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New ceramic superionic materials for IT-SOFC applications

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The syntheses of new ceramic superionic materials based on Bi_2O_3 (BIMEVOX and δ-Bi_2O_3), their elemental analyses, thermodynamical stability, and electrical properties are presented. The materials show high ionic conductivities (ca. 0.1 S/cm) at a relatively low temperature (600 °C), which makes them applicable as electrolytes in IT-SOFC fuel cells. Ionic conductivity measurements of these materials were performed with the DC (four probe configuration) and IS (impedance spectroscopy) methods, whereas structural research was performed using X-ray spectroscopy. Investigations of the thermodynamic stability of the elaborated materials in oxygen-free atmosphere were also performed. Based on the results of the investigations, the most suitable superionic conductors for fuel cell were selected.

Key words: *impedance; ionic conductivity; fuel cells; membranes*

1. Introduction

In recent years, continuous development and an increase in the amount of energy produced from alternative sources is observed. Among others, special attention is paid to intermediate temperature solid oxide fuel cells (IT-SOFC) due to their high efficiency of conversion of chemical energy stored in a fuel into electricity (ca. 60%) [1], quiet and pollution-free operation, the possibility of supplying energy from different kinds of fuels, high resistance to unfavourable atmospheric phenomena and natural disasters, making them very attractive in terms of their application. High working temperature enables easy recovery of waste heat in combined heat and power systems.

The element of the cell having the greatest impact on the fuel cell efficiency, production cost, and stable operation is the electrolyte. It should be characterised by high ionic conductivity (at least 0.1 S/cm) at relatively low temperature, impermeability to

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gases, high mechanical strength, good resistance to thermal shock, and thermodynamic stability (especially in a reducing atmosphere).

Until now, stabilized ZrO_2 was the most often used electrolyte in SOFC. It has satisfactory mechanical and electrical parameters, but a very high working temperature (ca. 1000 °C), limiting its commercial applications. The present authors investigated the possibility of applying Bi_2O_3-based solid solutions and the BIMEVOX family of electrolytes, being good ionic conductors (O^{2-}) at relatively low temperatures (ca. 600 °C). A high-temperature and highly ionically conductive (O^{2-}) modification of δ bismuth oxide could be stabilized at lower temperatures by adding rare earth oxides (L_2O_3, where L = Gd, Er, Dy, Y, Ho, Nd, Sm) [2]. No sudden decrease in the ionic conductivity of doped δ-Bi_2O_3 is observed, which takes place during the phase transitions $\delta \to \gamma$ and $\delta \to \alpha$ when a sample of pure Bi_2O_3 is cooled. The doped samples, however, are reactive in oxygen-free atmosphere or at a very low oxygen concentration in atmosphere; the reduction of oxide to metallic Bi takes place [3–5]:

$$(Bi_2O_3)_{1-x}(Me_2O_3)_x \to (Bi_2O_3)_{1-x-\alpha}(Me_2O_3)_x + 2\alpha Bi + 3\alpha/2O_2$$

Thus the use of Bi_2O_3-based oxide-doped electrolytes requires that a “safe” oxide concentration range be known precisely.

The BIMEVOX (BI – bismuth, ME – additive metal, V – vanadium, OX – oxygen) family of electrolytes belongs to the newest generation of electrolytes based on Bi_2O_3. The basic compound of the BIMEVOX family is γ-$Bi_2VO_{5,5}$. A high-temperature, highly ionically conductive modification of γ-$Bi_2VO_{5,5}$ is stabilized to lower temperatures by adding an oxide of another metal (e.g. Cu, Ni, Zn, Fe, Co, Mg) [6–10]. Moreover, these electrolytes have the ability to dynamically self-transform into electrode materials under polarization [11], so a BIMEVOX membrane could be used without other electrode materials.

