7-5-2006

Dielectric Constant of Particles Determined by Impedance Spectroscopy

Vladimir Petrovsky

Abhishek Manohar

Fatih Dogan
Missouri University of Science and Technology, doganf@mst.edu

Dielectric constant of particles determined by impedance spectroscopy

Vladimir Petrovsky,[a] Abhishek Manohar, and Fatih Dogan
Department of Materials Science and Engineering, University of Missouri-Rolla, Rolla, Missouri 654509

(Received 21 December 2005; accepted 26 March 2006; published online 5 July 2006)

Electrical characterization of slurries prepared by mixing dielectric powders with solvents can be used to estimate dielectric properties of the particles. In particular, dielectric constant of the particles can be calculated from effective dielectric constant of the slurry measured at high frequency by using the Lorentz-Lorenz or similar equations based on mixing rules. Unfortunately, this approach leads to high margin of errors in dielectric constant estimation and is very sensitive to any slurry nonidealities such as sedimentation or agglomeration of particles. Impedance spectroscopy techniques are introduced to measure dielectric properties of particles at different frequency ranges. Dielectric constant of strontium titanate particles, suspended in butoxyethanol, was determined reproducibly by impedance spectroscopy using an appropriate equivalent circuit model. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2206411]

INTRODUCTION

Various dielectric materials used in capacitor industry can be considered as two-phase systems such as polymer capacitors filled with ceramic particles (3-1 composites). Even pure ceramic capacitors often behave as two-phase systems because of significant differences between the grain and grain boundary properties.[1] Hence, it is important to distinguish contributions of individual phases to electrical properties from overall properties of two-phase systems. Regarding polymer-particle composites for electronic applications, although the dielectric properties of the polymeric phase can be measured simply using a bulk sample, it is a challenging task to determine the dielectric properties of ceramic filler particles.

Various approaches have been used to estimate the dielectric constant of ceramic particles. One of the approaches is based on electrical characterization of sintered dense ceramic materials. This approach allows precise characterization of the sintered material, but cannot be used to estimate the dielectric properties of loose ceramic particles. For example internal stresses which may exist within the polycrystalline sintered ceramics could alter the dielectric properties of the material, whereas loose particles are not mechanically constrained in the form of powders. Furthermore, the dielectric properties of particles in nanometer size scale may be significantly different than those in micrometer size scale. Although the dielectric properties of sintered ceramics as a function of grain size are widely studied, such investigations for particulate materials have been limited mainly due to the lack of reliable characterization methods to determine the permittivity of particulate materials.

Another approach to estimate the dielectric properties of particles is to conduct capacitance measurements on powder compacts or slurries (particles suspended in a liquid) as two-phase systems, followed by application of theoretical models based on mixing rules.[2] In particular, the Lorentz-Lorenz equation[3] allows estimating effective dielectric constant $\varepsilon_{\mathrm{eff}}$ of two component composite composed of uniformly distributed spherical particles with dielectric constant ε_1 and volume fraction x_1 in the host media with dielectric constant ε_2:

$$\frac{\varepsilon_{\mathrm{eff}}-\varepsilon_2}{\varepsilon_{\mathrm{eff}}+2\varepsilon_2}=x_1\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+2\varepsilon_2}. \tag{1}$$

Unfortunately, powder compacts do not represent an ideal system for which the mathematical models such as Eq. (1) would be applicable. Effective dielectric constant of the compacts is highly sensitive to particle-particle interaction, which can lead to errors in estimation of the permittivity of particles based on mixing rules.[2]

Characterization of slurries may be a more suitable approach to evaluate the dielectric constant of particles. In slurries the particles are dispersed in a liquid so that the application of Lorentz-Lorenz equation (1) would be more reasonable. Using liquids with a high dielectric constant ε_2 would result in more accurate estimation of ε_1 for particles with high dielectric constant (>1000) such as ferroelectrics. However, availability of liquids with high permittivity is limited ($\varepsilon_2 \sim 70$ for pro pylene carbonate or other highly polarizable liquids) so that calculating the permittivity of particles from the effective dielectric constant of slurry may involve high margin of errors.

