Permittivity Spectroscopy – an Insight Into Materials Properties

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Abstract

Permittivity Spectroscopy is a branch of the Impedance Spectroscopy specially tuned for measurements and analyses of dielectrics permittivity properties. The present paper presents experimental results on permittivity properties of composite objects in which a polarizable dielectric is distributed in a fine non-polarizable matrix (solid or liquid) measured in frequency range 1 MHz down to 0.01 Hz. Two types of objects are studied – water in porous functional ceramics and lubricating oils. In both systems gigantic enhancement of the effective capacitance is observed. The first series of experiments was performed on porous membranes of yttrium doped barium cerate, which is a proton conducting ceramics with hydrophilic properties. At a given level of watering the measured capacitance is sharply increasing (3 to 5 orders of magnitude) in the lower frequency range. The second example covers permittivity study of lubricating oils, where the increase is 2–3 orders of magnitude. The phenomenon of gigantic enhancement of the effective capacitance could be related to a formation of dipole volume structures induced by the external alternating electrical field.

Keywords: Permittivity Spectroscopy, Impedance Spectroscopy, gigantic enhancement of the capacitance, dual membrane fuel cell, lubricating oils.

1. Introduction

Electrochemical Impedance Spectroscopy quickly enters into new scientific fields due to the continuous sophistication of both the measuring instrumentation and the techniques for data analysis. [1–6] The large variety of objects – solid, liquid, conducting, semi-conducting or isolating, small and large batteries, pharmaceuticals and biosamples, opens new niches for its further improvement. This work was preceded by some screening measurements on motor oils and food products such as fats, alcohols, cheese and honey, applying one promising approach – the Permittivity Impedance Spectroscopy. It ensures contact-less measurements of a wide variety of objects with respect to their physical behavior and conductivity without the need of any reference electrode.

The Permittivity Spectroscopy is a special branch of the Impedance Spectroscopy which is tuned for measurement and analysis of dielectrics permittivity properties. In general permittivity is the ability of a space (free or filled with dielectric) to be polarized under external electric field. For dielectrics this ability is the ground for their property to conduct alternative current.

According to the general theory,[7] dielectrics could be classified in three categories: (i) non-polarizable; (ii) polarizable and (iii) ionic crystals. Non-polarizable dielectrics do not contain dipoles. Polarizable dielectrics contain dipoles (primary or induced) which follow the orientation of an external electric field. When such a field is applied by external electrodes, the dipoles near the electrodes are oriented correspondingly and compensate the external electric field.

The classical applications of the permittivity spectroscopy are typically related to the dipole properties studies of pure gases and liquids. The applied frequency range is from 1000 MHz down to 1 MHz and requires special measurement instrumentation.[8–13]

The studies reported here concern different objects – polarizable dielectrics, highly dispersed in a matrix of non-polarizable or weakly polarizable dielectric and require different frequency range. The accumulated expe-

rience has shown that important interactions between the two materials are well observable in the range of 1 MHz down to 1 Hz.[14,15] It should be noted that in this frequency range the penetration depth of the alternating electric wave is much larger than the object's thickness.[11] As a result the electric field strength is practically equal in the full volume of the object.

The pure capacitive impedance follows the dependence:

$$\mathbf{Z}(i\omega) = -i(\omega C)^{-1} \qquad (1)$$

where *C* is the capacitance. For parallel plate capacitor, it can be expressed as:[7,8]

$$C = \frac{\varepsilon\varepsilon_0 S}{d} \qquad (2)$$

where ε is the relative dielectric permittivity and ε_0 is the permittivity of vacuum, *S* is the surface area of the capacitor electrodes and *d* is the distance between them.

Taking into account the polarization losses, when the A.C. signal is applied, the relative permittivity can be expressed as a complex number:[7, 11]

$$\boldsymbol{\varepsilon} = \varepsilon' - i\varepsilon'' \qquad (3)$$

where ε' and ε'' denote the real and the imaginary (loss factor) components of the complex value of ε.

