Modelling of electric current flow in 1D Pd-C nanostructure: comparison with experiment

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Abstract. In this paper we propose a model of electric current flow through one-dimensional palladium-carbon nanostructure (nanowire) and compare the results of numerical computations with the experimental data. We focus on two aspects: 1) calculation of the current flow through the nanowire model, 2) determination of the macroscopic parameters in the nanocomposite in our model. Because of a complex micro-geometry of a nanowire, we apply the homogenization method to perform the numerical computations.

Key words: nanocomposites, palladium, carbonaceous matrix, homogenization.

1. Introduction

In many physical and material issues we meet the problem of finding effective physical properties for composite or non-homogeneous materials. Small regions of non-homogeneity of the material contained in its whole volume, but with diameters much smaller than this volume, impede or even prevent finding analytical solutions to the problems such as charge transport, heat transfer or stress transfer. Nanocomposites are examples of such materials. The regions of homogeneity in this materials have different compositions, structures and properties and their sizes are from a few to several hundred nanometres. In particular, a large number of regions with sizes of the order of a few nanometres has a strong influence on the effective properties of the whole material and their dissimilarity to the characteristics of the material in a macroscopic form. For instance, the existence of nanograins of various diameters can be the cause of a change in the mechanical properties of the material. In [1] the authors analyse the changes of mechanical properties caused by e.g. fragmentation of crystallites of material to the size of nanometres. It is a result of the increase of a number of boundaries of grains, a number of triple junctions and the increase of disorder in existing layers. In [2] and [3] the authors use the notion of coefficient of nanograins packing of material. The small packing coefficient means that the nanograins are located far away from each other. The effects mentioned above also influence a change of macroscopic properties such as charge or heat transfer.

For the phenomenon of the transfer of electric charges in nanocomposite materials, there are various models used connected with the classical (diffusion) or quantum (tunnelling) approach. In this paper we propose the model of electric charges transfer in the nanocomposite material based on a

diffusion equation with the homogenization theory applied to obtain the macroscopic properties of the nanocomposite material. We assume that the considered material is isotropic in all respects. This assumption allows us to consider only the one-dimensional problem (in arbitrary direction with respect to the geometry of the material). The cross-section of such a material is shown in Fig. 1a and a model of it in Fig. 1b.
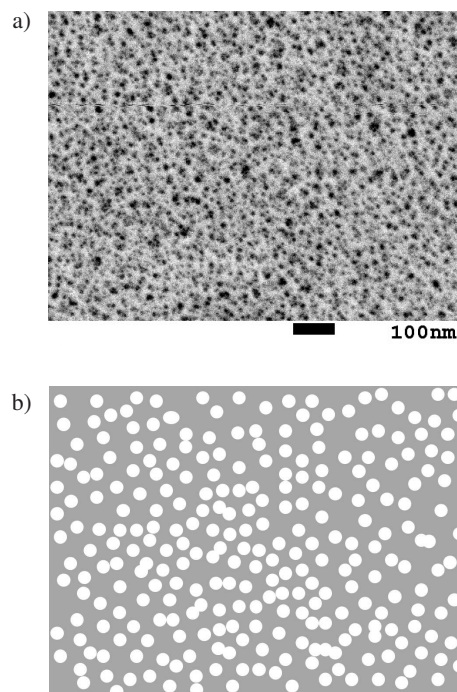

Fig. 1. a) Image of nanocomposite palladium-carbon layer (dark grey spots depict palladium nanocrystals), b) two-dimensional model of the nanocomposite material

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The model shown in Fig. 1b was constructed under the assumption that the nanocomposite consists of two materials: palladium (white circles) in the form of nanocrystallites and carbon (grey region) forming a matrix in which the nanograins of palladium are embedded. The problem of the transport of electrons through such material can be considered, similarly as in [2,3], as a flow of electrons along the conductivity paths formed by nanocrystallites.

