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Impedance spectroscopy advances and future trends: A comprehensive review

Abstract: Impedance spectroscopy is a highly performant measurement method, which is often used in many fields of science and technology. It refers to the measurement of the complex impedance over a range of frequencies and provides possibilities for separating relaxation effects, accurate measurements and measurements of non-accessible quantities. In material science, impedance spectroscopy allows the characterization of the complex conductivity. Impedance spectra of battery cells allow to get information in a non-destructive way and to separate different phenomena concerning electrolyte and electrodes. In the biomedical field, it has the decisive advantage by providing a lot of information non-invasively and for long time intervals. For sensors, decisive improvements of measurement accuracy can be reached and multifunctional sensors can be realized, which allow measurements of more than one measurement quantity at the same time and same state of a material or a device.

In this contribution, after an introduction about the fundamentals of the measurement method, the links and differences between a wide range of application areas of impedance spectroscopy are shown for the first time. In each of these fields, we highlight the specific strengths of impedance spectroscopy and report on recent advances and future trends.

Keywords: Impedance spectroscopy, electrochemical impedance spectroscopy, relaxations, battery diagnosis, bioimpedance, sensors, biosensors, inductive sensors, capacitive sensors, nanocomposite, corrosion, signal processing

1 Introduction

The complex impedance of a material or a system provides information about its composition, interfaces and geometry and helps to follow changes of its state. Impedance measurement has therefore decisive benefits compared to other characterization methods, as it is experimentally efficient, because of the relative reduced time, hardware and software needed. It delivers more information than only resistive, capacitive or inductive measurements, because it considers at the same time both the real and the imaginary part of the complex impedance. It provides the possibility to separate

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effects having linearly independent dispersions and dominating in different frequency ranges.

Impedance spectroscopy has shown a high potential for many years and has so far demonstrated its potential in a big number of applications, such as characterization of energy storage units [1], biomedical and biological applications [2] , [3] , [4], material testing [5–7], corrosion and coatings [8] and inductive [9, 10], capacitive [11] and conductive sensors [12]. The range of applications is very broad and the advantages it provides are significant under the condition that it is applied in the right manner. In every application, field-specific strengths of the method are in the focus of interest, even if the method can provide more advantages.

Impedance spectroscopy is non-invasive, as it uses small amplitudes of the excitation signal. It is capable to achieve real-time measurement by using wide frequency band signals. Even if it is generally known as a method for materials and systems characterizations in laboratory environments, impedance spectroscopy is increasingly used for real-time measurements in portable and embedded solutions due to the favorable developments in the field of microelectronics.

In this contribution, we give an overview about different aspects of the method in relation to a wide range of application fields. The aim is to demonstrate the potential of impedance spectroscopy and to show the link between the different application areas. In each context, the reasons for the particular strengths of the method are discussed and special potentials are shown. Then, recent developments are explained by means of selected examples.

2 Theoretical background

Impedance spectroscopy belongs to the so-called system identification techniques, where the frequency-dependent transfer function of a system is determined. In impedance spectroscopy, the complex impedance of a material or a system is measured at different frequencies or in a certain frequency range. Thereby both the real and the imaginary part of the complex impedance can be considered as useful sources of information, where certain phenomena are dominating in certain frequency ranges and can therefore be characterized. In general, the real and the imaginary part of the impedance show a different frequency dependency and therefore provide a comprehensive source of information. This is why manifold information regarding electrical and electrochemical properties of the investigated system or material can be extracted.

A wide frequency band helps to gain more information at a given working point of the i - u characteristic (see Fig. 1 (a) and (b)). If the measurements carried out correspond to the same phenomena (see Fig. 1 (c)), impedance spectroscopy helps to realize a better characterization of the phenomena. The measurements are from a physical point of view redundant and provide possibilities to have a better measurement

Fig. 1: Principle of impedance spectroscopy. (a) Excitation with a single frequency at a given working point. (b) Example for excitation with a varied frequency with a sweep. (c) Improvement of measurement information by redundancy. (d) Improvement of measurement information by diversity through a wide band excitation signal.

accuracy, as it becomes possible to reduce the influence of random deviation, such as noise, and systematic deviations, e. g., temperature, and to benefit from a detailed modeling of the characteristic.

If the impedance measurement is carried out in a wider frequency range (see Fig. 1 (d)), the information gained thereby becomes more probable to have diversity, as different physical/chemical phenomena can be dominating in different frequency ranges. If different spectral behaviors are included in the impedance spectrum referring to different phenomena, impedance spectroscopy provides interesting opportunities to measure more than one quantity at the same time. The conditions for this are (i) to have sufficient measurement data in the spectral regions where the individual effects are dominating and (ii) for the time constants corresponding to these phenomena to be sufficiently distant.

3 Extraction of information from impedance spectra

Several aspects should be specifically addressed on the design process for an impedance measurement system, such as measurement procedures, investigations of physical and chemical phenomena taking place, development of suitable impedance models and extraction of target information by optimization techniques.

In general, there are different approaches, which can be considered for information extraction from impedance spectra. Physical methods are interesting and allow profound insights in a material or a system (see Fig. 2). Mathematical methods have also been proposed, such as data mining, principal component analysis [13], neural networks and fuzzy logic [14].

For physical modeling, it is necessary to understand the physical and chemical phenomena taking place within the system and to formulate the necessary model equations by combining the descriptions of partial phenomena, e. g., in series, par-

Fig. 2: General approach of impedance spectroscopy and for information extraction from impedance spectra.

allel or cascade. Thereby, different formulations can be mathematically equivalent, but only some of them provide a meaningful model and are therefore physically relevant. The extraction of information is carried out, in this case, by determination of the model parameters, which are directly related to the corresponding physical phenomena. If the formulation of the model is suitable and the parameter extraction is successful [15], the model parameter provides information about the measured quantity and shows a physically expected behavior. In this case, extracted parameters inferring the measurement quantity are directly used for the calculation of the measurement quantity.

