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Impedance Spectroscopy Spectra Simulation of Yttria-Stabilised Zirconia / Alumina Composites

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Abstract. To simulate impedance spectra of yttria-stabilised zirconia/alumina composites a digital-image-based model has been developed. The computer simulation generates the polycrystalline microstructure of the material exploiting the Voronoi tessellation technique. Then a 3-D network of cubes is superimposed to the simulated polycrystalline microstructure and the edges of each cube substituted with discrete RC parallel electrical circuits. The composite is, in such a way, converted into a three-dimensional electrical network whose impedance has been calculated at different frequency values. The numerical solution has been performed via an iterative method based on a matrix non-linear recursion relation. Results of the simulation are presented and compared with experimental data.

Keywords. YSZ/Al_2O_3 composites, impedance spectra simulation

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1. Introduction

In recent studies [1-3], composites based on cubic yttria-stabilised zirconia (YSZ)/alumina have been proposed as electrolyte for planar SOFC; in fact, the presence of alumina as second phase improves the mechanical properties of the electrolytic layers.

Microstructural, mechanical and electrical properties of cubic 7.54mol%YSZ/Al_2O_3 with alumina contents of 5-10-15wt% have been recently investigated [4,5]. It has been shown that the bending strength is maximum at 10wt% Al_2O_3 and, in agreement with Fukuya et al. [2] and Mori et al. [3], the ionic conductivity decreases with increasing alumina content. In the same work [4], complex impedance spectra show large anomalous grain boundary semicircles which have been attributed to a relatively high impurity content in the alumina powders [6] .

Although large efforts have been spent to investigate the role of the grain boundary phase and its influence on resistivity in ZrO_2-based electrolyte systems [7-12], no definitive conclusions have been reached. The present work might be a contribution to a better understanding of the above mentioned problem.

2. Experimental

Powders of 7.54mol%YSZ have been mixed with 5 (5AZ), 10 (10AZ) and 15wt% (15AZ) of Al_2O_3 by ball milling for 4 hours; then uniaxially pressed and sintered at about 1500 °C for 4 hours, in air[4,5].

The phase composition in the sintered pellets has been checked by x-ray diffraction; the microstructure investigated by scanning electron microscopy (SEM) and the electrical conductivity obtained by Impedance Spectroscopy.

3. Computational techniques

A digital-image-based technique has been used to develop the model. This approach presents the advantage to show if the simulated microstructure is able to reproduce an actual SEM image, at once. Generally, these models need large computer resources which are usually provided by parallel systems. Preliminary results concerning the simulation of a limited dimension specimen and obtained on a scalar computer are here presented.

The computer simulation goes through three steps: the material microstructure construction, its conversion into a 3-D electrical network, and the calculation of the impedance spectrum.

3.1 Microstructure simulation

The sample microstructure has been obtained using the three-dimensional Voronoi tessellation [13], a well known technique to simulate polycrystalline materials [14]. A set of sites A_j (with co-ordinates randomly generated in the present case) are located in a volume V_m having parallelepipedal shape; then the whole volume is partitioned in convex hulls. Each set of points, in V_m, assigned to the nearest site A_j generates a convex hull (Voronoi assignment model)whose ensemble is the so-called Voronoi diagram of the sites set. As an example, in figure 1 is reported a 2-D Voronoi diagram of a set of ten A_j sites. An original algorithm to create Voronoi tessellation has been developed and used.

In the present simulation the volume V_m stands for a block, with defined dimensions, of composite and the convex hulls represent its grains. Once assigned the geometrical dimensions of the block, the homogeneous grain size distribution is obtained constraining the distances among the first-neighbour sites A_j to be greater than a minimum value. The average grain size is achieved imposing the number of sites per unit volume; in this way the most relevant features of the microstructure of the YSZ are simulated. Then the alumina phase has been simulated randomly locating, at the YSZ grain boundary, additional hulls, whose dimensions and amounts are consistent with the above mentioned specimens.

