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Salinity (conductivity) sensor based on parallel plate capacitors

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Salinity (Conductivity) Sensor Based on Parallel Plate Capacitors

by

Shreyas Bhat

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering
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Keywords: Impedance, oscillator, dielectric, polarization, complex permittivity

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DEDICATION

This dissertation is dedicated to my parents, Gopal Krishna Bhat and Sulochana Bhat, my brother, Suraj and sister, Naina. Their love, support and patience have always been the inspiration of my life.
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TABLE OF CONTENTS

LIST OF TABLES.................................................................................................................................................v

LIST OF FIGURES .................................................................................................................................................. vi

ABSTRACT.......................................................................................................................................................... ix

CHAPTER 1: INTRODUCTION..........................................................................................................................1

1.1 Definitions of Salinity........................................................................................................................................2

1.2 Composition of Seawater..............................................................................................................................3

1.3 Processes Influencing Ocean Salinity........................................................................................................4

1.3.1 Processes Decreasing Salinity...............................................................................................................4

1.3.2 Processes Increasing Salinity..............................................................................................................5

1.4 Need for Salinity Sensing..........................................................................................................................5

1.4.1 Ocean Circulation......................................................................................................................................6

1.4.2 Marine Life...............................................................................................................................................7

1.4.3 Water Cycle..............................................................................................................................................9

1.5 Motivation....................................................................................................................................................9

1.6 Thesis Outline..............................................................................................................................................10

CHAPTER 2: LITERATURE REVIEW..................................................................................................................11

2.1 Conductivity................................................................................................................................................11

2.2 Practical Salinity Scale (PSS) of 1978.........................................................................................................12
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3</td>
<td>Current Approaches at Conductivity Sensing</td>
<td>13</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Contact Type Sensors</td>
<td>13</td>
</tr>
<tr>
<td>2.3.1.1</td>
<td>2-Probe Conductivity Sensors</td>
<td>13</td>
</tr>
<tr>
<td>2.3.1.2</td>
<td>4-Probe Conductivity Sensors</td>
<td>15</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Non-Contact Type Sensors</td>
<td>15</td>
</tr>
<tr>
<td>2.3.2.1</td>
<td>Single Transformer</td>
<td>16</td>
</tr>
<tr>
<td>2.3.2.2</td>
<td>Double Transformer</td>
<td>18</td>
</tr>
<tr>
<td>2.4</td>
<td>IDT Configuration in Measurement of Conductivity</td>
<td>22</td>
</tr>
</tbody>
</table>

**CHAPTER 3: THEORY AND UNDERSTANDING**

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Fundamentals of a Capacitor</td>
<td>25</td>
</tr>
<tr>
<td>3.2</td>
<td>Complex Permittivity and Dielectric Loss</td>
<td>26</td>
</tr>
<tr>
<td>3.3</td>
<td>Polarization of Materials</td>
<td>27</td>
</tr>
<tr>
<td>3.4</td>
<td>Types of Polarization</td>
<td>29</td>
</tr>
<tr>
<td>3.4.1</td>
<td>Interface Polarization</td>
<td>29</td>
</tr>
<tr>
<td>3.4.2</td>
<td>Electronic and Atomic Polarization</td>
<td>29</td>
</tr>
<tr>
<td>3.4.3</td>
<td>Ionic Polarization</td>
<td>30</td>
</tr>
<tr>
<td>3.4.4</td>
<td>Orientation (Dipolar) Polarization</td>
<td>30</td>
</tr>
<tr>
<td>3.5</td>
<td>Contribution of Polarization to Permittivity</td>
<td>31</td>
</tr>
<tr>
<td>3.6</td>
<td>Interfacial or Space Charge Polarization</td>
<td>32</td>
</tr>
<tr>
<td>3.7</td>
<td>Relaxation Time</td>
<td>33</td>
</tr>
<tr>
<td>3.8</td>
<td>Debye Theory of Dielectric Behavior</td>
<td>34</td>
</tr>
<tr>
<td>3.9</td>
<td>Cole-Cole Diagram for Complex Permittivity</td>
<td>35</td>
</tr>
<tr>
<td>3.10</td>
<td>Dependence of Permittivity on the Concentration of Analyte</td>
<td>36</td>
</tr>
</tbody>
</table>
3.11 Temperature Dependence of Permittivity ..............................................................37

3.12 Assessment of Barrier Properties of Polymeric Coatings on the Electrodes .......38

3.12.1 Impedance Spectroscopy ...............................................................................39

3.12.2 Double Charge Layer .................................................................................42

CHAPTER 4: DESIGN, OPTIMIZATION AND CONSTRUCTION ..............................44

4.1 Minimization of Fringe Field Effects Using Guard Rings ...............................44

4.2 Detection Circuit Employing Twin-T Oscillator ..............................................49

4.3 Construction of the Sensor ..............................................................................53

4.4 Equivalent Circuit Model for the Sensor ............................................................56

4.5 Alternate Detection Circuit for Capacitive Salinity Sensor ...............................57

CHAPTER 5: RESULTS ................................................................................................61

5.1 AZ5214 as the Insulation Layer ........................................................................61

5.1.1 Impedance Data for Varying Salinities at 22 °C ........................................62

5.1.2 Impedance Data for Varying Temperatures at Constant Salinity ...............65

5.1.3 Twin-T Oscillator Frequency Versus Salinity ..............................................67

5.1.4 Twin-T Oscillator Frequency Versus Temperature .......................................68

5.2 ACCUFLO Spin-on-Polymer as the Insulation Layer ....................................69

5.2.1 Impedance Data for Varying Salinities at 22 °C ........................................69

5.2.2 Impedance Data for Varying Temperatures at Constant Salinity ...............72

5.2.3 Twin-T Oscillator Response with Spin-on-Polymer as Insulation Layer .......73

5.2.4 Twin-T Oscillator Frequency Versus Temperature .......................................74

5.3 Response of F-V Converter Circuit .................................................................74

5.3.1 Output Voltage Versus Salinity at 22 °C ....................................................75
5.3.2 Output Voltage Versus Temperature at Constant Salinity

5.4 Comparative Study

CHAPTER 6: CONCLUSION AND FUTURE WORK

6.1 Conclusion

6.2 Future Work

REFERENCES
LIST OF TABLES

Table 5.1: Parameters for the Randel’s Cell Obtained from the Nyquist Plot ..................63

Table 5.2: Randel’s Cell Parameters for Varying Temperatures at Constant Salinity (34.821 psu) ........................................................................................................66

Table 5.3: Comparison Chart for Materials Used and Detection Techniques Proposed .76
LIST OF FIGURES

Figure 1.1: Major Constituents of Seawater...............................................................3
Figure 1.2: Energy Transfer through the Conveyor Belt...........................................7
Figure 2.1: 2-Probe Conductivity Sensor .................................................................13
Figure 2.2: 4-Probe Conductivity Sensor ..................................................................15
Figure 2.3: Single Transformer Conductivity Sensor Shown with Seawater as the Surrounding Media .................................................................16
Figure 2.4: Equivalent Circuit for Single Transformer Design.................................17
Figure 2.5: Schematic for a Double Transformer Conductivity Sensor....................19
Figure 2.6: Capacitor Configurations: (a) Cylindrical Set-Up, (b) IDTs .....................22
Figure 2.7: IDT Conductivity Cell and Equivalent Circuit ........................................22
Figure 3.1: Parallel Plate Capacitor Configuration ..................................................25
Figure 3.2: Loss Tangent Vector Diagram .................................................................27
Figure 3.3: Polarization Phenomenon in Dielectric Molecules ..................................28
Figure 3.4: (a) Dipole Rotation in Applied Field, (b) Macroscopic Representation of Orientation Polarization Under the Influence of an Applied Electric Field .........................................................30
Figure 3.5: Frequency Response of Various Polarization Mechanisms......................31
Figure 3.6: Transition in Polarization with Sudden Field Drop ...............................33
Figure 3.7: Debye Relaxation of Water at 30 °C .....................................................34
Figure 3.8: Cole-Cole Representation of the Debye Model of Water at 30 °C ..................35
Figure 3.9: Hydration Process in a Solute-Solvent Mixture ...........................................37
Figure 3.10: Typical Nyquist Plot of the Complex Impedance .......................................41
Figure 3.11: Randel’s Cell Circuit Model .........................................................................41
Figure 3.12: Gouy-Chapman for Metal-Electrolyte Interaction ......................................42
Figure 4.1: Capacitor Incorporating Kelvin Guard Ring ..................................................44
Figure 4.2: 2-D Model of the Sensor Developed in FEMLAB ........................................46
Figure 4.3: 2-D Meshed Model of the Capacitor ............................................................47
Figure 4.4: Potential and Electric Field Distribution of the Sensor in Seawater ..............47
Figure 4.5: Sensor with Guard Rings for Field Minimization ..........................................48
Figure 4.6: Simulated Result for Capacitor with Guard Ring ........................................48
Figure 4.7: Twin-T Notch Filter Circuit .................................................................49
Figure 4.8: Twin-T Filter Response Simulated Using Pspice ..........................................50
Figure 4.9: Schematic of Twin-T Oscillator .................................................................51
Figure 4.10: Oscillator Response Simulated Using Pspice ..............................................51
Figure 4.11: Set-Up for Twin-T Oscillator with Capacitive Sensor ..................................52
Figure 4.12: Process Flow Steps for Fabrication of the Sensor ......................................53
Figure 4.13: Fabricated Sensors Prior to Alignment .....................................................55
Figure 4.14: Top-View of the Completed Sensor ............................................................55
Figure 4.15: (a) Maxwell-Wagner Layered Capacitor Model, (b) Equivalent Circuit Model, (c) Reduced Model, (d) Equivalent Circuit for Reduced Model and e) Simplified Model ..........................................................56
Figure 4.16: Block Diagram of the Circuit Employing Two F-V Converters and a Differential Amplifier Stage ..........................................................57
Figure 4.17: Set-up for the Frequency-to-Voltage Converter Approach .........................58

Figure 4.18: Detailed Schematic of Sensor Detection Circuit with Calibration Adjustment ...................................................................................................................................59

Figure 5.1: Plot of Complex Impedance for Different Salinity Concentrations (psu) ....62

Figure 5.2: Plot of Capacitance Versus Frequency for Varying Salinities at 22 °C........64

Figure 5.3: Plot of Capacitance Versus Salinity for 40 KHz at 22 °C.............................65

Figure 5.4: Nyquist Plot for Varying Temperatures (Salinity = 34.821 psu).....................66

Figure 5.5: Plot of Capacitance Versus Frequency for Varying Temperatures at Constant Salinity ...................................................................................................................................67

Figure 5.6: Twin-T Oscillator Frequency Versus Salinity at 22 °C ................................68

Figure 5.7: Twin-T Oscillator Frequency Versus Temperature at 34.471 psu.................68

Figure 5.8: (a) Plot of Complex Impedance for Varying Salinities at 22 °C, (b) Equivalent Circuit Model for Metal-Electrolyte System corresponding to the Plot in (a)...................................................................................................................................70

Figure 5.9: Plot of Capacitance Versus Frequency for Varying Salinities at 22 °C .........71

Figure 5.10: Plot of Capacitance Versus Salinity for a 2 KHz Signal at 22 °C..............71

Figure 5.11: Nyquist Plot for Varying Temperatures at Constant Salinity (34.856 psu) ....72

Figure 5.12: Plot of Capacitance Versus Frequency for Varying Temperatures (34.856 psu) ...................................................................................................................................73

Figure 5.13: Oscillator Frequency Versus Salinity at 22 °C .......................................73

Figure 5.14: Plot of Oscillator Frequency Versus Temperature at Constant Salinity of 32.891 psu ...................................................................................................................................74

Figure 5.15: Output Voltage Versus Salinity at 22 °C ..................................................75

Figure 5.16: Output Voltage Versus Temperature at 34.65 psu ...................................76
SALINITY (CONDUCTIVITY) SENSOR BASED ON PARALLEL PLATE CAPACITORS

Shreyas Bhat

ABSTRACT

This work is aimed at developing a high sensitivity salinity (conductivity) sensor for marine applications. The principle of sensing involves the use of parallel plate capacitors, which minimizes the proximity effects associated with inductive measurement techniques. The barrier properties of two different materials, AZ5214 and Honeywell’s ACCUFLO T3027, were investigated for use as the insulation layer for the sensor. Impedance analysis performed on the two coatings using Agilent’s 4924A Precision Impedance Analyzer served to prove that ACCUFLO was a better dielectric material for this application when compared to AZ5214.

