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Solid electrolytes for gas sensors and fuel cells applications

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Abstract

Solid electrolytes are wider and wider used in electrochemical devices. They are of peculiar importance to gas sensors, membranes, pumps and fuel cells. The study of the conductivity of the thick film fast ion conducting systems (NASICON and BICUVOX) was carried out using ac impedance spectroscopy. Investigations of changes of electrolytes conductivity with temperature (Arrhenius plots) were carried out. Conducted research was confirmed through practical applications of NASICON in thick film NO_2 sensor and BICUVOX solid electrolyte in fuel cell (SOFC). © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The inorganic ionic conductors are commonly used in the novel electrotechnical devices such as gas sensors, membranes, pumps and fuel cells. These devices are of peculiar importance to environment protection. Gas sensors, in method of analysis being a concentration cell with solid-state electrolyte, enable the detection and measurement of hazard gases (SO_x, NO_x),[1] whereas solid oxide fuel cells (SOFC) are the effective (60%) environmentally benign source of electric energy.[2]

The systematic name: solid state electrolytes contain the chemical compounds exhibiting practically only the ionic conductivity which magnitude at high temperature is comparable to the conductivity of liquid electrolytes, i.e. it is in the range of 1 S/cm. The high value of ionic conductivity of this group of compounds is an effect of both: ion charge carrier high concentration and mobility. The high concentration and mobility of the charge carriers of these solid state electrolytes results from the crystal structure of these compounds. Their structure consists of the two kinds of ions: ones constituting the immobile space crystal lattice and the others easy moving inside this lattice and establishing the 'molten' sublattice.

The mobile ions generally come to be the small cations, so these kinds of conductor are usually cation conductors. The most popular one is the Na-Super-Ionic-Conductor (NASICON). The name NASICON contains the whole group of Na+ ionic conductors with chemical formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leqslant x \leqslant 3$), yet it was estimated that the composition with $x = 2.2$ gives the highest electrical conductivity.[3] NASICON constitute the essential part of broad range of electrochemical sensors of such hazard gases as: NO, NO_2, CO_2.[4] However, the research into the increase of the ionic conductivity of NASICON, in order to optimise the sensors parameters (dimensions, time of answers, stability), is still carried out.

Along with ionic conductors with molten sublattice there are some conductors in which the electrical conductivity is controlled by the total number of defects (concentrated defect type). The crystal lattice of these compounds constitutes two sublattices of close-packed ions where one of the sublattices is highly defected. The defected sublattice is usually the anionic one and that is why they are well known conductors (ZrO_2 and CaF_2) of O^{2-} and F^- ions. The novelty in this group of conductors, due to high O^{2-} conductivity at relatively low temperature are so called BIMEVOX[5] and BICUVOX in particular, the conductors based on stabilised Bi_2O_3. The electrical conductivity σ of BICUVOX.10 ($Bi_2V_{0.9}Cu_{0.1}O_{5.35}$), at 250–450°C temperatures is about two orders of magnitude higher then the best oxide ion

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conductors known up to now (YSZ $(Bi_2O_3)_{0.8}(Er_2O_3)_{0.2}$). For example, at 400°C the conductivity of BICUVOX.10 reaches 10^{-2} $\Omega^{-1}cm^{-1}$.[6] The solid state electrolytes oxygen ion conducting power is fully utilised in fuel cells (SOFC) to generate electricity from chemical energy with low emissions.

For high ionic conductivity the super ionic conductors in the electrotechnical devices are utilised above all in the form of high dense ceramic sintering bodies. These devices usually require the electrolyte layer 1 mm and less in thickness to assure the short paths for ion migration. Such sintered bodies are not easy to be handled without damage by mass production methods.

In this paper, a new method of manufacturing solid electrolytes is presented. Instead of the previously used ceramic method, thick film technology was applied. The work was aimed at estimation if the ionic conductivity of NASICON and BICUVOX electrolytes in devices made by thick film technology (thickness of electrolyte films ~200 μm) is sufficient for NO_2 sensors and SOFC applications.

2. Experimental

2.1. Preparation of thick film electrolyte layers of NASICON and BICUVOX

Because NASICON and BICUVOX are not commercially available the first step in this study was the synthesis of them. The NASICON ($Na_{3.2}Zr_2Si_{2.2}P_{0.8}O_{12}$) sample was synthesised from mixture of chemically pure $NaHCO_3$, ZrO_2, SiO_2 and $NH_4PO_4{\cdot}3H_2O$ powder (produced by POCH) by annealing at 210°C for 20 h (for decomposition of $NaHCO_3$ and $NH_4PO_4{\cdot}3H_2O$). Powder X-ray diffraction (XRD) analysis of annealing mixture identified Na_2CO_3 and Na_2HPO_4 and the amorphic SiO_2 in the mixture. DRON X-ray diffractometer with Co radiation filtered with Fe filter was used in this study. To decompose Na_2CO_3 and Na_2HPO_4 the mixture was further annealing at 1140°C for 3 h. Decomposition was confirmed by XRD analysis. Only ZrO_2 and Na_2ZrSiO_7 was found in it. The convert ZrO_2 and Na_2ZrSiO_7 into NASICON the mixture was milling again and annealing at 1260°C for 3.5 h. XRD analysis confirmed the synthesis of NASICON.

