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Dielectric Characteristics of Ionic Liquids and Usage in Advanced Energy Storage Cells

Attila Göllei

Additional information is available at the end of the chapter

Abstract

Before the application of ionic liquids, it is important to know their fundamental physical and chemical properties. Practical experience has shown that it is important to look at these materials in the behaviour of the function frequency and temperature. To understand obtained information understanding the molecular-physic bases is needed. Research and application of ionic liquids have attracted an increasing attention in the areas of nuclear industry, oil and gas industry, petrochemical industry, chemical and electrochemical industry. The number of studies dealing with the question is proliferating which opens up new horizons in the field of chemical operations in microwave field with ionic liquids (organic chemical synthesis, catalytic operations, etc.). As a result of the relatively high destroying temperature of ionic liquids, a wider temperature range of operations can be done and it offers environmental friendly solution in the replacement of the toxic solvents with generally low evaporating temperatures. The area of application is becoming more widespread as electrolyte of novel battery cells. Being aware of the physical and chemical properties of ionic liquids is necessary in order to apply them. The main goal of this research was to test the dielectric properties, viscosity and temperature dependence of the electrical conductivity. Based on our results, we can claim that significant temperature dependence of the three properties can be shown in the case of ionic liquids. These findings are crucial for the usability of applications, planning and preparing of production and optimization processes. The significance and importance of these results become even more obvious if we consider the fact that these energy storage cells are exposed to large temperature differences. The present study discusses the

sample materials, their usage possibilities and the results of the research from the previous work of the author. In the case of ionic liquids, it is important to know their behaviour in electric field. In lot of cases, there is no fundamental difference between the static and dynamic behaviours. Static state (like in accumulators) is similar to the dynamic. Ionic liquids are well characterized and grouped with their dielectric behaviour. First of all a short summarizing of basics of the electrical permittivity and then a modelling procedure will be shown modelling lots of parameters using dielectric characteristic of material. At the end the practical usage and application will be shown by using ionic liquids as the electrolyte of batteries.

Keywords: ionic liquids, energy storage cells, conductivity, temperature dependence, viscosity

1. The electrical permittivity of ionic liquids: the concept of dielectric constant

1.1. The introduction of the concept of the dielectric constant

Charge carriers in ideally sealants are not able to move. Perfect vacuum is considered to be an ideal insulation for the fluid. In reality, in the practical devices containing the vacuum (such as vacuum switches), the vacuum is always bounded with material that allocates charge carriers in the vacuum; therefore, they cannot be considered as perfect insulators in practice [2].

Dielectric is a solid, liquid or gaseous substance, which acts as an electrically insulating material. Resistivity is greater than 10^8 Ωm. In dielectric there are practically no free charge carriers. Polarization occurs in the dielectric materials as a result of electric field. It is the permittivity characteristics of the substances that affect the amount of electric field. The dielectric constant is a scalar value.

Electric field strength from the charge by r distance created by a point charge Q from the context of

$$E = \frac{Q}{4\pi \cdot \varepsilon \cdot r^2} \rightarrow \varepsilon = \frac{Q}{4\pi \cdot E \cdot r^2} \tag{1}$$

so:

$$[\varepsilon] = \frac{[Q]}{[E] \cdot [r^2]} = \frac{1As}{1\frac{V}{m} \cdot 1m^2} = 1\frac{As}{Vm} \tag{2}$$

The proportionality factor is between the electrical permittivity of the prevailing electric field of a given electrical offset (D) and electric field (E), which is characterized by filling the space at the point of medium volume and independent of the electric field in the material:

$$\varepsilon = \frac{D}{E} \tag{3}$$

The electrical permittivity of a point in space is a multiplication of the relative constant of the vacuum permittivity and the permittivity of room-filling material at the point:

$$\varepsilon = \varepsilon_0 \cdot \varepsilon_r \tag{4}$$

where $\varepsilon_0 \approx 8,852 \cdot 10^{-12} \frac{As}{Vm}$, the permittivity of the vacuum, the so-called dielectric field constant and ε_r is a value without dimension, the permittivity of the material, the so-called dielectric value of the material.

Most of the insulation applied in practice have the relative permittivity of insulation value of a digit. Water has particularly high value, due to the highly polar water molecules and high dipole moments.

In most computing procedures, the relative dielectric constant of air can be considered with the value of 1 because of its difference from one is in the order of 10^{-4}.

1.2. Electric field in the insulating material

The value of the field of the electric charge can be obtained from the very simple relationship:

$$\mathbf{D} = \varepsilon_0 \mathbf{E} \tag{5}$$

The introduction of the displacement vector, which is formally a simple relationship between the dielectric constant and the electric field strength [3]. The situation is complicated when the insulation material is placed in the chamber. This is a natural thing since the smallest building blocks of matter are charged particles, although they usually seem to be neutral in the outing direction. In a small part of the chamber, the same amount of positive and negative charges can be found, but we know that these charges are in influenced by the electric field force and the consequence of the previously neutral dielectric material that creates a force field as well. This effect of the external space will change the field of force.

1.3. Electrophysiological approach

The value of a capacitor can be calculated by the following equation:

$$C_0 = \frac{\varepsilon_0 \cdot A}{4\pi \cdot d} \tag{6}$$

where C is the capacitance, A is the surface area of opposing arms, d is the distance of armaments and ε is the dielectric constant of material positioned between the plates. If there

is a vacuum between the condenser armatures, the measured capacity of the condenser is marked C_0. If there is electrically insulating material between the armaments, the capacitance increases:

$$C = \varepsilon_r \cdot C_0 \tag{7}$$

The relationship shows that the value of the dielectric constant is at least one or greater than one value.

Then $\varepsilon_r = \frac{C}{C_0}$ or in relative units, $\varepsilon_r = \frac{C + C_0}{C_0}$

If the capacitance change is large($C \gg C_0$), the values of the two previous relationships do not differ significantly. The obtained dielectric constant value is marked ε' and this metric number characterizes the interaction between the material and the electromagnetic field. The dielectric constant is a number that shows how many times greater the capacity of a given capacitor filled with dielectric material is than in the vacuum.

1.4. Interpretation of the dissipation factor

If an ideal lossless capacitor is coupled in AC circuit, $\varphi = 90°$ phase shift is generated between the voltage and the current of the capacitor (**Figure 1**).
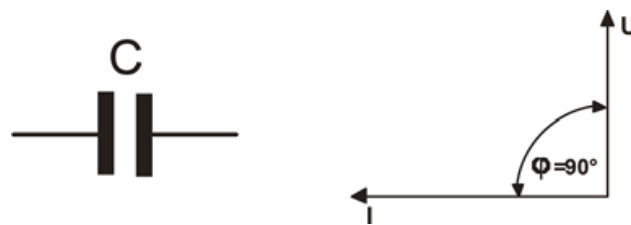
Figure 1. Phase between current and volt of capacitor.

In this case the capacitor behaves like a lossless impedance (reactive resistance). Accordingly, the capacitor does not absorb energy from the circuit. The context of the AC power load can be seen

W = U I cosφ where φ = 90° cosφ = 0 and so W = 0.

If there is a dielectric material between the capacitor armatures, the dielectric loss is created. This can be modelled with an ideal capacitor and a resistor coupled in parallel.

The value of the reciprocal of the resistance is often presented as electrical conductivity. In this case, the phase difference between voltage and current will be less than 90° (**Figure 2**).

The dielectric material absorbs electromagnetic energy from the space (directly from the circuit) and consequently the movement of the dielectric molecules increases. Part of the electrical energy is converted into heat, so dielectric loss occurs. The magnitude of the losses is called phase angle supplementary angle and it equals to the tangent of the loss angle:

$$\delta = 90° - \phi \tag{8}$$

The tan δ is an analytically similar electro-physical constant to ε. From the magnitude of tan δ, even more reliable conclusions can be obtained about the purity of a substance than some cases from the dielectric constants. The tan δ of a capacitor comprising a parallel loss resistance is calculated as follows:

$$tg\delta = \frac{1}{\omega \cdot C \cdot R} = \frac{G_a}{\omega_0 \cdot C_a} \tag{9}$$

where G_a is the electrical conductivity of the dielectric, measured together with the dielectric capacitance of C_a.

