

DIELECTRIC CHARACTERISTICS OF POLYANILINE BLENDS. COMPARISON OF DIFFERENT METHODS.

Milan Neubert¹, Jan Nedbal¹, Jaromír Fahnrich¹, Jaroslav Stejskal²

¹Charles University in Prague, Faculty of Mathematics and Physics, 180 00 Prague 8, Czech Republic

²Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06
Prague 6, Czech Republic

Abstract

Main attention of the contribution is devoted to polyaniline-poly(vinyl alcohol) cryogels and to the dependence of their dielectric characteristics on temperature and history (ageing, desorption), especially to non-Arrhenius behaviour around freezing point. Results obtained using standard contact methods (mainly broadband frequency analyser Novocontrol Alpha in frequency range 10^{-2} – 10^{+7} Hz) were compared with data obtained by developed contactless resonance method based on evaluation of eddy currents in samples exposed to changing magnetic field.

Key words: *conducting cryogels, polyaniline, dielectric properties, contactless method*

1. INTRODUCTION

Polymer hydrogels are chemically or physically crosslinked systems of polymer chains swollen with aqueous liquid phase. Conducting polymer hydrogels represent perspective materials containing a conducting polymer, e.g. polyaniline (PANI). The synthesis, characterization, and applications of conducting hydrogels have recently been reviewed (Guiseppe-Elie 2010). Among their interesting properties belong mixed electronic and ionic conductivity, flexibility at good mechanical integrity, non-toxicity and biocompatibility, high specific surface area, controlled morphology, macroscopic homogeneity connected with electrochemical switching between redox forms of conducting polymers and the transition between salt–base forms in conducting polymers.

PANI is often synthesized by the oxidation of aniline in acidic aqueous medium (Stejskal & Gilbert 2002). Conducting hydrogels based on PANI have usually been prepared by diffusion of the monomer into a standard hydrogel, e.g., poly(vinyl alcohol) (PVAL) with the goal to produce a hydrogel homogeneously penetrated with PANI. Nevertheless, it is observed in practice that the conducting polymer is produced mainly at hydrogel surfaces. One way bypassing this obstacle is to prepare a cryogel by the polymerization of aniline in the presence of PVAL in ice, followed by thawing (Stejskal 2016, pers. comm., ‘*Conducting polymer hydrogels*’, Chem. Pap., in press.).

Key physical property of conducting cryogels is their electrical conductivity (Quadrat et al. 1995). The four-point method is usually used to measure it. The cylindrical cryogel swollen with the aqueous phase is placed into a tube. Two flat electrical current carbon electrodes are put to contact with the fronts of the cylinder. Two other electrodes (platinum/iridium wires), inserted at various positions, are used to detect the electrical potential difference. Electric conductivity can be also measured in frequency domain by using an AC power supply. Usability of this method is in many cases restricted by the effect of electrode and interfacial polarization which plays a significant role, particularly in electrolytes. The contact effect problem opened the question of a contactless measurement of electrical and dielectric properties which will be solved in present contribution.

2. CONTACTLESS CONDUCTIVITY MEASUREMENT – THEORETICAL BACKGROUND

The basis of our contactless conductivity measurement method is an inductive coil converter wound around a thin-wall tube filled with the material to be measured. Such converters are usually very effective at high specific conductivity values, where the eddy (Foucault) currents manifest themselves very strongly. This regime was studied (Kulakov 1988, Lopatin 1980) in the past, connecting the

converter impedance with specific conductivity of samples, usually metals. To measure effectively specific conductivities under 1S/cm, a refined approach had to be developed and a measuring cell to be designed.