3.2 Three-dimensional electrical network construction

In order to simulate the electrical behaviour of the composite, a 3-D cubic units network has been successively superimposed to the above Voronoi diagram (see figure 2) and an electrical discrete circuit have been assigned to each edge of every cube. An electrical discrete circuit can be either a single element or a combination of them. To account for the electrical behaviour of the pure YSZ it seems reasonable to consider two different types of edges: one representing the bulk and the other the grain boundary. The edges inside YSZ grains (B) and those crossing two different grains (GB) are considered as representative of the bulk and the grain boundary electrical behaviour, respectively. To simulate the composites a third type of edge (A) has to be introduced to represent the alumina phase electrical behaviour.

The physically consistent electrical circuit assigned to each B and GB edge is a combination of resistance and capacitor in parallel, while a single capacitor is the equivalent circuit of A edge, considering the resistivity of alumina to be infinite. The electrical behaviour of the electrodes is not considered in the present simulation.

In figures 3 and 4 a schematic view of the 3-D network and a detailed electrical circuit of one part of its planar section are reported, respectively.

3.3 Algorithm for computing impedance

In the past several methods have been developed to solve numerically random electrical networks; the resolution of Kirchoff's equations by relaxation methods [15] and techniques based on the node elimination [16] were the most frequently used. The former is sometimes slow convergent while the latter needs very sophisticated computer codes; nevertheless both are computationally time consuming.

A different approach based on matrix non-linear recursion relations [17], similar to the transfer-matrix method of statistical mechanics, has been adopted to solve electrical networks. In the present case because the frequency is a variable, more sophisticated algorithms than those for d.c. regime are necessary.

4. Results

Experimental and computational results are here reported in two different paragraphs.

4.1 Experimental results

Cubic YSZ and alumina are the only phases present in the composites, as checked by x-ray diffraction spectra. Figures 5a and 5b are typical micrographs of the YSZ and the composite, respectively. As one can observe the average grain size of YSZ is about 6 μm. Alumina grains are randomly distributed in the composite and their average dimension is about 1μm.

Typical complex impedance spectra are reported for three different composites at about 610 K in figure 6. As one can observe three semicircles are present; moving from lower to higher frequency values the contribution of the electrode, grain boundary and bulk are represented.

4.2 Computational results

To perform the simulation the V_m (volume of the composite considered) has been chosen to be represented by a parallelepiped having a section of 600 x 800 pixels and length of 350 pixels (40 pixels correspond to 1 μm); inside V_m twenty-five A_j sites, having a minimum distance grater than 100 pixels, have been located. These figures are consistent with the experimental SEM micrograph . Fifty pixels is the dimension of the 3-D cubic units; such a value is a good compromise between reliable simulation and moderate computing time.

Using the pure YSZ Nyquist experimental diagram (see figure 7) the relative values, at 610 K, of the electrical elements (in arbitrary units) of the edge B and GB have been calculated: the ratios C_{GB}/ C_B and R_{GB}/R_B are about 10^5 and 10^6, respectively; these values are not relative to the actual specific conductivity. To the alumina capacitance it has been assigned a value 4 order of magnitude lower than that of pure YSZ bulk.

According to the above figures the simulation of impedance spectroscopy spectra of the three composites 5AZ, 10AZ and 15AZ has been performed, at 610 K, and the results reported in figure 8. According to the assumption of neglecting the electrical behaviour of the electrodes the simulated spectra present only two semicircles. Differences between experimental and simulated spectra are present. In the experiments [4] the grain boundary resistance increases with the alumina amount while the bulk conductivity is almost constant and grain boundary electrical resistance values are always greater than those of bulk. As above mentioned, the large grain boundary resistance was attributed to the presence of a relatively high impurity content in alumina powder.

In simulated spectra too the grain boundary conductivity values decrease with the alumina content and the bulk conductivity appears to be constant, but the grain boundary resistance values are never larger than those of the bulk. Such result, not in agreement with the experimental spectra, is however consistent with the electrical model used, in fact the influence of the alumina impurities have not been considered. Nevertheless it should be possible to reproduce the experimental results if the values of the electrical elements of the pure YSZ are used as parameters. Preliminary calculations (see figure 9) show that the model is able to modify the relative dimension of the semicircles.

