

Une Plate-Forme Sans Fil pour Electrochimique Spectroscopie D'impédance

Mémoire

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Résumé

Avec l'émergence soutenue de capteurs et de dispositifs électrochimiques innovants, la spectroscopie d'impédance électrochimique est devenue l'un des outils les plus importants pour la caractérisation et la modélisation de la matière ionique et de l'interfaçage des capteurs. La capacité de détecter automatiquement, à l'aide de dispositifs électrochimiques peu couteux, les caractéristiques physiques et chimiques de la matière ionique ouvre une gamme d'application très variée pour la compréhension et l'optimisation des procédés ou interviennent les processus électrochimiques.

Cette thèse décrit le développement d'une plate-forme microélectronique miniaturisée, connectée, multiplexée, et à faible coût pour la spectroscopie d'impédance diélectrique (SID) conçue pour les mesures électrochimiques *in-situ* et adaptée aux architectures de réseau sans fil. La plate-forme développée durant ce travail de maitrise a été testée et validée au sein d'une maille ZigBee et a été en mesure d'interfacer jusqu'à trois capteurs SID en même temps et de relayer l'information à travers le net Zigbee pour l'analyse de données et le stockage. Le système a été construit à partir de composants microélectroniques disponibles commercialement et bénéficie des avantages d'une calibration système *on-the-fly* qui effectue la calibration du capteur de manière aisée.

Dans ce mémoire de maitrise, nous rapportons la modélisation et la caractérisation de senseurs électrochimiques de nitrate; notamment nous décrivons la conception microélectronique, la réponse d'impédance de Nyquist, la sensibilité et la précision de la mesure électrochimique, et les résultats de tests de la plate-forme pour les applications de spectroscopie d'impédance relatives à la détection du nitrate, de la détection de la qualité de l'eau, et des senseurs tactiles.

Abstract

The emergence of the various applications of electrochemical sensors and devices, electrochemical impedance spectroscopy became one of the most important tools for characterizing and modeling of the material and interfacing the sensors. The ability to sense in an automatic manner enables a wide variety of processes to be better understood and optimized cost-effectively.

This thesis describes the development of a low-cost, miniaturized, multiplexed, and connected platform for dielectric impedance spectroscopy (DIS) designed for *in-situ* measurements and adapted to wireless network architectures. The platform has been tested and used as a DIS sensor node on a ZigBee mesh and was able to interface up to three DIS sensors at the same time and relay the information through the Zigbee net for data analysis and storage. The system was built from commercial microelectronics components and benefits from an on-the-fly calibration system that makes sensor calibration easy.

The thesis reports characterizing and modeling of two electro-chemical devices (i.e. nitrate sensor and optically-transparent electrically-conductive glasses) and also describes the microelectronics design, the Nyquist impedance response, the measurement sensitivity and accuracy, and the testing of the platform for in-situ dielectric impedance spectroscopy applications pertaining to fertilizer sensing, water quality sensing, and touch sensing.

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List of Acronyms

AC	Alternative current
ADC	Analog-to-digital converter
Ag	Silver
AFE	Analog Front End
BAWIS	Bulk acoustic wave impedance sensor
BEHP	Bis(2-ethylhexyl) phthalate
Cl	Chloride
CMOS	Complementary metal-oxide-semiconductor
CNT	Carbon nanotube
CPE	Constant phase elements
CSC	Co(II)-salophen complex
DC	Direct current
DDS	Direct digital synthesis
DFT	Discrete Fourier transform
DIS	Dielectric impedance spectroscopy
DME	Dropping mercury electrode
DPP	Differential pulse polarography
DUT	Device under test
EC	Electrical conductivity
EIS	Electrochemical impedance spectroscopy
FDR	Frequency domain reflectometry
I2C	Inter integrated circuit bus
IEC	International Electro-technical Commission
IoT	Internet of Things
IS	Impedance spectroscopy
ISO	International Organization for Standardization
ITO	Indium tin oxide
ITO	Indium-Tin-Oxide
KCI	Potassium chloride
Li	Lithium
LR-WPANs	Low rate wireless personal area network
MCU	Micro-controller unit
Mn	Manganese
Ν	Nitrogen
NEA	Nitrite electrodes
NED	N-(1-naphtyl) ethylenediamine dihydrochlorid
Ni	Nickle
NiTMTAA	Tetramethyl-cyclotetra-decanato-nickel

NO ₃	Nitric oxide
NPS	Nitrate, phosphate, sulfate sensor
0	Oxygen
ORP	Oxygen reduction potential
OSC	Oscillator
PA	Precision agriculture
PCB	Printed current board
ppm	Parts per million
PU	Polyurethane
PVC	Polyvinyl chloride
RF	Radio frequency
SA	Sulfanilic acid
SAMs	Self-assembled monolayers
SCE	Saturated calomel electrode
TDR	Time domain reflectometry
TDT	Time domain transmission
THF	Tetrahydrofuran
UART	Universal asynchronous receiver/transmitter
USD	United States dollar
VWC	Volumetric water content
YSZ	Yttria stabilized zirconia

List of Symbols

°C	Celsius
А	Area
С	Capacitance
d	Distance
E	Electrical potential
E_{ω}	Frequency-dependent potential
f	Frequency
i	Current
I_{ω}	Frequency-dependent current
Κ	Di-electric constant
L	Inductance
Q	Quality Factor
R	Resistance
V	Voltage
wt	Weight
Х	Reactance
Y	Admittance
Z[k]	Discrete-time impedance wave
Zi	Real part of impedance
Zq	imaginary part of impedance
Zω	Impedance
α	Frequency decency factor of CPE
ε0	Vacuum permittivity
θ	The angle between impedance vector and real impedance axis
ω	Angular frequency

Acknowledgment

This thesis is dedicated to my mother and sisters who always loved and supported me. A special acknowledgement should be made to my mother for her patience and love along completion of this degree. Words cannot express my gratitude or love to her. I could not have done this without support of my sisters; the angels who helped me in every step of my life. I cannot imagine my life without them. I would like to acknowledge my beloved father and dedicate this thesis to the memories he hacked in my heart, I can never be thankful enough for him and his great personality that influenced and will influence my entire life.

I would like to thank my supervisors, Prof. Messaddeq and Prof. Gosselin for guiding me and helping me to reach my potentials. Prof. Messaddeq is admirable for both personal and professional attribute that he has. This thesis would not have been possible without fruitful financial support of Canadian Excellence Research Chair in Enabling Photonic Innovations for Information and Communication. Many thanks to Prof. Gosselin for his helps to complete this degree, a brilliant, dedicated professor and head of Bio-microsystem's lab at Laval University. I learned a lot from his collaboration. Special thanks to Dr. Jeff Viens for his unswerving professional support through every trial and tribulations happened to me along this way. Dr. Viens understandings of science is astonishing; I was truly happy to spend at least one hour bi-weekly meeting with him. He was so kind to me to enable Skype meetings even when he was on leave. Finally, I like to thank Prof. Paul Fortier for his lovely and inspiring personality, he is one of the greatest scholars that I've met in my entire life. In addition I would like to thank him for his critical feedback as jury of my thesis.

I am grateful to Prof. Amine Miled, who supported me at every important moment of my M.Sc. experience at Laval University; he has keen understanding of microelectronic and microfluidic devices. I was truly blessed with our discussions and meetings we had when I was his teaching assistant.

Chapter One

Introduction

1 Introduction

Dielectric spectroscopy or electrochemical impedance spectroscopy (EIS) is a relatively new and powerful method of characterizing many of the electrical and ionic properties of materials and their interfaces with electronically conducting electrodes. In other words, EIS is a perturbative characterization of the dynamics of an electrochemical process and a tool for unraveling complex non-linear processes. It applies in a various applications and scientific fields such as fuel cell testing, bio-molecular interaction, microstructural characterization and measuring concentration of a content. Moreover, it can be applied for evaluation of reaction mechanism in an electrochemical process and to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic–ionic, and even insulators. The EIS technique can also be applied in a dielectric medium with high electrical resistance, as in crude oil and water-in-oil emulsions[1, 2].

Generally, EIS technique evaluates impedance of the solution, ionic transference resistance, electrode capacitance and others kinetic and thermodynamic parameters over the electrode and measures the dielectric properties of a content as a function of frequency. It is based on permittivity and the interaction of an external field with the electric dipole moment of the sample.

When EIS is developed in a potentiostat manner, a sinusoidal perturbation of potential is applied $\rightarrow \Delta E = |\Delta E| \sin (\Delta t)$ and consequently the current has a sinusoidal behavior too $\rightarrow \Delta i = |\Delta i| \sin(\Delta t)$. The relationship between both of these variables is defined as the impedance of the system. By measuring the impedance of a system over a range of frequencies, the frequency response of the system, the energy storage and the dissipation properties of system can be obtained. The term impedance refers to the frequency dependant resistance to current flow of a circuit element (resistor, capacitor, inductor, etc.). Impedance assumes an AC current of a specific frequency in Hertz. The main relation of impedance is defined below:

Impedance:
$$Z_{\omega} = E_{\omega}/I_{\omega}$$

where E_{ω} is the frequency-dependent potential and I_{ω} is the Frequency-dependent current. Impedance is the opposition to the flow of alternating current (AC) in a complex system.

A passive complex electrical system consists of two section, energy dissipater or resistor and energy storage or capacitor elements. Any physico-chemical system like mass-beam oscillators, biological tissues and electrochemical cells possesses energy storage and dissipation properties and EIS can be applied for examination of these systems. Briefly, for measuring the main concept of EIS, first a small sinusoidal perturbation (potential or current) of fixed frequency is applied. Then, the response and impedance of each frequency is computed[3].

The EIS method is complicated, however, it used more than other methods; EIS technique provides more information rather than other methods like DC technique and single frequency measurement. Moreover, it can distinguish more electrochemical reactions and reveal information on the capacitive behavior of the system. For validation of EIS method, the main criteria are linearity, stability and causality. First, the system must obey Ohm's Law, $V=Z\times I$. In addition, the system must be stable and not change with time and returns to its original state after removing the perturbation. The system must also be causal and respond only to the applied perturbation.

1.1 Motivation

Impedance Spectroscopy (IS) frequently used to carry out the modeling, characterization and measurements of numerous electrochemical devices. Electrochemical Impedance Spectroscopy (EIS) is a wining method in terms of cost and complexity compared to old characterization and modeling methods such as Electrical Conductivity, Frequency Domain Reflectometry and Time Domain Reflectometry. The presence of Alternative Current (AC) and Direct Current (DC) and capability of measuring the impedance in different range of frequency could lead to perfect characterization data. Variability of system response to different frequency and voltage level led to valuable characterization of the systems in terms of atomic conductivity, ionic conductivity, dipolar conductivity and electronic conductivity. Impedance is defined as the electrical energy dissipation in the material and many physio-chemical materials and animals biological tissues poses this property.

Electrochemical Spectroscopy techniques being widely employed in the past few years to fuel cell testing, bimolecular interactions, and structural characterizations.

Numerous sensors developed for various environment based on the EIS analysis such as NPS Sensors (Nitrate, Phosphate, Sulfate) for Precision Agriculture (PA) or for environmental analysis like water quality measurements. Characterizing and modeling of optically-transparent electrically conductive glasses is one other recent application of EIS in field of Optics and lasers. This glasses play tremendous role in manufacturing conductive fiber optics. While Fuel cell diagnostics, human glucose monitoring, corrosion monitoring and gas sensors is still commonplace application of impedance spectroscopy.

Nowadays arising demands for switching the old laborious, costly and bulky identification/ measurement techniques to reliable, miniaturized, low cost, digitally interfaced sensors led us to develop a wireless impedance spectroscopy platform, capable of being used for long distance measurements, hazardous environments or easily employed in the sensor networks. This platform benefits from Zigbee wireless connectivity which could be widely used for different application such as Building Management Systems (BMS) in order to interface smoke/gas sensors or could be employed in wide sensor networks which numerous sensor nodes is needed like agriculture fields and etc.

Beside wireless conductivity, on-the-fly calibration is other advantage of this platform. User can calibrate the device for different impedance measurements ranges with known on-board impedances through the wireless network. On-the-fly calibration and digitally controllable trans-impedance amplifiers feedback loop gives the ability to connect wide range of sensors to the device. The digitally controlled front-end can multiplex over 3 different sensors as Devices Under Test (DUT) and five calibration resistors, while digitally controlled feed-back loop can change over four feedback resistors in order to reach suitable gain-factor for internal trans-impedance amplifiers.

Ability of software switching between sweep mode and point to point impedance measurement mode is another advantage of this platform. The device can sweep in the frequency range of 5 KHz to 100 KHz with the resolution of 0.2 Hz. The platform is capable of exciting the Devices Under Test in different voltage levels, the DC voltage

level could be set through front-end and the AC voltage level is programmable with possible ranges of 200 mV, 400 mV, 1 V, 2 V.

This thesis devoted on explaining the system and design overview of this platform and calibrating and testing of it for two type of Impedance Spectroscopy application, the first application is in Photonic, Optics materials i.e. optically-transparent electrically conductive glass and the second application is in precision agriculture for developing nitrate sensor for tree nursery on special growing media.

1.2 Literature Review on EIS

There are many previous works based on impedance spectroscopy. Along with measurement of soil nutrition's (what has been done in this thesis); impedance spectroscopy has been used to provide precious data in fuel cell analysis, anticorrosion coating, biomedical application and molecular/bacterial biosensors. This section devoted to briefly review those applications.

Ramirez et al. proposed an EIS test for evaluating hydrocarbon-type pollutants contained in industrial waste soils by studying the interaction between hydrocarbon soil in organic and inorganic solvents. They developed a theoretical model and tried to optimize it with experimental results of soil electrodes. Their model was based on the polarity of solvents and they measure resistance changes of ionic transference which originates from the pollutants in the form of hydrocarbons. Because of salt presence, soil is an ionic conductor. When the composition or structure of soil is modified by the presence of other kinds of compounds, its constitution and related properties are changed. In this manner, EIS can indicate the change of the ionic transfer resistance in the soil by measurement of variation of particle size and the hydrocarbon [4].

