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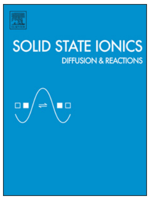

Effect of quenching method on Li ion conductivity of $Li_5La_3Bi_2O_{12}$ solid state electrolyte

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ABSTRACT

Effect of the quenching method on conductivity of $Li_5La_3Bi_2O_{12}$ ceramics prepared by sol-gel process was studied. In a synthesis process, lithium hydroxide, acetic bismuth, and acetic lanthanum were used as starting materials, while water was used as solvent. The temperature to synthesize the high density $Li_5La_3Bi_2O_{12}$ with cubic garnet type structure is 750 °C for 8 h in air with 10% excess lithium salt. The samples were prepared by the same synthesis route with the only difference from cooling methods. The samples were characterized by XRD, SEM, ^{6}Li MAS NMR and ionic conductivity measurement. The XRD patterns of $Li_5La_3Bi_2O_{12}$ ceramics showed that there was a single phase oxides with garnet-like structure by the furnace cooling and the quenching method. The $Li_5La_3Bi_2O_{12}$ electrolyte by the furnace cooling exhibits the highest total ionic conductivity of 2.0×10^{-5} S cm^{-1} at 22 °C, and that by the quenching method exhibits the highest conductivity of 2.0×10^{-4} S cm^{-1} with a motional activation energy of 0.36 eV, which is an order of magnitude higher than that by the furnace cooling. The reason is that the relative density of $Li_5La_3Bi_2O_{12}$ by the quenching method is higher than that by the furnace cooling. The SEM images are also shown that the density of $Li_5La_3Bi_2O_{12}$ is very high by the quenching method and there exists lots of pores by the furnace cooling. And the ^{6}Li-MAS-NMR results indicate the $Li_5La_3Bi_2O_{12}$ samples by the quenching method possess high Li ion mobility.

1. Introduction

Lithium ion batteries are the most promising candidate for mobile power sources of the newly arising application that there is a strong ongoing search for materials for energy conversion and storage. Fast lithium ion solid electrolytes have drawn much attention due to their potential application in all-solid-state rechargeable batteries and other solid-state electrochemical devices. Up to now, Lithium ion conduction has been reported for a wide range of metal oxide [1–4], e. g. $Li_{14}ZnGe_4O_{16}$, $Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$ and $Li_{3x}La_{(2/3)-x}\square_{(1/3)-2x}TiO_3$ ($0 < x < 0.16$) [5–7]. However, they cannot be used as solid state electrolyte due to their low ion conductivity or poor chemical stability. Therefore, it is important to find new types of lithium ion conductors to develop solid state lithium ion batteries.

Recently, a novel class of fast lithium ion conducting metal oxides with the nominal chemical composition $Li_5La_3M_2O_{12}$ (M = Nb, Ta) [8,9] and $Li_7La_3Zr_2O_{12}$ (LLZO) [10] possessing garnet-related structure has been reported. Based on these compounds, further investigations of conductivity optimization by chemical substitutions and structural modifications were initiated. The partial replacement of divalent alkaline earth ions for a trivalent La in $Li_5La_3M_2O_{12}$ extended the series of garnet-like structures by compounds with the general chemical formulas $Li_6ALa_2Nb_2O_{12}$ (A = Ca, Sr, Ba) [11,12] and $Li_6ALa_2Ta_2O_{12}$ (A = Sr, Ba) [13]. Recent studies on Y substitution at the M sites of $Li_5La_3M_2O_{12}$ produce Li-stuffed garnets with the general formula $Li_{5+2x}La_3M_{2-x}Y_xO_{12}$ [14,15]. The cubic LLZO shows a total conductivity of about 10^{-4}S cm^{-1}. Recently, lots of studies show that the substitution with Ta, Al and Ga [16–18], by using multiple sintering [19] and by adding some fluorine [20] to enhance the ion conductivity of LLZO.