Two separate detection circuits have been proposed for the salinity sensor. In the Twin-T filter method, a variation in capacitance tends to shift the resonant frequency of a Twin-T oscillator, comprising the sensor. Simulations of the oscillator circuit were performed using Pspice. Experiments were performed on calibrated ocean water samples of 34.996 psu and a shift of 410 Hz/psu was obtained. To avoid the problems associated with the frequency drift in the oscillator, an alternate detection scheme is proposed which employs frequency-to-voltage converters. The sensitivity of this detection scheme was observed to be 10 mV/psu.
CHAPTER 1
INTRODUCTION

Since archaic times, oceans have been used as a mode of transport and a source of food. However, it was not until late nineteenth century that oceans were perceived as information-rich reservoirs of scientific importance. The impetus for further oceanic studies began in the 1930s with the search for petroleum, continued with the emphasis for improved naval warfare and more recently expressed, to protect the ecosystem. Among the different facets of oceanography, physical oceanography relates to the study of physical properties and dynamics of the ocean, the primary interests being the ocean-atmosphere interaction, the oceanic heat budget and the coastal dynamics. No discussion on oceanography is complete without a mention of parameters such as salinity, temperature, pressure and density. Extensive research has been done to understand the role of these parameters in regular oceanic processes, but there is still a lot of latent information that seems to remain elusive to the oceanographers worldwide. This work is primarily aimed at developing a salinity sensor for marine applications and hence, in the following sections, we shall focus on salinity and its significance in oceanography.
1.1 Definitions of Salinity

Salinity (derived from the Latin equivalent salinus = salt) is commonly defined as the ratio between the weight of dissolved material in the sea water sample and the weight of the sample [1]. This ratio is generally expressed in parts per thousand. The dissolved material includes dissolved gases, because even gases dissolve in water. However, it excludes fine particles being held in suspension and other solids that are in contact with sea water. Salinity is also conveniently referred to as TDS or Total Dissolved Salts.

It is nearly impossible to determine the total amount of dissolved salts in a sample by direct chemical analysis. In addition, it is impossible to obtain reproducible results by evaporating seawater to dryness and weighing the residue as some of the material present, mainly chloride, is lost during the final stages of drying (Sverdrup, Johnson, and Fleming) [2]. Hence, it is logical to employ an alternate technique that yields reproducible results which albeit does not give the exact amount of salts dissolved, yet represents a quantity of slightly lower numerical value than TDS. The International Council for the Exploration of the Sea established a technique in 1902, according to which salinity is defined as the total amount of solid material in grams contained in one kilogram of sea water when all of the carbonate has been converted to oxide, the bromine and iodine replaced by chlorine, and all organic matter completely oxidized. This method is accurate but difficult to use routinely [3].

William Dittmar’s analysis of 77 ocean water samples, collected during the HMS Challenger’s circumnavigation expedition around the globe, led to the establishment of The Principle of Constant Proportions. This theory explains that the major dissolved constituents responsible for the salinity of sea water occur nearly everywhere in the ocean
in the exact same proportions, independent of its salinity. This constancy of composition was then exploited to deduce the salinity of sea water by measuring its single largest constituent, the chloride ion [1]. The weight of this ion in the water sample is termed as chlorinity. In 1966, a joint panel on Oceanographic tables and standards offered a more accurate definition of salinity based on its chlorinity, which is mathematically expressed by the relation,

\[ S = 1.80655 \text{ Cl} \]  \hspace{1cm} (1.1)

It is apparent that salinity is a ratio, and is hence, unitless. The Practical Salinity Scale (PSS) established in 1978, uses the term Practical Salinity Units (psu), as the standard unit for the salinity, and is essentially parts per thousand of sea water. The general representation for psu is ‰. An advantage of expressing salinity in psu is that decimals are often avoided and values convert directly to grams of salt per kilogram of sea water.

### 1.2 Composition of Seawater

Seawater is a solution of salts of nearly constant composition, dissolved in variable amounts of water.
The seawater is a mixture of more than 70 dissolved elements. However, only 6 of these constitute more than 99% of all the dissolved salts; all occurring as ions (electrically charged atoms or group of atoms) [1]. The major constituents of seawater are as shown in Figure 1.1.

1.3 Processes Influencing Ocean Salinity

Since, the salinity of seawater is not the same throughout the ocean, it maybe of relevance to know what processes actually influence salinity. Apparently, salinity can be altered by varying either of the two components – the amount of dissolved salts or the amount of water. Nonetheless, the salts occur in almost the same proportions. An overview of the processes that tend to decrease/increase salinity is given in the following sections.

1.3.1 Processes Decreasing Salinity

Precipitation, in the form of rain, snow, sleet and hail, is one of the processes that contribute towards a decrease in seawater salinity. About three-quarters of all the precipitation worldwide falls directly into the ocean. Thus, it increases the amount of fresh water, decreasing salinity. Runoffs from fresh water sources, like rivers and its tributaries also add fresh water. Icebergs are large chunks of glacial ice that have broken free from glaciers and flown into the ocean. Upon melting, they return fresh water to the oceans. Also, sea ice is formed at cold temperatures in high latitude regions and is primarily composed of fresh water [1].
1.3.2 Processes Increasing Salinity

Formation of sea ice causes an increase in salinity. This is owing to the fact, that when sea water freezes into ice, only around 30% of the dissolved components are retained in the sea ice. This effectively causes fresh water removal from the ocean. Evaporation of water removes pure water from the oceans, thereby increasing salinity. Volcanic eruptions produce large amounts of gases, the major ones being sulfates and chlorides, that eventually reach the oceans. Submarine eruptions spew gases directly into the ocean, increasing its salt concentration. Weathering of rocks on the continents releases silica and elements like sodium, calcium, potassium and magnesium into the ocean increasing its salinity [1].

It is interesting to note how these processes affect the variation of salinity over depths. Since, most of these processes are surface phenomena, they lead to larger variations of salinity at the surface, and cause little variation at greater depths.

1.4 Need for Salinity Sensing

Salinity influences a lot of physical and biological processes in the ocean, both directly and indirectly. The following sections will discuss in some detail, the vital information that can be inferred by determining seawater salinity. The key areas of salinity impact can be listed as:

1) Ocean Circulation.

2) Marine life.

3) Water Cycle.
1.4.1 Ocean Circulation

Before we proceed to appreciate ocean circulation and its impact on the global weather, it would be beneficial to comprehend the role of salinity in the determination of seawater density. Density of seawater is a function of its salinity, temperature and pressure and can be mathematically expressed as

\[ \rho = \rho(T, S, p) \]  

(1.1)

Where, \( T \) = temperature, \( S \) = salinity and \( p \) = pressure [3].

An increase in salinity implies an addition of more dissolved material into the seawater, which translates to a corresponding increase in density. Similarly, an increase in pressure increases the density, because seawater is compressible to some extent. Conversely, temperature increase causes a decrease in the density, due to thermal expansion. *Thermohaline* graphs (plots of salinity and temperature) are used extensively to determine the density of seawater along the sea surface and at various depths. Density differences make water masses sink or float, and hence determine the vertical position and movement of water masses. The ocean like the earth’s interior is *stratified* (layered), with low density waters existing at the surface and high density waters below [1].

Evaporation and precipitation continually change the salinity of the surface waters and hence its density. Thus, there is constant circulation of water between the different layers in the sea. This circulation of water over the depth of the ocean plays a significant role in the circulation of dissolved oxygen and dissolved carbon between the various layers, which is vital for deep-sea aquatic life.

Greater salinity, like lower temperature, causes higher density with a corresponding depression of the sea surface height. In warmer fresher waters, the density
is lower resulting in an elevation of the sea surface. These height differences are related to the circulation of the ocean between the Equator and the Poles [4].

Figure 1.2: Energy Transfer through the Conveyor Belt [4]

The changes in the density bring warm water from the Equator poleward to replace the dense sinking waters as illustrated in figure 1.2. Thus, the overall effects of surface current circulation and the deep-water thermohaline circulation lead to what is aptly called the \textit{conveyor-belt circulation} model. This transport of heat, over the surface has a moderating effect on the climate of Europe.

Current developments in mapping these parameters over broader areas, have indicated that changes in the thermohaline circulation can cause drastic climatic changes. As an instance, if surface waters stopped sinking, the surface water temperatures would be a lot higher, and consequently create hotter lands!! Salinity mapping can also give vital information about the buildup of greenhouse gases into the atmosphere, since these gases can alter the thermohaline circulations.

1.4.2 Marine Life

The sensitivity response of marine animals to changes in the physical parameters of the ocean (like temperature, pressure, salinity, light transparency, buoyancy) varies
between animals. Salinity in open ocean is less susceptible to large variations. Hence, evolution has led the deep-sea creatures to adapt to constant salinity and therefore, they can tolerate very small changes in the salinity levels. (*stenohaline* animals). However, variation in salt concentrations in the estuaries tends to be higher due to periodic rise and fall of tides. Hence, the aquatic diversity in the estuarine ecosystem has adapted itself to considerable variations in salinity levels. (*euryhaline* animals) [1].

To better understand the role of salinity in marine animals, it might be beneficial to introduce the term *osmosis*, according to which, when two solutions of unequal concentrations are separated by a semi-permeable membrane (animal skin, in this case), water molecules diffuse from the region of lower to the region of higher concentration. The pressure applied to the high concentration region to prevent water molecules from passing into it is called *osmotic pressure*. Marine organisms exchange nutrient molecules and waste molecules with their surrounding environment through osmosis. Unexpectedly large variations in salinity can lead to high osmotic imbalance, which may result in rupture of cells due to excessive pressure. Therefore, it can be inferred that a variation in salinity brought about by natural (precipitation etc.) or man-made factors (chemical spills etc.) can be consequential to the aquatic life.

As an example, a study on lobsters performed by Jury et. al. at the University of New Hampshire [5] reveals that drastic salinity variations can have fatal effects on their heart rates. Data like these aid in understanding the vertical and horizontal distribution of marine animals and their habitat preferences, and are widely used for purposes of fishing and conservation.
1.4.3 Water Cycle

As discussed in section 1.3, the salinity of seawater can be attributed to several physical, chemical and biological processes. Sea Surface Salinity (SSS) is a key parameter in understanding how fresh water input and output affect ocean dynamics. It is possible to monitor variations in the water cycle due to processes like land run-off, sea ice melting and freezing and, evaporation and precipitation over oceans, by tracking the variations in SSS [6].