In order to select the most appropriate electrolyte for IT-SOFC applications:

- 18 electrolyte bulks were synthesized and samples in the form of beams, tablets, and screen-printed layers were prepared;
- X-ray investigations of the composition and thermodynamic stability of the synthesized bulks were performed;
- the ionic conductivities of the electrolyte samples were measured using the DC and IS methods.

2. Experiments

Sample preparation. Electrolyte samples were prepared in the form of beams, pellets, and screen-printed layers (Fig. 1). Pellets and beams were pressed at 500 kG/cm^2 and then sintered. Thin layers were applied on an alundum base with a plotted Pt heater and Pt electrode (Fig. 2). This method is suitable for making relatively thin layers of electrolyte, ca. 0.1 mm thick. The composition of the electrolyte bulks and the preparation method are presented in Table 1.

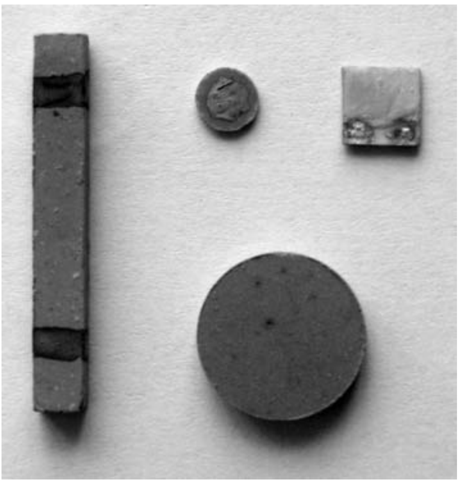


Fig. 1. Electrolyte samples: beam, tablet, and printed electrolyte layer

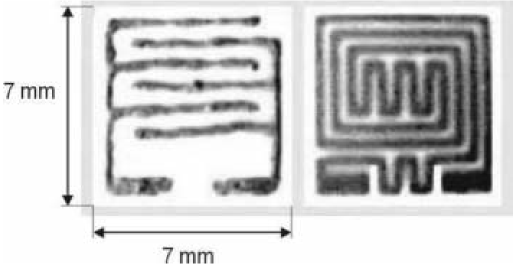


Fig. 2. Comb electrode and a heater, applied on an alundum base by using the screen-printing method (averse and reverse)

Table 1. Compound formulas and synthesis conditions of the investigated masses

No.	Compound formula	Name	Synthesis condition
1	$Bi_2V_{0.75}Cr_{0.25}O_{5.25}$	α-BIMEVOX	sintering 800 °C, 12 h
2	$Bi_2V_{0.9}Sb_{0.1}O_{5.4}$	γ-BIMEVOX	
3	$Bi_2V_{0.9}Co_{0.1}O_{5.4}$	BICOVOX	
4	$Bi_2V_{0.875}Ti_{0.125}O_{5.4375}$	BIMEVOX	
5	$Bi_2V_{0.86}Zn_{0.1}O_{5.25}$	BIMEVOX	
6	$Bi_2V_{0.73}Zn_{0.27}O_{5.095}$	BIZNVOX.27	
7	$Bi_2V_{0.9}Cu_{0.1}O_{5.35}$	BICUVOX.10	
8	$Bi_4V_2O_{11}$	BIVOX	sintering 830 °C, 12 h
9	$Bi_4V_{1.9}Co_{0.1}O_{10.85}$	BICOVOX	
10	$Bi_4V_{1.8}Co_{0.2}O_{10.7}$	BICOVOX	
11	$Bi_2Co_{0.1}V_{0.9}O_{5.35}$	BICOVOX	calcination 610 °C, sintering 800 °C, 12 h
12	$(Bi_{0.95}Zr_{0.05}O_{1.525})_{0.8}(YO_{1.5})_{0.2}$	stabilized δ-Bi_2O_3	830 °C, 12 h
13	$Bi_4V_{1.95}Fe_{0.05}O_{10.95}$	BIMEVOX	sintering 850 °C, 24 h, slowly cooled to room temperature
14	$Bi_4V_{1.9}Fe_{0.1}O_{10.9}$	BIMEVOX	
15	$Bi_4V_{1.8}Fe_{0.2}O_{10.8}$	BIMEVOX	
16	$Bi_4V_{1.5}Fe_{0.5}O_{10.5}$	BIMEVOX	
17	$Bi_4V_{1.75}Fe_{0.25}O_{10.75}$	BIMEVOX	
18	$Bi_4V_{1.7}Fe_{0.3}O_{10.7}$	BIMEVOX	