So $tg\delta = \frac{\varepsilon''}{\varepsilon'}$ than $\varepsilon'' = \varepsilon' \cdot tg\delta$.

Therefore ε'' is a value without dimension that characterizes the amount of absorbed energy by the material from the electromagnetic space.
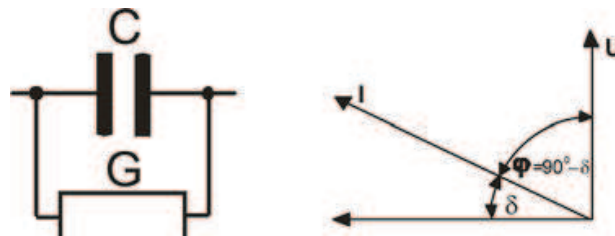

Figure 2. Lossless capacitor.

1.5. Molecular physics approach

Two groups of the dielectric structure are distinguished regarding the structure of materials.

a.   Non-polar molecules

In the case of non-polar molecules, the molecules of the insulating material are neutral if there is no outward electric field. The positive and negative electric charge centres of gravity are in the same point and they only constitute small dipoles, depending on the outer space's field strength. This group includes, for example, a symmetrical hydrocarbons without permanent dipole moment molecules (methane, acetylene, benzene, naphthalene) and molecules consist of two identical atoms (F2, Cl2) and the noble gases.

b.   Polar molecules

In the case of polar molecules, the molecules of the dielectric are situated in an unsettled manner without an electric field. The positive and negative potentials of the centre of gravity in these materials do not coincide and they have dipole moment without an electric field (permanent dipole moment). The electric field handles and deforms these

dipoles of the molecule and the electric field is trying to turn to the direction of the field despite of the heat movement. This group contains molecules that are related together with electrovalent or ion binding (e.g. water, alcohols, compounds containing a carboxyl group, an amino group). So polar molecules and materials can be polarized by the deformation and orientation effects of the outdoor electric space (**Figure 3**).
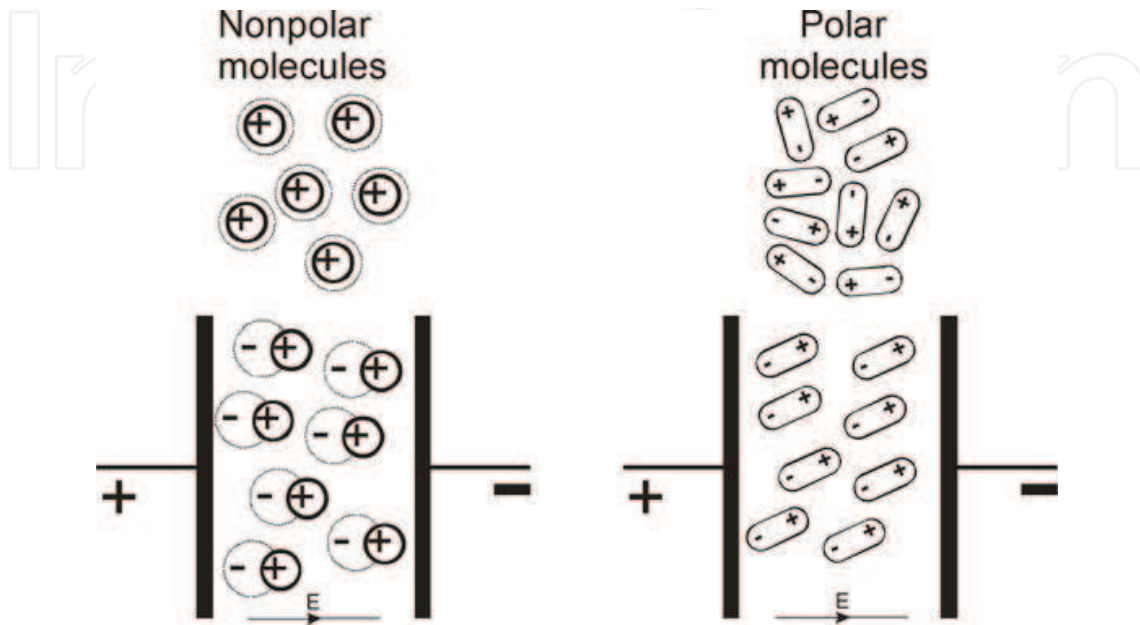
Figure 3. Arrangement of non-polar and polar molecules.

The dielectric polarization is composed of several parts:

Polarization shift

1. The electron cloud shifts from relative to the nucleus without having to change relative positions of the nuclei inside the molecule.

    (elektron polarization, Pe)

2. Atoms or ions are shifted relative to each other.

    (atomic or ion polarization, Pa).

    Orientation polarization.

    The dipoles are arranged in the effect of the outing field

    (-Po).

1.6. The effect of temperature on the dielectric constant (temperature dependence)

In non-polar solvents, the resulting dipole molecules are always arranged in the direction of the field and this state is not formed by the heat movement significantly; therefore, the dielectric constant of the non-polar material does not depend on temperature. In the case of

polar materials, the temperature increase causes dielectric constant decreasing (incoordination is increasing).

The polarization of polar materials, as has been previously mentioned, is made up of displacement and polarization orientation. In the case of polarization orientation, the thermal motion of molecules prevents the orientation effect of the field and prevents molecules from turning into the direction of the field.

This effect is greater when the temperature and the heat movement are higher.

The polarization level depends on the number and strength of the dipole and the intensity of the thermal motion. There are some liquid compound temperature coefficients in **Table 1**. As shown, the temperature coefficient increases with the increase of the value of polarity.

Material	Temperature coefficient
Benzene	0.00160
Chlorine-benzene	0.00174
Ethylene chloride	0.0553
Nitro-benzene	0.185
Pure water	0.366

Table 1. Temperature coefficient of the dielectric constant in case of liquid compounds.

1.7. The effect of frequency changing to the dielectric constant (frequency dependence)

The dielectric constant depends on many other things, mostly the frequency at measurement. This can easily be seen if we introduce the concept of the complex dielectric constant:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{10}$$

The ε'' is the dielectric power consumption from the electric field, thus referred to as the absorption coefficient or loss numbers sometimes. There is the following relation between ε', ε'' and tgδ:

$$tg\delta = \frac{\varepsilon''}{\varepsilon'} \tag{11}$$

The following figure shows the frequency dependence of ε'' and ε'. ε' retains its value by a certain frequency (approximately 10^8 Hz). Here the electric field and the polarization are in phase and the dielectric constant is maximum (**Figure 4**).This is called the quasi-static dielectric constant values [4].
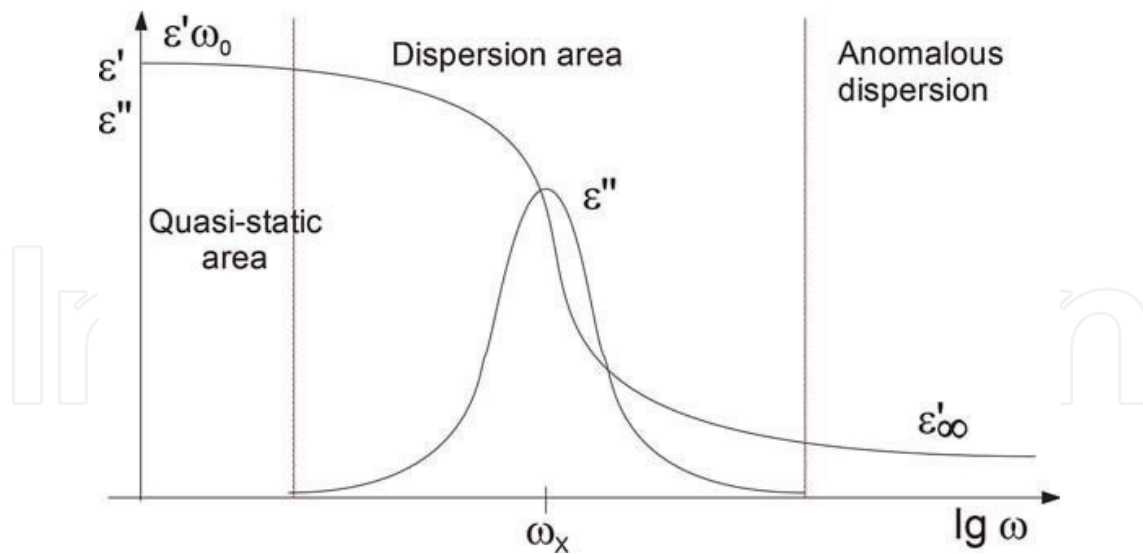
Figure 4. Frequency dependency of ε'' és ε'.

