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The effect of humidity on the electrical properties of Nasicon-type materials

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Nasicon $Na_3Zr_2Si_2PO_{12}$ samples were prepared by coprecipitation and solid-state reaction. Both methods lead to materials consisting of monoclinic Nasicon phases with small admixtures of ZrO_2 or $ZrSiO_4$. The differences of their behaviours and stabilities in long-term ageing tests in humid atmospheres are discussed in terms of their microstructures. Model equivalent circuits are proposed to explain observed phenomena.

Key words: *Nasicon; relative humidity; impedance spectroscopy; microstructure*

1. Introduction

Nasicon-type (Na^+ Super Ionic Conductor) materials are known to exhibit high ionic conductivity and relatively high chemical stability. These materials have been proposed to be used as solid electrolytes in solid-state electrochemical cells such as gas sensors, ion sensors, and Na–S batteries [1–3]. The highest conductivities of Nasicon samples ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) were observed in the range $1.8 < x < 2.4$, hence most studies have concentrated on the composition of $x = 2.0$. Moreover, the total electrical conductivity strongly depends on the density and nature of the grain boundaries [4–6]; the microstructure of samples is usually affected by the preparation method.

Initially, Nasicon was considered to be insensitive to moisture and stable in contact with water, since its structure prevents water molecules from penetrating the lattice. Nearly 20 years ago, Ahmad et al. [7] revealed that Nasicon reacts with water solutions, regardless of composition and the processing route.

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The purpose of this work was to study the influence of humid air on the electrical properties of $Na_3Zr_2Si_2PO_{12}$ obtained by coprecipitation and the solid-state reaction method. The experimental conditions of synthesis and their correlation with the results obtained from accelerated ageing tests were also discussed.

2. Experimental

2.1. Sample preparation

Nasicon samples with a general formula of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, with a stoichiometric composition of $x = 2$, were prepared by coprecipitation and the solid-state reaction method. In the case of coprecipitation, aqueous solutions of $ZrO(NO_3)_2$, $NaOHSiO_2$, and $(NH_4)_2HPO_4$ were used. These solutions were mixed at room temperature and stirred until the gel-like coprecipitate was formed. This precipitate was then slowly evaporated at 70 °C for 48 h, then dried at 150 °C for 12 h, calcined in 24 h at 750 °C, and then in 900 °C for 24 h. Powders were formed into pellets, then isostatically pressed at 300 MPa. Sintering was done at $T = 1175$ °C for 5 h. In the case of solid-state reaction, the mixture $Na_3PO_4\cdot 12H_2O$ and $ZrSiO_4$ powders in an appropriate stoichiometric ratio were pressed into pellets and calcined at 1150 °C for 24 h in one step. The obtained material was ground, pressed, and sintered under the same conditions as the material prepared by coprecipitation.

2.2 Measurements

X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) were used to determine the structural and microstructural properties of the prepared pellets. Electrical properties were determined basing on AC Electrochemical Impedance Spectroscopy measurements (EIS). Measurements were done in a typical sample holder at room temperature in air atmosphere with controlled humidity. In order to obtain humid atmosphere, dry synthetic air was passed through a water bubbler. Air humidity was measured at the gas outlet. The gas flow was kept at constant level in all measurements. Pt blocking electrodes were deposited by screen-printing on both sides of the Nasicon pellets. Prior to each measurement, samples were equilibrated for 24 h after each change of conditions.

3. Results and discussion

3.1. Phase composition

The calcination at $T = 750$ °C of the primary gel/coprecipitate prepared by coprecipitation leads to the formation of tetragonal ZrO_2, and no traces of other phases are observed. Further calcination at $T = 900$ °C and $T = 1175$ °C leads to the formation of a monoclinic Nasicon phase with a slight admixture of monoclinic ZrO_2. The sample prepared by the solid-state reaction method crystallises as a monoclinic phase just after calcination at 1150 °C for 24 h (with possible traces of tetragonal $ZrSiO_4$ and the usual slight admixture of monoclinic ZrO_2 phase).

3.2. Microstructure

Figures 1 A–D show the cross-section SEM micrographs of Nasicon samples, prepared by different methods; before (A, C) and after (B, D) ageing tests in a humid atmosphere. The samples obtained from powder prepared by the solid-state reaction method display much higher density (lower porosity) compared to the samples sintered from powders by coprecipitation. The grain boundaries are hardly visible in the case of Nasicon prepared by a solid-state reaction. This may suggest the presence of a liquid phase during sintering and a glassy-like phase after quenching. No significant difference in the microstructure before (C) and after (D) humidity treatment was observed.

