# Random-network simulation of an ultracapacitor based on metal-solid-electrolyte composite

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A random-network model of a dense (pore-free) metal-solid-electrolyte composite is developed. Real and imaginary parts of admittance are simulated as a function of frequency and composition by means of the transfer matrix algorithm on a cubic lattice. For a composite without a solid-electrolyte membrane in the middle (insulating with respect to electronic current) the results predict the capacity maximum at the percolation threshold in three dimensions and two maxima in two dimensions as a function of composition; they are compared with the predictions of the effective medium theory. For a composite with an insulating membrane in the middle, typical for ultracapacitors, the maximum of capacitance in three dimensions is at equal portion of metal and solid-electrolyte particles. In contrast to metal dielectric mixtures there are no giant enhancement effects in static capacitance as a function of composition: the upper estimates of the enhancement factor are proportional to the ratio of the size of the sample to the size of the grains.

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## I. INTRODUCTION

Dual phase composites of electronic and fast ionic conductors are the subject of great current interest as components of electrodes for solid oxide fuel cells,[1] separation membranes,[2] and ultracapacitors.[3] The special feature of these composites is that metal grains are conductive in electrons and solid oxide particles are conductive in ions. The do does not pass across the contact of metal and solidelectrolyte grains, unless an electrochemical reaction would mediate it. However, the ac passage would be possible, at high enough frequencies, because the metal-solid-electrolyte interface is not blocking for the relaxation currents.[4]

In the absence of Faraday processes, such a composite can be used as a filling material for ultracapacitors. Consider a tablet of such a composite, pressed between two metallic plates. The network of metal grains touching the plates effectively "continues" them inside the sample, increasing the effective electrode/electrolyte interface, and thereby the capacitance. This idea was utilized in a number of designs, including the composite-based ultracapacitors.[3] Note that not only surface determined effects are present here. The interplay of the surface and bulk effects deserves a serious study both under dc and ac conditions.

In Ref. 5 an effective medium theory was developed for the electrical admittance of the metal-solid-electrolyte composite. The theory predicted a large enhancement of the bulk dielectric constant of the composite near the percolation threshold in the metallic component. The effect was several orders of magnitude greater than the similar phenomenon for the metal dielectric mixtures. However, the mean-field theory cannot describe the systems of the finite size with boundary effects and the inhomogeneous field distribution. It addresses only to the electrical properties of the "bulk" which under do conditions do not exist as such, due to the Debye length screening near the effective electrode surface. At the same time, the consideration of bulk properties may have a right on existence under ac conditions. This would be true at frequencies so large that the electric double layer at the effective surface would not have enough time to be charged by migration of ions through the electrolyte bulk.

A random-network computer simulation is appropriate in this situation. It should answer the main questions concerning the capacitance dependence on the composition of the random mixture and frequency (for a given equivalent circuit of two grains junction). The particular advantage of the simulation is that it can treat the system with its real boundary conditions, thereby showing when the predictions of the bulklike effective medium theory are approved and when they are misleading. While this is a relatively easy task in two dimensions, it is numerically more complicated in three dimensions, due to a drastic growth of the simulation time with the increase of the system size. We study the twodimensional system first and then present the results in three dimensions. In the latter case, we were limited to rather thin samples, so that the clear cut between the "surface" and bulk properties cannot be made, but the main trends could nevertheless be seen.

## II. MODEL AND SIMULATION PROCEDURE

### A. The underlying model

In order to calculate the real and imaginary parts of the overall admittance of a metal-solid-electrolyte composite we use the model of a random network of complex resistors. Each resistor represents the admittance between two single grains in the composite. For simplicity of the network, we choose a square lattice with four nearest neighbors in two dimensions and a cubic lattice with six nearest neighbors in three dimensions. Since no pores are considered, we have only two kinds of sites representing the grains (metal and solid-electrolyte sites). With two different sites, we get three kinds of bonds: bonds between metal sites, bonds between solid-electrolyte sites, and bonds between metal and solid-electrolyte sites. The bonds represent the admittance between the connected sites (Fig. 1).[5]
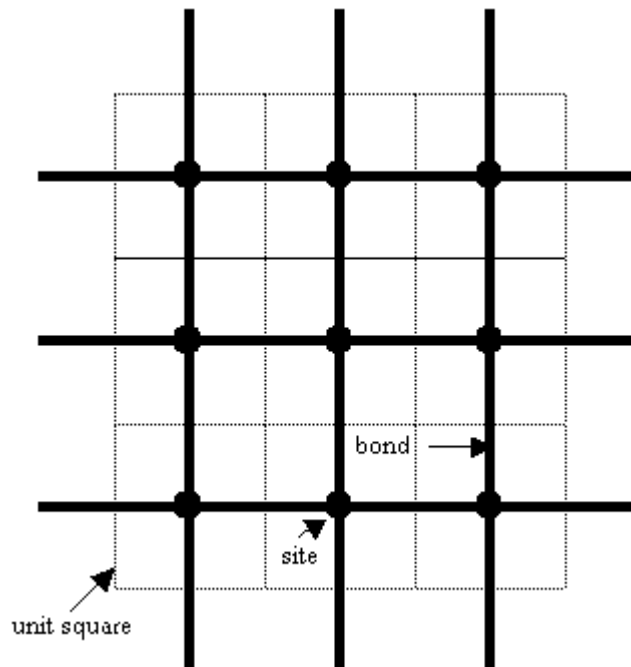


FIG. l. The model of a square grid, used in the two-dimensional simulation. In the middle of each unit square is a site, which is connected to its four nearest neighbors by bonds. Similar arrangement between sites and bonds is used in the three-dimensional simulation on a cubic lattice with six nearest neighbors.

In the simulation we calculate the overall admittance between the top and bottom line in two dimensions and top and bottom layer in three dimensions. These lines/layers represent the electrodes of the system and consist of metal sites. The other sites are randomly distributed with a constant probability to be occupied either by a metal or solid-electrolyte grain. We set the size of the system equal in all dimensions.

We shall also consider, as a special case, the system in which the middle layer consists only of solid-electrolyte sites. This will simulate the situation used in ultracapacitors, where the membrane, blocking the electronic current, is put into the middle of the sample.[3] The membrane prevents short cuts which in a finite size sample may emerge even below the percolation threshold.

## B. Bonds and circuits in the bulk and at the surface

The complex admittances represented by the bonds between two sites are realized by elementary circuits. The circuits of the three bonds are shown in Fig. 2. The circuit between metal sites is an Ohmic resistor. The circuit between solid-electrolyte sites is a circuit with an Ohmic resistor and a capacitor, connected in parallel. The capacitor here is responsible for the geometrical capacitance of the solid-electrolyte grain. The circuit between metal and solid-electrolyte sites is more complex.[4] It has an important new element: the blocking double layer capacitance of the interface between the metal and solid-electrolyte grains. The other elements of the circuit are the same as appeared before, but with a scaling factor, taking into account that only "half" of each particle takes part in the connecting bond. The last two circuits contain capacitors and depend therefore on the frequency $w$. Note that we use here the same basic equivalent circuits as in Ref. 5 (Sec. II) where the possible variations around them were discussed.