Applying equations (2) and (3), the capacitance can be also presented in a complex form:

$$C = C' - iC'' \qquad (4)$$

If Eqn. 1 is expressed as admittance

$$Y(i\omega) = 1/\mathbf{Z}(i\omega) \qquad (5)$$

Then

$$Y(i\omega) = i\omega C = i\omega (C' - iC'') = \omega C'' + i\omega C' \qquad (6)$$

The real component $\omega C''$ in Eqn. 6 can be regarded as dielectric conductivity,[7] which can be expressed also as equivalent resistance $R = 1/\omega C''$ directly monitored by the instrument. It involves the energy dissipative effects as ohmic conductivity, dipole's reorientation losses in electric field and others. is directly related to the dielectric permittivity, i.e. to the polarization ability.

This work aims at presenting the application of the Permittivity Impedance Spectroscopy in the studies of two different systems: (i) water in the highly porous matrix of functional ceramics and (ii) lubricating oils.

The interest in water behavior in porous functional ceramic media was inspired by the recently developed new design of solid oxide fuel cell (SOFC) named dual

membrane fuel cell (dmFC).[14–16] It eliminates the principle construction disadvantage of both SOFC and proton conducting SOFC (pSOFC) in respect to the effect of the water formation respectively on the anode or on the cathode side. The new design combines a pSOFC anode/electrolyte assembly that produces protons and a SOFC electrolyte/cathode that produces oxide ions. They are connected by a mixed ion conducting porous ceramic membrane – central membrane (CM), where the two types of ions meet and form water, evacuated through the porous structure of the CM. In this way hydrogen, oxygen and water are located in 3 independent chambers. The new design has important advantages: the fuel and the oxidizer are not diluted and water does not inhibit the catalytic activity of the electrodes.

The standard procedure for the construction of CM with mixed conductivity is to use composite from oxide ion conducting electrolyte – $Ce_{0.85}Y_{0.15}O_{1.925}$ (YDC15) and proton conducting one – $BaCe_{0.85}Y_{0.15}O_{2.925}$ (BCY15).[16] Due to the discovered mixed ionic conductivity of BCY15,[17,18] the composite CM was replaced with the so called monolithic membrane produced with BCY15. Since the kernel of the dmFC is the central membrane where the water is formed and evacuated, permittivity spectroscopy emerges as an important tool for water behavior studies in the porous mixed ion conducting ceramic media.

The first screening measurements of oils together with other similar objects as fats, butter, margarine, inspired the interest for permittivity studies of lubricating oils which could be a basis for further development of convenient and fast non-destructive methods for screening analysis and assessment of the changes in oils lubricating properties during exploitation.

The main function of motor oils is to lubricate those parts of the engine, which move closely and cause friction that wears them and converts energy to heat. The oil forms a film between the surfaces of the adjacent moving parts and thus minimizes the direct contact between them, decreasing friction, wear, and production of excessive heat.[19] Oils are made of a heavier petroleum hydrocarbon base stock derived from crude oil (the hydrocarbons are with between 18 and 34 carbon atoms per molecule).[20] They contain also additives which improve certain properties. Motor oils quality evaluation is based on a big number of parameters (over 40), applying time-consuming destructive physical and chemical tests.[21–26] Viscosity and oiliness are of leading importance for all types of oils. Viscosity is accepted as the basic physico-mechanical parameter, while oiliness can be regarded as a "hidden" potential quality parameter of the oil. It is evaluated with a set of properties which ensure lubricating effect at thickness of the film, which is small enough to eliminate the viscosity effect.[23,26] The leading factor is the strength of attachment of the thin oil layer towards the two moving parts, which preserves them from direct contact. It

depends on the oil's property to form layers with orientated molecules, i.e. on its polarization characteristics. The oiliness is higher when the polarization processes are easier. The addition of compounds with high polarization activity (oxygen-containing compounds as naphthene, carbonic acids, asphaltenes, tar, compositions with sulphur in their molecules) improves the strength of the fine oil layer, i. e. the oiliness increases. The procedure for oiliness testing is hard – the oil is tested on special traction stands, where the degree of wear of standard moving parts (for instance balls) is evaluated. Thus polarization ability studies by permitivity impedance spectroscopy are an original approach towards further development of a more convenient and fast non-destructive procedure for oiliness testing.