The resistivity $\rho(d, f, A)$ along such path is a function of a packing coefficient f, a coefficient A denoting agglomeration of nanograins and the diameter of a molecule d. This description is relevant to the model shown in Fig. 1b. For the considered two-component material, the two-dimensional problem can be reduced to the one-dimensional problem (see Fig. 2).

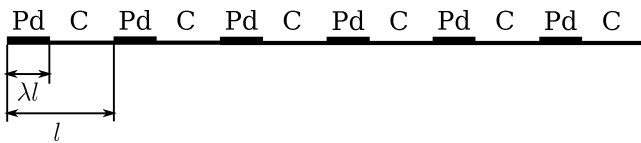Pd C Pd C Pd C Pd C Pd C Pd C

Fig. 2. One-dimensional model of the two-component material

An important assumption, which we make in our model, is the existence of the effective electrical conductivity (or resistivity) and substitution of this idea for the idea of conductivity paths. The key point is that we may replace two-component nanocomposite material with the homogeneous isotropic one. This assumption allows to consider the problem in one-dimensional case.

2. Mathematical model

In the proposed one-dimensional model, the nanowire has periodic micro-structure consisting of palladium nanocrystals embedded in a carbonaceous matrix. We assume that the nanowire is composed of the finite number of identical cells (comprising palladium and carbon) of the length l periodically repeated on the interval $[0, L]$. In every cell the palladium nanocrystal occupies the subinterval $[0, \lambda l]$, $0 < \lambda < 1$, and the rest of the cell is occupied by the carbon (see Fig. 2).

We model the electric current flow through the nanowire using the Laplace equation. Let the function $n : [0, L] \to \mathbb{R}$ denotes the electric field potential in the material. It satisfies the following diffusion equation:

$$\frac{\mathrm{d}}{\mathrm{d}x}\left(\sigma(x)\frac{\mathrm{d}}{\mathrm{d}x}n(x)\right) = 0 \qquad (1)$$

with the boundary conditions $n(0) = V_0$ and $n(L) = 0$, where V_0 is the voltage applied to the nanowire and the electrical conductivity of the nanostructure $\sigma : [0, L] \to \mathbb{R}$ is given by $\sigma(x) = \sigma_{Pd}\chi_\lambda(x) + \sigma_C(1 - \chi_\lambda(x))$, with the constants σ_{Pd} and σ_C denoting the electrical conductivity of palladium nanocrystals and the carbonaceous matrix respectively, and χ_λ is the characteristic function of the region occupied by the palladium. The current density $J : [0, L] \to \mathbb{R}$ in the material is given by

$$J(x) = -\sigma(x)\frac{\mathrm{d}}{\mathrm{d}x}n(x).$$

The above model of a palladium-carbon nanostructure still has a complex micro-geometry. Hence to simplify the study further we apply the asymptotic homogenization method (see Sec. 3) to the Eq. (1). We get the macroscopic electrical conductivity of the nanowire given by (cf. (16))

$$\sigma^* = \frac{\sigma_{Pd}\sigma_C}{\lambda\sigma_C + (1 - \lambda)\sigma_{Pd}} \qquad (2)$$

and the analytical formula for the current density (constant along the nanowire) $J(x) = \sigma^*\frac{V_0}{L}$, $x \in [0, L]$.

In the physical experiments the nanomaterial of the shape of a narrow rectangle was used as a model of one-dimensional nanowire. Thus we can calculate the electric current flow through the nanowire using the formula

$$I = sJ = s\sigma^*\frac{V_0}{L}, \qquad (3)$$

where s is the cross-section of the nanomaterial.

The proposed model allows to determine the palladium content in a nanowire using only the experimentally measured resistance of the material. To this end we calculate the experimental electrical conductivity of the nanowire

$$\sigma_e = \frac{L}{sR}, \qquad (4)$$

where s and R denote the cross-section and the resistance of the material, respectively. Thus it suffices to derive the dependence of λ on σ^* from Eq. (2).

