Metallic electrolyte composites in the framework of the brick-layer model

H. Lustfeld [a],*, C. Pithan [b], M. Reißel [c]

[a] *PGI-1 Forschungszentrum Jülich, D52425 Jülich, Germany*
[b] *PGI-7 Forschungszentrum Jülich, D52425 Jülich, Germany*
[c] *Fachhochschule Aachen, Abteilung Jülich, D52428 Jülich, Germany*

Abstract

It is well known that the already large dielectric constants of some electrolytes like $BaTiO_3$ can be enhanced further by adding metallic (e.g. Ni, Cu or Ag) nanoparticles. The enhancement can be quite large, a factor of more than 1000 is possible. The consequences for the properties will be discussed in the present paper applying a brick-layer model (BLM) for calculating dc-resistivities of thin layers and a modified one (PBLM) that includes percolation for calculating dielectric properties of these materials. The PBLM results in an at least qualitative description and understanding of the physical phenomena: This model gives an explanation for the steep increase of the dielectric constant below the percolation threshold and why this increase is connected to a dramatic decrease of the breakdown voltage as well as the ability of storing electrical energy. We conclude that metallic electrolyte composites like $BaTiO_3$ are not appropriate for energy storage.
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1. Introduction

The problem of storing electrical energy has been present for many years. But nowadays it has become more urgent due to the fact that (i) classical power supplies like coal- or atomic power plants are replaced by wind energy and solar energy (ii) oil production will decrease in the near future, so that the international community has to find alternatives. Apart from the conservative energy storage systems there are two promising lines of research possibly leading to new storage systems with high energy densities. One is the development of lithium and other alkali ion batteries, the other is the development of supercaps. In this paper we concentrate on supercaps being composites of electrolytes like $BaTiO_3$ and metallic (Ni, Cu, Ag) nanoparticles.

An enormous increase of the dielectric constant $\varepsilon \rightarrow \varepsilon_c = \alpha\varepsilon$ has been observed in various $BaTiO_3$ metallic composites.[1–3] α increases and nearly diverges when approaching the percolation threshold. However, it is very difficult to fabricate e.g. $BaTiO_3$ metallic composites in a reproducible way. The distribution of the metallic nanoparticles can be very inhomogeneous,[4]

shape and size of the nanoparticles affecting the properties[5,6] are not well defined, and a tendency to clustering has also been observed.[7] All these effects lead to a large mean variation of the dielectric properties[8] and to an uncertainty in determining the percolation threshold.

Fig. 1 gives a practical impression on how irregular the inclusion of metallic nanoparticles into a ceramic matrix of $BaTiO_3$ takes place. Fig. 2 demonstrates how dramatically the inclusion affects the dielectric constant of the overall composite. It should be noted here again that the distribution of the metallic nanoparticles in the ceramic phase will not only lead to strong fluctuations within one sample but also from one sample of identical average composition to another one. This serious problem can be recognized in the obvious scattering of the measured data in Fig. 2. In this context it should be noted that the experimental work, published earlier by Chen et al.[1] and Huang et al.[2], obviously neglects the fact that reproducibility of ceramic processing and material homogeneity represents a major issue. All their measured values of the dielectric constant seem to perfectly follow an empirical percolation law. No details on fluctuations (e.g. error bars) are given.

In spite of the experimental difficulties these composites are of great interest. One reason is the following: Since α can become very large[9] these composites seem to be candidates for

* Corresponding author. Tel.: +49 2461 61 4745; fax: +49 2461 61 2850.
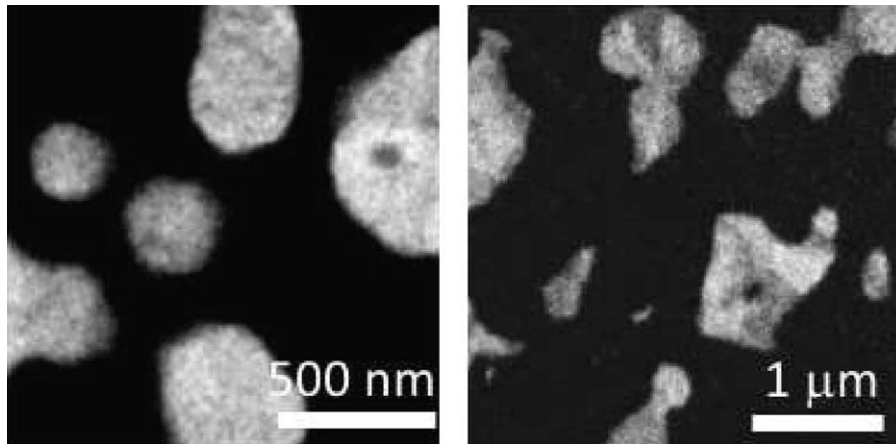*E-mail address:* H.Lustfeld@fz-juelich.de (H. Lustfeld).