Li Wang et al. applied EIS to investigate the electrochemical properties of a $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode. Electrochemical impedance spectroscopy technique has been used to study the electrode materials because it can reveal the relationship between the crystal lattice and the electrochemical properties. The information of electrolyte resistance, surface film resistance and charge transfer resistance are obtained by

modeling with two different equivalent circuits using Nyquist plots. They demonstrate that impedance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode changed with increasing cycles which helps to know the influence of the impedance of electrode on its cycling performance [5].

P. Saeung et al. used EIS technique to measure electrical properties of membranes as a function of frequency. A small signal of AC potential was applied to a charged chitosan membrane with an amplitude of 2 V over a frequency range of 100–300 kHz. They conduct an experimental set up and improved it by using two electrodes from vertical to horizontal direction to the membrane plane, and being closer to the membrane surface. Electrical properties of the membrane were investigated by immersing the membrane in a KCl solution [6].

Rodriguez et al. used Impedance spectroscopy as non-destructive test for evaluating bacterial biosensors. EIS allows evaluate bacterial activity by measuring the conductivity changes in the medium. EIS technique was deployed due to simplicity, suitability and being cost effective for measuring the chloride ions concentration inside of the wet media. This method of test was effective for validity test of the feasible, cost effective and miniaturized biosensors [7].

Characterizing and modeling of the fuel cells are one another important application of the impedance spectroscopy. Dhirde et al proposed electric circuit model of the 1.2 W proton exchange membrane fuel cell based on impedance spectroscopy. Various loading conditions were applied to the fuel cell and impedance data gathered and analyzed and equivalent circuit developed using impedance data by the basic electrical engineering elements. They studied various parameters of the fuel cell such as ohmic resistor of whole stack, double layer capacitance of the cell, anode and cathode charge transfer resistance. The inductive effect of the low frequencies was another important phenomenon which observed during the experiment [8].

Corrosion detection and anti-corrosion coating is one of the important application of the impedance spectroscopy. Jerry Hoja et al. used square pulse excitation for high impedance spectroscopy of anticorrosion coating. This method designed diagnostic of corrosion on the field. The range of impedance measurement in this study was 1 mHz to 1 MHz, they used different signal processing methods to handle the calculation of the

impedance spectra. Finally the equivalent circuit of the corrosion developed which can be used to detect early undercoat rusting [9].

Manickam et al. presented a A CMOS electrochemical Impedance Spectroscopy biosensor array implemented on metal-oxide semi-conductor process. This array of sensors is capable of detecting various biological analytics such as DNA and rotein in real time. They used bio compatible electrodes and embedded circuitry to measure the impedance of the associated interface. The chip is capabe of the measurements frequency renge of 10 Hz to 50 MHz [10].

Bernard et al. used high precision impedance spectroscopy for analyzing of the ionic and electric conductivity of lead zirconate titanate as a function of temperature and oxygen pressure. Since electrochemical spectroscopy is very powerful tool for understanding of the charge transfer in electrical or electrochemical systems; it contributes to better understanding of the material properties. In this study lead zirconate titanate is of interest because of its special properties in applications such as piezoelectric and ferro-electric materials [11].

Frank et al. published a review on using impedance spectroscopy as a tool for monitoring multicellular spheroid drug models. They claim that EIS is capable of modeling 2-D and 3-D cell cultures. The used it as a tool for automated screening of the cell drugs interactions[12].

1.3 Structure of This Thesis

This multidisciplinary thesis is devoted to modeling, characterizing and analysing various devices in field of impedance spectroscopy and to the design of a low-power, hand held, multiplexed and wireless impedance spectroscopy platform capable of being used in LR-WPANs for domestic or industrial applications.

Chapter 1 is a literature review on impedance spectroscopy and its application illustrating the direction of this study.

Chapter 2 presents common issues and method of measuring impedance to give the user a sense of what happens inside the measurements devices. Different models of the impedance loads and the effect of parasitic impedances, different probes and fixtures are studied in this chapter.

Chapter 3 explains the theory of impedance spectroscopy and cites previous works on nutrition measurements and analytical chemistry in soil.

Chapter 4 consist of modeling and characterizing of two ionic-conductive electrochemical devices; first a nitrate sensor for determining the trace amount of NO₃ in the growing media and second an optically-transparent electrically-conductive glass capable of being used for simultaneous electrical and optical stimulations. Chapter 4 is insertion of the journal paper [52] and [71] published by the author of this thesis.

Chapter 5 is a report on the design of general purpose, low cost, wireless impedance spectroscopy platform for *in situ* applications. Later on, this platform is calibrated for nitrate sensor, touch glass sensor and water quality sensor. Chapter 5 is insertion of the journal paper [80] published by the author of this thesis.

Chapter 6 and 7 are a brief conclusion of this research and possible future works.

1.4 Contributions

Four other students of Laval University contributed on this multidisciplinary project, Charles-O. Normandeau, William-O. Caron and Mathilde Loubier developed the nitrate sensor presented in Chapter 3 as part of their M.Sc studies and Maxime Rioux developed optically-transparent electrically-conductive glass as part of his Ph.D. studies under supervision of Professor Messaddeq. (Department of Chemistry)

Seyed Alireza Ghaffari (author of this thesis) devoted time to understand and characterize the electrical model, effect of electrodes and fixtures, effect of ionic conductivities of the mentioned devices in Chapter 3. He also designed the wireless impedance spectroscopy reported in chapter 4 under the supervision Prof. Gosselin and co-supervision of Prof. Messaddeq.

Dr. Viens had a substantial role as the director of this project in developing the idea and managing the students for accomplishing the goals of this study.

Chapter Two

Impedance Measurement Circuits and Methods

2 Impedance Measurement Circuits and Methods

2.1 Basics of Impedance Measurements

Impedance is an important parameter used to characterize electronic circuits. Over the recent years, this concept has been widely used to characterize the electrochemical phenomena. Impedance is defined as the total resistant of the substance to the flow of alternative current. Since the alternative current excite the substance in a given frequency, the impedance is related to the frequency. In Electrical Engineering, impedance is usually represented as a complex number R+jX, which R is the resistance and X is the reactance of the excited material. *Resistance* demonstrate resistive and *reactance* shows the inductive or capacitive behaviour of material.

Figure 1 (a) shows the representation of the impedance in the complex plane and the polar representation of the impedance.



Figure 1: (a) Impedance in a complex plane (b) inductive and capacitive impedance.

$$z = R + jX = |Z| \angle \theta \qquad \text{eq.(2-1)}$$

$$R = |Z| \cos \theta \qquad \text{eq.(2-2)}$$

$$|Z| = \sqrt{R^2 + X^2}$$

$$\theta = \tan^{-1}(\frac{X}{R}) \qquad \text{eq.(2-3)}$$

Reactance can be in two form, capacitive and inductive Figure 1 (b) shows the circuit legends related to these two types of reactance. The capacitive (X_c) and inductive (X_l) reactance can be represented as

$$X_{c} = \frac{1}{2\pi fC} = \frac{1}{\omega C} \qquad eq.(2-4)$$
$$X_{l} = 2\pi fL = \omega L$$

Another factor to be considered is the quality factor (Q). The quality factor shows how much reactance is pure, that means the ratio of stored energy in the device to the energy dissipated by device.

$$Q = \frac{1}{D} = \frac{1}{\tan(90 - \theta)} = \frac{|X|}{R}$$
 eq.(2-5)

The physical or chemical components are neither purely resistive nor reactive. In measuring the impedance of a material, many parasitic impedances are involved such as impedance of the connection wires, impedance of the probes and electrodes, etc. In addition, all the real world materials do not show pure resistive or reactive impedance and there are always unwanted parasitic behaviours associated with impedance measurements. Figure 2 shows the parasitic impedances of several electrical components.



Figure 2: Parasitic impedances associated with capacitive, resistive and inductive loads.

2.1.1 Real, Nominal and Measured Value of Impedance

The value obtained in impedance measurements must be completely understood by the operator, otherwise choosing inconvenient electrodes and probes could lead to significant error in the measurements. According to Figure 3: there are three values associated with each measurement.

1) Nominal value:

The nominal value is the value of the component or material provided by the vendor. This value excludes of the parasitic values. As an example, for capacitor of Figure 3(a) the nominal value is:

$$C = K\varepsilon_0 \frac{A}{d} \qquad eq.(2-6)$$

2) Real value:

Real value is the impedance of the components or material including the parasitic effect of the component.

3) Measured value:

The measured value is the impedance value measured by the impedance measurement device. This value includes the wiring and electrode impedances. Test fixture components (wires, probes and electrodes) must be chosen to have minimum effect on the measurements in the different range of frequencies.



Figure 3: Real, Nominal, Measured Value.

2.2 Material Dependency Factors

1) Frequency

Frequency is natural dependency of the impedance which cause by the excitation wave. Even resistive impedances show the frequency dependency. Over a wide span of the frequency different parasitic gets prominent.

2) AC level of excitation signal

According our measurements in ionic conductivity, the excitation AC level is important for making enough powerful electrical field to move the heavy ions. This dependency varies depending on the di-electric constant.

3) DC level of excitation signal

DC level affect the measurement in two ways, first it could saturates the input stage amplifiers of measurement device and second, it can affect the measurement of high value di-electric capacitive devices and in some cases it could cause di-electric breakdown. In addition it may cause magnetic flux saturation in the coil of inductive devices.

4) Temperature

As temperature varies, the atomic or ionic mobility vary. This make most of the components impedance temperature dependent.

5) Humidity magnetic field, electric field, light, atmosphere, vibration

Most of the materials with ionic conductivities are dependent to environments. For example for measuring ionic conductivity of nitrate, it is recommended to always agitate the solution.

6) Time

Time dependency is very visible in impedance spectroscopy of materials or devices, which depends on chemical reactions such as batteries

2.3 Measurement Accuracy

Most of the modern impedance measuring instruments basically measure vector impedance (R+jX) and convert it, into various parameters i.e. capacitance, inductance, quality factor, impedance modulus or admittance¹ modulus, etc. Since measurement range and accuracy are specified for the impedance and admittance, both the range and accuracy for the capacitance and inductance vary depending on the frequency.

¹ A measure of electrical conduction, numerically equal to the reciprocal of the impedance.

Figure 4 shows the accuracy of the Solartron Gain/Phase analyzer which we used in our experiments.



Figure 4: Measurement accuracy of Solartron 1260 gain/phase analyzer.

2.4 Theory of Practical Impedance Measurements

2.4.1 I-V Method

The I-V method relies on measuring the voltage and current across the DUT. By definition, the impedance is the ratio of measured voltage to measured current. In Figure 5, current is measured by measuring the voltage across the accurately known and relatively small resistor R_r . The obtained voltage and current vector can be transferred to a processor or a mixer for further analysis, such as separating the real and imaginary part of the impedance. This method will be discussed later in section 2.6.



Figure 5: I-V Method for measuring impedance.

2.4.2 Auto-Balancing Method

The auto-balancing method is common place in low frequency measurements. This method measures the voltage of the test signal and current flood through the DUT by a null detector as shown in the Figure 6. The equations are as follow:



Figure 6: Auto-balancing method for measuring impedance.

This method can be simplified by the using a multiplexer and a voltmeter as shown in Figure 7.



Figure 7: Simplified auto-balancing method for measuring impedance.

So basically, the measurement device switches between the test signal and output signal to measure V_r and V_x .

2.5 Measurement Functions

2.5.1 AC Level and Source Resistance

The oscillator level or AC level of the excitation voltage and source resistance are key parameters of the measurement instruments. This phenomenon becomes important especially in measuring low impedance devices. According to Figure 8 the applied voltage V_x is different from the open circuit nominal voltage.



Figure 8: Effect of source impedance.

$$V_x = \frac{Z_x}{R_s + Z_x} V_s$$

= 0.5 V
$$eq.(2-9)$$
In addition, the oscillator level must be stable to improve the signal to noise ratio. Depending on the nature of the measurements, the oscillator level must be different. For example the oscillator level must be high in capacitive and resistive loads but low in inductive loads. Measurement of semiconductor devices need more attention for choosing the AC level due to different working regions of transistors and threshold voltages. In such devices, AC level must be small enough to make sure it will not change the operating regions of the transistor.

2.5.2 DC level

DC bias level of the excitation device can make additional error in most of the measurements such as semiconductors and ionic conductive solutions; all the loads can be burnt out in high level of DC. Different devices show different behaviour in DC and AC. For example the dynamic resistance of diode in AC is different from its static resistance in DC.

As shown in Figure 9, another problem can be the leakage current in low DC resistance devices. If so, the bias current of the measurement device will flow through the R_r to the device, and make the measurements unstable or unreliable. Inductors are transparent to the DC currents. It means that ideally they bypass all the DC current, but in the real world they are fragile to high currents. This concept applies dually to capacitors; they are ideally open-circuit in DC voltage but really fragile to high DC voltage.



Figure 9: Leakage current in low-impedance devices.

2.5.3 Ranging

Since, sweeping a wide span of frequencies or sweeping between different devices cause large change in the impedance values, impedance measurements have several measurement ranges and the device or user can change the measurement range according to impedance of the device under test. A ranging function is usually realized by changing the gain multiplier and switching the gain resistor for the internal amplifiers. Figure 10 demonstrates the ranging function in the auto-balancing method. On any range for which the maximum accuracy obtained, the embedded software will return the value to the user. This method will be employed extensively in chapter 4 to design the Wireless Impedance Spectroscopy Platform.



Figure 10: Ranging circuit.

2.5.4 Compensation

Since optimum measurements results in time variant especially in the ionic conductors, most of the measurement devices have the ability to perform small statistical signal processing or averaging. In addition, using different electrodes and fixture makes a difference in measuring the impedance; specifically in high frequencies it is common place to consider two-port parameters of the probes, electrodes and fixture such as scattering parameters, impedance parameters and admittance parameters and compensate the test results by post processing.