With increasing the frequency, the dielectric constant $\left(\varepsilon'_{\omega 0}\right)$ is retained until you reach certain frequency areas, areas of anomalous dispersion, where the dielectric constant is reduced to a constant value $\left(\varepsilon'_{\infty}\right)$. This value of n is called the refractive index in the next context on the basis of Maxwell's equation:

$$\varepsilon'_{\infty} = n^2 \tag{12}$$

Theoretically, this can be explained by the electrons, atoms and atomic groups and the permanent dipoles can track slow changes of the field in the quasi-static area. Significant change occurs when the frequency of the alternating space is increased to a greater extent. Above a certain frequency, the permanent dipoles cannot follow the changes of space rapidly, so the orientation polarization no longer contributes to the total polarization. The dipole orientation cannot keep up with the force field and suffers delayed phase shift. Then we can talk about the anomalous dispersion of the dielectric constant. According to the Debye's theory of dispersion, this situation depends on the viscosity (η), the molecular radius (r):

$$\tau = \frac{4\pi \cdot \eta \cdot r^3}{k \cdot T} \tag{13}$$

τ is the so-called relaxation time τ ($\tau = 1/\omega x$), the measured value of the relaxation rate. This is the time period, while the orientation polarization reduces e-fold by switching off the static field afterwards [5].

The absorption coefficient ε'' behaves differently depending on the frequency. The quasi-static and high-frequency field ε'' are almost immeasurably small. Only the dispersion area can be measured and reaches its maximum at a frequency ω_x. The theoretical analysis of the frequency dependence of the dielectric constant begins to form detailed in Debye equations:

$$\varepsilon^* = \varepsilon'_{\infty} + \frac{\varepsilon'_{\omega 0} - \varepsilon'_{\infty}}{1 + j\omega\tau} \tag{14}$$

1.8. The Cole-Cole diagram

The real and the imaginary part is obtained by applying the following relationships:

$$\varepsilon' = \varepsilon'_\infty + \frac{\varepsilon'_{\omega_0} - \varepsilon'_\infty}{1 + \omega^2\tau^2} \qquad \varepsilon'' = \left(\varepsilon'_{\omega_0} - \varepsilon'_\infty\right) + \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{15}$$

Where ε'_∞ and $\varepsilon'_{\omega 0}$ are the high frequency and static dielectric constant and τ and ω are the frequency and relaxation time, which is characterized by the formation and cessation of the polarization ratio. These relationships are derived both from liquids and solids and can also be used, although they are from different models.

From the combination of relationships above, we can obtain the following relationships:

$$\left(\varepsilon' - \frac{\varepsilon'_{\omega o} + \varepsilon'_\infty}{2}\right)^2 + \left(\varepsilon''\right)^2 = \left(\frac{\varepsilon'_{\omega o} - \varepsilon'_\infty}{2}\right)^2 \tag{16}$$

The formula above gives the equation of the circle. Accordingly, in the diagram ε'' with as ordinate and ε' with as abscissa, a semicircle is obtained.

Figure 5 shows an ideal Cole-Cole diagram, when the behaviour of that material fits the above equations. In this case, the centre of the circle is at the abscissa and a different behaviour lies when the centre of semicircle lies below the abscissa. From the ideal Debye behaviour analysis of the differential structure, this is a useful research method.
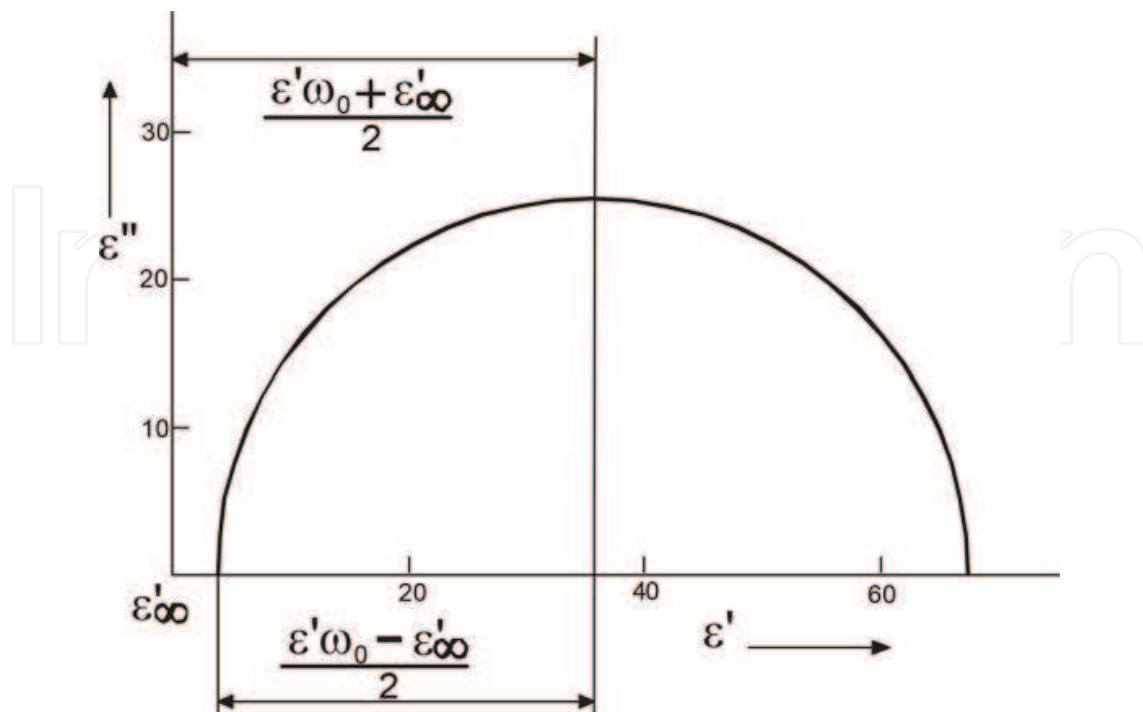
Figure 5. Cole-Cole diagram, ideal Debye behaviour.

2. Materials in electromagnetic field

During the microwave treatment, temperature of the sample continuously rises and its dielectric properties also change [6]. From the generator's viewpoint, the value of terminating impedance represented by the transmission line changes accordingly. For the microwave generator, the transmission line acts as an impedance terminator whose value depends on the wavelength and on the geometric properties of the transmission line [7]. The impedance of transmission line also depends on the dielectric properties of the material which are either partially or fully filling the transmission line. Since the temperature of the sample changes due to the energy impact, the value of the impedance terminator represented by parameters the transmission line also changes together with the sample properties. During the energy impact, the varying dielectric properties of the sample change the axial distribution of the microwave energy in the transmission line; therefore, the amount of energy absorbed in the sample also changes.

Because of the constant microwave energy input, temperature-dependent energy-, impedance- and dielectric conditions are developed. Some of them (e.g. temperature, dielectric property) are measurable; others can only be determined by computation [8]. By constructing a model containing the parameters of the transmission line and the sample placed in the transmission line, it is possible to determine the continuously varying parameters during the heating.