1.5 Motivation

Clearly, there is a need for salinity sensing. Salinity sensors are most often used in conjunction with pressure and temperature sensors for multi-parameter ocean monitoring. Integrated devices of this type are known as CTD (conductivity, temperature and depth sensors) sensors. Most current CTD sensors are sizeable and bulky devices, upto a meter in length [7]. In the oceanic environment, for reasons of corrosion protection, the smaller the surface areas the better. The sensor proposed here is fabricated at the meso-scale (<2cm). Also, the motivation to minimize the proximity effects manifested in inductive sensors which are commonly used to measure salinity, led to the use of capacitive sensors for salinity sensing, more of which is explained in Chapter 2. The use of a Twin-T oscillator for the detection circuit stems from its ability to produce a low distortion output and relatively high sensitivity.
1.6 Thesis Outline

This thesis has been segregated into 6 chapters. The first chapter gave a description of the definitions of salinity, parameters influencing it, and the need for salinity sensing. Chapter 2 gives an overview of the various approaches used at measuring salinity (conductivity). Discussed in Chapter 3 are the theories and processes governing the operation of this sensor. Chapter 4 talks about the design of the sensor, its optimization and construction details. The results are presented in Chapter 5. Chapter 6 is the conclusion to this work and also includes a brief discussion on the future work.
CHAPTER 2
LITERATURE REVIEW

The measurement of salinity has been done using several methods, both direct and indirect. The direct method for salinity measurement of a sample involves measuring its chlorinity, as discussed Section 1.1. The standard scheme adopted for estimating chlorinity is titration by the Mohr’s method [8]. The principle of this method involves taking equal volumes of standard seawater and of the sample, and determining the volumes of given silver nitrate solution to precipitate completely the halogens. However, due to the level of difficulty associated with its experimentation and repeatability, oceanographers use salinity’s dependence on conductivity, to their advantage [9]. An introduction to conductivity and the Practical Salinity Scale (PSS) precede the section on the current approaches at conductivity sensing.

2.1 Conductivity

Conductivity is a unit measure of electrical conduction; a property by which matter conducts electricity. Electrical conductivity is the reciprocal of electrical resistivity, and is denoted by the symbol $\sigma$, which is mathematically expressed by the equation

$$\sigma = \frac{1}{\rho} = \frac{L}{RA}$$  \hspace{1cm} (2.1)
Where, \( L \) = length of the material (in meters, m)

\[ R = \text{resistance of the material to the flow of current. (in ohms, } \Omega) \]

\[ A = \text{area of cross section of the material. (in meters, m)} \]

The unit for conductivity, \( \sigma \), is mhos / meter \((\Omega^{-1} \text{m}^{-1})\) or Siemens / meter \((\text{S.m}^{-1})\).

In an electrolyte, it is directly related to the total dissolved salts present in the solution. The more the dissolved salts, the higher is the conductivity of the electrolyte. Hence, conductivity is often measured to deduce the concentration of an analyte. The relation between conductivity and salinity for practical oceanographic purposes is given by the Practical Salinity Scale (PSS).

### 2.2 Practical Salinity Scale (PSS) of 1978

In 1978, UNESCO established the Practical Salinity Scale (PSS) which defines salinity in terms of a conductivity ratio, thereby, breaking its link with chlorinity. According to the PSS, salinity,

\[ S = 0.0080 - 0.1692 R_{15}^{1/2} + 25.3851 R_T + 14.0941 R_T^{3/2} - 7.0261 R_T^2 + 2.7081 R_T^{5/2} + \Delta S \]

\[ R_T = C(S,T,0)/C(KCl,T,0) \]

\[ \Delta S = [(T - 15)/(1 + 0.0162(T - 15))] + 0.005 - 0.0056 R_T^{1/2} - 0.0066 R_T - 0.0375 R_T^{3/2} \]

\[ + 0.636 R_T^2 - 0.0144 R_T^{5/2} \]

(2.2)

For \( 2 \leq S \leq 42 \)

Where \( C(S,T,0) \) is the conductivity of the seawater sample at temperature \( T \) and standard atmospheric pressure, and \( C(KCl,T,0) \) is the conductivity of the standard potassium chloride (KCl) solution at temperature \( T \) and standard atmospheric pressure [2].
2.3 Current Approaches at Conductivity Sensing

Modern conductivity sensors are broadly classified under two categories:

1) Contact-type sensors

2) Non-contact type sensors

2.3.1 Contact Type Sensors

As the name suggests, in these types of sensors there is a direct contact between the measurement probes and the surrounding media. There are 2 main types of contact-type conductivity sensors currently in use:

1) 2-probe conductivity sensor

2) 4-probe conductivity sensor

2.3.1.1 2-Probe Conductivity Sensors

A schematic of such a sensor is as shown in figure 2.1. It consists of two conducting electrodes (metal or graphite in some cases), spaced a fixed distance d, apart from each other.

![Figure 2.1: 2-Probe Conductivity Sensor](image-url)
The solution under test is allowed to flow between the electrodes. Upon application of an electric potential between the two electrodes, a current is generated between the electrodes and through the medium. The magnitude of this current is directly related to the electrical conduction of the solution. Thus, the amount of current flowing through the circuit is a measure of the conductivity of the solution. Transducers like these actually measure conductance of the solution. The probe/cell constant or K factor is what links the conductivity and conductance. K factor is determined by the geometry of the measuring cell and the distance between the electrodes. Mathematically, k is given by,

\[ K = \frac{\text{distance between the probes}}{\text{c/s Area of the probe}} \]

For the sensor in figure 2.1, if \( x = y = d = 1 \text{cm} \), then the probe constant would be \( 1 / \text{cm} \).

The relationship between conductivity and conductance can be expressed as,

\[ \text{Conductivity} = \text{Conductance} \times K \text{ factor} \quad (2.3) \]

K factor can vary from 0.01 to 100, but lies in the range 0.1 to 10 for most commercial probes [10].

The advantage of such systems is the simplicity of design. However, they suffer from a few drawbacks, which can cause significant errors in measurement. Since, the probe is exposed to the solution, corrosion and fouling effects are an issue. Also, the problem of space-charge polarization is pronounced in such systems since, the same probes are used for applying the input voltage and measuring the resultant current. The problem of polarization has been minimized, if not eliminated, using a better design employing 4 probes.
2.3.1.2 4-Probe Conductivity Sensor

This design makes use of 4 conducting probes. The alternating voltage is applied across two probes while the current is measured across the other two. The 4-electrode cell uses a reference voltage to compensate for any polarization or fouling occurring at the voltage probes [11].

![4-Probe Conductivity Sensor](image)

*Figure 2.2: 4-Probe Conductivity Sensor*

Figure 2.2 illustrates the 4-probe conductivity cell. An alternating voltage is applied to the two circular electrodes in the middle. The current is measured across the outer 2 electrodes. Sensors of this kind can be used for measuring solutions with a wider range of conductivities than the two probe method [11]. However, fouling is still an issue with such devices.

2.3.2 Non-Contact Type Conductivity Sensors

This classification of conductivity sensors arises from the fact that there is no contact between the analyte and the sensing device. This gives them an apparent advantage over the contact type sensors, whose long term stability is limited by polarization and fouling. The measuring principle for most non-contact conductivity sensors is inductive. The two commonly used types of inductive conductivity sensors are:
1) Single transformer

2) Double transformer

2.3.2.1 Single Transformer

This is the simplest form of inductive conductivity sensor.

![Single Transformer Conductivity Sensor Shown with Seawater as Surrounding Media](image)

Figure 2.3: Single Transformer Conductivity Sensor Shown with Seawater as Surrounding Media [12]

It consists of a magnetic induction device, a single coil which acts as the primary coil of the transformer as shown in figure 2.3. The secondary coil of the transformer is formed by the surrounding liquid whose conductivity is to be determined.

An oscillating current of known frequency and amplitude is used to drive the primary coil. The current circulating in the coil produces a time-varying magnetic field, called the primary field, which induces an electric field, as defined by Faraday’s law of magnetism. When the coil is brought close to a conducting body, seawater in this case, the electric field generates eddy currents in that body. The density of these eddy currents is directly proportional to the conducting ability of the medium (given by Ohm’s law). These eddy currents generate a secondary magnetic field, pointing in a direction opposite to the primary field, according to Lenz’s law. Again, by Faraday’s law, we have that a variation in the magnetic flux over time gives rise to an Electromotive force (emf) in the
coil, whose phase is $180^\circ$ relative to the driving current. The expression governing this relation is given by

$$E = -\frac{\Delta \phi}{\Delta t}$$  \hspace{1cm} 2.4

The conducting media is thus seen by the oscillator as a resistive load. Figure 2.4 shows the circuit representation of the single transformer. Knowing that the internal impedance of the oscillator is finite, a change in the load resistance brought about by a change in conductivity of the medium, causes the amplitude of oscillations to vary. Hence, a change in the oscillator amplitude is a measure of the change in conductivity of the analyte. Thus, the same coil acts as both the electromagnetic source and the receiver.

![Figure 2.4: Equivalent Circuit for Single Transformer Design](image)

The equivalent circuit for the single transformer is shown in fig 2.4 where $R_{eq}$ is the equivalent resistance as seen by the source.

The single transformer conductivity sensor has not been applied to oceanographic applications [12]. However, Lynn W. Hart et. al. (1988) have described the use of such sensors for non-invasive electromagnetic conductivity sensing in biomedical areas of research [13]. Their discussion involves the possible use of such sensors to detect brain edema induced by trauma to the skull. Brain edema is known to propagate from the point(s) of trauma, and hence detection is of prime importance in the treatment of injuries resulting from trauma to the skull. A general rule of thumb for such type of sensors is that
the depth of conductivity sensing is related to the radius of the sensing coil. The possible use of coils 2-5 cms in radius has been discussed. Initial experiments were carried out using HP 4275A LCR meter. The readings were taken at oscillator frequency, \( f = 10 \) MHz for a coil radius, \( R = 10.27 \) cm, and number of turns, \( N = 2 \). The plot of resistance change to the conductivity variations in the sub-skull matter yielded a sensitivity of 76.4 mΩ / (S/m). The Colpitt’s oscillator was chosen as an alternative to this expensive impedance meter, which gave a measurable dc output level change in response the change in conductivity of the analyte. A plot of the voltage change for variations in conductivity yielded a sensitivity of 77.2 mV / (S/m). The upper and lower bounds for conductivities for such detection lay in the range 0.10 S/m – 0.5 S/m. However, experiments have not been performed with this set up for analytes with higher conductivities comparable to those of seawater.

Robert Guardo et. al (1997) demonstrated the use of such contactless sensors in measuring thoracic conductivity [14]. This was an improved version of the contactless sensor developed earlier by Guardo et. al.(1995), with better linearity achieved due to its ability to keep the voltage amplitude constant using a feedback loop. The change in conductance recorded for 0.05 S/m variation was 0.8 % of the measured output signal.

### 2.3.2.2 Double Transformer

The double-transformer type of conductivity sensor was first introduced into physical oceanography by Relis (1951) and later on applied for Williams (1960) and Fatt (1962) [12].
The transformer consists of two transformers, namely the driver transformer and the pick-up transformer. In this system, the surrounding media (sea water in this case) forms the secondary coil of the driver transformer and the primary coil of the pick-up transformer.

![Diagram of the transformers](image)

*Figure: 2.5: Schematic for a Double Transformer Conductivity Sensor [12]*

A schematic of the design is as shown in the figure 2.5. The arrangement of the two coils is important in that the only coupling between them is by the common water loop. The voltage or current in the secondary coil of the pick-up transformer is the sensor output signal. Here again, a high frequency current excites the first coil that generates a current in the second coil. The amount of current generated depends on the amount of magnetic flux, which is coupled through the solution. Thus, the current in the second coil is proportional to the conductivity of the solution.

Another contactless toroidal sensor employing 2 coils was implemented by Natarajan et. al.[15]. The novelty with this approach however, lay in the RF detection employed. Most conventional double transformer sensors calibrate the medium’s conductivity, to the change in amplitude of the current in the sensing coil. The detection
strategy in this approach, involves measuring a phase shift that occurs in an alternating signal that couples between two closely held coils (drive and sense) placed in the conducting medium. The phase shift is detected using a phase detector circuit. Measurements taken at constant salinity of 36.15 ppt over varying temperatures show the device sensitivity to be 5mV for 1 S/m change in conductivity of the analyte. However, the device sensitivity for change in conductivity was recorded only for two different concentrations of the analyte.

