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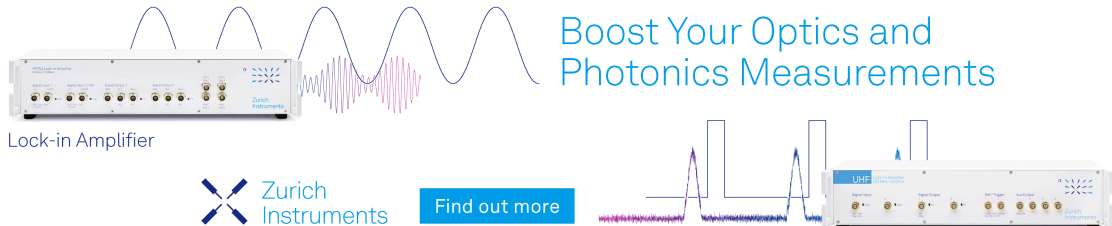


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# Effective dielectric constant of two phase systems: Application to mixed conducting systems

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Theoretical approaches to electrical characterization of two phase systems are mostly limited to the systems where the individual components exhibit the same type of conductivity (pure dielectric or pure conductive systems). In this article, the brick wall geometry is extended to the mixed conductive systems with percolation. Impedance spectroscopy techniques were used for experimental investigation of slurries. Various metal oxide powders and host liquids were analyzed using a wide range of solids loadings. Comparison of experimental results with theoretical predictions shows good fitting of the experimental data. Parameters (the values of permittivity for both phases and percolation threshold) calculated from this fitting match the corresponding values of components of two phase systems. Analysis of both low frequency (less than 10 kHz) as well as high frequency (10 kHz to 1 MHz) responses of impedance spectra allows determining of permittivity of dielectric powders suspended in various liquids. Low frequency response provides better accuracy for systems with high dielectric contrast between components, while high frequency response is more accurate for low contrast systems. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4743985>]

## INTRODUCTION

Various theoretical models have been implemented towards electrical characterization of two phase systems. After initial introduction by Lorenz and Maxwell, the effective media approach undergone series of improvements in application to pure conductive and pure dielectric systems.<sup>1-3</sup> Several other approaches were also developed including the brick wall model.<sup>1,4</sup> Important directions of further advancements in the theoretical field include extension of theoretical models on the systems with mixed conductivity and introduction of percolation.<sup>5-7</sup> These extensions in the modeling and systematic experimental investigation of mixed conducting two phase systems with percolation can provide useful information for various practical applications.<sup>8-11</sup> Such investigations of two phase systems were performed earlier in our laboratory using suspensions of metal-oxide powders in organic solvents (slurries) by impedance spectroscopy techniques.<sup>12-14</sup> Measurements using slurries have some obvious advantages for a broader-range investigation in comparison with other types of two phase systems such as polymer-ceramic composites. It is relatively simple to control the electrical conductivity of solvents in slurries so that impedance spectroscopy techniques can be implemented more efficiently as a characterization method. The dielectric contrast between the liquid and suspended particles in slurries can be adjusted by using solvents with different values of permittivity. Effects of particle sedimentation and agglomeration on dielectric properties of slurries can be minimized by using efficient dispersion techniques such as ultrasonic processing. Our previous studies were focused on the low frequency part of the impedance spectra (less than

10 kHz) and extracting the values for the permittivity of powders. Conclusions of these studies include the following: (1) impedance spectra of slurries consist of two relaxation processes, (2) low frequency relaxation is caused by the permittivity of powder, and (3) permittivity of the liquid does not influence the low frequency part of the spectra. Values of permittivity for different materials in powder form could be determined by analyzing the low frequency part of impedance spectra of slurries. Another conclusion of these studies was that high frequency relaxation in impedance spectra is caused by permittivity of the liquid and not affected by the permittivity of powders in the slurry. These findings were confirmed by using small ceramic cubes submerged in the liquid as a physical model of slurries.<sup>15</sup>

The focus of the present article is on the high frequency part of the impedance spectra obtained from two phase systems with mixed conductivity. Procedures allowing a detailed material characterization are described by analyzing impedance spectra along with the theoretical equations. Validity of the theoretical approach is confirmed by analyzing of experimental (real) mixed conductive systems using impedance spectroscopy techniques.

## PHASE DISTRIBUTION AND PERCOLATION

Effective media theory and brick wall methods are two fundamentally different approaches applied for two phase system modeling. Physical nature of effective media models (like Maxwell Wagner model) does not consider percolation, i.e., physical contacts between suspended particles irrespective of the suggested particle shape. The shape of particles influences effective permittivity of the mixture only through

dipole moments generated by particles. In these models, percolation parameters can be introduced only empirically (for example, by introducing partial clustering in the system<sup>16</sup>). The standard brick wall model describes a specific case of material distribution within a two phase system. Particles as the suspended phase are periodically distributed perfect cubes and they are disconnected in all ranges of particle volume fractions  $X_1$  until the entire volume is filled ( $X_1 = 1$ ) which describes two phase systems without percolation (percolation threshold  $X_p = 1$ ). A detailed comparison of Maxwell Wagner and brick wall models was discussed in Ref. 15 using physical modeling as experimental approach.