2.6 Separation of Real and Imaginary Parts of the

Impedance

There are two major method for separating the imaginary part and real part of the impedance, this section is devoted to explain these two methods.

2.6.1 Synchronous Detection Method

This method is based on mixing the wave by sine and cosine test phasors and integrating the mixed signal with low-pass filter. This method is widely used in [10] to design impedance measurement system on chips. The Figure 11 shows the overall idea and equations of this method.



Figure 11: Synchronous detection for separating real and imaginary parts of impedance.

Assume that $V_{in} = A_1 \sin(\omega \theta)$

The output of amplifier is considered such as $A_2 \cos(\omega t - \theta)$ which its amplitude and phase changed due to the change for impedance measurement and op amp frequency response.

Using $\cos(\alpha - \beta) = \cos(\alpha)\cos(\beta) + \sin(\alpha)\sin(\beta)$ and $A_1\sin(\omega t - 90) = A_1\cos(\omega t)$ we have $A_2\cos(\omega t - \theta) = A_2(\cos(\omega t)\cos(\theta) + \sin(\omega t)\sin(\theta))$

So the output of mixers will be:

Upper Mixer:

$$\begin{aligned} A_1 A_2 \sin(\omega t) \times [\cos(\omega t) \cos(\theta) + \sin(\omega t) \sin(\theta)] &= \\ A_1 A_2 \cos(\theta) \sin(\omega t) \cos(\omega t) + A_1 A_2 \sin(\theta) \sin(\omega t) \sin(\omega t) \\ &= \frac{1}{2} A_1 A_2 \cos(\theta) [\sin(\omega t + \omega t) + \sin(\omega t - \omega t)] + \frac{1}{2} A_1 A_2 \sin(\theta) [\cos(\omega t - \omega t) + \sin(\omega t + \omega t)] \\ &= \frac{1}{2} A_1 A_2 \cos(\theta) \sin(2\omega t) + \frac{1}{2} A_1 A_2 \sin(\theta) [1 - \cos(2\omega t)] \\ &= eq.(2-10) \end{aligned}$$

And after the low pass filter:

$$\int_{0}^{2T} \frac{1}{2} A_{1} A_{2} \cos(\theta) \sin(2\omega t) + \int_{0}^{2T} \frac{1}{2} A_{1} A_{2} \sin(\theta) [1 - \cos(2\omega t)] = \frac{1}{2} A_{1} A_{2} \sin(\theta) \qquad eq.(2-11)$$

For simplicity, we consider $A_1 = I$ so the output of the low pass filter corresponds to $A_2 \sin(\theta)$ which is the amplitude of the imaginary part.

Lower Mixer:

$$\begin{aligned} A_1 A_2 \cos(\omega t) \times [\cos(\omega t) \cos(\theta) + \sin(\omega t) \sin(\theta)] &= \\ A_1 A_2 \cos(\theta) \cos(\omega t) \cos(\omega t) + A_1 A_2 \sin(\theta) \cos(\omega t) \sin(\omega t) \\ &= \frac{1}{2} A_1 A_2 \cos(\theta) [\cos(\omega t - \omega t) + \cos(\omega t - \omega t)] + \frac{1}{2} A_1 A_2 \sin(\theta) [\sin(\omega t + \omega t) - \sin(\omega t - \omega t)] \\ &= \frac{1}{2} A_1 A_2 \cos(\theta) [1 + \cos(2\omega t)] + \frac{1}{2} A_1 A_2 \sin(\theta) \sin(2\omega t) \\ &= \frac{eq.(2-12)}{2} \end{aligned}$$

After integration of the low pass filter:

$$\int_{0}^{2T} \frac{1}{2} A_{1} A_{2} \cos(\theta) [1 + \cos(2\omega t)] + \int_{0}^{2T} \frac{1}{2} A_{1} A_{2} \sin(\theta) \sin(2\omega t) = \frac{1}{2} A_{1} A_{2} \cos(\theta) \qquad eq.(2-12)$$

Considering $A_1 = I$, output of the low pass filter corresponds to $A_2 \cos(\theta)$ which is the amplitude of real part.

2.6.2 Discrete Fourier Transform Method

The impedance response signal will be sampled by an ADC. A discrete Fourier transform (DFT) must be processed by the on-board engine, and the results will be sent to an online computer for data storage and analysis. The device should employ a transimpedance amplifier for amplifying the current and then use an N- point DFT algorithm for separating the real and imaginary parts of impedance. After digitalizing with the ADC, a discrete-time impedance wave, Z[k] (n= 0, 1, 2,..N-1), is obtained by the DFT:

$$F\{z[k]\} = Z(e^{j\omega}) = \sum_{n=0}^{N-1} z[k] \cdot e^{\frac{-j2\pi kn}{N}} = \sum_{n=0}^{N-1} z[k] \cos(\frac{-j2\pi kn}{N}) - j\sum_{n=0}^{N-1} z[k] \sin(\frac{-j2\pi kn}{N}) = Z_i - jZ_q$$

$$eq.(2-13)$$

Where Z_i and Z_q indicate, respectively, the real and imaginary parts of the impedance returned by the DFT. Equation 2-13 shows a digital implementation of multiplication of cosine and sine phasors to the main signal and extracting the real and imaginary part as it shown in Figure 11. This method has been used in AD5933 impedance analyzer IC by Analog devices and the more detail algorithm can be found in Texas instruments documents [13, 14].

Chapter Three

Theory of Impedance Spectroscopy

3 Theory of Impedance Spectroscopy

Impedance spectroscopy is a powerful technique for analysis and characterization of electrochemical systems. As shown in Figure 12, the devices under test will be excited by a small AC signal with specified DC level.



Figure 12: Demonstration of small-signal excitation in special DC work-point.

Recently, impedance spectroscopy (IS) frequently used to carry out the modeling, characterization and measurements of numerous electrochemical devices. electrochemical impedance spectroscopy (EIS) is a winning method in terms of cost and complexity compared to old characterization and modeling methods such as electrical conductivity (EC), frequency domain reflectometry (FDR) and time domain reflectometry (TDR). The presence of alternative current (AC) and direct current (DC) and the capability of measuring the impedance in different range of frequency can lead to near perfect characterization data. Variability of the system response to different frequency and voltage level lead to valuable characterization of the systems in terms of atomic conductivity, ionic conductivity, dipolar conductivity and electronic conductivity. Impedance is defined as the electrical energy dissipation in the material and many physio-chemical materials and biological tissues have this property.

Electrochemical Spectroscopy techniques have been widely employed in the past few years to fuel cell testing, bimolecular interactions, and structural characterizations. Numerous sensors have been developed for various environment based on the EIS

analysis such as NPS Sensors (nitrate, phosphate, and sulfate) for precision agriculture (PA) or for environmental analysis like water quality measurements. Characterizing and modeling of optically-transparent electrically conductive glasses is another recent application of EIS in field of optics and lasers. This glasses play tremendous role in manufacturing conductive fiber optics. Fuel cell diagnostics, human glucose monitoring, corrosion monitoring and gas sensors are commonplace applications of impedance spectroscopy.

3.1 Demonstrating the Impedance Spectra

Showing the Impedance as a function of frequency is called impedance spectra. There are two major methods to demonstrate the impedance spectra. The first and most celebrated method is the **Bode plot**. The Bode plot is a pair of plots, i.e. magnitude vs frequency and phase vs frequency. The bode plot is very helpful for determining zeros and poles of a system and understanding the capacitive, resistive or inductive behaviour is quite straightforward by looking at the phase diagram. Both quantities are plotted against a horizontal axis proportional to the logarithm of frequency. Moreover, the presence of large impedances can be identified easily. In the investigation of electrochemical devices and phenomena, especially the study of the ionic conductivity, bode diagrams are not enough to demonstrate the system. The Nyquist diagram is extensively used for understanding the impedance spectra. Distinguishing and classifying constant phase elements (CPE) and Warburg¹ elements are very easy in the Nyquist plot. A Nyquist plot is a parametric plot of a frequency response used in automatic control and signal processing. In Cartesian coordinates, the real part of the transfer function is plotted on the X axis. The imaginary part is plotted on the Y axis. The frequency is swept as a parameter, resulting in a plot per frequency. Alternatively, in polar coordinates, the gain of the transfer function is plotted as the radial coordinate, while the phase of the transfer function is plotted as the angular coordinate. Frequency is not obvious in a Nyqusit plot and small impedances can be swamped by large impedances.

¹ Defined in section 3.1.2

Figure 13 shows the demonstration of the Nyquist and bode of the simple Randles Cell. Randles cell is an equivalent electrical circuit that consists of an active electrolyte resistance R_1 in series with the parallel combination of the double-layer capacitance C_1 and an impedance of a faradaic reaction. It is commonly used in electrochemical impedance spectroscopy (EIS) for interpretation of impedance spectra.



Figure 13: Randle Cell (a) Equivalent Circuit (b) Bode plot (c) Nyquist plot.

3.1.1 Constant Phase Element

A constant phase element is one of the elements which invented to understand ionic conductivity and it is literally a demonstration of the impure capacitance and mathematically defined as:

$$z(j\omega) = \frac{1}{(j\omega)^{\alpha} C_{\alpha}}$$

A CPE can be reduced to resistance when α =0 and capacitance when α =1. However in the real applications α is between 0 and 1.

Figure 14 shows the deviation of the R-CPE circuits from R-C circuits as alpha decrease.



Figure 14: demonstration of CPE as impure capacitance as alpha decrease.

3.1.2 Warburg Element

Diffusion can create an impedance known as a Warburg impedance. This impedance depends on the frequency of the potential perturbation. At high frequencies the Warburg impedance is small since diffusing reactants cannot move very fast. In opposite, at low frequencies, the Warburg impedance increases.

On a Nyquist plot the infinite Warburg impedance appears as a diagonal line with a slope of 0.5. On a Bode plot, the Warburg impedance exhibits a phase shift of 45 degree.

$$z_{warburg}(j\omega) = \frac{A_w}{\sqrt{\omega}} + \frac{A_w}{j\sqrt{\omega}} \qquad \qquad \left\| z_{warburg}(j\omega) \right\| = \sqrt{2} \frac{A_w}{\sqrt{\omega}}$$

3.1.3 Exploring Several Example of Nyquist Plots in Impedance Spectroscopy

3.1.3.1 Absorption

Electrochemical behaviour could be observed in absorption of the platinum in 0.5 M H₂SO₄. Figure 16 gives an example of the experimental data and fitted curve of this process. This is one of the common example of the ionic conductivity which happened in the absorption procedure



Figure 15: Absorption (a) Equivalent Circuit (b) Bode plot (c) Nyquist plot.

3.1.3.2 Mixed Kinetic Diffusion

Most of the batteries and fuel cells can be studied using impedance spectroscopy. Batteries generate electrical energy with a combination of the diffusion and kinetic procedures. The Figure 16 shows the equivalent model and the impedance data of the typical fuel cell.



Figure 16: Fuel cell (a) Equivalent Circuit (b) Bode plot (c) Nyquist plot.

3.1.3.3 Polycrystalline Electro-Ceramics

In the study of Polycrystalline electro-ceramics, there are three different conductions in frequency sweep: (I) grain boundary conduction, (II) and electrode Reaction (III) ceramic grain. This three process are shown in the equivalent circuit and bode diagrams in Figure 17.



Figure 17: Polycrystalline electro-ceramics (a) Equivalent Circuit (b) Bode plot (c) Nyquist plot.

3.2 Dielectric Mechanisms

There are a number of different dielectric mechanisms, connected to the way a studied medium reacts to the applied field. Each dielectric mechanism is centered on its characteristic frequency, which is the reciprocal of the characteristic time of a process. Generally, the dielectric mechanisms is divided into relaxation and resonance processes including:

- Electronic polarization: it comes out from an applied field and refers to electron density. This mechanism consider an atom as a point nucleus surrounded by spherical electron cloud of uniform charge density. The resonant process occurs in a neutral atom when the electric field displaces the electron density relative to the nucleus it surrounds [3].
- Atomic polarization: it happens when the nucleus of the atom reorients in response to the electric field. It is intrinsic to the nature of the atom which is derived from an applied field. Compared to electronic polarization, atomic polarization is relatively small [3].
- **Dipole relaxation**: this originates from permanent and induced dipoles aligning to an electric field. Thermal noise disturbs the orientation polarization (which misaligns the dipole vectors from the direction of the field), and the time needed for dipoles to relax is determined by the local viscosity. These two facts make dipole relaxation heavily dependent on temperature, pressure and chemical surrounding [3].
- **Ionic relaxation:** it comprises ionic conductivity and interfacial and space charge relaxation. Ionic conductivity predominates at low frequencies and introduces only system losses. Interfacial relaxation occurs when charge carriers are trapped at interfaces of heterogeneous systems. The charges may be separated by a considerable distance and therefore make contributions to the dielectric loss that are orders of magnitude larger than the response due to molecular fluctuations [3].
- **Dielectric relaxation:** it is a whole result of the movement of dipoles (dipole relaxation) and electric charges (ionic relaxation) due to an applied alternating

field, and is usually observed in the frequency range 10^2 - 10^{10} Hz. Comparing to resonant electronic transitions or molecular vibrations, which usually have frequencies above 10^{12} Hz, relaxation mechanisms are relatively slow [3].

3.3 An Introduction on Nitrogen Measurement in Soil

For improving farming and plants demands, reducing NO₃ content and measuring N rate to match spatial and temporal crop demands are necessary. Actually, one basic need is to measure and monitor spatial and temporal loss pathway for N. The conventional methods for measurement of the existing soil NO₃ concentration like soil sampling are time-consuming and impractical for large-scale or high-resolution monitoring. Furthermore, soil sampling method is not reliable or consistent because it depends on equipment and tools. Other manual method like plant tissue testing is also not accurate because it is not possible to monitor the dynamic nature of NO₃ in a timely manner [15]. So, these reasons lead scientist to develop real time measurement techniques. Bulk soil permittivity measurement has been used in environmental monitoring to estimate volumetric water content (VWC) and soil salinity [16]. Moreover, there are other practical methods as time domain reflectometry (TDR) techniques to estimate change in nitrate-nitrogen (NO₃-N) concentration in pore water both in a field and a laboratory within related sensors or probes.