3. Modelling of power and temperature dependence of ionic liquids

During treatment and usage, outing energy is transferred to a material sample placed in an applicator of given geometric parameters. As a result of the energy transfer, the sample absorbs energy from the microwave field depending on its dielectric properties. The degree of energy absorption is directly proportional to the dielectric loss and proportional to the square root of the dielectric constant. The temperature of the sample continuously increases due to the energy transfer and the dielectric properties of the sample also change with the rising temperature. Although the microwave energy supply is constant, time- and temperature-dependent energy impedance and dielectric relations are developed. A part of them is measurable, but the other part of them cannot be directly measured; they can only be computed from the previously measured ones. In a closed model which contains the parameters of the sample and the waveguide, the continuously changing parameters can be determined in relation of the temperature. These parameters are as follows: attenuation of the transmission line, temporal change of the sample temperature, dielectric properties of the sample, loss factor of the sample, penetration depth, impedance of the transmission line and standing wave ratio reflection factor. The modelling procedure was invented on the University of Pannonia by the research group. The above parameters can be modelled as a function of the sample's temperature or as a function of time [9].

The power leaving the generator enters and propagates in the transmission line as a wave. The medium in the transmission line—according to its dielectric properties—modifies the portrait of lines of force and takes energy from the electromagnetic field. The electromagnetic wave

reflected from the shortcut at the end of the transmission line leaves the line towards the generator. The ratio of forwarding and reflected waves is the standing wave ratio and it depends first of all on the dielectric loss of the medium filling the transmission line. The standing wave ratio is infinity in the ideal case (there is no sample, i.e. loss in the transmission line) if the transmission line is closed with the wave impedance of the line. Since the standing wave ratio is given as the ratio of forwarding and reflected waves, it is greater than one if the transmission line has loss and it equals to the ratio of powers entering and leaving the transmission line.

That is, knowing the standing wave ratio r and the generator power P_M, it is possible to determine the power entering the transmission line. Since the medium's (sample's) dielectric parameters are functions of the temperature, it is necessary to appear the temperature dependence in the formulae explicitly. Denoting the microwave power entering the transmission line by P_A and the generator's power by P_M, the following formula holds:

$$P_A(T) = \frac{1}{r(T)} P_M \tag{17}$$

A part of this, power will dissipate and heat up the sample placed inside the transmission line. The amount of power absorbed in the sample depends on the sample's dielectric properties: it is directly proportional to the dielectric loss and inversely proportional to the square root of the dielectric constant. The coefficient 0.5126 is an experimental value [10]:

$$P_D(T) = 0.5126 \frac{\varepsilon''(T)}{\sqrt{\varepsilon'(T)}} P_A(T) \tag{18}$$

The temperature dependence of the dielectric parameters is respected in the above formula. The power absorbed in the sample increases its temperature; the degree of warming depends on the specific heat (C_p) and the density (ρ) of the sample. A sample having greater specific heat or density warms slower. The change of temperature is given as follows:

$$\frac{dT}{dt} = K \frac{1}{C_p \rho} P_D(T) \tag{19}$$

where K is a coefficient regarding the volume of the sample and its unit is $1/cm^3$. The formula gives the speed of temperature change; on the other hand, the integral of the formula with respect to time gives the value of the temperature in the sample as a function of time. The temperature dependence of the dielectric parameters (ε', ε'') of the sample can be measured with a microwave dielectrometer designed by the author of this paper [11]; thus, it is possible to define the relationships $\varepsilon'(T)$ and $\varepsilon''(T)$ regarding the specific sample material by fitting polynomials on the resulted data.

The impedance of the transmission line is a function of its geometric parameters and the dielectric properties of the sample. The characteristic wave impedance Z_{0t} of the transmission line depends on the size of the transmission line sizes (in two dimensions) and the wavelength (λ_g) of the electromagnetic wave propagates inside according to the following formula:

$$Z_{0t} = \frac{2Z_{0l}b}{a\sqrt{1-\left(\frac{\lambda_g}{2a}\right)^2}} = 754\frac{4,4}{9,4\sqrt{1-\left(\frac{12,24}{18,8}\right)^2}} = 465\Omega \tag{20}$$

where Z_{0l} is the open air wave impedance of the air (377 Ω), is the electromagnetic wavelength a and b are the dimensions of the transmission line (9.4 cm, 4.4 cm), respectively. Note that Z_{0t} is independent of the sample properties and depends only on the transmission line geometry and wavelength. From Z_{0t} and the dielectric loss, it is possible to calculate the overall impedance (of the transmission line and the sample) as a function of temperature [12]:

$$Z_T(T) = \frac{Z_{0t}}{\sqrt{\varepsilon'(T)}}\left(1-\frac{3}{8}(\mathrm{tg}\delta(T))^2 + j\frac{1}{2}\mathrm{tg}\delta(T)\right) \tag{21}$$

From the overall impedance and the wave impedance, one can determine the reflection coefficient of the transmission line:

$$|\Gamma(T)| = \frac{Z_T(T)-Z_{0t}}{Z_T(T) + Z_{0t}} \tag{22}$$

Afterwards, it is possible to express the standing wave ratio:

$$r(T) = \frac{1 + |\Gamma(T)|}{1-|\Gamma(T)|} \tag{23}$$

From the standing wave ratio, it is possible to give the power entering the transmission line knowing the generator power, as it was mentioned before. Now, it is possible to build a model from the above equations, which has the following input parameters: microwave generator power, density of the sample, specific heat of the sample, sample specific dielectric characteristics as a function of temperature, transmission line and wavelength parameters.

3.1. Modelling set-up in filled cavity

Overall we can obtain an overall figure about modelling of microwave cavity filled with ionic liquid or other material (**Figure 6**).

The model structure has been implemented in MatLab® environment (**Figure 7**). First the pure water has been investigated. The temperature dependence of dielectric values of water is described by Eq. (24) This equation is from the literature [13] and showed in (**Figure 8**):

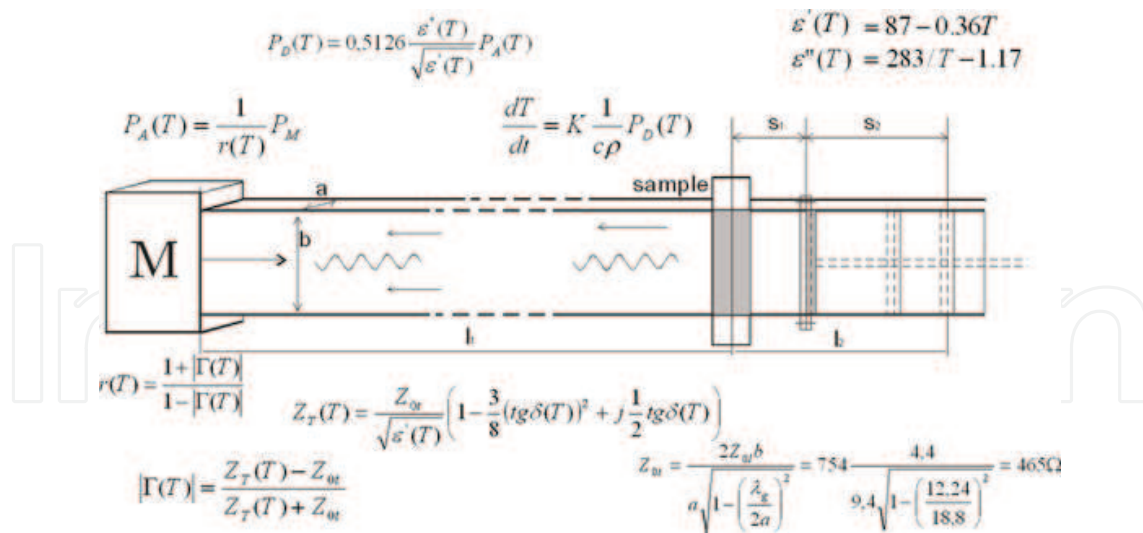$$\varepsilon'(T) = 87-0.36T \qquad \varepsilon''(T) = 283/T-1.17 \tag{24}$$

