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Analysis of the electrical behaviour of conductor/insulator composites using effective medium theories

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Abstract

Al_2O_3/8YSZ composites with a wide range of alumina compositions, from 0 to 50 wt.%, have been prepared and characterised. The electrical properties and the microstructure were studied by complex impedance spectroscopy and scanning electron microscopy techniques, respectively. Simple models derived from effective medium theories were used to predict the qualitative trend of electrical conductivity versus Al_2O_3 volume fraction and a comparison with the experimental data is reported. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3–YSZ; Effective medium theories; Impedance spectroscopy; Ionic conductivity; Solid electrolyte

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1. Introduction

Cubic stabilised zirconia is the most widely used high performance electrolyte in solid state electrochemical devices (oxygen sensors, solid oxide fuel cell). In fact, this material satisfies the primary requirements (high ionic conductivity, unitary ionic transference number and long time phase stability) for electrochemical applications. However, its use in high temperature solid oxide fuel cell (SOFC) shows some problems. In planar SOFC the stacking of the electrolyte sheets and of interconnect plates introduces high mechanical stresses which often results in fractures with loss of efficiency in the energy conversion. This is the case of cubic 8 mol% Y_2O_3–ZrO_2 (8YSZ) which suffers from relatively poor bending strength (200–300 MPa depending on sintering conditions).

In the last years, some efforts were devoted to increase the mechanical strength of 8YSZ. The addition to the 8YSZ matrix of a secondary phase with high elastic modulus, little partial solubility in ZrO_2 ($<1\%$), high temperature phase stability and electrical insulating behaviour was suggested. Alumina was the most extensively used secondary phase and it was demonstrated that small amounts could influence the electrical conductivity of the composites. Mori et al.[1] reported that the electrical conductivity of 20 wt.% Al_2O_3/8YSZ composite is 0.10 S/cm at 1000 °C and 0.03 S/cm at 830 °C, about 40 and 50% lower than the values they measured in 8YSZ (about 0.16 and 0.06 S/cm at 1000 and 830 °C, respectively). Navarro et al.[2] found that at 1000 °C the conductivity of 20 wt.% Al_2O_3/8YSZ is 0.10 S/cm, about 65% less than pure 8YSZ (0.30 S/cm); Natali Sora et al.[3,4] studied the electrical behaviour of Al_2O_3/8YSZ composites up to 15 wt.% of alumina: at 850 °C the conductivity of 10 wt.% Al_2O_3/8YSZ was found to be 0.03 S/cm, about 50% lower than 8YSZ. Unlike the previous works, a recent paper of Feighery and Irvine[5] showed that at 1000 °C up to 10 wt.% of alumina can be added without any significant decrement in the electrical conductivity, while Yuzaki and Kishimoto[6] reported a slight increase in conductivity with alumina addition up to 10 mol% (about 8.5 wt.%). Fukuya et al.[7] found excellent high conductivity at high temperatures for both 8YSZ and 5% mol Al_2O_3/YSZ (about 4.5 wt.%) composites (0.22 and 0.19 S/cm at 1000 °C, respectively), anyway decreasing with the alumina content. Recently, Ji et al.[8] stated that the

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conductivity has a maximum at 4 wt.% of alumina as secondary phase.

The conflicting and inhomogeneous results suggest that the role of alumina in 8YSZ-based composites is still far to be confident; so Al_2O_3/8YSZ composites with a wide range of alumina amount (0–50 wt.%) were prepared and characterised. The electrical conductivity and the microstructure were investigated by complex impedance spectroscopy and by scanning electron microscopy, respectively. In order to predict the electrical behaviour of ionic conductor composites simple semi-empirical models derived from effective medium theories (EMT) were used to analyse the qualitative trend of the electrical conductivity data versus Al_2O_3 volume fraction.

2. Experimental

2.1. Sample preparation

The starting powders were 13 wt.% (~8 mol%) Y_2O_3–ZrO_2 fully stabilised zirconia (Unitec Ceramics) and Al_2O_3 (Sumitomo Chemical). The chemical composition of nominal 13 wt.% Y_2O_3–ZrO_2 powder is: Y_2O_3 12.7 wt.%, SiO_2 <0.02 wt.%, Al_2O_3 0.02%, Fe_2O_3 0.04 wt.%, TiO_2 0.12 wt.%, ZrO_2+HfO_2 86.95 wt.% and MgO <0.05 wt.%. The chemical analysis performed on the Al_2O_3 powder gave: SiO_2 0.16 wt.%, Fe_2O_3 0.03 wt.%, Na_2O <0.005 wt.% and $K_2O<0.005$ wt.%; the particle sizes were 2 μm for 8YSZ and 0.5 μm for Al_2O_3, on average.

