How to forecast the electrical behaviour of ionic conductor composites?

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The theoretical models that might be used to forecast the electrical behaviour of ionic conductor composites for application in SOFCs are reviewed. A comparison of the different models is performed and comparative analysis of their power is presented on the basis of a case simulation (YSZ (7,54 mol%Y_2O_3)-Al_2O_3 (5 wt%) composite). The lack of systematic experimental works makes a wide comparison with the theoretical results very difficult, so the real power of the models can not yet be fully assessed and only introductory considerations are tentatively given. Nevertheless from the preliminary results, it seems possible to affirm that Electrical Network Models are able to better sustain the simulation of the electrical properties of YSZ-Al_2O_3 composites. Certainly many other improvements have to be done before ENMs became confident tools for tailoring "*ab initio*" the electrical properties of two phase mixtures.

1. Introduction

In recent years, the practical importance of solid ionic conductors has continuously increased in view of their application in batteries and fuel cells, devices whose role is strategic in the development and exploitation of new large and small power sources [1–3]. Nowadays only a few well-established solid electrolytes are on the market and the research is very active either in looking for new compounds (i.e. polymer proton conductors and intermediate-temperature oxide ion conductors [4, 5]) or in improving the properties of the utilised materials. The recent investigations on the yttria stabilized zirconia (YSZ)-Al_2O_3 composites are certainly a proper case for giving an example of the latter statement.

Up to now a zirconia-doped (8%mol Yttria, 8YSZ) ceramic is the only electrolyte actually used in Solid Oxide Fuel Cell (SOFC) prototypes and forthcoming commercial devices [6, 7]. During the last twenty years many research efforts [8–28] have been devoted to optimise electrochemical, thermal and microstructural properties of YSZ. Nevertheless some problems arose in developing planar configuration devices [29, 30], where the stacking of electrolyte sheets and interconnect plates induces high mechanical stresses, which often results in fractures; indeed, cubic 8YSZ suffers from poor mechanical properties [26, 29, 31].

In order to strengthen the YSZ the addition of a secondary phase (chromia [32–34], sodium β-alumina [35], silicon carbide [36] and α-alumina) was suggested; the attention was mainly focused on α-alumina for its high elastic modulus, low partial solubility in ZrO_2 (<1%), high temperature stability and electrical insulating behaviour.

The α-alumina, originally added in small amounts (less than 2%mol) as a sintering aid [8], showed an increase in the electrical conductivity [37], acting as a SiO_2 impurity scavenger [9]. However larger amounts of secondary phase have to be blended in order to reach sufficient bending strength [38]; unfortunately high concentrations of this insulating phase increase the electrical resistance of such composites. The influence of the α-alumina on the electrical conductivity of the composites is not yet well explained and poor agreement is observed in experimental results. For instance, Mori *et al*. [39] found the conductivity of 10wt% Al_2O_3 composites to be ∼0.1 S/cm at 1000 °C and of ∼0.04 S/cm at 830 °C, about 30% lower than that observed in 8YSZ, at the same temperatures. Navarro *et al*. [40] measured ∼0.16 S/cm, about 50% less than 8YSZ, at 1000 °C; Natali Sora *et al*. [41] ∼0.03 S/cm, at 850 °C. On the contrary, Feighery and Irvine [42] showed that at 1000 °C up to 10wt% of alumina can be added without any significant decrease in the conductivity; Yuzaki and Kishimoto [43] reported a slight increase in conductivity with alumina addition up to 10mol%; Ji *et al*. [44] stated that 4 wt% of alumina gives the highest grain boundary conductivity.

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These conflicting and inhomogeneous data might result from the actual purity of the added insulating phase as well as from the shortage of a detailed analysis of the composites microstructure, which can play an important role in the total (bulk + grain boundary) conductivity. If one gives credit to the latter hypothesis, a rational approach might be taken into account for an optimised tailoring of the above mentioned composites. Unfortunately few models were and have been developed to predict the electrical behaviour of two phase systems and still less to manage the YSZ-Al_2O_3 composites.