In this method, a sample scale electrical sensor or a dielectric sensor is used as a reference to characterize the media. Then, microwave remote sensing will be used which relies on electromagnetic response of transmitted wave to the media wet contents such as nitrate ion. However, one challenge in designing dielectric sensor is measuring the bulk soil dielectric permittivity, which is commonly used to estimate soil moisture content.

Time domain reflectometry (TDR) and time domain transmission (TDT) techniques have proved to be reliable methods for determining soil water content. In general, TDR and TDT systems measure the propagation velocity of a step voltage pulse with a bandwidth of around 20 kHz to 1.5 GHz along a pair of electrodes to determine the permittivity of the material through its travels [17]. The quality and volume of TDR measurement depends on probe design, accuracy of calibration and its construction [18, 19]. There are several available TDR systems for soil moisture monitoring like TRASE (Soil Moisture Equipment Corps), Trime (IMKO), the Acclima (Acclima Inc) and CS-TDR100 (Campbell Scientific).

Also, researcher performed numerous experimental works on evaluation of NO₃ concentration of soil solution from bulk soil electrical conductivity measurements using the TDR probe. Proper calibration of probe leads to reasonable agreement between NO₃-N concentration and the bulk electrical conductivity sensed by the TDR probe.

Dalton et al [20] measured bulk soil electrical conductivity from the amplitude of the reflected waveform with TDR probes and demonstrated measurement of the apparent permittivity and the bulk soil electrical conductivity using the same instrumentation, probes, and same soil volumes. The bulk soil electrical conductivity is influenced by several soil parameters, including the pore water conductivity, the water content, the surface conductivity of the surface particles, and the tortuosity of the electrical flow paths. Hilhorst et al. [21] proposed a linear model for measurement of dielectric permittivity and conductivity of the bulk soil to the pore water conductivity, simultaneously.

Amente et al. [22] concluded there is no advantage to the use models for measuring the soil solution electrical conductivity to the bulk soil conductivity for sandy based on soil hydraulic properties compared to the simpler models that do not require them. Rhoades and Oster [23] determined total ionic concentration of the soil solution from the measurement of the bulk soil conductivity. They concluded that calibration is necessary to estimate ionic concentration and it is soil and solution specific.

Kachanoski et al. [24] assumes an empirical linear relationship between the concentration of solutes and the bulk conductivity measurements. But, numerous scientists used another simple approach to determined solution concentration from the bulk soil conductivity. They consider an intermediate step of secondary calibration so that the solution concentration is determined from the soil solution conductivity.

Nissen et al. and Krishnapillai and Ranjan [25, 26] estimated NO₃ concentration of soil solution from the bulk soil electrical conductivity measurements using calibrated TDR probe. They did not apply any electrolytes to the soil during these experiments, except NO₃-N, and any change in the solution conductivity was mostly from the changes on the NO₃-N concentration.

Das et al. [27] simultaneously evaluated volumetric soil water content, soil solution electrical conductivity, and soil NO₃-N concentration in an irrigated peppermint field using TDR methods. They compared obtained results of NO₃-N concentration with experimental results from direct soil measurements (soil cores and soil solution samples).

Payero et al. [28] concluded that TDR probes could be used to measure NO₃-N in nonsaline soils and water after the proper calibration over a long enough period of time. Their results include the expected variations in volumetric water content (VWC), temperature and NO₃-N.

Despite the advantage of using TDR methods, there are many problems associated with TDR such as extracting accurate parameters from the received waveforms, difficulties in detecting the reflected signal in saline soils, measurement dependence on the coaxial cable and probe lengths and waveform analysis applied to the collected data. So, alternative solutions for enhancement of TDR probe performance are using frequency domain reflectometry (FDR) and capacitance-type probes. Both frequency domain technique (FDR) and capacitance type probes measure the electrical capacitance of a capacitor that uses soil as a dielectric. An oscillator which is connected to this capacitor in a circuit, generating repetitive electric waveforms at a characteristic frequency. Soil moisture content of the capacitor affects the circuit operating frequency making it possible to detect changes in VWC. In capacitance-type sensors, the dielectric permittivity is evaluated by measuring the charge time of a capacitor made with the medium.

From the experimental works of Knoll et al., Andrade et al., and Kelleners et al. [29]– [31] we can conclude that electrical conductivity of soil has a negligible effect on the permittivity measurements at frequencies above 50 MHz. So, it makes most of the capacitance-type sensors insensitive to soil salinity, but with decreasing measurement frequency, the effect of the soil electrical conductivity becomes stronger.

Generally, dielectric sensors operating at an effective frequency above 500 MHz have stable permittivity region, while at frequencies below 50 MHz dielectric permittivity measurements are biased by the electrical conductivity and require calibration. Results of various studies have shown that besides water content, soil salinity and temperature, capacitance-type probes are sensitive to soil type, bulk density, clay and organic matter content. However, errors can be compensated if the bulk soil electrical conductivity and temperature have been considered.

Another problem related to dielectric probes is they measure the apparent permittivity rather than the real permittivity. Unlike the real part of permittivity, the apparent permittivity is also influenced by the imaginary part of permittivity, which affects accuracy and reliability of soil moisture estimates. It should be noted that the real (capacitive) part of the permittivity is mainly related to the soil water content, while the imaginary (conductive) part is related to the soil bulk electrical conductivity and the dielectric relaxation.

Carr et al. [32] studied the effect of dissolved ions in the soil water on the permittivity measurements using the capacitance type probes ECH₂O EC₋₅ and EC₋₁₀ operating at fixed frequencies of 70 and 5 MHz, respectively. They found that the EC₋₁₀ probe was more sensitive to ionic conductivity than the EC₋₅, hence illustrating a potential to estimate soil salinity using the low frequency capacitance probe. They concluded that at lower frequencies, contribution of conductive is stronger than capacitive part of permittivity and apparent permittivity is changed by dielectric loss, including changes in the bulk soil conductivity.

One important problem related to commercial capacitance probes is their limitation in measuring at a single frequency which is adequate for a single soil properties. But, the bulk soil permittivity measured using capacitance type probes is sensitive to multiple physical and chemical properties of soil. So, measuring at multiple frequencies (from low kHz to couple of hundreds MHz) can integrated all effects and evaluate several physical and chemical properties of soil. Zhang et al. tried to develop a capacitance type of sensor to cover multi-frequency measurements ranging from 1 Hz to 15 MHz and measure most of the conductive part of the permittivity spectra [33].

As mentioned, there are a few type of sensor available that can measure both the VWC and soil bulk EC by independent measurements of the conductive and capacitive components of the complex dielectric permittivity of a porous material. However, most of the commercially dielectric sensors respond to the soil bulk permittivity, also called the apparent permittivity, which incorporates both real and imaginary parts in the measurement. So, at low frequencies the apparent permittivity is influenced by the conductive behavior and it overestimates the volume water content.

One approach is based on using the cumulative effect of soil moisture and frequencydependent ionic conductivity on the soil bulk permittivity measurement to estimate the change in individual ion concentrations during continuous monitoring of agricultural fields. Specifically, combining measurements at several frequencies rather than using a single frequency would allow to partition the dielectric response into components associated with the VWC, salinity, and concentrations of individual ions (NO₃ in our case).

Chighladze tried to test the validity of measuring the effect of ion-specific conductivity on the dielectric response of bulk soil using off-the-shelf technology. Also, he evaluated the sensitivity of these capacitance probes to changes in the soil solution NO₃ concentration at environmentally relevant levels at two fixed measurement frequencies (70 and 5 MHz) for a range of soil moisture contents. Furthermore, he determined the effect of other soil solutes on capacitance probes and examined the differences in sensor response between soil samples wetted with NO₃, Cl, and NO₃–Cl solutions at both measurement frequencies. While high-frequency dielectric measurement is a good predictor of soil water content, they also used low-frequency measurements to estimate several soil solution properties, such as salinity (at very low frequency) and the concentration of individual ion species (at ion-specific characteristic frequencies) [34].

3.4 Electrochemical Methodologies for Nitrite Detection

Electrochemical detection techniques have been investigated for *in situ* quantitative analysis and real-time monitoring of environmental parameters. Technologies used to detect nitrite can be divided into a number of categories including voltammetric, potentiometric and impedimetric electrodes.

Voltammetric electrodes: while a potential field is applied to the working electrode, a voltammetric or amperometric electrode provides a current signal to represent the rate of reactions on the probe surface. To avoid oxygen interference and obtaining a strong electrode response to nitrite oxidation including sensitivity and response time, it is necessary to determine the applied potential to the working electrode [35]. A current-to-voltage converter and a voltage amplifier are used to convert the working probe current to voltage and amplify it to a suitable range for the analog-to-digital converter (ADC) to sample. Then, related results can be calculated, saved, transmitted and displayed on instruments or monitors.

Since the early 1900s, this method have been utilized to detect and monitor nitrite, when glassy carbon electrodes were used that continuously detect without additional agent consumption [36].

For voltammetric detection and improving electrode performance, substrates such as copper, nickel, boron-doped diamond, platinum, carbon, cadmium, alloys, gold, lead and indium tin oxide have been used. The main problem of these material is related to the low electrode transfer rate and also species which is formed during the electrochemical process and they influence the electrode passivation and cause poisoning of the electrode. [37], [38].

For solving this problem, various solutions are proposed including surface modification and adding organic/inorganic modifier. The most useful technique is surface modification which considerably improve selectivity and sensitivity of the electrode. The other method is also applicable while using organic/inorganic catalysts and enzymes as modifiers can improve the sensibility and selectivity of electrodes by enhancing the reduction or oxidation of nitrite.

Ag nanoplates inserted into the surface of a glassy carbon electrode may be used as a sensitive sensor for the assessment of nitrite. Ag nanoplate-modified electrodes (AgNP/GC), which have high current response to the electrooxidation of NO2-, benefit from the enhanced surface area and high specific activity of AgNP/GC due to the exposure of many defect sites [39].

The carbon nanotube-based electrode is another substrate that has been investigated as a nitrite sensor with a number of modifiers. Zhang et al. constructed a composite film of α_2 -K₇P₂VW₁₇O₆₂•18H₂O (P₂W₁₇V) and carbon nanotubes (CNTs) that was used as a sensitive amperometric nitrite sensor [40].

Beside variety of modifications, photochemical catalysis is another applicable method. First, Chen et al. and XiuTing et al. investigated and suggested photo-catalyst technology to facilitate the performance of electrodes and obtain a rapid response [41], [42].

Nanoparticle electroplating technique is based on constructing and exposing a large and highly active surface area which can increase the sensitivity of the electrode response. Appropriate ions are dissolved in an electrolyte with a potential sweeping the immersed electrode in the cathodic direction. The metal ions are then plated onto the electrode, providing a fresh surface for nitrite to undergo the oxidation-reduction reaction. Due to freshly reaction of nitrite in deposited metal layer, the analysis is relatively independent of the base electrode material. Ag nanoplate-modified electrodes (AgNP/GC), which have high current response to the electro oxidation of NO2-, benefit from the enhanced surface area and high specific activity of AgNP/GC due to the exposure of many defect sites [39].

Polarography is another approach which is introduced for detection of nitrite, as the behavior of a dropping mercury electrode (DME) is relatively independent of its past history. Having high accuracy and reproducibility are advantages of polarography,

because liquid working electrode can be repeatedly used and then refresh and remain unpolluted from contamination without interference among polarographic waves. Yilmaz et al. tried to apply this method and detected nitrite trace using differential pulse polarography (DPP) with a dropping mercury electrode (DME). Materials such as indium tin oxide (ITO) and gold or diamond electrode are not suitable for batch manufacture and application because they are fragile, expensive and make fabrication difficult [43].

For detection of biological tissue, it is not possible to use large electrode stick. So, microelectrodes have been fabricated and investigated to extend the detection area in this case. In order to clean electrodes and eliminate the harmful effects that are caused by deposition of oxides, gas bubbles and ions of chemical, sonotrodes¹ have been introduced in electrochemistry detection systems. By using sonotrodes, the *in situ* detection system can continuously work longer with a self-cleaning ability and nitrite electrodes can detect solutions with highly passivating² materials [44].

Potentiometric electrodes: they detect ions with the assistance of organic membranes that contain an appropriate ionophore or ion-exchanger with specific binding affinity for the target ion and carry a particular charged species from the sample to the electrode area. A potential difference is formed between the reference and indicator electrodes with the appearance of a charged species. No species are consumed or produced between electrodes and no current flow is generated. If the concentration of the ion is low and the activity coefficients can be considered constant, the potential difference would vary with the logarithm of the concentration and there is no need to calibrate the response curve.

Potentiometry with ion-selective electrodes has tremendously improved in recent years. The main benefits of this method are signal selectivity, the ability to explore a large range of species that are not redox-active in aqueous environments, low detection

¹ A sonotrode is a tool that creates ultrasonic vibrations and applies this vibrational energy to a gas, liquid, solid or tissue. A sonotrode usually consists of a stack of piezoelectric transducers attached to a tapering metal rod.

² As a technique, passivation is the use of a light coat of a protective material, such as metal oxide, to create a shell against corrosion.

limit and applicability to colored and turbid samples. The required instrumentation is also simply fabricated, easily accessible, cheap and portable [45].

Recent researches for the detection of nitrite concentrations relied on fabrication ionselective electrodes, covered with membranes incorporated with suitable ionophores. The common problem related to potentiometric methods are low electrode response, interference with other species, and unfeasible miniaturization-due to unstable potential when the electrode approaches micrometer- dimensions, common fluctuation of reference potential and potential drifts with time.

In potentiometric methods, two type of electrodes are applied including a reference electrode and working electrodes. A saturated calomel electrode (SCE)¹ or Ag/AgCl electrode is typically employed to provide a reference for the working electrode. The working electrode, which provides selectivity and sensitivity towards the species, is more complex than the reference electrode. A number of nitrite ion-selective electrodes have been reported, but strong interference effects existed from anionic species such as perchlorate, thiocyanate and iodide in a polymeric membrane doped with Co-salen as an ionophore and acetate salts of three Co(III)-tetraphenylporphyrin derivatives [46], [47].