In several studies,[4–8] dielectric measurements using slurries are conducted at high frequency (10–20 MHz) range to ensure low dielectric losses so that the effective medium theory [such as Lorentz-Lorenz equation (1)] would be applicable. However, the dielectric constant of the slurry $\varepsilon_{\mathrm{eff}}$ should be measured very precisely with an accuracy of several decimal points in order to be able to calculate the dielectric constant of particles ε_1 with a small margin of error. Other factors affecting the reliability of measurements using slurries include size, shape, agglomeration, and sedimentation of the particles. Nonideal slurries with respect to particle dispersion could lead to significant errors in the calculated value of the dielectric constant of particles ε_1. Hence, the theoretical models have been modified by introducing various parameters based on, e.g., particle shape and size factors

[a]Electronic mail: vpetrovs@umr.edu

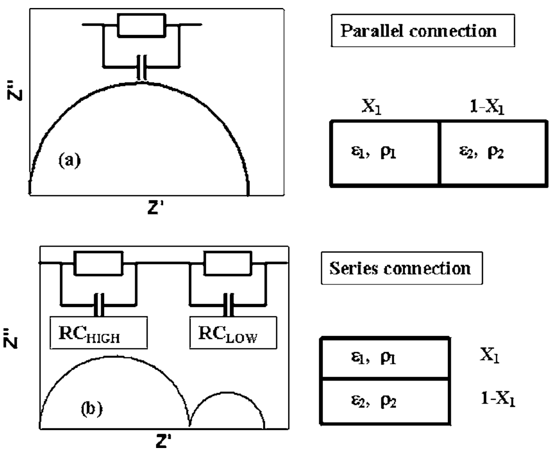

FIG. 1. Impedance spectra of a two-phase system with two extreme cases: parallel (A) and series (B) connections between phases.

to minimize deviations of slurries from ideal systems. Lorentz-Lorenz equations or fine element models which are modified by incorporating such parameters are used to calculate the dielectric constant ε_1 of particles.[4–10]

Impedance spectroscopy is a well established method to investigate electrical properties of materials particularly multiphase systems. The objective of this study is to introduce the impedance spectroscopy techniques as viable methods for reliable and accurate measurement of the dielectric constant of particles suspended in appropriate liquids.

THEORETICAL CONSIDERATION

Impedance spectroscopy techniques are applied to characterize slurries as two-phase systems, similar to the methods used to analyze polycrystalline materials, e.g., bulk and grain boundary conductivities. Theoretical models considering the parallel and series connections between each phase are two extreme cases to analyze the impedance spectra. In the case of parallel connection [see Fig. 1(a)], the impedance spectra will consist of only one ideal semicircle with an effective dielectric constant of two phases:

$$\varepsilon_{\text{eff}} = \varepsilon_1 x_1 + \varepsilon_2 (1 - x_1). \quad (2)$$

If phases are connected in series [see Fig. 1(b)], the impedance spectra reveal two ideal semicircles. The effective dielectric constants defined by the first (ε_H high fr equency) and second (ε_L low fre quency) semicircles are expressed by

$$\varepsilon_H = \varepsilon_2/(1 - x_1), \quad (3a)$$

$$\varepsilon_L = \varepsilon_1/x_1. \quad (3b)$$

Semicircles in impedance spectra of slurries may overlap, since dispersion of particles in slurries is not ideal (or uniform). The effective dielectric constant retrieved from the high frequency semicircle would follow the Lorentz-Lorenz equation (1) or Eq. (3a) depending on the slurry characteristics and particle volume fraction x_1. The low frequency semicircle is coupled with the dielectric constant of particles ε_1 in the slurry. The effective dielectric constant, retrieved from the low frequency semicircle, can be expected within a range from ε_1 to ε_1/x_1 [see Eq. (3b)].

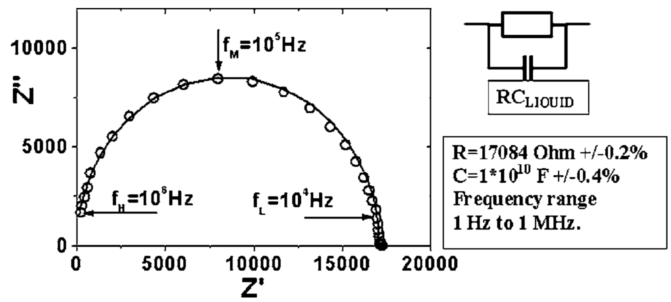

FIG. 2. Impedance spectra of butoxyethanol; open circles represent experimental data, and line represents fitting with an ideal RC circuit [$R = 17\ \text{k}\,\Omega(\pm 0.2\%)$; $C = 1 \times 10^{-10} F(\pm 0.4\%)$].

EXPERIMENTAL CONFIRMATION

An electrochemical cell with aluminum electrodes (electrode diameter: 44 mm, distance between the electrodes: 1.1 mm) was built to conduct electrical measurements using slurries with different liquids and $SrTiO_3$ powders. An automated Solartron system (1255b frequency response analyzer and 1470 cell tester) was used to collect data of the impedance spectra.