The other solid electrolyte BICUVOX.10 ($Bi_2V_{0.9}Cu_{0.1}O_{5.35}$) was prepared by solid-state reaction from stoichiometric amounts of the following chemically pure oxides (from POCH): Bi_2O_3, V_2O_5 and CuO using the method described by Simner.[6] The mixture of starting powders was dispersed in methanol and ball-milled for 15 h. The resulting mix was dried, thoroughly ground to break up any large agglomerates, and then fired at 800°C for 5 h in air. To ensure complete reaction the material was ground and refired at 800°C for 5 h. By correlation with X-ray diffraction studies carried out by other workers[6] XRD analysis of mixture confirmed the synthesis of BICUVOX.

To obtain the pastes applicable for printing thick films the NASICON and BICUVOX powders were mixed with organic binder (vehicle). Then the pastes were screen-printed on alumina substrates and sintered.

2.2. Electrical conductivity of thick NASICON and BICUVOX films

The electrical conductivity of the electrolytes was analysed in function of temperature by complex impedance spectroscopy. An ac two-point impedance measurement technique using a computer-controlled Hewlett-Packard precision LCR meter Model HP 4284A, with 20 mV_{rms} test signal over the frequency range 20 Hz to 1 MHz with 10 point per frequency decade was employed. Pt porous thick film electrodes were applied.

2.3. Thick film NO_2 sensors and SOFCs

The thick film electrolyte layers along with printed Pt electrodes constituted electrochemical cells. The galvanic cells using NASICON were intended for NO_2 sensors. Their design and principle of operation are described elsewhere.[7] NO_2 concentrations were established by measuring of cell emf. The sensors response times were also at spotlights.

The BICUVOX electrolytes were used for SOFCs realisation. For this purpose the perforated alumina plate with printed on the BICUVOX layer were placed in a steel tube through which the CH_4 was flowing. The cell emf was measured.

3. Results and discussion

3.1. Electrical conductivity

The Nyquist plots for a thick film NASICON sample at 23, 50 and 100°C are shown in Fig. 1. At higher frequencies the well resolved semicircular arc appears. This arc is attributed to the bulk properties of electrolyte and diminishes with increase of temperature. At lower frequencies the start of the other semisecular is traceable and can be ascribed to the electrode polarisation effect. On the basis of Nyquist plots the resistive component of the total impedance was established.[8] This resistive component was used to derive the values of conductivity in the function of temperature for thick film NASICON sample. A typical Arrhenius plot for this thick film electrolyte is illustrated in Fig. 2. As expected, the conductivity increases with increased temperature but generally it is much lower in comparison to ceramic bodies

conductivity. The conductivity of NASICON thick film at 300°C corresponds to 0.001 Ω^{-1} cm^{-1} whereas conductivity of NASICON ceremal 0.159 Ω^{-1} cm^{-1}.[3] The discrepancy is the result of differences in sample densities (the pores retard the ion transition in material).

The typical Nyquist plot for a thick film BICUVOX sample at 300°C is shown in Fig. 3. The Arrhenius plot for BICUVOX (Fig. 4) was traced in the same manner. In the temperature range 150–400°C the conductivity of BICUVOX thick film is much lower than the conductivity of BICUVOX sintered pills. However, at higher temperatures (>400°C) the BICUVOX ceramic body has no advantages over thick film and the conductivity is approximately 0.01 Ω^{-1} cm^{-1} at 400°C and 0.1 Ω^{-1} cm^{-1} at 600°C.

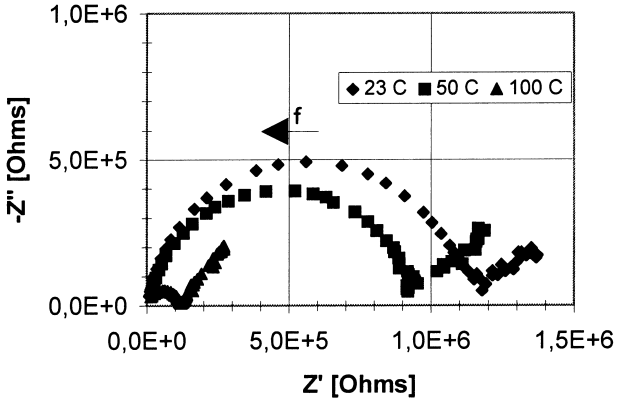

Fig. 1. Nyquist plots for a thick film NASICON sample at 23, 50 and 100°C.