Mathematical methods are also possible, but need a big data base with relevant experiments in order to build the necessary basis for signal processing and extraction of information. Suitable feature extraction and classification methods need to be developed in this case to discriminate between the different classes corresponding to the state of the system [14]. For this purpose, the training data and the experimental data need to be representative for the real scenario and include all relevant cases that could influence the results, such as environmental parameters, aging and contamination effects.

4 Impedance spectroscopy in measurements and sensor solutions

Impedance spectroscopy provides the possibility to follow the state of a system and to track its changes, e. g., due to aging or chemical reactions taking place. This is the case, e. g., for corrosion, battery diagnosis and bioimpedance. Especially for bat-

tery diagnosis and bioimpedance analysis, impedance spectroscopy allows to non-invasively get information about the state of a cell or a battery and to determine specific information concerning parts of it or phenomena taking place within it. In the case of conductive, capacitive and inductive sensors, impedance spectroscopy allows to measure quantities in spite of experimental limitations, to improve the accuracy or even to measure more than one quantity at the same time.

The applications for impedance spectroscopy are therefore manifold. In the next sections, we present a selection of the most important applications for impedance spectroscopy (see Fig. 3) and show the potential of this measurement method in the corresponding fields in comparison with other classical methods.

Fig. 3: Selection of impedance spectroscopy applications in measurement and sensor solutions.

5 Material characterization

For materials, impedance spectroscopy provides interesting possibilities to characterize the complex electrical behavior including resistive, capacitive and inductive behavior [5]. Thereby, it is sensitive to both surface phenomena and changes of bulk properties including conduction mechanisms.

For example, impedance spectroscopy is a well-established method, which allows quantitative characterization of corrosion processes as well as the evaluation of the anti-corrosion performance of protective coatings on corrosive metals [16]. It can be used for several purposes, among which the detection of surface and material changes due to exposure, prediction of the lifetime of corrosion protection, evaluation of coating systems, identification of the corrosion processes that lead to failures, measurement of water uptake by coatings and the development of models for coating/metal system performance.

One of the important advantages of this method is that it is a non-destructive technique. It can follow the evolution of coated metals as they undergo either natural or

artificial exposure to conditions that cause corrosive failure to provide information about the corrosion kinetics. Impedance measurements allow the prediction of the long-term performance of the coatings and track very effectively the effects of temperature, water ingress, coating plasticization and the glass transition temperature in coatings [17].

Impedance spectroscopy is interesting for electrical characterization of almost every material. It has played a big role for many years in the field of nanocomposites, which are becoming increasingly important in the field of lightweight structures and sensors. Flexible films of carbon nanotubes (CNTs) can be prepared for several sensor applications, such as strain gauges or pressure sensors showing a high sensitivity and performing under low costs. With less than 1 % filler material, input conductive and percolation-based CNT polymer composite sensors can be fabricated. Thereby, a suitable composition and homogeneity are highly demanded and should be fulfilled by the fabrication process including choice of materials, preparation of dispersion, substrate treatment and deposition techniques.

Impedance spectroscopy enables to deeply investigate the complex conductivity of the nanocomposite materials, so that they can be better optimized for certain required properties [5, 18]. For example, for highly sensitive pressure sensors based on CNT polymer nanocomposites, it is very important to realize nanocomposites at the percolation ratio [19]. The percolation ratio is the nanofiller concentration at which rarely conductive paths can be built through the nanofillers without tunneling through the polymer. At this concentration, the nanocomposite becomes more sensitive to pressure, because an increase of pressure leads to a reduction of the distance between the CNTs and therefore increasingly leads to percolation. These concentrations cannot be determined easily by experimental methods due to fluctuating processing parameters during the fabrication process.

Impedance spectroscopy is suitable for characterization of the percolation behavior, as it includes the information about both resistive and capacitive behaviors of the nanocomposite [5]. Especially the imaginary part of the impedance gives information about the average gap between nanofillers and is therefore very important for investigating percolation (see Fig. 4).

In [5] it has been shown that impedance spectroscopy measurements allow the experimental determination of the percolation threshold of the nanocomposite. At concentrations lower than the percolation ratio, the nanocomposite shows an almost purely capacitive behavior. Due to inter-tube distances, the share of capacitive behavior dominates the conduction behavior (see Fig. 4 (a)). Beyond the percolation ratio, the conductive paths dominate (see Fig. 4 (b)) and show a frequency independent behavior. The percolation region is exactly the region where the transition between these two extreme cases takes place abruptly.

This example shows that, by means of impedance spectroscopy, the percolation ratio can be determined experimentally even after film deposition. This allows tailor-

Fig. 4: CNT polymer composite. (a) Relaxed: tunneling effect, the capacitive behavior is dominating. (b) Under pressure: resistive behavior is dominating due to increasing contacts between CNTs.

ing of the piezoresistivity of strain-sensitive films based on nanocomposites for different nanofillers and even by fluctuating processing parameters.

6 Battery characterization and diagnostics

Modern battery management systems need accurate information concerning the state of charge (SoC) [20], the state of health (SoH) [21], the battery lifetime, the internal temperature and fault diagnosis within cell packs. Other methods are, e. g., voltage measurement and coulomb counting, which bring some challenges in the case of Li-ion batteries. In particular, the SoC-vs-voltage curve is very flat, so that the sensitivity of the voltage to the SoC is very low. The direct voltage measurement is not sufficient for a comprehensive diagnosis as it is dependent on SoC, temperature and current level at the same time. In general, the open-circuit voltage (OCV) provides an alternative, which can be determined at offline state, where the battery is isolated from the external circuit for a long time. In online measurement, it can be estimated from the voltage measurement by considering the internal resistance multiplied by the current [22] Coulomb counting integrates the current over time to estimate the remaining battery charge. But, due to the limited sampling rate, several current impulses may not be tracked with a high accuracy. Therefore, the coulomb counting drifts over time due to the cumulative deviation.

