Impedance and Dielectric Spectroscopy of Nanoparticulate Films and Composites
R.A. Gerhardt

*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, USA, rosario.gerhardt@mse.gatech.edu

ABSTRACT

Nanoparticulate materials are becoming ubiquitous in a wide range of industrial applications. Such materials can be used as individual devices with appropriate 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 are 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 themselves 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
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 permittivity, admittance and electric modulus as
shown below:

1. \( Z^* = 1/j\omega \varepsilon_0\varepsilon^* \)
2. \( Y^* = j\omega C_0\varepsilon^* \)
3. \( M^* = 1/\varepsilon^* \) where

\[ \omega = 2\pi f \]

In addition to using log \( Z^* \) vs log \( f \) plots, one also often
uses complex impedance plots. Unless materials are very
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

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

In Fig. 1(d), 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 \( > 10^{14} \) \( \Omega \)cm,
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.

3 REFERENCES