X-ray stability investigations. X-ray measurements of the phase composition of the electrolyte bulks and investigations of the thermodynamic stability in reducing atmosphere were performed with an X-ray diffractometer DRON-2 with Co radiation filtered with Fe. XRD was measured in the 2Θ range from 10 to 95°.

Four-probe DC measurements of ionic conductivity. A scheme of the four-probe configuration for ionic conductivity measurements using Wagner's method is presented in Fig. 3. The measurements were made with the samples prepared from the synthesized material in the form of beams with platinum electrodes. Ionic conductivities were measured during the heating and cooling of the samples (the current – 0.1 and 1 mA).

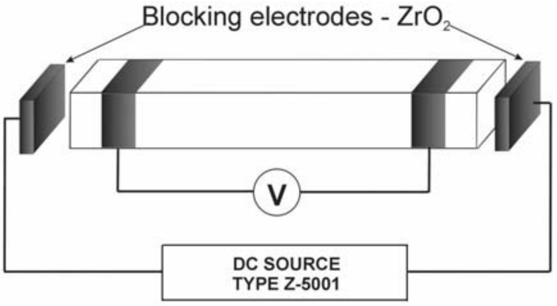


Fig. 3. Scheme of the system used for measurements of ionic conductivity, DC four-probe Wagner method

IS measurements of ionic conductivity. Impedance measurements of ionic conductivity [12] were performed for electrolyte layers applied on an alundum base using the screen-printing method. The real and imaginary part of the impedance (impedance spectra) were measured at frequencies from 20 Hz to 1 MHz and in the temperature range from 20 to 700 °C. The amplitude of the sinusoidal sampling signal was 20 mV. An RLC meter (HP 4284A) was used. The samples were heated with a platinum heater, placed on the reverse side of the alundum base. Temperature was determined based on the measured linear dependence of the heater resistance on temperature. A schematic diagram of the test stand is presented in Fig. 4.

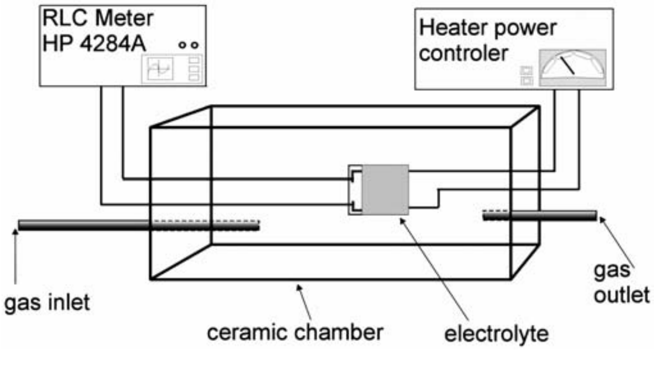


Fig. 4. Scheme of the test stand used for measurement of ionic conductivity, IS impedance spectroscopy method

3. Results and dicussion

3.1. X-ray investigations of the composition and thermodynamic stability of selected electrolytes

X-ray spectra of selected electrolytes are presented in Figs. 5–8.