So far, the reported lowest synthesis temperature of $Li_5La_3Bi_2O_{12}$ [21] is about 775 °C for 48 h. Recent research on the ionic conductivity of 10^{-5}S cm^{-1} by partial substitution of Bi and by other strategies were reported [22,23]. How to enhance the ionic conductivity of electrolyte is the key issues in development of solid state batteries. The quenching method is one of the most conventional techniques to prepare materials [24]. The method can eliminate internal stress, narrow cracks and increase in crystallinity of the phase. Some glass electrolytes by quenching methods can improve ion conductivity [25]. However, there are few reports on enhancing ion conductivity of solid state electrolytes by the quenching methods. Therefore, in the present study, the primary work motivation is to explore effect of the quenching methods

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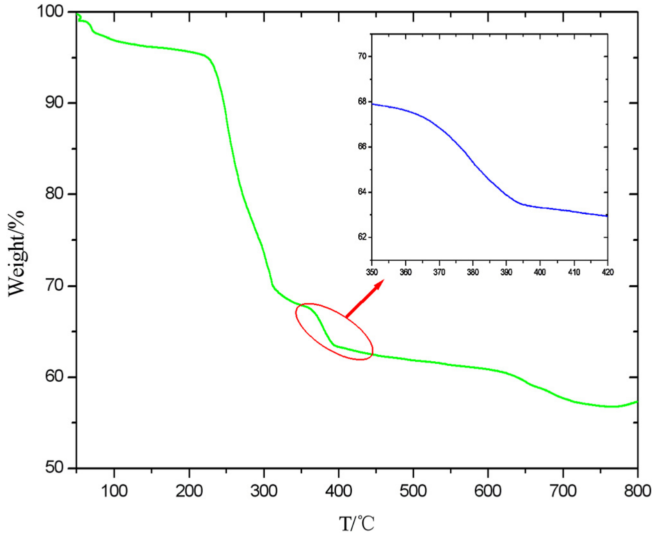

Fig. 1. TGA curves of the dried precursor obtained by the sol-gel method. The inset shows variation of weight in the temperature range of 350–420 °C.

on ionic conductivity of the $Li_5La_3Bi_2O_{12}$ electrolyte, compared to that by the furnace cooling.

2. Experimental

2.1. Preparation of $Li_5La_3Bi_2O_{12}$

The compound $Li_5La_3Bi_2O_{12}$ were prepared by using appropriate amounts of high-purity LiOH (99.3%), $LaAc_3.1.5H_2O$ (98%), $BiAc_3$ (98%) and ethylene-diaminetetraacetic acid (EDTA, 99.5%) as precursors. A relatively large amount (10%) of excess lithium salt was added to compensate for the loss of lithium during heat treatment. The overall synthesis procedure is outlined as follows: the required amounts of LiOH, $LaAc_3 \cdot 1.5H_2O$ and $BiAc_3$ were dissolved in water to prepare precursor. At the same time, a suitable amount of EDTA (5 mol%) was added to the above solution as complexing agent. The heating temperature and stirring speed were controlled in order to cool the solvent slowly until dried gel was obtained. Then the dried gel was dwelled at 750 °C for 8 h (heating rate 5 °C min^{-1}) to prepare $Li_5La_3Bi_2O_{12}$ powders. The quenching method process is different from the furnace cooling. In the courses of cooling, the powder was allowed to rapidly cool to 400 °C in 5 min, kept at 400 °C for 30 min, then rapidly cool to room temperature in air. The samples were uniaxially pressed into discs 12 mm in diameter in a stainless-steel die at 5 MPa. The pressed discs were sintered from room temperature to 750 °C at 2 °C min^{-1}, kept at 750 °C for 4 h, and then allowed to cool down in the furnace to room temperature.

Table 1
Lattice constants, ionic conductivity, activation energy and relative density of $Li_5La_3Bi_2O_{12}$ compound by the furnace cooling(a) and the quenching method(b).

Compound	a/Å	Ionic conductivity/Scm^{-1}	Activation energy/eV	Relative density/%
$Li_5La_3Bi_2O_{12}^{a}$	13.052	2.2×10^{-5}	0.42	88.3%
$Li_5La_3Bi_2O_{12}^{b}$	13.049	2.0×10^{-4}	0.36	93.2%

2.2. Characterizations

Thermal gravimetric analysis (TGA 7, Perkin-Elmer) was employed to analyze the reaction processes during heating and to find the proper temperature range for the synthesis. The measurements were performed in flowing air from room temperature to 800 °C at a heating rate of 2 °C·min^{-1}. A sample weight of 25–30 mg was used.

