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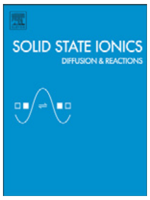

$Na_{1+x}Al_xGe_{2-x}P_3O_{12}$ (x = 0.5) glass–ceramic as a solid ionic conductor for sodium ion

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ABSTRACT

Sodium-ion conducting glass–ceramics composed of $Na_{1+x}Al_xGe_{2-x}P_3O_{12}$ (x = 0.5) crystalline conducting phase were successfully prepared by heat-treating the parent glass at different temperature and time, and were characterized with DSC, XRD, CV, SEM and alternative current impedance. The relationship between the ionic conductivity and crystallization conditions (time and temperature) of the sodium aluminum germanium phosphate (NAGP) glass–ceramic was investigated. Results show that the NASICON phases containing Al^{3+} in all these glass–ceramics are isomorphous with $NaGe_2P_3O_{12}$ and stable against sodium metal. The highest total conductivity of the glass–ceramic material, 9.27×10^{-5} S cm^{-1} at 140 °C, is obtained by highly crystallizing the glass at 750 °C for 12 h. The reasons for the enhancement of the ionic conductivity in the glass–ceramics are discussed in view of the dependence of microstructure morphology on the heating condition. It could be attributed to its good crystallization of the conductive phase NAGP, uniform grain size and possible optimizing conductive pathway of Na^+ ions.

1. Introduction

Sodium-ion batteries (NIBs) have attracted great attentions particularly in electric vehicles (EVs) and large scale electrochemical storage for biomass, solar radiation, wind and waves and so on because of the huge abundant sodium resources,low cost (Na_2CO_3 0.07–0.37 € kg^{-1} *vs.* Li_2CO_3 4.11–4.49 € kg^{-1}) and very suitable redox potential ($E^o_{(Na+/Na)} = 2.71$ V *versus* standard hydrogen electrode; only 0.3 V above that of lithium) [1–7]. The very high reactivity of sodium with moisture and oxygen, the quest for safer and more reliable electrolyte systems is therefore urgent, and solid electrolytes (SEs) are promising candidates in this regard [8–10].

However, most polymer electrolytes coupling a polymer with a plasticizing organic solvent for NIBs still present some drawbacks [11,12]. In this respect, inorganic solid electrolytes (solid sodium ion conductors) present potential advantages like a large electrochemical stability window, highly thermal stability, absence of leakage and pollution, a high resistance to shocks and vibrations and the possibility of easy miniaturization [13,14]. One prominent example of the solid Na^+ ion conductor is Na-β″-Al_2O_3 that is mostly used in the high temperature sodium batteries (sodium–sulfur batteries) as an electrolyte with an ionic conductivity of 0.2–0.4 S cm^{-1} at 300 °C [4]. Another extensively studied Na^+-conducting solid electrolytes are NASICON (Natrium (Na) Super (S) Ionic (I) Conductor (C), general formula is $AM'M''P_3O_{12}$) type compounds which demonstrate sodium ionic conductivities in three-dimensional frameworks (any crystallographic direction) in comparison with Na-β-Al_2O_3 (layer structure) possessing only two-dimensional Na^+ mobility [15,16]. Solid solutions of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ (NZSP, $0 \le x \le 3$), firstly reported by Hong and Goodenough [17,18], are typical examples of NASICON-type compounds which are characterized by relatively large ionic conductivities in the order of 10^{-1} S cm^{-1} at 300 °C and 10^{-4} S cm^{-1} at ambient temperature [8,19]. Hence, the properties of the chemically stable Na^+-conducting SEs with high sodium-conductivity at room temperature, good cation-exchange with electrode materials and so on should make them possible for applications in room temperature all-solid-state NIBs with high safety [20].