We take the experimentally measured value of conductivity σ_e as the macroscopic conductivity of the nanowire $\sigma^* := \sigma_e$ and invert the formula (2) for λ to get the palladium content in the nanowire model

$$\widetilde{\lambda} = \frac{\sigma_{Pd}(\sigma_e - \sigma_C)}{\sigma_e(\sigma_{Pd} - \sigma_C)}. \qquad (5)$$

From the Eq. (2) we can also calculate the dependence of the model electrical conductivity of the carbonaceous matrix on the experimental conductivity σ_e of the nanomaterial

$$\widetilde{\sigma}_C = \frac{(1 - \lambda)\sigma_{Pd}\sigma_e}{\sigma_{Pd} - \lambda\sigma_e} \qquad (6)$$

3. Homogenization method

Having in mind a complex microstructure of Pd-C nanocomposite we apply a homogenization method to study the problem. Homogenization means deducing the macroscopic equations and relations from properties of its microscopic constituents. The reader can find methods of the homogenization theory in [4] and [5].

In the paper [6] a homogenization was performed for an electric conductor with material coefficients being periodic functions of spatial variables. In a description of the electric conductivity the Joule-Lenz heat production was taken into account. Hence, in reality, two cross-linked equations, one for the electric current and one for the heat were considered. An assumption of the stationary flow of the electric current permitted to preserve the qualitative form of the primary system of equations.

We assume that the considered body is characterized by a periodic microstructure. It means that a large body with a

characteristic dimension L consists of a number of periodic cells whose characteristic dimension is l. Let $\frac{l}{L} \ll 1$; we introduce into our considerations a small parameter $\varepsilon = l/L$.

The homogenization method [4, 5, 7, 8] means finding an asymptotic solution of the equation

$$\mathcal{A}_\varepsilon u^\varepsilon \equiv \frac{d}{dx}\left(A^\varepsilon(x) \frac{du^\varepsilon}{dx} \right) = f(x), \qquad (7)$$

where $\mathcal{A}_\varepsilon$ is a second order differential operator of diffusion with variable coefficients $A^\varepsilon(x)$ namely,

$$\mathcal{A}_\varepsilon = \frac{d}{dx}\left(A^\varepsilon(x)\frac{d}{dx} \right).$$

In a periodic setting we write $A^\varepsilon(x) = A\left(\frac{x}{\varepsilon}\right)$ and we will identify $\frac{x}{\varepsilon} = y$, where y is referred to as a microscopic variable. The microstructure is periodic with the period ε, if we extend the body to the whole space. So we have $A\left(\frac{x}{\varepsilon}\right) = A(y)$, where the function A is periodic with respect to microscopic variable y. In other words, if we have a function $A(y)$ defined on $(0,1)$ we extend the function A to $\mathbb{R}$ by a periodic way, namely $A(y) = A(y+1)$, for all $y \in \mathbb{R}$, for one-dimensional structures.

3.1. Two-scale asymptotic expansion. We distinguish two scales: macroscopic and microscopic; the former is a scale of x called macroscopic variable, and the latter $y = \frac{x}{\varepsilon}$, called a microscopic one.

The homogenization procedure consists in the elimination of the microscopic variable by the appropriate averaging or by passing to zero with a small parameter ε.

In order to obtain a macroscopic description of the problem, we look for a solution u^ε of the problem (7) in the form of a two-scale asymptotic expansion

$$u^\varepsilon(x) = u_0(x) + \varepsilon u_1(x, y), \qquad (8)$$

where for $x \in [0, L]$ the term $u_1(x, y)$, is a periodic functions with respect to microvariable $y \in Y = [0, 1]$. Usually Y is referred to as a *cell of periodicity*.