We will work with a finite system with no periodical boundary conditions and use dimensionless units in this simulation. The resistance is measured in the unit of $R_{se}$ and the capacitance in the unit of $C_d$. The admittances of the three circuits (Fig. 2) have the following form:

circuit between metal particles

$$Y(w) = \frac{1}{R_{me}},$$

circuit between solid-electrolyte particles

$$Y(w) = \frac{1}{R_{me}} \text{ and}$$

circuit between metal and solid-electrolyte particles
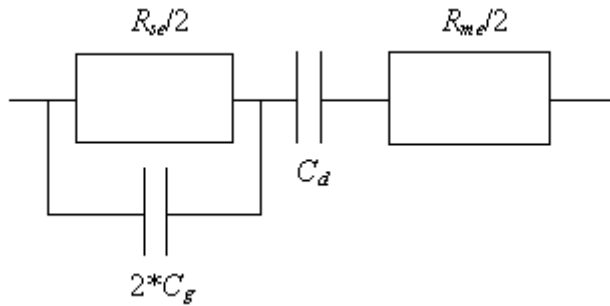
$$Y(w) = \frac{1}{R_{me}},$$

where the frequency is measured in the unit of $\vee$; $\vee = 1/(C_d R_{se})$. Settings are $R_{se} = 1$, $C_d = 1$, and $R_{me} = 10^{-3}$, $C_g = 10^{-4}$. The last two values represent some typical ratios between the conductivities of metals and solid electrolytes, and between the double layer and geometrical capacitances of the grains of 10 μm size.
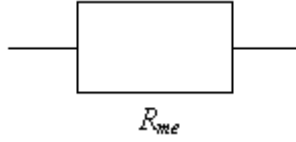
(a)
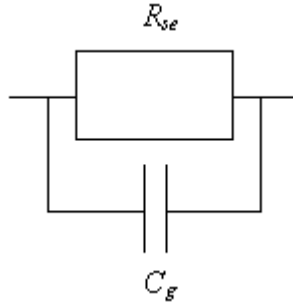
(b)

(c)

FIG. 2. Equivalent circuits for bonds between metal sites (a), between solid-electrolyte sites (b) and between metal and solid-electrolyte sites (c).

## C. Random-network generation

The overall lattice represents a three-dimensional network of complex circuits. Each elementary circuit of the network is determined by the two corresponding sites. Therefore the sites distribution totally determines the system. We want to simulate the effect of the portion $x$, $1 \geq x \geq 0$, of the metal sites in the total number of sites, i.e., the effect of different mixtures, on the admittance of the lattice. Each site of the lattice is randomly generated with a probability of $x$ being a metal site and a probability of $1-x$ being a solid-electrolyte site, since there are no pores. Exception is for the sites of the top and bottom layers, which are always metal sites. In the simulation of capacitor with the "solid electrolyte membrane" in between, the middle layer will consist of solid-electrolyte sites. Since the bonds of the lattice are functions of the corresponding sites, they are determined by this procedure too.

## D. Transfer matrix algorithm

The algorithm used to calculate the admittance of the network is a special version of the transfer matrix algorithm described in Refs. 6 and 7. We want to calculate the admittance from the top to the bottom layer of the cube. The bottom layer is connected with the ground. The top and bottom layers consist of null resistors. We build our cube by adding two-dimensional layers from the left to the right part of the cube. A layer is added by adding each bond of the layer to the already existing strip of the cube.

Each time we add a bond we calculate its contribution to the admittance of the strip: we add to all sites except to site $j$ a grounded wire. To site $j$ we add a voltage $U_j$. The current through a grounded wire at site $i$ is given by $I_i = A_{ij} U_j$. $A$ is a ($n$ x $n$) x ($n$ x $n$) matrix (n is the size of one dimension) and describes the admittance of the lattice. How does matrix $A$ change to matrix $A'$ if we add a new bond to the existing strip? First we add the horizontal bonds. A new horizontal bond $R$ is added to the stripe to site a and we get

$$I_i = U_j (A_{ij} - (A_{ia}A_{aj}R) / (1 + A_{aa}R)).$$

Therefore matrix $A'$ is given by

$$A'_{ij} = A_{ij} - (A_{ia}A_{aj}R) / (1 + A_{aa}R).$$

When we add the vertical bonds between site a and $\beta$ we get three cases:

(1) $i \neq j$; $a = i$; $\beta = j$: $I_i = U_j (A_{ij} - (1 / R))$ and therefore $A'_{ij} = A_{ij} - (1 / R)$;

(2) $i = j$; $a = i$; $\beta \neq i$: $I_i = U_j (A_{ij} + (1 / R))$ and therefore $A'_{ij} = A_{ij} + (1 / R)$;

(3) all other cases: $I_i = U_j A_{ij}$ and therefore $A'_{ij} = A_{ij}$.

So matrix $A$ is recursively calculated each time a bond is added to the already existing lattice. The admittance from the top to the bottom layer of the cube is then given by $A_{00}$ if the last bonds added to the strip are nonconducting bonds.


## III. RESULTS

We now present the results for the real part of the admittance and its imaginary part divided by frequency which represents the system capacitance. We give them separately for two-dimensional and three-dimensional systems and in each case we show the graphs with the dependence on the frequency (w) and on the composition ($x$). Frequencies will be given in the units of $\vee$ [Eq. (4)], which is the inverse time needed to polarize one solid electrolyte grain. The value of $\vee$ varies for different metal-solid-electrolyte combinations. Typical values belong to the range $10^5$ - $10^8$ Hz [4]. Unless otherwise stated, the results would refer to the system without an isolating membrane in the middle of the sample.

All the figures displaying the frequency dispersion will show two main dispersion ranges. The first one is around $\vee$. Here the blocking capacitance of the interface between the metal and solid-electrolyte grains drops down, since the frequencies are already too high for the ion migration through the bulk of the solid-electrolyte grain in order to form the equilibrium double layer at the opposite sides of this grain. The second frequency is much greater and it corresponds to $w = 1 / (R_{se}C_g)$, the characteristic frequency at which the geometrical capacitance of solid-electrolyte grains starts to contribute the shunt transmitting the current.[4]

The error bars shown correspond to the mean square deviation, determined in the multiple random simulation runs.
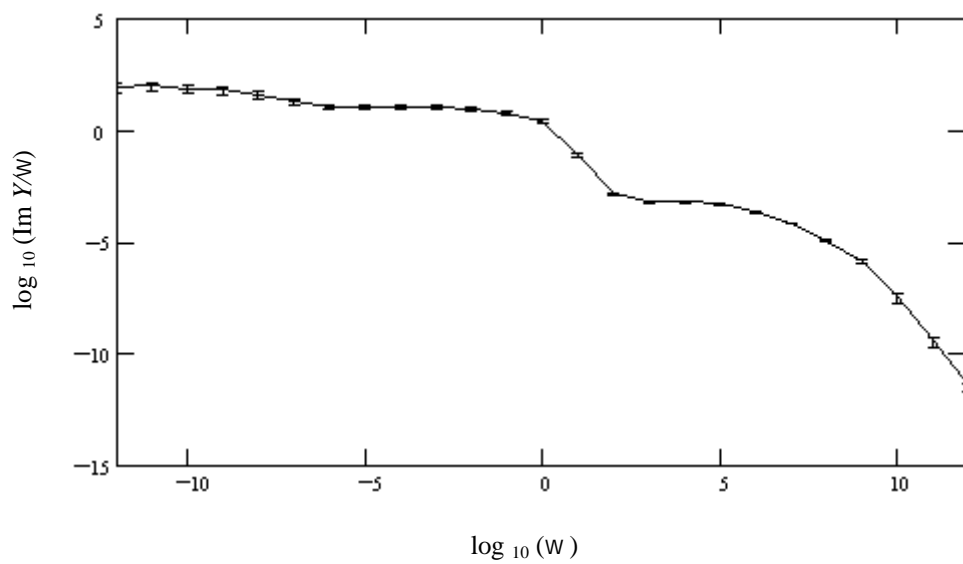
## A. Two-dimensional system