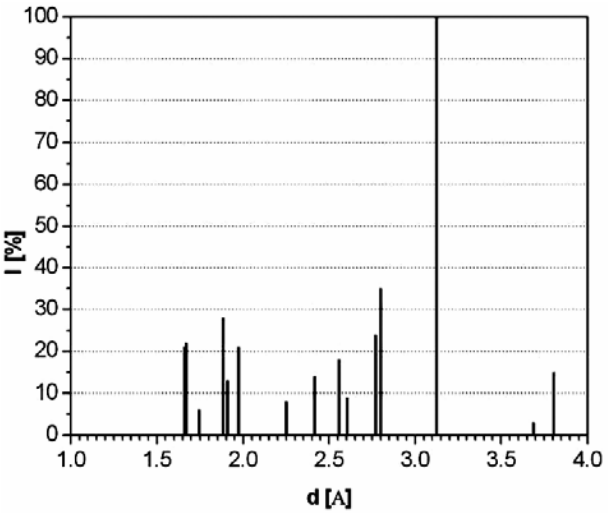


Fig. 5. X-ray spectra of the sample made of mass No. 8, identified as $Bi_4V_2O_{11}$

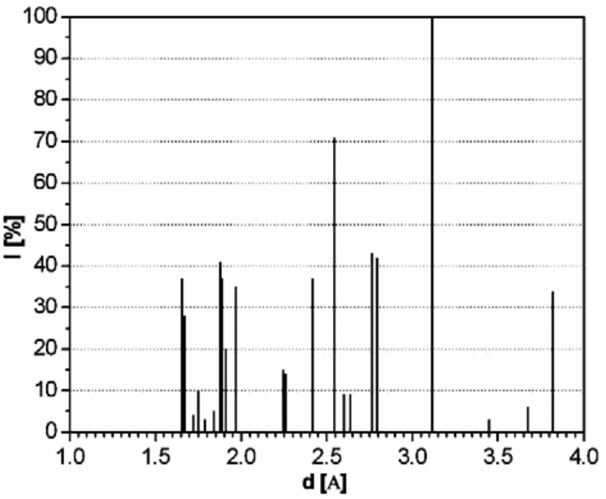


Fig. 6. X-ray spectra of the sample made of mass No. 8
after curing in a reducing atmosphere, identified as $Bi_4V_2O_{11}$

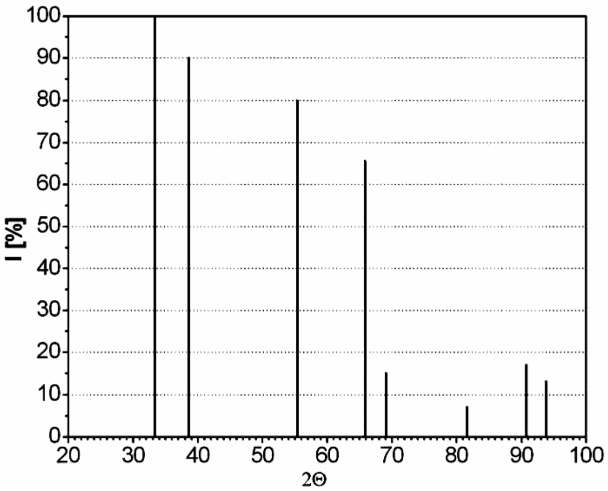


Fig. 7. X-ray spectra of the sample made of mass No. 12, identified as $Bi_{1.5}Y_{0.5}O_3$ or δ-Bi_2O_3

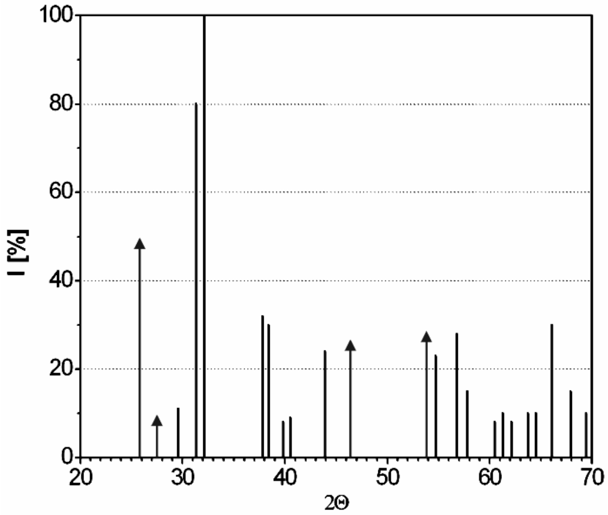


Fig. 8. X-ray spectra of the sample made of mass No. 12 after curing in a reducing atmosphere, identified as α-Bi_2O_3 and Bi (▲)

