Dielectrics Newsletter

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Dielectric measurements on attograms and zeptograms of matter

Afef Houachtia, Gisèle Boiteux, Gérard Seytre, Jean-François Gérard, Anatoli Serghei*

Introduction

There are two key-points characterizing the strength of Broadband Dielectric Spectroscopy in investigating the electrical and dielectric properties of materials:

(a) Due to its extraordinary broad frequency range covering more than 10 orders of magnitude, this technique provides a direct experimental access to a variety of physical phenomena taking place at different length and time-scales: density fluctuations and phase transitions, molecular fluctuations, charge transport processes in the bulk and at interfaces, flow processes etc. The broad frequency range accessible by BDS offers the possibility of investigating physical phenomena that show large variations – over many orders of magnitude – in their characteristic time with temperature, such as for instance molecular relaxation processes. A further essential point is related to the fact that different physical phenomena exhibit different frequency dependencies. Being able to vary the frequency of a dielectric measurement represents thus a very straightforward mean of discriminating different contributions showing up in the dielectric spectra.

(b) The high accuracy in measuring electrical currents by BDS allows one to characterize, with high resolution, the electrical and dielectric properties of materials. This is the essential factor that makes Broadband Dielectric Spectroscopy one of the most powerful methods in investigating samples of nano metric dimensions.

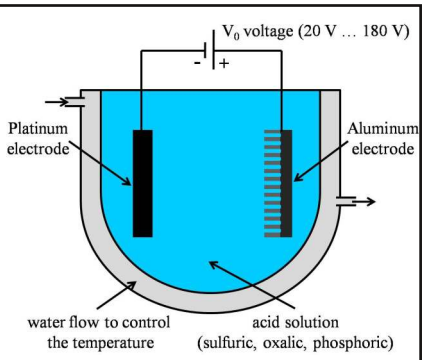

Figure 1: anodization reactor to prepare ordered nanoporous membranes. A Platinum electrode and an Aluminum electrode are immersed into an acid bath at a constant temperature and a dc voltage is applied to carry out the anodization process. The pore diameter and the distance between the pores are controlled by adjusting the anodization conditions: type of electrolyte, concentration of the electrolyte solution, temperature and applied voltage. The length of the pore is controlled by the anodization time. Typically, an anodization time of 3 minutes leads to nanopores with a length of 180 nm.

gram	g	1 g
milligram	mg	10^{-3} g
microgram	µg	10^{-6} g
nanogram	ng	10^{-9} g
picogram	pg	10^{-12} g
femtogram	fg	10^{-15} g
attogram	ag	10^{-18} g
zeptogram	zg	10^{-21} g

Table 1: Subdivisions of gram. For a density value of 1g/cm^3, the equivalent volume of 1 attogram corresponds to 10 nm x 10 nm x 10 nm, while the equivalent value of 1 zeptogram corresponds to 1 nm x 1 nm x 1 nm.

Dielectric investigations on samples of reduced dimensionality, however, require the development of novel approaches and procedures. The most essential aspect to be considered in these developments is that the measurement cells used for dielectric investigations must have a comparable dimensionality with the samples that are investigated. In studies on nano metric thin films, for instance, sample cells with a nano metric separation distance between the electrodes have been developed, using nano structures as spacers. Here we show that dielectric measurements on attograms and zeptograms of matter (table 1) are possible using a recently developed experimental approach which employs nanocontainers as dielectric cells.

Preparation of nanocontainers as dielectric cells

The nanocontainers are prepared in a two-step anodization process of pure aluminium in acid solutions (Figure 1). The pore diameter and the distance between the pores can be controlled by adjusting the anodization conditions: type of electrolyte (oxalic acid, sulfuric acid, phosphoric acid), concentration of the electrolyte solution (typically in the order of 0.3 M), temperature and the applied voltage. The first anodization process, initially taking place in a random manner, undergoes with the time a self-ordering phenomenon which leads, at the end of anodization procedure, to highly ordered (hexagonally packed) arrays of nano pores with a narrow distribution of pore diameters and interpore distances. The porous membranes obtained after the first anodization are removed by chemical etching in a solution of chromic acid,