We recall that the rule of differentiation is as follows

$$\frac{d}{dx} = \frac{\partial}{\partial x} + \frac{1}{\varepsilon}\frac{\partial}{\partial y}.$$

Thus we have

$$\mathcal{A}_\varepsilon u^\varepsilon \equiv \frac{d}{dx}\left(A(y)\frac{d}{dx} \right)(u_0 + \varepsilon u_1)$$

$$= \left(\varepsilon^{-2}\mathcal{A}_0 + \varepsilon^{-1}\mathcal{A}_1 + \mathcal{A}_2 \right)(u_0 + \varepsilon u_1),$$

where

$$\mathcal{A}_0 = \frac{\partial}{\partial y}\left(A(y)\frac{\partial}{\partial y} \right),$$

$$\mathcal{A}_1 = \frac{\partial}{\partial y}\left(A(y)\frac{\partial}{\partial x} \right) + \frac{\partial}{\partial x}\left(A(y)\frac{\partial}{\partial y} \right),$$

$$\mathcal{A}_2 = \frac{\partial}{\partial x}\left(A(y)\frac{\partial}{\partial x} \right) = A(y)\frac{\partial^2}{\partial x^2}.$$

Equating the power terms of a small parameter ε we obtain the following system of equations:

$$\mathcal{A}_0 u_1 + \mathcal{A}_1 u_0 = 0, \quad \text{in} \quad Y = (0, 1), \qquad (9)$$

$$\mathcal{A}_1 u_1 + \mathcal{A}_2 u_0 = f \quad \text{in} \quad Y. \qquad (10)$$

Now we deduce from (8) and (9) that

$$\frac{\partial}{\partial y}\left(A(y)\frac{\partial u_1(x, y)}{\partial y} \right) = -\frac{dA(y)}{dy}\frac{du_0(x)}{dx}. \qquad (11)$$

Linearity of the last equation allows us to assume that the solution $u_1(x, y)$ may be represented in the form

$$u_1(x, y) = N(y)\frac{du_0(x)}{dx} + \widetilde{u}(x), \qquad (12)$$

where $\widetilde{u}(x)$ is an arbitrary function depending on x. Applying (12) to (11) we obtain

$$\frac{d}{dy}\left(A(y)\frac{dN(y)}{dy} \right) = -\frac{dA(y)}{dy}. \qquad (13)$$

This is *a local equation* defined on the periodicity cell Y to an unknown (*auxiliary* or *local*) function $N(y)$, periodic with respect to the microscopic variable y.

We observe that the Eq. (13) may be rewritten as

$$\frac{d}{dy}\left(A(y)\left(1 + \frac{dN(y)}{dy} \right) \right) = 0.$$

The solution of the equation exists, so in fact we have

$$u^\varepsilon(x) \simeq u_0(x) + \varepsilon u_1(x, y) = u_0(x) + \varepsilon N(y)\frac{du_0(x)}{dx}.$$

Taking into account (10) we can derive the macroscopic equation corresponding to (7).

The Eq. (10) may be written in the form

$$\int_Y (\mathcal{A}_1 u_1 + \mathcal{A}_2 u_0)\, dy = f(x). \qquad (14)$$

Applying (12) to (14) we obtain

$$\left[\int_Y \left(A(y) + A(y)\frac{dN}{dy}(y) \right) dy \right] \frac{d^2 u_0}{dx^2} = f. \qquad (15)$$

It is shown, e.g. [4, 5], that the term in square brackets is a harmonic mean of the known function $A(y)$. However we note that it holds for 1D case only. Thus the simplest version of (15) may be written as follows

$$A^* \frac{d^2 u_0}{dx^2} = f \quad \text{in} \quad (0, L)$$

and the homogenized diffusion coefficient has the form

$$A^* = \left(\int_0^1 \frac{1}{A(y)}\, dy \right)^{-1}. \qquad (16)$$

The homogenization method is commonly used to obtain macroscopic relationships knowing the properties of the microscopic behaviour of the medium. Many physical and mathematical problems can be solved using this method, we will mention only a few: fluid flow, thermal flow, current flow, porous media, see [9, 10].