Let us consider a conducting sample inside a solenoid. If it is contained inside the region where the magnetic field of the coil, fed by an AC current I with the frequency ω , can be considered as homogeneous with magnetic induction $\vec{B}$, the sample attains (Landau & Lifshitz 1960) a magnetic moment

$$\vec{m} = \tilde{\alpha} V \vec{B} / \mu \quad (1)$$

where V is the sample volume, μ is the permeability of the surroundings of the coil (usually the air) and $\tilde{\alpha}$ is so-called magnetic polarizability of the sample. This complex quantity determines both the magnitude of the magnetic moment and its phase shift with respect to the generating field $\vec{B}$. The magnetic polarizability does not depend on the volume, but it has different values for different shapes of the sample (sphere, cylinder) and has generally tensor character. For a given shape of the homogeneous sample, magnetic polarizability depends only on one dimensionless parameter – let us denote it x – which is a ratio of the sample dimension (e.g. radius R_V of the sphere or cylinder) to the skin effect depth δ in the sample:

$$x = \frac{R_V}{\delta} = k_r R_V = R_V \sqrt{\frac{\omega \mu_V \sigma_V}{2}} \quad (2)$$

where μ_V is the sample permeability, σ_V its specific conductivity and k_r we have denoted the real part of the complex wave number $k = k_r(1 - i)$. Expressions for calculation of magnetic polarizability for three cases can be found (Landau & Lifshitz 1960): a sphere, an infinite cylinder polarized in parallel to its axis and a cylinder polarized perpendicularly to the axis.

The voltage induced in the coil by the sample magnetic moment can be expressed on the basis of symmetry of interaction between coil and magnetic moment

$$U = i\omega m \frac{B}{I} = i\omega \alpha V \frac{B}{I} \cdot \frac{B}{\mu}, \quad (3)$$

where m is the projection of $\vec{m}$ in the direction of magnetic field and α is the corresponding diagonal component of $\tilde{\alpha}$. The voltage U results in an apparent change of the coil impedance

$$\Delta Z = \frac{U}{I} = i\omega \mu \alpha V \left(\frac{B}{\mu I} \right)^2. \quad (4)$$

The induction B is proportional to the current I , the fraction in the parentheses is thus independent of the current and is given only by the arrangement geometry; it characterizes the interaction (coupling) between the sample and the coil. For a long solenoid with N turns on the length l_L its value will be N/l_L .

The expression (4) represents the change of the coil impedance detected by the measuring device as a consequence of inserting the sample into the coil. Let us compare this change with the total impedance $Z_L = R_L + i\omega L$ of the coil with self-inductance L and equivalent serial loss resistance (ESR) R_L . If we neglect the loss resistance and estimate the inductance of the (long) solenoid as

$$L = \mu N^2 \cdot V_L / l_L^2, \quad (5)$$

where V_L is the solenoid “volume“, we obtain for the impedance relative change ΔZ simply

$$\frac{\Delta Z}{|Z_L|} \cong \frac{\Delta Z}{\omega L} = i\alpha \frac{V}{V_L}. \quad (6)$$

Apart from the last fraction (“filling factor”), characterizing, how the sample fills in the volume of the coil, the relative change in the coil impedance is given by the value of the sample magnetic polarizability α . For samples with low conductivity, this can be a relatively small change, hardly directly measurable. We can enhance the sensitivity by completing the coil to a resonant circuit.

Let us connect the coil in series with a capacitor of impedance $Z_C = R_C + 1/(i\omega C)$, where C is the capacitance and R_C the loss ESR of the capacitor. Then the series circuit impedance at resonance frequency, $Z_S = Z_L + Z_C = R_L + R_C$, will be in the ratio 1: Q lower than that of the coil, where $Q = \omega L/R_L$ is the resonant circuit quality factor. Thus the relative change of the circuit impedance will be Q times larger than expression (6):

$$\frac{\Delta Z_S}{|Z_S|} \cong iQ\alpha \frac{V}{V_L}. \quad (7)$$

But, even so, the measurement of the very low impedance changes of the order of small fractions of ohm might be difficult with ordinary equipment. Huge improvement may be achieved by using a parallel resonant circuit (Figure 1). Its impedance is

$$Z_P = \frac{Z_L Z_C}{Z_L + Z_C}. \quad (8)$$

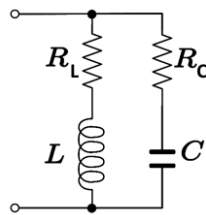


Figure 1: Parallel equivalent circuit of the measuring cell

Both factors in the numerator in (8) vary slowly in the resonance region and their magnitudes are approximately ωL . The expression in the denominator coincides with Z_S and at resonance attains the value $R_L + R_C$. The magnitude of the parallel circuit impedance is thus approximately Q -multiple of the coil impedance at resonance, or Q^2 -multiple of that of series circuit:

$$|Z_P| \cong Q\omega L = Q^2(R_L + R_C). \quad (9)$$

Such values are already easily measurable by common devices. As the change of Z_P is predominantly due to the change in the denominator in (8), in resonance region the small relative change of Z_P , after inserting the sample, is the same as in (7), with opposite sign:

$$\frac{\Delta Z_P}{|Z_P|} \cong -iQ\alpha \frac{V}{V_L}. \quad (10)$$

More accurately, however, the change of the coil impedance can be determined by fitting the experimental resonance measurement to theoretical formulae for the parallel resonance circuit in Figure 1.

For small values of x , i.e. for low frequencies or conductivities, approximate expressions for α are given (Landau & Lifshitz 1960), e.g., the formulae

$$\alpha = -\frac{i}{5}x^2 - \frac{4}{105}x^4 \quad \text{and} \quad \alpha = -\frac{i}{4}x^2 - \frac{1}{12}x^4 \quad (11)$$

are valid for the sphere and for the cylinder polarized in the direction of its axis, respectively. Evidently, for small x the first term on the right hand side is predominant and the α is almost pure imaginary. In this case, the dominant effect is the increase in the real component of Z , corresponding to the increase in the equivalent resistance R_L and lowering the quality of the resonant circuit. Using only the first term in (11), formulae can be written for the calculation of specific conductivity from the measured impedance change (6):

$$\sigma_V = \frac{8}{R_V^2 \omega \mu_V} \cdot \frac{V_L}{V} \cdot \frac{\Delta Z}{\omega L} = \frac{8V_L}{\pi R_V^4 l_V \omega \mu_V} \cdot \frac{\Delta Z}{\omega L} \quad (12)$$

for a long cylinder (with length l_V) and

$$\sigma_V = \frac{10}{R_V^2 \omega \mu_V} \cdot \frac{V_L}{V} \cdot \frac{\Delta Z}{\omega L} = \frac{15 V_L}{2 \pi R_V^5 \omega \mu_V} \cdot \frac{\Delta Z}{\omega L} \quad (13)$$

for a sphere.

At larger values of x , the effect of decreasing imaginary component of Z becomes important, with corresponding decrease of the inductance (effect “short-circuited turn”) and shifting resonance toward higher frequencies.

3. EXPERIMENTAL

PANI cryogel containing 5 wt.% of PVAL and 2 wt.% of PANI immersed in Q-Milli water or 0.1 M sulfuric acid was prepared in different geometrical shapes. Two main methods were used: impedance (dielectric) spectroscopy using broadband frequency analyser Novocontrol Alpha in the frequency range 10^{-2} – 10^{+7} Hz and temperature range -100°C ... $+100^\circ\text{C}$, and in contrast with that, a newly developed contactless method based on evaluation of eddy currents in conducting samples exposed to changing magnetic field.

The solenoid of the measuring cell was wound from 1 mm thick high-frequency cable (litz wire consisting of 900 single copper wires) on an auxiliary cylinder with diameter 13 mm and casted with mechanically and thermally stable non-conductive two-component resin with a $100\ \Omega$ platinum thermometer attached. Class 1 ceramic capacitor 2 nF, type NP0 with zero temperature coefficient and very low ESR (dissipation factor < 0.0008) with working temperature range -55 ... $+125^\circ\text{C}$ short-circuited the solenoid in its vicinity. The resulting measuring cell is presented in Figure 2.