### 1. Frequency dependence

Figure 3 shows the conductivity (a) and capacitance (b) of the system as a function of frequency for $x = 0.5$, i.e., below the percolation threshold in two dimensions for this lattice ($x < x_c = 0.59$).
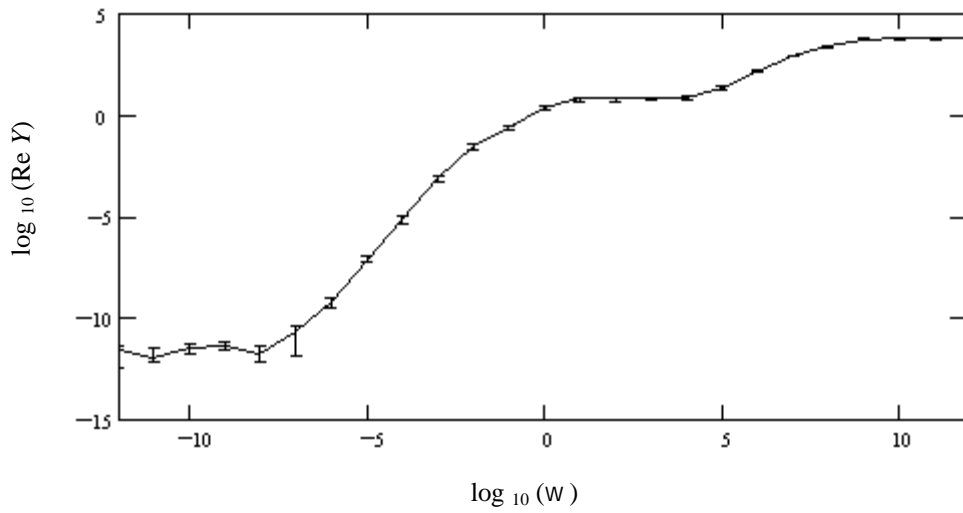


(a)



(b)

FIG. 3. Frequency dependence of conductivity (a) and capacity (b)

for a two-dimensional system of size 80 x 80 with fraction of metal particles $x = 0.5$.

*2. Composition dependence*

Figure 4 shows the full composition dependence of conductivity (a) and capacitance (b) plotted for the frequency $10^{-4}$v, i.e., at the first, low frequency plateau of Fig. 3. The conductivity plot shows the known percolation threshold, $x_c = 0.59$.

The capacitance plot is quite nontrivial. It shows two peaks, first rather shallow one around $x = 0.34$ and the other peak around the percolation threshold. On the same plot for the frequency $10^{-4}$v [Fig. 5(b)], the first peak disappears. The change in conductivity with the frequency increase [Fig. 5(a)] seems to pose no questions; the tail of low (solid electrolyte level) conductance is seen below the percolation threshold because the double layer capacitance is no longer blocking for transient currents.
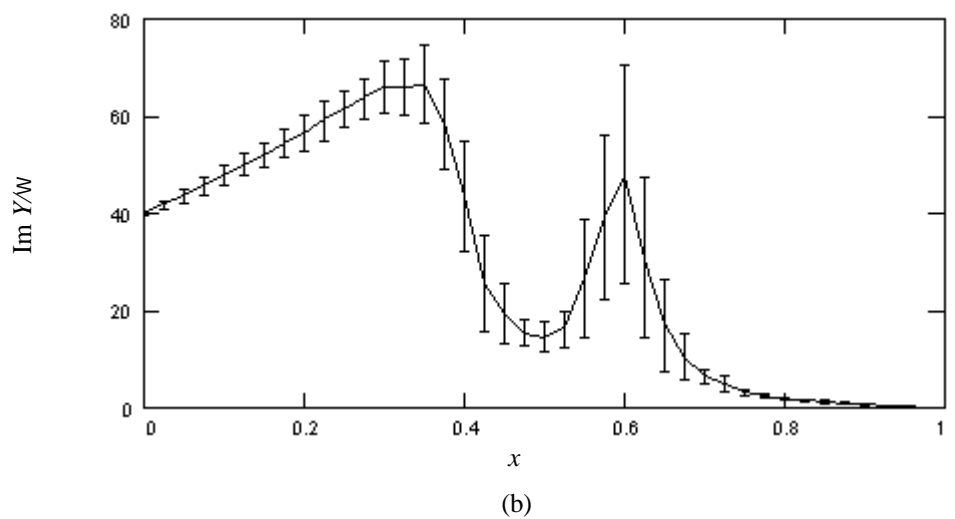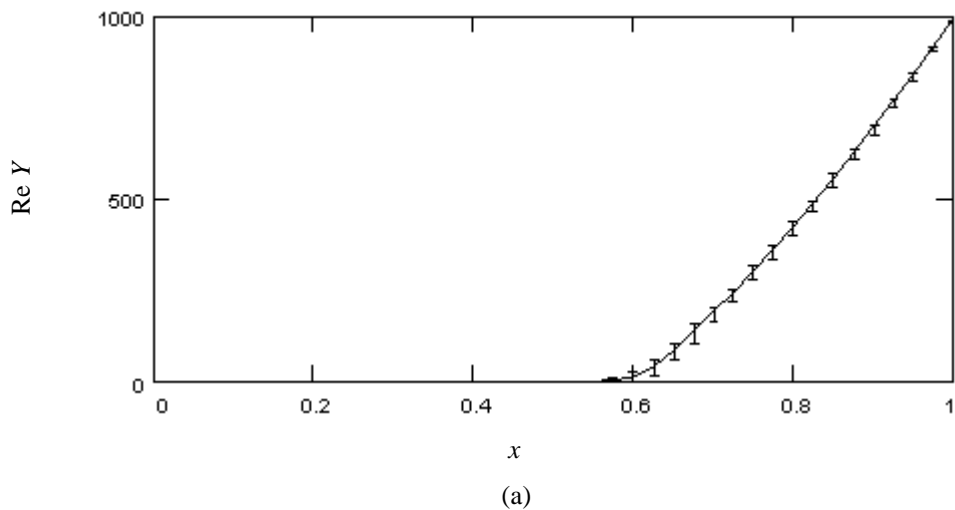
(a)

(b)