The theoretical interest in simulating the electrical properties of ionic conductor composites largely arose after Liang [45] observed an improvement of three orders of magnitude in the ionic conductivity of LiI when mixed with Al_2O_3; such behaviour was later confirmed in many other compounds [46]. The phenomenon was attributed to a space-charge layer formation along the internal interfaces between the different phases [47, 48]. Models based on random resistor networks and percolation theory [49] were, for the first time, used to define the macroscopic aspects of the electrical properties of these heterogeneous solid electrolytes [50–52]. Successively similar random resistor network models were extended to simulate the a.c. behaviour of the same composites [53, 54]. Since then, several approaches were designed to investigate the a.c. electrical response of inhomogeneous systems [55–64].

The aim of the present paper is to review the theoretical models, which were and might be used to forecast the electrical behaviour of ionic conductor composites for application in SOFCs. The different models and the comparative analysis of their power is presented. The lack of systematic experimental works makes a comparison with the theoretical results very hard, so the real power of the models is not yet fully assessed and only preliminary considerations are given.

2. Modelling review

The problem of simulating the electrical behaviour of two phase systems and composites can be managed in a rigorous way calculating the impedance by the actual potential distribution within the material; in other words solving the classical Laplace's equation:

$$\nabla \cdot \vec{j} \equiv \frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial^2 \Phi}{\partial z^2} = 0 \qquad (1)$$

where $\vec{j}$ is the current density and Φ the scalar electrical potential.

The puzzling geometry of the composites makes the solution of the equation very difficult. Nevertheless the conductance of a two-phase mixture is evaluated by solving the equation within each phase and forcing the continuity for potential and flux at their boundaries. In principle, the resulting differential problem is numerically solved with any desired accuracy, but in practice it cannot be done for its complexity. The numerical solution of this type of differential equation has been reconsidered recently. The powerfulness of the Finite Element Method (FEM) [65], which can be applied to any geometrical domain and optimised by using adaptive algorithms, has been the key element. The FEM solves systems of differential equations by approximating the solution through a sequentially continuous polynomial function. This technique was very recently also applied to outline the grain boundary influence on impedance spectra of polycrystalline solid electrolytes [66–69]. Unfortunately, in the case of composite materials the application of FEM is even more difficult for the larger number of interfaces and grain boundaries.

For the above mentioned reasons, the simulation of the electrical behaviour of composites was performed by less rigorous approaches, namely: continuous and discrete medium models. Generally, the continuous models starting from the classical Maxwell equations, through some assumptions, generate an analytic equation where any composite property (i.e. the conductivity) is a function of the analogous properties of the pure components: $\sigma_c = f(\sigma_1, \sigma_2)$. Effective Medium Theory (EMT) and percolation theory are the most common rationalisations.

The discrete medium models, much more complex approaches, simulate the electrical behaviour converting the composite into a 2D or 3D network (constituted of discrete electrical elements) and solving a set of algebraic equations. The classical Laplace's condition on static current distribution ($\nabla \cdot \vec{j} = 0$) becomes, as outlined by Kirkpatrick [49], the simple Kirchoff's current law equation, thus providing the theoretical foundations of these models. The main differences among these models can be ascribed either in the way of arranging the discrete electrical elements inside the electrical networks or in the choice of the representative circuits.

Some other semi-empirical models have been developed *ad hoc* to describe particular phenomena or to simulate specific materials [55, 64, 70]. In the following, only the models that were, are and might be used to forecast the electrical behaviour of oxygen ionic conductor composites will be considered and discussed.

2.1. Continuous medium models

Several methods have been developed to describe the electrical behaviour of heterogeneous materials [71, 72], among which the most widely applied in the past years were the Maxwell and the Bruggeman models. They were mainly used to describe the d.c. or low-frequency electrical properties of composites [73, 74], and only occasionally extended to the a.c. behaviour [56, 75, 76].

The two- or brick-layer model (BLM), designed by Maxwell [77], is the simplest way to outline the a.c. behaviour of a composite that is pictured as two contiguous sheets of different media. An attractive feature of this model is its physical simplicity: the two phases are arranged as a set of alternate flat sheets, perpendicular to the current flow, so that low conductance regions are accounted for. The analytical expression of the overall admittance, Y_C, is:

$$\frac{1}{Y_C} = \frac{\varphi_1}{Y_1} + \frac{\varphi_2}{Y_2} \qquad (2)$$

Y_1 and Y_2 ($Y = \sigma + j\omega\varepsilon, \sigma$ the conductivity, ω the angular frequency and ε the permettivity) are the

admittance of the two phases, φ_1 and φ_2 their layer thickness, which can be converted into the volume fractions of the two constituents, by normalisation. The electrical response fits a two RC parallel circuit.