The cobalt (III)-based complexes cannot sufficiently withstands against lipophilic anions such as thiocyanate and salicylate. But, a PVC-based membrane nitrite sensor based on the Co(II)-salophen complex (CSC) shows good selectivity over fluoride, bromide, iodide, sulfite, nitrate, thiocyanate, triiodide and perchlorate. The best nitrite selectivity and longest functional lifetimes were obtained with membranes doped with carboxylated PVC and Rh-tBTPP, respectively. The response time can be partially shortened by employing polymer matrix additives such as polyurethanes or carboxylated PVC [48].

PVC membrane electrodes covered with nitrite-selective carriers have been fabricated as a nitrite-responsive detector with good selectivity. However, the PVC membrane has

¹ The Saturated calomel electrode (SCE) is a reference electrode based on the reaction between elemental mercury and mercury(I) chloride

poor adhesion on certain solid substrates, such as silicon chips; thus, other polymeric matrices have been explored, including functionalized PVC, polyurethane (PU), silicone rubber and poly (acrylate or methacrylate), accompanied by poor electrochemical performance and limited plasticizer compatibility. Significant potentiometric anion response and selectivity of the metal (III) porphyrin membranes were also observed in the presence of endogenous cationic sites in PU. On the contrary, the anionic sites in PVC have no added exogenous lipophilic sites [49].

Impedimetric electrodes: in electrochemical sensors, the impedance is proportional to an increase in nitrite concentration. It is necessary to perform simulations to obtain the impedance of this electrode type. When a voltage stimulation is applied to the electrode, the current from the electrode must be detected, and current stimulation requires voltage detection. A few inorganic impedimetric nitrite electrodes have been investigated and stability data acquired.

Wang et al. immobilized NEA onto a gold electrode to form positively charged selfassembled monolayers (SAMs). The positive charges on the electrode facilitated access of the negatively charged $[Fe(CN)_6]^{3-/4-}$ probes to the electrode surface. The nitritemediated Griess¹ reaction between NEA and sulfanilic acid (SA) on the electrode surface lead to the formation of negatively charged SAMs, which produced a barrier to electron transfer between the redox probe and the electrode. This Griess reaction-based method has been demonstrated, achieving a detection limit of 20 n Mol [50].

A flow-injection system has been developed based on the use of a zinc-filled reduction column and a bulk acoustic wave impedance sensor (BAWIS) as detector. Both nitrate and nitrite are converted on-line to ammonia with water as a carrier stream, but only nitrate is converted to ammonia with sulfamic acid as a carrier. The formed ammonia diffuses across membrane and is trapped in an acid stream, causing a change in the solution conductance. The system achieves a detection limit of 1.8μ Mol for nitrite [51].

¹ The Griess test is a chemical analysis test which detects the presence of organic nitrite compounds

Chapter Four

Impedance Spectroscopy of Nitrate sensor

4 Impedance Spectroscopy of Nitrate sensor

The journal paper presented in [52] by the author of this thesis has been included in chapter 4.

The advent of smart cities allows sensor owners to register and connect their devices to feed data into an online database for storage, and to allow developers to connect to the database and build their own applications [53]. Interest in smart cities is motivated by major challenges pertaining to sustainable growth, including the growth of urban infrastructure and rising urban populations, which, amongst other things, are putting pressures on food production, water supplies, and the environment. The need to reduce costs and resource consumption, to minimize fertilizer usage in the environment, and to optimize crop production worldwide have motivated the development of low-cost, online digital sensor technologies for monitoring the concentration of ionic nutrients in agriculture, notably nitrate, phosphate, and potassium [54]. Nowadays, the detection and identification of nutrients still rely on conventional sampling laboratory techniques, which are costly, laborious, and not always suitable for real-time monitoring in farm or large-scale industry settings. Therefore, a research challenge in this field is focused on the need to develop rapid, reliable, specific, and sensitive methods to detect and monitor these nutrients cost-effectively [55], [56], while large scale analysis implies improved miniaturization, reduction of analysis time and cost, and multi-ion detection [57].

Precision agriculture (PA) is a farming management concept based on observing, measuring and responding to field variability in crops [58]. Crop variability typically has both a spatial and temporal component which makes data acquisition, computational treatments, and statistical analysis ubiquitous. The objective of precision agriculture research pertains to the ability of optimizing returns on inputs while preserving resources (water, fertilizer, *etc.*). The practice is enabled significantly by the development of digital sensor technologies arrayed across the field that communicate in real-time to a central management system the amount of phosphate, nitrate, or potassium in the soil or in other growing media. The system's ability to determine and locate in real-time the precise nutrient content allows for the creation of maps of the spatial/temporal variability of nutrient for specific crop management, which may be specific to open farm lands, tree nurseries, or greenhouse settings, *etc.* Measuring the

spatial and temporal variables of crop using an array of nutrient sensors is key to defining smart strategies for efficient resource use and sustainable growth.

Many ion sensors or different methods have been developed in recent years to perform crop monitoring. Among these, electrical conductivity (EC) meters have been used extensively to measure soil salinity [59], however the lack of ion selectivity for this method makes it inadequate for the quantitative measurement of specific ions. In addition, EC measurement techniques such as time domain reflectometry (TDR) and frequency domain reflectometry (FDR) relate to the propagation of a voltage pulse and measurement of the reflected wave; however, they are usually power hungry and processor intensive, which are sets of attributes inappropriate for low-cost sensors. Digital sensor technology based on electrical impedance spectroscopy (EIS) is becoming a powerful tool in precision agriculture because it involves a relatively simple electrical measurement that can readily be automated and whose results may often be correlated with many complex materials variables: from mass transport of fertilizers, rates of reactions with the growing medium, and local ion concentrations [60]. While EIS analysis has been used to perform tasks such as corrosion monitoring [61], fuel cell analysis [62], bio-sensing [63], mineral nutrient detection in plants [64], [65], breast cancer detection [66], and glucose determination [67], this section describes a novel, low-cost, and portable nitrate sensor based on EIS for the determination of trace amounts of NO₃⁻ in selected growing media used in tree nurseries. The nitrate sensor can be integrated to conventional digital microelectronics or CMOS platforms to perform online nitrate sensing continuously, and feed data into a database for storage and analysis. This section describes the structural design, the Nyquist impedance response, the measurement accuracy, and the field testing of the EIS nitrate sensor performed within a tree nursery setting under the International Organization for Standardization (ISO) and the International Electro-technical Commission (IEC) certifications #17025.

4.1.1 Chemistry of the EIS Sensor

4.1.1.1 EIS Nitrate Sensor Structure

The electrochemical nitrate sensor comprises a set of electrode wires surrounded by an ion selective polymer membrane, as shown in Figure 18a. The polymer membrane is inserted into the growing medium (preferably wet) and interacts locally with the medium under test. This sensor configuration provides two different electrical conduction paths, one within the polymer membrane and the other into the medium under test, depicted as paths 1 and 2 in Figure 18b, respectively. The equivalent electrical circuit of the sensor is described in Figure 18c. The polymer membrane is composed of high molecular weight polyvinyl chloride (PVC—from Aldrich) and of a plasticizer bis(2-ethylhexyl) phthalate (BEHP-also from Aldrich). PVC-BEHP is an attractive scaffold for the development of low-cost, non-toxic, and chemically-stable sensors, and provides ease of fabrication and solubility in tetrahydrofuran (THF). Ion-selectivity is provided by adding two components to the polymer membrane: an ionophore and ionic sites. For the nitrate sensor, the ionophore consisted of tetramethyl-cyclotetra-decanato-nickel (II) complex (NiTMTAA), and the ionic site consisted of trioctylmethylammonium chloride (TOMAC-from Aldrich). Both of these have been chosen according to the reversibility, selectivity (>4 $pK_{NO_{3},A^{-}}^{pot}$, where A⁻ stands for NO₂⁻, HPO₄²⁻, SO₄²⁻, or Cl⁻) and efficiency reported in previous potentiometric studies [68]. All chemicals, except the synthetized ionophore, were reagent grade and used without further purification. Together, this polymer membrane composition can be dissolved into THF and molded into any desired shape prior to drying, which brings mechanical strength, environmental endurance, and abrasion resistance, and which defines a stable baseline of electrical conductivity to the system. The membrane exhibits low polarity in order to limit the entry of water and ions in the system. Also, the plasticizer reduces the glass transition temperature Tg of the polymer, and brings molecular mobility to the membrane; this property is necessary to enhance the speed of interaction with the medium under test.

The sensors were fabricated using a dip-coating process to cover the electrodes uniformly with the polymer membrane. The electrodes were made from copper wires (923UL-9 from Consolidated Electronic Wire and Cable), and inserted into a 5 mm-diameter 100 mm-long alumina rod comprising two parallel hollow cavities spaced by a gap of 0.6 mm. Alumina has been chosen for its dielectric, mechanical, and chemical strength properties. The copper wires protruded out of the alumina rod over a length of 5 mm along which the polymer membranes were coated. The dip-coating process consisted of immersing the protruding copper wires into a THF-dissolved polymer

solution of abovementioned composition, followed by a 24-h drying at room temperature in order to let the THF evaporate and the polymer membrane solidify. Successive dipping and drying were performed until all the electrodes were fully covered by a 1 mm-thick membrane.



Figure 18: (a) Picture of the polyvinyl chloride-bis(2-ethylhexyl) phthalate (PVC-BEHP) electro-chemical nitrate sensor, (b) Schematics of the main electrical conduction paths, one within the polymer membrane and the other into the medium under test, and (c) Equivalent electrical circuit of the sensor.

4.1.1.2 Medium Under Test

Laboratory measurements were performed by immersing the PVC-BEHP electrochemical nitrate sensors in 10 mL of KNO₃-containing (Aldrich—selectophore grade) deionized water (18 M Ω ·cm) solutions set at 20 °C room temperature, while making sure to avoid sensor contact with any glassware surface. The sensors were left immersed in the solution for about 5 min to provide enough time for interaction and equilibrium with the ions. Field test measurements were performed in a white spruce (*Picea glauca* (Moench) Voss) seedling tree nursery setting. The measurement method consisted of immersing the sensors in about 300 mL of sampled growing medium (peat-vermiculite 80/20% v/v, density of 0.11 g/cm³, pH_{H=O} 3.8, pH_{CaCl=} 3.1, C.E.C. 106 meq/100 g, N_{min} 53 mg/Kg, N_{NO⁵} 6 mg/Kg, P 13 mg/Kg, K 20 mg/Kg) mixed with water to reach saturation at about 92% weight of water content. The nitrate measurements obtained from the electrochemical sensors were compared with normalized colorimetric laboratory measurements, which consisted in sampling, centrifuging, and treating the

growing medium using an ISO/IEC 17025-certified methodology described in Section 3.2.3.

4.1.2 Experimental Setup and Results

4.1.2.1 Measurement Setup

Impedance measurement and data collection for the PVC-BEHP electrochemical nitrate sensors were performed using a Solartron Impedance/Gain-phase Analyzer (model 1260A) through an AC frequency range from 1 Hz to 1 MHz. The Solartron measurements exhibited less than 5% error in the real part of impedance and less than 1.5% in the imaginary part of impedance, in the AC frequency range from 1 Hz to 1 MHz, and in the nitrate concentration range from 0 ppm to 6000 ppm. The AC amplitude of the driving signal was set at 200 mV to provide as low-signal, linear regime, and high S/N ratio as possible to the impedance measurements; however, the sensor exhibited impedance non-linearity as further described in Section 3.2.2.3. The connection of the Solartron impedance analyzer to the sensor followed standard procedures described in Section 6.5 of the Solartron 1260 manual [69]. All the probes used during the tests were coaxial cables and the accuracy of the measurements was $\pm 1\%$ for the impedance magnitude and ± 1 degree for phase. The measured impedance referred to the real and imaginary parts of the electrical impedance of the immersed sensors: $Z(\omega) = R(\omega) + jX(\omega)$, where $\omega = 2\pi f$, f is the AC frequency of the measurement in Hertz, and Z is the compounded sum of resistances R and reactances X of the immersed sensor. The modulus of impedance is given by $||Z(\omega)|| = \sqrt{R(\omega)^2 + X(\omega)^2}$

and the phase is given by $\langle Z(\omega) = \tan^{-1}(\frac{X(\omega)}{R(\omega)})$. Studying the impedance spectra of

the system through a wide range of AC frequencies provides an objective and quantitative tool to assess medium variables such as nitrate ion concentration and water content, which may relate to specific elements of an equivalent circuit model for quick processing into useful data [5], [70].

4.1.2.2 Measurement Results



Figure 19: Real (a), Imaginary (b), Phase (c), and Nyquist (d) impedance spectra of the immersed PVC-BEHP electrochemical nitrate sensors, at 200 mV AC amplitude, through a wide range of nitrate (NO3–) concentrations using KNO3-containing water solutions.

Figure 19 shows the impedance spectra results of the immersed PVC-BEHP electrochemical nitrate sensors through a wide range of nitrate (NO₃⁻) concentrations, under laboratory conditions using KNO₃-containing water solutions. Measurement stability was reached after ~1 min immersion. These results show that the impedance spectrum of the PVC-BEHP sensor was strongly dependent on nitrate concentration throughout the range 0.01 ppm to 1000 ppm. The measured Nyquist profiles at the range of AC frequencies from 1 Hz to 1 MHz are indicative of a resistance-capacitance parallel circuit behavior that comprises phenomenological constant phase elements (CPE) as depicted in Figure 18c. A CPE is a component that models impedance elements exhibiting distributed materials properties, and has been proposed to explain the behavior of ionic charges in ionic conductors [71]. A conductivity dominated by the polymer membrane (Path 1) is key to obtaining selective nitrate sensor response; this

membrane-related impedance was dominant at high frequencies and low NO_3^- concentrations, while the impedance of the medium (Path 2) became prominent at low frequencies and high (>100 ppm) NO_3^- concentrations, which leads to a non-selective nitrate sensor response at these conditions.