2. Experimental

Complex permittivity and impedance measurements were performed on Solartron 1260 FRA in the frequency range 1 MHz – 0.1 Hz at room temperature with amplitude of the signal 1 V for the ceramic sample and 300 mV for the lubricating oils at density 5 points/decade.

The experimental cell consists of two coaxial cylindrical electrodes with coplanar working surfaces. For the ceramic samples they are prepared from brass and for the motor oils – from iron. Additional plastic spacer ensures distance of 0.2 mm for the oil between the two electrodes (diameter 96mm), which are spring fixed in the cell mounting.[14,15] The precise determination of the object's permittivity/impedance is ensured by a preliminary calibration procedure, which eliminates the parasitic components coming from the measuring cell.[14,15]

Preliminary screening measurements showed that the two investigated systems are not sensitive to d. c. bias polarization, i. e. they behave as linear systems. The experimental data are presented in C'/f and R/f plots, where f is the frequency.[27] A logarithmic scale is applied (Fig. 1).

Two types of mixed conducting porous ceramic pellets were prepared: BCY15 (monolithic) and composite based on 50 : 50 vol. % of BCY15 and YDC15. The initial powders were mixed with pore former graphite or starch. After homogenization the mixtures were cold pressed and sintered in air at 1450 °C for 5 hours. Samples with diameter and thickness respectively about 2 cm and 1,5 mm were obtained. The exact dimensions are given in Table 1.

For more convenient analysis of the experimental results the exact dimensions of the samples are presented in volume units (Table 1). Porosity was determined by mercury porosimetry (AUTO 9200 "MICROMERITICS").

The BCY15 pellets stability in water was tested by Differential Thermal Analysis and Thermogravimetry combined with Mass Spectroscopy in the temperature range 20–600 °C. A good chemical stability was observed.[28] The good reproducibility and reversibility of the permittivity measurements confirmed the stability of the samples in the selected experimental conditions.

3. Results and Discussion

3. 1. Water Behavior Studies in Porous Functional Ceramics

Since the study concerns the influence of the water on the permittivity of the ceramic sample, the measurements were performed first on dry membranes (with humidity equal to that of the ambient atmosphere), followed by a series of measurements with increasing quantity of the water introduced in the volume of the samples with micropipette. For dry central membrane approximately no frequency dependence of C' is observed, while the parallel effective resistance is increasing, which indicates decrease of the losses (Fig. 1).
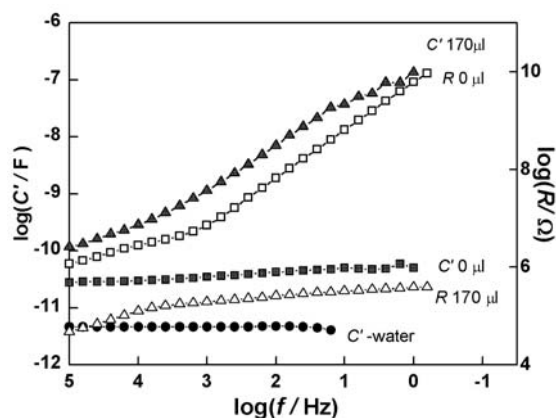
Fig. 1. Permittivity measurements of composite membrane with pore-former 2 wt% starch. Frequency dependence of: C' for pure water (in spacer with the dimensions of the sample), C' and R for dry sample and for sample with 170 µl water.

Table 1. Measured samples

№	Sample type	Pore former 2 wt%	Diameter/Thickness mm	Geom. Volume mm³	Porosity %
1	Composite sample	Starch	22/1,5	~ 570	45
2	Composite sample	Graphite	23/1,6	~ 664	30
3	Monolithic sample	Graphite	22/1,15	~ 437	30

The same behavior is registered for measurements in which the ceramic sample is replaced with pure water in special spacer with the dimensions of the sample (Fig. 1). This indicates that C'_{H20} is practically frequency independent (in the applied frequency range). The dielectric permittivity of the water derived from the experimental data is 82 (at 1 kHz), which is in agreement with data from the literature.[8] The addition of small quantities of water in the CM slightly increases the value of *C'* up to a given level of watering, at which sharply increases in the lower frequency range, combined with increase of the losses. The additional watering moves the kink that marks this sharp increase of *C'* ($10^3 - 10^4$ times at 1 Hz) towards higher frequencies (Figs. 2a, 2b). This general behaviour has specific differences for samples with variation of the porosity, including pore morphology, which depends on the poreformer quantity and origin (starch or graphite). Samples which differ only in the type of the pore former have different microstructure and perform different behaviour in respect to the frequency dependence of *C'*.

