The Power of Electrochemical Impedance Techniques

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Introduction

Electricity and electrical phenomena pervade our lives. Electricity lights and heats our homes, powers our industrial society, is at the heart of the electronics and IT revolutions and is the basis of much of biology. Without electricity our cells and organs could not function.

Many physical or chemical phenomena give rise to a specific electrical response on application of an electrical stimulus. Consequently, electrical measurements are widely used in a variety of environments that include test and measurement applications in such fields as corrosion, batteries and fuel cells, electroplating, coatings, medicine and materials characterisation in general. The application of these measurements may use either AC or DC based methods.

All electrical measurements involve the application of a voltage and the measurement of the resulting current, or vice versa. In the case of DC measurements a constant voltage or current is applied. However, by adding the simple variable of frequency (or its reciprocal time) i.e. making AC measurements, this gives a wealth of information on the electrical properties of a system compared to DC measurements. AC measurements have long been used in the semiconductor industry to characterise devices, but in other industrial and medical sectors its use has been much more limited than DC. For example, DC measurements dominate the on-line quality control of batteries in the factory where cells are subjected to DC drain tests. Despite the theoretical ability of AC to give diagnostic information about materials, devices and in medicine, its use has been limited because traditionally it has required large complex equipment, relatively long data collection times (up to several hours) and complex analysis of the results.

Electrochemical Impedance Spectroscopy (EIS)

The Measurement Method

In recent years the specific AC measurement technique of Electrochemical Impedance Spectroscopy (EIS) has established itself as a key method in fundamental and applied electrochemistry as well as in materials science. The measurement relies on the application of a small alternating signal through the sample while monitoring the response. In many systems the response varies as the frequency of the applied signal changes.

By changing the frequency of the applied signal, an impedance spectrum is obtained that is unique to the sample under investigation, thus providing valuable insights into its physical and chemical properties.

For portable use most existing EIS devices are not practical, and any clinical system used must comply with General Medical Safety requirements such that medical applications are limited to systems that include suitable protection for a patient and user. Traditional impedance measurement systems generally remain a significant size and weight which certainly hinders mobility and application in the field.

There are generally two approaches for measurement of impedance spectra [1]. The first is in the frequency domain based on a series of sequentially applied small amplitude sinusoidal signals to a sample each at a known frequency. The response of a system to a DC voltage is expressed by the opposition to the flow of charge $R = V / i$, where R is the resistance, V is the voltage and i is the current. In the case of AC the response has two parameters, the opposition to flow of charge (same as DC) given by $Z = V_{max} / i_{max}$, and the difference in phase between the sinusoidal voltage and sinusoidal current, θ, as shown in Figure 1.

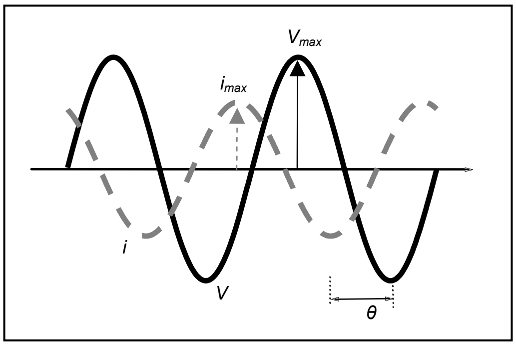

Figure 1 Representation of applied and response waveforms in an ac technique.

The impedance (combination of magnitude and phase difference) can be expressed as Z and θ by the in-phase (real) and out-of-phase (imaginary) components. To construct an impedance spectrum, this single-sine technique requires a number of measurements to be performed at discrete frequencies in a sequential manner as represented in Figure 2. The total measurement time is therefore the sum of the application times of all the waveform cycles.

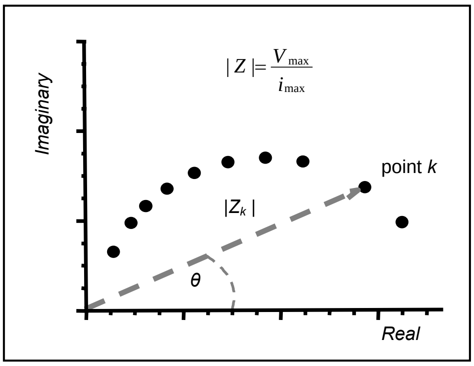

Figure 2 Impedance spectrum in the Nyquist (or Cole-Cole) plane.

