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Solid lithium ion conducting composites based on $LiTi_2(PO_4)_3$ and $Li_{2.9}B_{0.9}S_{0.1}O_{3.1}$ glass

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ABSTRACT

The $LiTi_2(PO_4)_3$–based ceramic composites with addition of $Li_{2.9}B_{0.9}S_{0.1}O_{3.1}$ (LBSO) were formed and investigated by means of X–ray diffractometry, thermogravimetry, scanning electron microscopy, impedance spectroscopy and density methods. Significant enhancement of total ionic conductivity of the formed composites could be observed after sintering the material at high temperatures. The maximum conductivity of 1.79×10^{-4} S·cm^{-1} at 30 °C was achieved for the LTP–0.3LBSO material sintered at 900 °C compared to 5.15×10^{-8} S·cm^{-1} of the ceramic LTP.

1. Introduction

Nowadays, increasing number of electronic devices which requires the external source of energy generates demand in lithium ion batteries (LIBs) with high energy density. The market expresses the need on still better batteries in the context of higher specific capacity and lifetime. Commonly used rechargeable batteries contain liquid electrolyte, which, in fact, impede progress of technology because of their flammability and limited width of electrochemical window [1–5]. The solution of presented problems, and introduction of above amendments as well, could be possible if the liquid electrolyte will be replaced by the solid one. However, this concept might find application, when few major criteria will be fulfilled. First of all, high Li–ion conductivity exceeding 10^{-4} S·cm^{-1} at operating temperatures is required [5,6]. The proposed materials, which will act as solid electrolyte need to be thermally and chemically stable. Other, worthy of attention features, especially for commercially oriented mass production are simplicity of preparation and low prices of the reagents [1–5].

Among many examined compounds, the highest value of the lithium ion conductivity was reported for Li_2S containing glasses. Unfortunately, from the practical point of view, application of the materials containing sulfides might be problematic due to their hygroscopicity [4,5]. Better chemical stability in air exhibit materials based on metal oxides. However, their ionic conductivity is slightly lower, ca. 10^{-4} S·cm^{-1}. Within this group, $LiTi_2(PO_4)_3$ (LTP) seems to be a perspective material [7–23]. It crystallizes in NASICON–type structure with rhombohedral symmetry and belongs to R–3c space group. High chemical and thermal stability, inflammability and environmental benign are the main advantages of the LTP, which predestines it for application in the LIB technology as functional material working as solid electrolyte. Ion conductivity of the LTP grains at room temperature is reported to be in the range of 10^{-4}–10^{-3} S·cm^{-1} [12–19]. But total ion conductivity of the ceramic LTP, which is the most vital parameter for the practical purposes in the LIBs technology is poor, having values in the range of 10^{-8}–10^{-6} S·cm^{-1} at room temperature [12–22]. A highly resistant grain boundary phase inside the ceramic material is responsible for that. There were various attempts to enhance conductivity of the grain boundary to obtain a low–-total–resistivity LTP material. It has been reported that high values of total ionic conductivity could be obtained by crystallization of the NASICON–based glass [24,25]. Unfortunately, that method requires very high temperatures for the vitrification and the prepared glassy material is too fragile for the large scale production. Other approach claims that some additional, foreign phase introduced among the LTP grains could lower the grain boundary resistance [19,23,26,27]. Therefore, the useful lithium ion conductors should be sought among composites. For their preparation is necessary to choose a suitable material – an additive.

One of the most studied additive is glassy Li_3BO_3 (LBO) [28–34]. K. Tadanaga et al. and N.C. Rosero–Navarro et al. investigated a family of garnet type materials with addition of the LBO. Both groups reported the increase of the total ion conductivity of the formed composites [28–31]. They also noticed densification of the ceramic materials after sintering at 900 °C. A. Hayashi et al. [32,33] and M. Eom et al. [34] reported high values of electrical conductivity of the sulfide composites. The latter authors suggested that the conductivity enhancement could be caused by increased of the effective concentration of lithium ions in the composite due to addition of Li_3BO_3 [34].