Basing on the analysis of the spectra, it was established that:

- Electrolytes of the BIVOX and BIMEVOX families are generally thermodynamically stable in the presence of reducing gases (oxygen-free atmosphere), although in some cases the samples of BIMEVOX electrolytes decomposed (Fig. 9).
- The electrolyte based on stabilized bismuth oxide δ-Bi_2O_3 (mass No. 12) is unstable thermodynamically and decomposes to α-Bi_2O_3 and finally to pure Bi (Fig. 10).

Fig. 9. Decomposed tablet made of mass No. 5 after a hazard in a reducing atmosphere

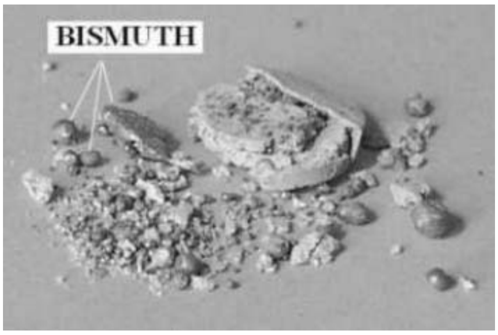


Fig. 10. Decomposed tablet made of mass No. 12 after a hazard in a reducing atmosphere

3.2. DC measurements of ionic conductivity

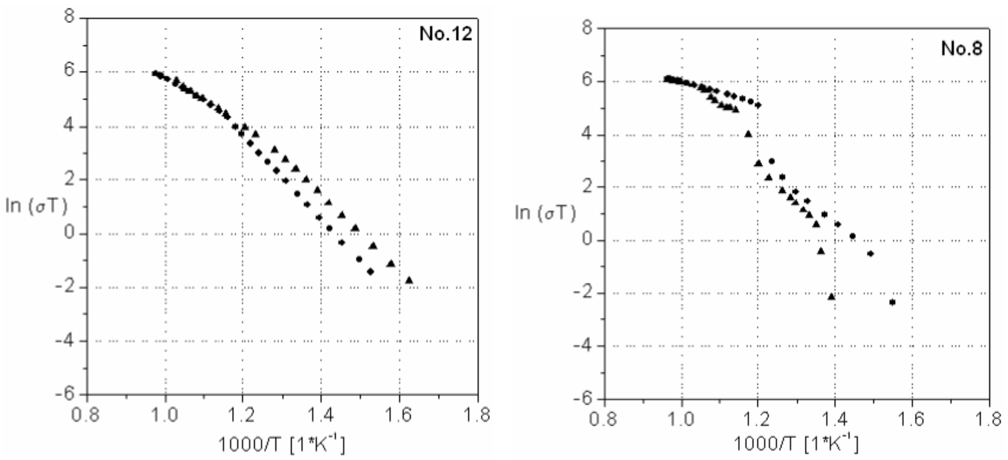
The temperature dependences of the ionic conductivities of selected electrolytes (mass No. 8, 12 and ZrO_2) are presented in Fig. 11. Measurements were performed during the heating and cooling of the samples. The ionic conductivities for all electrolytes investigated are presented in Table 2.