The second approach operates in the time domain where a multi-frequency waveform is applied to the sample [2,3]. The measured response is then converted by Fast Fourier Transform (FFT) to the frequency domain and the impedance spectrum is calculated. In this multi-sine technique the source waveform is constructed by the summation of sinusoids. An example construction of a pseudo-random noise output waveform for an EIS measurement is shown in Figure 3.

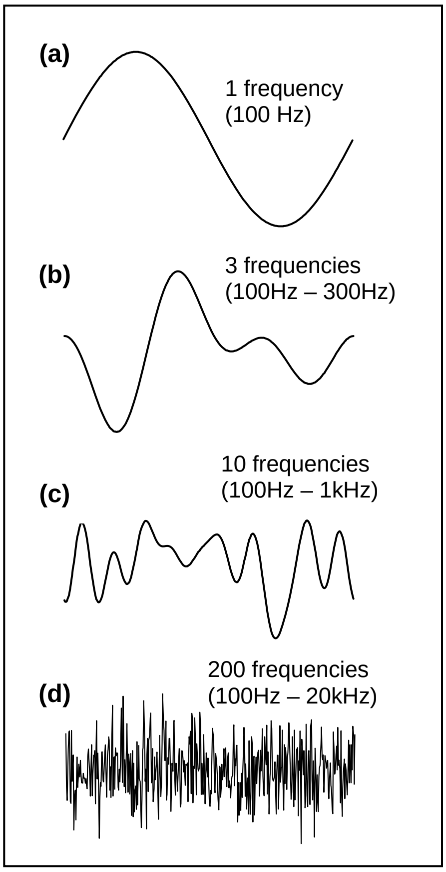

Figure 3 Construction of example pseudo-random noise output waveforms.

While the generated composite source signal resembles noise, it is actually a highly structured waveform that combines the characteristics of each discrete frequency. The most significant advantage of this multi-sine method is the measurement speed since the entire spectrum of frequencies is applied in only a cycle period of the lowest frequency.

Analysing the Measurements

The electrical behaviour of any material, biological or otherwise, can be described in terms of a combination of electrical components known as an equivalent circuit [1,4]. Each component, usually a resistor or capacitor, represents a separate response of the material to the electrical stimulus. This can be illustrated by a simple example. The electrical characteristics of an ionically conducting solution are represented by a resistor corresponding to the drift of the ions in parallel with a capacitor corresponding to the polarisation of the immobile atoms. On application of an alternating current the solvated ions move back and forth in phase with the applied electric field, alternately accumulating and depleting at each electrode surface. The energy required to move the ions through the solution depends on the ion mobility and the physical properties of the solvent. The opposition to the flow of charge during migration of ions through the bulk solution creates an electrical resistance, termed the bulk resistance, R_b. In addition to the movement of ions through a solution, there are also polarisation contributions from solvent molecules and solvated ions that orientate themselves with the applied field on a time-averaged scale. Under appropriate conditions (frequency range and cell geometry), this molecular polarisation is observed as a capacitive contribution termed the bulk capacitance, C_b. The migration of ions and the orientation of solvent molecules occur simultaneously in the solution and so the bulk resistor and capacitor are placed in parallel in the equivalent circuit model of an ideal system, shown in Figure 4.

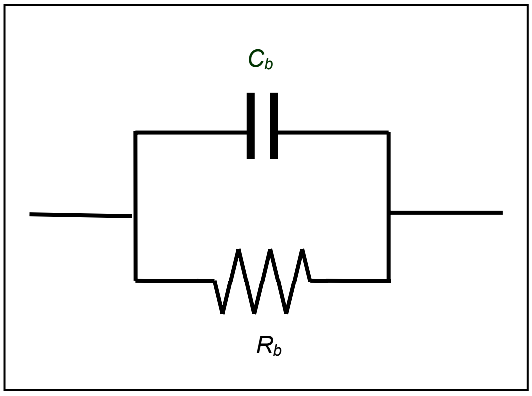

Figure 4 Equivalent circuit model for an ideal electrolyte solution.

More complex materials are represented by more complex equivalent circuits. However these are generally more complex arrangements of resistors and capacitors, and the principles are the same. The key point is that with DC only the total of the resistances can be obtained whereas by varying the AC frequency each resistor and capacitor can be measured allowing a complete characterisation of the material or device.