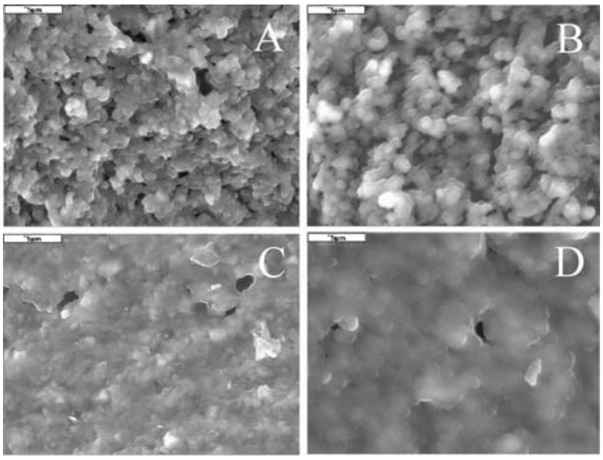

Fig. 1. SEM micrographs of $Na_3Zr_2Si_2PO_{12}$ sintered at 1175 °C for 5 h, prepared by coprecipitation before (A) and after (B) humidity treatment, and prepared by solid state reaction before humidity treatment (C)

As can be shown on the microstructure pictures of Nasicon obtained by coprecipitation (Fig. 1A, B), a smaller amount of glassy-like phase at the grain boundaries was visible, compared to the Nasicon prepared by the traditional method. Grains seem to be smooth and not uniform in size. After the ageing test, however, Nasicon prepared by coprecipitation looses its mechanical strength and easy crumbles. Similar behaviour was observed earlier by others [8, 9] and could be related to the dissolution of traces of glassy phase at grain boundaries or, on the contrary, to the formation of a hydronium Nasicon protonic conductor surrounding Nasicon particles. No additional Nasicon-like phase was found in our samples, so the first explanation of this phenomenon seems to be more feasible.

3.3. Electrical properties – the influence of humidity

Fig. 2 (A, B, C) shows examples of the admittance spectra of $Na_3Zr_2Si_2PO_{12}$ (prepared by coprecipitation) in dry and humid atmospheres, measured at room temperature. The proposed equivalent circuit is shown in Fig. 3a and consists of a CPE_{dl} element (double layer capacitance at the surface), R_b (bulk resistance), R_{gb} and CPE_{gb} (grain boundary resistance and capacitance), and R_g and CPE_g (glass resistance and capacitance). The diagram for Nasicon prepared by coprecipitation before the ageing test in a humid atmosphere (Fig. 2a) is represented by two semicircles (in the $Y''(Y')$ representation). On the left, a low frequency semicircle corresponds to electrode polarisation, and on the right, a high frequency semicircle reflects the grain boundary polarisation (the semicircles related to $RCPE_{gb}$ and $RCPE_{glass}$ are not separated due to similar R and CPE values). Additionally, to illustrate the difference between the low and high frequency ranges of the spectra, impedance diagrams were also used. The

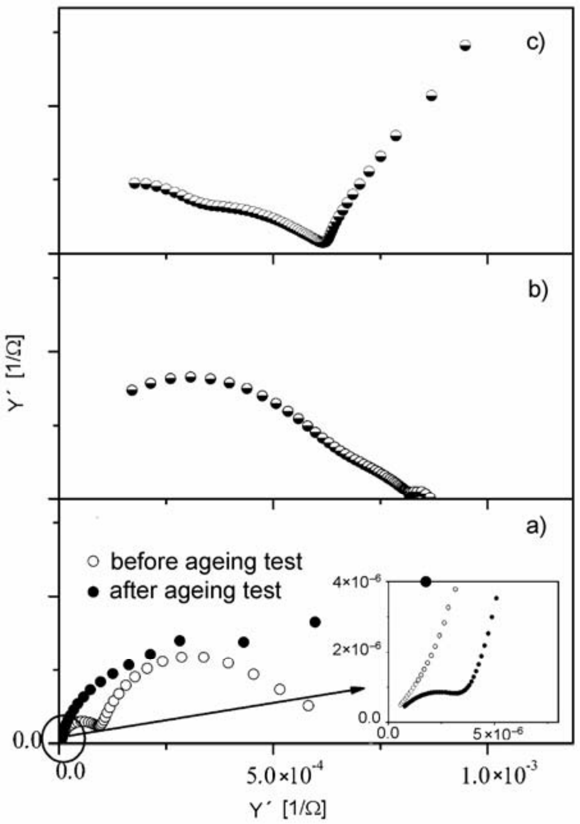

Fig. 2. The admittance spectra of $Na_3Zr_2Si_2PO_{12}$ prepared by coprecipitation:
a) 0% RH, b) ~90% RH, 400 h in wet air flow, c) ~90% RH, 768 h in wet air flow

