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IMPEDANCE SPECTRA MEASUREMENTS OF SOLIDS

Vítězslav ZIMA
Joint Laboratory of Solid State Chemistry
of Academy of Sciences of the Czech Republic and University of Pardubice

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A system for impedance spectra measurement is described. Two examples (polycrystalline sample of $VOPO_4$ *intercalated with sodium cation and* As_2Se_3 *glass doped with silver) are given to demonstrate the possibilities of this method.*

Recent development of solid state batteries, electrochemical devices, catalysts, anticorrosion media leads to the necessity to investigate electronic properties of systems with solid-solid or solid-liquid interfaces of materials, having often character of solid ionic conductors. In many cases, one of the important electronic properties - conductivity - cannot be determined by conventional d.c. method due to the polarization effects at the interface or even due to the polarization effects inside the sample if this is polycrystalline. To avoid these problems, it is convenient to use impedance spectroscopy.

Impedance, as a function of frequency ν or angle frequency $\omega = 2\pi\nu$, is a complex quantity, which is composed from real (Z') and imaginary (Z'') parts

$$Z = Z' + jZ'' \tag{1}$$

In polar coordinates, it can be expressed as modulus of impedance $|Z|$ and phase angle φ

$$Z = |Z|\exp(j\varphi) = |Z|\cos\varphi + j|Z|\sin\varphi \tag{2}$$

where j is an imaginary number[1].

The experimental impedance data can be analyzed by the impedance of an equivalent circuit made up of ideal resistors, capacitors, or various distributed circuit elements. In such a circuit, resistance can be associated e.g. with bulk conductivity of the material and capacitance with space charge polarization. In Nyquist plot (i.e. plot of imaginary vs. real part of impedance at various frequencies), an ideal circuit, consisting of resistance R connected in parallel with capacitance C, is represented by a semicircle lying on x-axis. Total impedance Z of this circuit is then given by the equation

$$Z = \frac{R}{1 + j\omega RC} \tag{3}$$

However, in real systems, which have its physical properties often distributed, the Nyquist plot shows an arc with a center depressed under x-axis. In the corresponding equivalent circuit, the capacitance is then replaced by the so-called constant phase element CPE. The impedance of the CPE depends on angular frequency according to the equation

$$Z_{CPE} = \frac{R}{(j\omega\tau_R)^{\psi}} \tag{4}$$

where τ_R is the mean relaxation time ($\tau_R = \omega^{-1}$ when Z'' reaches its maximum value), and $\psi = 1 - \alpha$, where α is a measure of distribution of relaxation times τ. The total impedance of the parallel R-CPE circuit is given by the expression

$$Z = \frac{R}{1 + (j\omega\tau_R)^{\psi}} \tag{5}$$

The impedance of more complex systems could be described by a proper combination of circuit elements i.e. resistances, capacitances, and CPE.

The dependence of impedance on frequency can be obtained experimentally. Let divide the function $Z = f_t(\omega; \boldsymbol{P})$ (describing the behaviour of corresponding equivalent circuit) into two parts: $Z' = f_t'(\omega; \boldsymbol{P})$ and $Z'' = f_t''(\omega; \boldsymbol{P})$, which are functions of both angular frequency ω and a set of parameters $\boldsymbol{P}$. Consider $i = 1, 2, \ldots, k$ data points associated with ω_i. The values of parameters τ and α are then estimated by a complex non-linear least squares method (CNLS). This procedure consists in optimization of the error function

$$S = \sum_{i=1}^{k} \left\{ w_i'[f_{ei}' - f_t'(\omega_i; \boldsymbol{P})]^2 + w_i''[f_{ei}'' - f_t''(\omega_i; \boldsymbol{P})]^2 \right\} \tag{6}$$

where w_i' and w_i'' are weights associated with the i-th data point and f_{ei}' and f_{ei}'' are the real and imaginary parts of impedance found experimetally. In literature[1], the values of the weights w_i' and w_i'' are recommended to be set equal to the reciprocal values of f_{ei}' and f_{ei}'', respectively.

New instrumentation techniques allow us to measure impedance characteristic in wide range of frequencies, from mili- to megahertz. Impedance spetra are usually measured in dependence on temperature, composition of atmosphere in the cell, and applied static voltage or current bias.

In our case, an impedance meter Tesla BM 653 working in the frequency region from 20 to 5×10^5 Hz connected on-line with a personal computer through A/D interface is used. The impedance meter provides values of modulus $|Z|$ (max. 10 MΩ) and phase angle φ. The data obtained are transformed to the real and imaginary part of impedance. In the computer program developed, parameters of four equivalent circuits (Fig. 1) can be fitted by the simplex optimization using CNLS method described above. The weights $w\,'$ and w_i'' are taken to be unity, ensuring a sufficient accuracy of the parameters estimation. The drawing of the cell used for impedance measurement is given in Fig. 2. The construction of the cells allows to warm up the sample up to 300 °C and to vary the composition and humidity of the gas surrounding the sample. The cell is connected to the impedance meter by a coaxial cable.