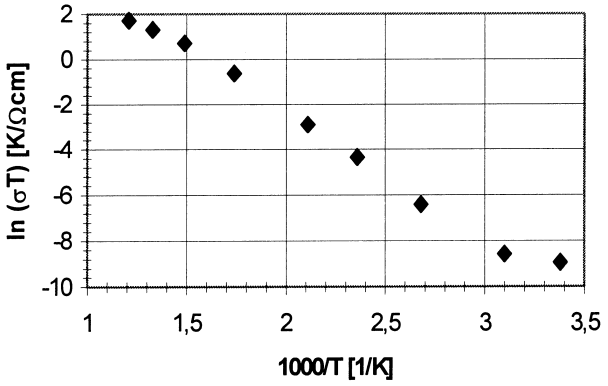

Fig. 2. Arrhenius plot for a thick film NASICON sample.

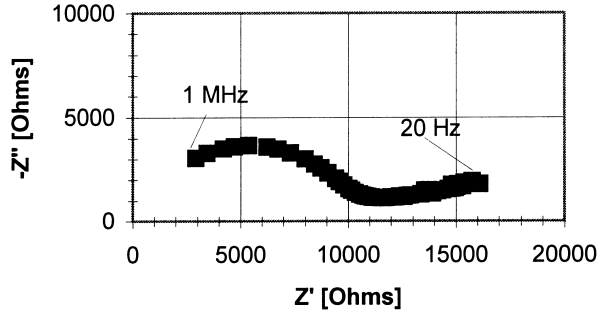

Fig. 3. Typical Nyquist plot for a thick film BICUVOX.10 sample recorded at 300°C.

3.2. Parameters of thick film NO_2 sensors and SOFCs

Fig. 5 illustrates the performance of the sensor base on the thick film NASICON. The cell emf response to the logarithm of NO_2 in the wide range of NO_2 concentrations (10–1000 ppm) was linear and corresponds to the Nernst equation.[9] The response time of sensor was determined for the NO_2 partial pressures varied between atmospheric and 17 ppm (Fig. 5). The response time depends sharply on solid electrolyte thickness.[10] Application of thick film electrolyte (film thickness 0.2 mm) instead of the ceramic one[4] allows to make the response time significantly shorter due to the electrolyte thickness decrease.

The emf quantity delivered from cells based on BICUVOX electrolyte (screen printing executions) — 0.3 V at

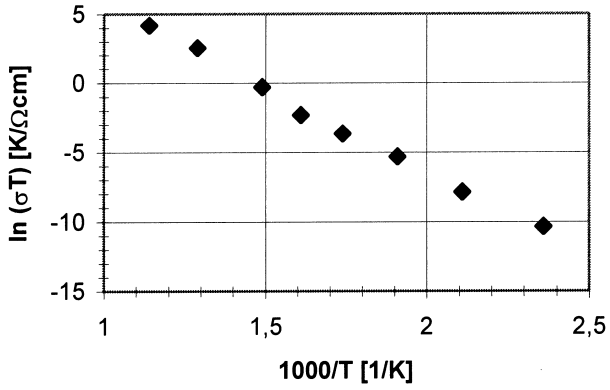

Fig. 4. Arrhenius plot for a thick film BICUVOX.10 sample.

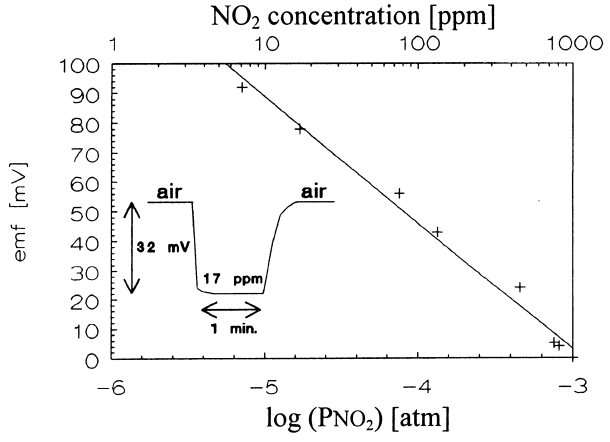

Fig. 5. Performance of sensor based on thick film NASICON electrolyte at 200°C: emf vs. NO_2 concentration and response transient to 17 NO_2 ppm.

400°C — arouse the trust to come, in the pursuit of increase of energy efficiency, to commercial resolutions.

4. Conclusions

The following conclusions can be drown from our experiments:

- Thick film technology allows for the manufacturing of solid electrolytes such as NASICON or BICUVOX.
- The conductivity of thick film electrolytes in general is lower than the conductivity of electrolytes ceramic body. Thick film electrolytes are suitable for gas sensors and fuel cells applications.
- Application of thick film (layer thickness 0.2 mm) instead of the ceramic technology significantly decreases the response time of NO_2 sensor, due to the decrease in the electrolyte thickness.

Acknowledgements

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