Fig. 1. Left figure[3]: microscopic picture of Ni nanoparticles (concentration 27%) in BaTiO$_3$. Right figure[3]: microscopic picture of Cu nanoparticles (concentration 27%) in BaTiO$_3$. Both figures demonstrate that the metallic nanoparticles are not even approximately of uniform size or shape.

an immense energy storage provided the metallic particles do not lead to a significant increase of dc-conductivity and a significant decrease of the breakdown voltage V_b. It is the purpose of this paper to discuss both these issues.

In a good electrolyte the dc-conductivity is negligibly small and the conductivity practically remains zero as long as the metallic particle concentration is small enough. If the thickness h of the electrolyte is much larger than the averaged size of the metallic particles s_0, i.e. $h \gg s_0$, everything is simple: conductivity sets in only if the metallic particle concentration p passes the percolation threshold[10] p_c. At this concentration the percolation length ξ diverges following the power law

$$\xi = b_1 s_0 (1 - x)^{-\nu}, \quad x = \frac{p}{p_c} \tag{1}$$

Here b_1 is a parameter depending on the material and ν is a universal exponent of percolation theory.[10] However, if $h \gg s_0$ is not fulfilled, then the conductivity sets in before the percolation

Fig. 2. This plot[3] demonstrates the enormous increase of the dielectric constant with increasing concentration of Cu nanoparticles in BaTiO$_3$. Obviously the mean variation is not small, which is not surprising when looking at Fig. 1.

threshold is reached and depends on h as well. Since this situation is of practical interest, we will discuss it in some detail in Section 2 using the BLM.[11–13] This model neglects the detailed shape of the metallic particles completely. More seriously, it is a one dimensional model and therefore the critical concentration is given by $p_c = 1$. However, we think that it contains the essential physics for thin layers in a simple way. Therefore, we calculate the limit p_σ, for which the conductivity is no longer negligible. Of course, p_σ is much too high. We take care of this shortcoming by looking at the relative change

$$\Delta x_\sigma = x_c - x_\sigma = \frac{p_c - p_\sigma}{p_c} \tag{2}$$

and by inserting instead of $p_c = 1$ the actual percolation threshold. This is concededly a crude approximation but we think it leads to correct estimates.

In Section 3 we compute the dielectric constant ε_c of a composite, the breakdown voltage V_b and the maximum storable energy U_A as function of the relative concentration x in the framework of a brick-layer model, in which we include percolation (PBLM). This modification takes the scaling results of 3d percolation theory into account. The PBLM is therefore much more realistic than the original BLM.

Approaching the percolation threshold we get the following results

$$\varepsilon_c \rightarrow \infty, \quad V_b \propto \frac{1}{\varepsilon_c}, \quad U_A \propto \frac{1}{\varepsilon_c} \tag{3}$$

This result is important and marks the essential point of our paper. The PBLM predicts that metallic particles can increase the dielectric constant of an electrolyte considerably. Therefore, when being interested in high capacitances, metallic composites like those of BaTiO$_3$ may be an option. On the other hand, using these composites for energy storing does not seem to be a good choice at all. Section 4 ends the paper.

