

A Modified Cole-Cole Model Used in the Evaluation of Low-Frequency Electrical Impedance Spectroscopy Measurements

Nina Gyorfi, Lili Nadasdi, Attila Toth, Mihaly Klincsik, Zoltan Sari, Bojan Kuljic, Akos Odry, Peter Odry, Zoltan Vizvari

Abstract— Electrical Impedance Spectroscopy is a widely applied material analysis technique which does not impair functionality nor lead to destruction. The greatest advantage of the cost-effective method is how it assesses the chemical compound of the material analyzed. The data acquired during the measurements are analyzed by equivalent electric models, in which the material parameters correlate with the model parameters. The pre-requisites for the model applied are primarily dependent upon the structure of the analyzed material and the frequency spectrum. Based on the experiments implemented through the considerably large number of low-frequency analyses (< 10 Hz) performed by our research team, we have modified the Cole-Cole relaxation model to fit it as precisely as possible to the low-frequency analyses. The present article demonstrates the modified Cole-Cole model, and includes an experimental measurement to support the efficacy and robustness of the self-developed analysis system and method.

Keywords—Electrical Impedance Spectroscopy, Cole-Cole model, relaxation models for material testing

I. INTRODUCTION

Electrical Impedance Spectroscopy (EIS) is a wide-spread procedure, during which electric current flowing through the electrodes as a result of the alternating voltage in a given frequency spectrum is measured. The complex impedance spectrum of the cell is determined by the coefficient of the applied potentials and the current developed as a consequence of which, can be presented on the Bode plot or displayed using the Nyquist spectrum [1]. In the analysis of any given datum point, however, it is not possible to identify precisely what frequency was applied to fix the point, which is one of the major drawbacks regarding the Nyquist plot. Distinctly, the Bode plot

presents frequency information [2].

One of the advantages in reference to the EIS as opposed to time-spectrum measures (e.g. impulse or quadrilateral wave measures) is the frequency response in the frequency spectrum can analytically be determined by applying equivalent electrical circuit elements or couplings. These equivalent electrical circuit elements can be represented by relatively simple mathematical functions [3].

Equivalent electrical circuit elements form the basis for developing equivalent couplings, among which resistance (R) and capacitance (C), well-known from electronics, can evidently be found. However, these are unable to describe several other physical-chemical procedures, such as diffusion or ion-transfer [3].

II. MODELS AND APPLICATION OF EIS TECHNIQUE

EIS data are usually assessed by fitting them to equivalent electrical circuit models. The polarization of certain dielectric materials is dependent upon the nature of the molecular and atom chemical couplings. Presently, there are no universal models which offer an explanation regarding polarization in any material [4]. Since the relaxation response reaction regarding several dielectric materials cannot be justified by the standard Debye-model, the demand in newer models soared. The most important models emphasize the Cole-Cole function, the Cole-Davidson function and the Havriliak-Negami function, all which consider the different distribution types of the relaxation times [5].

In 1929, Debye developed a simple model in describing the relaxation models, in which he presumed individual relaxation time for each molecule [4]. The Debye model is the simplest

This work was supported by grants GINOP-2.3.2.-15- 2016-00022 and EFOP-3.6.2-16-2017-00010.

Nina Gyorfi is with the Department of Environmental Engineering, Faculty of Engineering and Information Technology, University of Pécs, Boszorkány u. 2, H-7624 Pécs, Hungary (e-mail: gyorfinina@gmail.com).

Lili Nadasdi is with the Department of Environmental Engineering, Faculty of Engineering and Information Technology, University of Pécs, Boszorkány u. 2, H-7624 Pécs, Hungary (e-mail: nadasdililike@gmail.com).

A. Toth is with the Institute of Physiology, Medical School, University of Pécs, Szegedi str 12, H-7624 Pécs, Hungary (e-mail: attila.toth@aok.pte.hu).