Yttria-stabilised zirconia (8YSZ) and alumina (up to 50 wt.%) powders were mixed and ball-milled with isopropyl alcohol for 5 h and then dried for 12 h at 110 °C. The mixtures were uniaxially pressed and successively subjected to cold isostatic pressing (200 MPa for 60 s). The pellets were sintered at 1500 °C for 4 h in air (heating rate 10 °C/min) and then furnace cooled. The density of the specimens was measured by the Archimedes' technique.

2.2. X-ray powder diffraction

After sintering, the pellets were checked by X-ray powder diffraction (XRD). The data were collected at room temperature with a Philips MPD 1830 diffractometer using graphite monochromated Cu-K_α radiation. The scan step was 0.02°, with scan speed of 0.4°/min and angular range $4^\circ<2\theta<61^\circ$.

2.3. Scanning electron microscopy

Well-polished specimens (after thermally etching for 1 h at 1350 °C in air) were examined with a scanning electron microscope (SEM) equipped with an X-ray energy dispersive spectrometer (EDS). EDX analyses were performed at 13 kV over a 100 s count time and repeated twice on each spot, to ensure reproducibility.

2.4. Impedance spectroscopy

The conductivity of 8YSZ and Al_2O_3/8YSZ composites was obtained by complex impedance spectroscopy (IS) technique. Cylindrical samples, of approximately 11 mm in diameter and 3 mm thick, were sputtered with platinum on both faces. The complex impedance spectroscopy measurements were carried out by a Solartron 1255 Frequency Response Analyser (frequency range 1 Hz–10 MHz) in the temperature range 300–850 °C, in air.

3. Results and discussion

3.1. Microstructural characterisation

The relative densities of the composites, indicating the percentage of theoretical densities, are given in Table 1. All pellets sintered at 1500 °C have relative density of about 98%. The X-ray powder diffraction patterns show that all composites contain only Al_2O_3 and 8YSZ with a cubic fluorite type structure (see Fig. 1).

The SEM images are presented in Fig. 2. The black parts indicate alumina and the grey ones 8YSZ. The alumina grains tend to cluster and to mostly distribute at the 8YSZ grain boundaries. Furthermore, according to the grain growth inhibitor effect of the Al_2O_3[9–11] the grain size of the 8YSZ decreases as the secondary phase amount increases. EDX analysis agrees very well with the above mentioned XRD results.

3.2. Electrical conductivity

Typical impedance spectra are shown in Fig. 3. Moving from the lower to higher frequency values, the three semicircles represent the contributions relating to the electrodes, the grain boundary and the bulk, respectively. It should be remembered, however, that the electrode contribution is more clearly defined at higher temperatures; on the contrary bulk and grain boundary

Table 1
Nominal composition and relative density of the sintered specimens

Sample code	8YSZ (wt.%)	Al_2O_3 (wt.%)	Relative density (%)
8YSZ	100	0	98.1
5A	95	5	97.8
10A	90	10	97.7
15A	85	15	98.0
25A	75	25	98.5
35A	65	35	98.8
50A	50	50	98.5