Maier [78] suggested a set of three phases (ion conductor, insulating material and space-charge region) in parallel; so the overall admittance is:

$$Y_C = \beta_1\varphi_1 Y_1 + \beta_2\varphi_2 Y_2 + \beta_3\varphi_3 Y_3 \qquad (3)$$

where β_is are dimensionless parameters, describing the deviation from the ideal parallel switching. A similar approach was adopted by Uvarov *et al*. [59], which proposed an equation where the total conductance of a composite is expressed as the sum of the conducting phase bulk contribution and of the different space-charge regions (host-host and host-dispersoid).

Another model, proposed by Maxwell [71, 72, 77] for mixtures of purely resistive materials and later extended by Wagner (MWM) to mixtures of materials having dielectric and resistive behaviour [75], consists in a dispersion of particles (phase 1) in a continuous medium (phase 2). The particles are assumed to be sufficiently separated (dilute limit) and not interacting. When phase 1 can be pictured as spherical inclusions, the model gives:

$$Y_C = Y_1\frac{2Y_1 + Y_2 - 2\varphi_2(Y_1 - Y_2)}{2Y_1 + Y_2 + \varphi_2(Y_1 - Y_2)} \qquad (4)$$

φ_1 and φ_2 are again the volume fractions. This equation does not work in the case of binary mixtures close to percolation threshold. The model was later extended to cover spheroidal [79] and ellipsoidal particles [80].

Both the BLM and MWM are able to describe systems with two different relaxation processes so that they might be used when two semicircles appear in the experimental impedance spectra. Quite recently, Equation 4 was used to study the electrical response of YSZ/Al_2O_3 composites [76] on a qualitative basis.

Effective medium theory (EMT) is a self-consistent procedure to calculate the electrical properties of a composite through sequential approximations [71, 72], that 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 the d.c. regime. Among them Bruggeman's symmetric and asymmetric effective medium theories (BSEMT and BAEMT, respectively) are certainly the most famous [71–73].

In the BSEMT the two phases are depicted as different size spheres which are arranged in such a way as to completely fill the entire composite medium (Fig. 1); so [81, 82]:

$$\varphi_1\frac{Y_1 - Y_C}{Y_1 + 2Y_C} + \varphi_2\frac{Y_2 - Y_C}{Y_2 + 2Y_C} = 0 \qquad (5)$$

According to the above assumptions, at least one phase is always percolating; both of them have a 3-3 connectivity for intermediate (about $1/3 < \varphi_i < 2/3$) composition [73]. With the proper modifications, Equation 5 can be applied to systems of any dimensionality [72] as well as to ellipsoidal particles [83]. This model is also easily extended to multi-component systems [72].

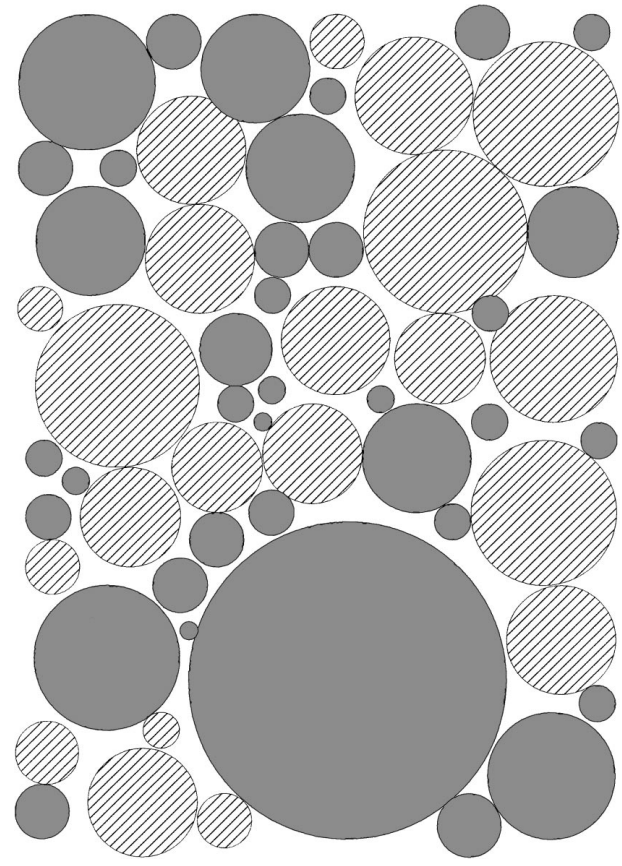


Figure 1 Schematic representation of the composite in Bruggeman's symmetric effective medium theory (BSEMT).