2. Conductivity in the BLM approach

Assume that the composite is an insulator with thickness h and an area A. The first approximation in the BLM consists in
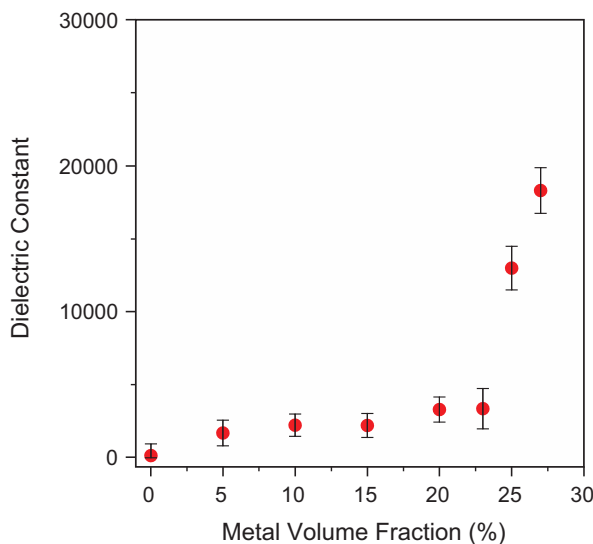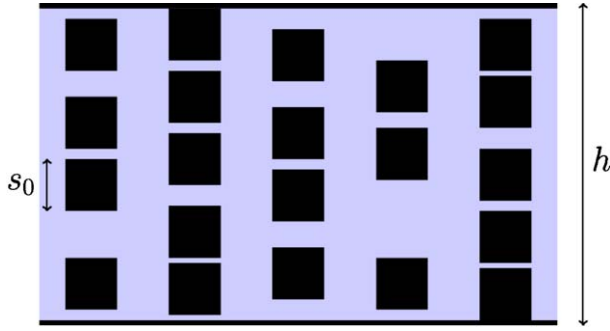
Fig. 3. Sketch of the (nearly filled) brick-layer model.[11,12] An electrolyte with thickness h is located between electrodes of area A. Embedded in it are 'bricks' (i.e. metallic cubes with edge length s_0) being arranged in columns. The distance between bricks in a column is arbitrary, however, bricks must not overlay each other. Any interaction between different columns (currents, capacitance etc.) is neglected.
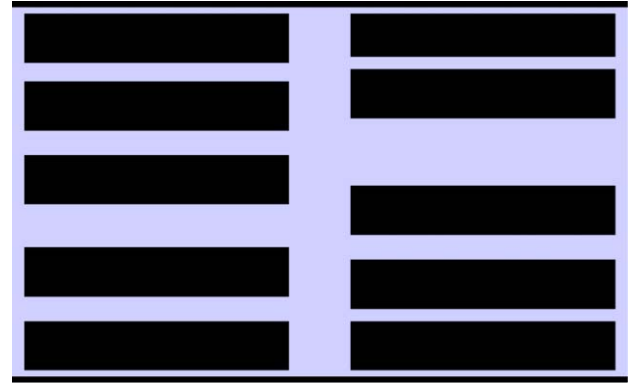

Fig. 4. The left and the right column contain the same number of bricks and the same electrolyte. The inverse of the total capacitances of both columns are equal in spite of different distances between the bricks.

treating the metallic particles as cubes with an edge length s_0. These cubes are called *bricks* building columns and step by step, with increasing brick concentration, filling the composite. If A is the area of the upper surface then the number N_S of these columns is given by

$$N_S = \frac{A}{s_0^2} \tag{4}$$

In the brick-layer model the distance of bricks within a column is arbitrary to mimic the randomness of the real metallic particles. The number N_{tot} of brick places is given by

$$N_{tot} = \frac{Ah}{s_0^3} \tag{5}$$

In this model any side effects, any transverse currents and any capacitances between columns are neglected. This is an approximation reducing the dimension of the problem to 1 and thus moving the percolation threshold to 1 as well, cf Fig. 3.

We are interested in the situation close to the percolation threshold. In this limit the BLM is nearly filled with bricks. Therefore, in analogy to switching from electrons to holes in semiconductors, we consider the distribution of the free, not yet occupied places M given by

$$M = \frac{(1-x)A \cdot h}{s_0^3}, \quad x = \frac{p}{p_c} \tag{6}$$

Let $w(k)$ be the probability that k places are free in a column. Then we obtain according to the Poisson distribution

$$w(k) = \frac{\lambda^k}{k!} e^{-\lambda}, \quad \lambda = \frac{M}{N_S} = \frac{h}{s_0} \cdot (1-x) \tag{7}$$

From this formula we get the dc-conductivity as follows: According to our assumption the electrolyte itself is an insulator. Conductivity in a column occurs as soon as it has no free places, which happens with a probability $w(0)$. Denoting the specific conductivity of the metal by σ_m, we obtain for the conductivity per area

$$\sigma_A \approx \frac{\sigma_m}{h} e^{-(1-x)h/s_0} \tag{8}$$

Note that the conductivity increases exponentially as soon as x approaches the percolation threshold.