Real systems always percolate earlier ( $X_p < 1$ ) since the particle shape and distribution are different from that used in standard brick wall model. An additional parameter (or parameters) needs to be introduced in the model to address these differences. Various theoretical approaches were used to address this issue in Ref. 17. It was shown that main advantage of the brick wall approach is the possibility of natural extension on percolating systems. The brick wall model considers physical contacts between particles so that percolation can be introduced simply by changing the shape of suspended particles as shown in Fig. 1. A cube cell with a unit size of composite material is depicted as an element of the periodic brick-wall structure. The suspended component is shown as a dark cube inside the cell. It can be elongated in direction of electrical field ( $\alpha > 1$ ) or suppressed ( $\alpha < 1$ ) resulting in a columnar or layered type percolation, respectively. Volume fraction of the suspended material ( $X_1$ ) is equal to  $X_1 = \alpha x a^3$ . Columnar type percolation will take place for  $\alpha > 1$  when suspended particles will touch each other vertically at  $\alpha x a = 1$ . Substitution of  $a = 1/\alpha$  in equation defining volume fraction of suspended material gives value of percolation threshold ( $X_p$ ) which will be equal to the inverse square of percolation parameter ( $X_p = 1/\alpha^2$ ). Layered type of percolation will dominate for  $\alpha < 1$  when suspended particles are in contact horizontally at  $a = 1$ . Substitution of  $a = 1$  in equation defining volume fraction of suspended material gives the value of percolation threshold ( $X_p$ ) which, in this case, will be equal to percolation parameter ( $X_p = \alpha$ ).

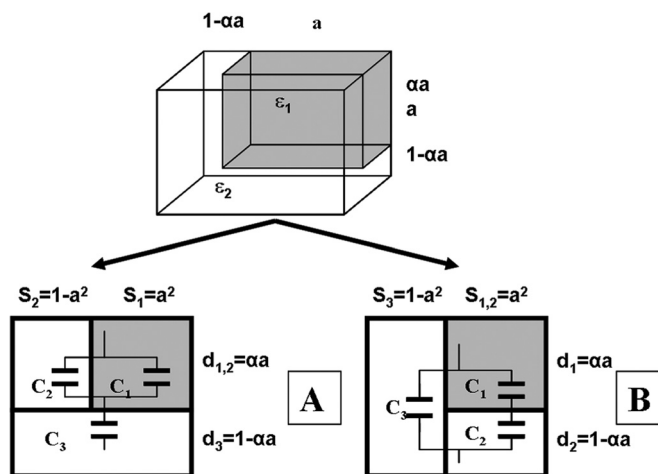


FIG. 1. Brick-wall model of two phase systems with elongated bricks causing percolation. Two possible transitions to equivalent circuit demonstrated: model 1 (a) and model 2 (b).

Additional advantage of brick wall model is natural transition from complex three dimensional distribution of electrical field to simple equivalent circuit which was described for cubic particles in Ref. 15 and extended on elongated particles in Ref. 17. It generates two models surrounding the exact solution as shown in Figs. 1(a) and 1(b). Corresponding equations as described in Ref. 17 are

$$\text{Model1}^*: \frac{\epsilon_{\text{EFF}}}{\epsilon_2} = \frac{1}{1 - (X_1 \alpha^2)^{1/3} + \frac{(X_1 \alpha^2)^{1/3}}{1 - \left(\frac{X_1}{\alpha}\right)^{2/3} \left(1 - \frac{\epsilon_1}{\epsilon_2}\right)}}, \tag{1}$$

$$\text{Model2}^*: \frac{\epsilon_{\text{EFF}}}{\epsilon_2} = 1 - \left(\frac{X_1}{\alpha}\right)^{2/3} + \frac{\left(\frac{X_1}{\alpha}\right)^{2/3}}{1 - (X_1 \alpha^2)^{1/3} \left(1 - \frac{\epsilon_1}{\epsilon_2}\right)}. \tag{2}$$

It is reasonable to suggest that averaging of Eqs. (1) and (2) will provide good fitting for real two phase systems with percolation

$$\text{Averaging: } \bar{\epsilon}_{\text{EFF}} = \left(\epsilon_{\text{EFF}}(\text{Mod.1})^* \epsilon_{\text{EFF}}(\text{Mod.2})\right)^{1/2}. \tag{3}$$

As shown in Fig. 2, brick wall model modified with percolation parameter (Eqs. (1)–(3)) was compared with experimental results.<sup>17,18</sup> The experimental data were obtained from measurements using barium titanate (BTO) slurries (blue up triangles) and porous bulk samples of barium titanate prepared by sintering of powders with various amounts of fugitive pore providers, so that the data cover the entire range of barium titanate volume fractions  $X_1$  from 0 to 1. A theoretical model (Eqs. (1)–(3)) was applied for nonlinear fitting using the software program in ORIGIN. This model presents  $\epsilon_{\text{eff}}(X_1)$  dependence with three parameters ( $\epsilon_1$ ,  $\epsilon_2$ , and  $\alpha$ ) which were calculated by the software program as a result of