5. Conclusions

The results of the simulation of the experimental YSZ/alumina composites complex impedance spectra seem to be unsatisfactory. Nevertheless the model works quite well: using the pure YSZ electrical elements, without taking into account the influence of the alumina impurities, the simulated spectra are different from the experimental ones and variations of the electrical elements values are able to modify the shape of the spectra. Because it has been demonstrated that the experimental electrical elements values play an important role it can be supposed that using proper experimental data the results of the simulation might be quite faithful to the reality. These preliminary outcomes are encouraging and it appears convenient to progress the work to verify the true capability of the model proposed.

6. References

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CAPTIONS TO FIGURES

Figure 1. Two-dimensional Voronoi diagram of a set of 10 sites.

Figure 2. View of a planar section of the simulated composite with the superimposed cubic network.

Figure 3. Schematic view of a part of the three-dimensional electrical network.

Figure 4. Section of the network: detailed view of the electrical circuit.

Figure 5. SEM micrograph of pure YSZ (a) and of 15AZ (b) composite.

Figure 6. Experimental Nyquist diagrams of 5AZ (a), 10AZ (b)and 15AZ (c) at about 610 K.

Figure 7. Experimental Nyquist diagram of YSZ at 610 K.

Figure 8. Simulated complex impedance spectra (in arbitrary units) of 5AZ (a), 10AZ (b) and 15AZ (c).

Figure 9. Simulated complex impedance spectra (in arbitrary units) of 5AZ obtained by electrical elements values different from pure YSZ (both C_{GB}/C_B and R_{GB}/R_B are about 10^9).