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In this work we decided to focus on $LiTi_2(PO_4)_3$–based composites with addition of $Li_{2.9}B_{0.9}S_{0.1}O_{3.1}$ (LBSO) glass. According to the studies of Japanese group of M. Tatsumisago, the ionic conductivity of the glass–ceramic LBSO is higher in comparison to LBO, equals 1.4×10^{-5} Scm^{-1} [35,36]. So, the LTP–LBSO system seemed to be promising in further improvement of total ionic conductivity. In the study we paid attention on correlations between density, sintering temperature and ion conductivity of the grains or grain boundary phase.

2. Experimental

The $LiTi_2(PO_4)_3$ material was synthesized by a conventional solid–state reaction method. Stoichiometric amounts of Li_2CO_3 (Sigma Aldrich), $NH_4H_2PO_4$ (POCh), TiO_2 (Sigma Aldrich) reagents were weighted, mixed with a mortar and pestle. The ground mixture was annealed at 900 °C for 10 h to synthesize the final compound. In the case of preparation of $Li_{2.9}B_{0.9}S_{0.1}O_{3.1}$ glass, stoichiometric amounts of Li_2CO_3 (Sigma Aldrich), H_3BO_3 (POCh) and Li_2SO_4 (Sigma Aldrich) were weighted, mixed with a mortar and pestle. Then, the formed mixture was placed in an alumina crucible and annealed at 1100 °C for 15 min. to obtain the molten glass. The process of vitrification was completed by quenching of the melt between two stainless steel plates. The obtained glass was ball–milled with rotation speed of 400 rpm for 1 h employing a planetary ball–mill Fritsch Pulverisette 7. The composites were formed by mixing the LTP as–prepared powder with the ball–milled lithium borate sulfate glass taken in a different molar ratio varying from 10 to 30 mol%. Further process of preparation involved ball–milling of both components at rotation speed of 400 rpm for 1 h. Ethanol was used as an immerse liquid. The obtained powder, after drying, was pressed under uniaxial 10 MPa pressure to form pellets 6 mm in diameter and ca. 2 mm thick. Such material, later in the text, will be called as a non–sintered composite. Then, the pellets were sintered at 700, 800 or 900 °C for 2 h forming final composites.

The X–Ray diffraction method (XRD) employing Philips X'Pert Pro (Cu Kα) was used for examination of the quality of both the composites and their components. Temperature dependent HTXRD were performed using Anton Paar HTK–1200 Oven in the temperature range of 30–900 °C. Data were collected in the range of 10° – 90° with 0.05° step and a count rate of 0.5 s at each step.

Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on the powdered composites using TA Instruments Q600 to observe thermal events in the studied materials during heating under air flow in the temperature range of 30 °C to 900 °C. The measurements were performed with heating rate of 10 $°C \cdot min^{-1}$ on samples, ca. 20 mg each.

Apparent density of the composites was determined using Archimedes method with isobutanol as an immerse liquid. We estimated the maximum accuracy of the used method as ca. 2%.

The microstructure was investigated by means of scanning electron microscopy (SEM) employing Raith eLINE plus microscope. Only freshly fractured pellets were used for the SEM imaging.

In order to perform electric investigations, both bases of the as–form pellets were, at first, polished and then covered with graphite as electrodes. Electric properties of the obtained composites were studied employing Solatron 1260 frequency analyzer in a frequency range of $1–3 \cdot 10^7$ Hz. Impedance data were collected in the temperature range from 30 °C to 100 °C, both during heating and cooling runs. The impedance spectroscopy investigations of the studied materials were performed in air atmosphere.