$$P_D(T) = 0.5126 \frac{\varepsilon''(T)}{\sqrt{\varepsilon'(T)}} P_A(T) \qquad \varepsilon'(T) = 87 - 0.36T$$
$$\varepsilon''(T) = 283/T - 1.17$$

$$P_A(T) = \frac{1}{r(T)} P_M \qquad \frac{dT}{dt} = K \frac{1}{c\rho} P_D(T)$$

$$r(T) = \frac{1 + |\Gamma(T)|}{1 - |\Gamma(T)|}$$

$$Z_T(T) = \frac{Z_{0t}}{\sqrt{\varepsilon'(T)}} \left(1 - \frac{3}{8} (tg\delta(T))^2 + j \frac{1}{2} tg\delta(T) \right)$$

$$|\Gamma(T)| = \frac{Z_T(T) - Z_{0t}}{Z_T(T) + Z_{0t}} \qquad Z_{0t} = \frac{2Z_0 b}{a\sqrt{1 - \left(\frac{\lambda_g}{2a}\right)^2}} = 754 \frac{4.4}{9.4\sqrt{1 - \left(\frac{12.24}{18.8}\right)^2}} = 465\Omega$$

Figure 6. Overall modelling of the filled cavity.
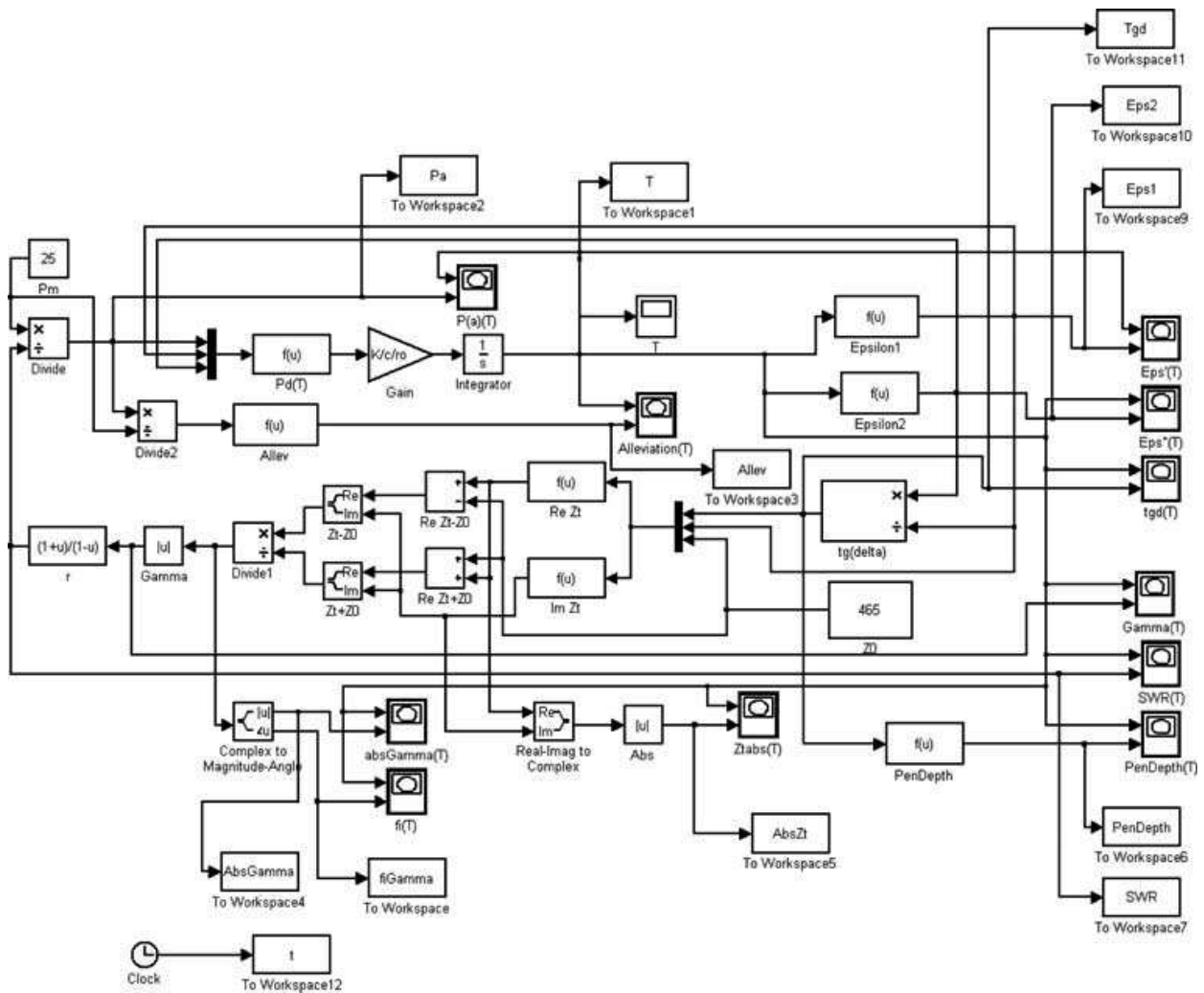
Figure 7. The MatLab model for simulation.
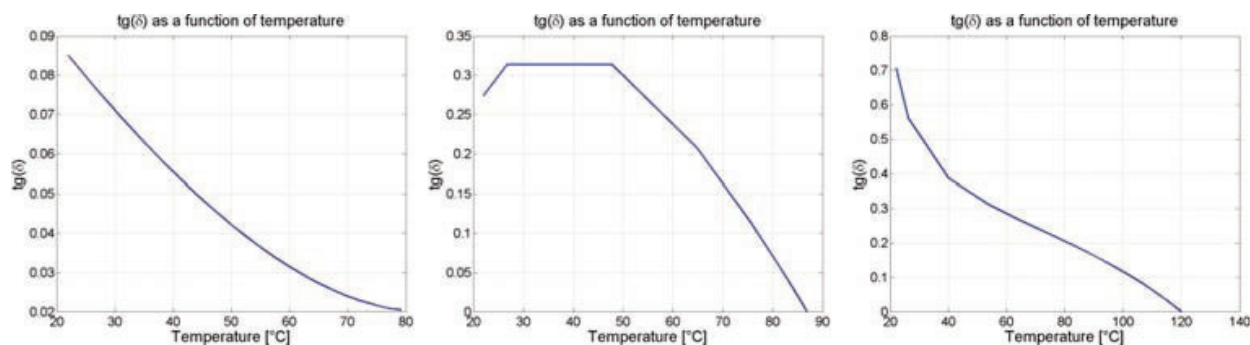
Figure 8. Results from the model. tgδ(T) values of different materials.

4. Introduction of battery cell

Dielectric constant and dielectric dissipation factors are the main parameters in the modelling of microwave behaviour of ionic liquids, in addition the parameters characterizing the polarizability and the microwave energy absorption. The static dielectric constant of ionic liquids cannot be approached with traditional measurement methods because they are characterized by high electrical conductivity which results in intense shortcut. Systematic study of these contexts has not been conducted so far because the subject is relatively new; however, the results are very important in the planning and controlling of chemical reactions.

At the end of the 1990s, the discovery of ionic liquids opened new ways of technological applications especially in the area of chemistry and in particular green chemistry. Their special chemical and physical properties make it very beneficial and important since the use of energy storage units, particularly mobile phones, electric vehicles and uninterruptible power supply systems, is widely used [1]. Recently, room temperature ionic liquids (RTILs) have been extensively studied as electrolytes of lithium ion batteries from cellular phones to electric vehicles. RTILs are good options for the electrolyte bases of a safe lithium battery due to their unique properties [14, 15].

RTILs are known for being thermally stable and non-flammable and they might have the capacity to improve the safety of electrochemical devices with aprotic solvents, such as Li batteries and supercapacitors in abuse.