FIG. 4. Conductivity (a) and capacity (b) dependence on the fraction of metal particles for a two-dimensional system of size 80 x 80 in the zero frequency limit, $w = 10^{-4}$ v.
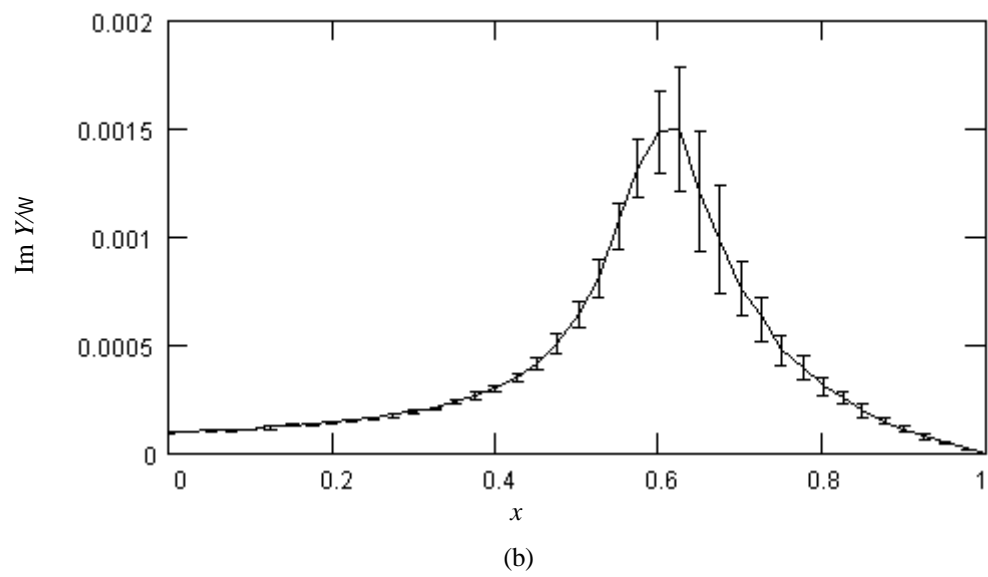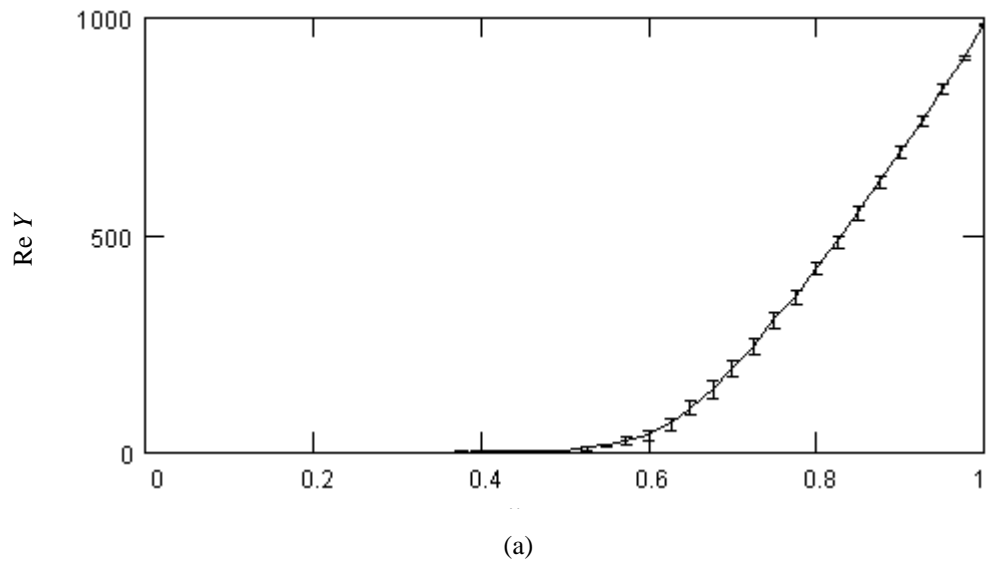
(a)



(b)

FIG. 5. Conductivity (a) and capacity (b) dependence on the fraction of metal particles

for a two-dimensional system of size 80 x 80 at frequency $w = 10^4 \vee$.