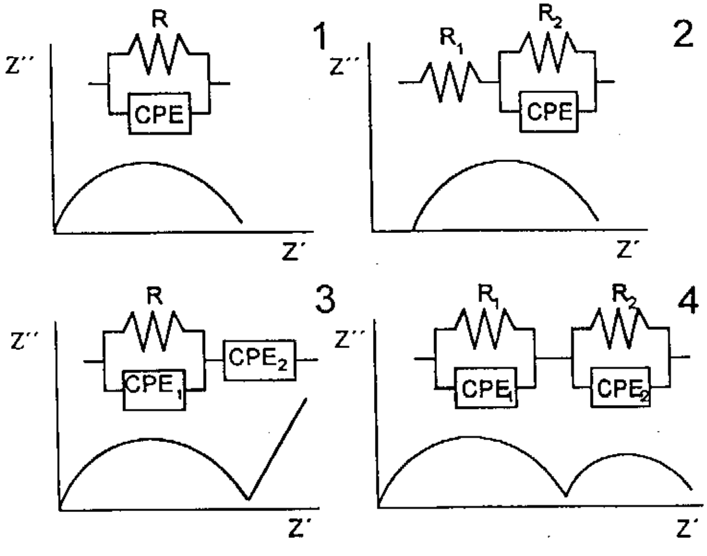

Fig. 1 Various types of complex impedance plots and their equivalent circuits

The impedance meter was used for AC conductivity measurements of layered compounds prepared by redox intercalation of alkali metals ions and hydronium ion into vanadyl phosphate dihydrate[2-4]. Samples under investigation were prepared by pressing of a dry powder product in rectangular matrix. Microcrystalline platelets of the intercalate were preferably oriented in one direction perpendicular to the direction of the pressure. In this way, a rectangular sample with dimensions 7×3×2 mm was obtained. The sample was placed between electrodes of the impedance meter so that AC conductivity was measured along the layer of the intercalate. The sides of the sample in contact with electrodes were coated with a graphite paste. In all the cases, the imaginary vs. real plot of impedance shows an arc shaped curve. This shape is typical of AC conductivity of solid ionic conductors and corresponds to impedance of the equivalent circuit consisting of resistance *R* connected in parallel with CPE. An example of the experimental data plot is given in Fig. 3 together with values of the parameters computed by the above-mentioned method. The conductivity of the samples decreases with increasing content of the ions intercalated.

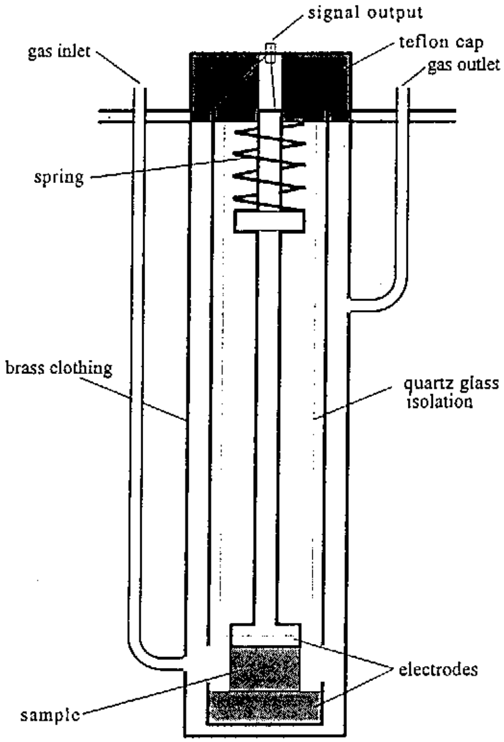

Fig. 2 Schematic drawing of the cell used for impedance measurements

Another example of impedance measurement is a study of AC conductivity of chalkogenide glasses. Two arcs were observed in the complex impedance plot of experimental data for As_2Se_3 glass doped with 9 at.% of silver (Fig. 4), in contrast to the As_2Se_3 glasses with different content of silver,