Conductivity sensors based on double transformers are the most widely used in oceanography. Contactless conductivity sensing technique serves to curb the limitations faced by the contact type electrodes, in that fouling and polarization of the measuring electrodes is not of much concern. The construction is robust and preservation of geometry factor is easily achieved by cleaning with soaps, solvents and a brush. The large inherent ‘hole’ in inductive sensors permits free flushing of solution.

However, inductive sensors suffer from a few drawbacks. The primary drawback of the inductive sensing approach is the problem of external fields. Apparently, the measuring field in this type of sensing is exposed to the surrounding media. However, this entire field is not coupled to the secondary coil of the transformer. Sea-bird Electronics Inc., in their comparative study on conductivity cells estimate that most of the inductive cells currently in use, have 11 to 20% of their field external [17]. The external fields lead to errors commonly known as proximity errors which can have major consequences on the data. Any material that has a conductivity value other than that of sea water can influence the calibration of the system. Cables, sensor housings and marine growth close to the conductivity cell can contribute to a shift in the system’s calibration.
It may be interesting to note that the antifouling coating on the cell is equally likely to cause errors. The simple reason for this is that any coating layer will alter the cell geometry. In the same study by Seabird, it is claimed that even a thin layer of coating (about 100 microns) will change the indicated salinity by approximately 0.7 psu, which is significant in systems aiming at achieving high-accuracy standards. Even if the system is calibrated initially considering the thickness of the antifouling coating, subsequent leaching of the paint will lead to errors in calibration.

The dependence of the sensor output on the coil inductance poses another problem in inductive sensors. In a study by Hinkelmann, it was shown that the permeability of the transformer core was susceptible to variability, caused by its temperature and pressure dependence [12]. However, precise electronic design employed in current inductive sensors can eliminate the undesired effects due to shift in the coil’s permeability, by calibrating the system using simplified assumptions. An alternate approach at minimizing the effect of permeability drift due to pressure variations has been the use of pressure-balance ports. However, they lead to significant escalation in costs.

The problem of external fields associated with inductive sensing can be overcome by employing capacitive principles for conduction sensing. Parallel plate capacitors rely on trapping the electric field in the region between the plates. This provides an inherent confinement of the measuring field between the two plates, with little interference due to external fields/objects. Only a small portion of the field is exposed to the external media on account of fringing effects at the corners and edges of the plates. More discussion on the minimization of fringe fields in parallel plate capacitor follows in Chapter-4. Parallel
plate arrangement is the simplest form of capacitor configuration. However, conductivity sensing using capacitors is not just limited to the parallel plate configuration. Various possible configurations have been discussed in [17] as shown in the figure 2.6.

![Figure 2.6: Capacitor Configurations, (a) Cylindrical Set-up, (b) IDTs](image)

From a fabrication engineer’s perspective, the cylindrical configuration is not much preferred due to the level of difficulty involved in depositing a uniform layer of metal for the electrode. The IDT structure is preferred due to its ease of fabrication as both the electrodes are coplanar.

### 2.4 IDT Configuration in Measurement of Conductivity

A schematic and equivalent circuit of the measuring cell is as shown in figure 2.7.

![Figure 2.7: IDT Conductivity Cell and Equivalent Circuit [18]](image)

The structure consists of two electrodes, the impedance across which gives a measure of the conductivity of the liquid between the combs. The equivalent circuit for
such a structure has been modeled as shown above. $R_{sol}$ is the solution resistance and is given by the equation,

$$R_{sol} = \frac{K_{cell}}{\kappa_{sol}}$$  \hspace{1cm} 2.5

Where, $K_{cell}$ is the cell constant of the conductivity cell and is dependant on its geometry. $\kappa_{sol}$ is the conductivity of the electrolyte. The direct capacitive coupling between the electrodes is represented by the cell capacitance $C_{cell}$ given by the relation,

$$C_{cell} = \frac{\varepsilon_0 \varepsilon_{sol}}{K_{cell}}$$  \hspace{1cm} 2.6

Where, $\varepsilon_{sol}$ is the relative permittivity of the electrolyte. $C_{dl}$ represents the double layer capacitance and is attributed to the formation of a layer of charge at the electrode, due to the electrode-electrolyte interaction. A plot of the complex impedance can be used to compute each of these parameters, more of which has been discussed in Chapter 3. However, the measurement of electrolyte of high concentrations has not been discussed in this study on IDTs.

Fritz Wolter and Fritz Thom have demonstrated the use of a parallel plate capacitor to determine the complex permittivity of supercooled aqueous solutions in the 1 MHz range [19]. The electrode material used was copper, with a coating of platinum to avoid polarization effects. Studies were performed on absolute ethanol and aqua bidest for low conductivity ranges ($< 0.02$ S/m). The permittivities were obtained using the Schlumberger 120 impedance analyzer. The conductivity of the solutions was varied by varying its temperature. In the temperature range 10 °C- 19 °C, the change in capacitance observed for the sensor was 0.033 pF for every 1 °C change in temperature (=0.85%
change in capacitance for every 1 °C). The response of the sensor was measured for different liquids. However, no data has been presented for change in conductivity for a particular solution of varying concentrations, at a constant temperature.

Hilland [21] presented a simple sensor system to measure the dielectric properties of saline solutions. A co-axial probe was used to measure the dielectric properties of saline. The use of Sucoplate alloy has been demonstrated to avoid corrosion of the probes. Measurements were performed in the frequency range 500 MHz – 40 GHz, at 20 °C using the Network Analyzer HP8722C. The conductivity of the analyte was obtained as 0.126 S/m for every psu change in salinity.
3.1 Fundamentals of a Capacitor

The most common form of capacitors is the parallel plate capacitors. It consists of two conducting plates, across which a potential difference is applied as shown in figure 3.1. The gap between the plates is filled with a material known as the dielectric.

![Figure 3.1: Parallel Plate Capacitor Configuration](image)

Capacitance for a parallel-plate capacitor is given by the expression,

\[ C = \frac{A \varepsilon}{d} \]  \hspace{1cm} (3.1)

Where, \( A \) = overlapping area between the two conducting plates,

\( d \) = distance between the plates.

\( \varepsilon \) = dielectric constant (permittivity) of the material

Permittivity is given by the relation,

\[ \varepsilon = \varepsilon_0 \varepsilon_r \]  \hspace{1cm} (3.2)
where, $\varepsilon_0 = \text{Permittivity of free space (vacuum).} \ (= 8.854 \, F / m^2)$

$\varepsilon_r = \text{Relative permittivity of material.}$

The term dielectric is usually used to signify materials with low conductivity and high insulation characteristics. The electric field distribution within the gap of a parallel plate capacitor depends on the type of dielectric and its resistivity. Application of voltage across the plates leads to distribution of equal and opposite charges on the surface of the plates (from Gauss’ Law, it is known that charges cannot reside within the bulk of a conductor).

### 3.2 Complex Permittivity and Dielectric Loss

It is desirable to have dielectric materials with zero loss, so that they confine more charge. However, in practical cases, no material (except vacuum) behaves as a perfect dielectric and is associated with a finite loss. One of these losses is the conduction loss, representing the flow of actual charge through the dielectric. The other is a dielectric loss and arises due to movement or rotation of molecules in a time-varying electric field, more of which will be evident following a discussion on polarization in the next section. One way of describing dielectric losses is to consider the permittivity as a complex number, defined as

$$\varepsilon = \varepsilon' - j\varepsilon'' = \left|\varepsilon\right| e^{-j\delta} \quad (3.3)$$

where, $\varepsilon' = \text{ac capacitivity}$,

$\varepsilon'' = \text{dielectric loss factor}$

This treatment would necessitate the introduction of a complex capacitance, defined as

$$C' = C' - jC'' \quad (3.4)$$
Where, $C$ and $C''$ are the real and imaginary parts of the complex capacitance respectively. This definition of complex capacitance permits us to use this complex value in any equation derived for real capacitance in a sinusoidal application, and get the correct phase shifts and power losses by applying the usual rules of circuit theory.

![Fig 3.2: Loss Tangent Vector Diagram](image)

When specifying lossy capacitors, the complex permittivity is generally expressed by $\varepsilon'$ and $\tan\delta$, where

$$
\tan\delta = \frac{\varepsilon''}{\varepsilon'}
$$

(3.5)

Where, $\tan\delta$ is called the *loss tangent* or simply, *dissipation factor* (DF), as shown in fig 3.2. A practical capacitor is more than pure capacitance. It is associated with a series and parallel resistance. Dissipation factor can also be expressed as,

$$
DF = \frac{\text{Energy lost by the capacitor}}{\text{Energy stored by the capacitor}} = \frac{\varepsilon''}{\varepsilon'} = \frac{R}{X}
$$

(3.6)

Where, $R = $ resistive component of the capacitor

$X = $ capacitive reactance of the capacitor

### 3.3 Polarization of Materials

The fundamental difference between a conductor and a dielectric is that a conductor has free electrons (loosely bound to the atom), whereas in a dielectric the electrons in the outermost shells are tightly bound to the nucleus. For any material in the
absence of an electric field, the electrons form a symmetrical cloud around the nucleus, with the center of this cloud being at the center of the nucleus, as shown in figure 3.3(a). The electric field generated by the positively charged nucleus attracts the electron cloud around it, and the mutual repulsion of the electron clouds of adjacent atoms provides matter its form.

![Figure 3.3: Polarization Phenomenon in Dielectric Molecules [22]](image)

The electrons in a conductor behave differently upon the application of an electric field. When subjected to external electric fields (dc), the loosely bound electrons in the conductor can jump from one atom to the other, causing an electric current. However, this is not possible in a dielectric. An external field $E_{\text{external}}$ cannot cause mass migration of electrons in a dielectric medium. However, it can polarize the atoms of the dielectric. This process involves distorting the center of the electron cloud and the nucleus, so that the atom is no longer symmetric as evident from figure 3.3(b). This distortion causes the negatively charged portion of the atom to be displaced from the positive part, creating a dipole where the nucleus maybe represented as $+Q$ and the center of mass of the electrons maybe represented by a charge $-Q$. The formation of dipole is illustrated in Figure 3.3(c). This kind of polarization is termed as electronic polarization.
Thus, an externally applied field, causes an induced electric field (due to the formation of dipoles), called the polarization field, $E_{\text{pol}}$. $E_{\text{pol}}$ is lesser in magnitude and opposite in direction to the $E_{\text{external}}$. Apparently, the induced field tends to reduce the magnitude of the total electric field on the material. This reduction factor in the electric field is referred to as \textit{dielectric constant} of the material.

3.4 Types of Polarization Mechanisms

The interesting aspect of polarization in dielectrics is that the contribution of the different polarization mechanisms to the overall permittivity is frequency dependant. There’re four basic types of polarization, of which, however, not all are relevant in this study of dielectric behavior in electrolytic samples.

3.4.1 Interface Polarization

Surfaces, grain boundaries and interphase boundaries (which include the surface of precipitates) may be charged. In other words, they contain dipoles which may become oriented to some degree in an external field and thus contribute to the polarization of the material. However, there is no simple method to determine the charge at the interfaces or their contribution to the total polarization of the material [25].

3.4.2 Electronic and Atomic Polarization

The polarization behavior referred to in figure 3.3 is also known as \textit{electronic polarization} because it results from the shift of electronic charges within the atom, under
the influence of an electric field. In atomic polarization, adjacent positive and negative ions “stretch” under the influence of an applied field.

3.4.3 Ionic Polarization

This is generally seen in solids with some degree of ionic character. They have internal dipoles, which cancel each other out and are pretty much unable to move under the action of an electric field. The external field then induces net dipoles by slightly displacing the ions.

3.4.4 Orientation (Dipolar) Polarization

This kind of polarization is generally associated with liquids and gases. A molecule is formed when one or more atoms combine to share their electrons, forming a single entity. A non-polar molecule is one in which the centers of positive and negative charges coincide. However, polar molecules have their positive and negative centers of charges displaced from each other, creating a permanent dipole moment. In the absence of an electric field, these dipoles are oriented in a random fashion so that no polarization exists. However, under the action of an electric field, the dipole will tend to rotate and align itself with the electric field, causing orientation polarization to occur as shown in figure 3.4a.