4.1.2.3 Measurement Non-Linearity

Electrochemical impedance spectroscopy involves the study of the variation of the impedance of an electrochemical system with the frequency of a small-amplitude AC perturbation. In practice, for the impedance measurement data to be reproducible, three main conditions have to be fulfilled. *Linearity*: the applied AC amplitude must be small enough so that the response of the system can be assumed to be linear, in first approximation, but still large enough to measure a response. Although highly reproducible under given conditions, the impedance spectra of the nitrate sensors did not fulfill the linearity assumption; Figure 20 shows that the recorded spectra exhibited a dependency with respect to the applied AC amplitude. The sensor had to be calibrated at a specific AC amplitude value, which was set at 200 mV with 0 V bias, as lower amplitudes led to poor S/N response and poor measurement accuracy. Stability: the overall state of the system must not change significantly during the acquisition of the data. This condition was fulfilled as the sensor exhibited a level of impedance stability of about $\pm 5\%$ during field tests in tree nursery settings, over a period of 1 month in airslit containers of 25 square-shaped cavities (320 cm³/cavity, IPL 25-320, IPL Inc.) filled with moistened 3:1 (v/v) peat-vermiculite. Over this period of time, the sensors were subjected to temperature fluctuations ranging from -2 °C to +29 °C in air, +1 °C to +23°C inside the medium (obtained from thermistors), and to a cumulative irrigation of 65 mm (obtained from a rain gauge model No. TE525M, Texas Instruments). Causality: The measured AC response of the system must be directly correlated to the applied AC stimulus. This correlation implies selectivity to nitrate. Nitrate selectivity was not fulfilled when immersing the sensors in medium containing similar concentrations of Cl^{-} ions. As previously shown in Figure 19, the impedance of the medium (Path 2) becomes prominent at low frequencies and high (>100 ppm) NO₃⁻ concentrations, which leads to a non-selective response of the sensors at these conditions. In order to

alleviate ion cross-detection and achieve good measurement accuracies, this study used simple and controlled growing media such as substrates of peat moss and vermiculite, which relaxed selectivity requirements.



Figure 20: Impedance spectra (Modulus and Phase) of the PVC-BEHP electro-chemical nitrate sensors, at 10 mV (green dots), 200 mV (red dots), and 1 V (black dots) AC amplitudes, showing the measurement dependency with respect to the applied AC amplitude.

4.1.2.4 Equivalent Electrical Circuit

Equivalent electrical circuits greatly aid in the process of fitting observed impedance data for elements with distributed properties. The equivalent electrical circuit model that represented the AC electrical conductivity of the PVC-BEHP electrochemical sensor is illustrated in Figure 18c. It is worth mentioning that both the PVC (path 1) and medium (path 2) are predominantly dielectric materials in nature and therefore exhibited poor DC electrical conductivities. Their electrical properties relate to various delocalized electrical carrier conduction mechanisms at play in non-crystalline materials such as short-range carrier mobility, defect hopping/trapping, and carrier diffusion, which manifest themselves negligibly in DC but may become significant and easily measured at AC frequencies in the kHz and MHz range [71]. In this context, the equivalent electrical circuit model contained both resistance and reactance (capacitive) elements which governed carrier mobility over a broad driving frequency range in AC. Specifically, the electrical circuit model assigned resistances and capacitances related to the nitrate-selective polymer membrane (Path 1: R_1 , C_1) and to the non-selective medium under test (Path 2: C_2 -CPE₁-CPE₂) which comprised phenomenological

constant phase elements (CPE). This electrical model could be applied accurately for all nitrate concentrations investigated in the present study, as demonstrated in Figure 21. The curve fitting had been done using an EIS analyzer software [72]. Overall, it can be seen that the electrical impedance of the polymer membrane was dominant at high AC frequencies and low nitrate concentrations, whereas the electrical impedance of the medium became dominant at low AC frequencies and high nitrate concentrations. As expected, the polymer membrane exhibited a negative phase in the impedance spectra indicative of a resistance-capacitance material response (Path 1), which, however, became strongly attenuated by the non-selective impedance of the medium at NO_3^- concentrations higher than 100 ppm (Path 2).



Figure 21: (Red dots) Nyquist response at 200 mV of the PVC-BEHP electro-chemical nitrate sensor through wide a range of nitrate (NO3–) concentrations. (Green lines) Fitting results using the equivalent electrical circuit model illustrated in Figure 18c.
4.1.2.5 Sensor Circuit Miniaturization

An AD5933 microelectronics platform from Analog Devices was used to obtain a lowcost (~\$60), compact (~ $8 \times 8 \text{ cm}^2$), and portable (~30 g) digital sensor technology that could be deployed, connected, and multiplexed at large scale during field tests. The AD5933 platform is a precision impedance converter circuit board that uses an autobalancing method [73], [74] for impedance measurements up to 10 MΩ, and that combines an AC frequency generator from 5 kHz to 100 kHz, with a 12-bit analog-to-digital converter (ADC). The frequency generator allows an external complex impedance (*i.e.*, sensor) to be excited with a known frequency. The impedance response signal was sampled by the ADC, a discrete Fourier transform (DFT) was processed by the on-board engine, and the results were sent to an online computer for data storage and analysis. The AD5933 employs a trans-impedance amplifier for amplifying the current and then uses the 1024 point on-chip DFT algorithm for separating the real and imaginary parts of impedance. After digitalizing with the ADC [75], a discrete-time impedance wave, Z[n] (n = 0, 1, 2, ...N-1), is obtained by DFT:

$$F\{z[k]\} = Z(e^{j\omega}) = \sum_{k=0}^{N-1} z[k] e^{\frac{-j2\pi kn}{N}} = \sum_{n=0}^{N-1} z[k] \cos(\frac{-j2\pi kn}{N}) - j\sum_{n=0}^{N-1} z[k] \sin(\frac{-j2\pi kn}{N}) = Z_i - jZ_q$$

where Z_i and Z_q indicate respectively the real and imaginary parts of impedance returned by the DFT, both of which could be calibrated with respect to NO₃ concentration in the medium at a specific AC amplitude, with best calibration resolution usually obtained when using the impedance modulus. To our knowledge, this is the first time the AD5933 device was used along with a chemical sensor for environmental analysis; for sake of carefulness this warranted comparison with other known and well calibrated impedance meters. As shown in Figure 22, the AD5933 impedance measurements have been compared with the Solartron impedance analyzer under the same laboratory conditions as described previously, but under a range of frequency limited from 5 kHz to 100 kHz according to restrictions determined by the oscillator module within the AD5933 device [76]. The AD5933 device exhibited higher measurement errors when operating close to upper or lower frequency limits of 5 kHz and 100 kHz, or far from the 200 k Ω calibration resistance. Overall, good agreement in impedance measurements was obtained between the AD5933 and Solartron, to within a ±10% comparative error level, through wide a range of nitrate concentrations. The comparative errors were about $\pm 2\%$ at 200 mV AC amplitude between 0.1 ppm and 100 ppm nitrate, which was the useful measurement range of field tests in tree nursery settings.



Figure 22: a) Comparative sensor impedance measurements made between the AD5933 microelectronics platform and the Solartron Impedance Analyzer b) Measurement setup.

4.1.3 Field Testing in Tree Nursery Under ISO/IEC 17025 Certifications

Ppm-level measurement sensitivity and accuracy, environmental reliability and nontoxicity, and compatibility to ISO certifications are attributes sought for defining smart strategies for efficient and sustainable management of farm lands, tree nurseries, or greenhouses. For the nitrate sensors under study, field test measurements were performed in growing medium selected from a tree nursery of white spruce (Picea glauca [Moench] Voss) species of evergreen coniferous [77], [78], shown in Figure 23. The sensors were inserted into the growing medium and could be used and calibrated under different nursery conditions, such as (1) in-situ under low irrigation conditions (~50% wt water), (2) *in-situ* after irrigation (~75% wt water), or (3) after sampling under water saturation (~90% wt water). For this study, an ISO/IEC 17025-certified methodology was adopted [79]. The measurement method consisted of immersing the sensors in about 300 mL of sampled growing medium (peat-vermiculite 80%/20% v/v, density of 0.11 g/cm³, pH_{H2}O 3.8, pH_{CaCk} 3.1) in a 600 mL beaker; this growing medium was then mixed with deionized water to reach saturation at about 92% wt of water content. The nitrate measurements obtained from the electrochemical sensor were made at that point, and later compared with normalized UV-V is colorimetric laboratory measurements taken of the same growing medium. The colorimetric measurements consisted of filtrating and centrifuging three samples of growing media, passing the aqueous centrifuged filtrate through a reductive column of copper-coated cadmium, and mixing with sulfanilamide and N-(1-naphtyl) ethylenediamine dihydrochlorid (NED). The reduction changed nitrate to nitrite which reacted with sulfanilamide, forming a diazonium compound that gave purple coloration with NED, yielding a specific optical absorption at 520 nm calibrated to provide a precise nitrate concentration. Figure 23 shows the sensor results (made after ~1 min measurement time in the sampled peatvermiculite medium) compared to the UV-Vis colorimetric laboratory measurements of the filtrates (made after ~1 h of filtration, centrifugation, and reduction processes). The sensor results are indicative of ppm-level measurement sensitivity and accuracy for nitrate detection, with much improved ease, versatility, and economy as compared to conventional sampling laboratory techniques. The real part of the measured sensor

impedance provided an accurate correlation with ISO/IEC 17025 certified measurements, in the tested range from 0.4 ppm to 130 ppm of NO_3^- concentration, to within a measurement accuracy of about ±1 ppm (95% confidence level) in the range 1–10 ppm, and about ±10 ppm in the range 50–100 ppm.



Figure 23: Field test results performed in growing medium selected from a white spruce tree nursery, showing the real part of the measured sensor impedance (in M Ω) at 1 kHz AC frequency compared against the ISO/IEC 17025-certified colorimetric NO3– concentration measurements.

4.2 Electrochemical Spectroscopy of Optically

Transparent, Electrically Conductive Glasses

The journal paper presented in [71] by the author of this thesis has been included in section 3.3 and all of its subsections.

The development of multi-material optical fibers that transmit both light and electrical current represents one of many challenges in the field of multifunctional fibers. Phosphate-based glasses, depending on the glass composition, exhibit high solubility to metallic ions, high chemical and mechanical stability, and high glass transition and crystallization temperatures. In particular, the well-studied phosphate glasses belonging to the xAgI–(1x)AgPO3 pseudo-binary system provide high ionic AC conductivities at room temperature. This set of attributes are of great interest to science and technology, as these glasses may form the basis for electro-optics modulator for telecommunication applications where an electrical field applied to the solid can modulate the phase, the

frequency, the amplitude, or the polarization of the incident light passing through the material. They may also be used as microprobes to measure the electrical activity of nervous cells of the brain,10 or into smart textiles where electrically conductive fibers can be integrated inside yarns for different uses in biomedicine.

In recent years, extensive research has been conducted in the Field of ion conductive glasses based on metal halides owing to their fast ion conduction properties. The best known metal halide superionic conductive crystalline compounds are rubidium silver iodide (RbAg4I5) and silver iodide (AgI). The latter is used extensively for ion-conductive glasses because of its low cost and high conductivity compared to RbAg4I5. The alpha phase of crystalline AgI (a-AgI) is stable above 147 C and can reach very high electrical conductivity owing to its body-centered cubic structure (bcc). The silver ions (Ag+) may be in either the octahedral sites, the tetrahedral sites, or between two adjacent iodide ions. It has been demonstrated that this crystalline structure includes 42 sites that provides mobility to the silver ions. Moreover, the coordination around the ions is weak which enables the silver ions to move from one site to another at very weak activation energies. The I anions are also highly polarizable, which enables the silver ions to move easily near the anions by the deformation of the electronic cloud.

4.2.1 Bulk Glasses Electrical Characterizations

We investigated the complex impedance of the glasses to characterize the materials under AC current. Figure 24 shows two examples of Nyquist complex impedance spectra recorded at three different temperatures on samples. The measured Nyquist profiles are indicative of a resistance–capacitance parallel circuit behavior that comprises a phenomenological constant phase element (CPE). The CPE is a component that models impedance elements exhibiting distributed materials properties, and has been proposed to explain the behavior of ionic charge carriers in ionic conductors. Equivalent circuits greatly aid in the process of fitting observed impedance data for elements with distributed properties. It has been shown in different studies that CPE behavior could represent the ions mobility in Li-ions borate conductive glasses and yttria stabilized zirconia (YSZ). The CPE was an essential element that provided accurate modelization of the AgI–AgPO3–WO3 glass complex impedance of Figure 24 , for all range of compositions studied. The equivalent circuit that represents the conductivity of the glasses is schematized in Figure 24c. This simple electrical model could be applied for all glass compositions investigated. The model assigns resistances and capacitances related to the electrodes (R1, C1) and to the glass (CPE–C2–C3–R2). Toward high frequencies, the glass-related capacitances (CPE–C2–C3) are less dominant and the contribution of the electrodes is negligible, which mainly let the effect of the conduction resistance of the glass (R2). At low frequency, the response due to the electrodes becomes more prominent.



Figure 24 (a) Nyquist complex impedance spectra of the 45AgI–(55 x)AgPO3–xWO3 glasses as a function of temperature for x=0 (b) and x=25, and (c) equivalent circuit consisting of electrode (R1, C1) and glass material contributions (R2, C2, CPE, C3) (c). Applied voltage: 100 mV.

Chapter Five

A Wireless Multi-sensor Dielectric Impedance Spectroscopy Platform

5 A Wireless Multi-sensor Dielectric Impedance Spectroscopy Platform

The journal paper presented in [80] by the author of this thesis has been included in Chapter 4.