## B. Three-dimensional system

### *1. Frequency dependence*

Figure 6 shows the conductivity (a) and capacitance (b) of the system as a function of the frequency for $x = 0.27$, i.e., below the percolation threshold in three dimensions for this lattice ($x < x_c = 0.31$). Both plots look qualitatively similar to those of Fig. 3 for two dimensions.
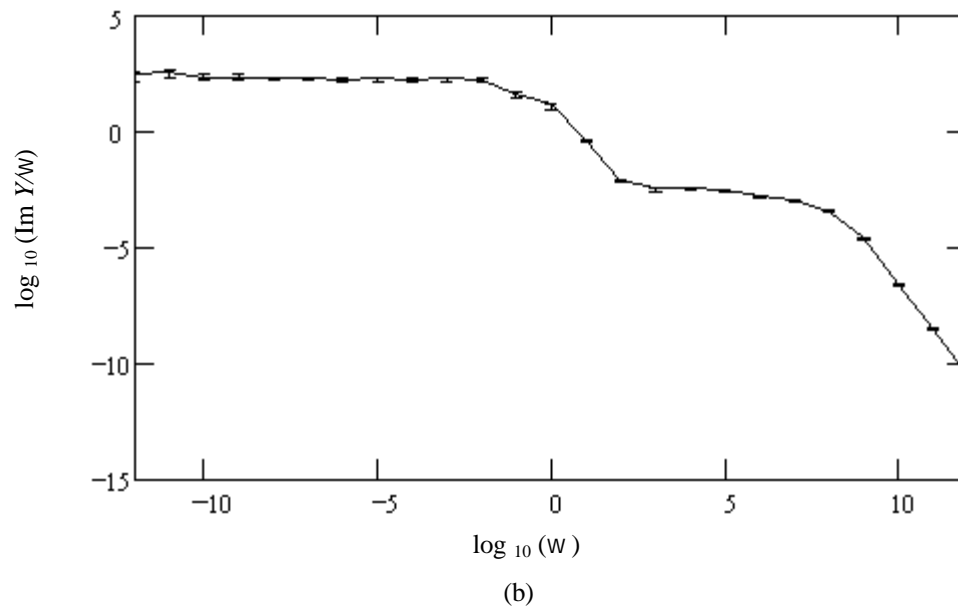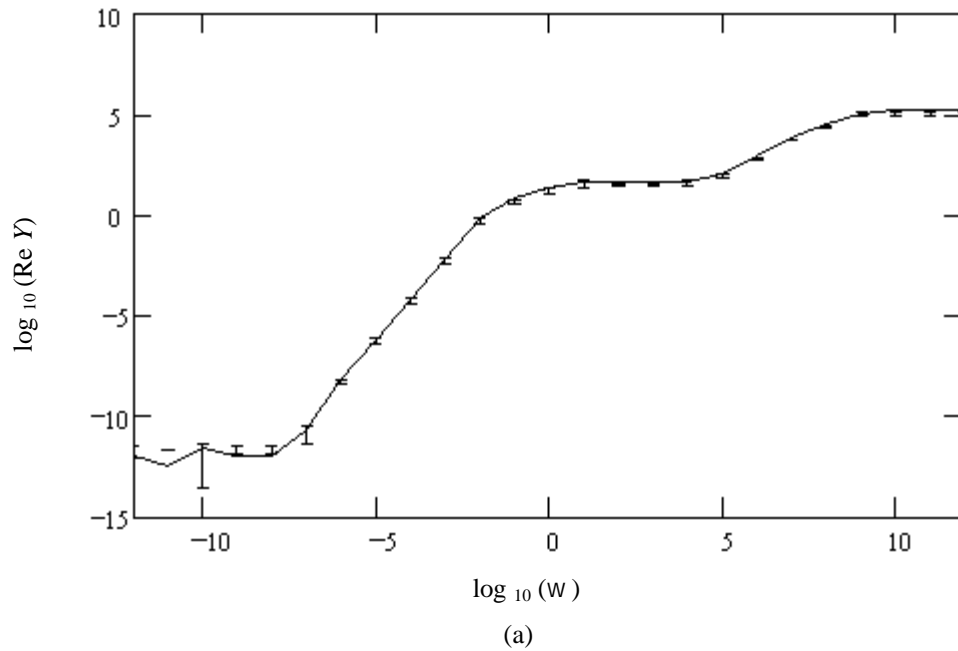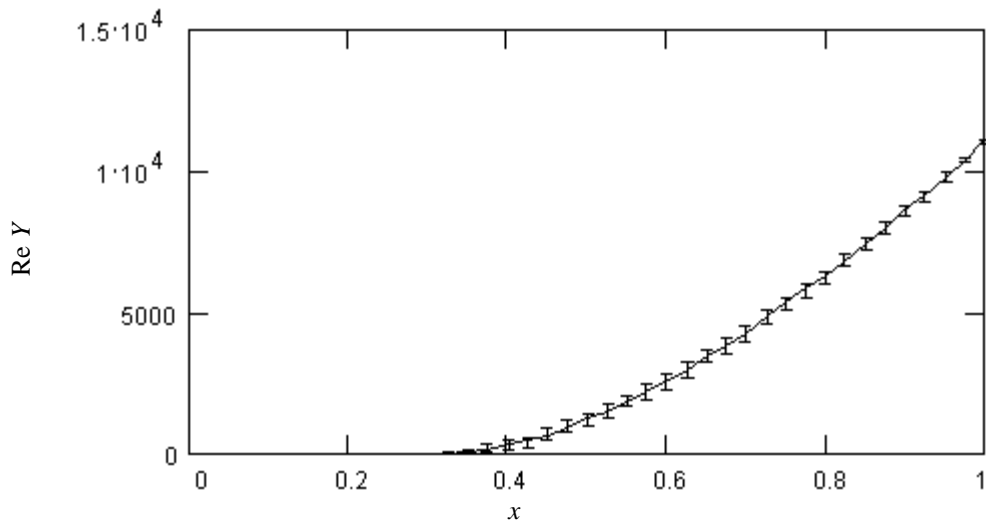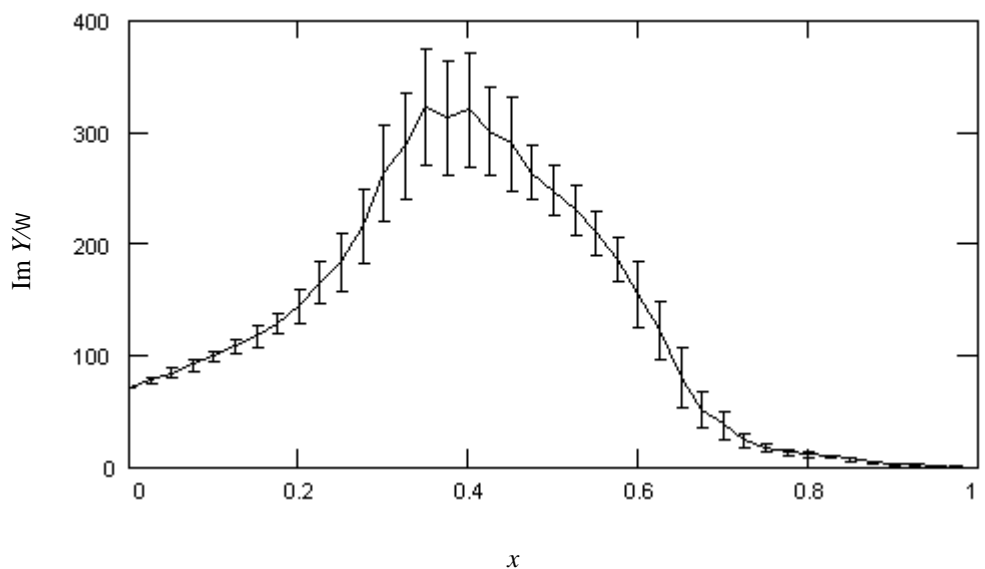