M. Klincsik is with the Department of Mathematics, Faculty of Engineering and Information Technology, University of Pécs, Boszorkány u. 2, H-7624 Pécs, Hungary (e-mail: klincsik@mik.pte.hu).

Z. Sari is with the Department of Information Technology, Faculty of Engineering and Information Technology, University of Pécs, Boszorkány u. 2, H-7624 Pécs, Hungary, (e-mail: sari.zoltan@mik.pte.hu)

Bojan Kuljic is with the College of Applied Sciences, Subotica Tech, Marka Oreškovića 16, 24000 Subotica, Serbia (e-mail: bojan@vts.su.ac.rs)

Akos Odry is with the Institute of Information Technology, University of Dunaujvaros, Tancsics M. u. 1/A, H-2401 Dunaújváros, Hungary (e-mail: odrya@uniduna.hu).

P. Odry is with the Institute of Information Technology, University of Dunaujvaros, Tancsics M. u. 1/A, H-2401 Dunaújváros, Hungary (e-mail: podry@uniduna.hu).

Z. Vizvari is with the Department of Environmental Engineering, Faculty of Engineering and Information Technology, University of Pécs, Boszorkány u. 2, H-7624 Pécs, Hungary (e-mail: vizvari.zoltan@mik.pte.hu).

model describing dielectric polarization procedures [5]:

$$Z(j\omega) = R_\infty + \frac{(R_0 - R_\infty)(1 - j\omega\tau)}{(1 - \omega^2\tau^2)} \quad (1)$$

where

Z is the measured impedance,
 R_∞ is the resistance corresponding to infinity frequency,
 R_0 is the DC resistance,
 τ is the time constant,
 ω is the angular frequency and
 j is the imaginary unit.

Debye's response function was the first theoretical model to describe the dielectric behavior of certain materials. Due to its limitations, it cannot annotate an adequate picture referencing low-frequency spectra, in which the real relaxation behavior may differ from the traditional Debye pattern. This was the primary reason why, in the ensuing years following the appearance of the Debye model, several other response functions were introduced, which may serve as a model effectively revealing the dielectric relaxation regarding several forms of material [4]. In comparison to the Debye model, the Cole-Cole model, developed by the Cole brothers, features an α parameter ranging between the values 0 and 1 [5]:

$$Z(j\omega) = R_\infty + \frac{(R_0 - R_\infty)}{1 + (j\omega\tau)^\alpha} \quad (2)$$

The α exponent parameter ensures the description among various spectral shapes possible. When $\alpha=0$, it represents the standard Debye model [5]. Due to its simplicity and good fit associated with the data measured, the Cole-Cole impedance model is applied in several areas of research, ranging from geophysics to evaluate biochemical or the pursuit of various biological material. Four parameters are required to evaluate a given tissue: R_0 , R_∞ , α and τ [6].

Cole's and Davidson's scientific achievements fulfilled a nearly entire determination and increased precision regarding quantitative description of the dielectric parameters possible. In consideration of the invention of the Cole-Cole model, a more complex model was soon thereafter developed on the basis of the dielectric experimental data:

$$Z(j\omega) = R_\infty + \frac{(R_0 - R_\infty)}{(1 + j\omega\tau)^\beta} \quad (3)$$

In review of the equation above, note the distribution of the relaxation times is not symmetrical. The β parameter, ranging between the values 0 and 1, ensures a possibility for the description of the dispersion spectrum. When $\beta=1$, the function is simplified in the form of a Debye function [5].

The Havriliak-Negami model can be considered as the

generalization of the previous models, as the general expression of the universal relaxation law. Consequently, the frequency dependence of the complex permittivity is generally determined referencing the following two-parameter formula:

$$Z(j\omega) = R_\infty + \frac{(R_0 - R_\infty)}{\left[1 + (j\omega\tau)^\alpha\right]^\beta} \quad (4)$$

in which the α and β exponents determine the symmetry of the given spectrum and the range of the dispersion. When $\beta=1$, it represents the Cole-Cole function, when $\alpha=1$, it represents the Cole-Davidson function, and when $\alpha=\beta=1$, it results in Debye's original model [5].