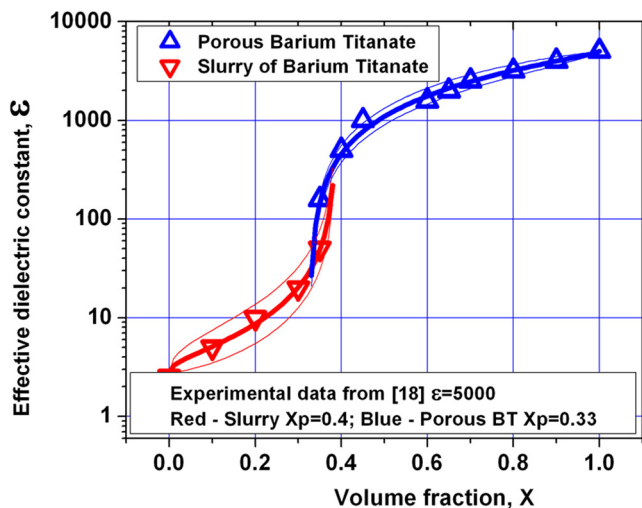


FIG. 2. Introduction of percolation in brick wall models allows extending this approach on real two phase system.<sup>17</sup> Down triangles and red lines are for slurries; up triangles and blue lines are for porous ceramics; thin lines are for models 1 and 2 and thick lines for their averaging.

this fitting. Percolation thresholds  $X_p$  were calculated using  $\alpha$  and equation  $X_1 = \alpha^3$ . Equations (1) and (2) with these values of calculated parameters were then used to demonstrate areas of possible deviations in the model (thinner lines in Fig. 2).

Fig. 2 shows that application of the modified brick wall model results in a good fitting of experimental data for dispersed powder (red curves) as well as for porous ceramic (blue curves). Model 1\* and Model 2\* surrounds experimental data points over the entire range of  $X_1$  (thin lines) while the averaging equation (3) follows exactly the experimental points. Calculated values of percolation threshold,  $X_{1P} = 0.4$  for slurries and  $X_{1P} = 0.33$  or  $X_{2P} = 0.67$  for porous ceramics, are reasonably within the range of percolation for spherical particles. These results indicate that the modified brick wall model (Eqs. (1)–(3)) can be suggested as a universal model for dielectric two phase systems at least within a reasonable range of percolation thresholds. This model has a clear physical background, and insures good fitting to experimental data obtained from actual two phase systems.

### EXTENSION ON MIXED CONDUCTING SYSTEMS

In the above discussion, both phases in a two phase systems were considered as pure dielectrics, i.e., both phases are electrically insulating (no leakage current) or the data were collected at frequencies high enough to neglect the impact of material's conductivity (usually in the range 100 kHz to 10 MHz for slurries<sup>19–21</sup>). Under these assumptions, the effective permittivity  $\epsilon_{\text{eff}}$  has no frequency dependence. It is the only parameter which can be determined using Eqs. (1)–(3) from experimental measurements of two phase

system. Several samples with different ratios between the phase volumes should be measured to obtain additional information on individual components of two phase systems (such as percolation threshold  $X_p$  and the values of permittivity of each phase).

Presence of some leakage in one of the phases leads to frequency dependence of  $\epsilon_{\text{eff}}$  so that impedance spectroscopy technique can be applied to extract additional parameters from impedance spectra of slurries. The shape of impedance spectra depends on the phase that is leaky or electrically conductive. A transition from brick wall model to equivalent electrical circuit can be accomplished by similar way as for pure dielectric systems explained earlier. Notations used in equivalent circuits are combinations of R and C parameters as well as distributed elements (like constant phase element CPE) which are standard notations for equivalent circuits and corresponding fitting software (like z-VIEW). Transition from this notation to effective parameters of composite material is achieved by normalizing of all parameters to sample geometry to obtain  $\rho_{\text{eff}}$  and  $\epsilon_{\text{eff}}$ . Physical models as Eqs. (1)–(3) can be applied to extract parameters of each component from the effective parameters of the two-phase system.