The evolutionary progress of information and communications technology is enabling continuous improvements on *in-situ* sensor technology. Internet connectivity allows physical objects (e.g. household goods, industrial equipment, food and agriculture settings, etc.) to be sensed and controlled remotely across existing network infrastructure such that embedded computing system can collect up-to-date information on objects and processes, creating opportunities for more direct integration between *in-situ* measurements and computer-based systems [81]. In this scenario, often coined the Internet of Things (IoT), objects are provided with identifiers and with the ability to transfer data over a network without requiring human interaction. This enables many aspects of everyday objects to be monitored *in-situ* at a previously unattained level of detail and be interoperable at low cost wirelessly within the existing Internet infrastructure. The ability to sense and react to events in the physical world in an automatic, rapid and informed manner not only opens up new opportunities for dealing with complex or critical situations, but also enables a wide variety of processes to be better understood and optimized cost-effectively [82].

The adoption of connected *in-situ* sensors is largely driven by opportunities to increase productivity, cost-efficiency, monitoring and control of assets [83]. Sensor devices based on dielectric impedance spectroscopy (DIS) or electro-chemical impedance spectroscopy (EIS) exhibit compatibility to IoT architectures as they can be designed to offer low-cost, miniaturized, multiplexed, and connected functionalities, which are key attributes to defining smart strategies for efficient technology scaling and sustainable growth [52]. Network connectivity of DIS and EIS sensor devices is a core function for future service and application development; thanks to the rapid development of microelectronics technology, the cost of wireless network connectivity is no longer a significant factor. Instead of giving DIS or EIS sensor devices conventional standalone operating controls and displays, it becomes progressively more cost-effective to fit them

with a wireless interface such as ZigBee and export their interaction components to the Internet or cellular networks. Of particular interest are the sensor platforms addressing the IEEE 802.15.4 protocol, enabling low-power low-rate wireless personal area networks (LR-WPANs) for the use of 2.4 GHz radio frequency (RF) channels [84]. The interconnection of embedded DIS platforms onto ZigBee meshes is expected to usher in automation in nearly all fields, enabling advanced applications like smart homes, smart grid, and Smart city in order to interface multiple end-point sensors to control and monitor a range of assets. To illustrate such sensor connectivity to Smart homes, Figure 25 depicts a ZigBee wireless network architecture that can be adapted to the connectivity of DIS and EIS sensor devices, which may include sensing end-points such as water quality sensors, fertilizer sensors, and touch sensors, etc., that find applications in many smart household or building environments.



Figure 25: Network Architecture for smart homes using ZigBee platform that can be adapted to the connectivity of DIS and EIS sensor devices such as water quality sensors, fertilizer sensors, and touch sensors.

This chapter presents a low-cost, miniaturized, multiplexed, and connected platform for dielectric impedance spectroscopy (DIS) and electro-chemical impedance spectroscopy (EIS) designed for *in-situ* measurements and adapted to wireless network architectures. The DIS platform was built from commercial off-the-shelf microelectronics components comprising a calibration multiplexer, a DIS analyser, a digital signal controller, and a ZigBee transceiver. The platform has been tested for *insitu* measurement applications pertaining to fertilizer sensing, water quality sensing, and touch sensing, and the concept can be scaled cost-effectively to much larger networks of dielectric impedance sensors.

5.1 Description of the Wireless DIS Platform

5.1.1 System Overview

The developed dielectric impedance spectroscopy platform consists of three main building blocks: (1) an on-the fly calibration and digitally controlled feedback loop, (2) a wireless connectivity module consisting of a ZigBee module, and (3) a dielectric impedance spectroscopy unit. This three-block architecture provides the interface that links *in-situ* DIS sensors with wireless networks. The three blocks are connected to a 16-bit dsPIC33fj128 digital signal controller [85] that carries out the command/data handling and impedance measurement for this system. Figure 26 schematizes the functional block diagram of the DIS platform.

The first block is an analog front end for setting the DC level of the excitation voltage of the sensors. On-the-fly calibration is a microelectronics functionality that allows DIS and EIS sensor devices to be multiplexed to the same microelectronics platform, thus providing the advantage of monitoring multiple sensors at the same time using the same microelectronics board. The user can calibrate the sensor devices for different impedance measurements ranges with known on-board impedances. On-the-fly calibration and digitally controllable trans-impedance amplifiers feedback loop give the ability to connect multiple different sensors to the device, while a digitally controlled feed-back loop reaches a suitable gain-factor for internal trans-impedance amplifiers. For the DIS platform developed in this work, the digitally controlled front-end is designed to multiplex over 3 different DIS sensors labelled as devices under test (DUT) with five calibration/etalon resistors, all connected to a n8:1 multiplexer. This circuit allows on-the-fly switching between the sensors, and the different calibration resistors prevent saturation of the AD5933 dielectric impedance measurement unit.

The second block consists of a wireless connectivity through a ZigBee Mesh consisting of a commercial XBee radio module [86] from Digi International, designed for point-to-point communications at data rates of 250 kbit/s.

The third block is a dielectric impedance measurement unit comprising an AD5933 precision impedance converter circuit from Analog Devices that uses an auto-balancing method [73], [74] for dielectric impedance measurements up to 10 M Ω , with a 12-bit analog-to-digital converter (ADC). The frequency generator allows an external complex impedance (*i.e.*, sensor) to be excited with a known frequency. The impedance response signal is sampled by the ADC, and a discrete Fourier transform (DFT) is then processed by the on-board engine [76]. The AD5933 employs a trans-impedance amplifier for amplifying the current and then uses the 1024 point on-chip DFT algorithm for separating the real and imaginary parts of the impedance. The AD5933 range of frequency for dielectric impedance measurements is limited from 5 kHz to 100 kHz, with the resolution of 0.2 Hz, according to restrictions determined by the 16 MHz oscillator module linked to the AD5933 device [76].

The DIS platform comprises two multiplexer components, the ADG804 and ADG608, which are used for feed-back multiplexer and on-the-fly calibration multiplexer, respectively. These two multiplexers allow the user to change the range of impedance measurement through a ZigBee network. The user can calibrate the platform with different range of impedances and even measure three sensors while using just one calibration resistor. This multiplexing technique helps reduce the overall price of the platform, and can be scaled to multiplexing values much larger than the n8:1 figure chosen in this work. Figure 27 shows an actual picture of the wireless DIS platform. This platform weight only 18 grams, exhibits small dimensions (4cm \times 6cm), and costs less than 110 CAD.



Figure 26: Functional block diagram of the dielectric impedance spectroscopy (DIS) platform.



Figure 27: Picture of the wireless dielectric impedance spectroscopy (DIS) platform.

5.1.2 Dielectric Impedance measurement unit

The dielectric impedance measurement unit consists of the AD5933 network analyzer device and 16 MHz external clock for its internal direct digital synthesis (DDS) engine. The DDS engine produces a programmable frequency sine wave as the excitation wave for the DIS sensors (i.e. DUT). The DDS is capable of exciting the DUT at different voltage levels, wherein the DC voltage level is set at the front-end and the AC voltage level is programmable to values of 200 mV, 400 mV, 1 V, and 2 V. The AD5933 network analyzer device must be calibrated with etalon resistors exhibiting resistance values similar to the impedance range of the DIS sensors. For example, if the DIS sensor provides dielectric impedances ranging from 800 Ω to 1200 Ω , then the ideal calibration resistor would be a 1 k Ω load. The calibration must be done with resistive load in order to determine the internal AD5933 phase. AD5933 does have the phase offset due to internal zeros and poles of the DDS engine, therefore calibration with a known resistor helps to extract this phenomenon.

Figure 28 shows the detailed Schematic of the AFE and Impedance measurement unit. Two multiplexers. U3 and U7. (i.e. AD804YRM and ADG608BRU) are used for multiplexing the feedback resistors and calibration resistors. An AD8606 is used as operational amplifier in the circuits for biasing the DC level of the AFE. AD8606 is an IC which integrate two operational amplifier in one package. The capacitor C17 helps to filter the DC bias generated by the AD5933 and R14, R15, R17 and R19 force the AFE DC level to the $V_{DD}/2$. Changing the DC level of the AFE is straightforward by changing the value of this four resistors and any mistake in choosing this values causes additional leakage current to the DUT and affects the accuracy of the measurements. The connections of the AD5933 is depicted in Figure 28 use of two separated ground plane for analog and digital grounds are mandatory for reaching the best accuracy in the measurements. In this design the analog ground (AGND) is connected to the digital ground (GND) by using inductor L2 to filter impulsive currents sinks of the GND caused by the microcontroller or other digital devices. The I2C bus is used by AD5933 for communications, therefore SCL and SDA pins need pull up resistors according to I2C standards depending on which MCU are used. If the MCU has an internal pull up resistors there is no need to install pull up resistors, otherwise it is mandatory for having



Figure 28: Detailed Schematic of AFE and Impedance measurement unit.

for having a functional I2C bus. In addition, an ASTX-H11, 16 MHz crystal-oscillator (U8) is used as reference clock for AD5933 which generates stable, clear CMOS enabled output for the internal digital signal processing core of the device.

5.1.3 Wireless Connectivity through ZigBee Mesh

The DIS platform is equipped with a ZigBee communication transceiver capable of being used in a ZigBee mesh network with thousands of nodes. As shown previously on Figure 25, the ZigBee mesh is composed of three main category of nodes: ZigBee end points, ZigBee coordinators, and ZigBee routers. ZigBee end points correspond to specific DIS sensors; these nodes communicate with their parent router nodes, and are able to be switched off into a low-energy consumption (sleep) mode. ZigBee coordinator nodes control the formation and the security of the networks, whereas ZigBee routers are the range extenders toward the broader communication network. Routers are usually multi-function nodes which can be reserved as a sensor node and still route the data to other nodes. The DIS platform described in this work can perform all three functionalities of the ZigBee nodes i.e. end node, coordinator, and router, by loading suitable firmware on its ZigBee transceiver.

5.1.4 Digital Signal Controller

All the command and data handling functionality of the analog front-end, impedance measurement unit, and ZigBee transceiver are accomplished by an on-board 16-bit micro-controller unit (MCU) dsPIC33fj128 shown in the Figure 26. The MCU communicates through the I2C bus with impedance measurement unit and employs a UART to communicate with the ZigBee transceiver. The microcontroller firmware sends the appropriate command to the different units of the platform, collects the data, and sends it back through the ZigBee network to the superior nodes. The firmware is designed to provide all the functionalities of the board such as calibration setting, voltage level setting, frequency and sweep parameters setting, and calibration resistor setting. The MCU unit sends back the raw data of the impedance and gain factor at each stage of the calibration command and acknowledges the user of the healthy functionality of the board. Figure 29 shows the flowchart of the DIS platform embedded firmware.

After each hard reset, the platform will send the device health acknowledge to the superior node and waits for the command. The received command is normally contained in the frequency sweep settings or calls for getting the sweep frequency setting at the beginning of the communication. The device enters calibration mode if the user select one of the on-the-fly calibration resistors in the front-end and it goes to the measurement mode if one of the devices under test is being chosen. In the calibration mode, the device calculates the gain factor and save it as a variable for measurement mode routine. In the measurement mode, the device will sweep over the defined frequency span and send the data back to the superior node.

Figure 30 depicts the detailed schematic of the digital section. The P2 port enables the MCU programmer's communication to the board. The SW-PB push-bottom switch enables the hard reset for the MCU core. The U4 Microcontroller is connected to the 8 MHz Y2 crystal to generate the clock which is needed for MCU's internal operations. Capacitors C19 to C24 and C27 to C29 help regulate the voltage of the microcontroller and reduce the impulsive current sinking of the ground due to digital switches. Connections of the Xbee transceiver module and LM1117 voltage regulator are straightforward. A USB bridge (U2) used in the circuit for optional debug of the board in case of malfunctioning of Zigbee transceiver.

The stability of the DIS platform signal versus time is invariant due to nature of the digital design; the time stability of the signal is predominantly limited by the material/environment/temperature stability of the sensors connected to the DIS platform. The platform's power consumption depends on the functionality of the nodes in ZigBee mesh. The ZigBee module is the most power hungry part of the board, drawing 75 mA electrical current during data acquisition (50 mA of which is attributable to the wireless communication functionality), which represents 250 mW power consumption at 3.3 Volt driving potential. A single data acquisition is usually performed in less than 2 second, after that the board will draw around 25 mA current in stand-by mode. The platform may be turned to power-down mode at the end-points of the ZigBee mesh with a current consumption of less than 5 mA.



Figure 29: Flowchart of the DIS platform embedded firmware.



Figure 30: Detailed schematic of MCU and Xbee transceiver.



Figure 31: a) Button layer b) Top layer c, d) 3D representation of the PCB.

5.1.5 Experimental Testing of the DIS Platform for in-situ Dielectric Impedance Spectroscopy

This low-cost, miniaturized, multiplexed, and connected platform has been tested and used experimentally as a DIS sensor node on a ZigBee mesh. It interfaced three DIS sensors at the same time and relayed the information through the Internet for data analysis and storage. Specifically, the platform has been tested for *in-situ* dielectric impedance spectroscopy applications pertaining to fertilizer sensing, touch sensing, and water quality sensing, that find applications in many smart household, building, and industrial environments. To our knowledge, this is the first time a wireless platform featuring an AD5933 device was used along with touch and chemical sensors for environmental monitoring. For the sake of carefulness this warranted comparison with other known and well calibrated impedance meters, such as the 1260 Solartron impedance analyzer that provides accurate complex impedance measurements in the AC frequency range from 1 Hz to 1 MHz.

5.1.6 Electro-Chemical Impedance Spectroscopy (EIS) Nitrate Sensors

Fertilizer sensors, such as nitrate sensors, controlled by DIS platforms find many applications in agriculture and allow the feeding of sensor data into online databases for continuous crop monitoring, production optimization, and data storage. A research challenge in this field is focused on the need to develop rapid, reliable, specific, and sensitive methods to detect and monitor these nutrients cost-effectively [52], while large scale analysis implies improved miniaturization, reduction of analysis time and cost, and wireless connectivity [52].



