Conductivity in disordered structures: Verification of the generalized Jonscher's law on experimental data

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Abstract. The generalized Jonscher's law for complex conductivity (derived earlier) is tested on available experimental data. We suggest some criteria which are used for verification of the analytical expression describing the data related to complex conductivity. It is shown that the generalized Jonscher's law is suitable for description of the electrode polarization phenomenon.

1. Introduction
In paper [1] we derived the analytical expression generalizing the well-known Jonscher's law. This formula describes the contribution of the different charge carriers to the complex conductivity in the frequency region. In [1] the dependence of the complex conductivity against frequency was defined as the generalized Jonscher's law (GJ'sL). This dependence described well the complex conductivity data of the sodium nitrite embedded into the porous glass having mean pore size about 7 nm [2-4]. At derivation of the GJ'sL we did not use any specific model associated with concrete substance. The basic point was associated with the supposition that the substance has a self-similar structure [5-8]. This general supposition leads us to the idea that the GJ'sL should take place in a wide class of different heterogeneous substances. This fact, in turn, forced the authors of this paper to analyze attentively the scientific papers where the reliable data of the complex conductivity (or the complex dielectric permittivity (CDP)) were presented. The analysis of these frequency data could confirm or reject the "universality" of the GJ'sL put forward earlier as an alternative hypothesis. In this work we concentrate our attention only on analysis of experimental data of complex conductivity.

The basic aim of this paper is the verification of the GJ'sL on available experimental data that describe the behaviour of the complex conductivity against frequency.

2. The specific criteria of the generalized Jonscher's law that can be recognized in measured data
Preliminarily we reproduce the basic steps that led us to the analytical expression describing the GJ'sL [1]. Alongside with usual current associated with free carriers \( j_0 = \sigma_0 E \) and polarization current \( j_p = \partial P / \partial t \) we determine the so-called "fractal" current \( j_{frac} = \sigma_{frac}(\omega)E \). In result the total current is determined by expression

\[
j_{tot} = \sigma_{tot}(\omega)E = j_0 + j_p + j_{frac} = \left( \sigma_0 + \frac{i\omega}{4\pi} (\varepsilon(\omega) - 1)\varepsilon_v + \sigma_{frac}(\omega) \right)E ,
\]

(1)
here the value \( \varepsilon_v = 8.887 \times 10^{-13} \text{ F/m} \) determines the dielectric permittivity of the vacuum. If one takes into account the contribution of the connected charges \( \varepsilon_v (\varepsilon_{\infty} - 1) i \omega / 4 \pi \) then instead of (1) we obtain finally

\[
\sigma_{\text{tot}}(\omega) = \sigma(\omega) + \varepsilon_v (\varepsilon_{\infty} - 1) i \omega / 4 \pi \quad [9]
\]

Here we normalized the expression \( \left[ \sigma(\omega) - \sigma_0 - \sigma_{\text{frac}}(\omega) \right] \) on the constant \( \varepsilon_v / 4 \pi \). The fractal current \( j_{\text{frac}} \) figuring in (1) describes the slow/retarding dynamics of the carriers that is created by the fractal structure of the medium considered. It is defined by the following expression [1]

\[
j_{\text{frac}} = \sigma_{\text{frac}}(\omega) E = -\omega D_1^\nu P_2, \quad 0 < \nu < 1.
\]

where the fractional derivative \( \omega D_1^\nu \) [10] is taken from the delayed part of the polarization \( P_2(t) \). It is defined by expression [1]

\[
P_2(t) = \frac{\chi E(t)}{1 + (i \omega \tau)^\nu}, \quad E(t) = E_0 \exp(i \omega t).
\]

Here the value \( \chi \) defines the dielectric susceptibility. Inserting (4) into (3) we obtain

\[
\sigma_{\text{frac}}(\omega) = \frac{\chi \tau^\nu}{1 + (i \omega \tau)^\nu}, \quad 0 < \nu < 1.
\]

In the result the total expression for complex conductivity accepts the form

\[
\sigma(\omega) = \sigma_0 + i \omega (\varepsilon(\omega) - \varepsilon_{\infty}) + \frac{\chi \tau^\nu}{1 + (i \omega \tau)^\nu}.
\]

In the case of small frequencies the fractal conductivity from (5) reproduces the conventional Jonscher's law

\[
\sigma_{\text{frac}}(\omega) \approx \chi (i \omega)^\nu.
\]

The limiting expression (7) coincides with results of the paper [11]. In this paper it was shown that the classical correction (7) (suggested in [12]) coincides with the low-frequency solution of the functional equation that describes the self-similar electric circuit. This circuit takes into account the influence of the fractal surface of electrodes.