Table 2. Ionic conductivities of the electrolyte bulks

No.	σ [1/(Ω·cm)]	
	400 °C	660 °C
1	–	0.006
2	0.0397	0.084
3	0.0062	0.079
4	0.0010	0.095
5	0.0008	0.054
7	0.0003	0.047
8	–	0.536
9	0.0020	0.322
10	0.0016	0.118
12	0.0009	0.694
13	–	0.510
14	0.0011	0.328
15	0.0010	0.255
16	0.0001	0.016
17	0.0013	0.088
18	0.0007	0.065
ZrO_2	–	0.005

Basing on the results obtained it was affirmed that:

- In the temperature range from 200 °C to 700 °C, ionic conductivities of electrolytes based on Bi_2O_3 are ca. 3 orders of magnitude higher than the conductivity of the traditional electrolyte ZrO_2.
- In the temperature range of 400–700 °C (the range of operation of fuel cells), the highest ionic conductivity measured was for the electrolyte bulks No. 8, 9, 12, 13.
- The most linear Arrhenius characteristic, without any histeresis, was exhibited by the mass No. 12. This confirms that no phase transformations take place during its heating in air.
- The lowest value of ionic conductivity was measured for mass No. 1, in which X-ray composition analysis showed the presence of the poorly ionically conductive phase α-Bi_2O_3.



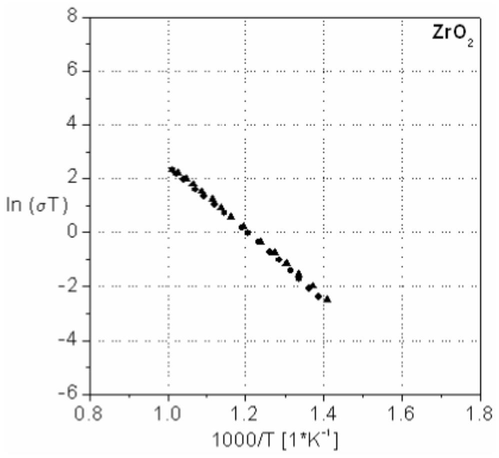


Fig. 11. Temperature dependences of ionic conductivities for selected electrolytes (No. 8 and No. 12), current range 1 mA, for cooling (●) and heating (▲). In the last figure, the Arrhenius plot for stabilized ZrO_2 is presented

3.3. IS measurements of ionic conductivity

Using the DC method it is impossible to determine the ionic conductivity of electrolyte layers prepared with the screen-printing method, it was thus decided to apply the AC method for ionic conductivity measurements. Examples of impedance spectra measured in function of temperature (350–600 °C) for the mass No. 5 are presented in Fig. 12.