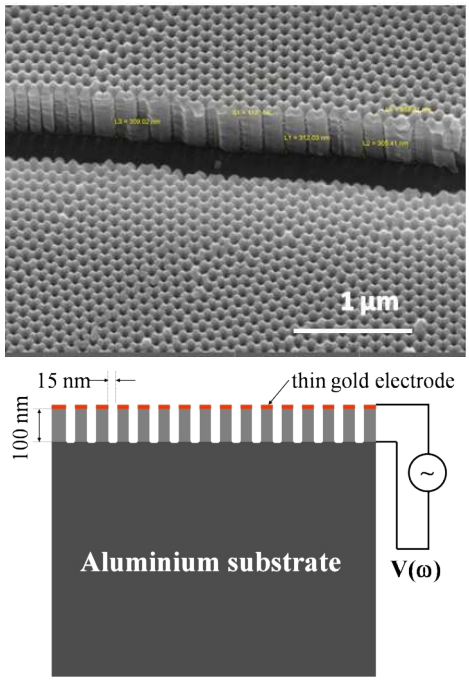

Figure 2: (upper part) SEM image showing a highly ordered array of nanocontainers. The fracture observed in the middle of the image was produced intentionally in order to characterize the cross section of the nanopores. (lower part) Nanocontainers employed as dielectric cells. The nanoporous layer produced by anodization on top of the aluminium substrate is insulating (Al is turning into Al_2O_3 due to anodization) and can be therefore used for dielectric measurements. The nanocontainers can be completely or partially filled by solution, giving rise, after the evaporation of the solvent by thermal treatment, to attograms or zeptograms partitions of matter.

leading to aluminium surfaces exhibiting an ordered structure of nano pits which replicate the anodization paths of the nano pores. Using these pre-structured aluminium surfaces, a second anodization procedure is carried-out to fabricate highly ordered arrays of nano pores, with controlled distribution of pore diameters and interpore distances. The length of the nano pores can be adjusted by changing the anodization time. Short anodization times (typically in the order of 1 to 5 minutes) lead to nano pores with a length between 100 nm and 500 nm. The resulting short nano pores ("nano-containers") are insulating (because, due to anodization, Al turns into Al_2O_3) and have all three dimensions on the nanometric length-scale. They can be thus used as dielectric cells (Fig. 2), to hold and measure extremely small amounts of material.

The nanocontainers can be completely or partially filled, usually by solution, with the material to be investigated. The filling process takes place in the following way: the empty nanocontainers are firstly cleaned by rinsing with pure acetone, dried and then cleaned again by a plasma treatment to remove any organic residues. The cells are completely immersed into the solution of the material that has to be investigated, sonicated for 30 minutes in an ultra-sound bath, and then let in the solution for several days. After this, the samples are taken out of the solution and the liquid present on the surface of the membranes is rapidly removed by using microporous cellulose filters. Since the pore diameter of the nanocontainers is by a factor of 1000 smaller than the diameter of the microporous cellulose filters, the capillary forces in the nanocontainers are dominating, with the consequence that the liquid inside the nanopores does not get absorbed into the filters during this procedure. The amount of matter hold in the nanocontainers can be thus controlled by considering the volume of the nanocontainers – adjusted by changing the anodization conditions – and the concentration of the solution used for the sample preparation. Alternative filling procedures are possible as well, by a solvent exchange process under controlling the miscibility between the solvent of the solution and the solvent used for the rinsing.

After filling, the solvent is evaporated by heating the sample in vacuum or/and in a pure nitrogen atmosphere at temperatures well-above the boiling point of the solvent and well-above the melting point (or the glass transition temperature) of the investigated material. For connecting the measurement cell with the dielectric spectrometer, the aluminium substrates that have been used for the anodization (and into which nanocontainers have been etched) are used as lower electrodes. The upper electrodes are prepared by metallizing the surface of the nano-porous membranes by gold

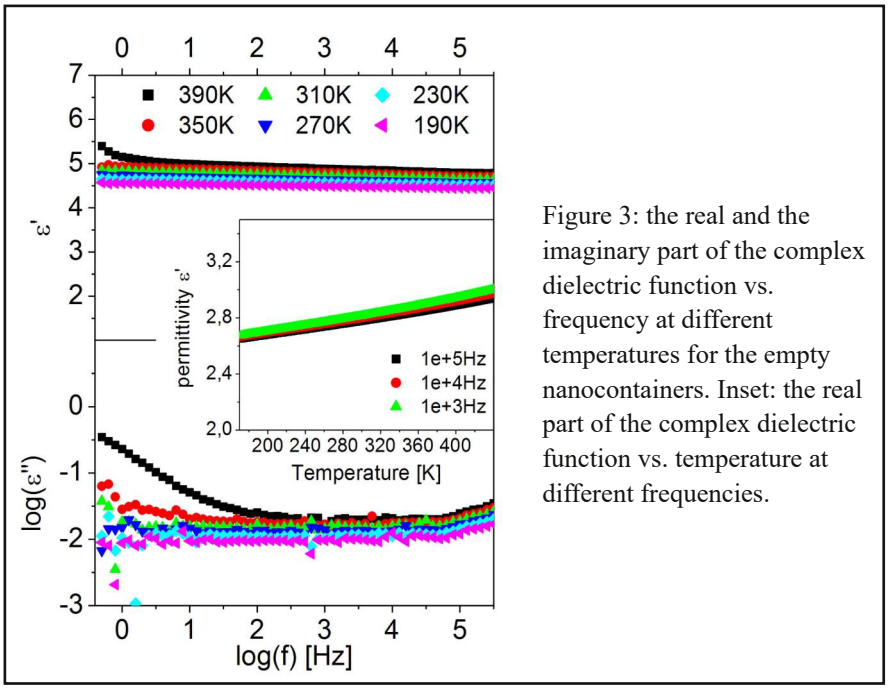

Figure 3: the real and the imaginary part of the complex dielectric function vs. frequency at different temperatures for the empty nanocontainers. Inset: the real part of the complex dielectric function vs. temperature at different frequencies.

