Impedance and Dielectric Spectroscopy of Nanoparticulate Films and Composites

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ABSTRACT

Nanoparticulate materials are becoming ubiquitous in a wide range of industrial applications. Such materials can be used as individual devices with appropiate doping and contacting methods. They are often made into films or used as one of the functional components in a nanocomposite. They are made into nanoparticulate films via vacuum filtration, layer by layer assembly, spin coating, dip pen nanolithography and many other techniques. When they are used in composites, they are often dispersed inside a polymer matrix via melt-extrusion, solution dispersion or microcontact printing to name a few. In all cases, these materials behave as combinations of two or more materials. Therefore, their electrical characterization is challenging due to the extreme smallness of the nanoparticulate materials and/or the properties of the materials that they are surrounded by. In this paper, we will focus on the usage of impedance and dielectric spectroscopy as an ideal method for characterization of such materials.

Keywords: ac measurements, nanoparticles, films, composites, time constants, equivalent circuits,

1 INTRODUCTION

Impedance and Dielectric Spectroscopy (IS/DS) is an electrical characterization method that uses alternating current to probe the electrical response of materials and devices at all length scales (i.e. from macroscopic dimensions down to the nanoscale). It can be used to measure the electrical behavior of insulating, dielectric, semiconducting as well as conducting materials and their mixtures[1]. IS/DS has been used to characterize a wide range of materials ranging from high temperature solid electrolytes for fuel cells, to ferroelectric thin films, bulk piezoelectric ceramics as well as insulator-conductor ceramic and polymer composites. As a result, it is an excellent technique for characterizing the properties of nanodevices, nanoparticulate thin films and nanoparticulate composites. Solid state impedance spectroscopy should not be confused with Electrochemical Impedance Spectroscopy also known as EIS, where the surface reactivity of the material being measured is probed with a liquid electrolyte. This is the method of choice for detecting corrosion of metals, formation of oxide scales as well as the sensitivity of biosensors and other materials. IS/DS is designed to detect the properties of the materials themselves rather than their interaction with a liquid electrolyte. While the surface reactivity of materials being measured can also affect the solid state electrical response detected, the underlying structure of the material can be probed by carefully controlling the atmosphere during the measurement.

Most IS/DS measurements are carried out at frequencies ranging from mHz up to the GHz range, depending on the specifications of the equipment used and the information one desires to obtain. Besides frequency, one can use temperature, atmosphere control, mechanical pressure, optical excitation or magnetic excitation as additional variables during the measurements. This paper provides some of the important information one needs to have in order to ensure that the properties that are being probed as those of the materials in question and not that of the electrical contacts or surface reaction layers that the nanomaterials form by interacting with their environment.

In addition to the external variables, one can keep the measurement conditions constant and instead vary the electrode contact size and shape[2] as well as the direction of the electric field with respect to important features of the nanostructure[3,4]. Material parameters such as the composition, the size and shape of the nanoparticles theimselves or their arrangement in 2D or 3D space as well as the quality of contact between the nanoparticles[5-10] can provide a rich canvas for study. In this paper, impedance simulations that illustrate characteristic responses for different conducting and insulating nanoparticulate thin film materials and composites will be provided.

2 IMPEDANCE RELATIONSHIPS

Most materials responses can be represented by combinations of equivalent circuit elements that include resistors (R), capacitors (C) and inductors (L). Before describing the more complex impedance plots, it is important to describe the primary trends expected.

(1) For log |Z| vs. log f Bode plots response is
   a. Flat for R
   b. Increases for L
   c. Decreases for C
(2) For phase angle θ, it is positive for inductive circuits and negative for capacitive circuits
(3) Nyquist plots (complex Z” vs Z’ plots) show semicircles only when RC or LR circuits occur in parallel.

It turns out that the ability of an experiment to detect the complete spectrum depends on the time constant of the

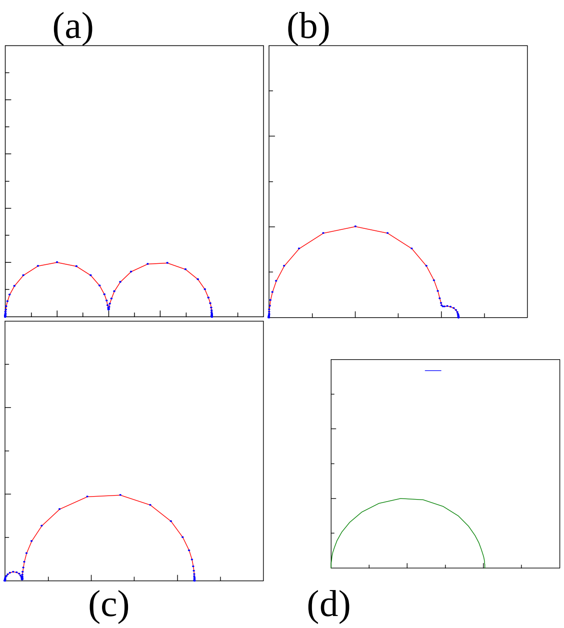

Figure 1. Effect of varying the resistance value on the Expected response of a nanomaterial.