In order to emphasize the phenomenon capacitance enhancement and to eliminate the influence of the cell, of the sample geometry and other unknown initial factors which can influence the measurements, a coefficient of enhancement γ_t which is dimensionless parameter, can be introduced:

$$\gamma_i = \frac{C'_i}{C'_0} \tag{7}$$

where is the capacitance at a given frequency ω_i and C'_0 is the capacitance at the highest measured frequency. In the rest of the examples this form of the experimental data presentation will be used (Fig. 2).

The sharp increase of *C'* starts at lower water concentration in composite membranes with higher porosity – at 45 µl for 45% porosity (Fig. 2a), while for membrane with 30% porosity it starts at 90 µl (Fig. 2b).

The monolithic CM which is pure BCY15-based matrix has higher polarization ability. The sharp increase starts at lower water content and reaches much higher values – at 1 Hz the enhancement is up to 5 orders of magnitude (Fig. 2c). Even the room humidity in the calibration "dry sample" measurements marks a small increase of *C'*. This result confirms the hypothesis that the polarization effect is strongly related to the hydrophilic properties and defect structure of the BCY material in the CM.

The phenomenon observed in porous BCY15-based membranes can be described as gigantic enhancement of the real part of the capacitance with the decrease of the frequency, which is dependent on the degree of wetting. One possible explanation of the results is the formation of 3-D structures of organized dipoles at the pores walls which are re-orienting synchronously with the alternating perturbation signal. This hypothesis was additionally confirmed by classical impedance measurement directly on a dual mem-
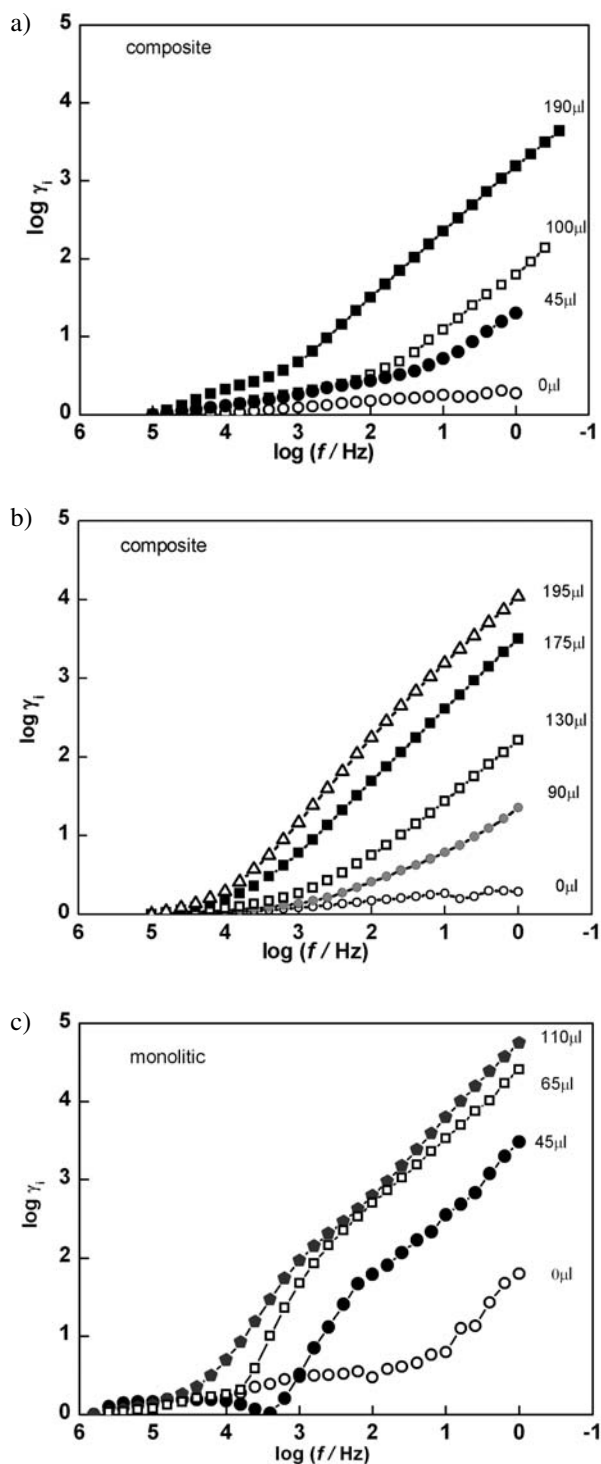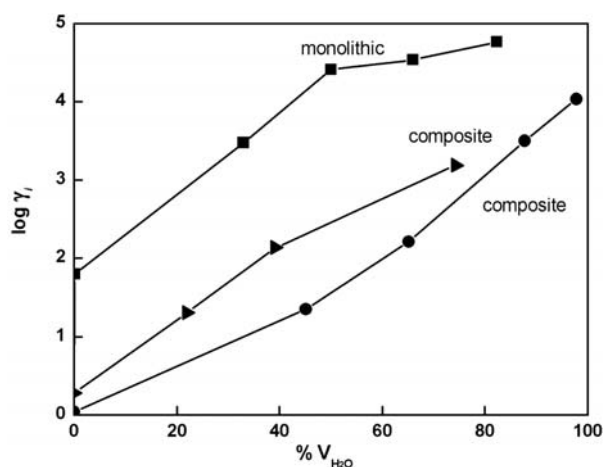