It should be noted that at least one of the slurry components should be conductive to obtain an impedance spectrum with distinctive semicircles. Since the conductivity of particles would remain constant, liquids with proper conductivity are used for slurry preparation. It is desirable to use liquids with ideal or close to ideal impedance spectra so that the analysis of the impedance spectra of slurries would be simplified without introducing parameters for correction of measured data. Various liquids meet these requirements which allow dispersing of particles in nonaqueous slurries. Butoxyethanol was used in this study to prepare relatively stable slurries.

The impedance spectra of butoxyethanol are depicted in Fig. 2. It is shown that single RC circuit allows a good fitting with experimental data in the frequency range from 100 Hz to 1 MHz (relative error for resistance is 0.2% and for capacitance is 0.4%). Using the capacitance value in Fig. 2 the dielectric constant of butoxyethanol is calculated to be 10.

Slurries with different solid loadings in the range from 5 to 35 vol % were prepared by mixing $SrTiO_3$ powder with butoxyethanol for impedance spectroscopy measurements. Strontium titanate powder with particle size $<5\ \mu$m was purchased from Sigma-Aldrich (product No. 396141). Figure 3 shows experimental data (open circles) and fitting results (two solid semicircles) for the slurry with 5 vol % solid loading. Two distinct semicircles can be extracted from the spectra even at low solid loadings so that the model with two RC circuits connected in series ensures a good fitting (fitting errors are $\Delta R_{\text{high}} = 1.2\%$, $\Delta C_{\text{high}} = 0.7\%$, and $\Delta R_{\text{low}} = 3.5\%$, $\Delta C_{\text{low}} = 8\%$ for high frequency and low frequency semicircles, respectively). The presence of additional semicircles, which may be related to other possible effects such as interfaces between particles and the liquid, was not observed using slurries investigated in this study.

The dielectric constant calculated from high frequency semicircle is equal to the dielectric constant of butoxyetha-

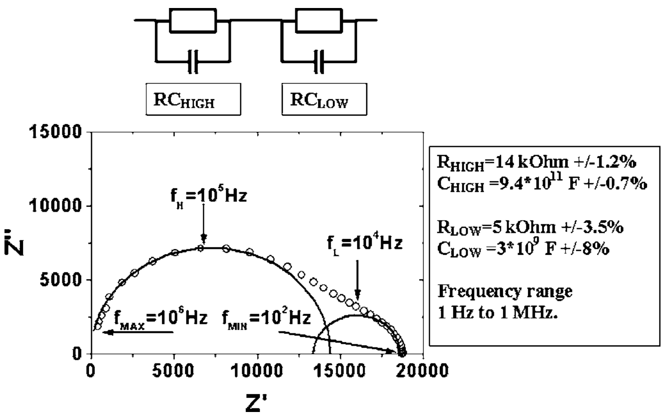

FIG. 3. Impedance spectra of 5% $SrTiO_3$ slurry in butoxyethanol: open circles represent experimental data, and lines represent fitting by two ideal *RC* circuits [$R_h=14$ k $\Omega(\pm 1\%)$; $C_h=0.94\times 10^{-10}F(\pm 0.7\%)$; $R_l=5$ k $\Omega(\pm 3\%)$; $C_l=3\times 10^{-9}F(\pm 8\%)$].

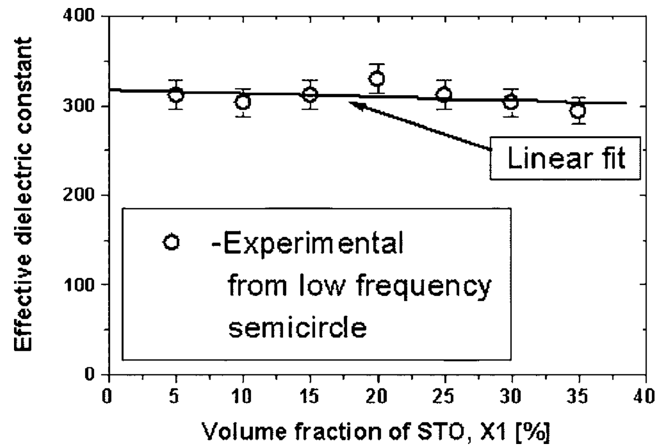

FIG. 4. Effective dielectric constant of $SrTiO_3$ particles (in butoxyethanol) determined from low frequency semicircle in Fig. 3 as a function of solid loading in slurries. Error bars correspond to standard deviation of effective dielectric constant $\Delta=5\%$.