A. Application of EIS Technique

Electric Impedance Spectroscopy is applied in several fields since it is rapid, simple and cost-effective. In the paint- and coating-industry, it proves to highly beneficial in consideration of the improved quality control measures regarding the various coatings [7] and to detect any potential corrosion [8] – [9].

Furthermore, it is used in several biosensor systems, such as a method to measure bacterium-concentration [10], and in the detection of potentially harmful pathogens, such as the Escherichia Coli O157: H7 [11] and the Salmonella Coli [12].

In agriculture, it has been verified as an excellent method to follow-up growth and in quality control. Several research studies have been performed to investigate its role in detecting the maturity of different kinds of fruits [13] – [14], vegetables [15] – [17] and meats [18] – [19], in diagnosing plant diseases [20] – [21], in analyzing wine- and milk-compounds [22] – [23], and also in monitoring olive oil extraction [24]. Compared to traditional chemical methods, its application in the food-industry explicitly reduces the investigation time and increases precision.

Multi-layer earth structures, including their spatial distribution can be determined by effective implementation regarding this method [25].

Additionally, it is applied to estimate the composition and different parameters of the human body, such as fluid content, total body fluid and free fat mass [26] – [27].

III. A MODIFIED COLE-COLE MODEL IN ACQUIRING LOW FREQUENCY MEASUREMENTS

Our research team has mainly specified to perform low-frequency (<10 Hz) measures. Due to the behavior of the impedance data at low-frequency, the Cole-Cole model can only be applied with limitations in this frequency spectrum. The team has modified the Cole-Cole model to ensure a proper, precise fit in reference to the data collected. Thus, the equivalent electrical circuit illustration representative of the modified Cole-Cole model is represented below (Fig. 1.).

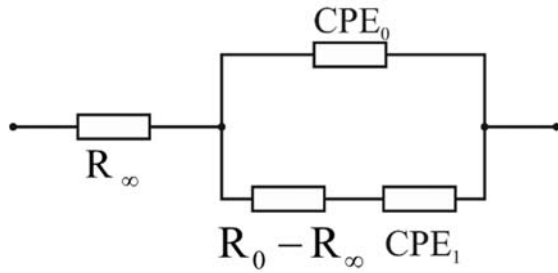


Figure 1 The modified Cole-Cole model equivalent circuit

Compared to the original model (2), the most remarkable difference regarding the modified Cole-Cole model is how CPE_1 cascaded with the $R_0 - R_\infty$ resistors is a non-linear element. The equivalent electric circuit has two time constants ($\tau_1 > \tau_0$), since

$$Z_{CPE0} = \frac{1}{(j\omega C_0)^\alpha}, Z_{CPE1} = \frac{1}{(j\omega C_1)^\beta} \quad (5)$$

the behavior regarding the coupling in the frequency spectrum is primarily determined by these parameters. When $\omega \rightarrow 0$, the impedance of the coupling approaches to infinity, while, when $\omega \rightarrow \infty$, the impedance equals to R_∞ , which is illustrated by the following figure (Fig. 2).