The high ionic conductivity of 1-Ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF$_4$) is comparable to those of organic solvent electrolytes and its viscosity is low which makes it a good electrolyte for Li batteries. Li battery applications can benefit from these and we also found that a Li/LiCoO$_2$ cell with RTILs as an electrolyte base works reversibly, indicating that QAimide RTILs are quite stable even at the Li reduction potential. We can claim that RTILs improve the safety of Li-ion batteries with carbon-negative electrodes. For improving the safety of Li-metal batteries, RTILs seem to be the most promising and applicable electrolytes, which could also be important for higher energy densities [16].

A set of four imidazolium ionic liquids (solid at room temperature) and one imidazolium ionic solid were screened for their potentials as electrolytes in manganese dioxide-free Leclanché batteries, equipped with a zinc anode and graphite cathode [17].

It is important to note that the ionic liquid 1-ethyl-3-methylimidazolium hydrogen sulphate (EMIM-HSO$_4$) similar to many other ionic liquids, such as those based on nitrate and dihydrogenphosphate anions, has also been found to work well in this battery design. Novel batteries are designed using standard cathode materials such as MnO$_2$, PbO$_2$, NiO and AgO and anode materials such as Zn, Sn and Pb. Additionally, by using a solid polymer electrolyte composed of polyvinyl alcohol and anionic liquid, new types of solid-state batteries are demonstrated with discharge voltages ranging up to 1.8 V, depending upon the type of cathode and anode used [18].

Ionic liquids like 1-butyl-3-methylimidazolium tetrafluoroborate (IMIM-BF4) or hexafluoro-phosphate (IMIM-PF6) and 1-butyl-4-methylpyridinium tetrafluoroborate (PyBF4) were mixed with organic solvents such as butyrolactone (BL) and acetonitrile (ACN). A lithium salt (LiBF$_4$ or LiPF$_6$) was added to these mixtures for possible application in the field of energy storage (batteries or supercapacitors). Viscosities, conductivities and electrochemical windows at a Pt electrode of these electrolytes were investigated. All the studied electrolytes are stable towards oxidation and exhibit a vitreous phase transition, which has been determined by application of the conductivity measurements. Mixtures containing the BF$_4$− anion exhibit the lowest viscosity and the highest conductivity [19].

Aromatic cations, such as 1-ethyl-3-methylimidazolium (EMI), have been used for as the cationic component of the RTILs. The EMI cation is the best cation to form the RTIL, which has a low viscosity and low melting point, with various anions. However, the electrochemical stability as a lithium battery electrolyte was not satisfactory since the cathodic limiting potential is ca. +1.0 V versus Li/Li+ and additives, such as thionyl chloride, were essential for improving the coulombic efficiency for lithium deposition in an RTIL based on EMI [20].

There are several combinations of alkylimidazolium cations and inorganic and organic anions have been investigated to date. A survey of these salts including fluoroanions will be given in [21].

4.1. Methods

Several properties of ionic liquids should be examined before its application in batteries; therefore, we used different measurement methods at our disposal on a number of ionic liquids. The different microwave measurements included processes such as checking the temperature rise in microwave field and measuring microwave dielectric properties at 2.45 GHz frequency, electrical conductivity according to temperature and viscosity changes depending on the temperature.

We used CEM Discover unit to measure the velocity of temperature rise of ionic liquids. The CEM Discover unit is a widely used and available apparatus in microwave chemistry. The device has a cylindrical operating space and on the cylindrical peripheral surface, there are many slots where microwave energy can enter; this way the high homogeneity of the microwave field is ensured. We measured the temperature at the bottom of the compartment with an infrared thermometer. The amount of the tested samples was 0.5 g, which were placed in an inner diameter of 12.5 mm of borosilicate cylindrical glass flask.

It is important to note that during microwave treatment, a conversion process takes place in which the microwave energy interacts with the treated material and the material converts the electric energy into thermal energy according its characteristic of dielectric properties. During this process, the measurable increase of the temperature in the treated material is the macroscopically observable result. The rate of the temperature increase depends on the microwave field and the treated material properties, which is described in the following equation:

$$\Delta \mathbf{T}/\Delta \mathbf{t} = P_v/\rho \mathbf{Cp} = jE^2 f \varepsilon''/\rho \mathbf{Cp} \qquad (25)$$

where the $\Delta T/\Delta t$ is the velocity of temperature rising in Kelvin per second, P_v is the absorbed power in the sample, ρ is the density of the sample, Cp is the specific heat of the sample, E^2 is the strength of the electromagnetic field in the sample, f is the frequency of the field and ε'' is the dielectric loss; j means this is a complex value [15]. This formula shows that the temperature of the treated material is influenced by a number of factors. Testing their effects separately is not simple, because ρ, ε Cp features themselves are temperature dependent and it is difficult to measure this value accurately inside the material. In the case of strictly homogeneous series of examined compounds, the situation is more simplified, because some simplifications are permissible.

Assuming ρ and Cp do not change significantly in the function of temperature, the multiplication ρ Cp was almost considered to be constant, so that the rate of temperature rise is determined by E and ε'' only. Further simplifications can be made if the device is single mode with the same volume and shape and the microwave energy is constant during the investigation. The value of E is determined by ε' and ε' and ε'' and the rate of temperature rise is essentially determined by ε'' value.

4.2. Measurement set-up of ionic liquids

Figure 9 depicts the schematic representation of the self-designed experimental set-up applied for automatic and online measurement of dielectric properties of ionic liquids in a definite temperature range. It is composed of the following devices and instruments: cylindrical sample holder unit, thermostat, peristaltic pump, waveguide, temperature sensor, displaceable piston, stepper motor, magnetron, detectors, control unit and a PC.

The IL sample, which is placed in the thermostat to keep it at the desired constant temperature, is flown across the waveguide having a length of about 3λ through the sample holder tube with the help of a peristaltic pump. The electric energy is transformed into microwave energy by the magnetron. The stepper motor is controlled by a microprocessor control unit, which contains an Intel 8-bit microcontroller, 12-bit A/D converters for receiving the four diode-detector signals, a stepper motor driver and a RS-232 serial interface to connect it to the PC. The control unit collects the detector signals and the temperature data determined by the temperature sensor and sends them to the PC. Furthermore it controls the position of the short circuit displaceable piston on the basis of algorithm software elaborated for this purpose.
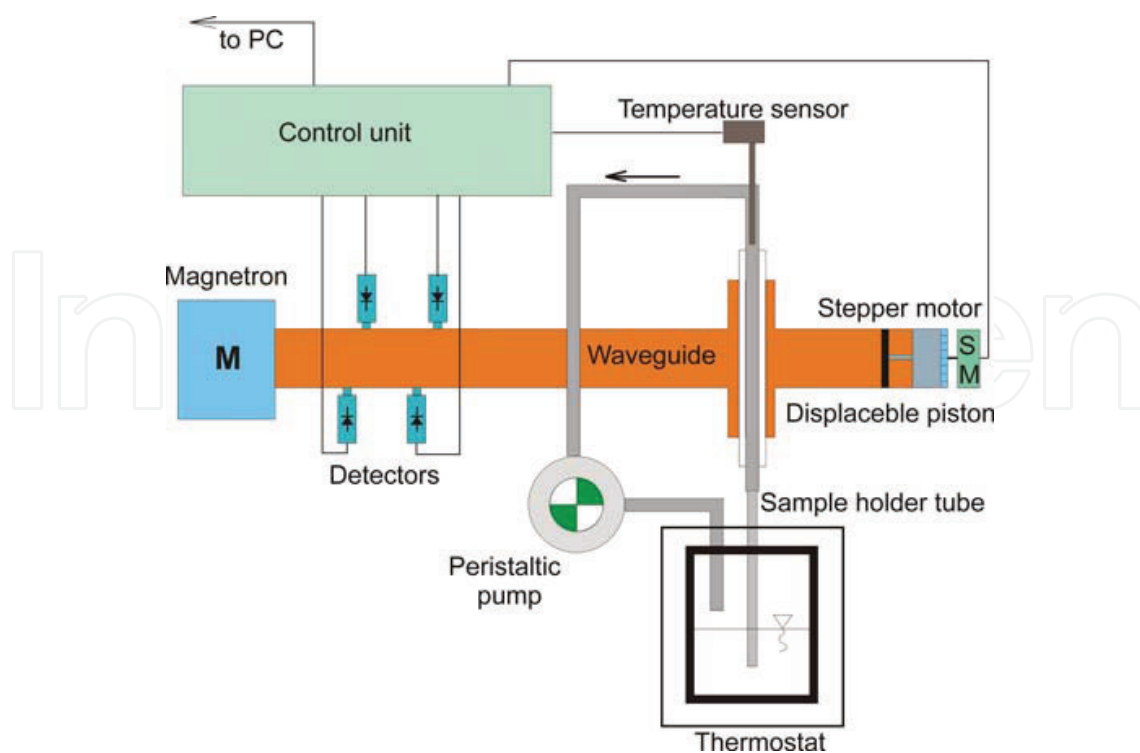
Figure 9. Scheme of the experimental set-up.