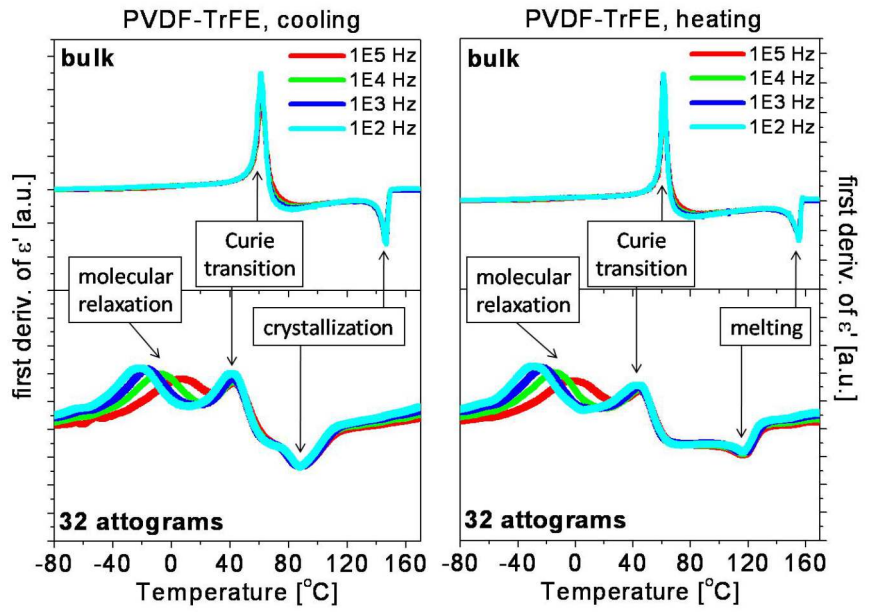

Figure 4: first derivative of the real part of the dielectric permittivity ε' in respect to temperature at different frequencies, as indicated, showing the phase transitions of PVDF-TrFE measured for the bulk (upper graphs) and for 32 attograms (lower graphs), on cooling (left graphs) and on heating (right graphs). For 32 attograms, a new relaxation process is observed, which is not detected in the bulk.

sputtering. Depending on the nature of the sample and the objectives of the study, two different approaches to realize the metallization can be used: (a) the empty nanocontainers are filled first with the material under study and then the surface of the measurement cell is metallized; (b) the empty cell is metallized by sputtering a thin layer of gold without closing the nanopores, and then the nanocontainers are filled by solution. The advantage of the second approach is that the filling process can be carried-out under an applied electric field.

The validation of this method of measuring attograms and zeptograms of matter is based on three essential conditions that are fulfilled: the nanocontainers are identical, independent and additive. The additivity is resulting from the fact that the applied electric field is parallel to the long axis of the nanopores. This orientation, imposed by the geometry of the sample cell (pore diameter are much smaller than the pore length), leads to a parallel arrangement of elementary capacitors, with the consequence that the global response represents an arithmetic sum of the local responses of the constituting units. In this way, attograms and zeptograms partitions are realized and investigated by measurements that are directly reflecting a statistical ensemble.

After realizing the electrical contacts, the samples are first annealed for several hours at high temperatures under flow of pure nitrogen and their dielectric properties are continuously monitored in time until sample equilibration is reached. Afterwards, the dielectric measurements are carried out as a function of frequency and temperature.

Results and discussion

The dielectric properties of the empty nanocontainers are shown in figure 3. In a broad frequency and temperature range, low dielectric losses (typically in the order of 0.02) and no dielectric dispersions are detected, indicating that the nanocontainers can be employed as dielectric cells.