In contrast, impedance spectroscopy is a non-destructive method, which can estimate the remaining charge of the battery, also known as SoC and the state of health (SoH) of the battery. This is due to the fact, that battery impedance increases with aging and changes due to temperature and also different phenomena taking place at low, middle and high frequencies. Therefore, impedance spectroscopy can be used as a diagnostic tool and accurate analytical technique for measuring different critical battery parameters. It provides the possibility to get information about the inner state of the battery, including both the electrolyte and the electrodes, non-invasively and in a relatively short measurement time, without needing to carry out any cycling processes.

Impedance spectroscopy offers a solution that is independent on the leakage currents and the fluctuating voltage. This method is experimentally efficient and provides the possibility to separate effects having linear independent dispersions and dominating in different frequency ranges. It is capable to achieve real-time measurement in a relatively short measurement time as it can use wide frequency band excitation signals. As a battery ages, several phenomena occur, accompanied by a change of the overall impedance of the battery [22–24]. The SoC of the battery can be also estimated by means of impedance spectroscopy [25–28].

The battery impedance spectrum includes information about the electrolytes, diffusion layer and electrode reactions, as explained in Fig. 5. At low frequencies, in the range of mHz, processes with a high time constant are stimulated, such as migration and diffusion. Diffusion effects are dominating in this frequency range. At middle frequencies, electrode reactions dominate and may show a constant phase behavior due to electrode porosity. At high frequencies, inductive effects in the battery wiring and porous structure are dominant.

Fig. 5: Typical impedance spectrum of a battery in an exaggerated Nyquist plot. Here, R_s is the series resistance, R_1 and R_2 are the charge transfer resistances of the electrodes, C_{dl1} and C_{dl2} are the double layer capacitances of the electrodes, σ is the Warburg coefficient, R_3 is the intersection of the diffusion characteristic with the real impedance axis and L represents inductive effects.

The individual phenomena in the impedance spectrum of a cell have their own models, which can be expressed analytically or in form of equivalent circuits. Models based upon concentrated circuit elements such as capacitors, resistors and inductors can simulate some internal electrical properties of the cell. Nevertheless, especially for diffusion processes and due to electrode porosity, elements with distributed param-

ters, such as constant phase elements and Warburg impedance, are also necessary to model the impedance behavior accurately.

The impedance spectrum of a battery cell includes manifold information and the method is therefore very interesting for diagnosis. Nevertheless applying it on a battery cell involves many challenges. The low-frequency measurements at mHz frequencies need a long measurement time and involve therefore a risk of charging or discharging the battery cell and changing its state thereby. The battery impedance is low and needs to be measured with a high resolution. A big challenge in modeling impedance spectra is that the individual phenomena may overlap in the impedance spectrum. This overlapping is strongly dependent on the cell technology and also on the cell state. In the case of overlap, the separation of effects and the parameter calculation become more difficult, especially if the measured frequency is limited. The AC current distribution within cylindrical Li-ion cells depends strongly on the frequency and the temperature [29]. This may lead to limitations for deep interpretation. The cell design may overshadow some active material impedance by local inhomogeneity due to lithium plating or advanced aging. The spectrum may change its structure due to aging and models need to be adaptively adjusted to consider this effect.

Yet, the latest developments allow to realize embedded solutions for impedance spectroscopy, which realize a comparable measurement quality like sophisticated laboratory devices [21, 30] having low cost and a significantly short measurement time. This development allows to use impedance for real-time measurements on site and to determine useful information for intelligent battery management systems, such as SoH [22], SoC [20], the internal cell temperature [31] and the remaining useful battery life [32].

7 Biomedical applications and food characterization

For non-invasive tissue characterization, pathological health status investigation and diseases diagnosis, bioimpedance spectroscopy is one of the most important methods. In comparison with classical non-invasive techniques used in clinical research, such as optical spectroscopy, ultrasound and X-ray, bioimpedance spectroscopy is easy to use and safe. It can give information on the deepness of a material and helps to avoid interferences with substances reacting in the same wavelength. Therefore, impedance spectroscopy is gaining importance in the biological and food sectors and will play a more important role for the food industry in the future.

Impedance spectroscopy can be used for characterization of different biological tissues and for medical [33–37] and food applications [11, 14, 38–41], because the complex impedance gives information about the composition and the state of a biological tissue or organ. Although there are many different methods, impedance spectroscopy is often preferred.

The impedance of a muscle includes three areas of dispersion: the α dispersion at low frequencies between some Hz and some kHz, β dispersion at middle frequencies in the range from some kHz to MHz and γ dispersion at higher frequencies [14, 33, 38, 39]. The β dispersion is very informative about the state of the muscle as it provides information about the cell membranes. Therefore, impedance spectroscopy is a very promising method for assessment of meat freshness and meat characterization in general.

A lot of challenges should be overcome in the measurement of muscle impedance in order to guarantee reproducible measurements. For this, an electrode configuration has been developed to avoid influence of anisotropy and in order to realize a good contact to the biological material in spite of its fibrous structure [4, 42]. The developed probe consists of one central cylindrical electrode and eight surrounding needle electrodes made of gold-plated steel (ϕ of 1 mm) in order to avoid corrosion.

The β dispersion, corresponding to radio frequency, is strongly dependent on the dielectric properties of the cell membranes and their interactions with the extra- and intracellular electrolytes, as the current passes through the cell membranes at these frequencies. It includes information referring to the behavior of the cell membrane integrity, which changes significantly with aging (s. Fig. 6). One of the phenomena that contributes to the β dispersion is the Maxwell–Wagner effect related to the interfacial relaxation process occurring in systems where the electric current passes at the interface between two different materials.

Fig. 6: Bioimpedance measurement of a beef longissimus dorsi muscle for 14 days [14].

