

Oxide-ion conductors for fuel cells

F. KROK^{1*}, I. ABRAHAMS^{2**}, W. WROBEL¹, A. KOZANECKA-SZMIGIEL¹, J. R. DYGAŚ¹

¹Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662, Warsaw, Poland.

²Centre for Materials Research, Department of Chemistry,
Queen Mary, University of London, Mile End Road, London E1 4NS, United Kingdom

The principal materials used in the construction of solid oxide fuel cells (SOFCs) are discussed. Some of the problems encountered with high temperature fuel cells (HT-SOFCs) might be overcome by lowering the operating temperature to 500–700 °C, through the development of suitable materials for intermediate temperature fuel cells IT-SOFCs. Candidate electrolyte materials are discussed, including cerium gallium oxide, lanthanum strontium gallium magnesium oxide, and electrolytes based on doped bismuth oxide. While high ionic conductivities can readily be achieved in these materials at intermediate temperatures, stability in reducing atmosphere is still a problem. This might be overcome by careful chemical design of electrolytes containing stabilising dopants. Two zirconia-doped bismuthate systems are discussed in this respect. In both cases, the obtained materials exhibit different structures – one is $\text{Bi}_3\text{Nb}_{1-x}\text{Zr}_x\text{O}_{7-x/2}$ of the $\delta\text{-Bi}_2\text{O}_3$ type, and the other, $\text{Bi}_4\text{V}_{2-2x}\text{Zr}_x\text{O}_{11-x}$, has a layered structure of the Aurivillius type.

Key words: *fuel cell; solid electrolyte; bismuth oxide*

1. Introduction

Fuel cells are the most efficient power-generating devices; they convert the chemical energy of fuel directly to electrical energy, without the need for intermediate conversion to thermal energy. Therefore, the efficiency of a fuel cell is not subject to the Carnot limitation. The principal components of a fuel cell are an ion conducting electrolyte and two electrodes: an anode and a cathode. For practical applications, single cells are typically connected in series. The connectors between cells (called interconnectors or bipolar separators) are therefore also important parts of the device. Electrolytes allow the fast conduction of ions between the two electrodes but the conductivity of electrons should be negligible. Electronic conduction occurs in the external circuit and can be used for

*Corresponding author, e-mail: fkrok@mech.pw.edu.pl

**Corresponding author, e-mail: I.Abrahams@qmul.ac.uk

external load applications. The critical component of any fuel cell is the electrolyte, the choice of which dictates the choice of the other components.

There are various types of fuel cells, depending on the type of electrolyte used. The most intensively studied fuel cells are polymer electrolyte-membrane fuel cells (PEMFCs), also called proton exchange-membrane fuel cells as they are based on proton conducting electrolytes and solid oxide fuel cells (SOFCs) based on solid oxide electrolytes. There are several of comprehensive reviews on recent developments in fuel cells (see eg. [1–3]).

Pure hydrogen represents the ideal fuel for fuel cells. There are many problems, however, associated with the production, storage, and distribution of pure hydrogen [1], and if the widespread use of fuel cells is to be achieved then other fuels need to be considered at least in the short term. Suitable alternatives include methanol and hydrocarbons such as methane. For these fuels, optimal cell operating conditions generally occur at high temperatures, i.e. within the normal operating range of SOFCs. This is one of the main reasons for the growing interest in SOFCs as alternatives to PEMFCs, which have lower operating temperatures.

Well-established high temperature (ca. 1000 °C) SOFC technology (HT-SOFCs) is based on the oxide-conducting yttria-stabilised zirconia (YSZ) electrolyte. In recent years, however, the need for smaller low-power SOFCs (up to a few tens of Watts), which could be operated at intermediate temperatures (ca. 500–700 °C, IT-SOFCs), has been expressed. The operation of SOFCs at intermediate temperatures would for example enable their application in electric vehicles. In this paper, the principal materials relevant for IT-SOFCs are discussed. In this respect, oxide ion conductors studied in our own work are examined in terms of their potential application in IT-SOFCs.

2. General requirements for fuel cells

Target power densities of fuel cells are typically of the order of $1 \text{ kW}\cdot\text{kg}^{-1}$. To meet this goal, the area specific resistivity (ASR) of the combined system (electrolyte plus both electrodes) should not exceed $0.5 \text{ ohm}\cdot\text{cm}^2$ [2]. Assuming approximately equal contributions from each component to the ASR, the requirement for the electrolyte alone is about $0.15 \text{ ohm}\cdot\text{cm}^2$.