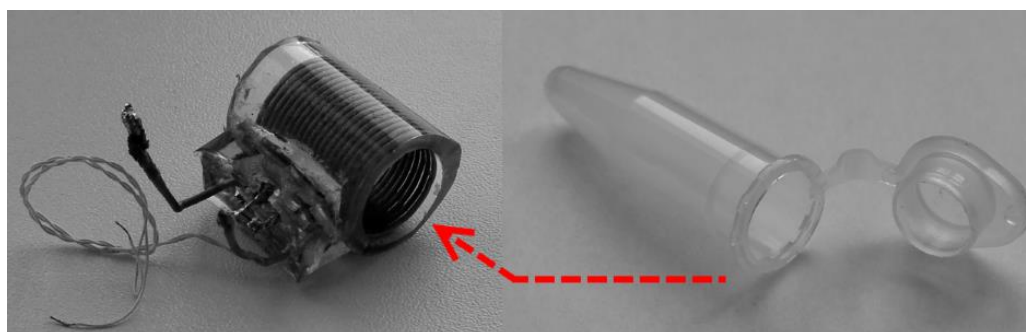


Figure 2: Measuring cell with a common test tube

Measuring cell could be filled either with pressed sample tablets (diameter 13 mm), or with test tubes, shown in Figure 2, containing original cryogels or cryogels partially squeezed out of water.

Novocontrol Alpha Analyzer along with Novocontrol Quatro Cryosystem was used to measure the resonance impedance curves and to control the sample temperature.

The resonance frequency of the empty cell was 2.25 MHz and its quality Q was higher than 750. The specific conductivity of samples was computed using the relations stated above and compared with results obtained for several reference samples, e.g., a set of hydrochloric acid solutions. Two examples of resonance curves (empty and 35% hydrochloric acid measured at 20°C) are presented in Figure 3. Considering the change in half-width and amplitude, it can be concluded that the newly designed measuring cell enables to measure specific conductivity well under 0.1 S/cm (35% HCl solution has 0.57 S/cm at 20°C).

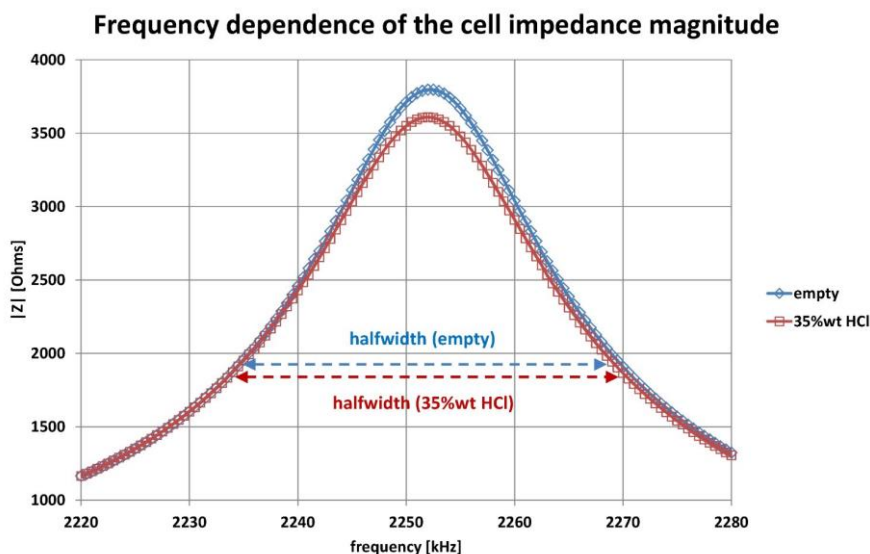


Figure 3: Frequency dependence of the cell impedance magnitude (empty and with 35% HCl solution at 20°C)

Main goal of our paper was to compare measurement results of the newly developed method with results obtained using standard impedance (dielectric) spectroscopy having in mind that a few other results on this topic are given (Dutta et al. 2002, Dutta, Biswas & De 2002). At this point we had to solve several problems. The first contact problem was connected with sample temperature stabilization and thermal stability of measured samples. Novocontrol Quatro Cryosystem uses for both cooling and heating nitrogen vapours what results in continuous loss of water in samples under test, thus in diminishing the sample thickness and in subsequent loss of electrical contact between the sample and the upper measuring electrode. The last uncomfortable effect for the measurements performed was partially eliminated by developing a pressure electrode using a spring exerting constant pressure upon sample during the measurement (Figure 4).