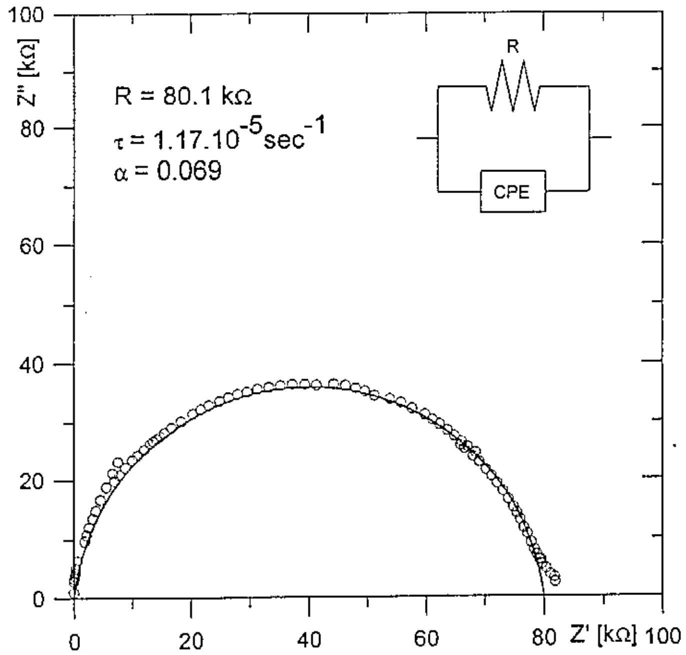

Fig. 3 Complex impedance plot of the pellet of $Na_{0.259}VOPO_4.2H_2O$ measured at room temperature

where only one arc was observed. The parameters of equivalent circuit (shown in Fig. 4) were calculated. As it was found out from thermal behaviour of AC conductivity, the values of activation energy (calculated from the slope in the Arrhenius plot) are equal for both resistances. This phenomenon can be explained by Bauerle's easy path theory. According to this theory, a sample is composed from grains with grain boundary regions, where good intergranular contact is established; these regions are called easy paths. Thus the first, smaller parameter R_1 (Fig. 4) expresses resistance in an interior of the grains, while the second parameter R_2 is resistance of the grain boundary. By heating of the sample up to 120 °C, the greater arc disappears and only one arc is observable in the complex impedance plot (fig. 5). The parameter values of this arc are close to the values of the smaller arc in Fig. 4. It is pressumed that a sintering occurs at higher temperature, making the glass more homogeneous.

As one can see from the above-given examples, impedance spectroscopy provides more information about electrical properties of materials than DC methods and can be a good complementary method for characterization of solids.

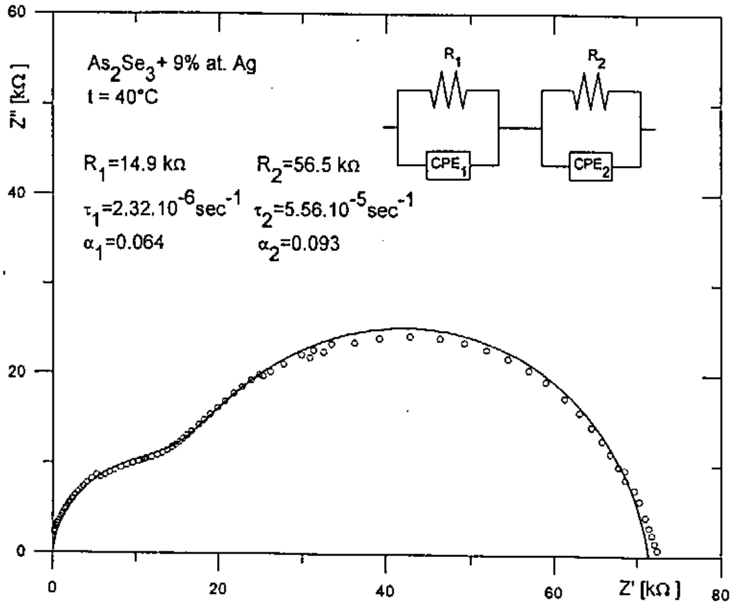

Fig. 4 Complex impedance plot of the arsenic selenide glass doped with 9 at.% of silver measured at 40 °C

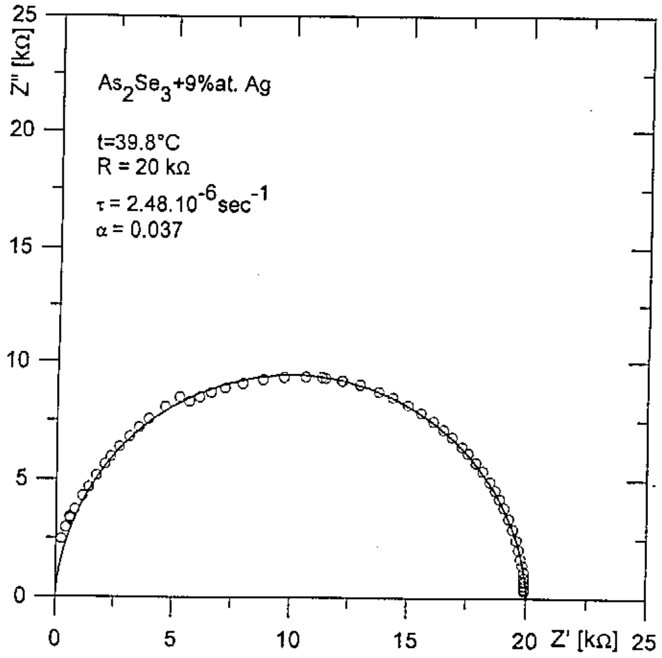

Fig. 5 Complex impedance plot of the As_2Se_3 glass with 9 at.% of silver heated to 120 °C; measured at 40 °C

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