders A. It was found that the samples with smaller ratios of powders A contain more well-defined grains than those samples with higher ratios of powders A. This observation is in agreement with the aforementioned argument which stated the well-defined grains originated from powders C. The relative density of samples with varied weight percentage (10%, 20%, 30%, 40% and 50%) of powders A, measured to be 73%, 75%, 77%, 76% and 75%, was found to change with the weight percentage of powders A. It seems the relative density peaked at 30% of powders A, which proves the role of powders A as binders in some way.

3.2. XRD patterns

The doping of trivalent Al has been reported to increase the conductivity of system by introducing more mobile Li-ions. In addition to that, the XRD patterns of samples show that the doping of trivalent Al also changed the crystallographic structure of samples. Sample $LiZr_2(PO_4)_3$, absence of Al, sintered at 900 °C show a triclinic phase, while samples upon doping of Al tended to forms a rhombohedral phase as shown in Fig. 3. Some impurity phase ($Zr_3(PO_4)_3$) appeared on compositions $x = 0.2$ and 0.8. According to Catti et al. [7], the rhombohedral phase of $LiZr_2(PO_4)_3$ can only be obtained above 1200 °C and will transform to a distorted triclinic phase upon cooling. It was found that the doping of trivalent Al helped to form the rhombohedral phase at 900 °C and stabilize it upon cooling in this study. The conductivity of the rhombohedral phase was reported to be higher than that of the triclinic phase [8]. Therefore it can be expected that the samples doped with Al will attain higher conductivities compared to the undoped one.

The cell parameters of doped samples are shown in Table 1. The a-lattice constant was found to increase with Al amount and the c-lattice constant did not show a clear trend with Al doping. The unit cell volume increased with the doping of Al, peaked at $x = 0.6$ and then dropped after that.

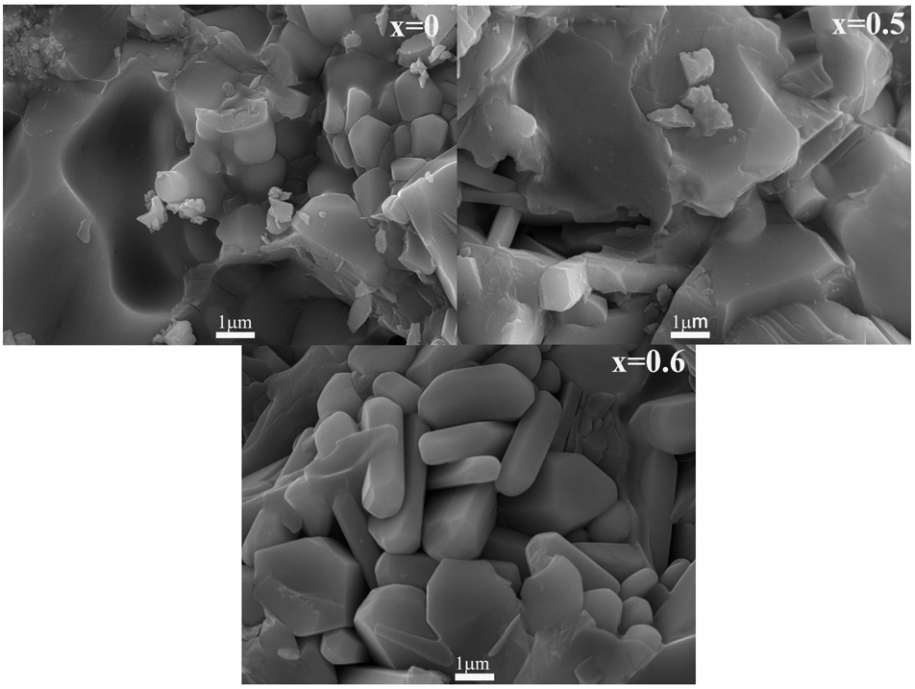

Fig. 1. SEM photographs of $Li_{1+x}Al_xZr_{2-x}(PO_4)_3$ samples (the ratio of A/C is 50%:50%) sintered at 900 °C.