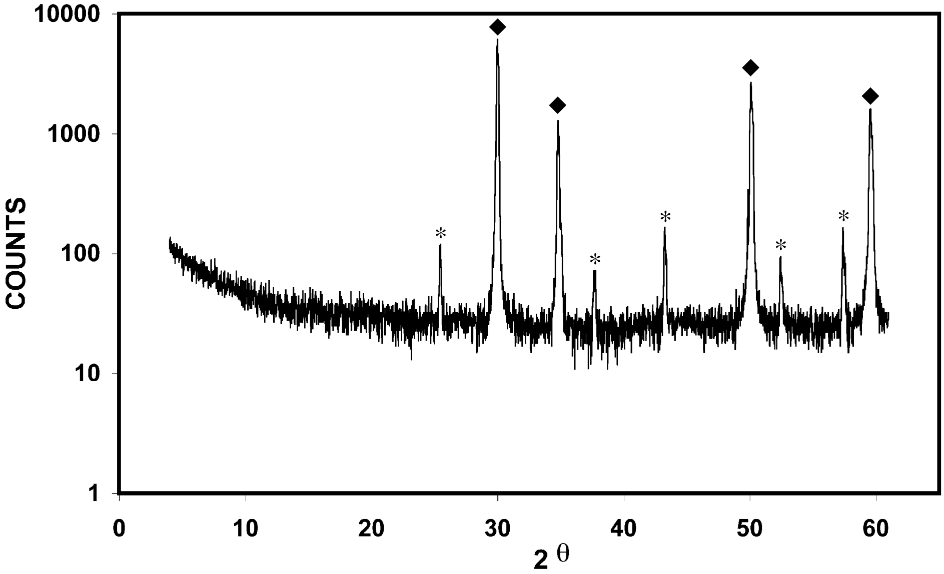

Fig. 1. XRD pattern of 15 wt.% Al_2O_3/8YSZ composite; (◆) 8YSZ and (∗) Al_2O_3 peaks.

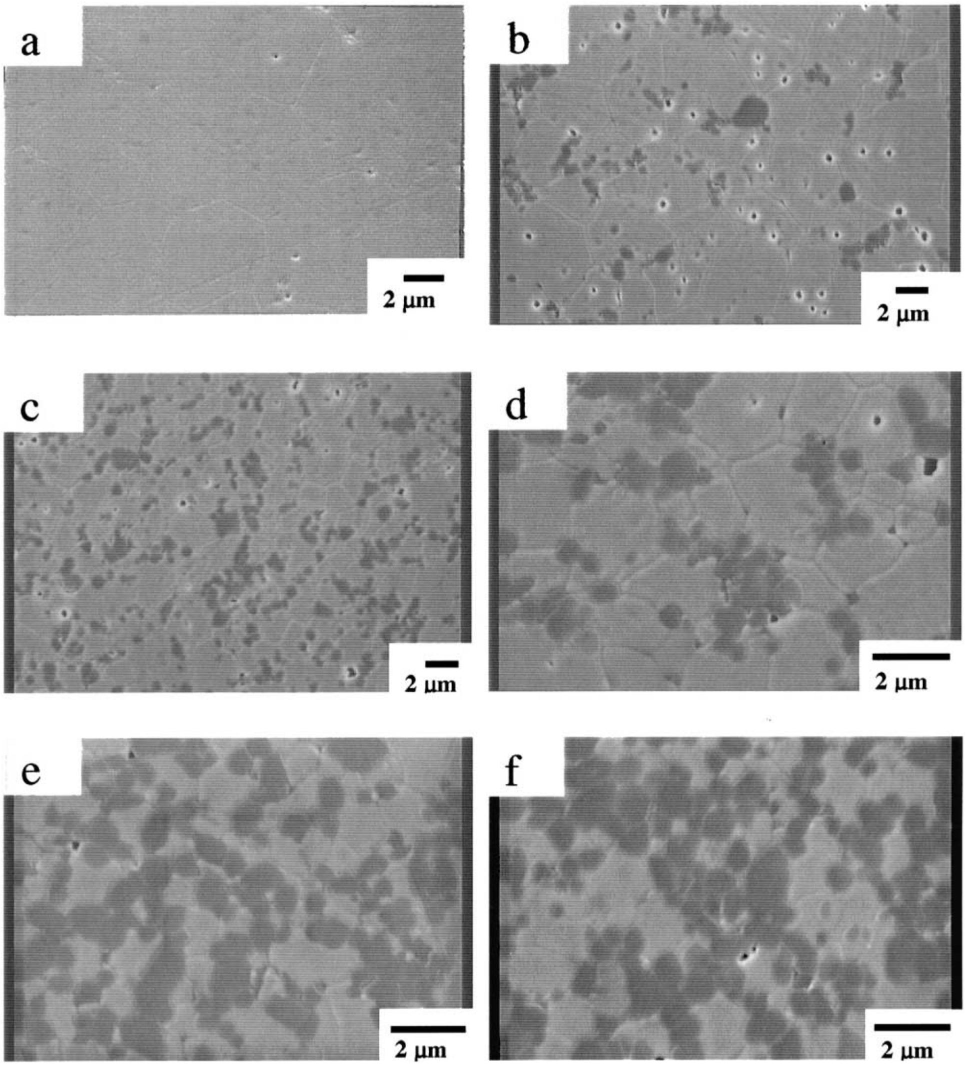

Fig. 2. Backscattered SEM images of: (a) 8YSZ; (b) 5A; (c) 15A; (d) 25A; (e) 35A and (f) 50A.