Fig. 2. Frequency dependence of the enhancement coefficients γ at different levels of watering for: a) composite membrane with pore former 2 wt% starch; b) composite membrane with pore former 2 wt% graphite; c) monolithic membrane with pore former 2 wt% graphite.

brane fuel cell with monolithic CM operating at 600 and 700 °C, where the presence of "quasi" liquid water film, absorbed in the pores, was experimentally proved.[29]

An informative presentation of the measured data is the single-frequency analysis which gives the relation between *C'* (expressed as log γ_i) and the quantity of added water for a chosen single frequency. The quantity of the water can be related to the volume of the pores in the ceramic matrix. The data from Table 1 that give information about the measured porosity can be used for recalculation the percentage of the pores volume (V_{H2O}) filled with water. Fig. 3 is presenting the results obtained for the three samples from Table 1, which ensure some conclusions for the influence of the matrix chemical composition and of the pore-former on the phenomenon gigantic enhancement. In the composite samples the pore-former starch is supporting a faster increase of the capacitance *C'*. The initial level of the enhancement for the pure BCY porous membrane could be attributed to the pre-humidification of the sample by the surrounding atmosphere which is related to the well known high hydrophilic properties of the BCY material.[30]

The obtained results – experimental data and their processed presentations ensure a description of the processes taking place in the pores during their filling with water, which explains the phenomenon of gigantic enhancement of *C'*. Under AC electric field which is perturbing the state of the sample, structures of oriented dipoles are formed inside the pores partially filled with water. The duration of this effect is defined by the half period of the AC signal which is varying between half microsecond and half second. Taking into account that the external signal is changing every half period, a formation of quite different dipole structures (in volume and morphology) can be expected. For very short duration (high frequencies), small clusters (2 and 3D) of oriented dipoles could be expected to develop at the pores surface. This process is decisively activated by the hydrophilic behaviour of BCY and its property to absorb water, dissolving it to proton and OH– ion which take different places in the crystal lattice ($H_2O_{(g)} + V_O^{\bullet\bullet} + O_O^X \rightarrow 2OH_O^\bullet$)).[18] Thus the pores surface has active centres for nucleation and formation of 3D water dipole structures – a process forced by the external field. At lower frequencies the initially formed clusters of structured dipoles have time to grow, which is registered by the permittivity measurements as increase of the capacitance. When the period of the AC half period is enough long the clusters start overlapping which leads to the increase of the capacitance enhancement slope. This hypothesis explains well the two slopes in *C'* frequency dependence. It also fits well to experimental results on operation of dual membrane fuel cell with monolithic central membrane. It was found that after initial operation and formation of the first small quantities of water in the CM (which is in quasi-liquid state),[27] the resistance of the cell starts decreasing substantially.[29] Obviously the produced water inside the membrane is filling preferably the "necks" of the pores improving the grains contacts due to the oriented dipole structures of the water-based film clusters.