The general requirements for the principal components of fuel cells are as follows:

Electrolyte: high ion conductivity with negligible electronic conductivity; dense non-porous microstructure (to avoid the permeation of neutral gas fuel molecules).

Electrodes: high mixed ionic-electronic conductivity (ionic – to ensure good electrical contact with the electrolyte, electronic – to ensure good electrical contact with the interconnector); porous microstructure (to allow gas transport to and from the electrolyte).

Interconnector: high electronic conductivity with negligible ionic conductivity; dense non-porous microstructure (to prevent gas mixing).

Moreover, a high stability (both temperature stability and phase stability in contact with reducing and/or oxidising atmospheres and other cell components) of each component and similar thermal expansion coefficients for components to avoid cracking during operation are required.

3. SOFCs based on YSZ

The most commonly used electrolyte material in HT-SOFCs is YSZ. Suitable electrodes for this cell are nickel/YSZ cermet for the anode and doped lanthanum manganite perovskite for the cathode. The component materials are discussed below.

Electrolyte: YSZ is a solid solution formed between ZrO_2 and Y_2O_3 with a general formula of $\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}$, with the highest conductivity around $x = 0.1$ [4]. The structure is based on that of fluorite (CaF_2), with a cubic close-packed Zr/Y and O located at the tetrahedral sites, resulting in eight-coordination for the cations. The introduction of subvalent Y^{3+} for Zr^{4+} is compensated for by vacancies created on the oxide ion sublattice. High vacancy concentration combined with high mobility results in a very high oxide-ion conductivity in this material at temperatures above 800 °C.

Anode: To provide the desired properties of the anode, usually a composite (cermet) of the electrolyte material (in this case YSZ) and powdered metal is used [5]. Nickel metal is commonly used due to its low cost. The role of the YSZ electrolyte in the cermet anode is to support the nickel-metal particles and prevent their agglomeration and coarsening. The content of nickel in the cermet anode has to be higher than the percolation threshold of this system to assure the high conductivity of the material. The percolation threshold for conductivity in this system is about 30% vol. of nickel content [5].

Cathode: Many oxides have been examined as potential cathodes in SOFCs. The crucial parameters which have to be taken into account in the assessment of suitability are electrical conductivity, phase stability, and the coefficient of thermal expansion. On this basis, strontium-doped lanthanum manganite, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM), was found to be particularly suitable [6]. Partial substitution of La^{3+} by Sr^{2+} in LaMnO_3 is charge compensated by the oxidation of Mn^{3+} to Mn^{4+} and results in an increase in electronic conductivity.

If the cell design is to be based on self-supporting YSZ, the minimum electrolyte thickness needs to be about 150 μm [2]. Thinner membranes can be produced, but only as thin layers supported on substrates. For self supporting YSZ, a target ASR of 0.15 $\text{ohm}\cdot\text{cm}^2$ is obtained only at temperatures higher than about 950 °C, and there are many problems associated with cell construction at these temperatures. For example, under these operating conditions there is a limited choice for the interconnector material. Co-doped LaCrO_3 is commonly used [7]. There is concern, however, over the use of chromium poisoning the cathode performance.

Lowering the fuel cell operating temperature through the design of novel SOFCs operating at intermediate temperatures (IT-SOFC) could solve many problems associated with HT-SOFCs.

In order to keep YSZ as the electrolyte material and to maintain the assumed target ASR of $0.15 \text{ ohm}\cdot\text{cm}^2$ at lower temperatures, much thinner electrolyte membranes are required. The minimum useful thickness for the YSZ membrane is about $15 \mu\text{m}$, since thinner membranes exhibit significant levels of gas permeation [1]. For the YSZ membrane of $15 \mu\text{m}$, the ASR of $0.15 \text{ ohm}\cdot\text{cm}^2$ can be obtained at 700°C [2]. For IT-SOFCs based on YSZ, the same electrodes as for HT-SOFCs can be used. In this case, however, there is no need to use a Cr-containing perovskite material for the interconnector, since at 700°C simple stainless steel will suffice.

4. New materials for IT-SOFCs

There are other materials that exhibit electrical conductivities higher than that of YSZ at temperatures lower than 700°C , and these materials can be considered as potential electrolytes in IT-SOFCs. The Arrhenius plots of conductivities of some candidate materials are presented in Figure 1. The most intensively studied materials in terms of the above-mentioned application are gadolinium-doped ceria (CGO) [8] and lanthanum-strontium-gallium-magnesium perovskites (LSGM) [9]. The best oxide ion conductors at low temperatures are based on Bi_2O_3 [10], and these also have to be considered in this respect.