The dielectric properties for 32 attograms of a ferroelectric polymer (PVDF-TrFE, polyvinylidenefluoride-co-trifluoroethylene) are shown in fig. 4, and the results are compared to the dielectric properties of this polymer in the bulk. In order to analyze the phase transitions, the data are represented as the first derivative of the permittivity in respect to temperature. In the bulk, a crystallization process and a ferroelectric Curie transition is observed on cooling, while a Curie transition and a melting process is detected on heating. Upon vary the frequency, the data are showing an identical shape and position, which is characteristic for phase transitions measured by the first derivative of the dielectric permittivity. The data for 32 attograms of PVDF-TrFE measured on cooling show a crystallization pro-

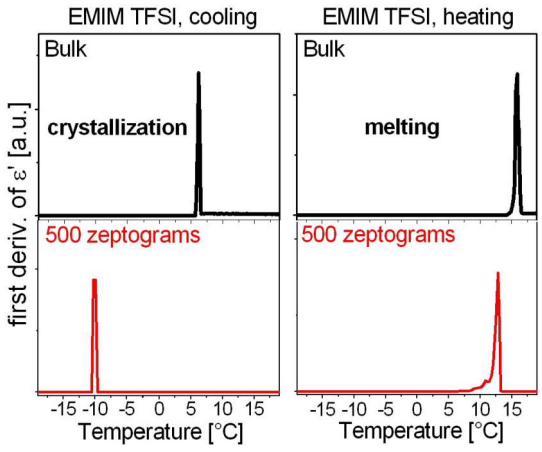

Figure 5: first derivative of the real part of the dielectric permittivity ε' in respect to temperature, on cooling (left graphs) and heating (right graphs), indicated the phase transitions of the ionic liquid 1-ethyl-4-methylpyridinum bis(trifluoromethylsulfonyl)imide in the bulk (upper graphs) and in partition of 500 zeptograms (lower graphs).

cess and a Curie transition that are shifted to lower temperatures by 58 °C and 19 °C, respectively. Additionally, a novel relaxation process is detected, which is not observed in the bulk. On heating, the Curie transition appears at the same temperature position as for the measurement on cooling, thus, the Curie transition for 32 attograms of PVDF-TrFE is shifted by 19 °C to lower temperatures as compared to the bulk. The melting point appears at 117 °C, by 38 °C lower than in the bulk.

Dielectric measurements for sample quantities in the range of zeptograms are presented in fig. 5, showing the crystallization and the melting process for an ionic liquid (EMPy TFSI, 1-ethyl-4-methylpyridinum bis(trifluoromethylsulfonyl)imide). As compared to the bulk, the crystallization of 500 zeptograms of EMPy TFSI is shifted by 16 °C to lower temperatures, while for the melting a shift of 3 °C is observed.

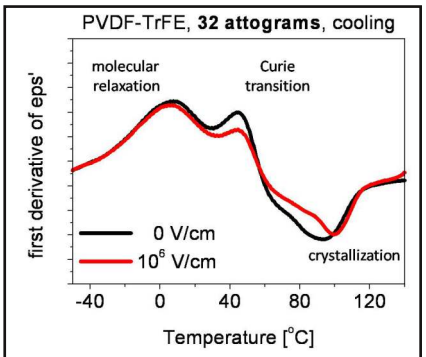

Figure 6: first derivative of the real part of the dielectric permittivity ε' in respect to temperature for 32 attograms of PVDF-TrFE measured on cooling without and with an applied DC electric field.

The fact that the length of the nanocontainers is in the nanometric range offers a unique possibility: high electrical fields can be obtained by applying small voltages. For instance, a voltage of 10 V applied on nanocontainers with a length of 100 nm, gives rise to an electric field of 10^6 V/cm. This can allow, for the first time, to investigate ionic liquids under high electric fields, without exceeding the voltage limitations related to their electrochemical window (typically in the order of ±5 V, higher voltages leading to a red-ox reaction of the material under study). The effect of high fields on the crystallization of 32 attograms of PVDF-TrFE is shown in figure 6: upon applying the dc field, a shift to higher temperatures and a narrowing of the crystallization process is observed, indicating an ordering phenomenon that takes place in attograms partitions of matter.

Conclusions

A novel experimental approach to carry-out dielectric investigations on attograms and zeptograms of matter was described in the present contribution. The approach relies on the concept of using nanocontainers as experimental cells. The method presents several important advantages:

(i) It allows dielectric measurements of extremely small amount of material, down to the level of zeptograms.

(ii) The handling of the sample cells does not require special conditions. The electrical contacts are straightforward to realize, and no special mechanical contacts are required.

(iii) Because the cells have nanometric dimensions, dust particles cannot enter inside, thus, there is no need to work in a controlled environment (white room etc.)

(iv) High electric fields can be applied with low voltages. This opens unique perspectives, such as, e.g, the possibility to investigate ionic liquids under high fields without exceeding the electrochemical windows of the materials under study.

Afef Houachtia, Gisèle Boiteux, Gérard Seytre, Jean-François Gérard, Anatoli Serghei*
Université Lyon 1, Ingénierie des Matériaux Polymères, CNRS-UMR 5223,
69622 Villeurbanne, France
Email: anatoli.serghei@univ-lyon1.fr

Phecos – the new Peltier-based heat/cool temperature control system

Today, most materials and devices are required to operate without failure in a certain temperature range. The so-called industrial range, e.g., is usually considered to extend from -40 °C to 85 °C, the automotive range from -40 °C to +125 °C.