(a)



(b)

FIG. 6. Frequency dependence of conductivity (a) and capacity (b)
for a three-dimensional system of size 12 x 12 x 12 with fraction of metal particles $x = 0.27$.

*2. Composition dependence*

There is no sign of any peak in the capacitance plot other than the one close to the percolation threshold [Figs. 7(b) and 8(b)]. With the frequency increase the height of the peak decreases, but its qualitative shape and position stay about the same. The conductance behavior is the same as before. In Fig. 9, the result for capacitance is shown for a system with a monolayer of solid-electrolyte particles in the middle.



(a)



(b)

FIG. 7. Conductivity (a) and capacity (b) dependence on the fraction of metal particles for a three-dimensional system of size 12 x 12 x 12 in the zero frequency limit, $w = 10^{-4} v$.

(a)



(b)

FIG. 8. Conductivity (a) and capacity (b) dependence on the fraction of metal particles

for a three-dimensional system of size 12 x 12 x 12 at frequency $w = 10^4 \vee$.

(a)



(b)
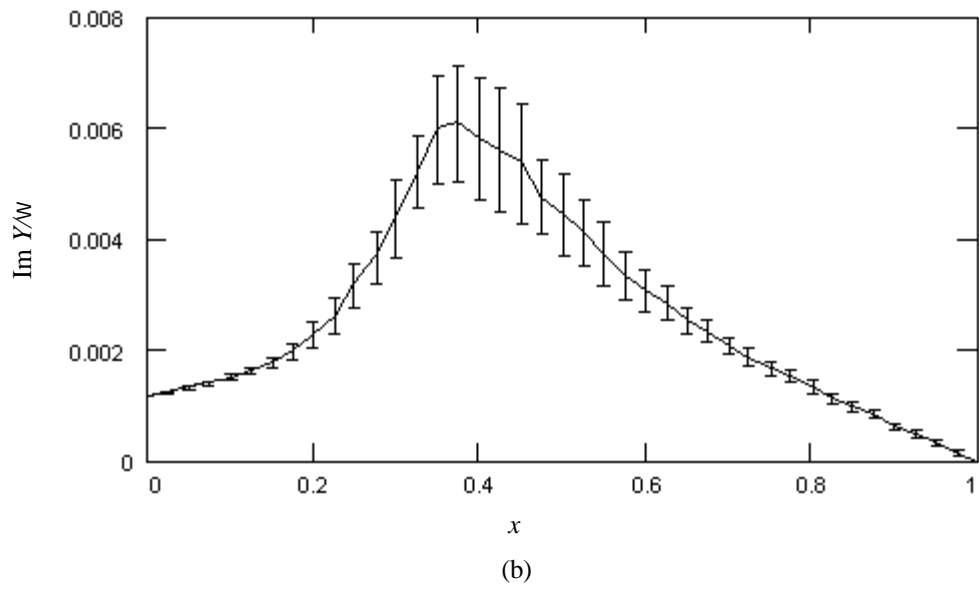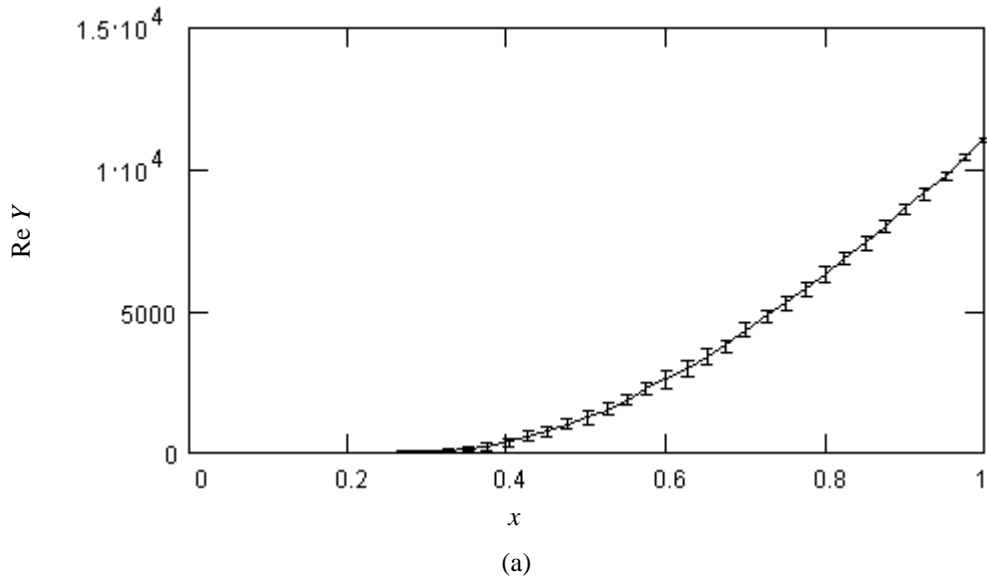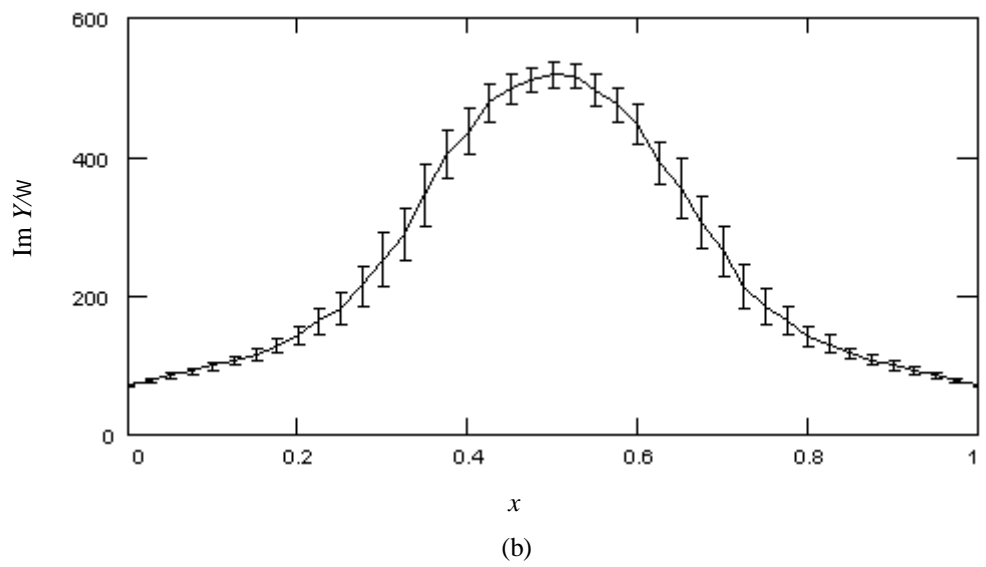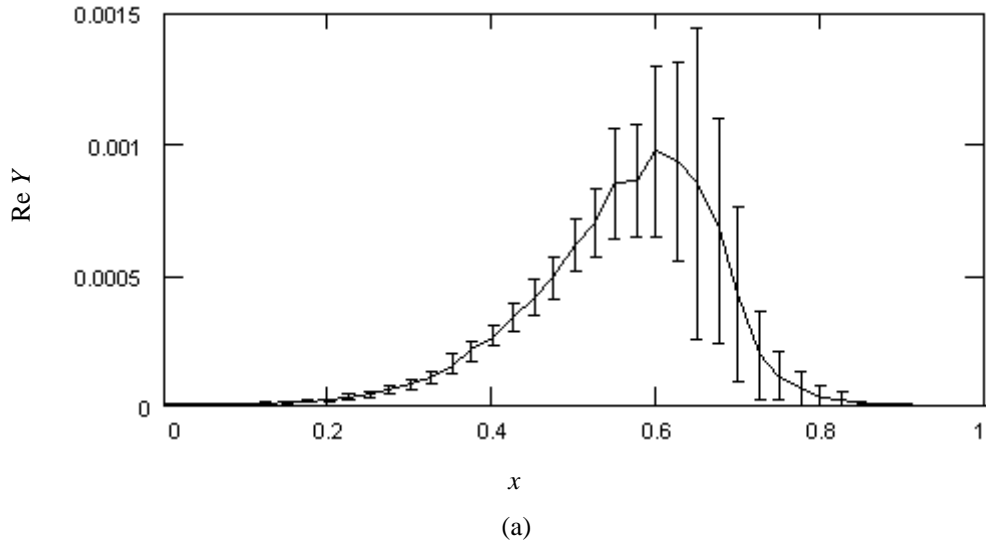
FIG. 9. Conductivity (a) and capacity (b) dependence on the fraction of metal particles

for a three-dimensional system of size 12 x 12 x 12 with an isolating membrane in the middle in the zero frequency limit, $w = 10^{-4}$ v.

## IV. DISCUSSION

The existing theoretical background for the electrophysical properties of metal-solid-electrolyte composites is due to effective medium theory (EMT).[5] In EMT, quasistationary Kirchhoff equations are solved for a system in which one bond or a group of bonds is considered explicitly and all the rest as an effective medium complex resistor. The admittance of the latter is then self-consistently determined by equalizing it to the admittance of the chosen bond or a group of bonds. Solutions have been obtained for the single bond approximation (SB), in which only one bond is considered explicitly, and for the low concentration cluster approximation (LC), which considers explicitly a cluster of bonds with a common site.[9] The latter takes into account at least part of the correlations between the admittance values of the neighboring bonds.

For a mixture of Ohmic resistors and ideal insulators, EMT equations for SB and LC approximations lead to qualitatively correct results for conductivity, though the exact position of the percolation threshold and the conductivity exponent near the threshold are far from the exact solution. The position of the threshold may be improved by treating the parameter $q$ in the Bernasconi-Wiesemann equation [9] as free parameter, being fitted to reproduce the correct threshold value. For a cubic lattice this would give $q = 9.4$ (which is equivalent to an introduction of the effective dimensionality in the Kirkpatrik equation,[8] $d = 10.4$). Of course, improving the position of the threshold in this way, may lead out of control other system properties.

Figures 10 and 11 show the results of the EMT and modified EMT at zero frequency in two dimensions and three dimensions, respectively, for a random mixture metal and solid-electrolyte sites. The sets (a) and (b) display real (conductive) and imaginary (capacitive) parts of admittance. The set of the complex admittances of the bonds is the same as considered above. In Fig. 10, the results are plotted for $q = 1.05$ and 1.8 (at $q = 1$ the first, lower $x$ peak in the capacity diverges). The $q = 1.05$ curve has a two peak shape, similar to the simulation result. In Fig. 11, the three-dimensional results are shown for $q = 2$ and 9.4. There is only one peak structure left here, which is also in agreement with the simulation.

The EMT curve has a small ionic conductivity tail at $x < x_c$ in three dimensions and at $x > 1 - x_c$, which could be seen in logarithmic coordinates for the conductivity in the (a) set. The simulation, of course, does not have such a tail: at $w = 0$ it allows only the electronic current passage through the system, and thus $s = 0$ at $x < x_c$. This discrepancy is an artifact of EMT which, in essence, does not distinguish the kind of charge carriers.