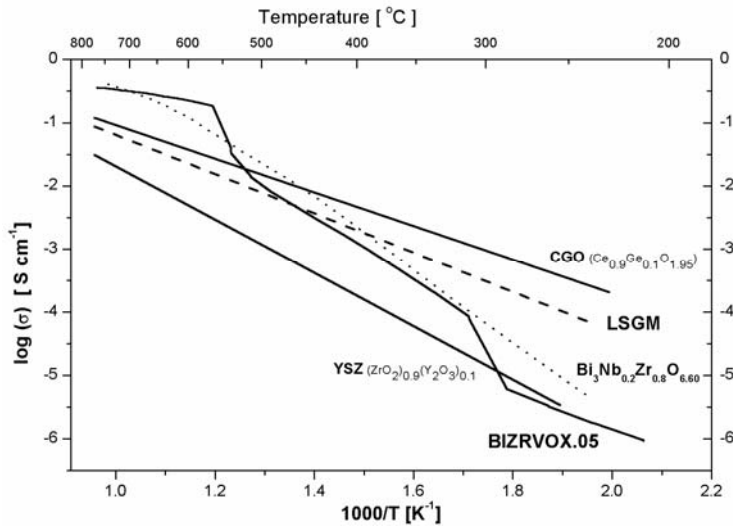


Fig. 1. Arrhenius plots of conductivities of selected oxide-ion conducting electrolytes

Like YSZ, ceria (CeO_2) exhibits a fluorite-type structure which is well suited for high oxide-ion conductivity [11]. Doped CeO_2 can exhibit even higher conductivity than stabilised zirconia [8]. This material shows a significant electronic conductivity at high temperatures, however, which results in cell short-circuiting. Electronic con-

ductivity arises from the reduction of Ce^{4+} to Ce^{3+} in the reducing atmosphere of the cell. At sufficiently low temperatures (about 500 °C), the electronic contribution can be neglected for some compositions, e.g. $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ [12].

Another potential electrolyte for IT-SOFCs is doped lanthanum gallate LaGaO_3 [9]. The introduction of the divalent ions Sr^{2+} and Mg^{2+} into trivalent La^{3+} and Ga^{3+} sites, respectively, results in the creation of oxide ion vacancies and consequently in an increase of ionic conductivity in the obtained system (LSGM). The best electrical properties have been found for the composition $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ [9]. It is very important that this compound is a purely ionic conductor over a very wide oxygen partial pressure range (large ionic domain). The main problem with LSGM is the difficulty in obtaining a single-phase material.

For IT-SOFCs based on both CGO and LSGM electrolytes, alternative electrodes are required.

5. Bi_2O_3 -based electrolytes

There is a natural temptation to use the materials based on the best oxide ion conductor, $\delta\text{-Bi}_2\text{O}_3$ [10], as electrolytes in IT-SOFCs. Bi_2O_3 shows a significant polymorphism with two stable phases, α and δ [13]. High conductivity appears only in the high-temperature δ -phase of a fluorite-type structure. Numerous studies have been carried out on stabilising the δ -phase to room temperature through the substitution of Bi by various metals [10]. Besides the δ -phase, these studies have revealed a number of new phases. The main drawback of Bi_2O_3 and related compounds is the lack of stability in contact with reducing atmospheres. However, there is a possibility of applying highly conductive Bi_2O_3 -based conductors as solid electrolytes in single-gas chamber SOFCs, where reducing conditions for electrolytes are not that strict since they operate in a gas mixture of fuel and oxygen [14]. Moreover, there are several of possible ways to overcome the problem of the instability of Bi_2O_3 -based materials, for example by covering them with a thin passivating layer resistant to reduction, e.g. of ZrO_2 [15]. Another possibility is a suitable doping of the Bi-based oxide which can lead to a material with a wider ionic domain. For example, $\text{Bi}_{1.6}\text{Er}_{0.4}\text{O}_3$ doped with zirconium is reported to have enhanced the stability to reduction [15]. Below, we present examples of the results of such studies carried out in our laboratories.