If the electrolyte is very thin, the electric flow moves mainly in vertical direction. Transverse currents are less important and thus the main approximation of the BLM is less serious. Therefore, we think that Eq. (8) can be applied for estimating the dc-conductivity just by replacing the threshold of the BLM (which is 1) by the actual value. Here we present a result for a multilayer capacitor containing Ni nanoparticles of size $s_0 \approx 10^{-7}$ [m]. The typical thickness of one layer is $h = 3 \times 10^{-6}$ [m], the conductivity of Ni is $\sigma_{Ni} = 1.43 \times 10^7 [S/m]$. Then we obtain

$$\sigma_{A|Ni} = e^{30-(1-x)\cdot 300}[\text{S/m}^2], \quad x = \frac{p}{p_c} \tag{9}$$

Therefore, the conductivity is expected to increase exponentially fast for $x > 0.9$.

3. An expanded brick-layer-model, results and discussion

The BLM has a peculiarity making the computations of dielectric properties very simple: In a column the electric field E is the same between two adjacent bricks, independent of the distance d_i between them. Therefore, the total voltage and the stored energy per area can easily be obtained in this model since only the sum of the distances between all bricks in a column matters. The individual distances between the bricks are irrelevant, cf Fig. 4.

The main shortcoming of the BLM is the neglect of 3 dimensional percolation. This becomes obvious by looking at the percolation threshold p_c. It is always 1 in this model whereas in reality p_c depends on the material[14,15] and typical values are in the range $p_c \approx 0.3 \pm 0.1$. Here we suggest a procedure of including 3 dimensional percolation without removing the above mentioned simplicity of the model. The correlation length

$$\xi = b_1 s_0 (1-x)^{-\nu} \quad : \quad \text{coherence length}$$
$$\nu = 0.88 \quad\quad\quad\quad : \quad \text{universal critical exponent} \tag{10}$$

is the diameter of typical clusters, the consistent expression for the number of metallic nanoparticles in a typical cluster with universal dimension $1/\rho$ is then

$$N_{clus} = b_2 \xi^{1/\rho} : \qquad \text{number of particles in a cluster} \quad (11)$$

N_{clus} is well known as the *z-average of molecular weight*,[10,16] b_2 as b_1 are nonuniversal constants depending on the material.

The idea is now quite simple, we suggest to replace the bricks of the BLM by the typical clusters of percolation theory. We call this the percolation-brick-layer model (PBLM) and the typical clusters *quasi-bricks*. Of course this model is still a crude one and more sophisticated models exist for calculating resistivity[17] and the dielectric constant.[18] However, in view of the experimental uncertainties (uniqueness of the percolation threshold, shape of the metallic particles etc.) mentioned above, this crudeness need not be a serious disadvantage. More important, crude as it may be, the model demonstrates the striking and for energy storage crucial connection between dielectric constant and breakdown voltage, as will be shown below.

There are three further objections against this procedure we will shortly discuss:

- clusters are not massive objects but *fractals*. However, there is a difference between dc-conductivity which depends on the detailed structure and dielectric properties which do not. In our opinion this makes the quasi-brick approximation less severe. In fact it is well known (e.g. from Faraday's cage) that the electric field of a grid has similar properties as an electric field of the corresponding continuous plane.
- the distance between clusters is not well defined since the clusters are not clearly separated from each other. So the effective size of the clusters may be smaller than ξ and neglecting this effect would mean an underestimation of the breakdown voltage and the maximum storable energy. On the other hand this is balanced, at least partly, by the fact that we neglect the possibly sharp edges of the clusters reducing the breakdown voltage etc.
- The PBLM (like the BLM) neglects the fields between adjacent columns. But this is a kind of surface effect between columns, and the larger ξ the less important it will be, we think.

Therefore, in spite of all these objections, we think that using typical clusters as quasi-bricks in the BLM will be a reasonable approximation, at least when looking into dielectric properties.