![Figure 3.4: (a) Dipole Rotation in an Applied Field [24], (b) Macroscopic Representation of the Orientation Polarization Under the Influence of an Applied Electric Field [22]](image-url)
The friction accompanying the rotation of the dipole results in dielectric losses. Water, being a polar molecule, exhibits strong orientation polarization.

### 3.5 Contribution of Polarization to Permittivity

Having discussed the various polarization mechanisms, we shall now try to explain their response to different frequencies of the applied field.

![Image of frequency response of various polarization mechanisms](image-url)

*Fig. 3.5: Frequency Response of Various Polarization Mechanisms [24]*
Electrons have much smaller masses than ions. This allows them to respond more rapidly to a time-variant electric field. For electric fields of high frequencies (like light), only electronic polarization can occur. At smaller frequencies, relative displacement between positive and negative ions can occur. Orientation of permanent dipoles requires the rotation of bulky molecules. This can occur only if frequency of applied field is relatively low (i.e. in the MegaHertz range or lower).

3.6 Interfacial or Space Charge Polarization

In addition to these polarization mechanisms, the existence of interfacial effects such as macroscopic discontinuities in the material result in another form of polarization called the space-charge polarization [24]. Charge carriers also exist that can migrate over a distance through the material, upon the application of low frequency fields. Space-charge polarization occurs when the motion of these migrating charges is impeded. This can occur due to trapping of charges at the interfaces of materials, or when charges cannot be freely discharged or replaced at the electrodes. The field distortion consequential of the accumulation of these charges increases the overall capacitance of the material which appears as an increase in $\varepsilon'$. The behavior of this polarization to the frequency of the applied field is intuitional in that, at low frequencies the charges have sufficient time to accumulate at the borders of the conducting regions resulting in an increase in $\varepsilon'$. Conversely, at higher frequencies the charges do not have time to
accumulate and hence polarization effects are minimal. These low frequency effects are often referred to as the *Maxwell-Wagner Effects*.

### 3.7 Relaxation Time

It may be expected that as the applied electric field, $E$, is brought to zero, the polarization field, $P$, will follow instantaneously. However, it takes a certain finite amount of time for the dipoles to revert to their original state of randomness (such that $P = 0$). This time is known as the *relaxation time* ($\tau$).

![Figure 3.6: Transition in Polarization with Sudden Field Drop [25]](image)

Figure 3.6 illustrates the relaxation time observed in dielectrics due to a drop in the applied field. All of the polarization mechanisms discussed so far can only operate up to a limiting frequency, after which a further frequency increase will result in their disappearance. Because of the spring-like nature of the forces involved, electronic and atomic polarization are accompanied by resonance type absorption. However, for orientation polarization, the disappearance accompanied by a broader peak in the loss factor, is more gradual, because the mechanism involved is of the relaxation type, and may involve a broad distribution of relaxation times. Indeed, the decline in $\varepsilon'$ may be so
slow that $\varepsilon'$ may appear almost constant, and be correspondingly small, over a wide
frequency range.

3.8 Debye Theory of Dielectric Behavior

Figure 3.7 shows the dielectric behavior of water obtained for an input signal
swept over a range of frequencies.

Figure 3.7: Debye Relaxation of Water at 30°C [24]

The curves shown above follow the Debye theory of complex permittivity given by the
following equations,

$$\varepsilon' = \varepsilon_s + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega \tau)^2} \quad 3.7$$

$$\varepsilon'' = (\omega \tau) \frac{\varepsilon_s - \varepsilon_\infty}{1 + (\omega \tau)^2} \quad 3.8$$

Where, $\omega = 2\pi f$ (f being the frequency of sweep)

And, $\tau = 2\pi f_0$ ($f_0$ being the relaxation frequency).

$\varepsilon_s = \varepsilon$ (at $\omega = 0$) and $\varepsilon_\infty = \varepsilon$ (at $\omega = \infty$).
From the Debye relation, the dependence of permittivity on the frequency of the applied field is evident. As frequency increases, $\varepsilon'$ decreases and this drop in $\varepsilon'$ is necessarily associated with a peak in $\varepsilon''$. Except for exceedingly high applied fields, $\varepsilon$ is independent of the magnitude of the applied electric field for all dielectric materials used in practice, except ferroelectrics [24].

### 3.9 Cole-Cole Diagram for Complex Permittivity

Although, the Debye equations for permittivity are hailed as one of the most significant advancements in the realm of dielectric behavior, the Cole-Cole plots act as a better approximation in most cases. It is a plot of $\varepsilon''$ (on the X-axis) versus $\varepsilon'$ (on the Y-axis). The equation governing the Cole-Cole plot is given by,

$$\varepsilon^* - \varepsilon_\infty = \frac{(\varepsilon_s - \varepsilon_\infty)}{[1+(j\omega\tau_0)^{1-\alpha}]}$$

Where, $\varepsilon^* = \varepsilon' - j\varepsilon''$

And, $\alpha(\pi/2) =$ angle between the real axis and the line drawn to the center of the circle from the high-frequency intercept.

![Cole-Cole Diagram for Complex Permittivity](image)

*Figure 3.8: Cole-Cole Representation of the Debye Model of Water at 30C [24]*
The above plot is for a dielectric with single relaxation frequency and the maximum value for $\varepsilon''$ is as shown in the plot.

### 3.10 Dependence of Permittivity on the Concentration of Analyte

Minute concentrations of electrolyte usually impart significant conductivity to a liquid medium. Besides conductivity, addition of electrolytes can influence the dielectric behavior of the medium in two ways. Firstly, its ions may associate, generating an ion-pair or similar solute species of appreciable dipole moment. Such species will then be expected to make their own contribution to the dielectric polarization and dispersion. Secondly, the ions or their aggregates in the medium can, by the virtue of their strong localized electric fields, influence the solvent’s molecular interactions. A corollary to the second aspect could be the explanation that solvent molecules may firmly bonded to the ions, and so imparted the new character of molecules of solvation. It is the second aspect that we are concerned with, during this discussion on the effect of electrolyte concentration on the permittivity of the solution [26]. The electrostatic field in the immediate neighborhood of the sodium or chloride ion is such that the interaction energy between the water-molecule dipole greatly exceeds that of the typical hydrogen bond between the solvent species. This means that an appreciable number of water molecules will be ‘frozen’ around each of the solute ion, and this produces a molecular pattern in the liquid. This process is called *hydration*. Figure 3.9 shows the hydration process in a solvent upon introduction of salt ions. The hydrated salt ion is a bulkier entity than a non-hydrated ion. The hydrate sheath around the dipoles prevents them from orienting
themselves with the changing electric field. This is the principal cause for the reduction in permittivity with addition of salt.

Figure 3.9: Hydration Process in a Solute-Solvent Mixture [27]

3.11 Temperature Dependence of Permittivity

The temperature dependence of polar materials is different than that of non-polar materials. While in non-polar materials, a change in temperature is associated with a fall in permittivity, due to the change in density of the material, the temperature dependence in polar materials is attributed to orientation polarization [26]. The dipoles in a polar solvent, are arranged randomly (such that \( P = 0 \)) and are constantly moving, due to thermal motion. It may then be expected that as the temperature increases, the thermal energy of the individual molecule increases. Hence, increasing the thermal motion
reduces the alignment of the permanent dipoles by the electric field, thereby reducing the orientation polarization. This causes a drop in permittivity of the sample.

As may be apparent from the construction of the sensor, to be discussed in Chapter-4, there exists a thin layer of dielectric separating the sensor plates from the conducting solution. Having learnt the effects of frequency, temperature and concentration on the dielectric properties of materials, it is of relevance to understand the yardsticks in assessing the stability and barrier properties of the dielectric under consideration.

3.12 Assessment of Barrier Properties of Polymeric Coating on the Electrodes

Polymers are high molecular weight molecules composed of repeating units (monomers), linked together to form long chains. Polymeric layers, coated on electrodes to prevent metal corrosion are thought to act as perfect barriers separating the metal from the surrounding media. However, the reliability of these materials is limited largely by the fact that over time, diffusion of ions through the coating can establish contact between the media and the electrode surface. This can have undesired effects, particularly, in capacitive sensing applications where the absorption of water by the dielectric film can effect an alteration in its dielectric properties. Absorption of water generally tends to increase the dielectric constant of the polymer. This can lead to erroneous results in calibration of the device. Another adverse effect of this diffusion process is the deformation in the geometry of the film [28]. Water molecules fill the voids that are formed between polymeric chains and consequently induce relaxation or simply, swelling of the polymer. This effectively changes the thickness of the dielectric film. Hence, it
becomes imperative to study the effects of the surrounding media on these barrier layers before making a final selection on the type of coating. One of the most trusted techniques for barrier layer analysis is impedance spectroscopy.

### 3.12.1 Impedance Spectroscopy

Film breakdown results from ion transport through it and the resulting failure is best understood in terms of the oxidation and reduction reactions at the metal-fluid interface. It is logical make an assessment of film properties using electrochemical test methods. Although, ion diffusion and mass absorption (slow processes) have been identified as the causes for swelling degradation, another consideration often neglected, is the surface morphology of the coating. Pores in the polymer during its application process, can act as direct channels between the fluid and metal and can cause localized corrosion, ultimately leading to film failure (fast process) [29].

Of the several methods for the assessment of barrier properties viz. film resistance measurement, film capacitance measurement, polarization resistance measurement, the electrochemical impedance spectroscopy, or AC impedance spectroscopy, is the most significant. It is clear that several processes take place at the metal-solution interface (like electrochemical reactions, diffusion, adsorption etc.). DC measurements average all these processes, from the slowest to the fastest. However, in AC measurements only those processes are taken, which have sufficient time to occur between the alternating fields of the applied signal. Hence, each of the processes can be traced by sweeping an input signal over a range of frequencies.
Electrochemical impedance is determined by applying a sinusoidal excitation of low amplitudes. This is done to keep the cell’s response pseudo-linear, where the resultant measured current signal follows the input signal in frequency but is shifted in phase relative to it [29]. Mathematically expressed, if the input voltage signal is represented by,

\[ E(t) = E_0 \cos(\omega t) \]  \hspace{1cm} 3.10

Where, \( \omega = 2\pi f \), (f being the frequency of the sinusoid),

Then, the response current signal, can be expressed as

\[ I = I_0 \cos(\omega t - \phi) \]  \hspace{1cm} 3.11

Where, \( \phi \) is the phase difference between the input and output signals.

The impedance, \( Z \), of the system can then be deduced from relation,

\[ Z = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)} \]  \hspace{1cm} 3.12

The impedance can be expressed in terms of real and imaginary terms as,

\[ Z = Z' + jZ'' \]  \hspace{1cm} 3.13

Or in polar form as,

\[ Z = |Z| \angle \theta \]  \hspace{1cm} 3.14

A graphical method of representing complex impedance data is the Nyquist plot as shown in figure 3.10. A Nyquist plot is obtained by plotting \( Z' \) on the X axis and \( Z'' \) on the Y axis. Such a plot is representative of the elements forming the equivalent circuit model of the electrode-medium interface. The length of the vector gives the magnitude of the impedance.
Figure 3.10: Typical Nyquist Plot of the Complex Impedance

The graph represented above is typically the representation for a coated electrode where the coating properties have started to degrade due to absorption of water. The equivalent circuit model for such a representation is called the Randel’s cell and is shown in figure 3.11 [30].