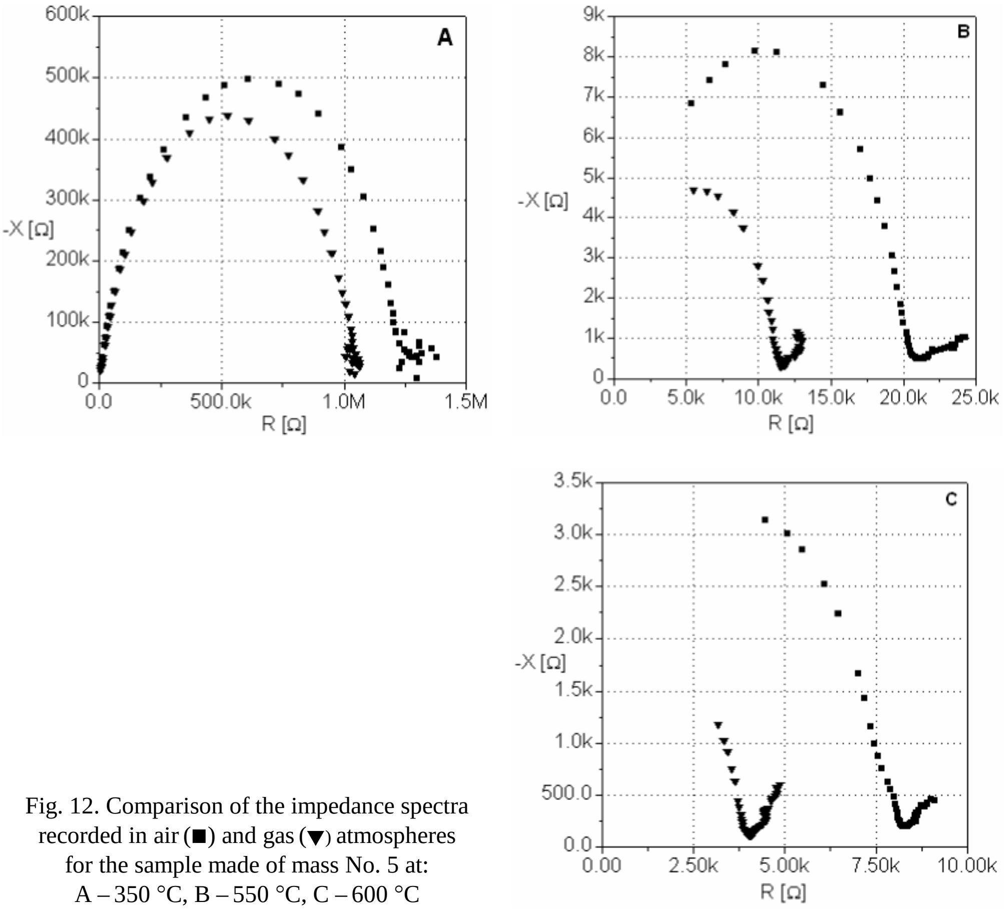


Fig. 12. Comparison of the impedance spectra recorded in air (■) and gas (▼) atmospheres for the sample made of mass No. 5 at: A – 350 °C, B – 550 °C, C – 600 °C

In order to determine the influence of a reducing atmosphere on the ionic conductivity of the electrolytes, impedance spectra measurements were performed in both air and gas (propane butane atmospheres. The results of these measurements are presented in Fig. 13 and Table 3.

Basing on impedance spectra analysis, it was confirmed that the ionic conductivity of all electrolyte bulks measured in air is higher than that measured in a reducing atmosphere. It was also proved (similar to the DC method) that the highest ionic conductivity were exhibited by samples No. 8 and 12. The reason for the differences in the ionic conductivities measured by the DC and IS methods is probably the different densities of the samples, prepared using pressing and screen-printing methods. Screen-printed layers have an ionic conductivity two order of magnitude lower than traditionally pressed samples.

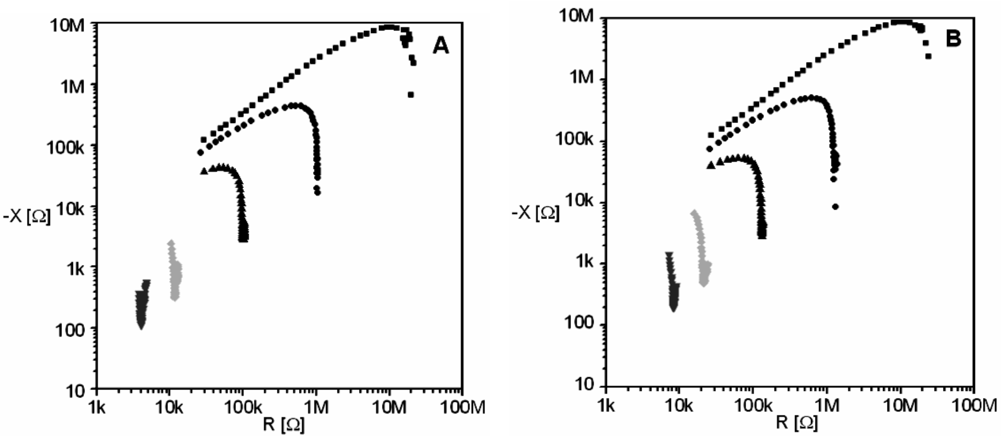


Fig. 13. Impedance spectra of mass No. 5 measured in air (A) and in a reducing atmosphere (B) at: ■ – 250 °C, ● – 350 °C, ▲ – 450 °C, ◆ – 550 °C, ▼ – 600 °C