Applications

Overview

In many systems the impedance varies as the frequency of the applied signal changes in a way that provides valuable insights into its physical and chemical properties [1]. Therefore multi-frequency techniques such as EIS provide much more information about a system under study than other methods that apply a signal at only a single frequency. For this reason, variable frequency techniques have uses in industries that include civil engineering [5], aerospace, automotive, defence, battery R&D [6-9], biomedical [4,10,11] and non-destructive testing with applications ranging from corrosion prevention and control [12] to dental caries diagnosis [13-15] and electrochemical impedance tomography (EIT) in medicine [16].

Electrical impedance of biological matter, also known as bioimpedance, depends on many physiological parameters and phenomena that are difficult to model. Impedance characterisation is, however, still suitable for many medical applications because it provides high sensitivity, is minimally invasive and gives real-time measurements with relatively easy and practical implementation. In terms of the design of future products, the key device features will likely be small size (hand-held), non-invasive, and portable. These features are all important for applications on the point of care market, which will drive the diagnostic sector in the future.

There are a number of applications where EIS is already in routine use and others where opportunities may exist for such a method to satisfy an unmet need. While the following examples are by no means exhaustive, the diversity of such applications discussed briefly highlights the importance of electrochemical impedance spectroscopy.

Material Characterisation

The AC response of the simplest material, an ideal insulator (dielectric) is represented by a pure capacitor corresponding to orientation of the dielectric's dipoles in the electric field. In reality dielectrics will exhibit a leakage current and this is represented by a resistor in parallel with the capacitor. Relaxation of the dielectric is represented by a resistor in series with the capacitor. Conductors, whether electronic or ionic, are represented by a parallel combination of a resistor and capacitor (as discussed above). If the material is a polycrystalline ceramic, then two parallel RC elements in series are required to represent the bulk (intra-grain) and grain boundary (inter-grain) conduction processes.

Energy Storage

Electrochemical techniques are very helpful for evaluation of batteries and cells during charge and discharge, and in service, since the nature of chemical and electrochemical processes occurring in these devices can be determined [6-9]. In comparison with DC electrochemical techniques, EIS has some significant advantages offering information such as:

- Analysis of state-of-charge
- Early identification of possible cell failure
- Early identification of cell aging
- Study of reaction mechanisms
- Change of active surface during operation
- Separator evaluation
- Passivating film behaviour
- Identification of possible electrode corrosion processes

Due to the advantages of EIS, this technique is now widely applied to the study of batteries and fuel cells in the laboratory. However, there is major scope for the use of modern, fast, EIS measurements in quality control as well as in cell monitoring as part of the battery management system. The market is moving to higher performance batteries, lithium batteries in particular. These now dominate the high value consumer electronics sector with production reaching 2 billion in 2006 and growing. This is a $10 billion industry annually. Storing more energy than traditional batteries is the key to their success. However, manufacturing such high energy density batteries requires much stricter quality control than before. The Sony share price dropped by 3% due to a recent highly publicised safety incident, so ensuring safe operation is vital to the business. EIS techniques have the potential to give much improved quality control. In the future lithium batteries will be used in vehicles (hybrid and electric vehicles) with 200 cells per battery. Safety is the most important issue.. Batteries have to be continually monitored and controlled and EIS can provide a valuable diagnostic tool embedded within the Battery Management System.

Corrosion inspection

Corrosion is a widespread and costly process. It is the ultimate end of life for most metal structures and costs businesses and economies billions of dollars. Few methods of corrosion inhibition can be applied and then left unattended. Corrosion protection of engineering structures with selected coatings is commonly used worldwide but degradation of such coatings does occur leading to an underlying metallic corrosion problem. Successful long-term anti-corrosion measures require monitoring so that early problems may be detected and dealt with. Catastrophic failure can be avoided, which would otherwise lead to expensive replacement (bridges) or loss of life. Some DC electrochemical techniques have already been applied in the evaluation process with only limited success. A field portable inspection unit applying EIS measurements, however, could provide a fast, non-destructive and quantitative method of assessing coating properties and identify the early onset of steel corrosion.