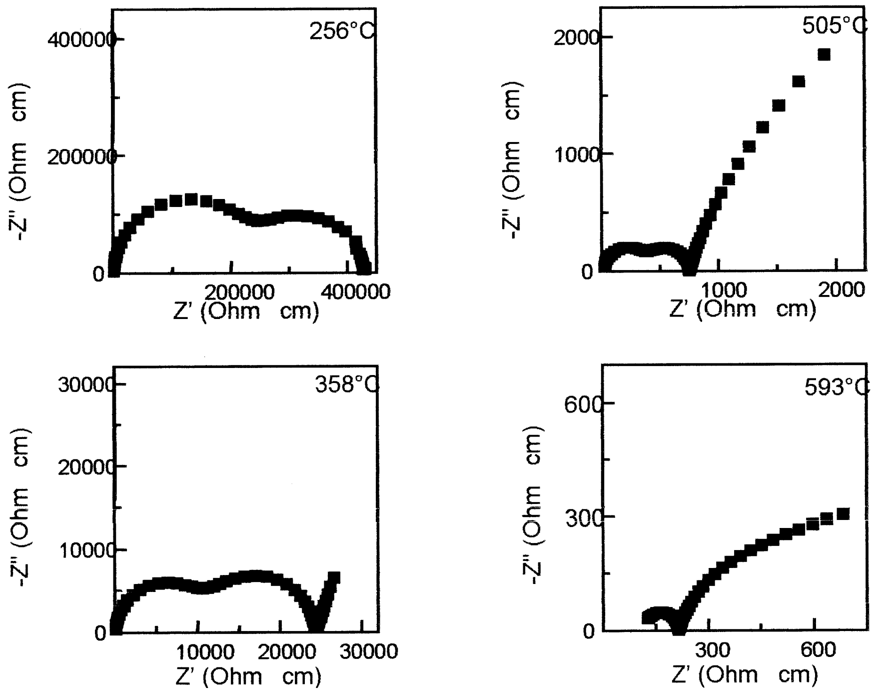

Fig. 3. Impedance spectroscopy diagrams of 15A sample at different temperatures.

are better resolved at lower temperatures. Spectra collected at constant temperature show that increasing the alumina quantity the grain boundary conductivity (σ_{gb}) decreases, while the bulk electrical properties (σ_b) do not differ significantly. In Fig. 4 IS patterns measured at 620 °C and differing only by quantity of alumina are shown.

To aid in comparing the data in the following diagrams the conductivity of pure 8YSZ is also reported[3] in addition to those of Al_2O_3/8YSZ composites. In Fig. 5 the Arrhenius plots for the bulk conductivity are reported: the σ_b of those composites which have the secondary phase amount higher than 5 wt.% it is unaffected by the composition. From these measurements, it was found that the σ_b highest values are observed in pure 8YSZ, while those of 5A composite are intermediate between 8YSZ and all the other composites. For instance, at 1000 K the average bulk conductivity—obtained by least square fitting of experimental data—of samples 50A, 35A, 25A and 15A is 1.48×10^{-2} S/cm, while those of 5A and 8YSZ are 2.71×10^{-2} and 4.29×10^{-2} S/cm, respectively. The bulk activation energy values were calculated by fitting the conductivity data and were about 0.95 eV for all the composites, while for 8YSZ the value obtained was 0.86 eV [Fig. 9(a)].