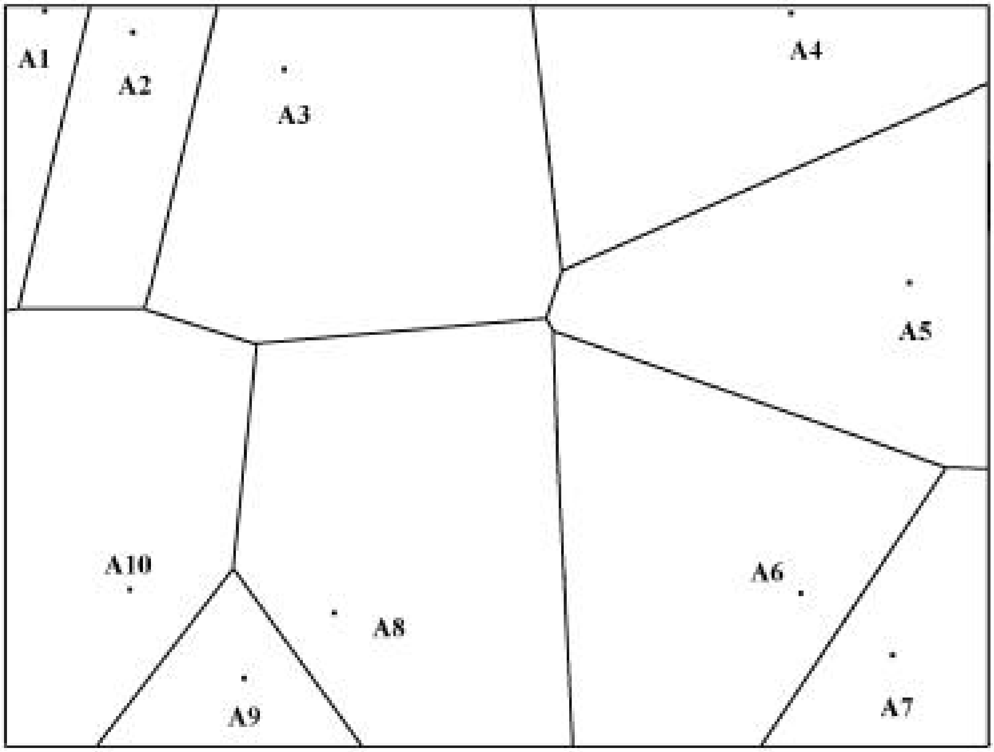


Figure 1