3. 2. Lubricating Oils Studies

Complex permittivity and impedance studies were carried out on motor oils from the three main types – natural, semi-synthetic and synthetic, produced by renowned companies and available on the market (Table2). The measured permittivity data of typical fresh samples from the three types of lubricating oils are presented in Fig. 4. The shapes of the effective capacitance frequency dependences and the equivalent resistance (presented in log scales) are different.

Fig. 3. Normalized plot of the enhancement coefficient γ_i (1 Hz) dependence on the relative pores filling with water : (●) composite membrane with pore former 2 wt% graphite; (▲) composite membrane with pore former 2 wt% starch; (■) monolithic membrane with pore former 2 wt% graphite.

Table 2. List of motor oil samples

| №	Firm	Name of the oil	Type	Status
1	Mobil	Mobil Delvac MX 15W40	natural	fresh
2	Mobil	Mobil Delvac MX 15W40	natural	after 10000 km
3	Castrol	Castrol TXT 5W40 mit	semi-synthetic	fresh
4	Castrol	Castrol RS 0W40	synthetic	fresh
5	Mobil	Mobil ATF (for automatic gear box)	natural	fresh
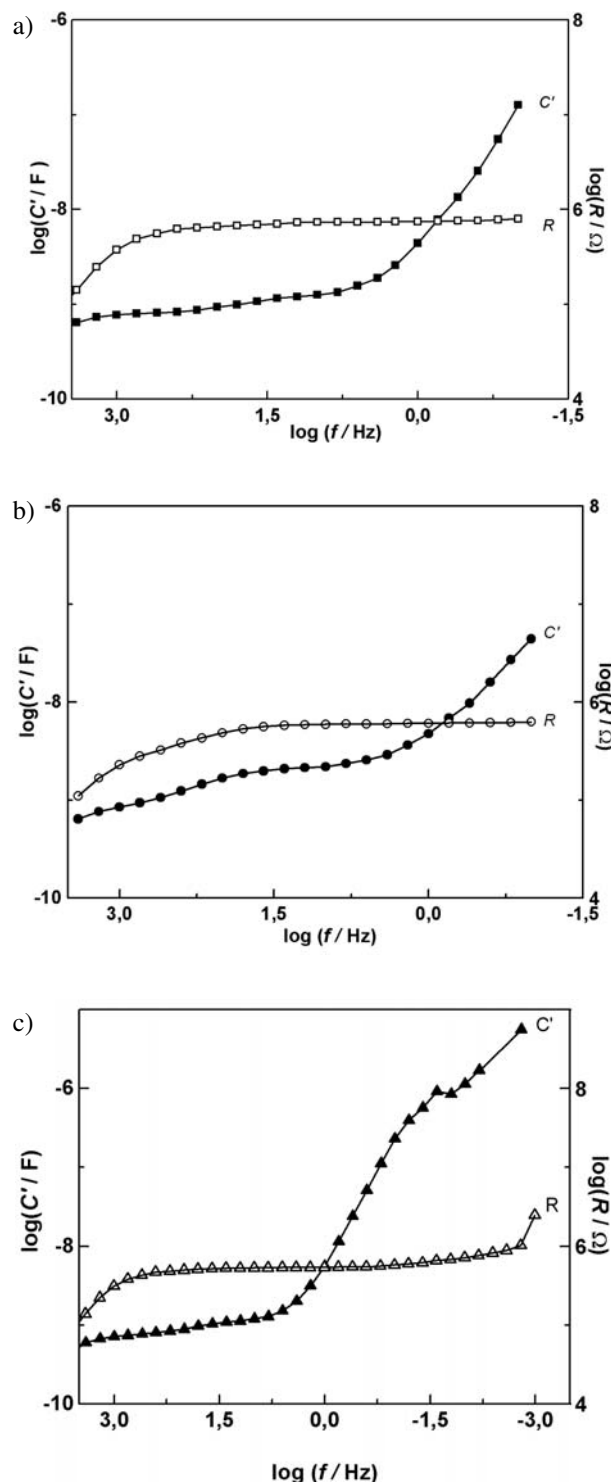
Fig. 4. Frequency dependence of *C'* and *R* for: a) natural (Mobil Delvac MX 15W40) , b) semi-synthetic (Castrol TXT 5W40) and c) synthetic (Castrol RS 0W40) lubricating oils.