Figure 4: Pressure electrode using a spring

Nevertheless, application of the electrode even with a gentle string led to another unpleasant consequence – to initial loss of some portion of water in samples under study. It restricted the extent to which both methods could be fully compared. Additional gravimetric measurements have to be done.

The second problem was non-linearity (non-ohmic contact resistance) of wet samples. It could be overcome by applying low effective voltages (usually up to 100 mV). Typical non-linear electric behaviour of a cryogel containing 5 wt.% of PVAL and 2 wt.% of PANI even after having lost considerable amount of water (estimation 70% given by weighing) with stainless steel electrodes is presented for several values of effective voltage in Figure 5.

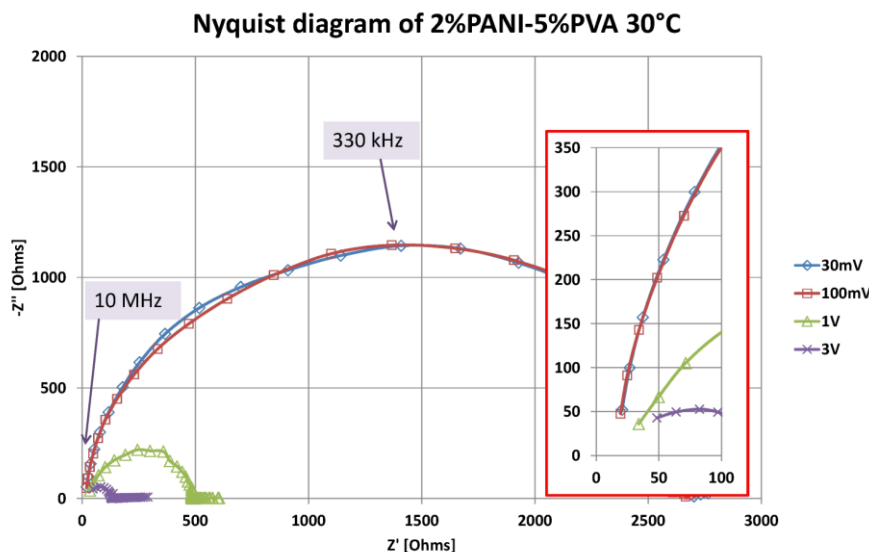


Figure 5: Nyquist plot for cryogel PVA-PANI at 30°C and several values of effective voltage (details of high frequency behaviour in inset)

Almost semi-circular plots correspond to a strong electrode or interfacial effect that depends on the effective voltage applied. The high-frequency limit of the real part of the sample impedance gives the volume resistance of the sample. From the knowledge of sample dimensions we can estimate the minimum value of the specific conductivity as 2 mS/cm, admitting that there might be further dispersion at higher frequencies (out of frequency region monitored).

Different behaviour of the samples can be obtained using silver electrodes. The electrode effect is suppressed and we have the possibility to study the changes of the sample impedance during initial desiccation (Figure 6). The initial value of 0.1Ω corresponds to the apparent sample specific conductivity 0.15 S/cm. It should be noted that the impedance remains constant in a broad frequency range.