In the BAEMT the entire composite medium is filled with different size spheres of one component and a uniform shell of the other one surrounds each of them (Fig. 2); only the shell component is able to percolate. The following equation is obtained [72]:

$$\frac{(Y_C - Y_2)^3}{Y_C} = \frac{(1 - \varphi_1)^3(Y_1 - Y_2)^3}{Y_1} \qquad (6)$$

where 1 and 2 refers to core and shell phase, respectively. Unfortunately this equation which becomes manageable only in the d.c. regime is not as easily solved as Equation 5.

It is interesting to note that BSEMT and BAEMT become the already described MWM model when very dilute mixtures are considered.

Another tool to picture the conductivity in both conductor-insulator blends and high-low conductivity phase mixtures is the percolation theory [84] that leads to:

$$\sigma \approx \sigma_1(\varphi_1 - \varphi_c)^t \qquad (7)$$

where σ_1 is high conductivity phase electrical property and φ_c the critical volume fraction. The latter parameter as well as t can be numerically calculated according to bond or site percolation models [73, 84, 85]. Equation 7 can be applied near to the percolation threshold

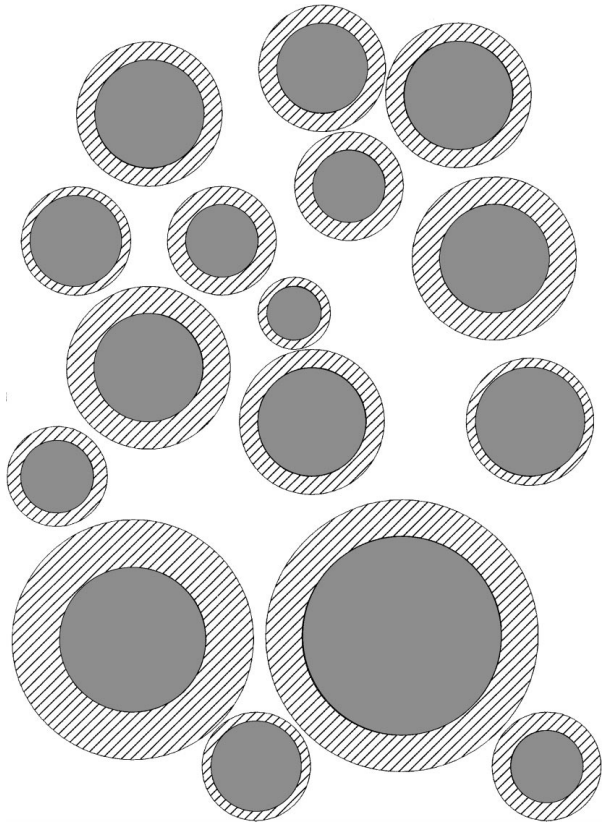


Figure 2 Schematic representation of the composite in Bruggeman's asymmetric effective medium theory (BAEMT).

and it is only able to correlate experimental data, so no predictions can be drawn. The model has been extended to issues where the conductivity is frequency dependent [57, 86].

In the eighties, McLachlan [73] proposed a general effective media equation (GEM) to describe composite systems. The GEM, in addition to usual independent variables (Y_i and φ_i), contains the same parameters (φ_c and t) of the percolation equation:

$$\frac{\varphi_1\left(Y_1^{1/t} - Y_C^{1/t}\right)}{Y_1^{1/t} + AY_C^{1/t}} + \frac{\varphi_2\left(Y_2^{1/t} - Y_C^{1/t}\right)}{Y_2^{1/t} + AY_C^{1/t}} = 0 \qquad (8)$$

where $A = \frac{\varphi_c}{1-\varphi_c}$. The two parameters, φ_c and t, as in the percolation theory, are the critical volume fraction of the poorly conducting phase and the factor accounting for the distribution (oriented, partially oriented or random) and the shape of the particles. Unfortunately the two parameters, φ_c and t, are difficult to calculate and can only be obtained by fitting the GEM equation to experimental data; then the equation itself cannot be predictive.