From Fig. 6 it was seen that the σ_{gb} is a function of the alumina content at any temperature. The electrical resistivity smoothly increases with the secondary phase amount; a variation of about two orders of magnitude at the lowest temperature and about one at the highest is observed in the overall composition range. No sensible variation in the activation energy values (about

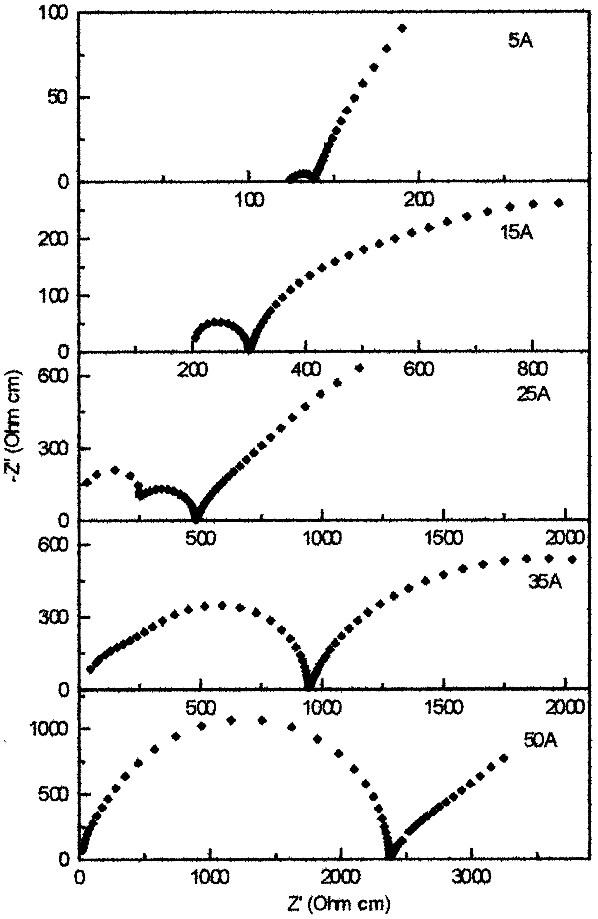

Fig. 4. Nyquist plots of Al_2O_3/8YSZ composites with different alumina content, at constant temperature (T = 620 °C).

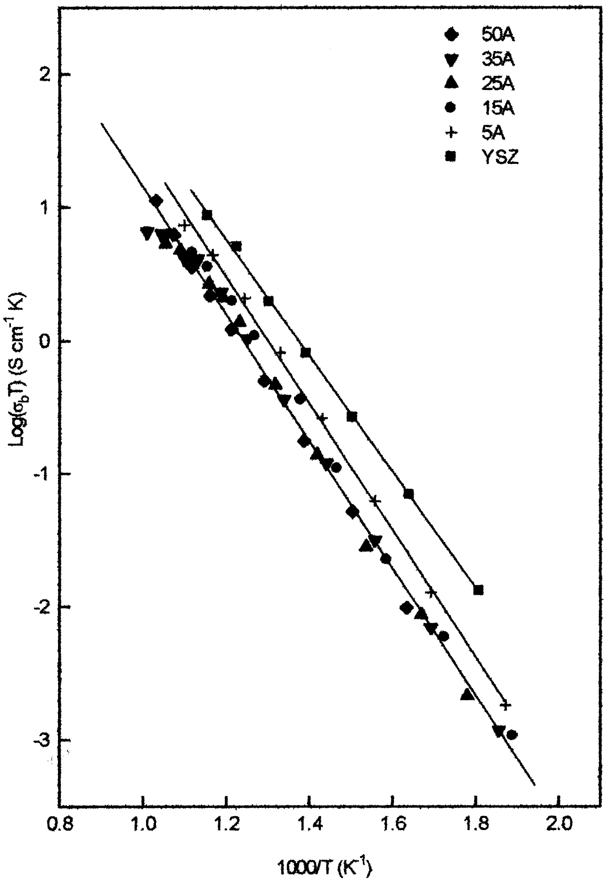

Fig. 5. Bulk electrical conductivity of Al_2O_3/8YSZ composites: log($\sigma_b T$) vs. 1000/T.

