Simulation of the Impedance Response of Materials with More than One Electrical Path

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Abstract: Materials and devices can often contain multiple interfaces that may or may not participate in the active function of a given material or device. However, they are often only evaluated at the specific frequency of application or in dc mode, which essentially disregards the rich information that the full frequency spectrum can contain. This causes a lot of useful information, which could be used to help understand their electrical behaviour, either for quality control, life prediction, reliability or basic understanding, to be lost. In this article, we utilize a combination of COMSOL Multiphysics simulations and equivalent circuit modelling to demonstrate the advantages of considering broadband ac measurements as a way to develop more detailed understanding of materials with more than one electrical path.

Keywords: COMSOL Multiphysics, impedance spectroscopy, polycrystalline materials, grain size effect, percolation

1. Introduction

Polycrystalline single phase materials often display electrical properties that are a function of their grain size. One of the best ways to characterize the properties of the bulk grains and the grain boundaries is to use an alternating current technique, known as impedance or dielectric spectroscopy[1]. This method is ideal for detecting the presence of more than one current path. The reasons for the different response from the grains and the grain boundaries is that electrically, the region around the grain boundaries is necessarily different due to the presence of defects, inadvertent impurities and segregation of certain materials towards or away from the boundary. It was originally thought that that it was necessary to have a completely different phase located at the boundaries[2], but minor compositional changes and/or the presence of defects can also give rise to different current patterns due to space charge build up or other effects[3]. However, because the properties of the boundaries are often very different than that of the bulk grains, it is useful to consider treating them as if they were made up of two different phases. Therefore, concepts developed to explain composite materials, such as effective media, connectivity of phases and percolation [4] may be able to be used to derive better understanding of the properties of polycrystalline materials as a function of grain size, defect density or the presence of inadvertent impurities.

Such a modeling effort becomes even more important in the case of nanocrystalline materials which have comparable volume fraction of grain boundaries and bulk grains due to the high surface areas these materials possess[5]. Such materials have been shown to display tremendous variations in their mechanical behavior[6], electrical properties[7] and sinterability as a function of grain size, heat treatment or other external forces[8].

The finite element model being used here was first developed to represent an ordered insulator-conductor composite with a segregated network microstructure[9]. Using such a model allows varying the grain size and grain boundary thickness easily. Additionally, this also permits assigning them different properties to evaluate their effect on the resultant response.

2. Use of COMSOL Multiphysics®

In this study, we use a finite element approach to solve the electric potential in the AC environment for an idealized two phase microstructure, as depicted in Figure 1. The faceted grains represent the main material phase and the boundary region has finite thickness and distinct electrical properties that may or may not percolate with itself[9]. A numerical calculation of the impedance, capacitance, and related quantities naturally requires the solution of the electric fields in the material under an applied electric potential or electric current. In the case of impedance measurements the potential/current is usually time harmonic[10]. Maxwell's equations, in terms of electric potential, can be simplified as equation (1), assuming no externally generated current.

$$\nabla \cdot \left(\sigma + \varepsilon_r \varepsilon_0 \frac{\partial}{\partial t} \right) \cdot \nabla V = 0 \qquad (1)$$

Equation (1) can be rewritten as equation (2) by replacing time derivative and electric potential by $1/j\omega$ operator and potential phasor, respectively, since time harmonic analysis is appropriate for the impedance calculations

$$\nabla \cdot \left(\varepsilon' - j\frac{\sigma}{\omega} \right) \cdot \nabla \tilde{V} = \nabla \cdot \left(\tilde{\varepsilon} \nabla \tilde{V} \right) = 0 \qquad (2)$$

where ε = $\varepsilon' - j\sigma/\omega$ is complex permittivity and $\tilde{V}$ is the potential phasor amplitude. The electric field can be obtained by evaluation the gradient of potential phasor amplitude[10].