4. Comparison with experiments

In the experiments the resistance and the current flow through the wires were measured. The wires were placed on a surface of a slab with the electrical connectors. The scheme of the experiment is given in Fig. 3. This figure also shows the composition of nanostructural C-Pd film built of palladium and carbonaceous nanograins. Such film in a form of thin wire was obtained by the PVD (Physical Vapor Deposition) method on a glassy substrate. The details of preparation method were described in paper [11].
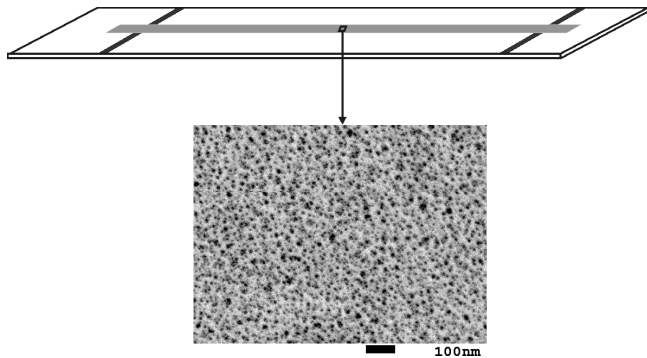

Fig. 3. The scheme of the wire with electrical connections and the image of a layer of nanomaterial (dark regions are palladium nanocrystals)

The preliminary results on the numerical study of 1D Pd-C structures using the homogenization method we presented in our first paper [12].

4.1. Modelling of current flow. In this experiment we observed the electric current flow through the wire. The sample of the length $L = 19.6$ mm with the cross-section $s = 3 \cdot 10^{-4}$ mm^2 (width 1 mm and thickness 300 nm) was used in physical experiments. The same dimensions were also used in the numerical computations. We assumed the electrical conductivity of palladium[1] and carbonaceous matrix to be $\sigma_{Pd} = 9.5 \cdot 10^6$ $(\Omega\text{m})^{-1}$ and $\sigma_C = 9.86 \cdot 10^{-4}$ $(\Omega\text{m})^{-1}$ (the value for fullerite C60[2]), respectively.

The experimental value of the electrical conductivity, obtained by (4), of the considered sample of the nanomaterial was $\sigma_e = 1.054 \cdot 10^4$ $(\Omega\text{m})^{-1}$. This value was used in (5), which gave the model palladium content in the wire $\widetilde{\lambda} = 1.0$.

In Fig. 4 we show the dependency of the current flowing through the studied wire of the nanomaterial on the applied voltage. Circles denote the experimentally measured values. The values computed numerically are shown by the line. In all the numerical computations we used the experimentally measured value of the conductivity σ_e. One can observe a good agreement between the experimental data and the numerical results of computations in our model approximately up to the value of the applied voltage $V_0 \approx 2$ V (the small deviations may be due to the inhomogeneities in the material

[1]http://www.palladiumcoins.com
[2]http://sesres.com/PhysicalProperties.asp

or the measurements errors). The reason for a deviation observed for the voltage higher than 2 V is not clear and may need another theoretical approach. It is possible that the conductivity paths are formed by palladium nanograins at higher voltages.
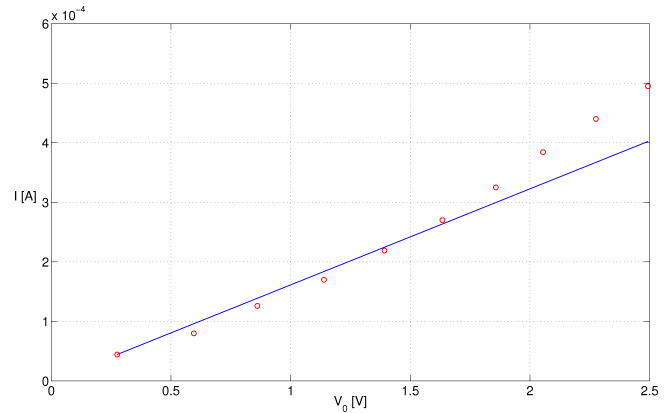

Fig. 4. The electric current in the wire as a function of applied voltage: dots – experimental data, solid line – numerical results

4.2. Modelling of macroscopic parameters. In this experiment we determined the macroscopic parameters of nanocomposites in our model: the palladium content and the conductivity of carbonaceous matrix.