However, high porosity and big grain boundary as well as the difficulties in obtaining the desired shapes of the sintered NASICON-type ion conductors affect their practical applications as SEs in NIBs [21]. Compared to the sintered materials, glass–ceramics can be made into desired shapes and sizes more easily because of their pore-free and small grain sizes [22]. So far, few reports were dedicated to sodium ionic conductors with NASICON-type structure containing Al cations, let alone the glass–ceramics with same composition. Only Li^+-conducting glass–ceramics composed with crystalline containing Al^{3+} NASICON phase have been reported [11]. Due to the close ionic radius of Al^{3+} compared to that of

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Ge^{4+}, the Al cation is likely within the tolerability limit of $NaGe_2(PO_4)_3$ framework. Furthermore, when NASICON-type sodium ionic conductors containing Al^{3+} are prepared, ALPO (aluminum phosphate) side-compounds can be easily formed. Phases such as berlinite (ALPO), with tetrahedral PO_4^{3-} groups, are very stable. Once formed, they do not react to yield desired NASICON-type products [23–25].

In this study, we report sodium ion conducting glass–ceramics containing crystalline NASICON phase, $Na_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$, and its preparation method. Al^{3+} in the glass–ceramics entered the structure of NASICON and partly substituted the Ge^{4+}. Sodium ionic conductivity of the solid electrolyte is up to 9.27×10^{-5} S cm^{-1} at 140 °C. Meanwhile, the effects of crystallization time and temperature on the ionic conductivity of the glass–ceramic have also been investigated. The prepared ion conductor extends the family of the $Na_{1+x}Al_xGe_{2-x}P_3O_{12}$ system and provides great promise for practical application in room-temperature sodium ion batteries or chemical sensors.

2. Experimental

A glass batch of $[18.75Na_2O\cdot6.25Al_2O_3\cdot37.50GeO_2\cdot37.50P_2O_5$ (mol%)] was prepared by using reagent-grade chemicals such as Na_2CO_3 (Sinopharm, China), Al_2O_3 (Sinopharm, China, particle size <10 μm), GeO_2 (Sinopharm, China) and $NH_4H_2PO_4$ (Sinopharm, China). The aforementioned chemicals were weighed, mixed, and ground for 10 min in an agate mortar. For further homogenization, the batch was milled in a glass jar for 1 h by using a ball mill. The milled batch was melted in a platinum crucible at high temperature (1350 °C) for 2 h to get a clear, homogeneous and viscous melt, which was poured onto a preheated (250 °C) stainless steel (SS) plate at room temperature and pressed by another SS plate to yield transparent NAGP glass sheets (thickness: ~200 μm). Subsequently, the pressed glass sheets were crystallized at different temperatures to release the thermal stresses and then cooled to room temperature to give $Na_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$ (NAGP) glass–ceramics.

Except stated, the following measurements were performed at room temperature. Thermal characterization of NAGP glass–ceramic samples was carried out using differential scanning calorimetry (DSC) in the nitrogen by Perkin-Elmer TGA7/DSC7 from room temperature to 800 °C at the rate of 10 °C min^{-1}. Based on the DSC data, thermal treatment was done in two steps. In the first step, the samples were heated to the temperature between glass transition temperature (T_g) and crystallization temperature (T_c) for 2 h in order to form the crystal nucleus. In the second step, the glassy samples were heated at the temperatures above T_c for different periods to reach the best treating conditions to optimize the conductivity of the glass ceramics. The heating and cooling rates for the crystallization were 3 °C min^{-1}. The crystallization process transformed the glass to glass–ceramic, which led to a change in the appearance of the glass from colorless transparent to grayish opaque. Elemental components were obtained from the analysis by using a Thermo E. IRIS Duo inductively coupled plasma atomic absorption spectrometer (ICP-AAS). X-ray diffraction (XRD) was performed on a Bruker D8 X-ray diffractometer (50 kV, 50 mA) with a copper target ($\lambda = 1.5405$ Å) and Ni filter at a scan rate of 5° min^{-1} from 10° to 80°. The surface morphology of the fractured and thermally annealed samples was investigated by Philips XL30 scan electron microscopy (SEM). All of the samples were sputtered with gold prior to the SEM measurement. The thickness of the membranes was measured with a micrometer (SM & CTW, Shanghai).