The steps used in the simulation include: (1) Selecting time harmonic-electric currents solver in the AC/DC module in COMSOL Multiphysics®, (2) Defining the electrical properties inside the grains and the grain boundaries, (3) Solving and finding the electric field distributions and (4) Using post-processing capabilities in COMSOL Multiphysics® to determine the impedance response.). An electric shielding boundary condition was applied to demonstrate thin grain boundary domains which can reduce the number of mesh elements.

A forced voltage port electrode was applied to the top edge as a Dirichlet boundary condition, while a ground electrode was applied to the bottom edge of the geometric model. The electrical insulation was applied to the side edges as a Neumann boundary condition $n \cdot J = 0$. An electric shielding boundary condition was applied to demonstrate thin grain boundary domains, which can reduce the number of mesh elements.

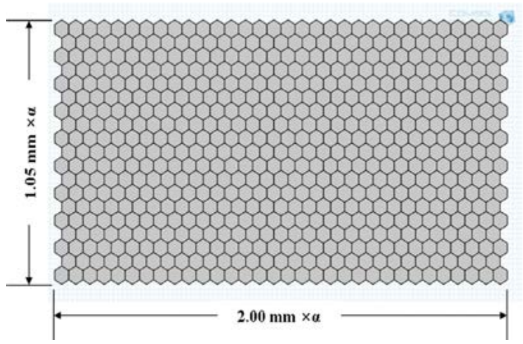
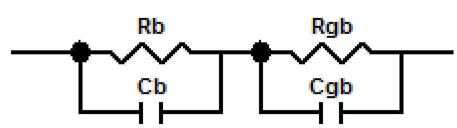


Figure 1. Schematic of the geometric model used for the simulations. The parameter α was used to modify the size of the grains and width of boundaries as well as the electrical conductivities of the two regions.

3. Impedance spectroscopy and equivalent circuits

Figure 2 illustrates simulated equivalent circuit complex impedance spectra for a series of cases where the grain boundary resistance, R_{gb}, is greater, equal to or smaller than the bulk grains, which have resistance R_{bulk}. The simulations utilized $C_{gb} > 10^3\, C_{bulk}$. The equivalent circuit is shown below.

Since most materials can be represented by a combination of a resistance R and a capacitance C in parallel, it has long been accepted that two distinguishable electrical paths in series can produce two semicircles if the RC time constants are separable [1,2]. It is clear that changes in the conductivity of the main grains may or may not be detected, depending on whether the grain boundaries are more or less conducting than the matrix grains.



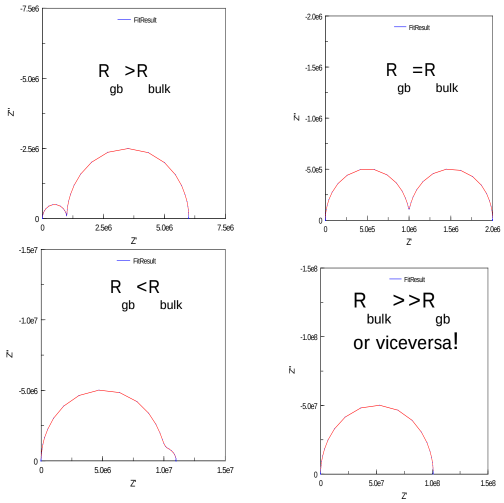


Figure 2. Simulated complex impedance spectra when the electrical response of the boundaries is equal, larger or smaller than the main phase grains. Modified from ref[1].

4. Results

The FEA results were obtained for four different percolated cases with 0.15 vol% occupied by the grain boundaries and one unpercolated case containing the same fraction of grain boundaries.

The majority of the simulations were obtained by keeping the size of the bulk grains constant at 100 μm and 60 nm for the grain boundary width. Some evaluations of changing the bulk grain size and the width of the grain boundaries were also conducted.