Every diagram has plateau in respect to *R* or/and *C'* in the mid-frequencies range, correspondent to the nature of the sample. The levels of the plateau- type regions are similar, which should be expected. All the diagrams have

segments where the capacitance is increasing significantly with the decrease of the frequency. However, the cross-over frequency points between the plateau and the next segment with increasing *C'* are different for every sample. The characteristic cross-over frequency for every single dependence can be calculated by determining the inflex point of its derivatives. The values could be correlated with the nature of the sample oil and/or with the oil viscosity. The parallel measurement of other oils from these 3 types produced by different companies, as well as measurement of gear-box oil with rather high viscosity (Table 2) showed however, that the viscosity is not the primary factor controlling the shape of the permittivity frequency dependences.

In order to go deeply in the studied phenomenon, the data were analyzed further in accordance with the algorithms of the Differential Impedance Analysis.[31–34] The equivalent time-constants have been calculated for every frequency point as a product of the measured capacitance and resistance. The resulting new parameters were plotted as functions of the inverse log-frequency. These new temporal functions (the argument is the time, i.e. the duration of the period of the sinusoidal perturbation) were then converted into the more illustrative spectral form,[31–34] shown in Fig. 5.
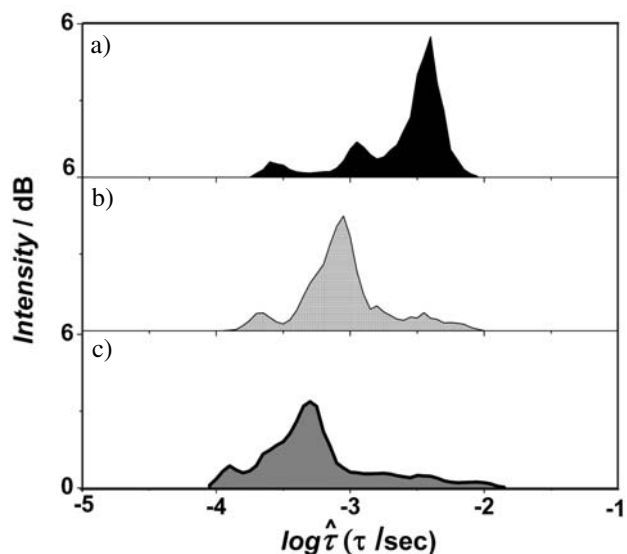
Fig. 5. Time-constant spectra from the middle frequencies segments for: a) natural (Mobil Delvac MX 15W40), b) semi-synthetic (Castrol TXT 5W40) and c) synthetic (Castrol RS 0W40) lubricating oils.

The spectra produced in this way give direct information about the mean values of the equivalent time-constants and their distribution. As it is seen, the time-constants differ significantly, decreasing in the range of two decades in the order: natural – semi-synthetic – synthetic oils.