In [43], a method for measuring bioimpedance non-invasively is presented. It consists of magneto-inductive measurement techniques, such as gradiometers. Gradiometers consist of a sending coil and two symmetrical receiving coils. For the detection of tissue impedance, they use the difference principle between the coil on the tissue side and the coil on the other side. They can therefore detect even small changes of electrical properties of a biological tissue. This high sensitivity has the drawback that they may have different levels of detuning, which cannot be easily adjusted. In [43], a concept for adjusting the gradiometer in a predefined initial state is presented. It uses ad-

ditional coils on both sides to adjust the detuning by a suitable current flow through the additional coils and realize an accurate measurement.

Measuring bioimpedance of living beings in medical applications brings several challenges. One is the limitation of the current, which must be applied without doing any damage [46]. The medical requirements imposed by the standard IEC-60601 claim that the current should be below the perception threshold of 0.5 mA at 5 kHz [44]. The perception threshold increases when the frequency increases following the equation [45]

$$I_{\max} = 10^7 f, \quad (1)$$

where the current is the root mean square value and the frequency is in Hz.

Therefore, for *in vivo* applications, a current excitation is preferred to a voltage excitation, which can be affected by contact impedance between the electrode and the tissue and high currents through the tissue due to impedance changes or temperature dependence of the tissue conductivity.

One further challenge is the fact that living beings change their state, e. g., due to breathing, moving and blood circulation. This is why one of the approaches which can be considered is to reduce the measurement time in order to maintain the system under test under quasi-static conditions. Many researchers investigated possibilities for using wide band signals including different frequencies in order to get a spectrum in a reduced measurement time [35, 47–49]. These are typically, e. g., chirp signals [35], multisine signals, binary chirp and binary multifrequency signals [49].

In [50], a novel measurement and identification approach, called the parametric-in-time approach, has been developed for time-varying bioimpedance systems with a quasi-periodic character. This allows to conduct myocardial impedance measurements *in vivo* and *in situ*.

8 Cable fault detection and localization

The increasing use of the wiring in vehicles, production plants, communication and power systems leads to a big need for wiring faults detection and location. Experience in this area indicates that the majority of the problems encountered are due to cable errors and increased contact resistance of connectors. If the cables are long, not all methods are able to detect the fault position as signals may become weak and even concealed by noise.

There are several methods for wire fault location and characterization, of which time domain reflectometry (TDR) is the most common one. In this case, a pulse signal is sent on the cable, which is supposed to be homogenous. If the cable has a fault, a signal is reflected and this reflection can be measured to detect the position of the fault by

estimating the time of flight and the type of the reflection includes information about the type of change of the cable impedance and therefore about the type of the fault.

Over the last decade, many methods, such as frequency domain reflectometry (FDR), ultra-wide band-based TDR, spectrum TDR (STDR) and impedance spectroscopy (IS), have been developed. They use different wide band incident signals and signal processing methods, but the aim was mainly to improve the accuracy of the fault location.

In [6], impedance spectroscopy was introduced to identify both position and type of cable errors. The innovation in this approach is that the load impedance of the wire fault can be quantitatively extracted from its input impedance, so that the types of the wire faults can be exactly identified. For that, a transformation to the pseudo-frequency domain is applied to localize the wire fault, which corresponds to the periodicity of the spectrum represented in Fig. 7.

Fig. 7: Impedance spectrum of a 10-m coaxial cable with different terminating resistors. The amplitude is influenced by the terminating resistors and the periodicity of the impedance is influenced by the error position [6].

The input impedance of the wire at low frequencies is applied to identify the types of wire faults. The imaginary part of the cable impedance can be applied to detect the type of the wire fault. In the case of an open circuit, it is the capacitance of the cable. In the case of a short circuit, the inductance of the cable helps to detect the fault type.

9 Conductive, capacitive and inductive sensors

Impedance measurement has decisive benefits, as it is experimentally efficient and can be realized in low-cost embedded systems. Its advantages are particularly important in sensor technology as it delivers more information than only resistive, capacitive or inductive measurements. This is due to the fact that it uses both the real and the

imaginary part of the complex impedance at different frequencies. It provides the possibility to separate effects having linearly independent dispersions and dominating in different frequency ranges.

Impedance-based sensors can have a variety of designs and can serve for the acquisition of various measured variables (see Fig. 8 and Fig. 9). These include, e.g., position, humidity, material properties and filling level. Very often, only the real part is measured in the case of conductive sensors and the imaginary part in the case of inductive and capacitive sensors. The other part of the impedance is considered as losses and is in general ignored, even if it includes also information about the “device under test”. In some cases, the amplitude of the impedance and the measured variable is determined at a suitable sensitive frequency [53].

Fig. 8: Electrode structures for capacitive and conductive sensors.

The measurement of the impedance with its real and imaginary part at different frequencies expands the information considerably [54]. The information obtained from the sensor is representative of the measurements of a sensor array, in which each sensor is fictitiously operated at a frequency. We know from the field of multisensors that this increases the quality and reliability of the measurement and helps to achieve a better accuracy [55].

Impedance spectroscopy provides interesting possibilities for realizing a multifunctional measurement, so that one sensor measures several quantities at the same time. This provides interesting possibilities not only to reduce costs, but also to extend the information diversity from one sensor. In [13], an impedimetric sensor has been developed for the measurement of soil moisture, having a design such as in Fig. 8 (c). It measures both the real and the imaginary part of the impedance at different frequencies and is thereby able to identify the type of the soil. Similar sensors measuring only

Fig. 9: Examples of inductive sensors for characterization of materials and non-destructive material testing. (a) immersion core principle, (b) Immersion core principle transformer principle, (c) inner wall characterization of a pipe, (d) material characterisation and testing by a reflective principle, (e) material characterisation and testing by a reflective difference principle, (f) material characterisation and testing by a transmissive principle.