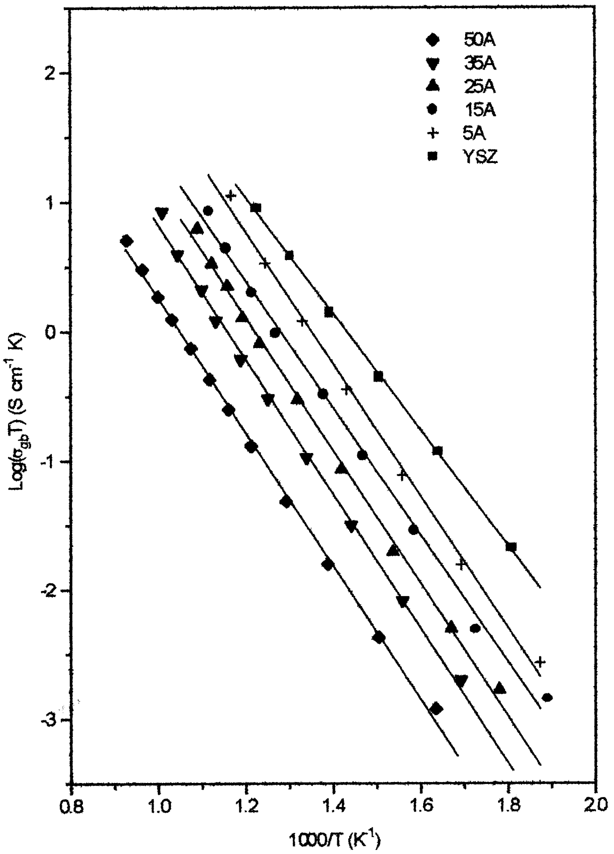

Fig. 6. Grain boundary electrical conductivity of Al_2O_3/8YSZ composites: log($\sigma_{gb} T$) vs. 1000/T.

1.00 eV) was observed for all the composites. 8YSZ presents a lower activation energy value for the conduction mechanism (0.90 eV) with respect to Al_2O_3/8YSZ composites [Fig. 9(b)].

The Arrhenius plots for the total conductivity is shown in Fig. 7. As one can observe the total electrical conductivity becomes smaller with increasing the amount of secondary phase in good agreement with some of the previous works[1–3,7] where similar composition ranges were investigated. For instance, both Mori et al.[1] and Navarro et al.,[2] who studied Al_2O_3/8YSZ composites containing up to 30 and 20 wt.% of alumina, respectively, observed a continuous decrease in total conductivity with increasing amount of insulating phase, with the exception of very small amounts of secondary phase (up to about 1 wt.%).[1] Natali Sora et al.[3,4] and Fukuya et al.,[7] who investigated composites with alumina content not exceeding 15 wt.%, also found similar results. Opposite results were found by Feighery and Irvine;[5] however, due to the low density (from 68 to 79% of the theoretical value) of their sintered composites (ranging from 0 to 24 wt.% of alumina), measured conductivities were corrected for the porosity and this may explain the controversial findings. In the work of Yuzaki and Khishimoto[6] changes in total conductivity due to alumina are very small; the lack of density data on sintered specimens and the use of alumina powders with different average diameter make difficult the comparison with the other literature results.

3.3. Semi-empirical modelling

The availability of a large amount of homogeneous experimental data obtained in a wide range of temperatures and compositions suggested the use of semi-empirical models to describe the electrical behaviour of ionic conductor composites. In order to enlighten the influence of the insulating phase on the overall conductivity of these composites, effective medium theories (EMT)[12,13] were tentatively used to account for experimental data. EMT is a self-consistent procedure to calculate the electrical properties of a composite through sequential approximations, which are related to the actual electrical property of each phase. The models coming from this theoretical approach had great success for their flexibility and good prediction results in insulator–electronic conductor systems. Among them Bruggeman's symmetric and asymmetric effective medium theories (BSEMT and BAEMT, respectively) are certainly the most famous.[14]