The importance of temperature control

Broadband Dielectric and Impedance Spectroscopy (BDS) is a perfect technique for the electrical characterisation of materials and technical samples like, e.g, membranes, sensors, batteries, and solar cells. Since many sample properties drastically change upon temperature variations, such measurements require a stable, reliable, and easy-to use temperature control system. In addition, it is desirable to have the option of performing fully automatic measurements of the electrical properties (like, e.g., complex permittivity, conductivity, and impedance) as a function of temperature in the frequency and time domains.

The relevance of a highly stable and reliable temperature control system is frequently underestimated. Researchers and engineers may waste tremendous amounts of time when applying inadequte means of temperature control, especially if simple ways of automation are not in reach.

The new Phecos system

Novocontrol announces its new desktop high-performance Phecos temperature control system for heat/cool operation (cf. Figure 1).

Since it is based on a dual-stage Peltier element whose sole resource is electrical power, no cryogenic fluids are required for the temperature control operation. Due to the low thermal mass, temperature changes are achieved quickly; the typical sample

Figure 1: The new Novocontrol Phecos temperature control system.

temperature stability is 0.1 K, and the absolute accuracy is 0.2 K. The Phecos system covers temperatures from -50 °C to +200 °C; a light version will operate from -40 °C to 160 °C. The system therefore is ideally suited for sample characterisations in the above mentioned industrial range and beyond. Gas connects allow operation under different atmospheres.

Performance: rapid changes and ultimate stability

Figure 2 provides an overview of the Phecos temperature control performance. The system quickly reacts to setpoint changes without significant overshooting, the typical time for stabilisation at a new setpoint being of the order of a few minutes only. The system easily stabilises to a precision of 0.1 K, allowing to monitor sample changes occuring in comparatively small temperature intervals.

Measurement examples

In the following, we will present results of two measurement taken for a dielectric and an electrolyte sample, respectively.

Conductivity measurement of a liquid electrolyte

As an example for a conductivity measurement, we monitored a standard water-based electrolyte solution (Hanna 70031) with a conductivity of 1413 µS/cm at 298 K. The commercial sample comes with a table of temperature-dependent conductivities for the range from 0 °C to 31 °C.

Data were taken using a Novocontrol Alpha-A analyzer with ZG4 test interface, the AC voltage set to 10 mVrms. The sample was filled into a Novocontrol parallel-plate cell for conductive liquids.

We obtained very good agreement between the measured conductivity values and the test sample manufac-

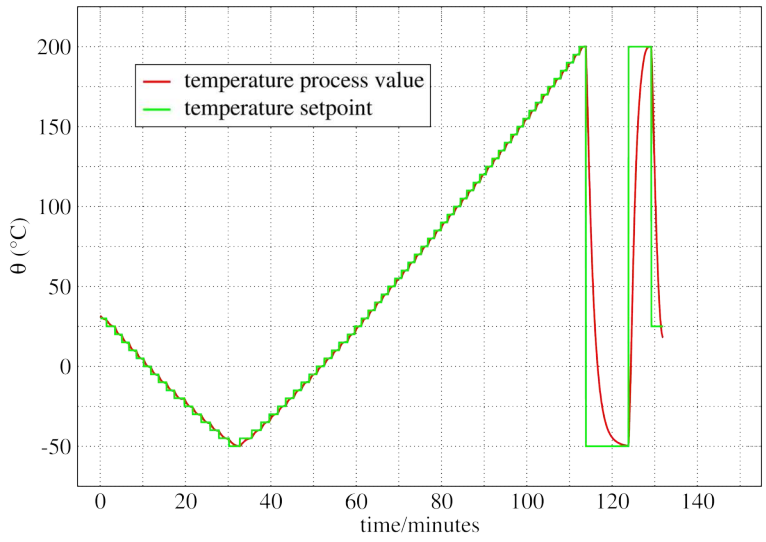

Figure 2: Stabilization characteristics of the sample temperature (red) compared to the temperature set point (green) . Set point step after sample temperature stabilization.

Phecos features

- High-quality temperature control system for dielectric and electrochemical impedance measurements
- Modular setup with several sample cell set-ups for e.g. dielectric and impedance material measurements, 2, 3 or 4 wire configurations for electrochemical samples and interdigit electrodes for e.g. monitoring of chemical reactions and curing of epoxies or glues or paints.
- Supports external gas inlets and outlets for defined atmosphere within the sample cell volume.
- Compatible with Novocontrol Dielectric / Impedance analyzers, potentiostats / galvanostats and high voltage interfaces.
- Compatible with Novocontrol WinDETA and WinCHEM software for electrical characterization of materials and technical samples in the frequency and time domains.
- Operating principle: Dual-stage Peltier heat/cool system
- T range: -50 °C to 200 °C
- T stability: 0.1 °C
- T accuracy: 0.2 °C
- temperature ramps from 0.01 °C/min up to 30°C/min
- temperature overshooting after set point step typically < 1 °C
- stabilization times typically below 5 minutes (for 0.1 °C stability)
- microprocessor controller with 24 bit ADC and IEC communication port