3. Results and discussion

Fig. 1 shows the XRD investigation results of the base material and composite with addition of 0.2 mol of LBSO glass. Positions and relative intensity of the reflections for the polycrystalline LTP powder presented at the bottom in Fig. 1 agree very well with those included in the database and referred to $LiTi_2(PO_4)_3$ (ICDD 00–035–0754). Also, one can notice some additional, weak diffraction peaks located at 2θ angles: 22.5°, 25.2° and 27.7°. They were attributed to the TiP_2O_7 (ICDD 00–038–1468) and TiO_2 (ICDD 00–021–1272). Formation of these undesired phases were reported also by other researchers [20–22] and they were related to some decomposition processes due to lithium evaporation occurring at high temperatures during synthesis of the material. In the case of a non–sintered composite material, the reflections corresponding to $LiTi_2(PO_4)_3$, TiP_2O_7 and TiO_2 are visible only. No additional diffraction lines were recorded. The results prove that a sequence of the processes: mixing and pressing does not cause formation of some, new phases in the composite. On the contrary, the sintering does, as the X–ray investigations reveal. Four additional, weak lines at 26.9°, 27.3°, 27.7°, 39.6° are visible on the X–ray patterns, whereas, surprisingly, the reflections attributed to TiP_2O_7, TiO_2 phases are absent. The new diffraction lines could be attributed to $LiTiPO_5$ (ICDD 00–044–0083). To learn more about phase changes, HTXRD was performed within the 30–900 °C temperature range. Up to 600 °C, there were no changes on the X–ray patterns. Starting at ca. 700 °C, the diffraction peaks related to TiP_2O_7 and TiO_2 phases began to decay and simultaneously those attributed to the $LiTiPO_5$ appeared. Their intensity increased with temperature. Taking into account that we did not detect any other phase or phases, the observations suggested that at high temperatures the TiP_2O_7 and TiO_2 phases were consumed in some reaction with the glass component.

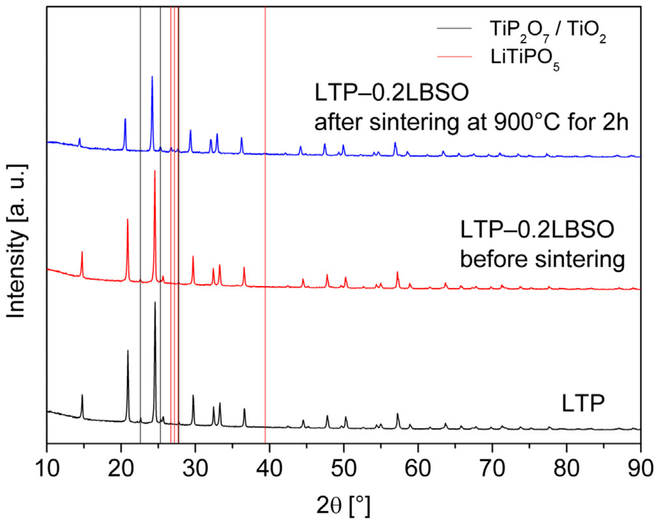

Fig. 1. X–ray diffraction patterns of the prepared: LTP, LTP–0.2LBSO (before sintering at 900 °C), LTP–0.2LBSO (after sintering at 900 °C).

More detailed information about the processes, which may occur during sintering was obtained by means of calorimetric (TGA/DTA) investigations performed on the LBSO and non–sintered composites as well. Fig. 2 presents the TG traces for the non–sintered LTP–LBSO powders. On each TG trace, between 30 °C and about 400 °C, one can observe the characteristic slope indicating some mass loss. The lost of the weight was estimated to be ca. 2 wt%. We attribute this very small mass loss to some dehydration processes caused by the release of moisture and, very likely, residuals of ethanol absorbed by the powdered components. Above 400 °C up to 900 °C no mass loss was detected.

The results of the DTA investigations of pure LBSO glass are shown in Fig. 3. For the heating run, the step–like change of the heat flow occurring at about 340 °C could be assigned to glass transition of LBSO. Two exothermic peaks at around 430 °C and 530 °C one can attribute to solidification processes. At about 670 °C some endothermic process starts with the peak at ca. 735 °C. It could be associated with some melting of the products of solidification. After cooling, during the next