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

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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.

Keywords: Percolation; Composites; Dielectric properties; $BaTiO_3$ and Titanates; Capacitors

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

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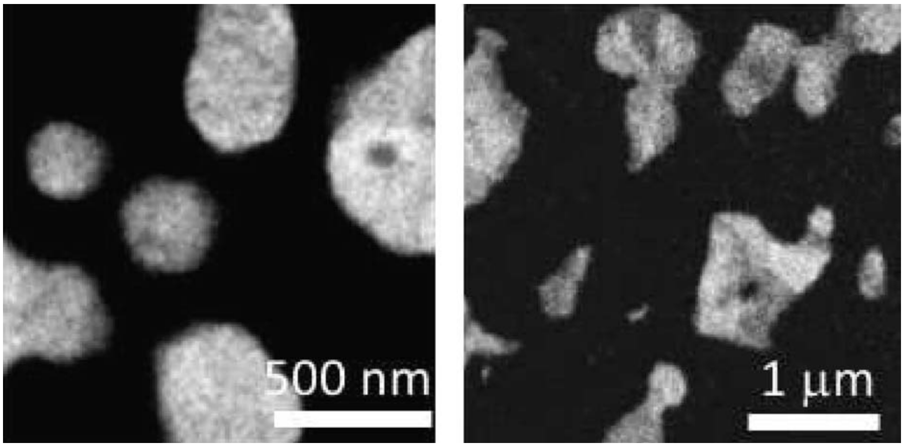

Fig. 1. Left figure[3]: microscopic picture of Ni nanoparticles (concentration 27%) in $BaTiO_3$. Right figure[3]: microscopic picture of Cu nanoparticles (concentration 27%) in $BaTiO_3$. Both figures demonstrate that the metallic nanoparticles are not even approximately of uniform size or shape.

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 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

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

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.

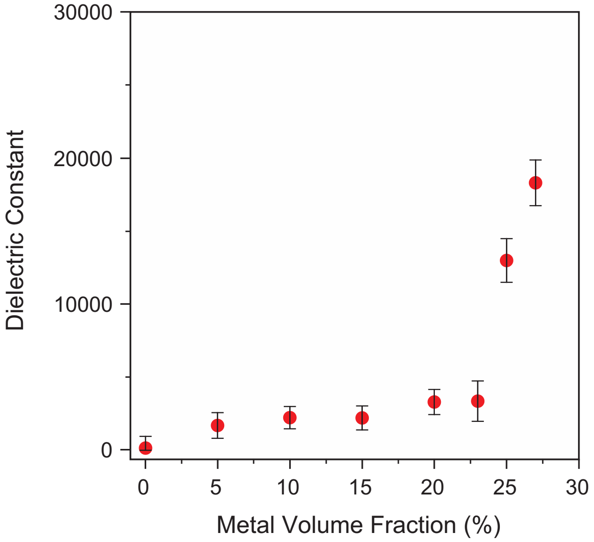

Fig. 2. This plot[3] demonstrates the enormous increase of the dielectric constant with increasing concentration of Cu nanoparticles in $BaTiO_3$. Obviously the mean variation is not small, which is not surprising when looking at Fig. 1.

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