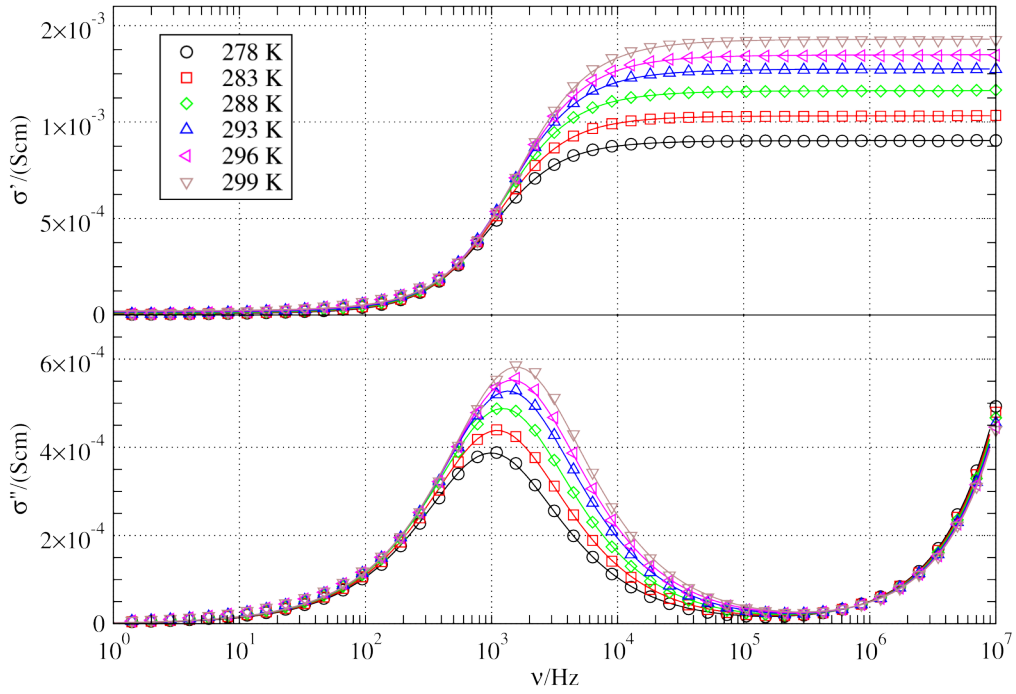

Figure 3: Fit results for the electrolyte solution measurements. Model described in the text. Solid lines: fit results. Symbols: measured data.
The fit shows very good agreement for both real and imaginary parts of conductivity.

turer's published data over the entire temperature range.

Data analysis using WinFIT

A first inspection of the conductivity data shows constant values of σ' at high frequencies. At lower frequencies, the conductivity reduces due to Maxwell Wagner polarization effects [1,2].

It is possible to directly extract conductivity data from the high-frequency plateau values (cf. Fig. 4, upper half). These already show good agreement with the values published for the Hanna conductivity solution.

To provide an even more detailed analysis of the data, we performed a non-linear fit of the conducivity spectra, using the following Novocontrol WinFIT model for the measured impedance: ((R1|CPE1)+R2)|C1 [3]. Here R, C, and CPE represent resistors, capacitors, and constant-phase elements, while the symbols | and + represent parallel and serial circuit connections, respectively.

In this model, R1 in parallel to the constant phase element represent the double-layer impedance, R2 reflects the bulk conductivity, C1 the bulk capacity. We use the complex conductivity data (linear representation) to determine the optimum fit and calculate the bulk conducivity from R2 and the cell constant. The results are highly convincing: all parameters exhibit physically reasonable values, the determined conductivities, as shown in Fig. 5, exhibit good agreement with the values published by the conductivity solution manufacturer with an absolute value accuracy below 1 % over the measured temperature range. It should be noted that no element of calibration was used. All data were exclusively calculated from the measured impedance and sample cell geometry (electrode diameter and spacing) without adjustments. With this, the system is especially suited for accurate and straightforward measurement of the internal bulk conductivity and polarization