XRD measurements were performed with a Philips PW 1830 diffractometer equipped with a CuK_{α} source operating at 40 kV and 30 mA. A Rietveld structure refinement was carried out with the Fullprof software package. A Philips SEM was used to obtain images of the pellet morphologies.

Impedance spectroscopy measurements over the frequency range of 1 Hz to 1 MHz with a Solarton Impedence Analyzer, model 1287, were made on ca. 1-mm-thick pellets having a diameter of 12 mm. Both parallel surfaces of the pellets were sputtered with a layer of gold. A 10 mV voltage was applied over the frequency ranges of the Solarton. The ^{6}Li-MAS-NMR spectra were acquired on a Bruker DSX 400 spectrometer at 9.4 T.

3. Results

3.1. Thermal analysis

Fig. 1 shows the TGA curve of the dry gel fired in air with a heating rate of 10 °C min^{-1} in the temperature range of 50 °C–800 °C. There are several weight loss steps, as evidenced more clearly by the peaks

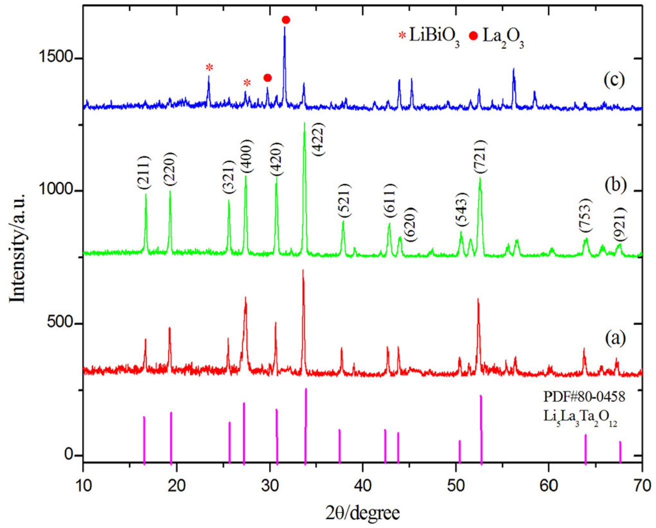

Fig. 2. XRD patterns of cubic nominal $Li_5La_3Bi_2O_{12}$ powders prepared by the furnace cooling (a) and the quenching method (b), $Li_5La_3Bi_2O_{12}$ calcined at 800 °C (c) in air.

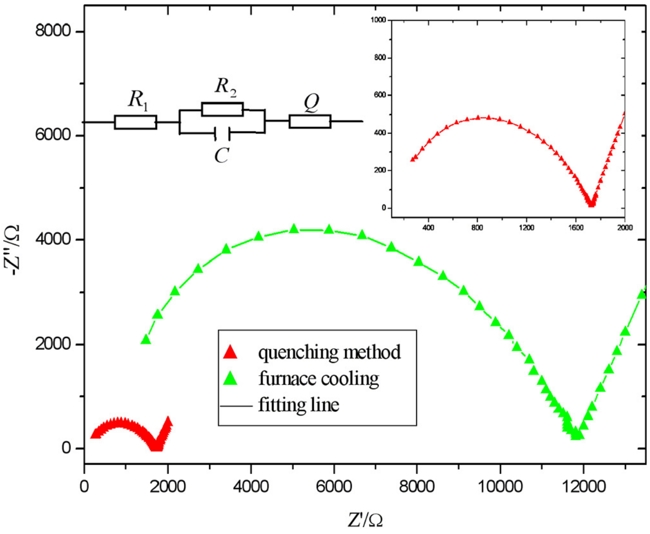

Fig. 3. Room-temperature impedance spectra of $Li_5La_3Bi_2O_{12}$ pellets prepared by the furnace cooling and the quenching method.