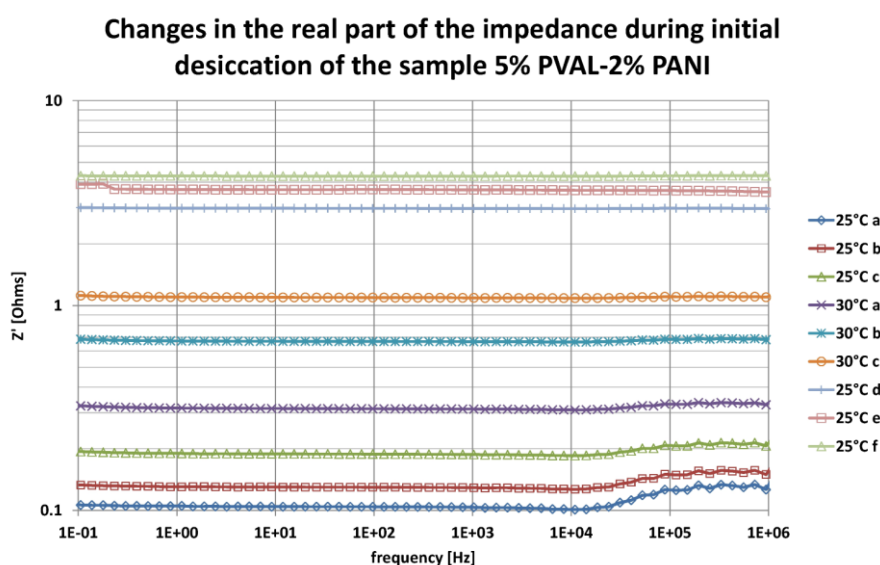


Figure 6: Time evolution of the impedance real part during initial desiccation (consecutive measurements at 2,800 s intervals are denoted alphabetically)

Temperature dependence of the sample impedance can be meaningfully obtained only after losing part of the bulk water. Such measurement was performed after the run covered by Figure 6 and the result is presented in Figure 7.

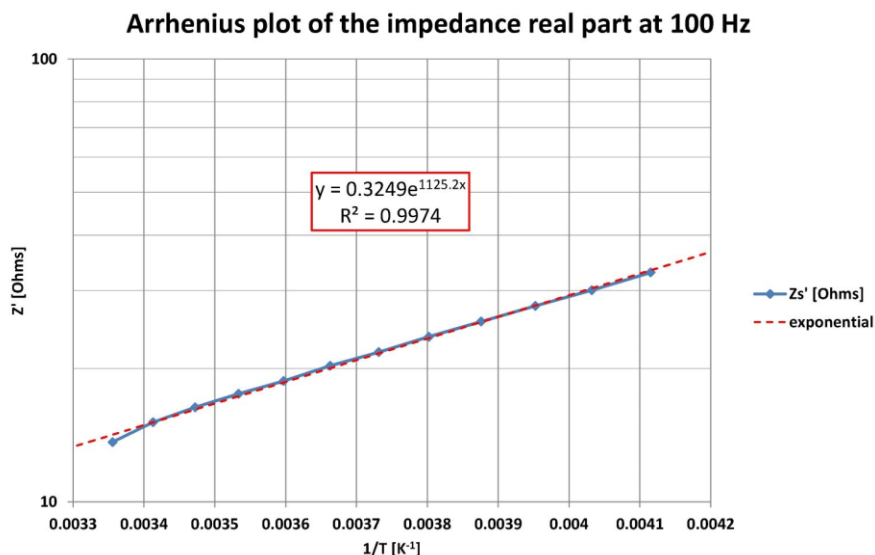


Figure 7: Arrhenius plot of the impedance real part at 100 Hz
(sample 5% PVAL-2% PANI after partial desiccation)

We can see a nearly Arrhenius-like dependence of the conductivity with activation energy 0.097 eV, well comparable to the value 0.05 eV obtained by Dutta, Biswas and De (2002). Such value of activation energy is often observed in systems with proton conductivity (Gao 2014, Matos 2014).

Impedance spectroscopy using Novocontrol Alpha with standard measuring capacitor did not give us the possibility to study temperature behaviour of PVAL-PANI cryogels without losing part of its bulk water as mentioned before. It is rational to suppose that the primarily lost water is the water filling the cavities produced during the cryogenic polymerisation. These water molecules should behave like free “volume” water, playing the role of an electrolyte solvent. If we do not want to get rid of this water, we have to close the cryogel samples hermetically and to protect them from any external pressure. For this reason we placed the samples to closable test tubes shown in Figure 2 and subjected them to developed contactless measurement described above.

The measurement results were at first glance surprising. All samples were subjected to the same temperature treatment – measurement began at +25°C and the temperature was then lowered in 5°C steps often with repeating measurements at certain temperatures up to –45°C. The temperature was then elevated again in 5°C steps up to +45°C and after short waiting a descent to +25°C followed. Each sample showed unique temperature dependence of its specific conductivity. Results for two samples, labelled A and B, with the same composition 5% PVAL–2% PANI, are presented in Figure 8, under (a) and (b), respectively. The samples had different mean value and dispersion of specific conductivity with slightly different overall temperature dependence. Despite all differences, three common features were observed:

- (1) During cooling process, the instability in the temperature range –10°C...–20°C, usually connected with the fall of conductivity, was recorded.
- (2) During rising the temperature instability was recorded in the temperature range +5°C...+20°C usually connected with the rise of conductivity.
- (3) A common rise of conductivity in the range +35°C...+45°C was observed.