Mixed conductive particles dispersed in a dielectric host material represent a simple case as shown in Fig. 3. Transition from brick wall model to equivalent electrical circuit  $C_{2B} - R_1 / (C_{2A} + C_1)$  is illustrated in Figs. 3(a) and 3(b) and corresponding impedance spectra is shown in Figs. 3(c) and 3(d). It is obvious that suspended particles behave as pure dielectric at high enough frequencies  $> 10$  kHz since resistor  $R_1$  is shorted by parallel capacitors  $(C_{2B} + C_1)$ , so that Eqs. (1)–(3) can be used. Series connection of  $C_{2B}$  and  $(C_{2A} + C_1)$  defines  $\epsilon_{\text{eff}}$  by neglecting the influence of resistor  $R_1$  on the

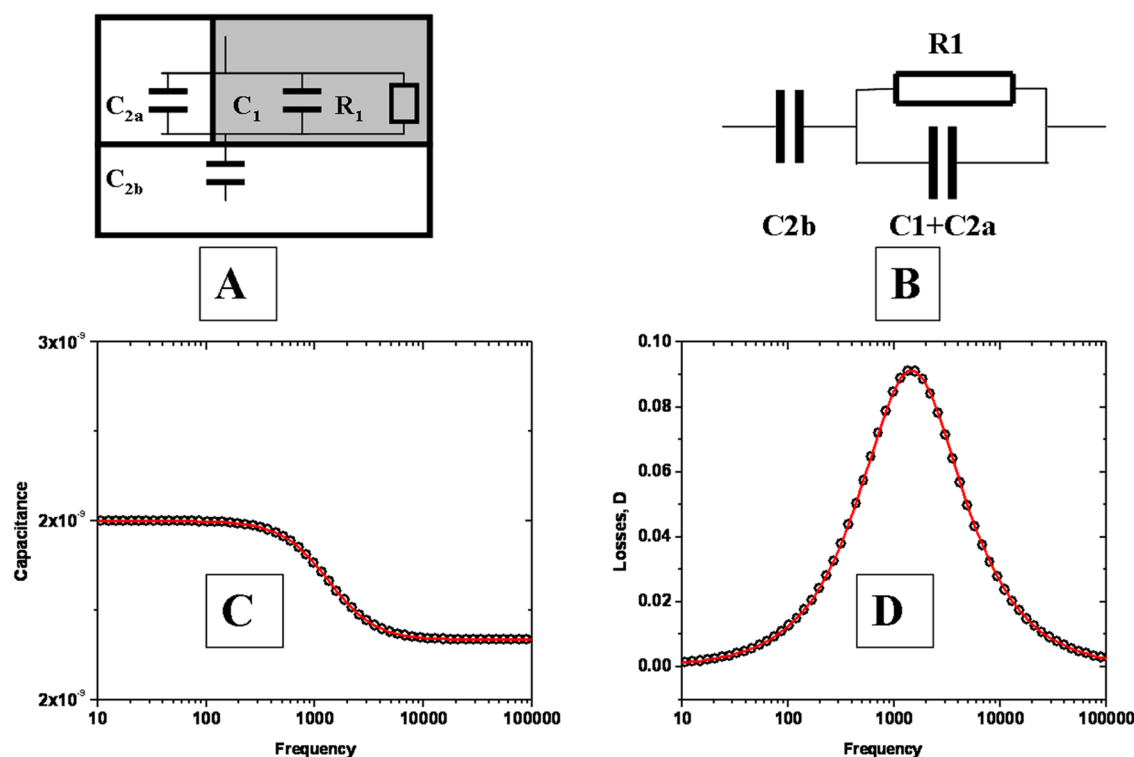


FIG. 3. Impedance spectra of two phase system with conductive suspended and nonconductive host phase (simulation). (a) Example of brick wall model; (b) corresponding equivalent circuit; (c) and (d) capacitance and dielectric losses spectra.

impedance spectra at high frequency. Suspended particles transform from a pure dielectric to a mixed conductor at the Maxwell relaxation frequency. The  $R_1/(C_{2A} + C_1)$  element relaxes due to domination of ohmic leakage  $R_1$  so that  $\epsilon_{\text{eff}}$  is defined only by  $C_{2B}$  at low frequencies  $<100$  Hz. The Maxwell relaxation frequency is described as

$$f = 1/(2\pi\rho\epsilon) = 1/(2\pi R_1^*(C_{2A} + C_1)). \quad (4)$$

The overall relaxation process is shown by frequency dependences of capacitance and dielectric losses in Fig. 3. Three parameters can be extracted from impedance spectra for each sample: (1)  $\epsilon_{\text{eff}}$  (H) at high frequency described by Eqs. (1)–(3), (2) transition frequency  $f$  described by Maxwell equation (4), and (3)  $\epsilon_{\text{eff}}$  (L) at low frequency described by Eqs. (1)–(3) with indefinitely high value of  $\epsilon_1$ , whereas the suspended phase 1 completely shorts the electrical field due to the dominating leakage current. The value of  $\epsilon_{\text{eff}}$  (L) can be derived from Eqs. (1)–(3) as

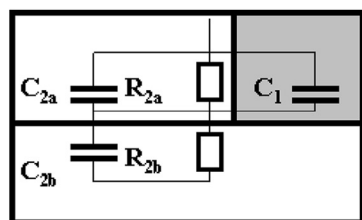
Averaging of models(1\*) and (2\*) for indefinitely high dielectric contrast ( $\epsilon_1/\epsilon_2 \rightarrow \infty$ ):

$$\frac{\bar{\epsilon}_{\text{EFF}}}{\epsilon_2} = \frac{(1 - (X_1\alpha^2)^{1/3} + X_1)^{0.5}}{1 - (X_1\alpha^2)^{1/3}}. \quad (5)$$