The ionic conductivities were measured by electrochemical impedance spectroscopy (EIS). A gold coating of 0.5 μm thickness was sputtered on both sides of these samples before measurement. The samples were measured in blocking-type cells where the gold-coated solid membranes were sandwiched between two stainless steel electrodes ($\Phi = 18$ mm). Impedance data were obtained with an electrochemical working station CHI660C (Chenhua) in the frequency range 1 Hz–100 kHz between 20 °C and 140 °C. At each temperature, the sample was equilibrated for 1 h prior to the impedance measurement. The ionic conductivity was calculated from the Eq. (1):

$$\sigma = l/(R_bA)(S\ cm^{-1}) \quad (1)$$

where σ is the ionic conductivity, R_b is the total electrolyte resistance (including both bulk and interfacial contributions) from EIS, l is the thickness of the solid electrolytes, and A is the area of the stainless steel electrode since the area of inorganic membrane is larger than that of the steel electrode.

The electrochemical stability of the glass–ceramic samples was determined from the linear sweep voltammogram by the electrochemical working station CHI660C (Chenhua) using a two-electrode cell. Stainless steel was used as the working electrode and sodium foil as the counter and reference electrode. The measurement was done between 0 and 5.5 V (*vs.* Na^+/Na) at the scan rate of 1 mV s^{-1}.

3. Results and discussion

The DSC curve of the glass batch NAGP from room temperature to 800 °C is shown in Fig. 1. The sample presents an inflection at 565 °C, which is related to the glass transition temperature (T_g). An exothermic peak (T_c) at 635 °C is attributed to the crystallization of the glass during its conversion to glass–ceramic. It should be noted that some crystallization does occur in the glass even before T_c, but at T_c rapid crystallization of the glassy matrix takes place. At this temperature range only one sharp peak was observed, indicating the formation of single crystalline phase. Based on the DSC data, the samples were heated to 600 °C for 2 h and then subsequently crystallized at 700, 750, 800, and 850 °C for 12 h, separately. Another two samples were crystallized at 750 °C for 8 and 24 h.

The ICP analysis data for the sample from heat-treatment at 850 °C show that the component is $Na_{1.49}Al_{0.50}Ge_{1.499}P_{2.99}O_{12}$, and the relative error is about 5%. It is almost consistent with the ratio for the precursors. Although some elements would evaporate during the heat-treatment at the high temperature up to 850 °C, the evaporated content is not much.

The XRD patterns of $Na_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$ glass-ceramics are shown in Fig. 2. It was observed that almost no impure phase can be detected. The XRD peaks coincided well with the data of JCPDS 33-1245 ($NaGe_2P_3O_{12}$), confirming the formation of a single crystallization phase indexed to rhombohedral NASICON-type structure. Therefore, it could be inferred that the added Al^{3+} ions entered the structure of $NaGe_2P_3O_{12}$ by replacing Ge^{4+} ions. The prepared glass-ceramics containing NASICON phase consist of crystal phase and amorphous region. So the exact number of Al^{3+} entering the NASICON structure needs to be tested further in the future if possible convenient measurement is available. These results also indicate that NASICON-type $Na_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$ is the major conductive crystal phase in the glass-ceramics.

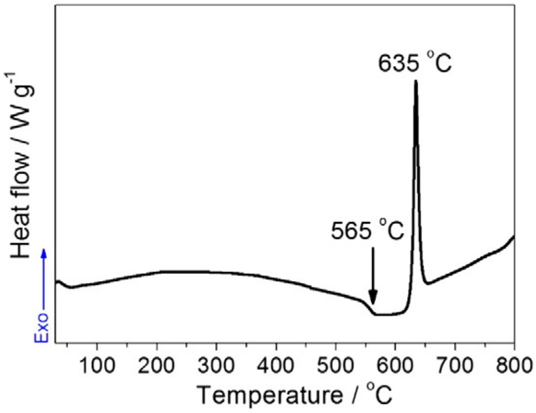

Fig. 1. DSC curve of $Na_{1.5}Al_{0.5}Ge_{1.5}P_3O_{12}$ glass sample.