Having expression (6) on can develop some important criterion for its checking. This criterion helps us to make the statement that the relationship associated with the classical correction in the form

\[
\sigma_j(\omega) = \sigma_0 + i \omega (\varepsilon_j(\omega) - \varepsilon_{\infty}) + \tau^{-1}(i \omega)^\alpha,
\]

is not realized in the data considered while the relationship (6) is the most probable and confirmed on the available data considered.
We consider only the real part of these expressions because this part is measured presumably in experiments. If the conductivity associated with polarization part is absent (the second terms in (6) and (8) are equaled zero) then for expression (8) we have usual power-law dependence. For the function (6) we have increasing function forming a plateau in high-frequency region. In the case of the presence of polarization part the real parts of both functions are increasing sharply at high-frequency region. Figure 1 demonstrates the dependencies of the real parts of expressions (6) and (8) in the absence/presence of polarization conductivity.

**Figure 1.** The model data for the real parts of the functions (6) and (8). As before the bold black line corresponds to function (6) the dotted-line corresponds to function (8). On the left we have two plots in the absence of the polarization current, on the right we have the plots when the contribution from the polarization current is taken into account. We used the following values of the fitting parameters: for function (6) \( \sigma_0 = 10^4 \), \( \nu = 0.4 \), \( \chi = 10^3 \), \( \lg \tau = -3 \); for function (8) \( \sigma_0 = 10^{2.1} \), \( \alpha = 0.65 \), \( \lg \tau = 5 \).

From this figure one can notice that the functions (6) and (8) have different behavior in the typical frequency range 10-10^8 Hz.

### 3. Verification of the generalized Jonscher’s law on real data

We think that the conditions of the fractal current appearance take place for example near the heterogeneous surface electrodes having self-similar (fractal) structure. This idea, as mentioned above, was realized in [11]. The same conditions can be realized also in materials having branching porous structure. So, one can expect that the dependence (6) should be closely associated with the electrode polarization phenomenon. In literature there are a lot of experimental papers that studied this phenomenon. So we have a good possibility to confirm/reject this new dependence (6) that can pretend on generalization of the conventional Jonscher’s law for complex conductivity.

Let us start from data of the paper [13]. Experimental data together with its fit to expression (6) is presented by Fig. 2.
Figure 2. Frequency dependence of real part of ac conductivity $\sigma'$ of the (PEO)$_{20}$-(LiClO$_4$·3H$_2$O+NaClO$_4$·H$_2$O)-x wt% MMT clay for nanocomposite electrolytes synthesized by melt compounded technique (see [13] for details). The solid lines correspond to the fit of data to modified expression (6).

As one can see the real part of conductivity has clearly expressed bend appearing at low-frequencies, which cannot be obtained from equation (8). In original paper [13] the authors fitted only the high-frequency part of the curve in the real part of conductivity based on the conventional Jonscher's correction. Their fit was not given here. Solid fitting lines presented on figure 2 are realized in the correspondence with expression (6) which describes well all these data.

Let us consider other data that are given in paper [14]. In this paper the authors studied the same substance as it was used in [13] but in another experimental conditions. Experimental data (triangle points) are presented in Fig. 3.

Figure 3. Frequency dependence of real part of ac conductivity $\sigma'$ of PVA-PEO blend-MMT clay nanocomposites hydrocolloids at varying MMT clay concentration (wt.%) (see [14] for details). Again, the solid lines correspond to the fit to expression (6).

Here we consider the data corresponding to two values of clay concentrations (wt.%) because other data do not have any peculiarities from the curves presented here. As one can notice from these figures the bend is exist at low-frequencies as it is shown on model data on fig 1 and so one can assert that these data confirm the validity of the GJ'sL. As an additional confirmation on Fig. 3 we give also the fitting curves (solid lines) corresponding to expression (6).
Below we will demonstrate only the qualitative behavior of the curves that correspond to the electrode polarization phenomenon leaving aside the direct fit of the data. Figures 4 and 5 reproduce a typical behavior of the real parts of the complex conductivity and permittivity that were taken from paper [15] for some conducting glasses. The behavior of experimental data of conductivity on these figure is like as on figure 1. The behavior of dielectric permittivity one can explain in frame of this approach that was be done in [1]. So, one can conclude that for the most experimental data we observe again the realizability of the GJ’sL that is closely associated with electrode polarization phenomenon.

**Figure 4.** The typical behavior that is observed for the electrode polarization phenomenon for the real part of the conductivity and the real part of the dielectric permittivity at high temperatures for a lithium-phosphate glass (see [15] for details).
Figure 5. The typical electrode polarization phenomenon that is revealed itself in behavior of the real part of the conductivity and the real part of the dielectric permittivity at high temperatures for a Na–Ca–phosphosilicate glass (see [15] for details).

4. Basic conclusions

In spite of the fact that the GJ’sL is realized in many heterogeneous and disordered substances we should remark that this law is not universal. Not all data can be described by expression (6). Formula (6) always contains the character slope at low-frequency range that is not observed for all cases analyzed. The contrary examples are collected in papers [15, 16]. Probably, in such cases it is necessary to use models that have been suggested earlier. Concerning the electrode polarization effect the formula (6) proved their applicability and we can conclude that the GJ’sL was totally justified itself in description of this phenomenon.

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