With the above introduced quasi-bricks we get the equation for the places $M^{(q)}$ not occupied by quasi-bricks

$$M^{(q)} = \frac{A \cdot h}{\xi^3} - x \cdot \frac{p_c \cdot N_{tot}}{N_{clus}} \quad (12)$$

and for the number N_S^q of columns containing quasi bricks:

$$N_S^{(q)} = \frac{A}{\xi^2} \quad (13)$$

From these relations we get the probability for k not occupied places in a column,

$$w^{(q)}(k) = \frac{\lambda^{(q)k}}{k!} e^{-\lambda^{(q)}} \quad (14)$$

$$\lambda^{(q)} = \frac{M^{(q)}}{N_S^{(q)}} \quad (15)$$

$\lambda^{(q)}$ depends now on x. From the *hyperscaling relation* of percolation theory[10] we get

$$\frac{\nu}{\rho} - 3\nu = -\beta = -0.41 : \quad \text{universal critical exponent} \quad (16)$$

and thus

$$\lambda^{(q)}(x) = \frac{1}{b_1} \frac{h}{s_0} \cdot (1-x)^\nu \cdot \left(1 - \frac{x}{x_h} \cdot \left(\frac{1-x}{1-x_h}\right)^{-\beta}\right) \quad (17)$$

Here x_h is a material constant derived from b_1 and b_2. Let $d(x)$ be the average over all distances in a column, then we get

$$d(x) = \sum \xi \cdot k \cdot w^{(q)}(k) = h \cdot \left(1 - \frac{x}{x_h} \cdot \left(\frac{1-x}{1-x_h}\right)^{-\beta}\right) \quad (18)$$

From this result we obtain three important relations. Let E_{max} be the maximum electric field of the pure electrolyte and ε its dielectric constant. Then the breakdown voltage $V_b^{(0)}$ in a column is given by

$$V_b^{(0)} = E_{max} \cdot h \quad (19)$$

Its maximum storable energy per area in a column, $U_A^{(0)}$, is

$$U_A^{(0)} = \varepsilon_0 \varepsilon E_{max}^2 \cdot h \quad (20)$$

Now the breakdown voltage V_b of the composite in a column depends on x and is given by

$$V_b(x) = E_{max} \cdot d(x) = V_b^{(0)} \cdot g(x) \quad (21)$$

$$g(x) = 1 - \frac{x}{x_h} \cdot \left(\frac{1-x}{1-x_h}\right)^{-\beta} \quad (22)$$

U_A, the corresponding maximum energy the composite can store per area, is given by

$$U_A(x) = \varepsilon_0 \varepsilon E_{max}^2 \cdot d(x) = U_A^{(0)} \cdot g(x) \quad (23)$$

The dielectric constant of the composite, ε_c, depends on x as well and can be obtained from the relation

$$U_A(x) = \frac{1}{h} \varepsilon_0 \varepsilon_c(x) \cdot V_b^2(x) \quad (24)$$

Setting this equal to Eq. (23) and using Eqs. (19)–(22) we get

$$\varepsilon_c(x) = \alpha(x) \cdot \varepsilon, \quad \alpha(x) = \frac{1}{g(x)} \quad (25)$$

The function $\alpha(x)$ has been plotted in Fig. 5 for various values of x_h.

We observe from Fig. 5 that the PBLM predicts an enormous increase of the dielectric constant ε_c for metallic composites of
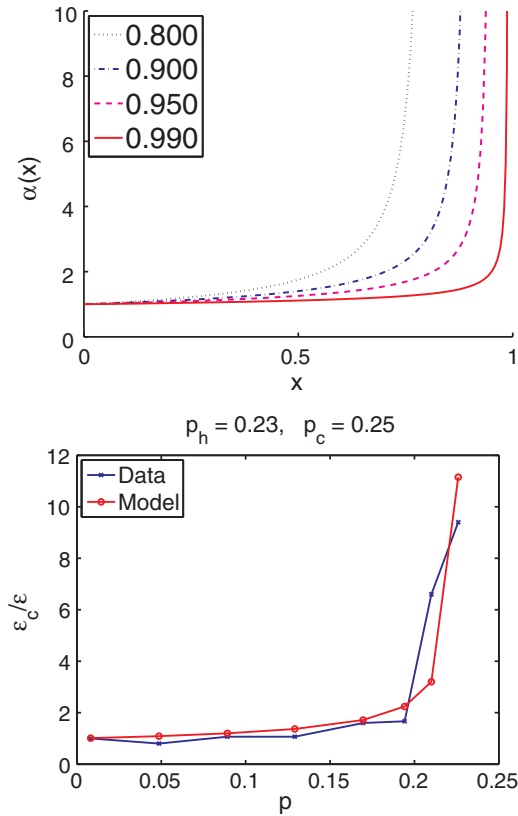
Fig. 5. Top: Plot of the function $\alpha(x) = \varepsilon_c/\varepsilon$, defined in Eq. (25), for various x_h values. Bottom: Comparison between measured dielectric constant of Fig. 2 and theory for $p_c = 0.25$ and $x_h = 0.92$. $p_h = x_h \cdot p_c = 0.23$.