Dental

Dental caries is the progressive demineralisation of tooth structure by organic acids produced from plaque bacteria and is the most prevalent disease of mankind. Early detection of dental caries is extremely important as it can allow treatment of the disease prior to the development of a cavity, increasing the effectiveness of existing preventive measures to remineralise the tooth surface and minimising the need for restorative treatment. The avoidance of restoration or removal of teeth due to caries has obvious advantages for patients, treatment providers and treatment funders. Traditional methods of caries detection based on visual, tactile or radiographic evidence are well known to be unreliable[17] and, due to the more recent changes in caries disease progression and epidemiology, it has become increasingly difficult to detect. There is a need for a detection system for dental caries that is more able to discriminate enamel loss or gain.

Impedance methods have been demonstrated as being capable of distinguishing between different dental sites that were sound from those that possessed early caries lesions or established caries [13]. This method was later discussed in the context of its application to clinical trials [14]. With the growing trend towards preventative dental care, a portable diagnostic aid provides practitioners with more opportunity to arrest or even reverse decay. Caries detection using EIS is comfortable for the patient and as a commercial system using this platform to detect decay, it has none of the inherent risks associated with ionising X-ray radiation.

Skin Cancer

The timely diagnosis and treatment of melanoma, during the earliest stages of its evolution, is of critical importance to patient survival. It is known that electrical impedance measurements can provide information about the physiological condition of living tissue [4,10,11]. The electrical impedance of biological tissue (bio impedance) is dependent on many parameters, including tissue dimensions, the ratio between extra and intra cellular volume, the ionic composition of cells and the manner in which the cells are packed. Some of these parameters are influenced by the pathological condition of the tissue. Accordingly, bioimpedance measurements may be used to diagnose abnormal tissue states, such as cancer.

Since the commercial use of electrical impedance techniques is attracting increased interest, there is a desire to provide an improved electrical impedance probe, monitoring system, and method of measuring that can provide accurate results at high resolution. While some early devices exist, they have not yet been widely accepted by the medical field mainly due to the partially invasive nature of the products. A compact and reliable device remains elusive that can be used by medical practitioners and scientists alike to make electrical impedance measurements on biological material.

Bone Mineral Density

Osteoporosis is a devastating disease that affects more than 10 million people in the US alone, with annual costs in excess of $13.5 billion. According to the US Surgeon General's Report [18] by the year 2020 half of all Americans older than 50 years will be at risk of an osteoporotic fragility fracture. Osteoporosis is characterized by low bone mass and structural deterioration of bone, leading to bone fragility and an increased tendency to fracture. Fracture resistance is determined by the strength of the bone, The most frequently used clinical indication of osteoporosis and fracture risk is bone mineral density (BMD) which is also the most readily accessible non-invasive measure of bone mineral content [19].

X-ray based methods have been used extensively for many years offering information on the bone geometry and, to some extent, its substructure geometry together with some information of general bone density. Dual Energy X-ray Absortiometry, or DEXA, is today's established standard. Another useful technique is that of magnetic resonance imaging (MRI) which can provide very detailed information upon the internal structure of the bone tissue. However, both X-ray and MRI techniques are required to be performed by trained staff and involve large, expensive hardware which are usually only available in well equipped laboratories and hospitals.

Sierpowska *et al* reported a correlation between electrical parameters and the composition of bones [20]. Electrical signals may be applied to a number of regions of the human body, including a hip, heel, selected vertebrae or to a forearm. A recent international patent submission [21] compares the analysis of impedance measurements against BMD values from DEXA using suitable statistical methods and therefore demonstrating the applicability of this impedance method.

Imaging

The medical application of impedance technology requires that the characteristics of 'normal' tissues are used as a reference for the measurements recorded from patient's tissues (either in-vivo or ex-vivo). The 'normal' characteristics of various tissues are a function of the integrity of the cellular structures within that tissue. Disease processes such as neoplasia have a fundamental impact on these characteristics. If point measurements taken from the sample tissue fall outside of the 'normal' range, then the tissue at the site of sampling can be identified as 'abnormal.'

Electrical Impedance Tomography (EIT) uses the same measurement of impedance as described earlier, but delivered via multiple electrode pairs to generate an image of the tissue being tested [4,16]. Using this technique, areas of 'abnormal tissue' can be identified and located within a defined anatomical structure such as a neoplastic lump within breast tissue. A multichannel impedance platform may therefore be applied to make point measurements or to provide images.