The method is based on the compensation of phase change due to the microwave energy absorption of the liquid sample. The short circuit piston situated behind the sample must be actuated for compensation. The energy conditions created by the wave front in the waveguide are measured by four diode detectors.

Dielectric constants, dielectric loss factors and the temperature dependence of the dielectric properties of ionic liquids intended to be used in batteries were determined by the above-described self-designed microwave dielectrometric apparatus (**Figure 3**) at the frequency of 2.45 GHz and at different temperatures (30°C, 40°C, 50°C, 60°C, 70°C, 80°C, 90°C, 100°C, 110°C and 120°C). The speed of the change in temperature depends on the electrical field strength in the material (E), the absorbed microwave power, (P_v) density (ρ), the specific heat capacity (C_p) and the dielectric loss factor ε'' and can be given by Eq. (1) [11].

4.3. Results and obtained characteristics

The temperature increase of the new type of ionic liquids was examined, as it is shown in **Figure 10** and in **Table 2**.
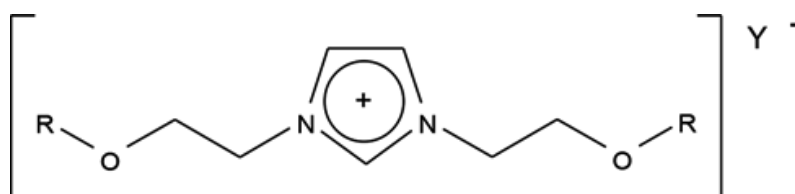

Figure 10. The structure of investigated ionic liquids.

Compound	R	Y	Compound	R	Y
1	CH_3	BF_4	8	C_4H_9	PF_6
2	C_2H_5	BF_4	9	C_2H_5	CI
3	C_3H_7	BF_4	10	C_2H_5	Br
4	C_4H_9	BF_4	11	C_2H_5	SCN
5	CH_3	PF_6	12	C_2H_5	$N(CN)_2$
6	C_2H_5	PF_6	13	C_2H_5	$N(SO_2CF_3)_2$
7	C_3H_7	PF_6			

Table 2. The formulas of investigated ionic liquids.

The effect of R groups was examined in the case of two anions—BF_4 (compounds 1–4) and PF_6 (compounds 5–8) at 3–5 watts of microwave energy.

Our results show that there is a negative correlation between the R group carbon number and the temperature elevation rate: a decrease in the previous increases the latter. By increasing the microwave power significantly, the temperature speeds converge to each other and sometimes change this order, but this is not typical in **Figure 11**. Overall, the rate of temperature rising follows the order of ε' and ε'' suggesting that in a strictly homologous series, the temperature rise of ionic liquids is determined by ε'' [18].
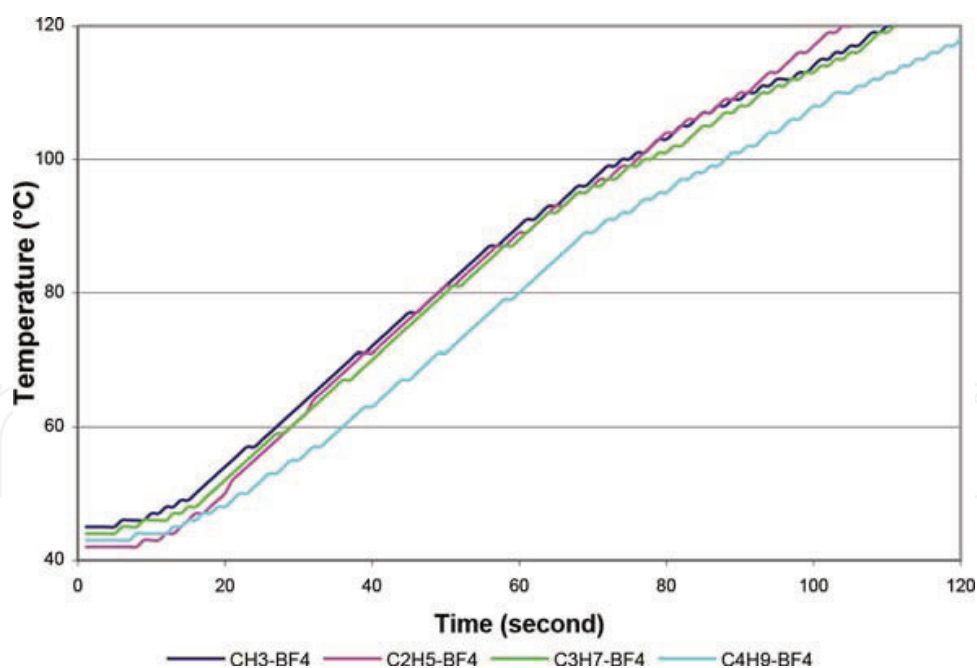
Figure 11. Temperature rising of 1-butyl-3-methylimidazolium tetrafluoroborates at 3 W.

After the temperature rising data rate, we investigated two additional parameters of the ionic liquids used in the advanced batteries, i.e. viscosity and electrical conductivity. Both properties are the functions of temperature and they were examined between 20°C and 100–120°C temperature range. The sample material was heated through a heat exchanger, so the viscosity

was measured up to 95°C. Water was used as a heat transfer material and it was not possible to achieve 100°C. The measurements were performed in a SV-10 type of vibration viscometer (A&D Ltd. Japan). The following figures show that the viscosity in room temperature is high, typically several hundred Pa*s and it decreases rapidly with the temperature rising similar to a y=1/x curve. Reaching the 100°C temperature, the value of viscosity can be ten times lower than at the initial value as we can see in **Figure 12**.
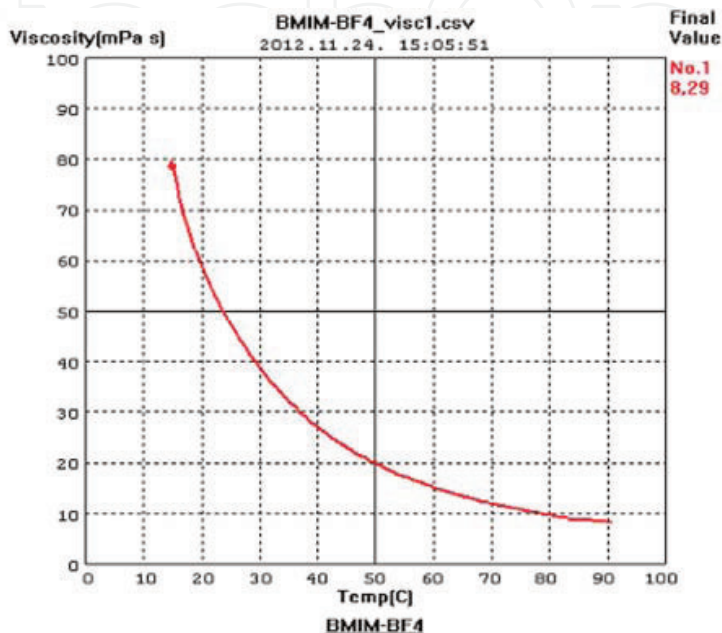
Figure 12. Viscosity of BMIM-BF4 in the function of the temperature.