5.1. $\delta\text{-Bi}_2\text{O}_3$ -type materials

The substitution of 25% of Bi in Bi_2O_3 by Nb results in a room temperature–stable $\delta\text{-Bi}_2\text{O}_3$ -related phase with a formula of Bi_3NbO_7 [16]. In this compound, there is a lower, but still significant, number of oxide ion vacancies. Using Bi_3NbO_7 as the base composition, it is possible to vary the vacancy concentration by suitable substitution of Nb. For example, substitution of pentavalent Nb by subvalent cations, such as

tetravalent Zr, results in an increase in vacancy concentration and consequently in an increase in ionic conductivity [17]. An X-ray diffraction study of the system $\text{Bi}_3\text{Nb}_{1-x}\text{Zr}_x\text{O}_{7-x/2}$ has revealed that in the composition range $0 \leq x \leq 0.4$ a single cubic $\delta\text{-Bi}_2\text{O}_3$ -type phase is observed. At higher compositions, a second fluorite-related phase (δ') appears. The δ' phase has a larger cubic cell parameter ($a \approx 5.51 \text{ \AA}$) than the original δ -phase ($a \approx 5.47 \text{ \AA}$). At compositions with $x \geq 0.6$, the system shows the presence of additional phases, viz. unreacted $\alpha\text{-Bi}_2\text{O}_3$, ZrO_2 , and $\beta_{\text{III}}\text{-Bi}_{2-x}\text{Zr}_x\text{O}_{3+x/2}$.

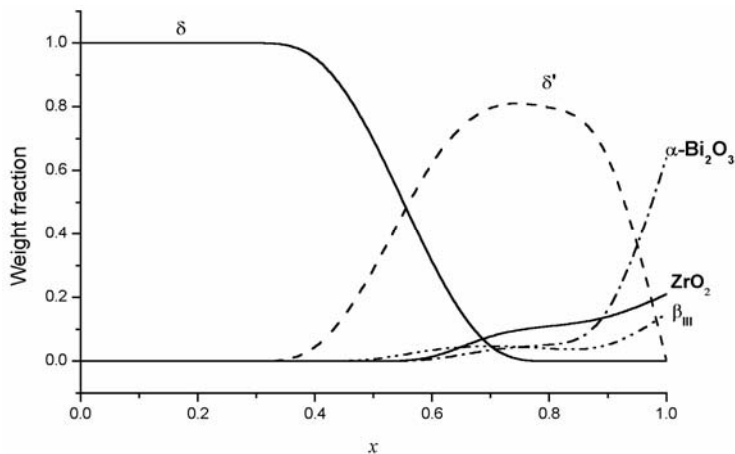


Fig. 2. Variation of the weight fractions of principal components with composition in the system $\text{Bi}_3\text{Nb}_{1-x}\text{Zr}_x\text{O}_{7-x/2}$

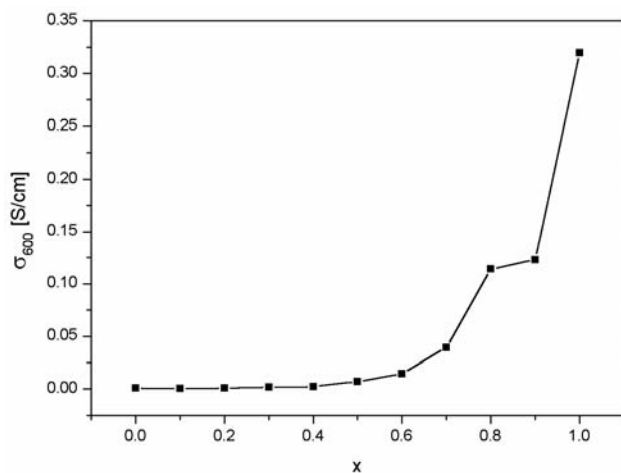


Fig. 3. Variation of total conductivity at 600 °C with composition in the system $\text{Bi}_3\text{Nb}_{1-x}\text{Zr}_x\text{O}_{7-x/2}$

The variation in the weight fraction of these phases in the studied system, presented in Figure 2, shows a gradual increase in their concentration with increasing Zr

content. The variation in electrical conductivity at 600 °C as a function of chemical composition is shown in Figure 3. The steep increase in electrical conductivity in the region corresponding to the appearance of the δ' phase cannot be explained only by the calculated increase in vacancy concentration with increasing x . It must also be associated with a change in structure between the δ and δ' phases. The higher conductivity of the δ' phase suggests a greater ionic mobility within this less dense structure.