This equation is, in principle, valid at any volume fraction and not only near the percolation threshold. In fact, it was not derived from any physical model, but from the extension of EMT to specific cases. It was demonstrated, just in the d.c. regime, that under proper assumptions Equation 8 becomes the BLM, BAEMT or BSEMT [73]. Until now GEM has been mainly applied to describe the conductivity of insulator and purely resistive conductor mixtures [73, 87, 88].

2.2. Discrete medium models

At the beginning, these models were used to calculate the parameters of the percolation equation [49, 85] and only later they became self-standing approaches to simulate the electrical properties [50–54]. Such a technique, named the electrical network model (ENM), has been used in computational materials science to simulate the electrical response of cement-based systems [89], Ni-YSZ cermets [90–92] and ionic conductor composites [60, 93–95].

The conversion of the system into a 2D- or 3D-electrical network (constituted of discrete circuit elements) and its solution by a computing procedure are the working principles. Generally, the electrical network is generated connecting the sites of a lattice, superimposed to the material, by discrete electrical circuit (i.e. parallel RC), each of them describing the electrical behaviour of any different phase. Random [90–92] and ruled [60, 89, 93–95] distributions of the electrical circuits characterise the different models.

Some distributions take into account the composite microstructural features that can be derived from digital image [89] or by simulation [93, 95]; the latter approach allows "*ab initio*" modelling and suitable tailoring of the composite might be hypothesised.

The electrical network characteristics are obtained by Kirchoff's current law, solving either a set of linear equations [96] or an iterative-adjusted matrix [97]. Both the methods have advantages and drawbacks; the former is less time consuming while the latter always gives convergence and is more stable. The use of these simulations is not trivial: the computing procedure is hard and the algorithms have to be developed *ad hoc*; nevertheless reliable results seem to be obtained. In particular, the impedance spectra of Al_2O_3/YSZ composites were simulated and good agreement with experimental data achieved [93, 95, 98, 99].

Other models are not considered here because some are useless for practical applications [100–103] and some others were designed for specific inhomogeneous materials [104, 105].

3. Results and discussion

In order to evaluate the reliability and the forecasting power of the different models they were tentatively applied to the Al_2O_3/YSZ composites. In particular, some Impedance Spectroscopy (IS) spectra were simulated and compared with the experimental data. Among the reviewed models only those having a predictive intrinsic nature have been chosen. Some can be easily used while others need a more structured approach; the latter are of course more time consuming. Such characteristics in addition to accuracy and flexibility might contribute to defining a figure of merit for each model.

Cubic YSZ (7,54 mol%Y_2O_3)-Al_2O_3 (5 wt%) composite, whose experimental electrical properties (bulk and grain boundary conductivity) [41] and microstructure [106] are known, was chosen as a reference to compare the results of the simulations.

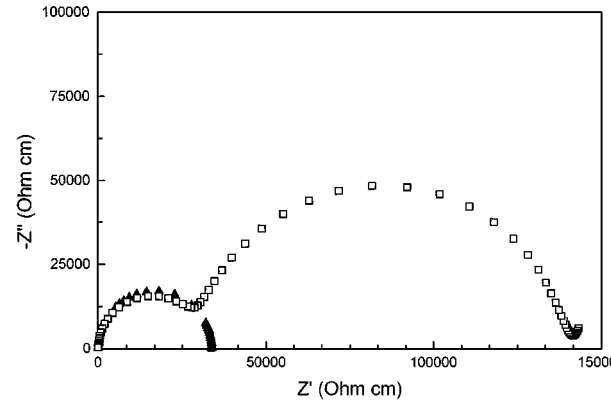
In the case of BLM, MWM and BSEMT it is impossible to take into account the grain boundary contribution,