Dielectric particles dispersed in mixed conductive host material represent a more complex case of two phase systems (Fig. 4). Transition from brick wall model to equivalent electrical circuit is illustrated in Fig. 4(a) and corresponding impedance spectra is shown in Figs. 4(b)–4(d). In this case, the equivalent circuit consists of two relaxing elements ( $R_{2B}/C_{2B}$

and  $R_{2A}/CPE$ ) so that at least four parameters can be extracted from impedance spectra.<sup>15</sup> First element of the equivalent circuit describes the Maxwell relaxation in host material (red curve marked as  $Z''$ -high frequency in Fig. 4(b)). This element contains information related with electrical properties of the host material. Equations (4) and (5) describe relationship between parameters of the semicircle corresponding to ( $R_{2B}$  and  $C_{2B}$ ) and properties of the host material ( $\epsilon_2$  and  $\rho_2$ ). The second element describes redistribution of electrical field around suspended particles (blue curve marked as  $Z''$ -high frequency in Fig. 4(b)). It was previously reported that permittivity of suspended particles  $\epsilon_1$  can be calculated directly from the low frequency semicircle.<sup>12–15</sup>

The low frequency semicircle appears in impedance spectra if conductivity of the host liquid is high enough to have a complete relaxation of the electrical field in the sample within the frequency range of the impedance spectrometer (0.1 Hz to 1 MHz).<sup>12</sup> In many practical cases, the conductivity of the host material is low so that only high frequency semicircle (or section of it) appears in real impedance spectra, so values of  $R_{2A}$  and CPE cannot be achieved from impedance spectra. For this case, the frequency dependences of capacitance and dielectric loss are shown in Figs. 4(c) and 4(d). Experimental data (black circles) and fitting for  $R_{2b}/C_{2b}$  relaxation (red curve) in Fig. 4(c) show plateaus at high frequencies, but the levels of these plateaus are different since the experimental data follow Eqs. (1)–(3) while the  $R_{2b}/C_{2c}$  fittings follow Eqs. (4) and (5), i.e., information about  $\epsilon_1$  still present in impedance spectra. Difference between values of  $\epsilon_{\text{eff}}$  measured directly at high



**A**

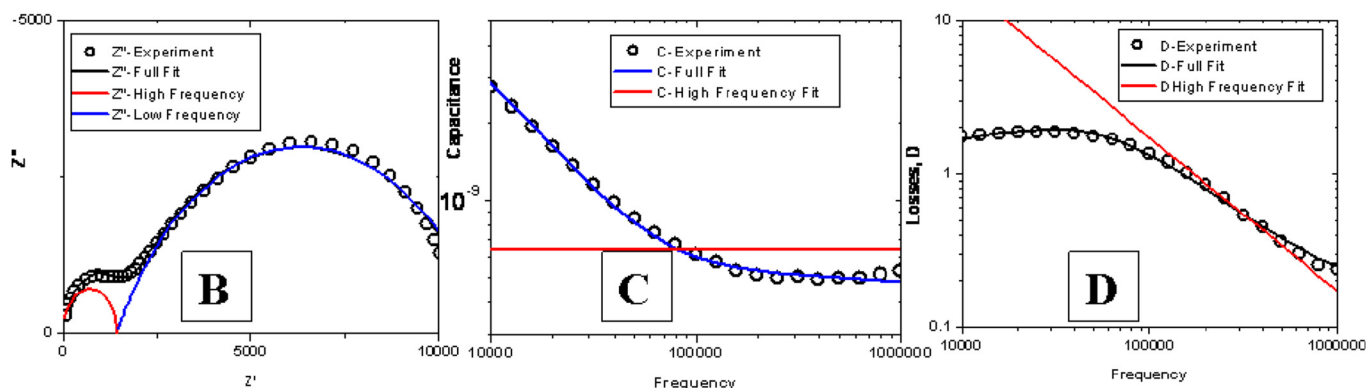
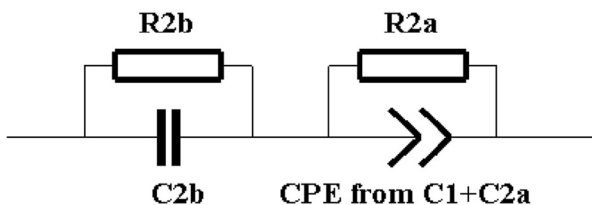


FIG. 4. Impedance spectra of two phase system with nonconductive suspended and conductive host phase (slurry of barium titanate powder dispersed in butoxyethanol). Circles—experimental data, black line—fitting by full equivalent circuit (a); red line—high frequency part of relaxation ( $R_1$ - $C_1$  element); blue line—low frequency part of relaxation ( $R_2$ - $CPE_2$  element). (a) Example of brick wall model and corresponding equivalent circuit; (b) experimental impedance spectra ( $Z'$ - $Z''$ , full frequency range); (c) and (d) capacitance and dielectric losses data in high frequency range.

frequency ( $\varepsilon_h$ ) and calculated from high frequency semicircle ( $\varepsilon_c$ ) allows calculating values of permittivity for both phases ( $\varepsilon_1$  and  $\varepsilon_2$ ) from the high frequency part of impedance spectra without analyzing of low frequency semicircle. This approach can be useful for various two phase systems which do not exhibit low frequency semicircle in the available frequency (0.1Hz to 10 MHz).