However, the application of EMT to metal-solid-electrolyte mixtures has another, principle shortcoming[5], which is pronounced in the results for capacitance. The EMT is a homogeneous treatment. It cannot describe the spatially heterogeneous structures near interfaces. Indeed, at $w = 0$ and $x < x_c$, the electric field would not penetrate into the bulk of the sample, but will be screened in the narrow layer near the surface of metal clusters connected with the metal plates. The screening distances are that of the Debye length in the solid electrolyte, which are few orders of magnitude smaller than the size of the grain. The system then simply behaves as a solid-electrolyte capacitor with a large surface area: the latter is formed by the surface of the clusters connected with the metal plates. The system capacitance is proportional to the surface area and inversely proportional to the Debye length. In the absence of an electric field, there is no current and the effective Kirchhoff equations of the EMT (Ref. 5) lose their meaning. Thus EMT may only describe the bulk contribution to admittance at nonzero frequencies or at $x > x_c$ but it cannot describe the surface contribution. This is especially well seen in the limit of $x = 0$, where the EMT gives a negligible small capacitance while it should level off to the value of the solid-electrolyte capacitor with flat metal plates, as is obtained in our simulation.

FIG. 10. Conductivity (a) and capacity (b) dependence on the fraction of metal particles

for a two-dimensional system at zero frequency, described by the effective medium theory with $q = 1.05$ (+) and $q = 1.8$ (•).
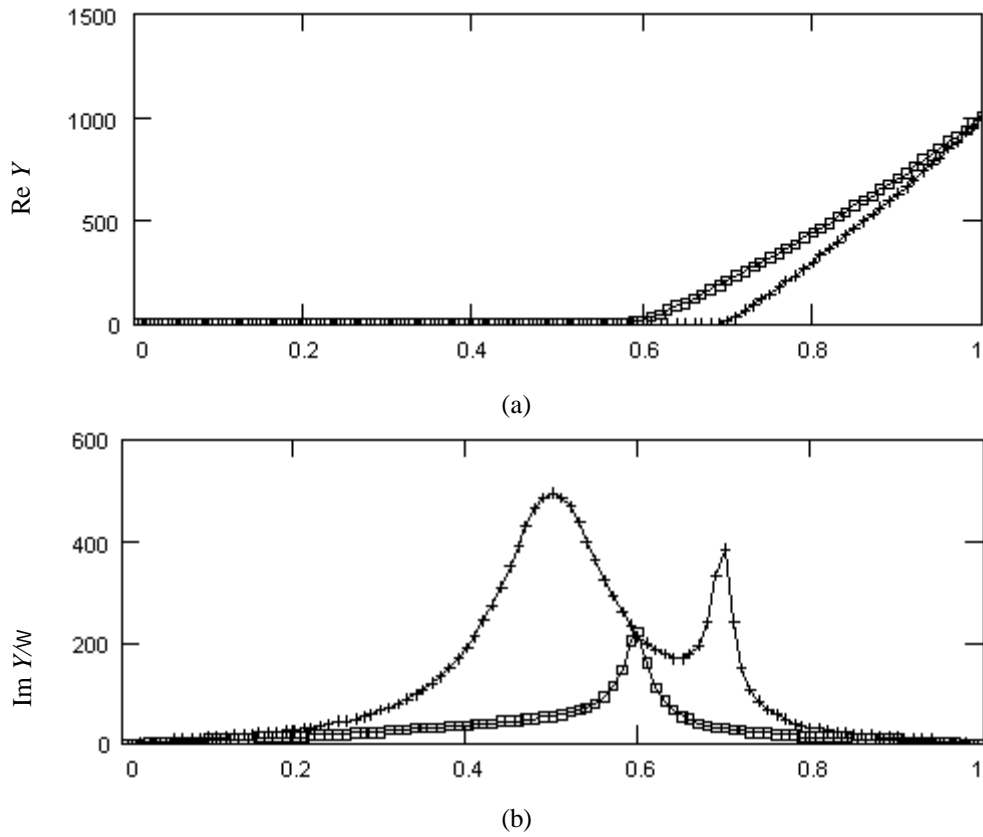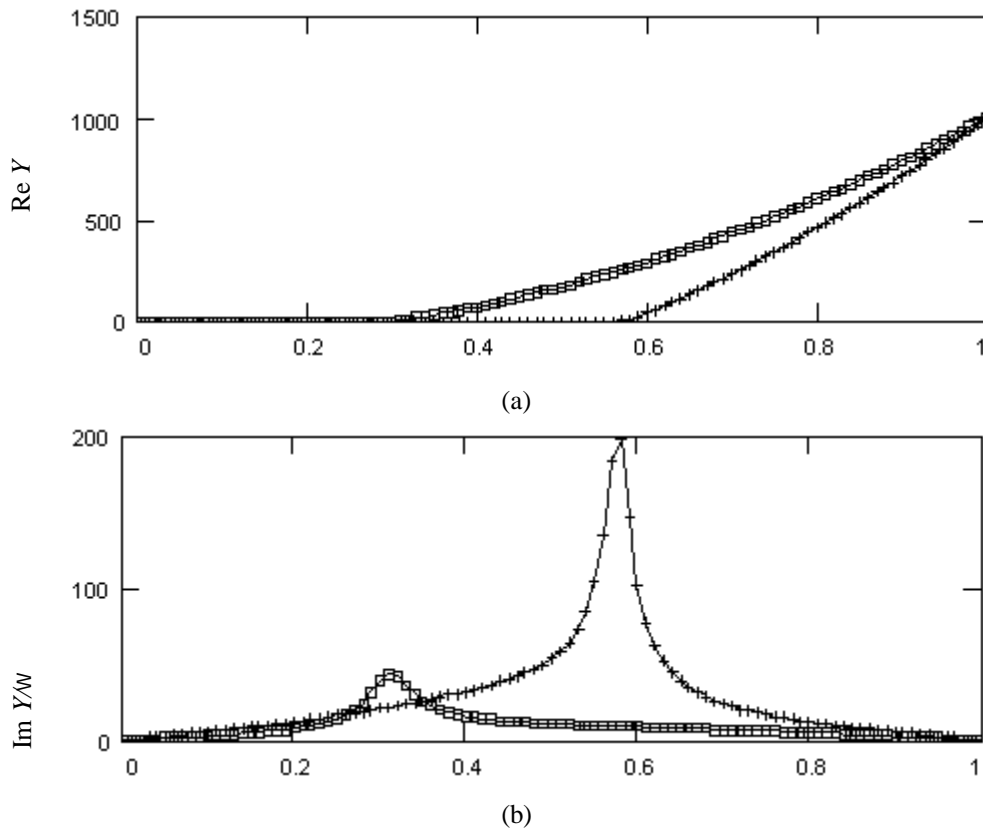


FIG. 11. Conductivity (a) and capacity (b) dependence on the fraction of metal particles

for a three-dimensional system at zero frequency, described by the effective medium theory with $q = 2$ (+) and $q = 9.4$ (•).

The small capacitance given by EMT at $x = 0$ is that of the dielectric capacitor with the dielectric constant, determine by the polarizability of the solid electrolyte at high frequencies at which the mobile ions may be regarded frozen for translational motions, but contribute to lattice vibrations.[5] Since the capacitance in Ref. 5 was scaled to this value, "giant enhancement" at $x = x_c$ was obtained. Our simulation shows that the enhancement is in fact quite moderate, because the correct value of capacitance at $x = 0$, i.e., the double layer at the metal-solid-electrolyte interface, is already large: orders of magnitude greater than that of the dielectric capacitor.