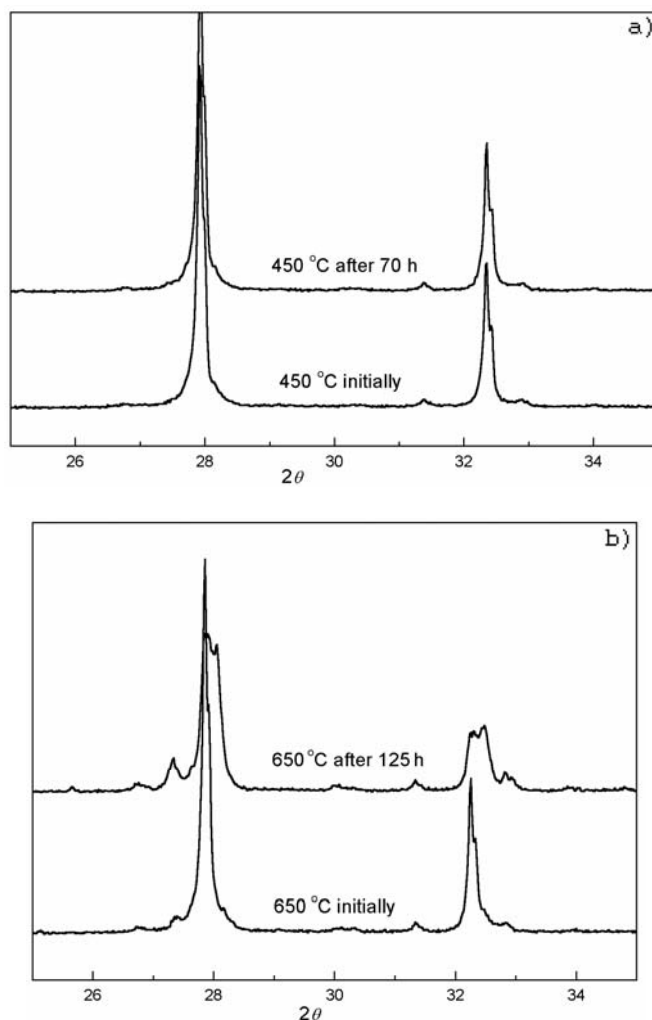


Fig. 4. X-ray powder diffraction patterns at 450 °C (a) and 650 °C (b) for a sample with the composition of $\text{Bi}_3\text{Nb}_{1-x}\text{Zr}_x\text{O}_{7-x/2}$ ($x = 0.7$)

The obtained high conductivity in the δ' phase is a positive feature of this system but it is not sufficient to warrant its application as an electrolyte in IT-SOFCs. The other requirements to be fulfilled are stability at high temperatures and the proper

ionic domain in conductivity (stability in contact with a reducing atmosphere). The first requirement has been examined – a material with the composition lying within the range of dominance of the δ' phase ($x = 0.7$) was subject to prolonged annealing at elevated temperatures [18]. The obtained results indicate that the δ' structure is maintained upon annealing at 450 °C. A significant degree of material degradation is evident, however, upon annealing at 650 °C (Fig. 4). The nature of this degradation, i.e. phase transition or phase separation, is now under study. The stability of the material under a reducing atmosphere is also being investigated.

5.2. Layered Aurivillius-type structures

Interesting results have been obtained in the system $\text{Bi}_2\text{O}_3\text{--V}_2\text{O}_5$, where the layered compound, $\text{Bi}_4\text{V}_2\text{O}_{11-\delta}$ (δ is associated with V reduction), is obtained [19]. This

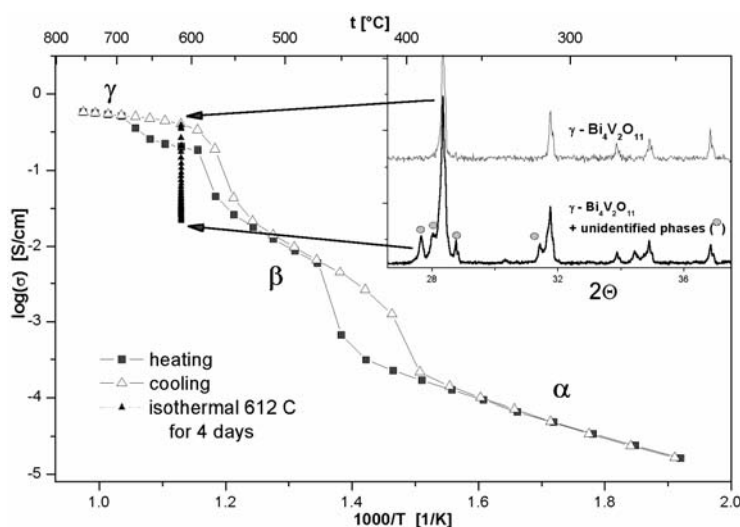


Fig. 5. Arrhenius plot of total conductivity for $\text{Bi}_4\text{V}_2\text{O}_{11-\delta}$, showing conductivity decay upon prolonged annealing at 612 °C. The insert shows initial and final (after annealing) X-ray powder diffraction patterns