electrical equivalent circuit taken to fit Nasicon spectra in a dry air flow, proposed earlier for samples prepared by solid state reaction [10], is typical of ceramic samples.

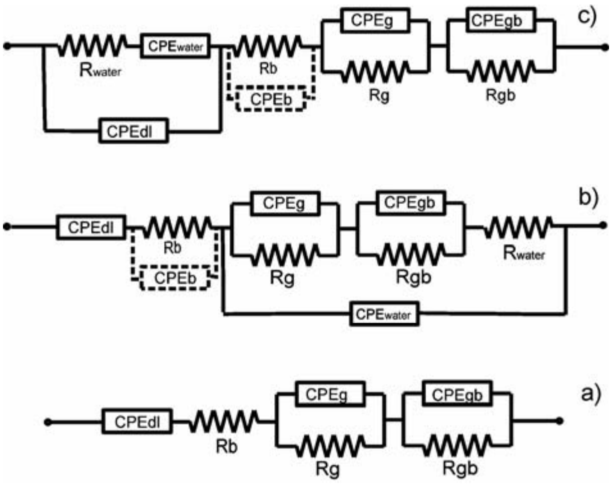

Fig. 3. Equivalent circuits proposed to fit the data obtained in dry (a) and humid atmospheres (b, c)

The presence of water vapour in an ambient atmosphere leads to a modification of the measured spectra (Fig. 2b, c) as compared to those obtained in dry air (Fig. 2a). Namely, the spectrum is shifted towards higher values of electrical conductivity; this effect can be attributed to the formation of conductive pathways along the ceramic pores due to water condensation, and was observed in Nasicon prepared by both methods. The shape of the spectra taken in a humid atmosphere (Fig. 2b) is the same for Nasicon prepared by both methods (Fig. 4b, c), but in the case of sample prepared by coprecipitation the spectrum is different after 500 h in a wet air flow (Fig. 2c). As can be seen in Fig. 3b and c, two possible circuits have to be taken into account to properly fit the obtained spectra. An additional electrode component related to water condensed at the electrode surface can be represented as a series-connected resistor and capacitor (R_{water}, CPE_{water}), connected in parallel with the double layer capacitance (CPE_{dl}). On the other hand, water condensation at grain boundaries has been considered, and the corresponding resistance and capacitance (R_{water} and CPE_{water}) may be included in series to the elements describing the bulk and grain boundary properties.

As can be seen on the spectra in wet flow for electrolytes obtained by coprecipitation, the grain boundary resistance (R_{gb}) decreases about one order of magnitude and the double layer capacitance (CPE_{dl}) is about two orders of magnitude higher compared to that of the sample in a dry atmosphere. The bulk resistance was initially lower, but after 700 h in a humid flow increased, probably due to the formation of new phase around Nasicon particles. To properly fit the spectra for Nasicon prepared by coprecipitation and measured after 500 h in a humid air flow, an additional CPE element connected with bulk capacitance is required (drawn by the dashed line and included in equivalent circuits describing measurements in a wet atmosphere in Fig. 3b and c). Additionally, higher values of grain boundary and glassy phase resistances suggest that longer humidity treatment leads to the formation of a so-called hydronium Nasicon surrounding the main Nasicon particles [9].