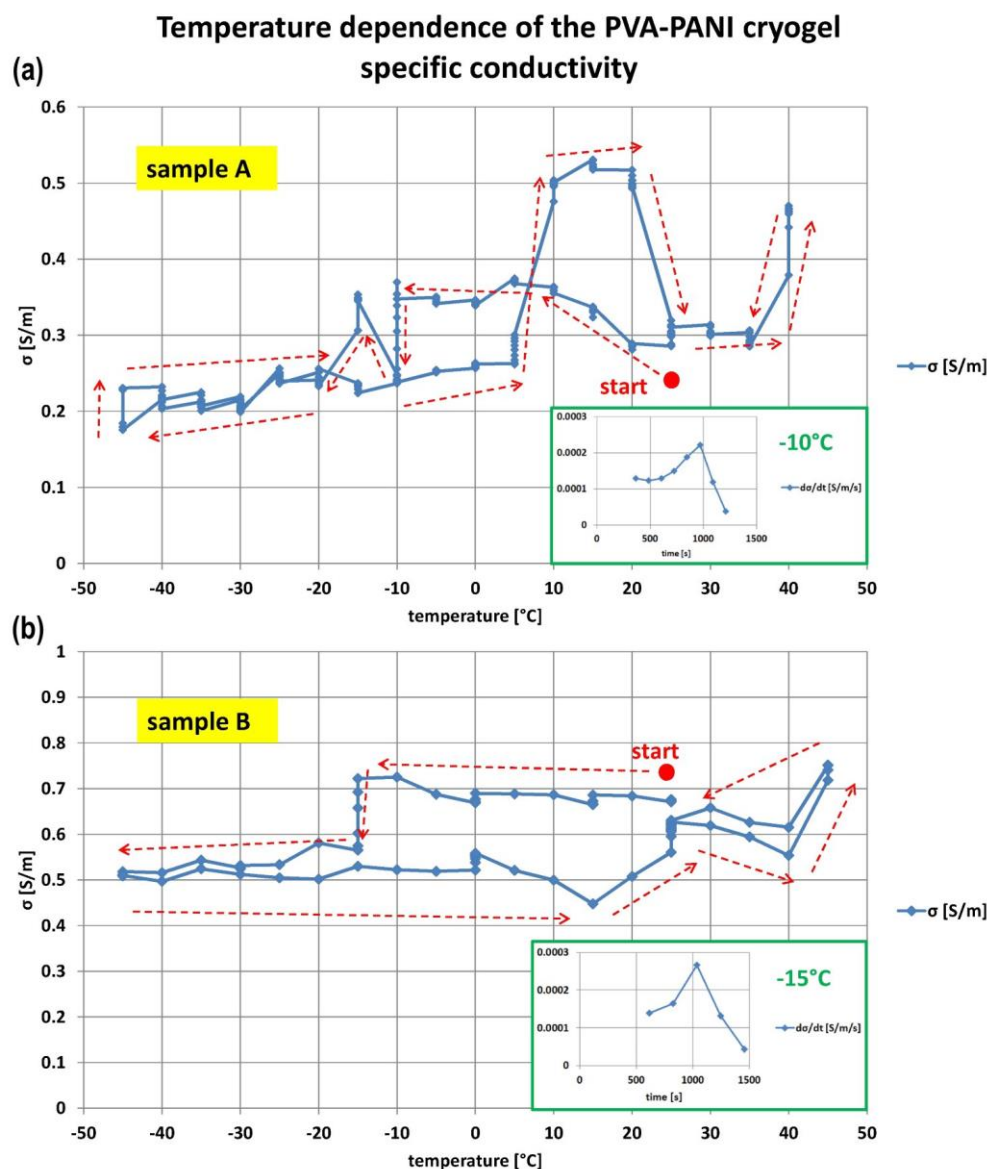


Figure 8: Temperature dependence of PVA–PANI cryogel specific conductivity measured by contactless method: (a) sample A; (b) sample B (time evolution of conductivity changes at -10°C and -15°C in insets)