Experimental studies of different slurries were conducted to confirm the theoretical approaches described above. Slurries were prepared by dispersing of various dielectric powders in several host liquids. Dielectric powders were BTO, strontium titanate (STO), calcium titanate (CTO), and titanium dioxide (TO). Butoxyethanol (BOE), ethylene glycol (EG), and propylene carbonate (PC) were used as host liquids. Preparation of slurries is described in detail in Ref. 13. Two values of effective permittivity were derived from the high frequency part of impedance spectra:  $\varepsilon_h$  was measured directly at 0.5 MHz while  $\varepsilon_c$  was calculated from the high frequency semicircle. While Eqs. (1)–(3) were used for fitting of  $\varepsilon_h(X_1)$  dependences, Eq. (5) was applied to fit  $\varepsilon_c(X_1)$  dependences for all samples investigated. It was suggested that parameters of slurries ( $\varepsilon_1$ ,  $\varepsilon_2$ , and  $X_P$ ) do not depend on solids loading for each type of slurry (i.e., they are not a function of  $X_1$ ).

The results of this study are summarized in Figs. 5 and 6. Fig. 5 (left) shows the results for slurries prepared by dispersing of different powders in the same solvent (BOE). Red down triangles and blue up triangles represent  $\varepsilon_c(X_1)$  and  $\varepsilon_h(X_1)$ , respectively. Corresponding curves are obtained by fitting of experimental data with Eq. (5) and Eqs. (1)–(3) for  $\varepsilon_c(X_1)$  and  $\varepsilon_h(X_1)$ , respectively. These fitting procedures generate parameters of slurry components ( $\varepsilon_1$ ,  $\varepsilon_2$ , and  $X_P$ ) shown as inserts for each type of slurry. It is revealed that the applied models result in good fitting with the experimental data and provide reasonable values of slurry parameters. The same experimental data were rearranged in Fig. 5 (right). Upper picture (E) shows  $\varepsilon_c(X_1)$  dependences for a different powder compositions. It can be seen that  $\varepsilon_c(X_1)$  is insensitive to the type of powder in the slurry which confirms the suggestion that only the host liquid is responsible for high frequency semicircle and justifies the use of Eq. (5). It allows calculating of permittivity  $\varepsilon_2$  of the host liquid and the critical volume fraction of powder at which percolation  $X_P$  takes place. Since the permittivity  $\varepsilon_1$  of powder is not considered in Eq. (5), it cannot be extracted from  $\varepsilon_c(X_1)$  dependences. In the contrary, the value of  $\varepsilon_h(X_1)$  is sensitive to the type of powder as shown in Fig. 5(f) so that Eqs. (1)–(3) should be used in this case to calculate the values of  $\varepsilon_1$ .