The total admittance of the system is determined by the interplay between the surface and bulk contributions. An attempt to take it into account was made in Ref. 5 by a construction of an interpolation formula in which the surface contribution is plainly added to the bulk contribution. The used dependence of the former on $x$ was aimed to approximate the behavior near $x_c$, neither giving the correct value at $x = 0$. Note that the two contributions are inseparable, when the system size is close to the correlation length (typical size of the metal cluster).

All this should be taken into account in the comparison of simulation results with EMT for different $x$. As expected at sufficiently large $x$, plots for the real part of admittance are qualitatively the same, as well as the behavior of capacitance. Particularly remarkable similarity is found for two dimensions where the unusual double peak curve for capacitance emerges. However, at small $x$ the difference is drastic.

The double peak structure in two dimensions, where one of the peaks is below $x_c$ and one practically coincides with $x_c$, can be rationalized as follows. The principle difference between the two-dimensional and three-dimensional percolation systems is that for two-dimensional systems ($x_c = 0.59$) there is a gap of $x$ values, $1 - x_c < x < x_c$, where there is no percolation neither for metal nor for solid-electrolyte particles. The low $x$ maximum of capacitance in two dimensions is not far from $x = 1-x_c$. Thus, with the increase of $x$ at $x < 1-x_c$, the surface of the metal clusters connected with the metal plates grows, at practically not disturbed path through the solid electrolyte from one surface to the other. At $x > 1-x_c$ the percolation on solid-electrolyte particles breaks down and the system splits into many not connected small clusters of metal and solid-electrolyte particles. The overall capacitance then drops due to emerging network capacitances, connected in series. At large $x$, approaching $x_c$ from below, the capacitance rises again, because the surface of the clusters, connected with the metal plates, grows while the number of small isolated metal clusters goes down. At $x > x_c$ the shortcut enters into play and the capacitance goes down again.

The tendencies in frequency dependence prescribed by the EMT and the simulation are qualitatively similar, except for the enhancement of the capacitance maximum at $x = x_c$, relative to the capacitance value at $x = 0$: in the simulation the enhancement grows with frequency due to the diminishing of the surface contribution.

One may expect that at zero frequency the capacitance in three dimensions for a large system (of a size much greater than the correlation length) cannot become larger than the surface capacitance. The largest value of the latter cannot exceed the capacitance of the flat interface times $(L / l)$ where $l$ is the grain size. Indeed, if there is a large bulk capacitance, its contribution in series will not be seen. For a smaller system, this limit is never reached, what we actually see from the simulation. The maximum on the capacitance plot may thus have a simple meaning. With the increase of $x$, the effective surface grows and so does the capacitance. After the percolation point is passed, there are short cuts through metal particles. Therefore, the capacitance goes down with the further replacement of solid-electrolyte grains by metal particles.

In the simulation of a system with a membrane in between (Fig. 9), the capacitance reaches its maximum at $x$ = 0.5, which is 50% higher than the maximum at the percolation threshold for a system without membrane. Even though the largest metal clusters in the system with membrane are smaller than in the membrane-free case, the maximum surface between the metal and the solid electrolyte, achieved at $x$ = 0.5, can be reached here without shortcuts.

Percolation phenomena in the composite of solid ion conductors (electrolytes) were also a subject of a number of publications.[10-14] However, Refs. 11-13 considered the mixture of solid-electrolyte and insulator particles. The equivalent circuits for the bonds in that system are different from those, which emerge in our metal-solid-electrolyte system. The former focused on a new element of the circuit, an enhanced ionic conductance along the imperfect insulator/solid-electrolyte interface. For considerably large graines, e.g., of a micron size or greater, typically used in metal-solid-electrolyte dual phase composites, this lateral grain boundary conductance is not dominating. The width of the grain boundary area is $10^3$ times smaller than the size of the grain, and so one should have > $10^3$ enhancement of the ion mobility along the surface of the solid electrolyte than across the bulk of the grain. This is usually not the case for dense metal/solid-electrolyte contacts. In Ref. 14, the mixture of solid-electrolyte and metal particles was studied. However, the interface between them was taken into account in the equivalent scheme of the solid-electrolyte grains, i.e., the double layer capacitance did not appear as a result of a contact between the metal and solid electrolyte. This allowed to map the system on a two bond model, but this type of mapping strongly exaggerates the imaginary part of the system admittance, particularly for the mixtures with large portion of solid electrolyte. With no claims that the circuits used in our paper exhaust all possible relaxation mechanisms (cf. Ref. 5, Sec. II), they take into account the main features, such as the blocking capacitance of the metal-solid-electrolyte interface. Possible extra elements when necessary can be introduced in additive manner within the same type of random network.

The complex admittance of the metal-solid-electrolyte composite was studied for a composite mixture of carbon and $Ag_4RBI_5$, without a solid-electrolyte membrane in between, as a function of the volume fraction of solid electrolyte in Ref. 15. The qualitative dependence of capacitance of this system (Fig. 3 of Ref. 15) is similar to the curves shown in Fig. 7 and 8; the same refers to its frequency dependence (cf. Fig. 1 of Ref. 15 and the Fig. 6 of our work). They report the maximum of capacitance close to the percolation threshold, which in their case is at smaller $x$ = 0.2, which corresponds to a face centered cubic lattice. The reported enhancement of capacitance is greater than in our simulation, because our system is much smaller.

## V. CONCLUSION

We developed a random-network model of pore free composite mixture of metal and solid-electrolyte grains and computed the electrical admittance of a composite slab disposed between two metallic plates. The results are in qualitative agreement with those of the effective medium theory except for the region of small portion of metal particles where the theory is invalid. The simulation proves that there is no giant enhancement of capacitance near the percolation threshold, relative to the zero metal component limit. The composition and frequency dependence of complex admittance exhibits interesting features, which would be worth of experimental investigation.

In the system without a membrane in the middle, blocking the electronic current, there is a pronounced maximum of capacitance near the percolation threshold. In a sample with such a membrane, the maximum is at equal portions of the metal and solid-electrolyte grains in the mixture. Below the percolation threshold there is practically no difference between these two cases.

The enhancement of the capacitance at the maximum, relative to the value for a metal-free composite, cannot be larger than the ratio of the size of the sample to the size of the grain. This gives $10^3$ for a sample 1 cm thick and the "typical" 10 µm grains, resulting in 0.01 F/cm$^3$ capacitance, which can be increased up to 1 F/cm$^3$, using superfine 0.1 µm grains. Roughening the interface between the individual grains and using metal/electrolyte combinations with particularly high interfacial capacitances may increase this value by one or two orders of magnitude. The scale of 100 F/cm$^3$ seems to be the theoretical limit for these type of systems.

The frequency dependence of capacitance follows the pattern, typical for metal-solid-electrolyte interface. We did not get any new characteristic frequency, other than coming from the equivalent circuit, which represents the two grain metal-solid-electrolyte junctions. The question remains open whether this will retain in the consideration of larger systems.

For the simplicity of computation, we have chosen a simple cubic lattice, which is not the best approximation for densely packed grains. The modification of the lattice would decrease the position of the percolation threshold.

Being limited to relatively small systems, we, nevertheless, could see the main trends in their properties. The results are instructive for the preparation of the dual phase capacitors or resistors with the composition determined properties. They also shed light on the possible frequency dependent impedance of such structures, which is relevant for the diagnostics of dual phase composites and invention of electronic designs based on them.

## ACKNOWLEDGMENTS

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