Fig. 10: Dependency of the imaginary part of the soil impedance on soil type and soil moisture. (a) Investigated soil types classified by their inorganic components [13]. (b) Soil imaginary part in dependence of the frequency for different soil types.

the capacitive part have massive problems with soil type influence, which leads to a high inaccuracy and needs therefore to be regularly calibrated to the corresponding soil. As can be seen in Fig. 10 (b), the changes of the imaginary part of the impedance due to moisture show a different behaviour depending on the soil type. Measuring the capacity at a certain frequency, leads to ambiguity as is not sufficient for realizing an accurate measurement. In the case of the impedimetric sensor, the measurement data serve first to the classification of the soil type by means of data reduction via principal components analysis and classification via the k-nearest-neighbor method. After soil type recognition, the moisture measurements become easy and accurate by using a linear characteristic of the imaginary part of the admittance [13].

Inductive sensors and especially eddy current sensors can be used in different manners for both distance measurement and material characterizations. The main advantages of these sensors are a.o. their robustness [56], their process capability and the fact that they operate contactless and in a non-destructive manner [57].

Yet, if the imaginary part changes more, also the real part includes interesting information. A change of frequency leads to a different penetration depth of the magnetic field in the target material (see Fig. 11) and the coil impedance can therefore give information about cracks and failures under the surface.

Fig. 11: Dependence of the eddy current effect on the frequency. (a) Schematic description of the penetration of a magnetic field in a target material in dependence of the frequency. (b) Numerical simulation of the magnetic vector potential in a ferric target material in dependence of the frequency.

10 Biosensors

Impedance spectroscopy has recently gained a high popularity for biosensing of a wide range of substances owing to its label-free measurements. It reaches thereby a superb sensitivity down to the femto- and attomolar ranges [58–60]. It allows rapid screening of biocompatible surfaces and monitoring pathogenic bacteria, as well as the analysis of biological cells and tissues.

The impedance spectroscopy transducer signal is in this case mainly based on the interactions between a certain biological receptor and the target species, which is selectively adsorbed from the solution (see Fig. 12) [61, 62]. Such interactions cause a change of the interfacial electron transfer kinetics between the solution species and the conducting electrode. The charge transfer resistance increases therefore with the increase in the quantity of targets bound to the receptive surface. Thereby, the selectivity, sensitivity, response time and detection limit are strongly dependent on the use of proper materials and catalysts [61, 63].

Fig. 12: Three-electrode electrochemical sensor. (a) Sensor element. (b) Selectivity enhancement by using template molecules. (c) Strategies for improving sensitivity by using nanoparticles and catalysts.

Because of their high affinity to biomolecules and high aspect ratio, nanomaterials, such as metal nanoparticles, CNTs and graphene, are revolutionizing electrochemical biosensors (see Fig. 12 (c)) [64, 65]. Nanomaterials are often used as electrode coating to increase their effective surface area and immobilize a large number of biomolecules such as enzymes and antibodies [65].

11 Future trends of impedance spectroscopy

The impedance spectroscopy is versatile as a method and its importance is in general increasing, as it provides interesting possibilities for characterizing materials, systems and sensors. Sensors themselves today tend to the use of high-speed and low-cost electronic circuits, allowing for increasingly more signal processing and advanced manufacturing technologies [52]. Similar aspects can be observed nowadays for impedance spectroscopy. Measurement devices use novel technologies and provide increasingly efficient solutions, enabling the use of the method in a wider range of applications.

11.1 Embedded and miniaturized solutions

Impedance spectroscopy was regarded as an electrochemical laboratory method for several decades. Today, due to the excellent developments in microelectronics, a cost-effective electronic realization becomes more and more possible. The most available embedded solutions are in general in the medical field and a lot of them are in medical implants. This trend is now increasing towards manifold solutions for sensors and diagnostic devices. In most cases, the aim is not to operate a large measuring range, but rather to find solutions that are usually limited by the requirements of a particular application.

11.2 Fast impedance spectroscopy and tomography

One of the important conditions for impedance spectroscopy is that the system does not change during measurement of the whole impedance spectrum. If the system has a higher dynamic, impedance measurement should be carried out within a short time to realize quasi-stable conditions. This is why reducing the measurement time is necessary to widen the scope of applications of impedance spectroscopy to more dynamic applications.

Many examples can be seen in impedance tomography. In this case, measurements with different electrode combinations contribute to the reconstruction of one image across the device under test. All these measurements need to be adjusted to the same system state. In order to fulfil this condition, in general only one or two relative high frequencies are measured. The development of fast impedance spectroscopy methods would enable tomography methods to better use the spectral information by involving more measurement frequencies.

11.3 Impedimetric sensors

Nowadays, in the sensor field there is an interesting trend towards multifunctional sensors, which are able to measure more than one quantity at the same time [51, 52]. Impedimetric sensors can provide more information as the impedance is measured and in a certain frequency range. The comprehensive data generated at one value of the measured quantity provide interesting possibilities to reduce influencing effects, improve the reliability of the information and even realize the measurement of more quantities at the same time. In this way, many classical capacitive, resistive or inductive sensors can reach a higher performance by using impedance spectroscopy.

Bibliography

- [1] U. Tröltzsch, O. Kanoun, and H.-R. Tränkler, "Characterizing aging effects of lithium ion batteries by impedance spectroscopy", *Electrochimica Acta*, vol. 51, no. 8–9, pp. 1664–1672, 20 January 2006.
- [2] D. Bouchaala, O. Kanoun, and N. Derbel, "Portable bioimpedance spectrometer for total frequency range of β dispersion", *Technisches Messen*, vol. 80, no. 11, pp. 373–378, November 2013.
- [3] M. Min, T. Parve, V. Kukk, and A. Kuhlberg, "An implantable analyzer of bio-impedance dynamics: Mixed signal approach", *IEEE Transactions on Instrumentation and Measurement*, vol. 51, no. 4, pp. 674–678, August 2002.
- [4] M. Guermazi, O. Kanoun, and N. Derbel, "Reduction of anisotropy influence and contacting effects in in-vitro bioimpedance measurements", *Journal of Physics Conference Series*, vol. 434, 12058, 2013.