We present the results for three samples of nanomaterial with different content of palladium, used in the physical experiments. All samples were of the length $L = 10$ mm with the cross-section $s = 3 \cdot 10^{-4}$ mm^2 (width 1 mm and thickness 300 nm). In Table 1 we give the measurements of resistance R and palladium content for all samples and the electrical conductivity σ_e computed using (4).

Table 1
Parameters of wire samples (experimental data)

Sample	Pd content [%]	Resistance R [Ω]	Conductivity σ_e [$(\Omega\text{m})^{-1}$]
I	9.87	$1.7 \cdot 10^7$	1.96
II	13.3	$2.5 \cdot 10^6$	$1.33 \cdot 10^1$
III	27.31	$5 \cdot 10^2$	$6.67 \cdot 10^4$

In all the computations we assumed, as in the previous subsection, the electrical conductivity of palladium $\sigma_{Pd} = 9.5 \cdot 10^6$ $(\Omega\text{m})^{-1}$. However the conductivity of carbonaceous matrix vary widely with the allotropic form of carbon and it is not known for the carbon form being the component of the considered nanomaterials. Thus we performed the computations for a number of carbon allotropes for which the known electrical conductivity values are given in Table 2.

Using (2) and the physical contents of palladium given in Table 1 we computed the electrical conductivity of nanocomposite samples in our model for a different carbon allotropes (see Table 2). We present the obtained values in Table 3.

Table 2
Electrical conductivity of carbon allotropes $[(\Omega m)^{-1}]$

fullerite C60	nanotubes[a]	amorphous carbon[b]	graphite[c]
$9.86 \cdot 10^{-4}$	$6.67 \cdot 10^2$	$3.33 \cdot 10^4$	$7.27 \cdot 10^4$

[a] http://en.wikipedia.org/wiki/Carbon_nanotube
[b] http://hypertextbook.com/facts/2007/DanaKlavansky.shtml
[c] http://invsee.asu.edu/nmodules/Carbonmod/thermprp.html

Table 3
Electrical conductivity of nanocomposites in our model $[(\Omega m)^{-1}]$

Sample	fullerite C60	nanotubes	amorphous carbon	graphite
I	$1.094 \cdot 10^{-3}$	$7.400 \cdot 10^2$	$3.693 \cdot 10^4$	$8.059 \cdot 10^4$
II	$1.137 \cdot 10^{-3}$	$7.693 \cdot 10^2$	$3.839 \cdot 10^4$	$8.375 \cdot 10^4$
III	$1.356 \cdot 10^{-3}$	$9.176 \cdot 10^2$	$4.575 \cdot 10^4$	$9.973 \cdot 10^4$

Table 4 presents the palladium content in the samples computed in our model for different carbon allotropes using (5) and the physical values of conductivity from Table 1. We note that in the case when the conductivity of the carbon allotrope is greater than the conductivity of the sample it is not possible to compute the palladium content coefficient. This is denoted using dashes in Table 4.

Table 4
Pd content in samples for different carbon allotropes (dash denotes that the conductivity of the allotrope is greater than the conductivity of the sample)

Sample	fullerite C60	nanotubes	amorphous carbon	graphite
I	99.95%	—	—	—
II	99.99%	—	—	—
III	100%	99%	50%	—

The considered model makes it possible to compute from the formula (6) the unknown value of the electrical conductivity $\tilde{\sigma}_C$ of carbonaceous matrix using only the content of palladium in a sample and the experimentally measured resistance of the material. The computational results are presented in Table 5.