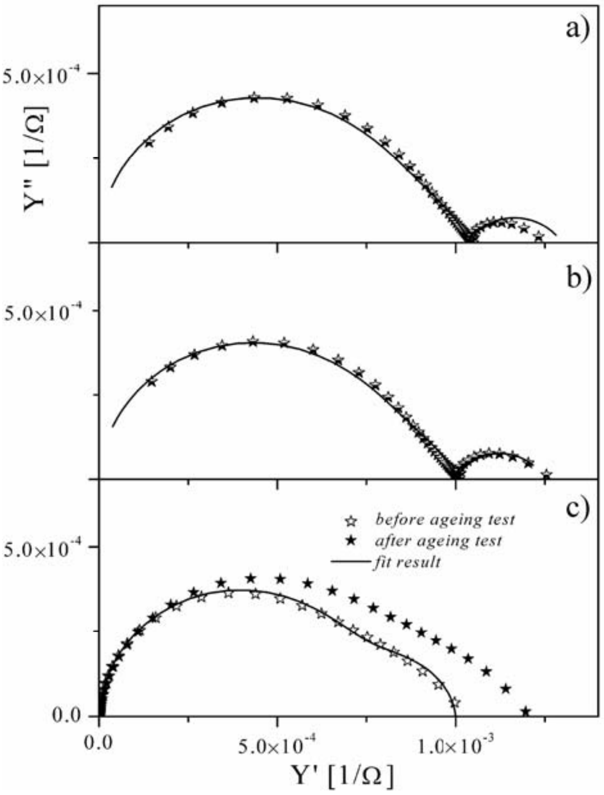

Fig. 4. The admittance spectra of $Na_3Zr_2Si_2PO_{12}$ prepared by solid state reaction:
a) 0% RH, b) ~90% RH, 420 h in wet air flow, c) ~90% RH, 768 h in wet air flow

Figure 4 illustrates the admittance spectrum of a sample prepared by solid state reaction measured at room temperature in a dry air flow, before and after the ageing test. The shape of the spectrum does not change and the absolute value of electrical conductivity is only slightly higher after long humidity treatment, probably as a consequence of additional conductive pathways due to water condensed at the Nasicon/Pt-electrode surface or along ceramics pores.

The influence of humidity on the electrical properties of Nasicon prepared by both methods is summarised in Figure 5. The presence of water vapour leads to an increase in electrical conductivity for times shorter than 200 h. This effect appeared for the more porous samples prepared by coprecipitation, and after 500 h their resistance increases again. The resistivity of Nasicon prepared by solid-state reaction remained unchanged even after 1000 h in a wet atmosphere. These observations may be attributed to differences in the microstructures, densities, and other properties of grain boundaries.

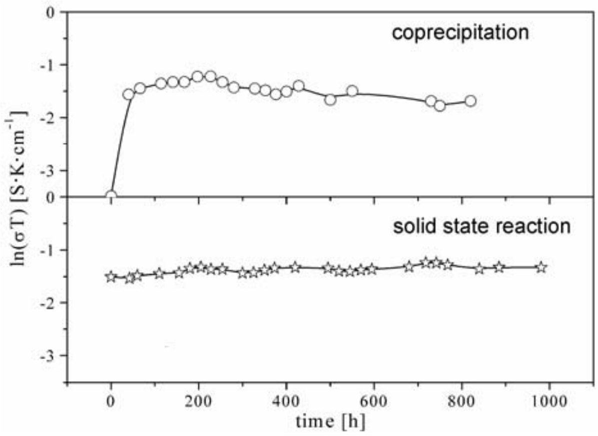

Fig. 5. The time dependence of the total conductivity of $Na_3Zr_2Si_2PO_{12}$, prepared by solid state reaction and coprecipitation in a humid atmosphere

4. Conclusions

The microstructure and phase composition of $Na_3Zr_2Si_2PO_{12}$ are strongly affected by the preparation method. Long-term measurements in a humid atmosphere indicate important differences in the stabilities of $Na_3Zr_2Si_2PO_{12}$ samples in contact with water vapour. In the case of Nasicon obtained by solid state reaction, the reversible modification of the admittance spectra after humidity treatment was noticed, contrary to the sample prepared by coprecipitation. This effect is strongly dependent on microstructure. No evidence of changes, such as the formation of a new phase, reduction of the glassy phase, or differences in the grain sizes, were detected after humidity treatment. Samples prepared by the solid-state reaction seem to be well-densified Nasicon and are more stable under a humid atmosphere. A behaviour typical of porous ceramics in contact with water vapour appeared in the case of Nasicon prepared by coprecipitation. The proposed equivalent circuits explain the effect of humidity on the Nasicon electrolyte. For samples obtained by solid state reaction, the wet atmosphere seems to modify rather the electrode/electrolyte surface, so an additional R-CPE$_{water}$ element should be connected to the low frequency part of the admittance spectra. On the contrary, for samples prepared by coprecipitation, when water may also condense inside, the modification can also be seen in the high frequency part of the spectra.

Acknowledgements

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