compound shows significant polymorphism, with three principal phases – α , β and γ – observed over particular temperature ranges. High electrical conductivity is characteristic only of the high temperature tetragonal γ -phase. A great deal of work has been carried out in the stabilisation of this phase at room temperature through the substitution of vanadium by aliovalent cations [20]. The resulting family of solid electrolytes have been termed the BIMEVOXes. In many cases, the BIMEVOXes show a significant enhancement of electrical conductivity at low temperatures in comparison to the parent $\text{Bi}_4\text{V}_2\text{O}_{11-\delta}$. We have examined the possible use of BIMEVOXes as electrolytes in IT-SOFCs. The zirconium member of the BIMEVOX family (BIZRVOX) [21–23] was investigated. As in the bismuth niobates, the reason for the choice of BIZRVOX

was the reported enhanced stability to the reduction of Bi_2O_3 -based compounds when doped with Zr [15]. The thermal stability of $\text{Bi}_4\text{Zr}_{0.1}\text{V}_{1.9}\text{O}_{10.95}$ in air at elevated temperatures was investigated by ac impedance spectroscopy upon prolonged annealing and compared to the behaviour of the parent material, $\text{Bi}_4\text{V}_2\text{O}_{11-\delta}$, under similar conditions.

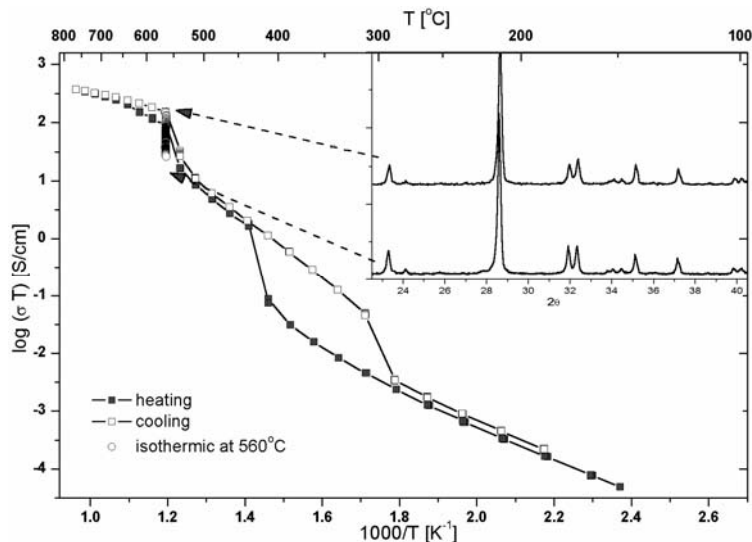


Fig. 6. Arrhenius plot of conductivity for $\text{Bi}_2\text{Zr}_{0.05}\text{V}_{0.95}\text{O}_{4.75-\delta}$, showing conductivity decay upon prolonged annealing at 560°C . The insert shows initial and final (after annealing) X-ray powder diffraction patterns

The results summarised in Figures 5 and 6 indicate that conductivity decay occurs in both materials upon prolonged annealing. The degree of conductivity degradation, however, is much smaller in BIZRVOX, where the partial substitution of V by Zr takes place. Parallel X-ray studies confirm the phase separation of these compounds upon prolonged annealing [24], but the degree of phase separation in BIZRVOX is significantly reduced.

6. Conclusions

New families of potential electrolytes for IT-SOFC applications continue to be developed. While high conductivities can be readily achieved at intermediate temperatures, much work still needs to be carried out on enhancing the stability of these electrolytes. Careful chemical design, including studies of doped systems, may offer a way forward in the development of novel IT-SOFCs. Two zirconia-doped bismuthate systems, $\text{Bi}_3\text{Nb}_{1-x}\text{Zr}_x\text{O}_{7-x/2}$ of a δ - Bi_2O_3 -type structure and $\text{Bi}_4\text{V}_{2-2x}\text{Zr}_{2x}\text{O}_{11-x}$ of a layered Aurivillius-type structure, are discussed in this respect. In the latter system, a signifi-

cant increase in thermal stability in the doped material in comparison to the parent compound was observed.

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