electrical process being detected, which depends on what circuit elements are present, whether they are in parallel or in a series arrangement, what are the values of the individual circuit elements and what dielectric function is being used[11]. Impedance spectroscopy is related to dielectric permittivitty, admittance and electric modulus as shown below:

(1) $Z^* = 1/ j\omega C_o \varepsilon^*$
(2) $Y^* = j\omega C_o \varepsilon^*$
(3) $M^* = 1/ \varepsilon^*$ where
$\omega = 2\pi f$ is the angular frequency

In addition to using log Z* vs log f plots, one also often uses complex impedance plots. Unless materials are vey conducting, they can generally be represented by a series of RC circuits in parallel.

For example, it is quite common for a nanomaterial to have a dual response: one for the main bulk part (i.e. individual nanoparticle, nanotube, platelet) and the other for the junction or interface between them. Even if the contact between two nano-objects is ideal, the junction or interface will always have a different response than the main part of the material, whether there is a material physically separating them or not[5-12]. Thus, this suggests that one might expect to see two semicircles on the complex impedance plots. However, as shown in Fig. 1, the ability of the measurements to be able to detect the two responses present depends on the time constants of the electrical processes that control the measurement and the equipment specifications as well as the contacting method being used. In the complex impedance formalism, the size of the semicircles is controlled by the size of the corresponding resistances giving rise to that measured response and one can obtain spectra that look as parts (a)-(c) above assuming capacitances that are about three orders of magnitude apart[1]. It is important to mention that even though one may have the two processes happening, the spectrum may only reveal one semicircle. This can be caused by the two resistances being so different that in the linear plot, one can only distinguish one. On the other hand, if both the resistances and capacitances give rise to the same time constant, even if the individual values are very are different, they will then merge and only show one semicircle as depicted in Fig. 1(d). This is where using the various dielectric functions can be very useful for discriminating between the various cases described here. It may also be useful to graph the complex plots in a log-log scale as first suggested by Jonscher[13], in order to determine whether more than one RC process is occurring or not.

Figure 2 displays examples of when one might obtain semicircles in the first and fourth quadrants. By convention, the complex impedance for capacitive circuits, which has a negative imaginary impedance, are plotted in the first quadrant. However, for inductive circuits, the imaginary impedance is positive and should therefore be plotted in the fourth quadrant to make it clear that a totally different type of response is being detected[1]. As shown in Fig.2, the size of the semicircles are still dominated by the magnitude of the resistance. As before, this means that one may not detect a second semicircle if the values of the resistances are orders of magnitude apart. Furthermore, it is difficult to determine a priori which of the two semicircles will show up first. As Fig. 2 indicates, this is related to the value of their time constants. Thus, when measuring materials that have different size features with very different conductivities, one needs to be very careful before jumping to conclusions about whether a semicircle is representative of the material being measured or not. Having such varied responses for seemingly similar scenarios can lead to confusion to the inexperienced user of this amazing technique.

It should be further mentioned that in this discussion, only parallel RC and parallel RL circuits have been presented. The reason is that the author intended to offer the most commonly sought after responses by users. Since series RC and series RL circuits do not lead to semicircles in the complex impedance plane, their response is often missed because most everyone who uses this technique focuses on generating complex impedance plots. The author has over 35 years of experience using this technique with all classes of materials and is in the process of writing a textbook where many of these nuances will be clearly described and explained. The reader should be reminded that material's resistivity is one of the most sensitive properties that exist, ranging from $<10^{-6}$ up to $> 10^{14}$ Ωcm, thus it should not be surprising that the frequency spectra measured can sometimes represent only a small fraction of what is occurring and that experiments need to be carried out with care and with a focused intention and that what works for one material need not work for another until the right variables have been explored.