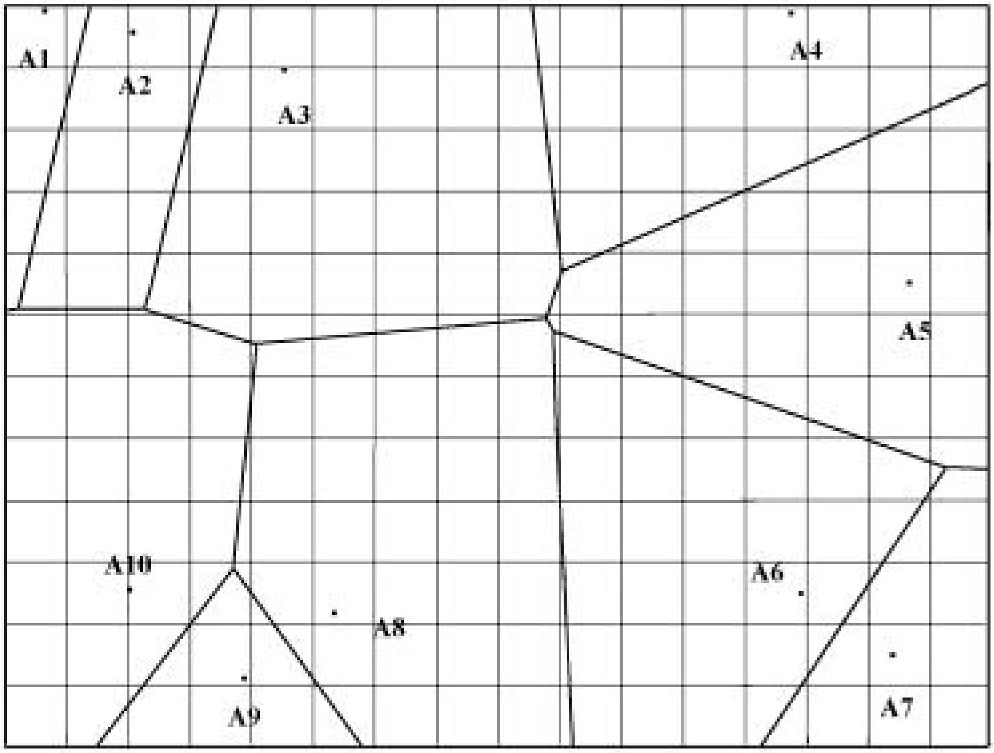
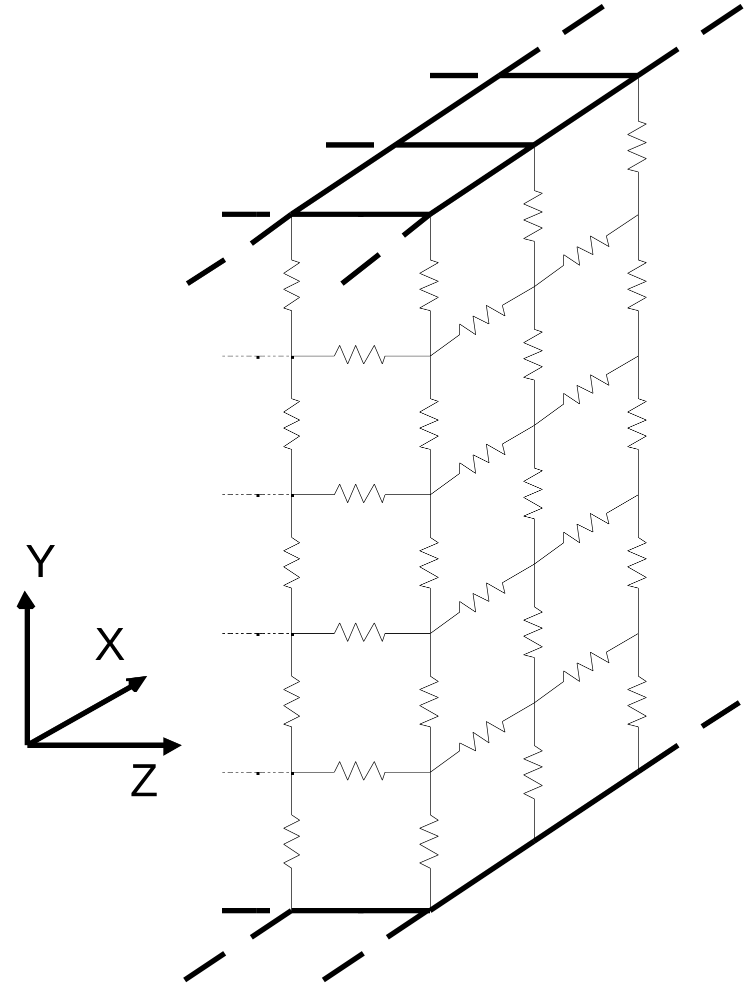