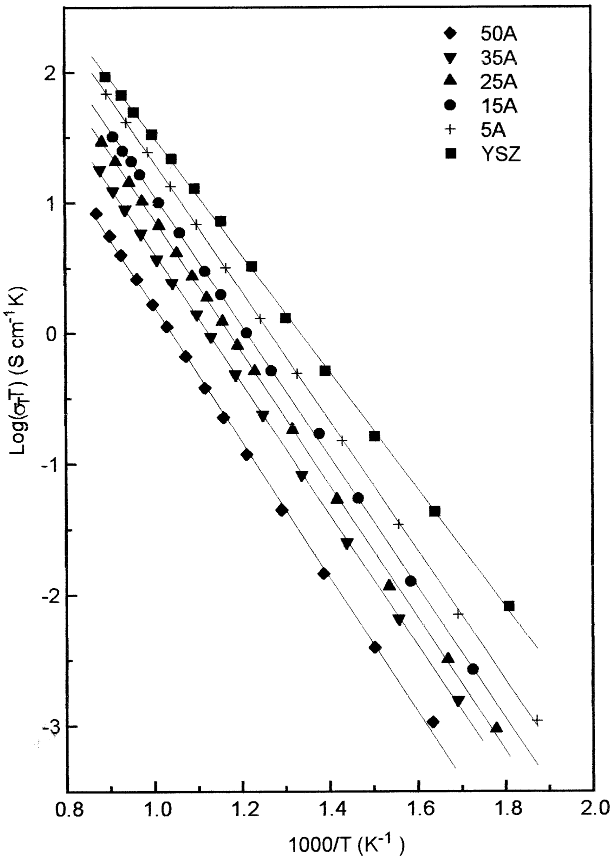

Fig. 7. Total electrical conductivity of Al_2O_3/8YSZ composites: $\log(\sigma_T T)$ vs. $1000/T$.

The BSEMT depicts a two-phase composite as a set of spheres of different sizes arranged in such a way to completely fill the space. According to this assumption, at least one phase is percolating, but for intermediate compositions (about $1/3 < \varphi_i < 2/3$, where φ_i is the volume fraction) both phases have 3–3 connectivity.[15] This model can be easily extended to the case of less regular shape particles and to multi-component systems.[12–14]

In the BAEMT the entire composite medium is filled with spheres of different sizes (component one) uniformly coated with the second component; therefore only the shell component percolates. This model can be also extended to systems where the particles have irregular shape, but only two-phase composites can be considered. Strictly, the BSEMT and BAEMT were developed for insulator–electronic conductor systems, and so they have been less widely used for insulator-ionic conductor systems.[16]

In the present work the secondary phase (α-alumina) was considered as a perfect insulator ($\sigma_A = 0$), thus the electrical property of the composite (σ_M) is only a function of both the alumina content (expressed as volume fraction, ϕ_A) and the conductivity of pure 8YSZ (σ_{8YSZ}) according to:

$$\sigma_M = \sigma_{8YSZ}(1 - \phi_A)^{1.5} \quad \text{BAEMT}$$

$$\sigma_M = \sigma_{8YSZ}(1 - 1.5\phi_A) \quad \text{BSEMT}$$

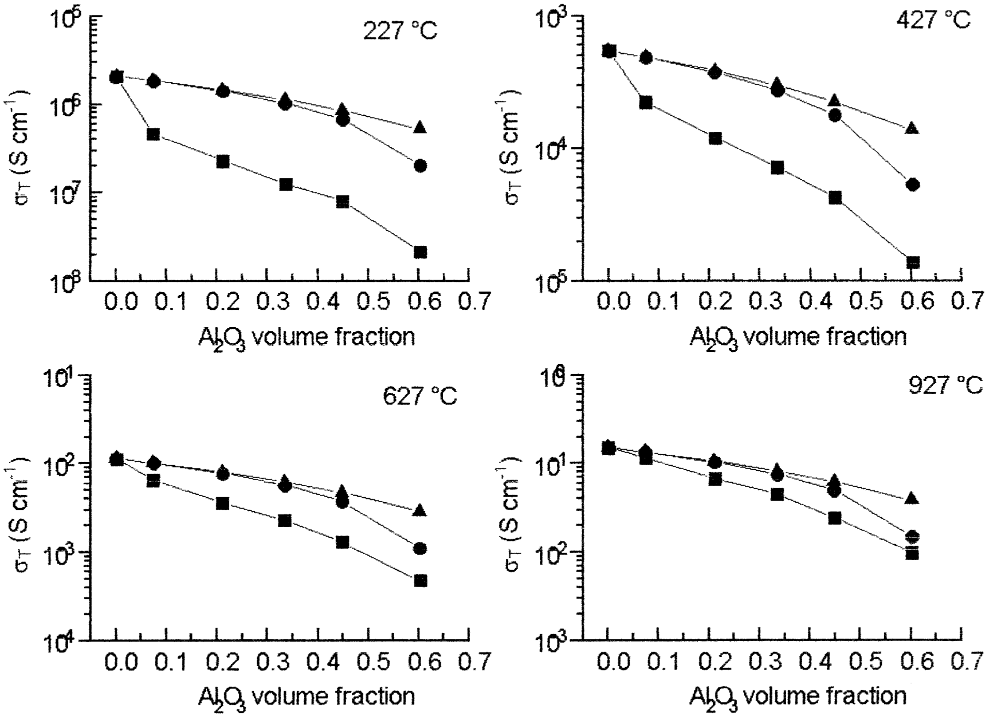

Fig. 8. Conductivity Al_2O_3/8YSZ composites (▲, experimental; ●, BSEMT; ■, BAEMT) vs. alumina volume fraction, at different temperatures.

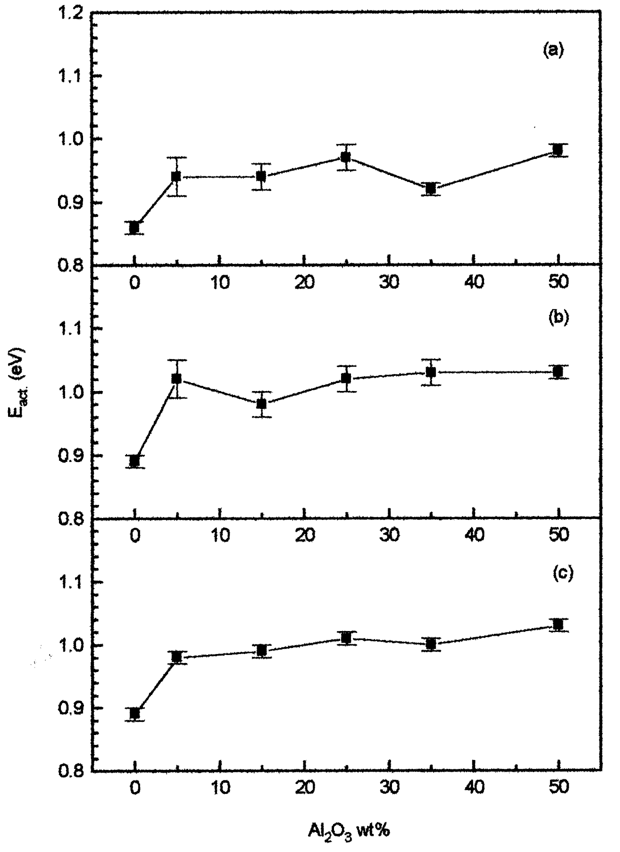

Fig. 9. Activation energy vs. alumina content: (a) bulk; (b) grain boundary; (c) total contribution.

Using the above reported equations, the total conductivity was calculated at different temperatures; the results are reported in Fig. 8. As it can be seen, experimental and theoretical data are in better agreement when the BSEMT approach is applied; both models yield large deviations from the actual conductivity values when the amount of insulating phase is bigger than $\frac{1}{2}$ volume fraction. The BAEMT fails to describe the electrical conductivity of composites also for small volume fraction of alumina.

4. Conclusions

The addition of α-alumina ($5 \leqslant$ wt.% $\leqslant 50$) to 8YSZ does not remarkably affect the bulk resistivity of the solid electrolyte. In particular, for amount of secondary phase larger than 5 wt.% no variation in σ_b is observed. Nevertheless, large decrease of the electrical conductivity takes place in the polycrystalline composites; such effect arises from the grain boundary contribution, which changes in an average of about two orders of magnitude in the investigated composition range. At any temperature, the electrical resistivity values continuously increases with the secondary phase amount, without any saturation effect.

The present results strengthen that the addition ($5 \leqslant$ wt.% $\leqslant 50$) of the α-alumina decreases the total conductivity of the composites and increases its activation energy. While the former effect is substantial, the latter is almost negligible as is detailed shown in Fig. 9; the best compromise between the amount of alumina and the mechanical strength of the composite is the important point of the planar SOFCs.

The simple models BSEMT and BAEMT appear inadequate in properly describing the electrical properties of ionic conductor composites. On the other hand, the microstructures of these systems generally are very complex and their modelling hard to be realised so that the present results are not so unexpected, as we recently hypothesised.[15]

Acknowledgements

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