Measurement Platform

A market ready impedance platform as a fully embedded handheld device has been developed [22]. The CarieScan PRO is a handheld device for dental caries detection implementing an impedance measurement system with multiple measurement channels that operates in the frequency domain. An earlier development phase from produced a further commercial platform using the rapid time domain approach also with multiple measurement channels. Both impedance platforms are protected by UK Patent[23]. Equivalent patent and design applications are pending in other countries.

This device applies a frequency sweep to the sample and analyses each spectrum in <1s. A custom algorithm is then implemented to extract the diagnostic score based on the recorded impedance values and mapped against a clinical reference. The system is intended to be run autonomously or be linked wirelessly via Bluetooth™ to a supporting pc for data acquisition and embedded software maintenance. This commercial device satisfies the requirements of the Medical Device Directive 93/42/EEC with primary product approvals and international standards fulfilled.

During development the measurement performance was benchmarked against a calibrated Solartron® frequency response analyzer (FRA) model 1260 which can be regarded as an industry standard. In this way the error response for the impedance and phase as a function of frequency was determined to be within ±1% for frequencies between 1kHz and 10kHz. At higher frequencies the error increases, due mainly to the effect of the parasitic capacitance. In general, however, the error remains below 3% in impedance magnitude and 3º in phase across the entire frequency range. A comparison of impedance spectra recorded by the CarieScan PRO and the benchmark Solartron FRA1260 is shown Figure 5.

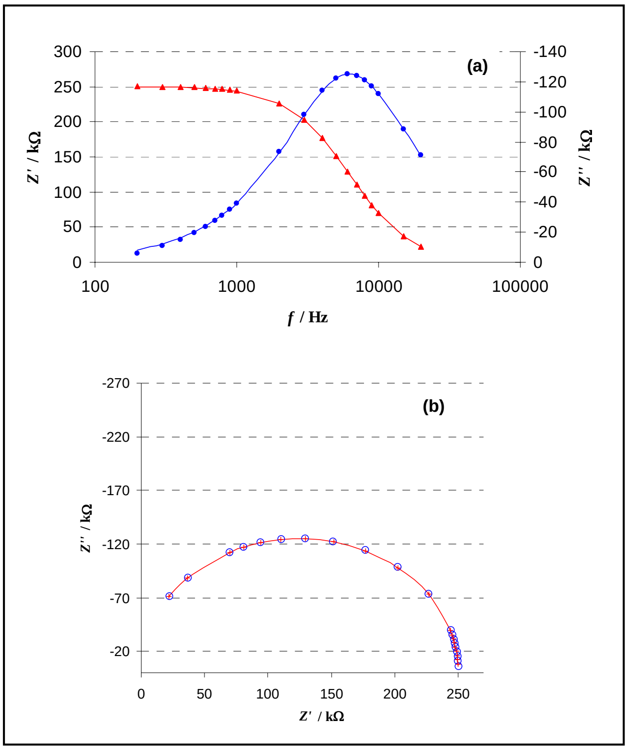

Figure 5 Comparison of CarieScan impedance platform (points) against the industry standard (line). (a) Bode plane and (b) Nyquist plane.

Summary

Electrical phenomena are ubiquitous in nature. Simple measurements of DC current are widely used to characterise many processes but are limited in the information they provide. AC measurements, especially electrochemicaal impedance spectroscopy (EIS), can, in contrast, characterise all the electrical responses of matter whether materials or biological. A sinusoidal voltage is applied and the corresponding sinusoidal current measured, with the relationship being described by the impedance. By measuring the impedance over a range of frequencies a wealth of diagnostic information is available in fields ranging from batteries to dentistry. As a portable platform, opportunities exist for development of devices for battery quality control and management, assessment of corrosion protection coatings, earlier detection of dental caries and other medical applications including cancer detection and screening for osteoporosis.

The CarieScan impedance platform is an electrochemical measurement system that provides a portable, cost effective alternative to existing benchmark equipment. It can collect, process, analyse and output the results of multiple frequency measurements in less than 1 second. While the first market ready product clearly demonstrates its applicability to dental diagnostics, it could be considered a platform for a number of diverse applications. Its measurement accuracy is >95% which, together with its small size, low power consumption and ultra-low applied current, makes it suitable for a wide range of medical and other applications.

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