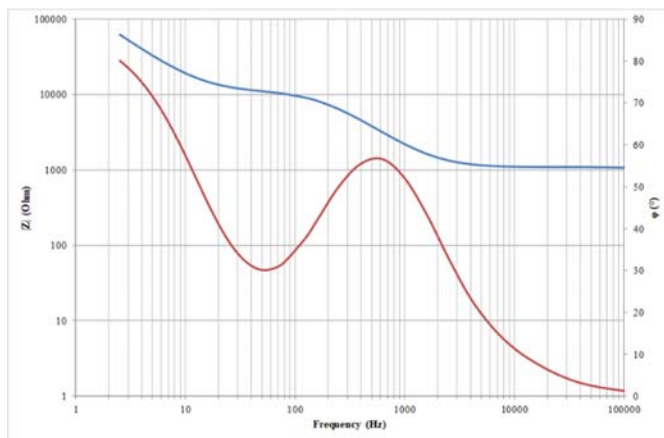


Figure 2 The impedance spectrum of the modified Cole-Cole model

IV. MATERIAL AND METHODS

To present the method representative in estimating the parameters of the modified Cole-Cole model, a linear system was established, in which the CPE elements simply turn to be capacitors by substituting $\alpha, \beta = 1$. The RC parameters are the following: $R_\infty = 1$ kOhm, $R_0 - R_\infty = 10$ kOhm, while the values of the capacitors are $C_0 = 0.1$ uF és $C_1 = 1$ uF. The resistors are ultra-precise resistors with less than 2 ppm thermic coefficients and 1% tolerance [28]. The tolerance of the capacitors is 5%, while the thermic coefficient is 200 ppm/°C [29].

A. The Measurement Method Applied

The experiment was performed using a self-developed multifunctional instrument, which can also be used regarding EIS and EIT measurements. The instrument [30] is capable of measuring impedance, impedance spectra, and Fast Fourier Transform (FFT) spectra on each channel independently. The excitation was a monochromatic sine wave in a frequency range between 1 mHz to 100 kHz, with a Total Harmonic Distortion + Noise (THD+N) greater than 100 dB. The maximum noise levels in the frequency range 0.1 Hz to 40 kHz are 150 fA eff for the current, while 1.5 μ V eff for the voltage. The range of applicable excitations is 110 dB in both current-generator and voltage-generator modes with maximum values of 10 mA peak to peak and 10 V peak to peak, respectively. The signals are digitalized by the receiver board applying 24-bit Analog-Digital (AD) converters and additionally processed using the digital platform controlled by the PC. During precise impedance calculations, (48 bit) resolution for both real and imaginary parts, all operations regarding signal manipulations and parameter extractions are performed in the digital domain. One of the most important features regarding sensitivity representative of the equipment is the accuracy of 1 ppm for amplitude and 0.01° for phase. Fig. 3 depicts the customized instrument.



Figure 3 The measuring instrument

The entire measurement procedure is implemented using PC software referred to as Embedded System for Impedance Measurement (ESIM). The ESIM displays the results on the screen and it is capable of saving all measurement data, whether on a Secure Digital (SD) card or Hard Disk Drive (HDD). Interestingly, the measurement system is independently operational without the use of a PC.

B. The Data Extracting and Evaluating Methods Applied

By measuring the test circuit shown in Fig. 4, it is possible to perform a statistical estimation of the accuracy of the system and the data evaluation method by calculating the relative error (ϵ) of the measured values, the correlation coefficient (R^2) and the Chi-square values (χ^2) for the model-fitting process.

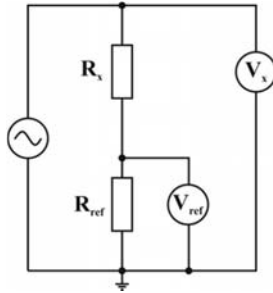


Figure 4 Passive test circuits (R_x symbolizes the measured model circuit)

In order to test the advantages of the self-developed impedance measurement technique, the test arrangement depicted on Fig. 4. was used (the same arrangement as in [31]). According to the patented method, R_x can be calculated by the following formula:

$$R_x = R_{ref} \cdot \frac{V_x - V_{ref}}{V_{ref}} \quad (6)$$

The EIS measurements were carried out by using lock-in averages in duration of 1 second at 100 distinct frequencies between 1 Hz and 10 kHz. In consideration of the evaluation regarding the measured frequency-impedance data-pairs, the Levenberg-Marquardt-based method, a non-linear optimization algorithm, was developed in a MatLab environment [32].