Figure 2



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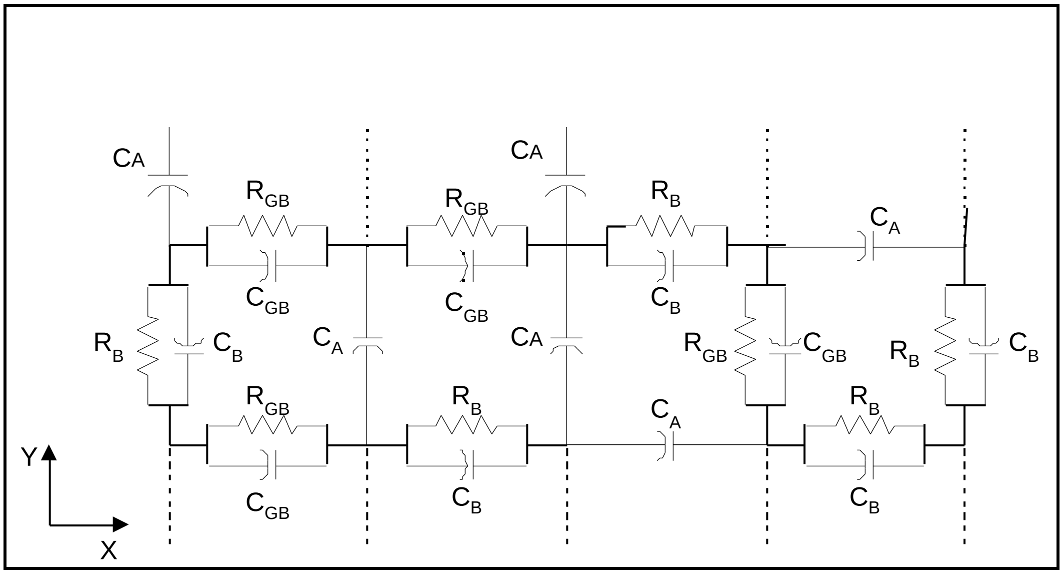
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