Figure 3.11: Randel’s Cell Circuit Model

For a Randel’s cell equivalent circuit, the individual circuit elements can be obtained from the Nyquist plot. The impedance of such a circuit can be expressed using the following equation

$$\text{Re } Z = R_s + \frac{R_t}{1 + \omega^2 R_t^2 C_r^2}$$
Im Z = $-\frac{\omega C_{dl} R_t^2}{1 + \omega^2 C_{dl}^2 R_t^2}$  

The right hand corner of the semi-circle in the Nyquist plot for the Randel cell is indicative of low frequency, while the left indicates the response at high frequencies. The point of intersection of the semi-circle with the X-axis on the right corner yields the component $R_{sol} + R_t$ while the point of intersection to the left yields the solution resistance $R_{sol}$. It may be observed at lower frequencies, the cumulative resistance is given by $R_{sol} + R_t$. This indicates that at lower frequencies the polarization resistance is significant. $C_{dl}$ represents the double charge layer. More on this layer is explained in the next section.

### 3.12.2 Double Charge Layer

The formation of this layer arises due to the interaction between the electrode and the electrolyte. The radius of the hydrated ions prevents direct contact between the ions in the electrolyte and the metal electrode and the diffusion of ions in the solution causes a non-linear charge distribution. The double charge layer can be best represented using the Gouy-Chapman model as shown in figure 3.12.

![Gouy-Chapman Model](image)

Figure 3.12: Gouy-Chapman Model for Metal-Electrolyte Interaction [18]
The following equation is used to compute the Randel cell parameters.

\[
\omega_{\text{max}} = \frac{1}{2\pi R_i C_{\text{dl}}}
\]

Where \(\omega_{\text{max}}\) is the frequency for which the peak of the curve occurs,

\(R_i\) is the charge transfer resistance or polarization resistance,

\(C_{\text{dl}}\) is the double layer capacitance.

Double layer capacitance can be formulated as shown below:

\[
\frac{1}{C_{\text{dl}}} = \frac{1}{C_{\text{Stern}}} + \frac{1}{C_{\text{diff}}}
\]

Where, \(C_{\text{Stern}}\) is the Stern capacitance, assumed to be a constant for most systems and is independent of the solution concentration, while \(C_{\text{diff}}\) is the diffusion layer capacitance, which is given by the equation,

\[
C_{\text{diff}} = \sqrt{\frac{2.10^{-3} \cdot z^2 \cdot \varepsilon_{\text{water}} \cdot \varepsilon_0 \cdot C \cdot N_A}{K T}}
\]

where, \(z\) is the valence of the ion, \(C\) is the ion concentration (mol/L), \(T\) is the absolute temperature, \(N_A\) is the Avagadro number, \(\varepsilon_0\) is the absolute dielectric constant of water, \(K\) is the Boltzmann’s constant and \(T\) is the absolute temperature.

It may be observed from the above equation that the diffusion capacitance increases as the ion concentration increases.
CHAPTER 4
DESIGN, OPTIMIZATION AND CONSTRUCTION

In this chapter, the design of the sensor, its optimization and fabrication have been described. Also, discussed are the detection strategies for the capacitive sensor.

4.1 Minimization of Fringe Field Effects Using Guard Rings

As already discussed in Chapter 2, the only fields external to a parallel plate capacitor are the fringe fields caused due to electric field bending at the corners and edges. The capacitance of a parallel plate capacitor is given by equation 3.1. However, in practice, the measured capacitance of a capacitor is generally higher than the calculated capacitance. This increase is attributed to the fringing fields at the plate edges. It is difficult to calculate the fringe field analytically and hence, it is in our best interest to minimize the fringe field using a suitable strategy. Kelvin guard electrodes (ring) are usually employed to minimize these effects. It is sufficient to use this ring around just one of the electrodes. A typical arrangement for Kelvin guard ring is as shown.

![Figure 4.1: Capacitor Incorporating Kelvin Guard Ring](image)
The use of Kelvin guard ring around the electrode serves two purposes:

1) It serves as a shield against external interference and,

2) It shifts the electric field out of the area of interest.

A general rule of thumb, as explained by Heerens [31], is that if the distance between the electrodes is comparable to the smallest dimension of the electrode, then the fringe fields are significant. In our case, the distance between the electrodes is ~600 microns, and the smallest dimension is 1 cm, which should make it less prone to fringe effects. However, a good design should incorporate strategies to eliminate the fringe fields. It should be noted that for excellent results in minimizing fringe effects, the following must be taken care of:

1) It must be ensured that the electrode and the surrounding guard ring should be totally in-plane with each other. Since, in this case, the electrode and guard ring are built on the same substrate, they can be assumed to be coplanar.

2) The distance between the guard ring and the electrode should be minimal for maximum minimization. For the salinity sensor, the gap was chosen to be 400 microns, due to limitations of the PCB fabrication set-up in the laboratory.

3) Ideally, the larger the width of the guard ring, the better the shielding. However, 5 mm was chosen as a convenient width for the guard ring for the capacitive salinity sensor.

4) The guard ring should be held at a potential equal to that of the opposite plate.

An attempt was made to quantify the reduction in fringe field due to the incorporation of the Kelvin guard ring. This was done using the ‘Finite Element Method’ tool FEMLAB. The sub-module ‘Quasi-static’ of the ‘Electromagnetic’ section was used for the simulation. The reason for having chosen the quasi-static mode is that the sensor
is intended to be used at low frequencies. This follows from the discussion on polarization in section 3.5. The frequency of the signal was specified as 1 KHz. The first step in the simulation was developing the 2-D model which is as shown in figure 4.2.

![2-D Model of the Sensor Developed in FEMLAB. The Boundary Conditions for the Materials Used are as Indicated](image)

Each shape in the geometry is assigned a sub-domain name. This facilitates the specification of materials used in the construction of the sensor. FEMLAB permits the use of user-defined materials, allowing the user to specify the material properties as indicated in figure 4.2. To simulate the seawater medium around the sensor, the capacitor was enclosed in a box with dielectric properties matching those of seawater. Next, the boundary conditions were specified, where the voltage for each of the interfaces was assigned. This is the most important step prior to simulation, because the nature of the boundary dictates the electromagnetic equation used for calculation of the electric fields in the system. The boundaries of the top metal plate were assigned a sinusoidal voltage, 5 Vp-p in magnitude, while those of the lower plate were assigned to ground. The junction of the liquid-dielectric interface was assigned as a continuous interface and is hence, governed by the equation,
\[ n \cdot (J_1 - J_2) = 0 \] (4.1)

Where \( n \) is the normal vector and \( J_1, J_2 \) are the current density vectors of the two adjoining materials in consideration.

In the next step, the mesh is developed with a predefined ‘normal’ mesh size for the mesh elements. The meshed structure is shown in figure 4.3.

![Figure 4.3: 2-D Meshed Model of the Capacitor](image)

The sensor was analyzed in the ‘time harmonic, small current’ mode and the solver used was ‘UMFPACK’. The simulated system results for the potential distribution and electric field are shown in figure 4.4.

![Figure 4.4: Potential and Electric Field Distribution of the Capacitive Sensor in Seawater](image)

Figure 4.4 shows the electric field distribution represented by the streamlines while the color gradient represents the potential distribution at various regions in the
capacitor. The post-processing operation involves computation of the sensor capacitance. One of the post-processing results obtained from a quasi-static simulation in FEMLAB is the energy density, $E$. We know that the energy stored by a capacitor is given by the expression,

$$E = \frac{1}{2} CV^2$$

Consequently,

$$C = \frac{2E}{V^2} \quad 4.2$$

Equation 4.2 computes the capacitance from the energy density and the simulated capacitance for the modeled capacitor was obtained as 4.608 pF.

The next logical step was the addition of guard rings (held at ground potential) around the capacitor as shown in figure 4.5.

![Figure 4.5: Sensor with Guard Rings for Field Homogenization](image)

![Figure 4.6: Simulated Result for Capacitor with Guard Ring](image)
Capacitance for this model was computed using the expression 4.2 and was obtained as 4.1026 pF. As expected, the capacitance for this system was found lower than the sensor without guard ring. The reduction in the computed capacitance was 10.9%.

4.2 Detection Circuit Employing Twin-T Oscillator

The capacitive sensor forms a part of a Twin-T detection circuit. The Twin-T consists to two arms, the high pass arm and the low pass arm. The high pass arm consists of two capacitors and a resistor while the low pass arm, consists of two resistors and a capacitor. This circuit functions as a notch filter by eliminating a particular frequency from the incoming signal. This can be achieved by adjusting the values of the constituent elements of the circuit. The notch frequency is given according to the expression [33],

\[ F = \frac{1}{2\pi RC} \]

Where \( R1 = R2 = 2R = R \), \( C1 = C2 = C3 / 2 = C \)

A schematic of this circuit is shown in figure 4.7.

![Figure 4.7: Twin-T Notch Filter Circuit](image)

A simulation of this circuit using Pspice, for an input frequency sweep from 100 Hz to 200 KHz, yields the following plot.
Figure 4.8 shows the simulated result for a Twin T notch filter circuit. It is observed that at ~64 KHz (given by the circuit components), the phase of the output undergoes a near 180° shift. By introducing an additional 180 degrees of phase shift around a closed loop, it is possible to configure this filter as an oscillator, in accordance with Barkhausen’s criterion for sustained oscillations. The oscillator circuit is as shown in figure 4.9. The capacitors in the circuit were replaced with the capacitive sensors fabricated in house. Also, the resistors used have a tolerance of 2%, to minimize drift in the oscillator response. This kind of a circuit incorporating R and C components can be utilized in applications requiring low frequencies of operation.

It can be observed from the expression 4.4 that for proper functioning of this circuit at the desired frequency, it is critical that the resistor and capacitor values are exactly matched. It is important to use resistors from the same manufacturer, as that will ensure closest matching. The resistor in the high pass arm (which is half the other two
resistors) can be realized by running the same two such resistors in parallel. A schematic of the oscillator circuit is as shown in figure 4.9.

![Figure 4.9: Schematic of Twin-T Oscillator](image)

The test set-up for the Twin-T oscillator comprising the sensor is as shown in figure 4.11. Calibrated IAPSO Standard seawater solution obtained from Ocean Scientific International, with a salinity of 34.996 psu, was allowed to flow through the gap between the plates.

![Figure 4.10: Oscillator Response Simulated Using Pspice](image)
It is worth noting that other oscillator networks could be chosen to read the capacitive data from the sensor. The advantage of Twin-T oscillator over other single-capacitor circuits is a lower distortion sine wave output. This is one of the prime reasons that this oscillator is very popular in audio electronic circuits. Sensitivity is defined as the slope of the output versus input curve for a system, or mathematically represented as

$$\text{Sensitivity} = \frac{\Delta \text{output}}{\Delta \text{input}}$$  \hspace{1cm} (4.6)

The sensitivity for the frequency response is given by $\Delta F/\Delta C$. Differentiating expression 4.3 with respect to $C$, we obtain

$$\text{Sensitivity} = \frac{dF}{dC} = \frac{-1}{2 \pi RC^2}$$  \hspace{1cm} (4.7)

It is interesting to see that the sensitivity varies inversely as the square of the capacitance. Certain other R-C oscillators that provide the same extent of sensitivity involve more complex designs and components.
4.3 Construction of the Sensor

The sensor consists of two parallel conducting (copper) plates. One of the plates has a dimension of 2cm x 1cm and the other plate is built with slightly larger dimensions (2.1cm x 1.1cm) for purposes of alignment. The sensor plates are constructed on copper clad FR-4 substrate boards. The use of FR-4 boards incorporating sensors exposed to solutions of high salt concentrations was done by Natarajan et. al. This fabrication procedure is similar to the process of patterning copper clad boards for electronic circuits. The process flow steps for the fabrication are as depicted in figure 12.