4.1 Effect of bulk grain and grain boundary conductivity

Figure 3 displays the impedance response for the case where the bulk grain conductivity was kept constant at 10^{-3} S/m and the conductivity of the grain boundaries was allowed to vary from 10^{-5} S/m up to 1 S/m. For such a situation, we found that the impedance is mostly dominated by the bulk grain properties until the conductivity of the grain boundaries exceeded the bulk grain conductivity by 10^{2} (i.e. σ_{gb} = 0.1 S/m).

One can see in Figure 3 that the overall impedance began to decrease in this case. Furthermore, once 1 S/m is reached, the contributions from the grain boundaries cannot be distinguished separately.

It is to be noted that the trends observed here do not follow the well accepted 2 parallel RC circuit in series described earlier. The reasons for this discrepancy have to do with the fact that the percolated path contains conductive channels that occur in the direction of the field and perpendicular to it so that neither semicircle observed in the impedance spectrum is directly related to the initial values of R_{bulk}, R_{gb}, C_{bulk} or C_{gb}. Transformation of the impedance into other dielectric functions such as admittance, electric modulus or permittivity would help to separate these different effects[11], but this is beyond the scope of this short paper.

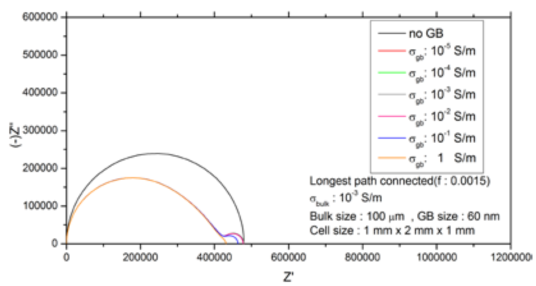
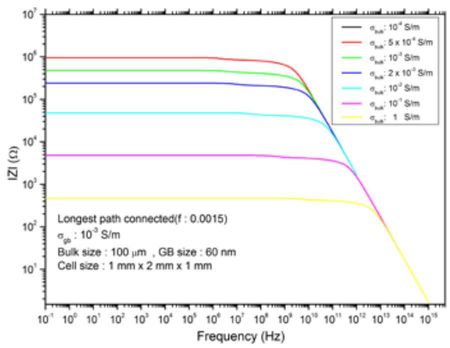


Figure 3. Complex impedance graph for a system with 100 μm size grains and 60 nm thick grain boundaries that percolate. Effect of changing the grain boundary conductivity is demonstrated.

In contrast, changing the bulk grain properties, while keeping the grain boundary properties constant at 10^{-3} S/m, causes much greater changes to be observed. In order to more easily demonstrate the several order of magnitude changes, we show the impedance magnitude vector in Figure 4(a) and the phase angle in Figure 4(b). These are frequency explicit plots that display how a four order of magnitude change in the bulk conductivity from σ_{bulk} = 10^{-4} S/m to 1 S/m causes a four order of magnitude change in the impedance vector value.

The switch over from a frequency dependent region to a frequency independent region occurs at higher frequencies as the conductivity of the bulk grains is increased. Additionally, one can see a more clearly defined frequency dependence in the phase angle plot displayed in Figure 4(b), which also highlights the inflection caused by switching from a frequency independent region to a frequency dependent region.

(a)



(b)

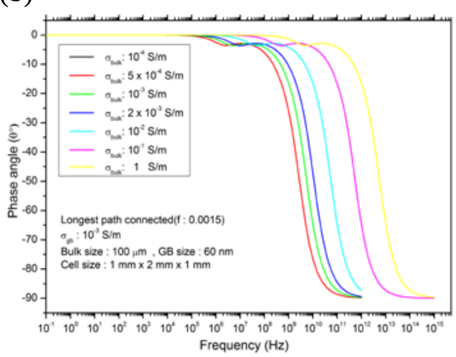


Figure 4. (a) Magnitude of the impedance vector Z plotted versus log of frequency demonstrates the huge changes observed as a result of varying the bulk grain properties. (b) Phase angle plotted versus the log of frequency for the same bulk grain indicates the huge changes obtained by varying the bulk properties.