The investigation of the viscosity may be important; therefore, it basically influences the mobility of ions in the electrolyte, which can affect the conductivity and thus the internal resistance of the battery cell. By cooling ionic liquids, the viscosity is increasing rapidly. Around freezing temperature the ionic liquids were already similar to a "honey density" mass.

Since the energy storage cells are used in a wide temperature range, it is important to know that the electrical conductivity of the electrolytes is a function of temperature.

In **Figure 13** five different electrical conductivity plots of ionic liquids in the function of temperature can be seen. It clearly shows that it is not BMIM-BF$_4$ which has the highest conductivity value, but the conductivity value, depending on the temperature of this material, increases with the greatest intensity [7].

Results in **Figure 14** are both new and impressive. The dielectric constant value of BMIM-BF4 reaches a value of 1 at close to 100°C, similarly to the value of the vacuum and if the temperature is raised further, the value will decrease to the negative range. This outcome suggests that the electrical conductivity is rising greatly with an increase in temperature and this compound is no longer an insulating material but a conductor. Therefore it is important to keep the temperature in an adequate range when batteries are used and especially in the charging period.
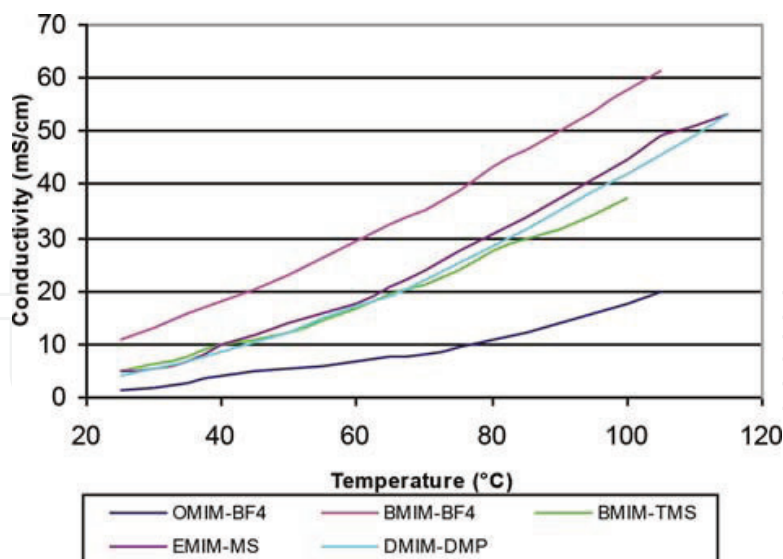
Figure 13. Conductivity of five compounds in a function of temperature.
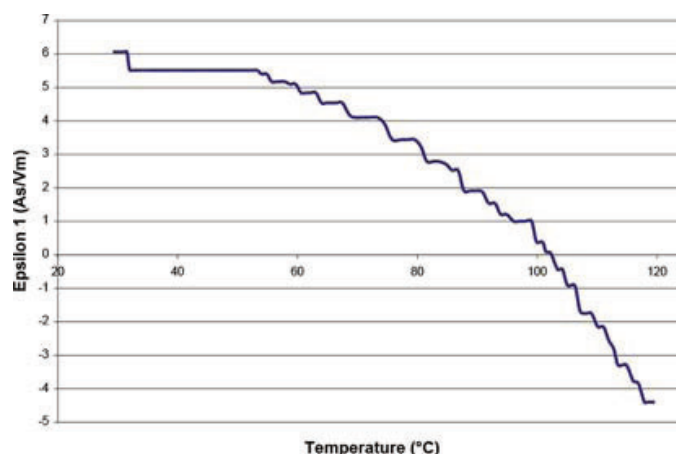

Figure 14. Dielectric constant of BMIM-BF4 in a function of the temperature.

The dielectric constant (E_1) and dielectric loss factor values of ILs built up of the same [BF_4] anion and six previously described cations containing alkyl chains with different lengths ([DiEtMeIm], [DiEtEtIm], [DiEtPrIm] and [DiEtBuIm]) at different temperatures between 30° C and 120°C are shown in **Figure 15**, respectively.

At the initial measuring temperature of 30°C, all four of the studied ILs have similar dielectric constants around 7. With the increase in temperature, the E_1 values for [DiEtMeIm][BF_4], [DiEtEtIm][BF_4] and [DiEtPrIm][BF_4] slightly increase up to 13, while the dielectric constant for [DiEtBuIm][BF_4] shows a sudden break at 90°C and at 120°C it reaches the value as high as 27. This could be explained with some sudden changes in the structure of the ILs or in the physicochemical interactions between the anion and the cation. Excluding the results for [DiEtBuIm][BF_4], the values at elevated temperature show that the highest E_1 value belongs to [DiEtMeIm][BF_4], followed by [DiEtEtIm][BF_4] and then by the [DiEtPrIm][BF_4]; hence, the dielectric constant increases with the decrease in the alkyl chain length of the cation.
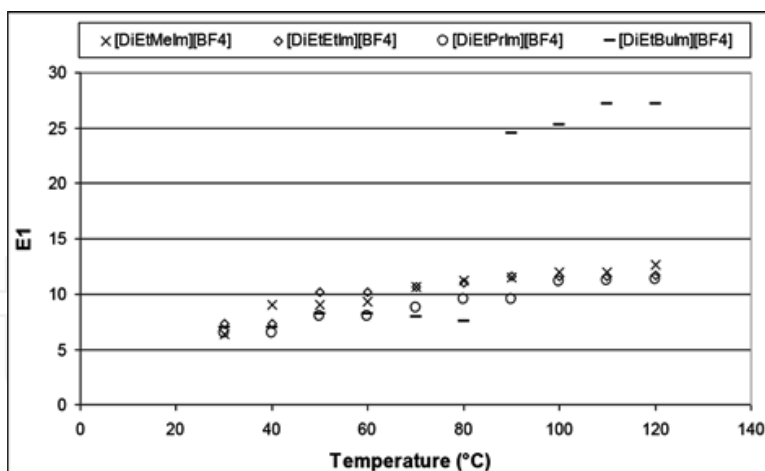
Figure 15. Dielectric constant of ILs containing common [BF$_4$] anion and different cations.

Taking into account the dielectric constant, dielectric loss and electrical conductivity results of all the investigated ILs, it can be concluded that the alkyl chain length of the cation and the structure of the anion strongly influence the dielectric properties of the ILs and that the highest *G* value is exhibited by the [DiEtMeIm][BF$_4$] IL at 30°C temperature; hence, it is the most suitable candidate for battery applications. Furthermore, it can be stated that implementing the knowledge about the connection between the IL structure and the dielectric properties another ILs should be studied in order to select the ones most adequate for electrolyte application.

5. Conclusion

Based on our study, ionic liquids turned out to be excellent candidates for environmentally sound, green electrolytes in batteries due to their useful features, such as wide electrochemical windows, high inherent conductivities, high thermal and electrochemical stability, tuneable physicochemical properties, etc. Before making decisions about their applicability, careful measurements on their dielectric properties should be done.

Although techniques aiming at the determination of the dielectric properties of ILs have been the main focus of several studies, so far no convincing findings can be found in the literature due to the fact that most measurements are based on classical methods. As it was detailed in this study, these methods are doomed to failure because of the high conductivity of ILs.

Based on the analyses of previous results, it can be concluded that the physical, chemical and electrical parameters of ionic liquids are greatly temperature dependent when used in energy storage cells. In any case, when they are applied, we should specify the range of application temperature. Stepping out of this range of the energy storage cell may not meet the expected specification values, or in the worst case, it may be permanently damaged.

Acknowledgements

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