![Figure 4.12: Process Flow Steps for Fabrication of the Sensor](image)

1) Presensitized FR-4 substrate
2) Patterning the board, using the required mask
3) Development stage
4) Copper Etch (in Ferric Chloride)
5) Spin coat Photosresist (masking tape on contact areas)
6) Solder contact wires
7) Spacing and alignment
The first step towards the fabrication of the sensor is the lithography step. The mask with the pattern was developed using AutoCAD 2002. The exposure step in the lithography process was done using a UV exposure box. This was followed by the developing stage. The developer used for this photoresist was aq. KOH (9 grams of KOH per liter of Deionized water). This process was performed at 50 °C in the presence of a magnetic stirrer for approximately 15 seconds. Since, positive photoresist is spun on the substrate, the areas exposed to the UV light were developed exposing the copper underneath. After development, the exposed copper was etched using Ferric Chloride solution. Subsequently, the photoresist over the copper was dissolved using acetone and the board was now patterned with the plates of required dimensions.

Next, a thin layer of a dielectric material was coated on the plates. Two sets of experiments were performed using two different dielectric materials (AZ 5214 and Honeywell’s ACCUFLO) for the purpose of insulating the copper plates from the conducting media. The other purpose served by this layer is the charge storage. Seawater can be considered as a lossy dielectric, because of its ability to conduct. Since, the surrounding media (in this case seawater) is conductive, there is a need to provide a layer of dielectric for minimizing losses through the conductive medium.

The first material used was the positive resist AZ5214. The intended thickness of the coating was ~5 microns. AZ5214 was spin coated on the substrate. The spin rate was set at 1000rpm and the spin time was 60sec. Once spun, the photoresist was baked on a hotplate at 140 C for 90 sec to dissolve the solvents and harden the layer. Next stage, in the fabrication was to connect wires to the contact pads. Tiny patches large enough to solder wires to the pads, were opened up on the dielectric layer, by careful application of
acetone using cotton swabs. The wires were soldered to the exposed pads. Figure 4.13 shows the top view of the fabricated sensor.

Figure 4.13: Fabricated Sensors Prior to Alignment

Next step was to conceal the exposed contact areas again with photoresist. This was done by drop-coating the photoresist over the contact areas. The plates intended to be arranged in parallel were fabricated on two separate substrates. The next stage was to align them face to face with a spacing of ~600 microns. The dimension of the bottom plate was chosen to be a little larger than the top plate, as already mentioned, to allow for visual alignment through the FR 4 substrate. The spacing between the two substrates was provided using two spacers, 600 microns thick, glued at each end of the substrate using marine glue. Figure 4.14 shows the completed sensor.

Figure 4.14: Top View of the Completed Sensor
4.4 Equivalent Circuit Model for the Sensor

As evident from the discussion on the construction, the sensor represents a complex dielectric system, comprising dielectrics of different permittivities and conductivities. A model of the sensor is shown in figure 4.15.

Figure 4.15: (a) Maxwell-Wagner Layered Capacitor Model, (b) Equivalent Circuit Model, (c) Reduced Model, (d) Equivalent Circuit for Reduced Model, (e) Simplified Model

Figure 4.15a shows the Maxwell-Wagner layered model for the sensor. According to the Maxwell-Wagner model, for a capacitor with alternate layers of dielectrics specified by their dielectric constants and conductivities, the complex dielectric can be simplified into 2 layers considering the aggregate thickness for both the materials. [32]. Assuming that the insulation coating has negligible conductivity, the equivalent model can then be represented as shown in figure 4.15c, where \(d_1\) represents the total thickness of the insulation coating and \(d_2\), the total ‘thickness’ of the seawater. The equivalent circuit model for the reduced capacitor is shown in figure 4.15d, where the bulk conducting solution is represented by a capacitor and resistor in parallel and the insulation layer is represented by a resistor.
4.5 Alternate Detection Circuit for Capacitive Salinity Sensor

An alternative circuit for the detection of the capacitive salinity sensor, based on frequency to voltage converters (F-V) has also been proposed. The advantage of this approach over the Twin-T circuit is that it eliminates the issue of frequency stability. Also, since this design employs only one capacitor, it resolves the issue of matching the circuit components, as required by the Twin-T. A block diagram of the circuit is shown in figure 4.16. The principal components of this circuit are:

1) Signal generator (or) voltage controlled oscillator chip.
2) Frequency to Voltage converters (NJM 4151)
3) Buffer and Difference amplifier (LM 6142)

![Figure 4.16: Block Diagram of Circuit Employing Two F-V Converters and a Differential Amplifier Stage](image)

The experimental set-up is as shown in figure 4.17.
A detailed schematic of this circuit is shown in figure 4.18. In the schematic shown, the square wave required for the operation of the circuit was generated using a 555 timer. This was done to ensure that the entire circuit could be driven from a single voltage source of 10 V. However, during this experiment the timer was replaced by a function generator. The dc voltage developed on the output of both the F-V converters U1 and U2 is a function of the frequency of the input square-wave, the pulse-width of the one shot inside the F-V converter, the value of the constant current sources internal to the two F-V converters, and the value of the resistor connected from the output to ground. R18 is a 20 turn precision potentiometer, provided for calibration. The potentiometer adjusts the pulse-width of the one shot internal to the reference F-V converter U2 during the calibration of the circuit.

The expression governing the output voltage of the F-V converters is given by equation 4.8. [34].

\[ V_{out} = F_{IN} \frac{R_b R_0 C_0}{0.486 R_S} \]  

4.8
From equation 4.9 it may be observed that the sensitivity of the circuit is obtained as,

$$\text{Sensitivity} = \frac{dV_{\text{out}}}{dC} = F_{\text{in}} \frac{R_5(R_{10} + R_{18})}{0.486 R_{11}} = \text{constant}$$

The sensitivity of this circuit is found to be independent of the capacitance.
CHAPTER 5

RESULTS

This chapter is broadly segregated into three main areas. The first section presents the data obtained upon the use of AZ 5214 as the photoresist. This includes an impedance analysis of the capacitor in seawater and the corresponding Twin-T oscillator response. The next section analyses the data obtained upon the use of Honeywell’s ACCUFLO Spin-on-polymer as the dielectric layer and the corresponding oscillator response. Also included are results obtained for the alternative detection circuit with ACCUFLO as the dielectric.

5.1 AZ 5214 as the Insulation Layer

AZ 5214 is a thick photoresist with a dielectric constant of 6. The barrier properties of this polymer were analyzed using the impedance analyzer Agilent 4294A Precision Impedance Analyzer. Impedance data were collected for the sensor for varying salinities and temperatures of the solution. Calibration of the cables was performed prior to the experimentation stage. The amplitude of the applied voltage was 100 mV p-p.
5.1.1 Impedance Data for Varying Salinities at 22 °C

Initial salinity of the solution was 34.996 psu. Subsequently, small amounts of water were added using a micropipette, to decrease the solution concentration. Figure 5.1 is the Nyquist plot for the sensor with the real part of the impedance plotted on the X axis and the imaginary on Y. The semi-circle shape observed clearly indicates that this circuit can be treated as a Randel’s cell as explained in Chapter 3.

![Nyquist plot](image)

*Figure 5.1: Plot of Complex Impedance for Different Salinity Concentrations (psu)*

This shape of the Nyquist plot implies a low pore resistance of the coating on the electrode [36]. It may be observed that at lower frequencies, the cumulative resistance is given by $R_{sol} + R_t$. This is indicative of the fact that, space charge polarization occurs at lower frequencies. It can be inferred that at higher frequencies the polarization effects subside and the only resistive component is the $R_{sol}$.

It is further observed from the above plot that as the salinity decreases, on the right corner, the curves tend to shift towards the left. This implies an increase in the polarization resistance as the concentration increases. This suggests that chloride anion
adsorption occurs on the electrode, favoring the blockage of active sites on the metal surface [36]. Also observed from the graph is the solution resistance at higher frequencies increases as the salinity levels decrease. This is logical, since, addition of ions decreases the solution resistance.

From the Nyquist plot the following parameters were obtained.

Table 5.1: Parameters for the Randel’s Cell Obtained from the Nyquist Plot

<table>
<thead>
<tr>
<th>Salinity (psu)</th>
<th>Rs + Rt</th>
<th>w_max</th>
<th>Rs</th>
<th>Rt</th>
<th>Cdl (=1 / (Rt * w_max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>34.996</td>
<td>8925.348</td>
<td>3.04E+03</td>
<td>406.1793</td>
<td>1.32E-08</td>
<td>1.39096E-08</td>
</tr>
<tr>
<td>34.961</td>
<td>8685.2300</td>
<td>3.29E+03</td>
<td>407.6288</td>
<td>1.4364E-08</td>
<td>1.43966E-08</td>
</tr>
<tr>
<td>34.926</td>
<td>8550.3440</td>
<td>3.29E+03</td>
<td>408.1606</td>
<td>1.47971E-08</td>
<td>1.47971E-08</td>
</tr>
<tr>
<td>34.891</td>
<td>8427.0640</td>
<td>3.29E+03</td>
<td>408.5595</td>
<td>1.48036E-08</td>
<td>1.48036E-08</td>
</tr>
<tr>
<td>34.856</td>
<td>8425.8980</td>
<td>3.54E+03</td>
<td>408.8128</td>
<td>1.48057E-08</td>
<td>1.48057E-08</td>
</tr>
<tr>
<td>34.821</td>
<td>8.42E+03</td>
<td>3.29E+03</td>
<td>4.09E+02</td>
<td>8.02E+03</td>
<td></td>
</tr>
</tbody>
</table>

From the above table, it is seen that the double layer capacitance increases with decrease in concentration of the solution. This is attributed to the increase in diffusion capacitance as explained in Chapter 3.

Figure 5.2 shows a plot of the capacitance versus frequency for varying salinity levels in seawater. The sweep frequency was 40 Hz to 100 KHz. It may be noted that there is a steep fall in the capacitance of the sensor with increasing frequency. This follows from the discussion on polarization in Chapter 3. At low frequencies, the effects of orientation polarization dominate and hence, the permittivity is high, leading to higher capacitance values. An interesting observation here is the level of magnitude increase at low frequencies. While at higher frequencies, the capacitance was observed to be in the nF range; the capacitances for frequencies < 1 KHz are in the µF range.
Figure 5.2: Plot of Capacitance Versus Frequency for Varying Salinities at 22 °C

This is due to two reasons. Firstly, the effects of orientation polarization come into play at lower frequencies. Secondly, a path linking the electrolyte to the electrode through the barrier layer was formed, causing space charge polarization. This leads to a tremendous and anomalous increase in permittivity at low frequencies [32]. This link between the electrolyte and electrode causes film degradation due to diffusion of ions, water absorption and can result in flaking of the film [28]. These are also responsible for greater variations in capacitance (with increasing salinity levels) at lower frequencies. Shown in figure 5.3 is a plot of the capacitance versus salinity for a 40 KHz signal at 22 °C.
This was plotted from the data used in figure 5.2. From this plot it is observed that with increasing salinity, the capacitance of the sensor decreases. This follows from the discussion in section 3.10, which states that as ions are added to water, the hydrate shell around them makes their rotation difficult. As a result, the permittivity of the solution decreases. The decrease in salinity from this plot was observed to be 0.02 nF (or 0.4%) for every 0.035 psu change in salinity. Hence, the sensitivity of the sensor was found to be 0.57 nF / psu.

5.1.2 Impedance Data for Varying Temperatures at Constant Salinity

The temperature response of the sensor was obtained at the final concentration of 34.821 psu, after dilution with de-ionized water. Temperature was varied using a hotplate. The solution temperature was measured periodically using a mercury thermometer and a magnetic stirrer was used to maintain uniformity in the temperature profile throughout the solution. The Nyquist plot for this experiment is as shown in figure 5.4. The semi-circles are observed to shift to the left with increasing temperatures. This is indicative of the fact that as temperature increases the resistance of the solution and the film decreases.
An explanation to this is that an increase in temperature increases the rate of diffusion of the electrolyte into the photoresist layer, thereby, reducing its resistance. Also, the rate of absorption of water in the film increases with increasing temperatures. This increases the effective dielectric constant of the film, increasing its capacitance.