V. RESULTS

These results demonstrate the capabilities and effectiveness of the entire equipment together with the data acquisition method. The error of impedance (R_x) values consists of two components: the constant error of analogue measuring channels and the resistor tolerance. The relative errors of the absolute value (Z) and phase (φ) of impedance are shown in the following formulae:

$$e_Z = 100 \cdot \frac{Z_i - Z}{Z}, \quad e_\varphi = 100 \cdot \frac{\varphi_i - \varphi}{\varphi}, \quad (3)$$

in which e_Z and e_φ are the relative errors (%), Z_i and φ_i represent the measured values corresponding to the i -th channel ($i = 1, \dots, 8$), while Z is the magnitude and φ is the phase of impedance (theoretical value based on equation (1), while $\alpha = 1$). The results of EIS measurement can be seen in Fig. 5. The maximum relative error regarding the magnitude of the impedance (calculated for the entire frequency domain of the measurement) is 0.57%. Regarding the measured phase values, the maximum relative error is 0.67%.

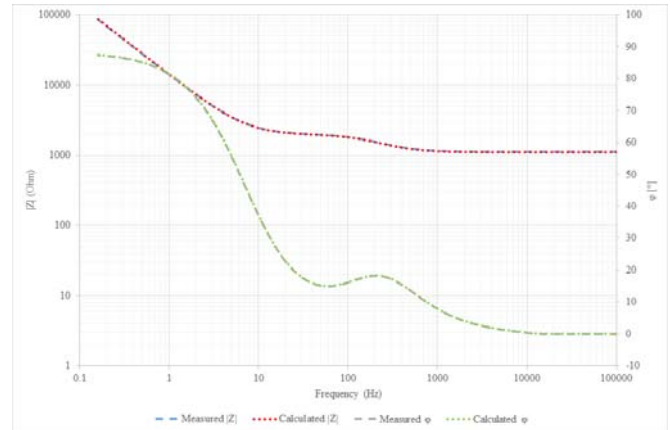


Figure 5 Result of EIS measurement performed on a test circuit compared to the theoretical values

The Table 1 depicts the results of a MatLab fit-algorithm. The relative error of the extracted model parameters is less than the tolerance of passive components.

Component name	Theoretical value	Extracted value	Relative error (%)
R_∞ (Ohm)	1 000	997	0.3
$R_0 - R_\infty$ (Ohm)	10 000	9 957	0.43
α (-)	1	0.9999	0.01
τ_0 (sec)	0.01	0.01012	1.2
β (-)	1	0.9999	0.01
τ_1 (sec)	0.1	0.0982	1.8

Table 1 The extracted model parameters compared to the theoretical value of components

The goodness of fit was measured using the R^2 value, which was 0.9999, while the χ^2 value was 0.24, which demonstrates the outstanding properties of the self-developed measurement system, the data recording method including the evaluation process.

VI. CONCLUSION

This article, in addition to illustrating the equivalent models applied to the Electrical Impedance Spectroscopy, presented the modified Cole-Cole model used for evaluating low-frequency measurements, which correspondingly fitted to our low-frequency data. Furthermore, the model was validated by an equivalent passive electronic system, in which several measurements were performed to evaluate the efficacy regarding the instrument and its methodology regarding theoretical values. The model parameters were determined by non-linear regression from the fixed frequency-impedance pairs, the standard deviation of which ranges within the tolerance of the constituents of the passive system. In consideration of all these various aspects, it was effectively and successfully demonstrated, in which our self-developed techniques are capable of evaluating measurement data

regarding Electrical Impedance Spectroscopy recorded at low-frequency levels, whether in the field of geophysics or biology.