nol, $\varepsilon_2=10$, within the margin of errors, so that there is no or minor influence of particles on impedance spectra at high frequency (at least for the slurry with 5 vol % solid loading). On the other hand, the dielectric constant calculated from low frequency semicircle is equal to that of $SrTiO_3$, $\varepsilon_1=300$, within the margin of errors. Similarly there is no or only minor influence of the liquid on the value of effective dielectric constant within the low frequency range. These results show that the permittivities of particles and the liquid phase in nonaqueous slurry can be extracted by impedance spectroscopy technique. Dielectric losses in the slurry are mostly connected with the conductivity of the liquid as dominating source of the losses for both high and low frequency semicircles. So, it is impossible to extract information about dielectric losses in the powder material at least for such good dielectrics as strontium titanate.

As mentioned above, determining the dielectric constant of particles by measurement of the effective dielectric constant of slurry and using effective medium models may result in significant differences of calculated values by several orders of magnitude. Minor variations of the solid loading in slurries or nonideal particle distribution can lead to significant errors in estimating the dielectric constant of particles. On the other hand, impedance spectroscopy techniques allow a reliable measurement of particle dielectric constant using slurries since different frequency ranges are selected to separate the contributions of the liquid and particles on impedance spectra.

Figure 4 shows the dielectric constant of $SrTiO_3$ particles dispersed in butoxyethanol at different solid loadings. The dielectric constant values were calculated from low frequency semicircle of the impedance spectra in Fig. 3. It is revealed that these values remain nearly constant for solid loadings from 5 to 35 vol % and equal to 309($\pm 3\%$). The measurements are quite insensitive to significant changes in the slurry such as solid loading or sedimentation of particles, so that the presented technique utilizing impedance spectroscopy offers a reliable and reproducible approach to measure the dielectric constant of particles.

SUMMARY

A common approach to estimate the dielectric constant of particles is based on the dielectric measurements of slurries and applying the mixing rules derived from the effective medium theory, such as the Lorentz-Lorenz equation and its modifications. However, these approaches often result in high margin of errors due to sensitivity of theoretical models to small deviations in measured values. Minor changes in measured values of slurry permittivity may lead to significant difference in calculated values of particle permittivity up to several orders of magnitude.

The present study shows that the impedance spectroscopy allows a reliable measurement of the dielectric constant of particles dispersed in liquids with an appropriate conductivity. This method allows calculation of the dielectric constant of particles with higher accuracy by analyzing the frequency dependency of the impedance spectra affected by dielectric properties of a slurry consisting of particles and liquid phase. The measurements are not significantly affected by slurry properties such as solid loading, agglomeration, and sedimentation of particles.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation, as part of the Center for Dielectric Studies, under Grant No. RG001083 and through a MURI program sponsored by the Office of Naval Research under Grant No. N000-14-05-1-0541.

[1] V. Petrovsky, P. Jasinski, H. U. Anderson, and T. Petrovsky, Mater. Res. Soc. Symp. Proc. **835**, 187 (2005).
[2] A. K. Goswami, J. Appl. Phys. **40**, 619 (1969).
[3] D. J. Bergman, Phys. Rep., Phys. Lett. **43**, 377 (1978).
[4] S. Wada, H. Yasuno, T. Hoshina, S.-M. Nam, H. Kakemoto, and T. Tsurumi, Ceram. Trans. **150**, 205 (2004).
[5] S. Wada, H. Yasuno, T. Hoshina, S.-M. Nam, H. Kakemoto, and T. Tsurumi, Jpn. J. Appl. Phys., Part 1 **42**, 6188 (2003).
[6] S. Wada, T. Hoshino, H. Yasuno, M. Ohishi, H. Kakemoto, T. Tsurumi, and M. Yashima, Ceram. Eng. Sci. Proc. **26**, 89 (2005).
[7] T. Tsurumi, T. Sekine, H. Kakemoto, T. Hoshina, S.-M. Nam, H. Yasuno, and S. Wada, Mater. Res. Soc. Symp. Proc. **833**, 243 (2005).

[8] A. Manohar and F. Dogan, *Advances in Electronic and Electrochemical Ceramic*, Ceramic Transaction Vol. 179, edited by F. Dogan and P. Kumta (The American Ceramic Society, Westerville, OH, 2005), pp. 93–102.
[9] T. Yamada, T. Ueda, T. Kitayama, J. Appl. Phys. **53**, 4328 (1982).
[10] Y. Rao, C. P. Wong, J. Qu, and T. Marinis, Proceedings of the International Symposium and Exhibition on Advanced Packaging Materials: Processes, Properties and Interfaces (IEEE, Piscataway, NJ, 2000), pp. 44–49.