4.2 Effect of changing grain size and grain boundary width

Figures 5 and 6 display the complex impedance response for a situation, where both the bulk grains and grain boundaries have the same conductivity of 10^{-3} S/m. Figure 5 evaluates the effect of changing the grain boundary width from 60 nm to 6 μm, while keeping the grain size constant at 100 μm. It can be seen that as the grain boundary width increases, the smaller low frequency semicircle shrinks in size. A third semicircle appears in between the two previous semicircles, and is believed to be due to bulk grain - grain boundary interactions. Except for the total impedance, which is mostly dominated by the bulk grain conductivity, none of these effects would have been predicted by considering only the bulk grain conductivity and the grain boundary conductivity properties. This suggests that percolated systems cannot be modeled by a simple series of parallel RC circuits and that one must use some additional parallel paths as was done recently for a glass-nanoparticle percolating system[12].

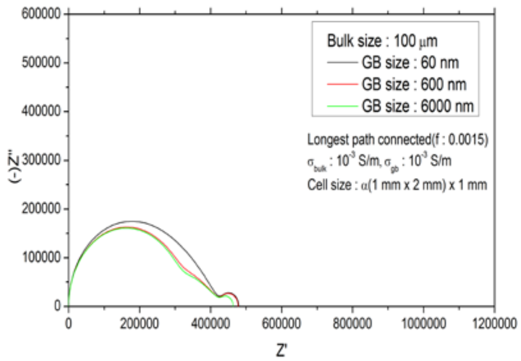


Figure 5. The effect of changing the grain boundary width in a percolated system, with 100 μm grain size.

Similarly, when we change the bulk grain size from 50 μm up to 300 μm, while keeping the grain boundary width constant at 60 nm, we can see that the overall low frequency resistance remains the same for all cases, but that the larger high frequency bulk semicircle appears depressed below the real Z' axis. A third semicircle appears in between the two and is more visible, the smaller the bulk grain size is. This is believed to represent the grain boundary-bulk interactions discussed earlier.

In all of the cases discussed above, the grain boundaries have been allowed to percolate, i.e. form an inter-connected conducting path within the structure. One interesting result is that in all of the conditions evaluated, the semicircles appear below the axis suggesting a wide variety of similar paths (often represented by a constant phase element or CPE[13]).

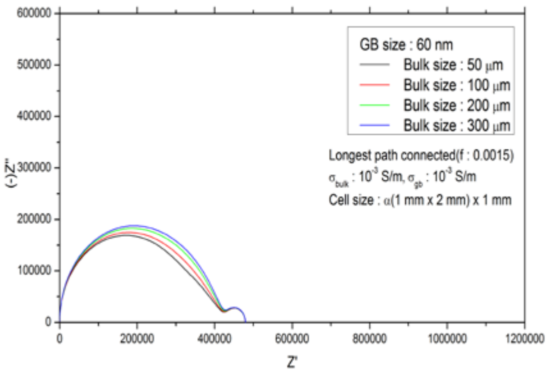


Figure 6. The effect of changing the bulk grain size, in a percolated system, with 60 nm grain boundary width.

Furthermore, these results suggest that any variation in the properties of real materials caused by different quality of contact between them or variations in their physical dimensions will always result in such deformed semicircles. This was recently demonstrated in a series of complex impedance curves for percolated glass-ATO composite specimens [12], which were fitted by a much more complicated equivalent circuit that includes some parallel RC circuits in series followed by an alternative parallel path and a series LR circuit as shown in Figure 7. It is easy to see how such variations may lead to a multitude of very similar but not identical contacting regions in between conducting particles that will give rise to result in the types of interfaces described. Other experimental evidence for differences in the quality of contact can be found in ref. [14].