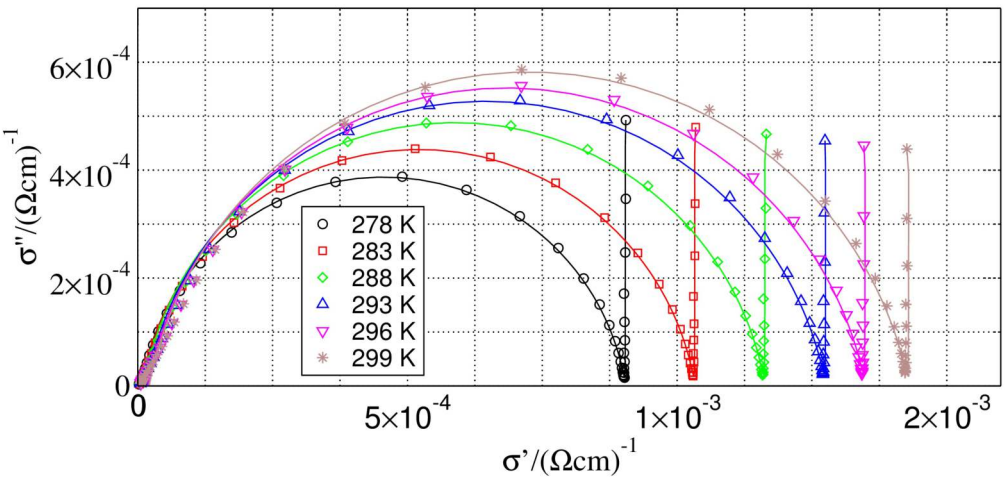

Figure 4: Fit results for the electrolyte solution measurements, shown in a complex conductivity plot. Model described in the text. Solid lines: fit results. Symbols: measured data.

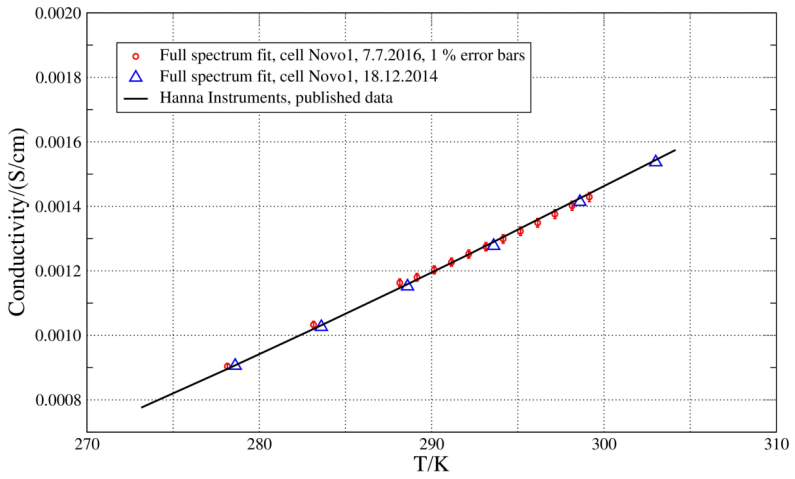

Figure 5: Conductivity values of the electrolyte solution. Solid line: published data. Symbols: measurement results.

properties of conductive liquids and electrolytes over temperature.

Dielectric measurement of a PMMA film sample

The second example shows measurement results of PMMA over a wide temperature range. A sample of 50 µm thickness equipped with 20 mm diameter silver electrodes on both faces was mounted between standard Novocontrol disposable electrodes (type BDS 1301). The measurements were performed using the standard AC voltage setting of 1 Vrms.

Results are presented in Figure 6. PMMA shows a broad relaxation strongly varying with temperature (both in position on the frequency sale and intensity) and thus constitutes a nice example of a temperature-dependent measurement.

References:

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[3] modified Randles circuit

Dirk Wilmer
Novocontrol Technologies

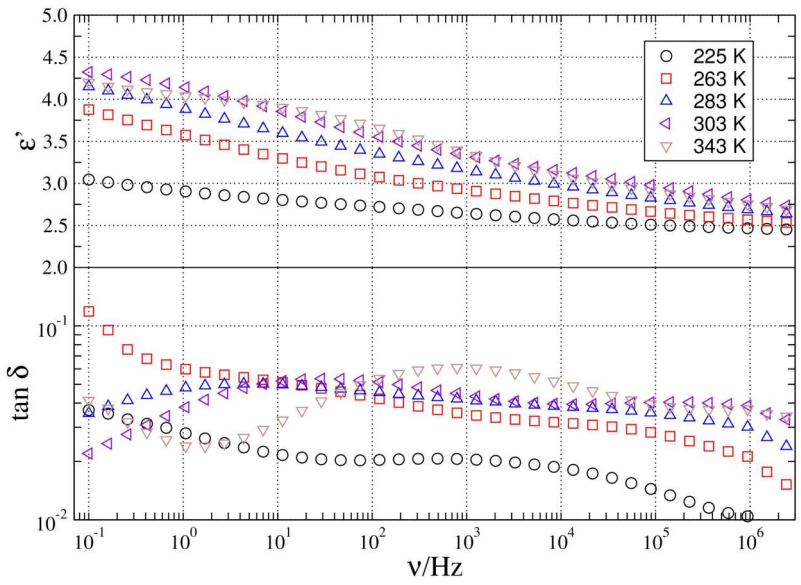

Figure 6: Results for dielectric measurements of PMMA using the new Phecos temperature control system.