Figure 32: (a) Picture of the EIS nitrate sensor head connected to the DIS platform, and (b) Schematics of the main electrical conduction paths of the EIS nitrate sensor: one through the polymer membrane and the other throughout the medium under test, with corresponding equivalent electrical circuits.

The tested nitrate sensor comprises a set of electrode wires surrounded by an ion selective polymer membrane, as shown in Figure 32a, and is controlled by the DIS platform described previously. The polymer membrane is inserted into the medium (preferably wet) and interacts locally with the medium under test. This sensor configuration provides two different electrical conduction paths, one within the polymer membrane and the other into the medium under test, depicted as paths 1 and 2 in Figure 32b, respectively. The polymer membrane is composed of high molecular weight polyvinyl chloride (PVC—from Aldrich) and of a plasticizer bis (2-ethylhexyl) phthalate (BEHP—also from Aldrich). Ion-selectivity is provided by adding two components to the polymer membrane: an ionophore and ionic sites. For the nitrate

sensor, the ionophore consisted of tetramethyl cyclotetra-decanato-nickel(II) complex (NiTMTAA), and the ionic site consisted of trioctylmethylammonium chloride (TOMAC—from Aldrich). Both of these have been chosen according to the reversibility, selectivity (>4 pK_{NO_3,A^-}^{pot} , where A⁻ stands for NO₂⁻, HPO₄²⁻, SO₄²⁻, or Cl⁻) and efficiency reported in previous potentiometric studies. Together, this polymer membrane composition can be dissolved into THF and molded into any desired shape prior to drying, which brings mechanical strength, environmental endurance, and abrasion resistance, and which defines a stable baseline of electrical conductivity to the system.

Impedance measurements were performed by immersing the EIS nitrate sensor in 10 mL of KNO3-containing (Aldrich—selectophore grade) deionized water (18 M Ω ·cm) solutions set at 20 °C room temperature. The sensor was left immersed in the solution for about 5 min to provide enough time for interaction and equilibrium with the ions. Figure 33a shows the impedance spectra of the immersed EIS nitrate sensors through a wide range of nitrate (NO3-) concentrations, revealing strong dependence on nitrate concentration throughout the range from 0 to 6000 ppm. The DIS platform measurements have been compared with the Solartron impedance analyzer under the same laboratory conditions, as shown in Figure 33b. The AD5933 device within the platform exhibited higher measurement errors when operating close to upper or lower frequency limits of 5 kHz and 100 kHz, or when the sensor exhibited an impedance value far from the 200 k Ω calibration resistance. Overall, good agreement in impedance measurements was obtained between the AD5933 and Solartron, to within a $\pm 10\%$ comparative error level, through a wide range of nitrate concentrations. The comparative errors were about $\pm 2\%$ at 200 mV AC amplitude between 0.1 ppm and 100 ppm nitrate, which is the typical measurement range of nitrate sensors for agriculture applications.



Figure 33: (a) Nyquist response of the EIS nitrate sensor by the Solartron gain/phase analyzer, tested through a wide range of nitrate (NO3–) concentrations, and (b) Comparative EIS nitrate sensor results obtained using the Solartron impedance analyzer and the DIS platform featuring an AD5933 device.

5.1.7 Water Quality Sensors

Besides being used as nitrate fertilizer sensors for agriculture, the abovementioned EIS nitrate sensors linked in tandem with the DIS platform can be used as a basis for water quality sensors, to the extent that these sensors become sensitive to a wide variety of ions in the medium under test when the conductivity of the medium (path 2) dominates the conductivity of the membrane (path 1), which occurs at ion concentrations higher than 100 ppm with the abovementioned sensor design. Water quality is a measure of the condition of water relative to the requirements of human consumption, and it is most frequently used by reference to a set of standards against which compliance can be assessed [87]. In North America, standards pertaining to the suitability of water for human consumption are usually regulated at the state level, and the following contaminant concentration limits in water may be found: Nitrates (NO3-) 45 ppm; Chloride (Cl-) 307 ppm; Sodium (Na+) 199 ppm; Sulfates (SO42-) 560 ppm. Contaminants that may be found at hundreds of ppm concentration in water include inorganic runoffs from agricultural activities (e.g. nitrate, phosphate, potassium) which are a major cause of water pollution in rural areas. The complexity of water quality as a subject is reflected in the many types of measurements of water quality indicators. Measurements commonly made on-site and in direct contact with the water source include temperature, pH, dissolved oxygen, conductivity, oxygen reduction potential (ORP), and turbidity [87]. Nowadays, citizens demand real-time information about the water they use daily and are drinking. Unfortunately, such information can be very expensive to obtain as water quality is usually sampled and analyzed at certified laboratories requiring water samples to be collected, preserved, transported, and analyzed at diverse locations.

The EIS nitrate sensor connected to the DIS sensor node on ZigBee mesh provides an affordable in-situ measurement technology for water quality sensing. In order to test the suitability of the DIS platform for water quality sensing, a set of water samples have been prepared with known concentrations of nitrate, chloride, sodium and sulfate contaminants. The abovementioned baseline of 45 ppm nitrate (NO3-), 307 ppm chloride (Cl-), 199 ppm sodium (Na+), and 560 ppm sulfate (SO42-) has been used to define contaminant concentration limit in water, wherein the water samples have been prepared by mixing selected molar quantities of potassium nitrate (KNO3) (Sigma-Aldrich-ReagentPlus \geq 99.0%), potassium sulfate (K2SO4) (Sigma-Aldrich, ReagentPlus \geq 99.0%), and sodium chloride (NaCl) (EMD chemicals, GR ACS crystals) in deionized water (18 M Ω .cm). Three water samples have been prepared with 0.1x, 1x, and 10x levels of contaminant concentration limit in water, respectively. The DIS platform measurements, along with comparative Solartron impedance analyzer measurements, have been obtained at 20oC room temperature, at 200 mV AC amplitude, at the AC frequency range from 30 kHz to 55 kHz, and are shown in Figure 34. Overall, good agreement in impedance measurements was obtained between the DIS platform and the Solartron, to within a \pm 15% comparative error level in impedance modulus, and the DIS platform signal-to-noise response was sufficiently high to allow a reliable differentiation between varying contaminant concentration levels in water, either below or above the quality limit set by state-level agencies. Although contaminants in water may come with many different ions and with varying relative concentrations, such DIS platform can be used, for example, as a non-selective distributed sensor for early detections of runoffs from agricultural/industrial activities, where sudden impedance anomalies in water can be detected within seconds and provide trigger for emergency measures.



Figure 34: Comparative EIS water quality sensor results obtained using the Solartron Impedance analyzer (solid lines) and the DIS platform (dotted lines), wherein the baseline of 45 ppm nitrate (NO3-), 307 ppm chloride (Cl-), 199 ppm sodium (Na+), and 560 ppm sulfate (SO42-) has been used to define the contaminant concentration limit in water.

5.1.8 Glass Touchscreen Sensors

The development of glass compounds that transmit both light and electrical current represents one of many challenges in the field of materials sciences. Phosphate-based glasses, depending on the glass composition, exhibit high solubility to metallic ions, high chemical and mechanical stability, and high glass transition and crystallization temperatures [71]. In particular, the phosphate glasses belonging to the AgI-AgPO3-WO3 system provide high ionic AC conductivities at room temperature (i.e. $10-2 \ge \sigma \ge 10-3 \text{ S} \cdot \text{cm}$ -1). This set of attributes are of great interest to science and technology, as these glasses may form the basis for electro-optics modulator for telecommunication applications where an electrical field applied to the solid can modulate the phase, the frequency, the amplitude, or the polarization of the incident light passing through the material [88], [89]. They may also be used as microprobes to measure the electrical activity of nervous cells of the brain [90], or into smart textiles where electrically conductive fibers can be integrated inside yarns for different uses in biomedicine [91].

In this section, the AgI-AgPO3-WO3 glass system [71] and the DIS platform have been used in tandem as the basis for a capacitive touch sensor. Many types of sensors use capacitive sensing, including interface devices such as trackpads and touchscreens [92] that can replace mechanical buttons on screens, doors, and windows. These interface devices are generally enabled by the use of conductive specialty thin films (like Indium-Tin-Oxide, ITO) that tend to be expensive due to containing elements like indium. However, the use of AgI-AgPO3-WO3 glasses could open new opportunities for interface devices such as touchscreens, smart doors, smart windows, etc., as they can be manufactured in large quantities at low cost. For this study, 10 mm diameter, 8 mm thick, 45AgI-(55-x)AgPO3-xWO3 glass samples (with x = 0, 12, and 20 mol%) have been used, as pictured in Figure 35a. Two copper electrodes were pasted on the side of each glass samples using silver paint; the silver paint used consisted of colloidal silver from Pelco® with a sheet resistance of 0.02-0.05 ohms/sq/mil Figure 35b and Figure 35c illustrate the principle behind glass touchscreens: an object (finger, conductive stylus) touches the conductive glass and alters the electrical coupling between the two electrodes, creating a grounded path

along the touch point, thus changing the overall impedance of the system as recorded through the electrodes. An equivalent electro-static model of the glass touchscreen is illustrated in Figure 35c, wherein the touch function actuates the grounded state of the glass system.



Figure 35: (a) Picture of the 45AgI-(55-x)AgPO3-xWO3 glass sample with x = 15 mol%, (b) Representation of the glass touchscreen setup, wherein the copper electrodes were connected to the DIS platform, and (c) equivalent electro-static circuit of the AgI-AgPO3-WO3 glass touchscreen.

First, we have investigated the complex impedance of untouched AgI-AgPO3-WO3 glasses to characterize the materials under alternate current (AC). Figure 36a shows the Nyquist complex impedance spectra recorded using the DIS platform on 45AgI-(55-x)AgPO3-xWO3 glass samples with x = 0, 12, and 20 mol%. The impedance measurements were performed at 22°C in ambient atmosphere. The measured Nyquist profiles are indicative of a resistance-capacitance parallel equivalent electrical circuit behavior [92] as illustrated in Figure 35c. The DIS platform measurements have been compared with the Solartron impedance analyzer as shown in Figure 36b. Overall, good

agreement in impedance measurements was obtained between the AD5933 and Solartron, to within a $\pm 10\%$ comparative error level in impedance modulus.



Figure 36: (a) Nyquist complex impedance of untouched 45AgI-(55-x)AgPO3-xWO3 glasses, using 200mV excitation voltage measured by Slartron gain/phase analyzer, and (b) Comparative impedance results obtained using the Solartron Impedance analyzer and the DIS platform featuring an AD5933 device.

Second, we have investigated the impedance effect of a touched AgI-AgPO3-WO3 glass to characterize the materials as the basis of a glass touchscreen. Figure 37 shows

the touch sensing response on a 45AgI-(55-x)AgPO3-xWO3 (x = 15 mol%) glass sample recorded using the DIS platform at an AC frequency of 100 kHz. The 12-second touches were clearly recorded using the DIS platform, The time plot clearly resolves successive 12-second touches applied to the glass, with "touch" corresponding to higher impedance, thus demonstrating that the DIS platform can be used for in-situ dielectric impedance applications pertaining to touch sensing, enabling advanced applications like smart doors and windows without the use of expensive specialty thin film coatings on the glass.



Figure 37: Touch sensing response of a 45AgI-(55-x)AgPO3-xWO3 (x = 15 mol%) glass sample recorded using the DIS platform at an AC frequency of 30 kHz, at 22°C in ambient atmosphere.

6 Conclusion

Precision agriculture allows the feeding of sensor data into online databases for continuous crop monitoring, production optimization, cost reduction, and data storage. This thesis reported a low-cost, compact, and scalable nitrate sensor based on electrochemical impedance spectroscopy. The nitrate sensor can be integrated to conventional microelectronics or CMOS platforms to perform online nitrate sensing continuously over a wide concentration range from 0.1 ppm to 100 ppm, with a response time of about 1 min, and feed data into a database for storage and analysis. Chapter three described the structural design and microelectronics scaling, the ppm-level measurement sensitivity and accuracy, and the reliable field testing of the nitrate sensors performed within a tree nursery setting under ISO/IEC 17025 certifications, which were attributes sought for such sensors in defining smart strategies for efficient and sustainable management of farm lands, tree nurseries, or greenhouses.

The ability to sense in an automatic manner enables a wide variety of processes to be better understood and optimized cost-effectively. Chapter four of this thesis described the development of a low-cost, miniaturized, multiplexed, and connected platform for dielectric impedance spectroscopy (DIS) designed for *in-situ* measurements and adapted to wireless network architectures. The platform has been tested and used as a DIS sensor node on ZigBee mesh and was able to interface up to three DIS sensors at the same time. The system was built from commercial microelectronics components and benefits from an on-the-fly calibration system that makes sensor calibration easy. The thesis described the microelectronics design, the Nyquist impedance response, the measurement sensitivity and accuracy, and the testing of the platform for *in-situ* dielectric impedance spectroscopy applications pertaining to fertilizer sensing, water quality sensing, and touch sensing. To our knowledge, this is the first time a wireless platform featuring an AD5933 device was used along with touch and chemical sensors for environmental monitoring.

7 Future Works

Nowadays sensors play important role in the civilized life. The type of sensor developed and characterized in the chapters 4 and chapter 5 can be used vastly in the smart homes and smart agricultures.

Developing the network suited for home applications or farm can be the next step of this work. Connecting this networks to the mobile networks can be another issue. In the smart cities it is imaginable that the user can monitor for example water quality of their home drinkable water with their cell phone. In smart agriculture, the farmer can measure different nutrition the different areas of the farm and take the proper action immediately on his phone or computer.

Another aspect of development of the sensors could be miniaturizing the sensors which is currently master project of Madam Mathilde Loubier under supervision of the Professor Messaddeq.

Electrically conductive, optically transparent glasses can be used for simulations optogenetics stimulation and recording in the neuroscience. This helps to integrate the electrode and stimulation LED/fiber together which can lead to improvement in the accuracy of the measurement. In this method, user can be sure that the measured data of the neuron's spiking activity is exactly recorded in the stimulation site.

8 Contribution to knowledge

During this project, the following papers have been published.

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