Table 5
Electrical conductivity of carbonaceous matrix in wires in our model

Sample	Conductivity $\tilde{\sigma}_C$ $[(\Omega m)^{-1}]$
I	1.767
II	$1.156 \cdot 10^1$
III	$4.855 \cdot 10^4$

5. Conclusions

In this paper we presented the method of calculation of the electrical conductivity in a material composed of many allotropic forms of carbon. This result is very important especially in the case of nanocomposite materials, where it is difficult to determine this parameter experimentally.

It is reasonable to take into account for further investigations the effect of formation of conductivity paths by palladium nanograins. This effect may change drastically the electrical conductivity of nanocomposite in higher electric fields.

It may happen that the properties of nanocomposite materials are different from the properties of component homogeneous regions having characteristics similar to the ones of the macroscopic counterparts. These properties depend strongly on the sizes of the homogeneous regions. In the considered case we have shown by calculations and experiment that classical diffusion equation describes well the electric current flow in Pd-C nanocomposite.

We used in this paper the two-scale asymptotic expansions method as a simple tool for calculations. However, more sophisticated methods can be used, for example the gamma-convergence method, see [13].

REFERENCES

[1] R.A. Andrievski and A.M. Glezer, "Size effects in properties of nanomaterials", *Scripta Mater.* 44 (8–9), 1621–1624 (2001).

[2] L.J. Chen, J.H. Tyan, and J.T. Lue, "The non-metallic conductivity of Nb$_3$Ge films sputtered on silicon substrates", *Phys. Chem. Solids* 55 (9), 871–879 (1994).

[3] G. Reiss, J. Vancea, and H. Hoffmann, "Grain-boundary resistance in polycrystalline metals", *Phys. Rev. Lett.* 56, 2100 (1986).

[4] A. Bensoussan, J.-L. Lions, and G. Papanicolaou, *Asymptotic Analysis for Periodic Structures*, North-Holland, Amsterdam, 1978.

[5] E. Sanchez-Palencia, *Non Homogeneous Media and Vibration Theory*, Springer-Verlag, Berlin, 1980.

[6] R. Wojnar, "Homogenization of electric conductor and Joule-Lenz's heat", *J. Techn. Physics* 35, 151–159 (1994).

[7] J.J. Telega and W. Bielski, "Stochastic homogenization and macroscopic modelling of composites and flow through porous media", *Theor. Appl. Mech.* 28–29, 337–378 (2002).

[8] J.J. Telega and W. Bielski, "Flows in random porous media: effective models", *Computers and Geotechnics* 30, 271–288 (2003).

[9] J.J. Telega and R. Wojnar, "Electrokinetics in random piezoelectric porous media", *Bull. Pol. Ac.: Tech.* 55 (1), 125–128 (2007).

[10] R. Wojnar, "Flow of Stokesian fluid through a cellular medium and thermal effects", *Bull. Pol. Ac.: Tech.* 62 (2), 321–327 (2014).

[11] E. Kowalska, E.Czerwosz, M. Kozłowski, W. Surga, J. Radomska, and H. Wronka, "Structural, thermal, and electrical properties of carbonaceous films containing palladium nanocrystals", *J. Thermal Analysis and Calorimetry* 101 (2), 737–742 (2010).

[12] W. Bielski, P. Kowalczyk, A. Idzik, E. Czerwosz, and E. Kowalska, "Modelling of a time dependent electron diffusion problem for nanocrystalline one-dimensional carbon-palladium structures via homogenization", *Numerical Analysis and Applied Mathematics ICNAAM 2011, AIP Conference Proc.* 1389, 1878–1881 (2011).

[13] B. Gambin and W. Bielski, "Incompressible limit for a magnetostrictive energy functional", *Bull. Pol. Ac.: Tech.* 61 (4), 1025–1030 (2013).