New Features of WinDETA 6.0

Our standard Windows program for dielectric and impedance spectroscopy, WinDETA, is currently prepared for its version 6.0 release. While maintaining the key features it is widely appreciated for, like extreme stability and reliability, it will receive additional features which are included in order to improve user experience and everyday usage.

WinDETA offers a huge variety of plotting configurations; to facilitate the switching between those, we have included a configurable short-cut option in the WinDETA Multigraphics menu. Multigraphics, the essential function for viewing the results of dielectric and impedance measurements, will be equipped with an easier-to-use zoom-in and zoom-out function. Moreover, WinDETA will now provide pre-defined standard plots, e.g., Bode and Nyquist plot for various complex parameters like permittivity ε, conductivity σ, impedance Zs, admittance Yp, capacity Cp, etc. The new graphics features are completed by the option to self-define short-cuts.

Multigraphics will show plotted data values when clicked, simplifying the extraction of particular data when discussing the results.

The most relevant WinDETA menu items are now equipped with pictograms which will allow faster orientation and use.

Needless to say that WinDETA 6.0 will support the new Novocontrol Phecos temperature control system.

WinCHEM upgrade to version 3.0

Novocontrol is preparing the release of its feature upgrade of WinCHEM, our software to control electrochemical measurements in the time domain. WinCHEM fully supports Novocontrol Alpha-A series analyzers combined with one of our high-performance potentiostat/gal-

vanostat interfaces, i.e, POT/GAL 30V-2A and POT/GAL 15V-10A.

In its upcoming version 3.0, WinCHEM will provide a substantial amount of new features in order to enhance and simplify the implementation of typical electrochemical experiments. For corrosion analysis, it will support Tafel plot fitting features (anodic, cathodic, and their combination) as well as polarisation resistance.

WinCHEM in general is a package which supports experiments in the time domain, i.e., a huge variety of voltage-current measurements which use particular pre-defined waveforms of one property (voltage or current) and measure the complementary one (current or voltage). WinCHEM version 3.0 will simplify the set-up of such measurements by providing easy-to-use set-up masks which aim to facilitate the entry of the key properties of each particular measurements. Currently included experiment types are

- cyclic voltammetry
- linear sweep voltammetry
- chronoamperometry
- chronocoulometry
- chronopotentiometry
- multi-step chronopotentiometry
- dc corrosion

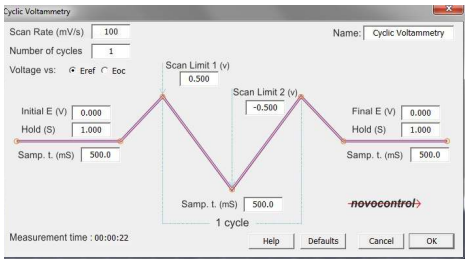

Figure 1: WinCHEM 3.0 Cyclovoltammogram set-up dialogue.

As an example, the CV set-up menu is shown in Figure 1. Beyond these pre-defined experiment types, the highly flexible waveform editor is used to create nearly any type of additional time-domain experiments.

Dirk Wilmer
Novocontrol Technologies

Book Review: Valerica Raicu and Yuri Feldman (Eds.): Dielectric Relaxation in Biological Systems [1]

Friedrich Kremer

In the eighties and nineties of the last century the dielectric properties of biological materials were in the focus of intense research as documented by the work of H. Schwan [2,3], S. Takashima [4], E.H. Grant, R. J. Speppard, G.P. South [5] and R. Pethig [6]. It is surprising and remarkable that it took more than 25 years before this subject became the topic of a novel study [1] again, which is edited by leading experts of in the field, V. Raicu and Y. Feldman. The book is organized in three parts "Theoretical background", "Experimental Methods and Techniques" and "Applications". In the first section after an elementary introduction, "the theory of particles in homogeneous fields" and "dielectric models and computer simulations for complex aggregates" are presented and discussed in detail. The second part is focused on "experimental methods and techniques" and especially "electrode polarization" which plays an eminent role in biological materials. Furthermore the "analysis of experimental data and fitting problems" are outlined. In the third section devoted to applications, classical, but also current topics are addressed, such as "the dielectric relaxation of water", "amino acids and peptides", "dielectric spectroscopy of hydrated biomacromolecules", "proteins in solutions and natural membranes", "dielectric properties of polyelectrolytes and lipid vesicles", "radiofrequencies dielectric properties of cell suspensions" or "dielectric properties of blood and blood components". As completely novel aspect "glucose detection from skin dielectric measurements" is described in detail.

The book sums up state of the art and is highly recommended to everybody who wants to inform themselves about the recent developments in this field of research.

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Prof. Dr. Friedrich Kremer
Universität Leipzig, Linnéstr. 5
04103 Leipzig, Germany