Table 3. Ionic conductivities of the electrolytes (flow of air and reducing gas)

No.	σ [1/(Ω·cm)]			
	In air		In gas	
	450 °C	600 °C	450 °C	600 °C
5	2.35×10^{-6}	5.9×10^{-5}	1.21×10^{-6}	2.87×10^{-5}
6	1.44×10^{-15}	3.48×10^{-14}	1.24E-15	3.29E-14
7	2.88×10^{-5}	2.19×10^{-3}	5.00×10^{-7}	1.21×10^{-3}
8	1.17×10^{-5}	2.41×10^{-3}	2.74×10^{-5}	2.92×10^{-3}
10	9.25×10^{-5}	–	7.66×10^{-5}	1.59×10^{-3}
12	3.26×10^{-4}	–	3.26×10^{-4}	9.65×10^{-3}
17	1.59×10^{-4}	1.90×10^{-3}	2.22×10^{-4}	2.85×10^{-3}

4. Conclusions

It is possible to operate SOFC fuel cells based on BIMEVOX or δ-Bi_2O_3 electrolyte, with a relatively low working temperature (ca. 600 °C). In the range of 200–700 °C, the ionic conductivity of electrolytes based on Bi_2O_3 is quite higher (ca. 3 orders) than for the conventional electrolyte ZrO_2.

Compounds from the BIVOX and BIMEVOX families (bulk No. 8) have suitable properties for fuel cell applications, since their ionic conductivity is high (ca. 0.,5 S/cm) at a relatively low temperature (650 °C) and they are thermodynamically stable in reducing atmospheres.

The material based on stabilized δ-Bi_2O_3 (bulk No. 12) is not thermodynamically stable in a reducing atmosphere, thus its application as an electrolyte in fuel cells is impossible.

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References

[1] BERG N., WILLE A., ALSTOM T&D Review, 1999.
[2] TAKAHASHI T., IWARA H., ESAKA, T., J. Electrochem. Soc., 124 (1977), 1563.
[3] YAREMCHENKO A.A., KHARTON V.V., NAUMOVICH E.N., TONOYAN A.A., Mat. Res. Bull., 35 (2000), 515.
[4] VERKERK M. J., BURGGRAAF, A.J., J. Electrochem. Soc., 128 (1981), 75.
[5] TAKAHASHI T., ESAKA T., IWAHARA, H., J. Appl. Electrochem., 7 (1977), 299.
[6] SHUK P., WIEMHOFER H.-D., GUTH U., GOPEL W., GREENBLATT M., Solid State Ionics, 89 (1996), 179.
[7] PAŚCIAK G., PROCIÓW K., MIELCAREK W., GÓRNICKA B., MAZUREK B., J. Eur. Cer. Soc., 21 (2001), 1867.
[8] LAZURE S., VERNOCHET CH., VANNIER R. N., NOWOGROCKI G., MAIRESSE G., Solid State Ionics, 90 (1996), 117.
[9] ABRAHAM F., BOIVING J.C., MAIRESSE G., NOWOGROCKI G., Solid State Ionics, 40–41 (1990), 934.
[10] KROK F., ABRAHAMS I., MALYS M., BOGUSZ W., DYGAS J.R., NELSTROP J.A.G., BUSH A.J., Solid State Ionics, 136–137 (2000), 119.
[11] PIROVANO C., VANNIER R.N., CAPOEN E., NOWOGROCKI G., BOIVIN J.C., MAIRESSE G., ANNE M., DOORYHEE E., STROBEL P., Solid State Ionics, 159 (2003), 167.
[12] BOGUSZ W., KROK F., *Solid Electrolytes, Their Electrical Properties and Methods of Their Measurement* (in Polish), WNT, Warszawa, 1995.

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