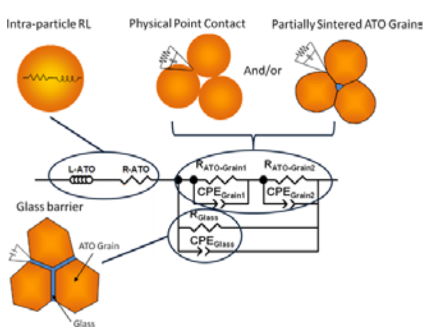
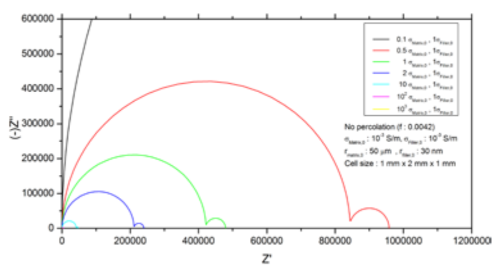


Figure 7. Equivalent electrical circuit that includes different types of paths and interfaces. Taken from reference[12].

4.3 Impedance spectra for specimens with percolated and unpercolated grain boundaries

The previous sections have presented the effects of varying the properties of percolated grain boundaries as a function of grain size, grain boundary width and bulk and grain boundary properties. In this section we will compare the expected complex impedance response for percolated and unpercolated structures using the same grain size and grain boundary area. Figure 8(a) and (b) present complex impedance spectra for a series of samples with different bulk grain conductivity and a constant grain boundary conductivity of 10^{-3} S/m. It can be seen that the series for the unpercolated grain boundaries give rise to perfect semicircles, while the percolated samples show semicircles depressed below the axis. As before, the total conductivity is mostly dominated by the bulk grain conductivity but neither value of the conductivity of the grains and/or grain boundaries is directly obtained. It is noteworthy that as the conductivity of the bulk grains increases, the two semicircles act in tandem.

(a)



(b)

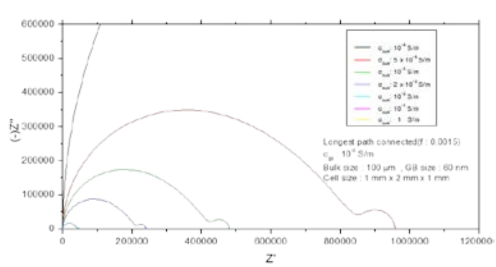


Figure 8. (a) FEA simulated complex impedance spectra for an unpercolated and a percolated material as a function of the conductivity of the bulk grains while keeping the grain boundary properties constant.

In Figure 9, we compare one of the unpercolated curves obtained with the same exact material parameters, as one of the percolated structures. It can be seen in figure 9 that the intercepts of the two semicircles fall at approximately the same value but that the percolated structure gives rise to high depression angles, all of which signify that percolated patterns provide even more possible alternate current paths that have ever so slightly different values and result in more deformed semicircles.

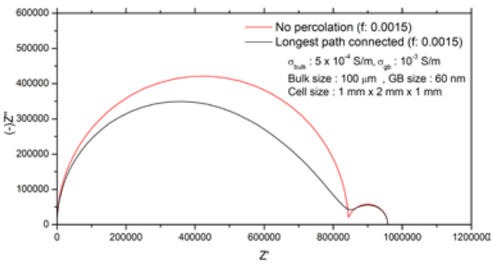


Figure 9. Comparison of the complex impedance curve for an unpercolated and a percolated grain-grain boundary system where all physical properties and dimensions are the same.

5. Conclusions

The FEA simulations have revealed that complex impedance semicircle shapes are very sensitive to the size and properties of the matrix grains and grain boundaries and whether the grain boundary properties are percolated or not. Combining equivalent circuit and FEA analysis will be very powerful in helping to understand the behavior of complex heterogeneous materials, as well as for any material that is undergoing a phase change or any other process that can affect the behavior of the grain boundaries separately from the matrix grains.

5. References

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