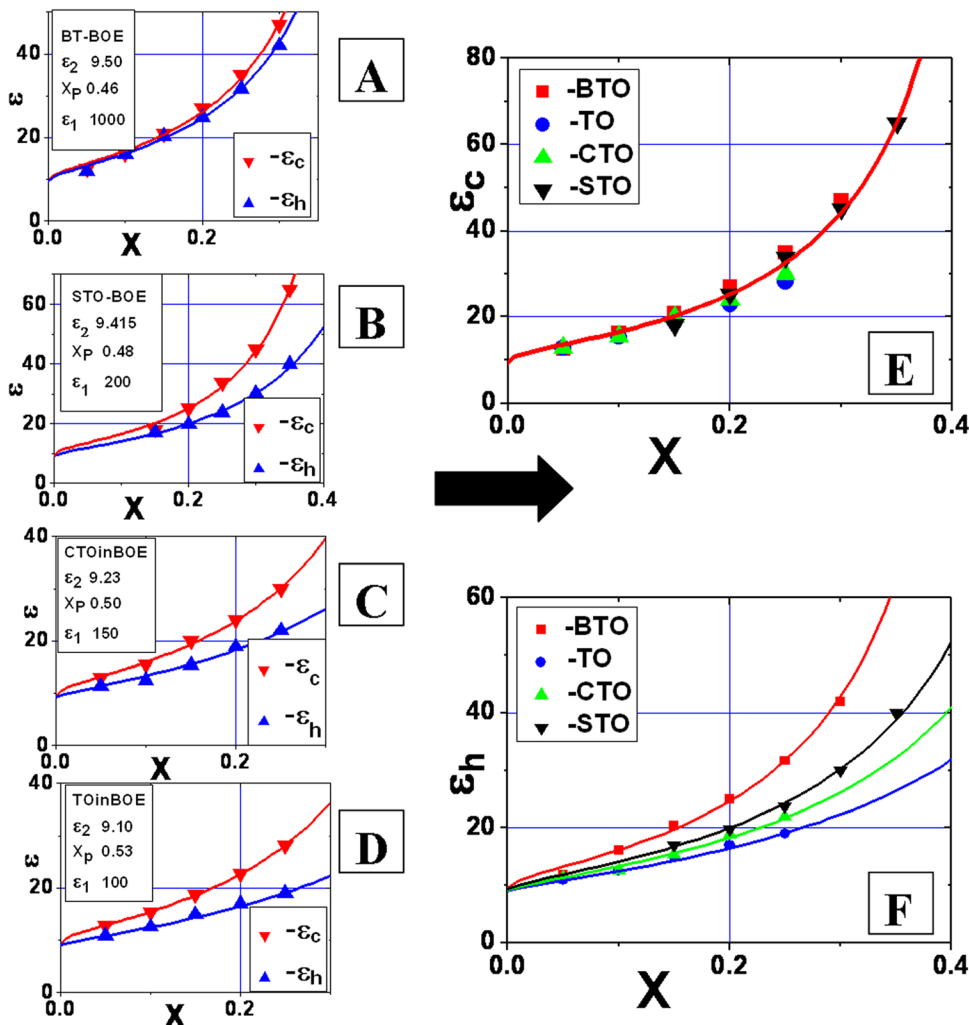


FIG. 5. Dependences of high frequency permittivity  $\varepsilon_h$  and permittivity calculated from high frequency semicircle  $\varepsilon_c$  for various powders in BOE. (a) BTO, (b) STO, (c) CTO, (d) TO; (e)  $\varepsilon_c$  dependence for all powders, (f)  $\varepsilon_h$  dependence for all powders.