- [5] A. Sanli, C. Müller, O. Kanoun, C. Elibol, and M. F.-X. Wagner, "Piezoresistive characterization of multi-walled carbon nanotube-epoxy based flexible strain sensitive films by impedance spectroscopy", *Composites Science and Technology*, vol. 122, pp. 18–26, 2016.
- [6] Q. Shi and O. Kanoun, "Wire fault location in coaxial cables by impedance spectroscopy", *IEEE Sensors Journal*, pp. 4465–4473, June 2013, doi: 10.1109/JSEN.2013.2269218.
- [7] Q. Shi and O. Kanoun, "Model-based identification of wire network topology", *Measurement*, vol. 55, pp. 206–211, September 2014, Elsevier.
- [8] H. Zarrok, A. Zarrouk, B. Hammouti, R. Salghi, C. Jama, and F. Bentiss, "Corrosion control of carbon steel in phosphoric acid by purpald – Weight loss, electrochemical and XPS studies", *Corrosion Science*, vol. 64, pp. 243–252, November 2012.
- [9] F. Wendler, P. Büschel, and O. Kanoun, "Efficient parameter estimation impedance-based sensors by local linear transformation", *Technisches Messen*, vol. 81, no. 9, pp. 450–456, 2014.
- [10] U. Tröltzsch and O. Kanoun, "Generalization of transmission line models for deriving the impedance of diffusion and porous media", *Electrochimica Acta*, vol. 75, no. 1, pp. 347–356, 2012.
- [11] A. Fendri, H. Ghariani, and O. Kanoun, "Dielectric spectroscopy for assessment of water content in edible oils", In: 14th International Multi-Conference on Systems, Signals and Devices, March 28–31, 2017, Marrakech, Morocco, 2017.
- [12] R. Gruden, A. Buchholz, and O. Kanoun, "Electrochemical analysis of water and suds by impedance spectroscopy and cyclic voltammetry", *Journal of Sensors and Sensor Systems*, vol. 3, pp. 133–140, 2014.
- [13] A. Tetuyev and O. Kanoun, "Method of soil moisture measurement by impedance spectroscopy with soil type recognition for in-situ applications", *Technisches Messen*, vol. 73, no. 7/8, 2006.
- [14] M. Guermazi, O. Kanoun, and N. Derbel, "Investigation of long time beef and veal meat behaviour by bio-impedance spectroscopy for meat monitoring", *IEEE Sensors Journal*, Sensors-9401, 2014.
- [15] P. Büschel, U. Tröltzsch, and O. Kanoun, "Use of stochastic methods for robust parameter extraction from impedance spectra", *Electrochimica Acta*, vol. 56, 2011, Elsevier.
- [16] G. Bierwagen, D. Tallman, J. Li, L. Hea, and C. Jeffcoate, "EIS studies of coated metals in accelerated exposure", *Progress in Organic Coatings*, vol. 46, pp. 148–157, 2003.
- [17] M. Tezeghdenti, N. Etteyeb, L. Dhouibi, O. Kanoun, and A. Al-Hamri "Natural products as a source of environmentally friendly corrosion inhibitors of mild steel in dilute sulphuric acid: Experimental and computational studies", *Protection of Metals and Physical Chemistry of Surfaces*, vol. 53, no. 4, pp. 753–764, 2017.
- [18] O. Kanoun, Chr. Müller, A. Benchirouf, A. Sanli, A. Bouhamed, A. Al-Hamry, and L. Bu, "Potential of flexible carbon nanotube films for high performance strain and pressure sensors", In: "Nanotechnology for Optics and Sensors", One Central Press, 2015, pp. 148–183.
- [19] A. Bouhamed, Chr. Müller, S. Choura, and O. Kanoun, "Processing and characterization of MWCNTs/Epoxy nanocomposites thin films for strain sensing applications", *Sensors and Actuators A, Physical*, vol. 257, pp. 65–72, 15 April 2017.
- [20] A. Cuadras and O. Kanoun, "SoC Li-ion battery monitoring with impedance spectroscopy", In: Sixth International IEEE Multi-Conference on Systems, Signals and Devices SSD'09, 23–26 March 2009, Jerba, Tunisia.
- [21] A. Otto, S. Rzepka, T. Mager, B. Michel, C. Lanciotti, T. Günther, and O. Kanoun, "Battery management network for fully electrical vehicles featuring smart systems at cell and pack level", In: 16th International Forum on Advanced Microsystems for Automotive Applications, AMAA 2012, pp. 3–14, 30–31 May 2012, Berlin, Germany.