Effects connected with phenomena (1) and (2) had often relaxation character with time constants of the order 10^3 s. Two insets in Figure 8 demonstrate this behaviour presenting the time dependence of the specific conductivity time derivative. We suppose that these effects can be connected with water supercooling under the freezing point (1) or with water melting (2) in single cavities with further cooperative rearrangement of the polymer matrix surroundings. The samples differ in their properties. This effect shows that the samples cannot be considered to be homogeneous, at least in the scale under study. Samples with different cavity dimensions will be studied in future experiments.

Similar instabilities were observed only for samples with “volume” water. When we used the contactless method for measuring conductivity of desiccated samples, these phenomena were not found. Besides PANI–PVAL cryogels, the contactless method was used during the study of “dry” pure PANI in a form of pressed tablets. In Figure 9, we present the temperature dependence of their specific conductivity without discussing its non-Arrhenius behaviour. In this contribution, we only want to

show that the newly developed method has enabled to detect reliably an unexpected behaviour of PVAL–PANI cryogels.

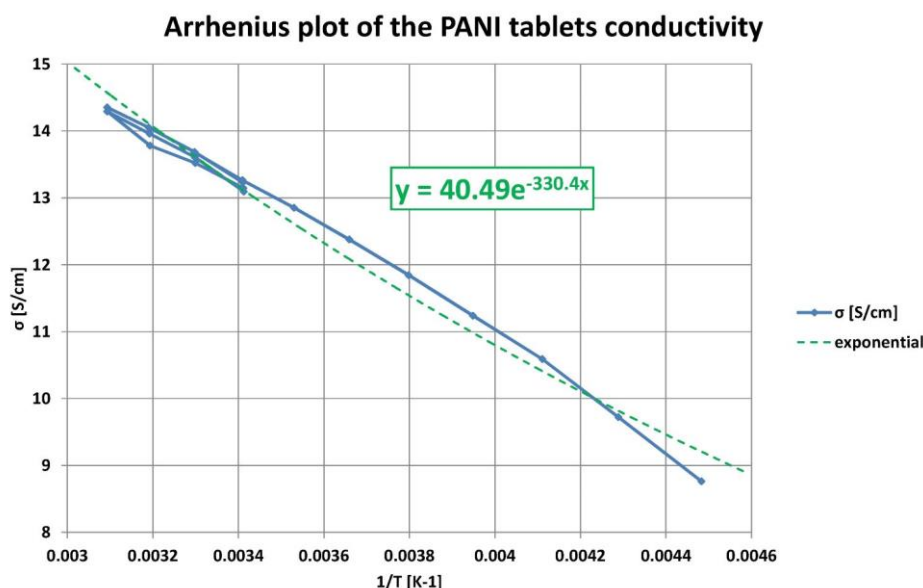


Figure 9: Arrhenius plot for the PANI tablets conductivity

4. CONCLUSIONS

We have designed and tested in practice a measuring method based upon evaluation of eddy currents in samples that enables to determine electric and dielectric properties of conducting polymer hydrogels having specific conductivity of the order 0.1 S/cm and higher. The main advantage of this method consists especially in the fact that it does not produce mechanical stress in samples. Cryogels under study often contain more than 90% of water. Some water (usually up to 30%) partially supports the stability of the 3D physical polymer net, but most of it fills the cavities emerging during the cryogenic polymerisation and can be irreversibly expelled by relatively low external pressure. The second advantage of developed method consists in eliminating electrical problems with electrodes (electrode polarisation effect, electrode material etc.).

Standard impedance (dielectric) spectroscopy works with higher sensitivity and uses very broad frequency range that is substantially more limited by the method developed. In the case of PANI–PVAL cryogels the frequency range was not decisive. Nevertheless, the actual production technology of ceramic condensers enables to cover frequency range of three decades ($10^4 \dots 10^7$ Hz). These frequency measurements along with the nonlinearity study will be subject of further contributions.

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