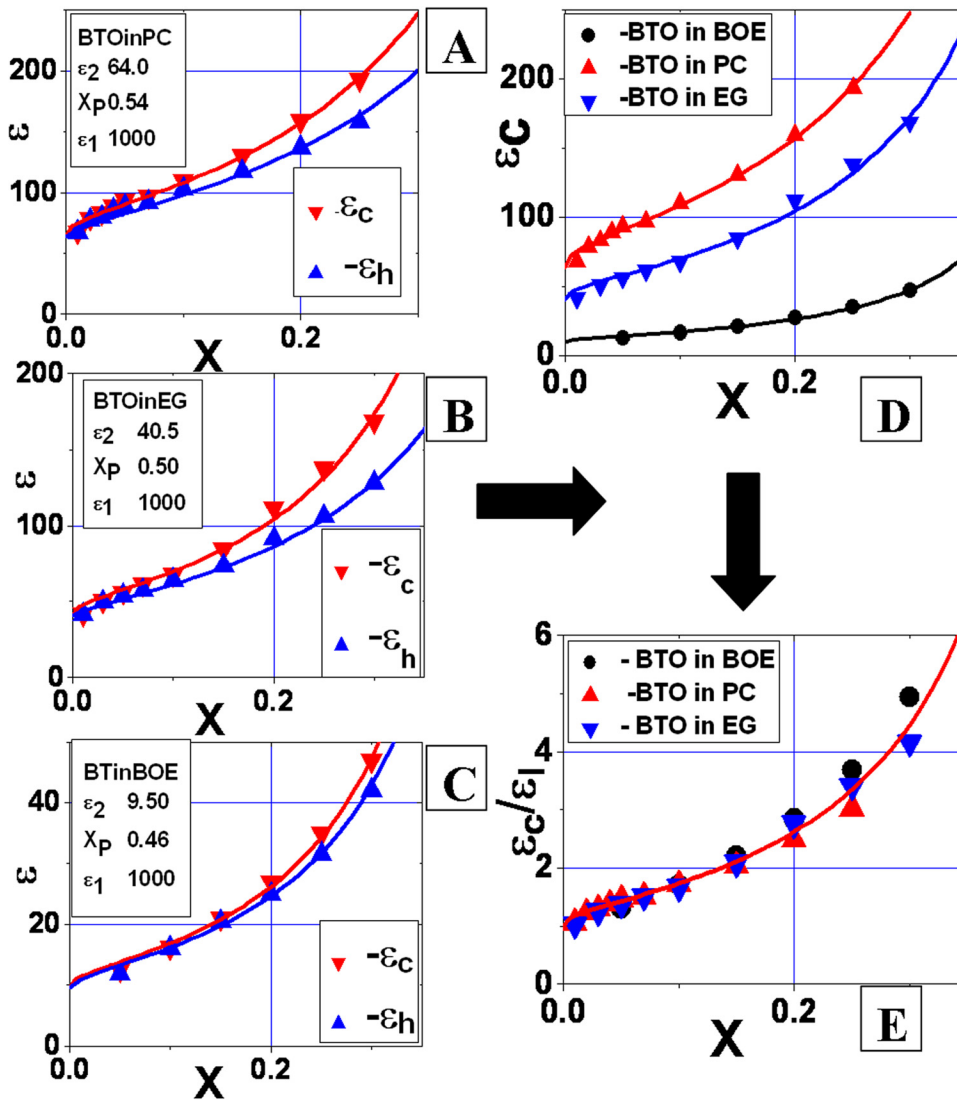


FIG. 6. BT powder dispersed in different liquids. Dependences of high frequency permittivity and permittivity calculated from high frequency semicircle. (a) PC, (b) EG, (c) BOE; (d)  $\epsilon_c$  dependence for all liquids, (e)  $\epsilon_c/\epsilon_1$  ratios for all liquids.

Influence of host liquid properties on the impedance spectra is shown in Fig. 6. Left three pictures in Fig. 6 show the results for slurries prepared by dispersing of BTO powder in different solvents. Red down triangles represent  $\epsilon_c(X_1)$ , blue up triangles represent  $\epsilon_h(X_1)$ , and corresponding curves were obtained by fitting of experimental data with Eqs. (1)–(3) and (5). Good fitting quality and reasonable values for slurry parameters were obtained. Fig. 6 shows also the same experimental data after rearrangement on right side of the figure. Fig. 6(d) reveals  $\epsilon_c(X_1)$  dependences for all three host liquids. It is shown that  $\epsilon_c(X_1)$  is shifted proportionally to permittivity of corresponding liquid. Normalized values of effective permittivity  $\epsilon_c/\epsilon_2$  are shown in Fig. 6(e) indicating that differences between the slurries are compensated and validating the use of Eq. (5) for  $\epsilon_c(X_1)$  dependences.

Table I shows permittivity values for various powders ( $\epsilon_1$ ) and liquids ( $\epsilon_2$ ) as well as percolation threshold ( $X_{1p}$ ). These values were calculated from high frequency part of the impedance spectra using Eqs. (1)–(3) and (5). For all slurries investigated, threshold values are close to 0.5 that are reasonable for well dispersed particles of nearly spherical shape. The calculated values of permittivity of liquids are reproducible and in good agreement with the literature data.

Fitting accuracy of permittivity for powders depends on the value of dielectric contrast. For a low contrast case (TO-BOE), the difference between  $\epsilon_c$  and  $\epsilon_h$  is large enough so that  $\epsilon_1$  is well defined while for high contrast (BTO-BOE), the difference between  $\epsilon_c$  and  $\epsilon_h$  is small so that the value of  $\epsilon_1$  can be only estimated. However, the relationships obtained from the high frequency part of impedance spectra are opposite to that for the low frequency part as shown in Table II. Values of permittivity  $\epsilon_1$  measured for bulk sintered samples and  $\epsilon_1$  calculated from the low and high frequency

TABLE I. The values of permittivity of liquids and powders and percolation parameters of corresponding slurries calculated from high frequency parts of impedance spectra.

| Liquid | Powder | $\epsilon_1$ | $\epsilon_2$ | $X_p$ |
|--------|--------|--------------|--------------|-------|
| PC     | BTO    | ~1000        | 64.0         | 0.54  |
| EG     | BTO    | ~1000        | 40.5         | 0.50  |
| BOE    | BTO    | ~1000        | 9.5          | 0.46  |
| BOE    | STO    | 200          | 9.4          | 0.48  |
| BOE    | CTO    | 150          | 9.2          | 0.50  |
| BOE    | TO     | 100          | 9.1          | 0.53  |

TABLE II. Comparison of permittivity values of bulk materials with the values calculated from low frequency<sup>13</sup> and high frequency parts of impedance spectra.

| Material  | TO      | CTO     | STO      | BTO       |
|-----------|---------|---------|----------|-----------|
| Bulk      | 86–173  | 198     | 300–310  | 1200–3000 |
| Low F sc  | 142 ± 5 | 210 ± 8 | 300 ± 10 | 1400 ± 50 |
| High F sc | 100     | 150     | 200      | ~1000     |

sections of slurry impedance spectra are compared. While the low frequency part of the spectra provides a better accuracy in determining the permittivity  $\epsilon_1$  of powders in slurries of low permittivity contrast, the high frequency part provides a better accuracy for slurries of high permittivity contrast.

## CONCLUSIONS

Extension of brick wall model on two phase systems with percolation provides a solid basis for theoretical characterization of pure dielectric systems. Corresponding equations can also be applied to the systems with mixed conductivity. The values of permittivity of both phases as well as percolation threshold can be calculated from low frequency as well as high frequency sections of the impedance spectra for a given two phase system. Experimental investigations of various slurries confirm the theoretical predictions. Theoretical equations, developed in this study, provide a good fitting to experimental data. Calculated parameters of slurry components are in good agreement with previous measurements of slurries and the literature data for corresponding bulk materials.

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