- [22] M. Bercibar, I. Gandiaga, I. Villarreal, N. Omar, J. Van Mierlo, and P. Van Den Bossche, "Critical review of state of health estimation methods of Li-ion batteries for real applications", *Renewable and Sustainable Energy Reviews*, vol. 56, pp. 572–587, 2016.
- [23] D. Stroe, M. Swierczynski, A. Stroe, and R. Teodorescu, "Lithium-ion battery power degradation modelling by electrochemical impedance spectroscopy", *IET Renewable Power Generation*, vol. 11, no. 9, pp. 1136–1141, 2017.
- [24] U. Tröltzsch, O. Kanoun, and H.-R. Tränkler, "Characterizing aging effects of lithium ion batteries by impedance spectroscopy", *Electrochimica Acta*, vol. 51, no. 8–9, pp. 1664–1672, 2006, doi: 10.1016/j.electacta.2005.02.148, issn: 0013-4686 (cit. on pp. 3, 159).
- [25] S. Srivastav, M. J. Lacey, and D. Brandell, "State-of-charge indication in Li-ion batteries by simulated impedance spectroscopy", *Journal of Applied Electrochemistry*, vol. 47, no. 2, pp. 229–236, 2017.
- [26] D. Stroe, M. Swierczynski, A. Stroe, and S. K. Kær, "Generalized characterization methodology for performance modelling of Lithium-Ion batteries", *Batteries*, vol. 2, no. 4, p. 37, 2016, doi: 10.3390/batteries2040037.
- [27] T. Kazuhiko, I. Masahiro, T. Kazuo, Y. Junichi, and O. Shigeto, "Quick testing of batteries in lithium-ion battery packs with impedance-measuring technology", *Journal of Power Sources*, vol. 128, no. 1, pp. 67–75, 2004.
- [28] A. Cuadras and O. Kanoun, "SoC Li-ion battery monitoring with impedance spectroscopy", In: *6th International Multi-Conference on Systems, Signals and Devices (SSD'09)*. 2009, pp. 1–5, doi: 10.1109/SSD.2009.4956761.
- [29] P. J. Osswald, S. V. Erhard, A. Noel, P. Keil, F. M. Kindermann, H. Hoster, and A. Jossen, "Current density distribution in cylindrical Li-Ion cells during impedance measurements", *Journal of Power Sources*, vol. 314, pp. 93–101, 2016.
- [30] T. Günther, P. Büschel, and O. Kanoun, "Eingebettetes Impedanzmesssystem für das Batteriemanagement in Elektrofahrzeugen", *Technisches Messen*, vol. 81, no. 11, pp. 560–565, 2014, doi: 10.1515/teme-2014-1052.
- [31] R. R. Richardson, P. T. Ireland, and D. A. Howey, "Battery internal temperature estimation by combined impedance and surface temperature measurement", *Journal of Power Sources*, vol. 265, pp. 254–261, Nov. 2014, doi: 10.1016/j.jpowsour.2014.04.129.
- [32] J. Wu, C. Zhang, and Z. Chen, "An online method for lithium-ion battery remaining useful life estimation using importance sampling and neural networks", *Applied Energy*, vol. 173, pp. 134–140, 2016.
- [33] U. G. Kyle, I. Bosaeus, A. D. De Lorenzo, P. Deurenberg, M. Elia, J. M. Gómez, B. L. Heitmann, L. Kent-Smith, J.-C. Melchior, M. Pirlich, H. Scharfetter, A. M. W. J. Schols, and C. Pichard, "Bioelectrical impedance analysis - Part I: Review of principles and methods", *Clinical Nutrition*, vol. 23, no. 5, pp. 1226–1243, October 2004.
- [34] U. M. Moissl, P. Wabel, P. W. Chamney, I. Bosaeus, N. W. Levin, A. Bosy-Westphal, O. Korth, M. J. Müller, L. Ellegård, V. Malmros, C. Kaitwatcharachai, M. K. Kuhlmann, F. Zhu, and N. Fuller, "Body fluid volume determination via body composition spectroscopy in health and disease", *Physiological Measurement*, vol. 27, no. 9, pp. 921–933, Article number 012, 1 September 2006.
- [35] M. Min and T. Parve, "Improvement of lock-in electrical bio-impedance analyzer for implantable medical devices: Contactless sensing of the conductivity of aqueous droplets in segmented flow", *IEEE Transactions on Instrumentation and Measurement*, vol. 56, no. 3, pp. 968–974, 2007.
- [36] B. Sanchez, G. Vandersteen, I. Martin, D. Castillo, A. Torrego, P. J. Riu, J. Schoukens, and R. Bragos, "In vivo electrical bioimpedance characterization of human lung tissue during the

- bronchoscopy procedure. A feasibility study”, *Medical Engineering and Physics*, vol. 35, no. 7, pp. 949–957, 2013.
- [37] H. Morgan, T. Sun, D. Holmes, S. Gawad, and N. G. Green, “Single cell dielectric spectroscopy”, *Journal of Physics D, Applied Physics*, vol. 40, no. 1, S10, pp. 61–70, 2006.
- [38] U. Pliquet, “Bioimpedance: A review for food processing”, *Food Engineering Reviews*, vol. 2, no. 2, pp. 74–94, June 2010, doi: 10.1007/s12393-010-9019-z.
- [39] M. Guerhazi, U. Tröltzsch, O. Kanoun, and N. Derbel, “Influence of meat aging on modified Fricke model’s parameter”, In: O. Kanoun, *Lecture Notes on Impedance Spectroscopy*, vol. 3. Taylor and Francis, 2012.
- [40] A. Chowdhury, T. Kanti Bera, D. Ghoshal, and B. Chakraborty, “Electrical impedance variations in banana ripening: An analytical study with electrical impedance spectroscopy”, *Journal of Food Process Engineering*, vol. 40, no. 2, Article number e12387, 1 April 2017, doi: 10.1111/jfpe.12387.
- [41] A. Abdelkafi, P. Büschel, A. Fendri, and O. Kanoun, “Impedance investigation of milk dilution”, In: *AMA Sensor and Test*, 19–21 May 2015, Nuremberg, Germany, pp. 156–159, doi: 10.5162/sensor2015/A7.2, 2015.
- [42] M. Guerhazi, U. Tröltzsch, O. Kanoun, and N. Derbel, “Assessment of beef meat aging using impedance spectroscopy”, In: *8th International Multi-Conference on Systems, Signals and Devices*, Sousse, Tunisia. 22–25 March 2011, pp. 1–6, doi: 10.1109/SSD.2011.5767450.
- [43] M. Heidary Dastjerdi, O. Kanoun, and J. Himmel, “Verfahren zum Abgleich von Gradiometern für medizinische Anwendungen”, *Technisches Messen*, vol. 83, no. 5, pp. 247–256, 2016.
- [44] D. Bouchaala, O. Kanoun, and N. Derbel, “High accurate and wideband current excitation for bioimpedance health monitoring systems”, *Measurement*, vol. 79, pp. 339–348, February 2016.
- [45] B. H. Brown, J. A. Tidy, K. Boston, A. D. Blacket, R. H. Smallwood, and F. Sharp, “Relation between tissue structure and imposed electrical current flow in cervical neoplasia”, *Lancet*, 2000, pp. 892–895, doi: 10.1016/S0140-6736(99)09095-9.
- [46] D. Bouchaala, M. Guerhazi, N. Derbel, and O. Kanoun, “Portable device design for in-vitro muscle tissue monitoring”, *tm – Technisches Messen*, vol. 82, no. 10, pp. 485–494, 2015.
- [47] M. Min, U. Pliquet, T. Nacke, A. Barthel, P. Annus, and R. Land, “Broadband excitation for short-time impedance spectroscopy”, *Physiological Measurement*, vol. 29, no. 6, pp. 185–192, 2008.
- [48] Y. Yang, F. Zhang, K. Tao, L. Wang, H. Wen, and Z. Teng, “Multi-frequency simultaneous measurement of bioimpedance spectroscopy based on a low crest factor multisine excitation”, *Physiological Measurement*, vol. 36, no. 3, pp. 489–501, 1 March 2015.
- [49] D. Bouchaala, E. Mekki, T. Guenther, P. Bueschel, O. Kanoun, and N. Derbel, “Study of excitation signals parameters for portable biomedical devices”, In: *IEEE International Instrumentation and Measurement Technology Conference*, 11–14 May 2015, Pisa, Italy, 2015, pp. 784–788.
- [50] B. Sanchez, E. Louarroudi, E. Jorge, J. Cinca, R. Bragos, and R. Pintelon, “A new measuring and identification approach for time-varying bioimpedance using multisine electrical impedance spectroscopy”, *Physiological Measurement*, vol. 34, no. 3, pp. 339–357, March 2013.
- [51] H.-R. Tränkler, O. Kanoun, and D. Pawelczak, “Technology, signal processing and applications: Charm of sensors”, In: *IEEE International Conference on Systems, Signals and Devices (SSD’07)*, 19–22 März 2007, Hammamet, Tunisia.
- [52] O. Kanoun and H.-R. Tränkler, “Sensor technology advances and future trends”, *IEEE Transactions on Instrumentation and Measurement*, ISSN 0018-9456, vol. 53, no. 6, 2004.