no term referring to it is contained in the analytical equations. It should be possible to add a third term, but the conductivity and the volume fraction amount of the grain boundary are difficult to define: particle size does not enter in the model and a true phase is not present. For this reason bulk electrical conductivity and the real part of the permettivity (dielectric constant) of each phase as well as the volume fractions were the only input parameters. The electrical properties of YSZ ($\sigma_{YSZ} = 2.9 \times 10^4$ Ohm cm, $\varepsilon_{YSZ} = 8.0 \times 10^{-11}$ F/cm) and Al_2O_3 ($\sigma_{Al2O3} = 1.0 \times 10^{14}$ Ohm cm, $\varepsilon_{YSZ} = 8.0 \times 10^{-13}$ F/cm) were obtained from experimental data performed on polycrystalline samples [41, 106] and from the literature [107], respectively. The models clearly fail in reproducing the electrical behaviour of the composite; the two semicircles of the experimental spectrum do not appear in the simulated ones (Fig. 3a, b and c). The total (bulk + grain boundary) experimental resistivity is always larger than the calculated one. One never obtains a complete separation of the two semicircles using the dielectric constants actual values; two distorted semicircles appear in the spectrum only when the insulating phase volume fraction is greater than 0.2. This is an artefact: the grain boundary is not simulated, but it is the contribution of the second phase that appears; the same behaviour has already been noted by Kleitz *et al*. [71].

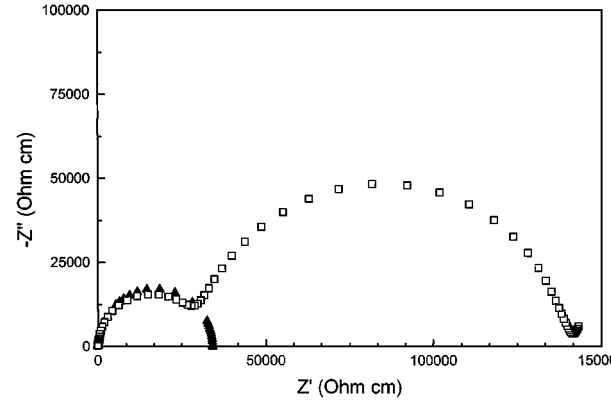
The simulation obtained by running the BLM (Fig. 3c) shows a straightline in the experimental frequency range (1–10^7 Hz). This is not surprising because, according to this model, the current flux is also forced to cross the small amount ($\varphi_{Al2O3} \approx 0.1$) of insulating phase and lower frequencies are necessary to observe the semicircle due to the alumina. A more detailed analysis points out the existence of a distorted semicircle, at the highest frequency (Fig. 3d), the presence of which is due to the YSZ. This model appears more powerful than MWM and BSEMT; the electrical properties of the two phases are evidenced. Again, the grain boundary can not be simulated.

To overcome the inadequacy of the models above mentioned, one might use Maier's model [78] that does not take into account the grain boundary contribution, but it introduces a term representing the space charge region. Nevertheless, the difficulty to manage this approach arises in assigning the grain boundary proper values of β_i, φ_i and Y_i. In particular, φ_i and Y_i might be evaluated according to assumptions similar to those proposed by Maier. The β_i value is really very difficult to forecast, being associated to the distribution topology of the dispersed phase. At the present, the lack of any method able to reliably define β_i values for ionic conductor composites invalidates the predictive nature of the model; for this reason Maier's model was not applied here. The same reasoning applies to Uvarov's model [59].

The ENMs work with *ad hoc* software codes that generally are not common knowledge; thus only one model was used to perform the simulation [93, 95]. The microstructure simulation, the conversion into a 3-D electrical network and the impedance calculation are the main steps of the procedure. The Voronoi tessellation



(a)