REFERENCES

- [1] O. Pänke, T. Balkenhohl, J. Kafka, D. Schäfer and F. Lisdat, "Impedance Spectroscopy and Biosensing", *Adv Biochem Engin/Biotechnol*, 109, pp. 195–237, 2008.
- [2] GAMRY Instruments: *Basics of Electrochemical Impedance Spectroscopy*, <https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/> 2019
- [3] B. A. Boukamp: "A Non-linear Least Squares Fit Procedure for Analysis of Immitance Data of Electrochemical Systems", *Solid State Ionics* 20, 31–44, 1986.
- [4] C. F. A. Rosa, C. D. Oliveira: "Relaxation Equations: Fractional Models", *J Phys Math* 6: 146, 2015.
- [5] G. Giannoukos, M. Min: "Mathematical and Physical modelling of the dynamic electrical bioimpedance", *International Journal of Circuits, Systems and Signal Processing*, Volume 8, 2014.
- [6] Y. Yang, Q. Sun, H. Wen, Z. Teng: "Improved Cole parameter extraction based on the least absolute deviation method", *Physiological Measurement*, 34(10), 1239–1252, 2013.
- [7] T. C. Da Silva, S. Mallarino, S. Touzain, I. C. P. Margarit-Mattos: "EIS and thermal fatigue of organic coatings", *Electrochimica Acta*, 2019.
- [8] T. Unsal, N. Cansever, E. Ilhan-Sungur: "Impact of biofilm in the maturation process on the corrosion behavior of galvanized steel: long-term evaluation by EIS", *World Journal of Microbiology and Biotechnology*, 35(2), 2019.
- [9] V. Encinas-Sánchez, M. T. de Miguel, M. I. Lasanta, G. García-Martín, F. J. Pérez: "Electrochemical impedance spectroscopy (EIS): An efficient technique for monitoring corrosion processes in molten salt environments in CSP applications", *Solar Energy Materials and Solar Cells*, 191, 157–163, 2019.
- [10] R. Maalouf, C. Fournier-Wirth, J. Coste, H. Chebib, Y. Saïkali, O. Vittori, N. Jaffrezic-Renault: "Label-Free Detection of Bacteria by Electrochemical Impedance Spectroscopy: Comparison to Surface Plasmon Resonance", *Analytical Chemistry*, 79(13), 4879–4886, 2007.
- [11] C. Ruan, L. Yang, Y. Li: "Immunobiosensor Chips for Detection of Escherichiacoli O157:H7 Using Electrochemical Impedance Spectroscopy", *Analytical Chemistry*, 74(18), 4814–4820, 2002.
- [12] V. Nandakumar, J. T. La Belle, J. Reed, M. Shah, D. Cochran, L. Joshi, T. L. Alford: "A methodology for rapid detection of Salmonella typhimurium using label-free electrochemical impedance spectroscopy", *Biosensors and Bioelectronics*, 24(4), 1039–1042, 2008.
- [13] A. A. Bakr, A. G. Radwan, A. H. Madian, A. S. Elwakil: "Aging effect on apples bio-impedance using AD5933", *3rd International Conference on Advances in Computational Tools for Engineering Applications (ACTEA)*, 2016
- [14] J. R. González-Araiza, M. C. Ortiz-Sánchez, F. M. Vargas-Luna, J. M. Cabrera-Sixto: "Application of electrical bio-impedance for the evaluation of strawberry ripeness", *International Journal of Food Properties*, 20(5), 1044–1050, 2016.
- [15] T. Watanabe, T. Orikasa, H. Shono, S. Koide, Y. Ando, T. Shiina, T., A. Tagawa: "The influence of inhibit avoid water defect responses by heat pretreatment on hot air drying rate of spinach", *Journal of Food Engineering*, 168, 113–118, 2016.
- [16] Y. Ando, Y. Maeda, K. Mizutani, N. Wakatsuki, S. Hagiwara, H. Nabetani: "Effect of air-dehydration pretreatment before freezing on the electrical impedance characteristics and texture of carrots", *Journal of Food Engineering*, 169, 114–121, 2016.