- [53] H.-R. Tränkler, O. Kanoun, M. Min, and M. Rist, “Smart sensor systems using impedance Spectroscopy”, *Proceedings of the Estonian Academy of Sciences*, vol. 13, no. 4, pp. 455–478, 2007, ISSN 1406-0175.
- [54] O. Kanoun, “Untersuchungen zu Sensoren mit variierter Anregung”, *Technisches Messen*, vol. 73, no. 7/8, pp. 382–392, 2006, 69(4/2002), doi: 10.1524/teme.2002.69.4.187.
- [55] H.-R. Tränkler and O. Kanoun, “Improvement of sensor information using multi-sensor and model-based sensor systems”, In: *IEEE Instrumentation and Measurement Technology Conference*, pp. 2259–2263, 17–19 Mai 2005, Ottawa, Ontario, Canada.
- [56] T. Morgenstern, R. Brodskiy, J. Weidenmüller, O. Kanoun, and J. Himmel, “3D Eddy current modelling for non destructive crack detection”, *Lecture Notes on Impedance Spectroscopy*, vol. 5: Taylor and Francis, 2015, pp. 65–71.
- [57] M. Heidary Dastjerdi, O. Kanoun, D. Rüter, K. Thelen, J. Weidenmüller, and J. Himmel, “Magnetic field topologies for fast impedance mapping of biological tissue”, In: *International Workshop on Impedance Spectroscopy (IWIS)*, 26–28 September 2012, Chemnitz, p. 52.
- [58] D. Grieshaber, R. MacKenzie, J. Vörös, and E. Reimhult, “Electrochemical biosensors - Sensor principles and architectures”, *Sensors*, vol. 8, no. 3, pp. 1400–1458, March 2008.
- [59] E. B. Bahadır and M. K. Sezgintürk, “A review on impedimetric biosensors”, *Artificial Cells, Nanomedicine, and Biotechnology*, vol. 44, no. 1, pp. 248–262, 2016, doi: 10.3109/21691401.2014.942456.
- [60] J. Munoz, R. Montes, and M. Baeza, “Trends in electrochemical impedance spectroscopy involving nanocomposite transducers: Characterization, architecture surface and bio-sensing”, *Trends in Analytical Chemistry*, vol. 97, pp. 201–215, 2017.
- [61] M. Hnaïen, F. Lagarde, J. Bausells, A. Errachid, and N. Jaffrezic-Renault, “A new bacterial biosensor for trichloroethylene detection based on a three-dimensional carbon nanotubes bioarchitecture”, *Analytical and Bioanalytical Chemistry*, vol. 400, no. 4, pp. 1083–1092, May 2011.
- [62] R. Pruna, F. Palacio, A. Baraket, N. Zine, A. Streklas, J. Bausells, A. Errachid, and M. López, “A low-cost and miniaturized potentiostat for sensing of biomolecular species such as TNF- α by electrochemical impedance spectroscopy”, *Biosensors and Bioelectronics*, vol. 100, pp. 533–540, 15 February 2018.
- [63] I. O. K’Owino and O. A. Sadik, “Impedance Spectroscopy: A powerful tool for rapid biomolecular screening and cell culture monitoring”, *Electroanalysis*, vol. 17, no. 23, pp. 2101–2113, 2005, doi: 10.1002/elan.200503371.
- [64] S. Z. Mousavisani, J.-B. Raoof, A. P. F. Turner, R. Ojani, and W. C. Mak, “Label-free DNA sensor based on diazonium immobilisation for detection of DNA damage in breast cancer 1 gene”, *Sensors and Actuators B, Chemical*, vol. 264, pp. 59–66, 1 July 2018.
- [65] B. Wang, U. Akiba, and J. Anzai, “Recent progress in nanomaterial-based electrochemical biosensors for cancer biomarkers: A review”, *Molecules*, vol. 22, no. 7, 2017.