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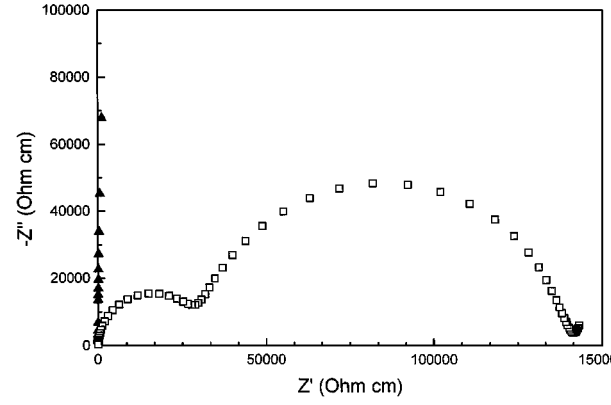
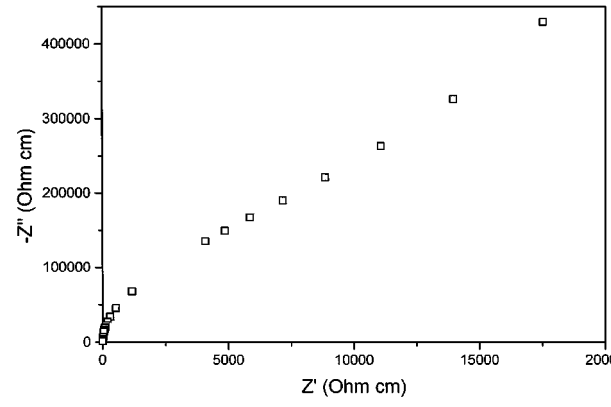


(c)



(d)

Figure 3 Experimental (□) and simulated (▲) IS spectrum of YSZ (7, 54 mol%Y_2O_3)-Al_2O_3 (5 wt%) composite, at $T = 614$ K. The simulated spectrum was obtained by: (a) MWM model, (b) BSEMT model and (c) BLM model; (d) expanded view, at lower frequencies, of (c).

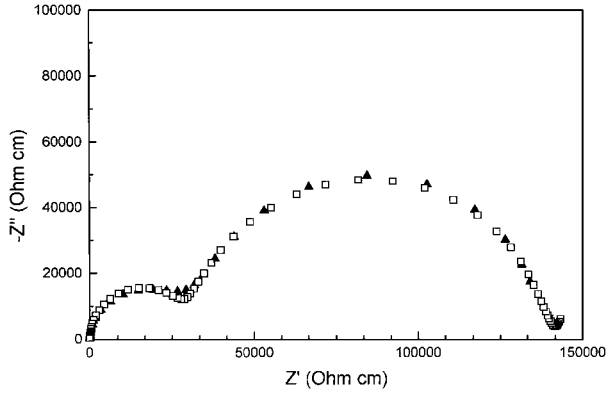


Figure 4 Experimental (□) and simulated (▲) IS spectrum of YSZ (7, 54 mol%Y_2O_3)-Al_2O_3 (5 wt%) composite, at $T = 614$ K.

was used to depict the polycrystalline microstructure, well defined rules were applied to generate the electrical network (constituted of RC parallel circuits) and the transfer-matrix method was run to calculate the impedance spectra. The grain boundary contribution was accounted for in the network generation.

By least square fitting of the experimental IS spectra of any YSZ-Al_2O_3 composite, the R and C values of YSZ grain boundary and bulk can be evaluated and successively used. The R and C value of YSZ bulk can be also obtained from polycristalline YSZ. The electrical properties of alumina were taken from literature. The microstructure simulation was performed in such a way to reproduce the experimental average grain sizes (YSZ $\approx 5\ \mu$m, $Al_2O_3 \approx 1\ \mu$m).

A comparison between simulated and experimental IS spectra is reported in Fig. 4; as one can observe a fairly good agreement exists; this model is able to generate a two semicircle spectrum, representing the bulk and the grain boundary of YSZ, respectively.

The forecasting power of the ENMs clearly appears from this result; the capability of simulating an experimental spectrum is not their unique prerogative, but the electrical properties of a composite as a function of its microstructure and composition is, in principle, an additional distinctive feature. The flexibility was previously shown when the influence of both YSZ and Al_2O_3 grain size on the electrical properties of the composites were simulated with promising and challenging results [99].

Unfortunately the lack of extended and systematic experimental works makes a wide comparison with the theoretical results very hard, so the real power of these ENMs can not yet be fully assessed. However from the preliminary results, it seems possible to affirm that the Electrical Network Models better sustain the simulation, even if they are much more demanding in software codes and in computing time.

The current version of the ENM is certainly not optimised and many other improvements have to be implemented before they might become suitable and confident theoretical tools for tailoring "*ab initio*" the electrical properties of composites, nevertheless this approach appears, at the present, to be very promising.

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