Another type of investigation is shown in Fig. 6. Two samples of the same oil – fresh and after 10000 km (approximately the end of its running live) are compared. After long time of exploitation the sharp pick disappears and the resulting spectral shape is rather dispersed in wider range of values covering faster relaxation times correspondent to smaller molecules – products of the oil degradation.
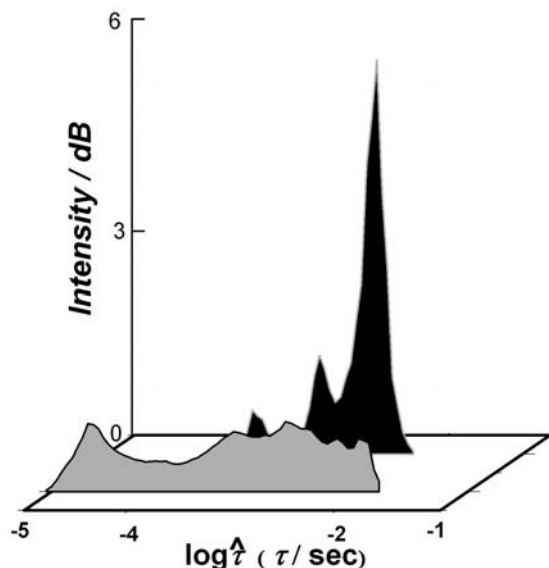

Fig. 6. Time-constant spectra of lubricating oil Mobil Delvac MX 15W40: new (black) and after 10000 km run (grey).

Discussing the observed phenomena, a general conclusion can be derived – the permittivity studies of lubricating oils have discovered again the phenomenon of gigantic enhancement of the effective capacitance. In comparison with the examples in the previous paragraph a smaller coefficient of enhancement can be marked. Obviously the observed phenomenon of capacity enhancement of lubricating oils is related to the presence of polarizable dipole molecules distributed in the non-polarizable (or weakly polarizable) dielectric of the fluid. Thus from electrostatic point of view these oils are highly dispersed mixtures of polar dipoles (fluid) in a fluid matrix of non-polarisable molecules. From practical point of view the observed phenomena can serve as a basis for the development of fast method for screening analysis of lubricating oils and related materials as well as for screening evaluation of the degradation degree the studied oil.

4. Conclusions

The application of the Permittivity Spectroscopy in the frequency range below 1 MHz is promising to be developed as a powerful approach for investigation of numerous materials: oils, food and beverages. The experiments described here cover two types of materials – water in porous ceramic membranes and lubricating motor oils. Even different in chemistry and morphology, these materials have a common physical property – a polarizable fluid is highly dispersed into matrix (fluid or solid) of non-polarizable dielectric. In both cases phenomenon of gigantic enhancement of the effective capacitance is observed.

This enhancement is very high and reaches 4–5 decades. The explanation is related to the formation of organized dipole structures called often dipole micelles. In both cases these structures support the practical applications of the material. The studies of the processes taking part and their deep understanding could serve as a tool for fast evaluation of the properties of the materials and for further improvement of their qualities.

5. Acknowledgements

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Povzetek

Permitivnostna spektroskopija je veja impedančne spektroskopije, ki je namenjena predvsem merjenju in analizi permitivnih lastnosti dielektrikov. Pričujoči članek prestavlja eksperimentalne rezultate permitivnostnih meritev kompozitnih vzorcev, v katerih je polarizabilen dielektrik porazdeljen v nepolarizabilni matrici (tekoči ali trdni). Frekvečno območje meritev znaša od 1 MHz do 0.01 Hz. Proučevali smo dva tipa vzorcev – vodo v porozni funkcionalni keramiki in mazivna olja. V obeh sistemih opazimo »gigantsko povečanje« efektivne kapacitivnosti. Prvi set eksperimentov smo opravili na poroznih membranah iz barijevega cerata, dopiranega z itrijem. Gre za znan trden protonski prevodnik s hidrofilnimi lastnostmi. Pri določeni stopnji navlažitve se izmerjena nizkofrekvenčna kapacitivnost strmo poveča, in sicer za 3 do 5 velikostnih redov. Podoben primer so mazivna olja, kjer porast kapacivnosti znaša od 2 do 3 rede velikosti. Fenomen gigantskega povečanja efektivne kapacitivnosti lahko razložimo s tvorbo dipolnih volumskih struktur, ki jih inducira zunanje spremenljivo električno polje.