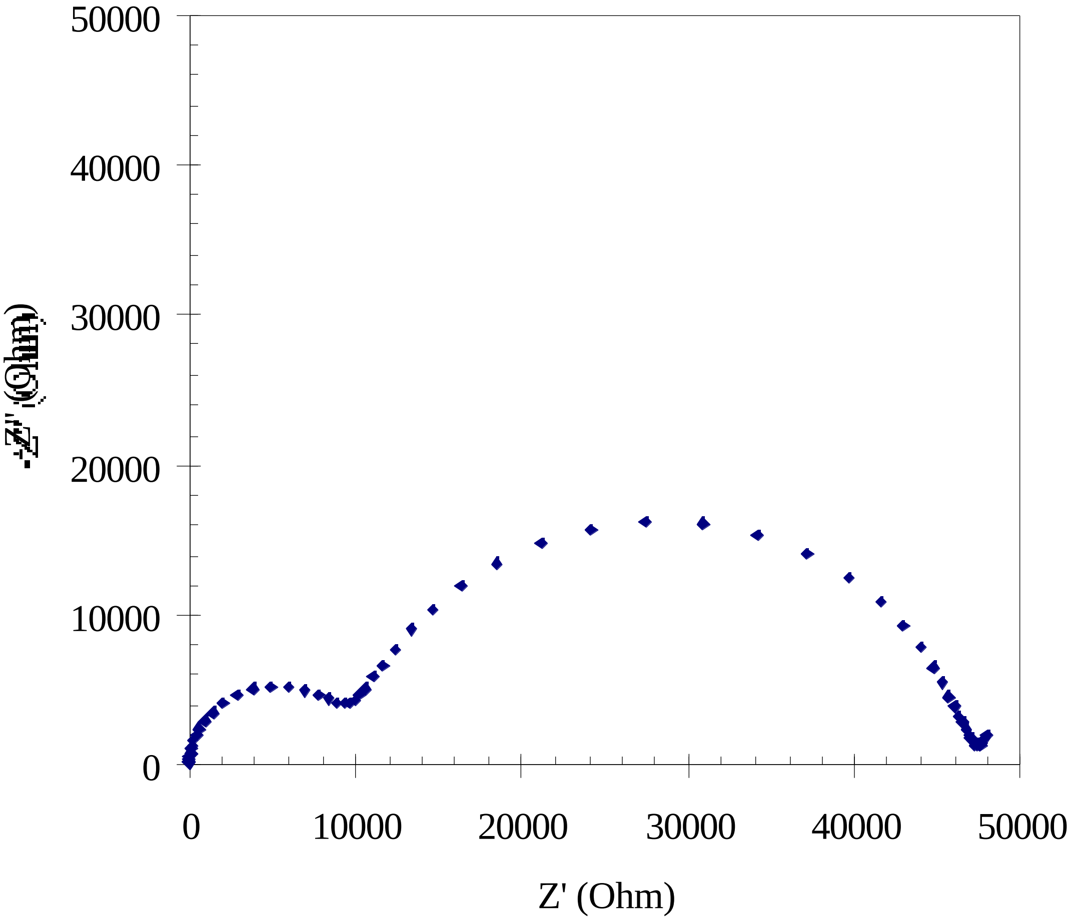
Figure 4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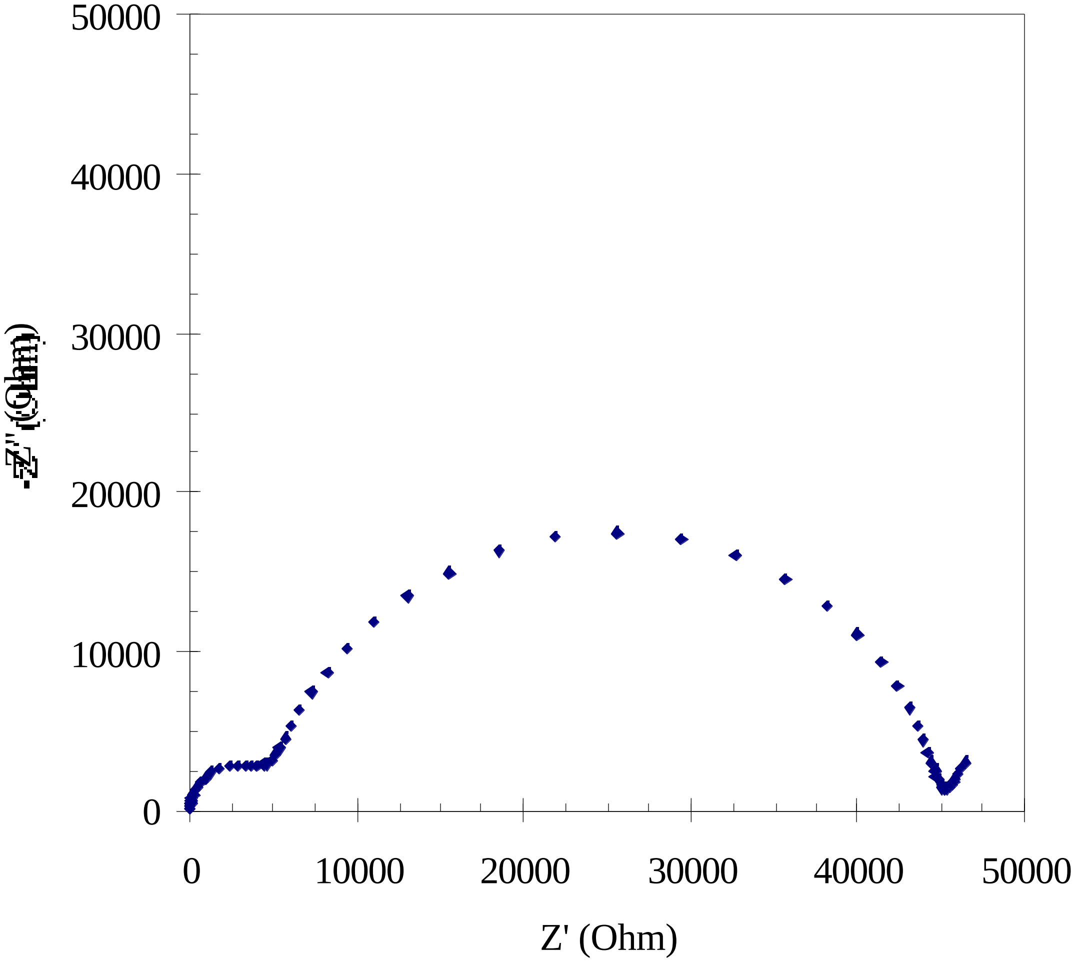
-Z'' (Ohm)
Z' (Ohm)