- [17] A. Kertesz, Z. Hlaváčová, E. Vozáry, L. Staroňová: "Relationship between moisture content and electrical impedance of carrot slices during drying", *International Agrophysics*, 29(1), 61–66, 2015.
- [18] J. L. Damez, S. Clerjon, S. Abouelkaram, J. Lepetit: "Beef meat electrical impedance spectroscopy and anisotropy sensing for non-invasive early assessment of meat ageing", *Journal of Food Engineering*, 85(1), 116–122, 2008.
- [19] X. Zhao, H. Zhuang, S. C. Yoon, Y. Dong, W. Wang, W. Zhao: "Electrical Impedance Spectroscopy for Quality Assessment of Meat and Fish: A Review on Basic Principles, Measurement Methods, and Recent Advances", *Journal of Food Quality*, 2017, 1–16, 2017.
- [20] C. Farber, M. Mahnke, L. Sanchez, D. Kourouski: "Advanced Spectroscopic Techniques for Plant Disease Diagnostics", *A Review. TrAC Trends in Analytical Chemistry*, 118, 43–49, 2019.
- [21] M. Khater, E. M. Alfredo de la, Q. G. Daniel, A. Merkoçi: "Electrochemical detection of plant virus using gold nanoparticle-modified electrodes", *Analytica Chimica Acta*, 2018.
- [22] A. M. Lopes, J. A. T. Machado, E. Ramalho, V. Silva: "Milk Characterization Using Electrical Impedance Spectroscopy and Fractional Models", *Food Analytical Methods*, 11(3), 901–912, 2017.
- [23] A. M. Lopes, J. A. T. Machado, E. Ramalho: "On the fractional-order modeling of wine", *European Food Research and Technology*, 243(6), 921–929, 2016.
- [24] S. Yang, I. Hallett, H. E. Oh, A. B. Woolf, M. Wong: "Application of electrical impedance spectroscopy and rheology to monitor changes in olive (*Olea europaea* L.) pulp during cold-pressed oil extraction", *Journal of Food Engineering*, 245, 96–103, 2018.
- [25] Z. X. Li, S. W. Rao: "Estimation of frequency domain soil parameters of horizontally multilayered earth by using Cole–Cole model based on the parallel genetic algorithm", *IET*, Volume 13 Pages 1746–1754, 2019.
- [26] M. Grossi, B. Riccò: "Electrical impedance spectroscopy (EIS) for biological analysis and food characterization: a review", *J. Sens. Sens. Syst.*, 6, 303–325, 2017
- [27] B. M. Carrion, A. Wells, J. L. Mayhew, A. J. Koch: "Concordance Among Bioelectrical Impedance Analysis Measures of Percent Body Fat in Athletic Young Adults", *International journal of exercise science*, 12(4), 324–331, 2019.
- [28] UPR resistors Token Passive Components Ltd. <http://www.4-direct.com/pdf/resistor-ppm/ultra-precision-resistor-upr.pdf>, (last visited 20 August 2016).
- [29] *Metallized polyester film capacitor d.c. multipurpose applications*, Kemet (Formerly Arcotronics) Distributor, R82 Series, 2016.
- [30] Z. Vizvari, T. Kiss, Cs. Ver, M. Klincsik, Z. Sari, K. Mathe, B. Kuljic, F. Henezi, P. Odry: "A multi-channel electrical impedance meter based on digital lock-in technology"; Pollack Periodica; (accepted) 2019.
- [31] K Borbas, T. Kiss, M. Klincsik, Z. Kvasznicza, K. Mathe, Cs. Ver, Z. Vizvari, P. Odry: Process and Measuring System for Data Acquisition and Processing in Soft-Tomography Studies, US20180374244A1, <https://patents.google.com/patent/US20180374244A1/en>
- [32] C. Richard, A. B. B. Clifford, H. Thurber: *Parameter Estimation and Inverse Problems*, 3rd Edition, Elsevier, 2018. (ISBN: 9780128046517)