electrolytes like $BaTiO_3$ as soon as their metal concentration approaches the percolation threshold. It can also be seen from Fig. 5 that, depending on the material parameter x_h, the curves of the model agree qualitatively with the experimental results,[1,2] in particular with those of Fig. 2. We conclude that the model describes the physics correctly.

Therefore we infer that the prediction of a simultaneous dramatic decrease of the breakdown voltage V_b and consequently U_A, the maximum energy to be stored, is correct as well. The
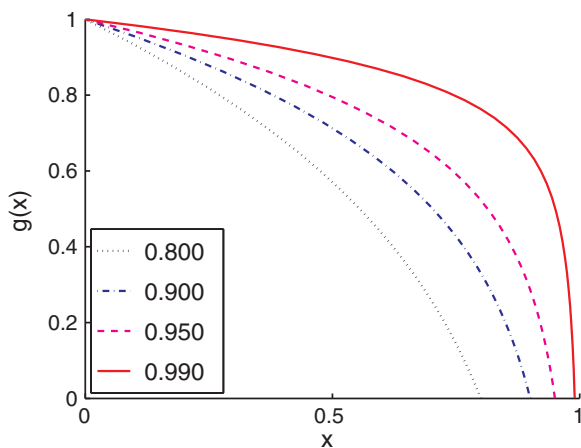

Fig. 6. Plot of the function $g(x)$, defined in Eq. (22), for various x_h values. Note the dramatic decrease when $x = p/p_c$ is approaching the percolation threshold.

relative decrease is shown in Fig. 6 and the following relations hold

$$V_b \propto \frac{1}{\varepsilon_c} \tag{26}$$

$$U_A \propto \frac{1}{\varepsilon_c} \tag{27}$$

Thus, according to the PBLM, there is no chance of using a metallic composite supercap with high capacitance as a device for energy storage.

One may object that the PBLM is a rather crude model. In fact, the critical concentration of the nanoparticles is some percent below the percolation threshold, which is an artefact of the model. On the other hand the PBLM includes the fundamental percolation relations and therefore should contain the essential physics.

We also want to point out that in the next better approximation for breakdown voltages, the nonuniform sizes and the irregular shapes of the metallic nanoparticles in these complex composites have to be taken into account. However, these important features are not part of the standard percolation theory.[10]

4. Conclusion

We have shown, that inclusion of metallic nanoparticles in supercaps with high dielectric constants ε will lead to remarkable changes of their properties. Of course, in particular in thin layers, the problem of increasing conductivity between the electrodes due to the metallic nanoparticles arises. Applying the brick-layer-model (BLM), we have shown that in fact the conductivity is increasing exponentially when approaching the percolation threshold. Apart from that, we have concentrated on the dielectric properties of those composites. To do that in a simple but qualitatively correct manner we have used the BLM again, however, extended it by including the fundamental relations of 3d percolation theory, which we call the percolation-brick-layer model (PBLM). Using that model, we detected a dramatic increase of the dielectric constant and thus of the capacitance when approaching the percolation threshold, which is *simultaneously connected* to a not less dramatic decrease of the breakdown voltage and the ability of storing electrical energy. From these results we infer that inclusion of nanoparticles is possibly an appropriate measure for increasing the capacitance but not at all an advantageous one for increasing the storage properties.

Acknowledgement

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