Figure 6a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Z' (Ohm)

Figure 6b

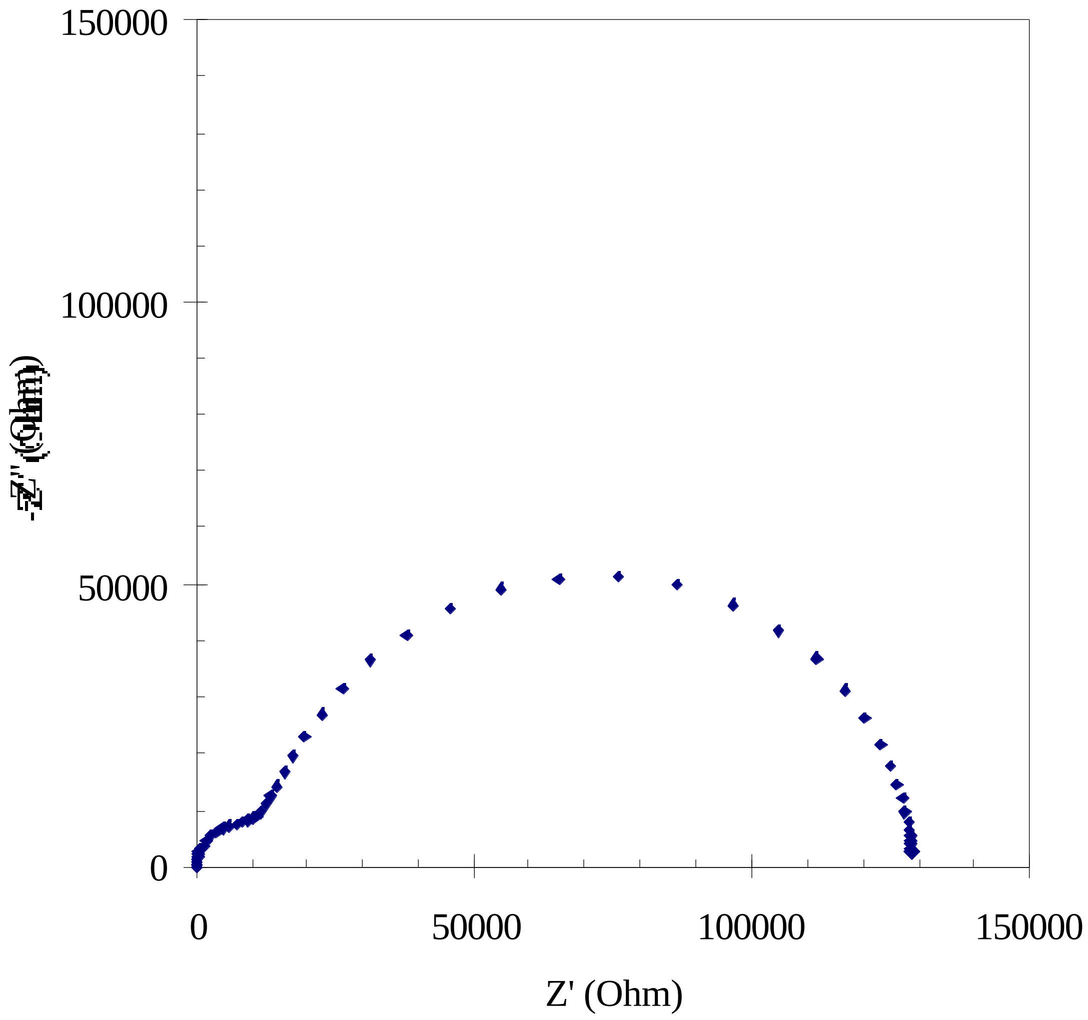

Figure 6c

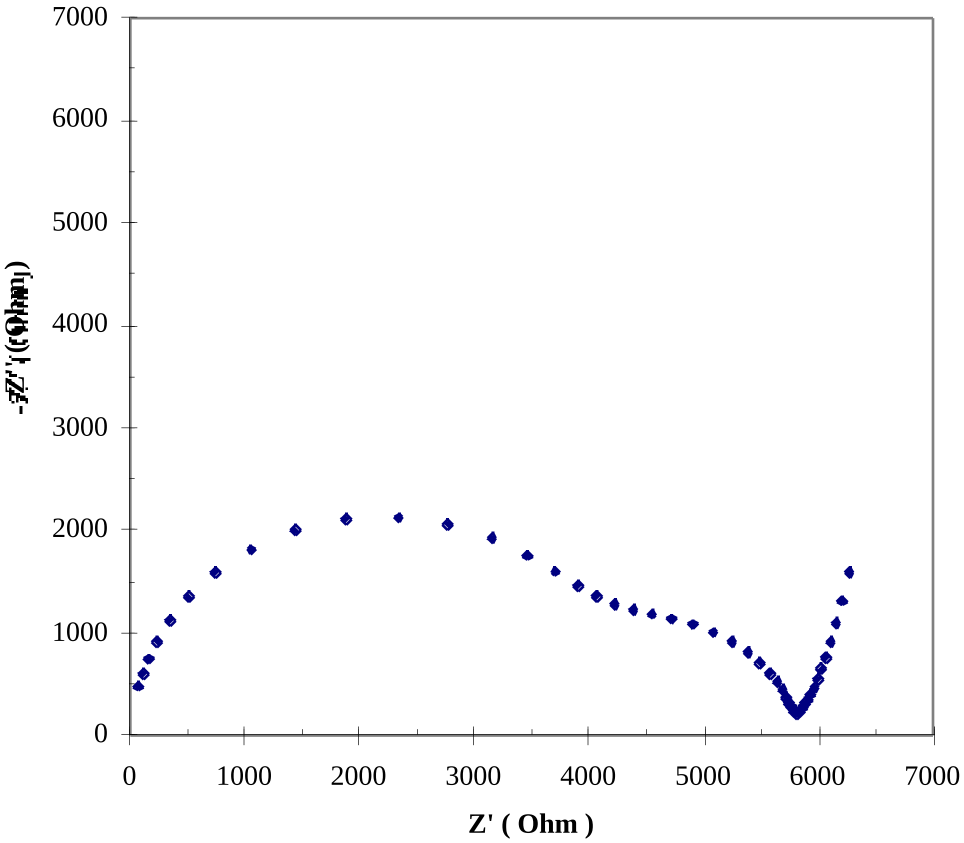

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Figure 7