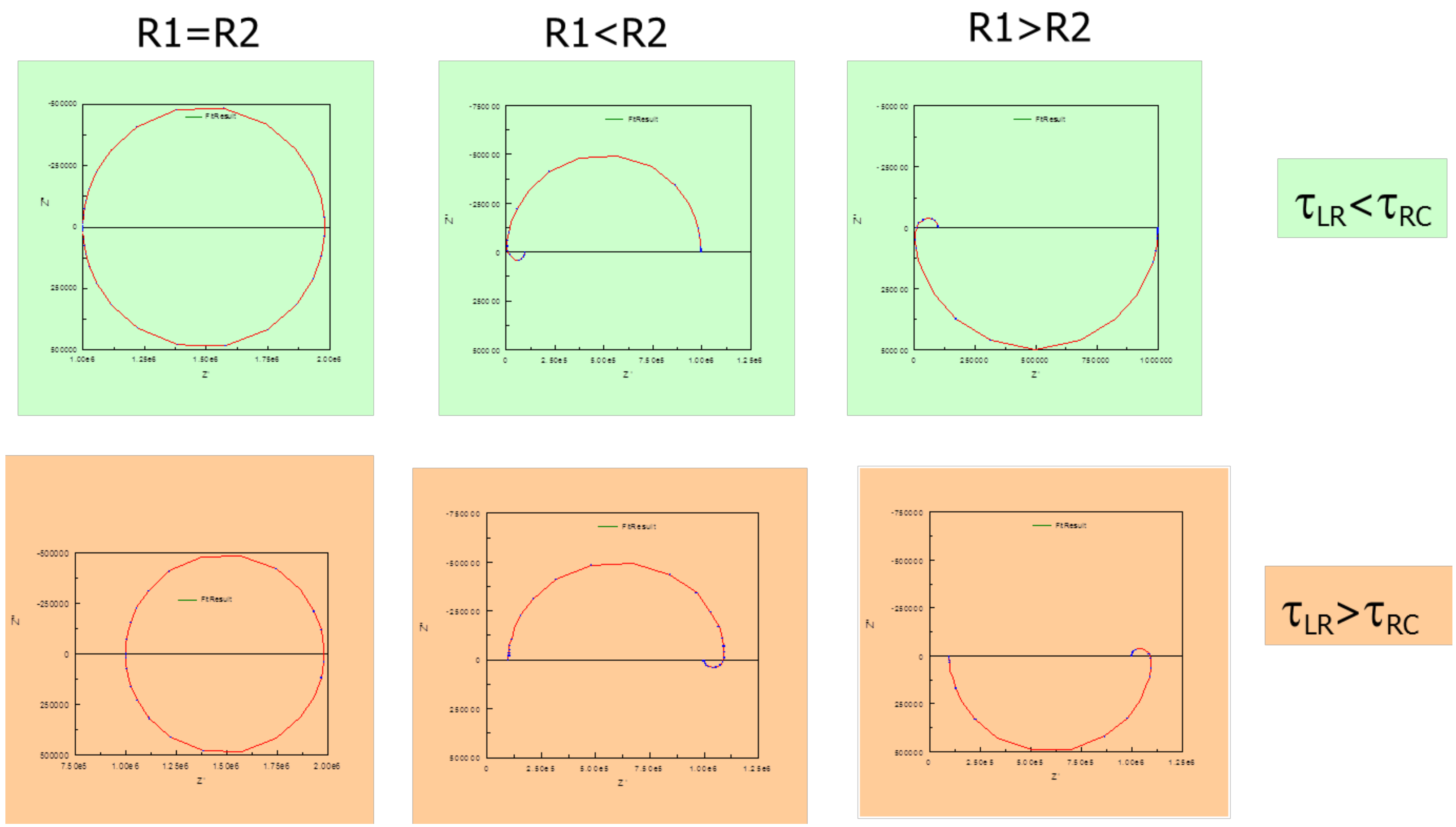

Figure 2. The complex impedance spectra for combinations of RC and RL parallel responses. The order in which these processes show up is determined by the corresponding time constants.

There are a number of research groups around the world who have successfully used IS/DS as an experimental method to characterize the bulk properties of many different types of materials. In particular, ferroelectric ceramics [14] , cement composites [15], general equivalent circuit interpretation[16] and interpretation of response of grain boundaries[17] to name a few. An excellent source of information for solid state measurements can be found in the book edited by Barsoukov and Macdonald[18]. As mentioned earlier, the emphasis in this article was on solid state materials and there are many well recognized researchers who conduct EIS measurements whose review articles are not included here for the sake of brevity.

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