![Nyquist plot for varying temperatures](image)

*Figure 5.4: Nyquist Plot for Varying Temperatures (Salinity = 34.821 psu)*

The Randel’s cell parameters for this plot and are as shown in table 5.2.

*Table 5.2: Randel’s Cell Parameters for Varying Temperatures at Constant Salinity (34.821 psu)*

<table>
<thead>
<tr>
<th>Temperature (C)</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs + Rt</td>
<td>8.55E+03</td>
<td>8.43E+03</td>
<td>8.32E+03</td>
<td>8.27E+03</td>
<td>8.26E+03</td>
</tr>
<tr>
<td>w_max</td>
<td>3.04E+03</td>
<td>3.29E+03</td>
<td>3.29E+03</td>
<td>3.29E+03</td>
<td>3.29E+03</td>
</tr>
<tr>
<td>Rt</td>
<td>8151</td>
<td>8033</td>
<td>7.93E+03</td>
<td>7941</td>
<td>7931</td>
</tr>
<tr>
<td>Rs</td>
<td>3.99E+02</td>
<td>3.97E+02</td>
<td>3.95E+02</td>
<td>3.92E+02</td>
<td>3.87E+02</td>
</tr>
<tr>
<td>Cdl (=1 / (Rt * w_max)</td>
<td>1.43E-08</td>
<td>1.47671E-08</td>
<td>1.51662E-08</td>
<td>1.52648E-08</td>
<td>1.52648E-08</td>
</tr>
</tbody>
</table>

Figure 5.5 shows the variation of capacitance of the sensor versus frequency for varying temperatures at a constant salinity of 34.821 psu. From the graph it was observed that with an increase in temperature the capacitance of the sensor was found to decrease. This can be attributed to the reduction of orientation polarization as temperature increases. The
change in capacitance at 40 KHz for a 5 °C change in temperature was observed to be 0.002 nF. Therefore, the sensitivity of the sensor was found to be 0.0004 nF/ °C.

![Capacitance Versus Frequency for varying temperatures at constant salinity (34.821 psu)](image)

*Figure 5.5: Plot of Capacitance Versus Frequency for Varying Temperatures at Constant Salinity*

### 5.1.3 Twin-T Oscillator Frequency Versus Salinity

Figure 5.6 shows the Twin-T oscillator response to the variation in salinity of seawater. The frequency drift in the output for constant salinity of the solution was ~400 Hz. The results obtained for the Twin-T oscillator with ACCUFLO as the dielectric will make clearer the fact, that this frequency drift can be attributed in part to the poor dielectric characteristics of the photoresist.
The resistors used in the Twin-T network were 1K resistors (2% tolerance). The frequency of the oscillator was observed to increase with increasing salinity. The oscillator frequency is inversely proportional to the capacitance of the sensor and hence, as salinity increased, the capacitance decreased resulting in increased frequencies. The change in frequency was observed to be ~500 Hz for 0.0875 psu change in salinity.

5.1.4 Twin-T Oscillator Frequency Versus Temperature

![Figure 5.7: Twin-T Oscillator Frequency Versus Temperature at 34.471 psu](image)
From the plot in Figure 5.7, it is observed that as temperature increases the oscillator frequency decreases. This is because the sensor’s capacitance decreases with increasing temperature. Hence, frequency of the oscillator increases with temperature. The frequency was observed to shift by 0.12 KHz for every 5 °C.

The sensor was removed from the solution after 48 hours of immersion. The photoresist seemed to have almost leached out of the electrode surface. There are two possible explanations for this. Firstly, the degradation of the film is caused due to water absorption and secondly, due to slow developing of the resist in the seawater. Photoresists are known to develop in alkaline solutions and seawater has a pH ~8 [1] making it slightly alkaline. This may have resulted in accelerated leaching of the resist layer.

5.2 ACCUFLO Spin-on-Polymer as the Insulation Layer

Honeywell’s ACCUFLO Spin-on-Polymer (T3027), was used for the second set of experiments. Impedance analysis on the sensor was performed to test the strength of the barrier layer in seawater.

5.2.1 Impedance Data for Varying Salinities at 22 °C

The Nyquist plot for the sensor with this coating is as shown in figure 5.8a. From [35], we have that the equivalent circuit model for this plot is as shown in figure 5.8b. According to GAMRY, this is the Nyquist plot for a good coating on the electrolyte as the impedance of the coating is found to be extremely high. This is because the film has not yet absorbed any water. Hence its permittivity is as expected and not anomalously
high. The impedance of the layer was found to reduce with concentration increase. Thus, it can be inferred from the Nyquist plots that ACCUFLO is more suitable as an insulation layer than AZ5214, for this application.

Figure 5.8: (a) Plot of Complex Impedance for Varying Salinities at 22 °C

(b) Equivalent Circuit Model for Metal-Electrolyte System Corresponding to the Plot in (a)

Figure 5.9 shows a plot of the capacitance versus frequency at varying salinities. Once again, capacitance is observed to fall as frequency increases. From this plot it can be seen that the capacitance drops as salinity increases. The reason for this drop is similar to that explained in the previous section. It may be noted that the variation of capacitance with frequency is not as pronounced as it was for the photoresist. Thus, it can be inferred that this coating exhibits better dielectric properties over wider frequencies than the photoresist.
Figure 5.9: Plot of Capacitance Versus Frequency for Varying Salinities at 22°C

Shown in figure 5.10 is a plot of the capacitance versus salinity for a 2 KHz signal at 20°C. This is from the data used for plotting figure B. For every 0.035 psu change in salinity, the change in capacitance observed was 0.01 nF. The sensitivity for this sensor was thus, obtained as 3.5 nF / psu.

Figure 5.10: Plot of Capacitance Versus Salinity for a 2 KHz Signal at 22°C
5.2.2 Impedance Data for Varying Temperatures at Constant Salinity

The Nyquist plot for varying temperatures of the solution is given in figure 5.11. The resistance of the film is found to decrease with increasing temperatures. The vertical lines obtained are indicative of the fact that the film has not yet absorbed any water from the medium.

![Nyquist plot](image)

*Figure 5.11: Nyquist Plot for Varying Temperatures at Constant Salinity (34.856 psu)*

Figure 5.12 shows a plot of the capacitance versus frequency for varying temperatures, at 34.856 psu. It is observed that for every 5 °C increase in temperature, the capacitance was found to decrease by 0.14 nF. Thus, the sensitivity of the device for varying temperatures is 0.028 nF / °C.
5.2.3 Twin T Oscillator Response with Spin-on-polymer as Insulation Layer

The Twin-T oscillator’s response was found for varying salinities at 22 °C and is plotted in figure 5.13. The oscillator frequency was observed to increase by 0.058 KHz for every 0.14 psu change in salinity which implies 0.41 KHz / psu.

Another point of interest with this material as the insulation layer was the good stability achieved in the output of the oscillator. The frequency was observed to drift only by ~10 Hz about a mean value at constant salinity and temperature.
5.2.4 Twin-T Oscillator Frequency Versus Temperature

The oscillator response for a constant salinity of 32.891 psu and varying temperatures is as shown in figure 5.14.

![Oscillator Frequency vs Temperature Graph](image)

*Figure 5.14: Plot of Oscillator Frequency Versus Temperature at Constant Salinity of 32.891 psu*

An interesting point to note is that for the same values of the R and C components in the Twin T network, the oscillation frequency can be made lower, by introducing a little positive feedback. This has a ‘latching’ effect on the op-amp, and it tends to stay in the saturated state for a longer duration, thereby, reducing the output frequency. However, there is no expression that can relate the frequency to the amount of feedback applied.

5.3 Response of F-V Converter Circuit

From the impedance analysis performed earlier, it was inferred that Honeywell’s ACCUFLO spin-on-polymer is more suitable as a dielectric layer for this application than photoresist AZ5214. Hence, this experiment was performed with ACCUFLO as the barrier layer.
5.3.1 Output Voltage Versus Salinity at 22 °C

The output voltage of the schematic shown in figure 4.17 is shown in figure 5.15. The output voltage was found to decrease with increasing salinity. This is because the output voltage for this circuit, as seen in expression 4.9, is proportional to the sensor capacitance.

![Output Voltage Vs. Salinity](image)

*Figure 5.15: Output Voltage Versus Salinity at 22 °C*

For a change in salinity of 0.07 psu, the change in output voltage was obtained as 0.7 mV. Thus, the sensitivity of this detection circuit is 10 mV / psu.

5.3.2 Output Voltage Versus Temperature at Constant Salinity

The effect of temperature on the output voltage was studied in this experiment, at constant salinity of 34.65 psu. The output voltage was observed to follow a decreasing trend with temperature due to the capacitance drop with increasing temperature.
Figure 5.16: Output Voltage Versus Temperature at 34.65 psu

Sensitivity of this approach to variations in temperature was found to be equal to 6.3 mV /°C.

5.4 Comparative Study

A comparison chart has been shown below, summarizing the results obtained for both the materials used as well as the detection techniques.

Table 5.3: Comparison Chart for Materials Used and Detection Techniques Proposed

<table>
<thead>
<tr>
<th>Barrier layer</th>
<th>Impedance Analysis using 4294 A Precision Impedance Analyzer</th>
<th>Twin-T Oscillator Detection</th>
<th>Frequency-Voltage Conversion Detection</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Salinity Variation (at 22 °C)</td>
<td>Varying temperatures</td>
<td>Salinity Variation</td>
</tr>
<tr>
<td>AZ 5214</td>
<td>Sensitivity 0.57 nF / psu (at 40 KHz)</td>
<td>0.0004 nF / °C (@ 34.821 psu)</td>
<td>500 Hz / 0.035 psu</td>
</tr>
<tr>
<td>Honey well's ACCU FLO</td>
<td>Sensitivity 3.5 nF/psu (at 2 KHz)</td>
<td>0.028 nF/°C</td>
<td>0.41 KHz /psu</td>
</tr>
</tbody>
</table>
6.1 Conclusion

A parallel-plate capacitive sensor was fabricated to detect varying salinity levels in the marine environment. Impedance analysis was done on the capacitor using two separate materials as the dielectric layer between the electrode and seawater. The spin-on-polymer ACCUFLO was found to have better dielectric properties over the photoresist AZ5214, which was inferred based on the Nyquist plots obtained for both materials. Optimization of the capacitor was performed using FEMLAB, by addition of guard ring around one of the electrodes. The capacitance was observed to fall by 10% offering fringe field reduction and minimized effects due to interference. Two detection strategies have been proposed for the sensor. The Twin-T oscillator provided a sensitivity of 500 Hz for every 0.0375 psu change in salinity with photoresist as the dielectric, while the sensitivity of the oscillator with ACCUFLO as the dielectric layer was obtained as 410 Hz/psu. However, frequency stability of the oscillator was enhanced upon the use of ACCUFLO. The frequency-to-voltage approach was suggested as an improvement since it eliminates the effects due to any drift in source frequency. The sensitivity of this detection circuit was obtained as 10 mV/psu.
6.2 Future Work

More robust materials need to be used as the dielectric layer for electrode protection. Parylene or Spin-on-Teflon may be tried as alternatives for the polymers used in this research, which provide more effective protection from corrosive media. Also, materials which exhibit negligible dielectric constant variation with temperature need to be investigated. This will assist to strengthen the argument that the change in permittivity caused by a corresponding change in temperature, is purely due to the conducting media, with negligible or no contribution from the insulation layer. Integration of the sensor and the electronics into one substrate will reduce the parasitic effects and capacitances due to the cables. Frequency stabilization circuits need to be incorporated to the Twin-T oscillator design to minimize the drift at constant salinity levels. A study of the temperature response of the sensor needs to be performed using a constant temperature bath, and for temperatures lower than 20 °C. This is because, in general, ocean temperatures can vary between 0 °C–45 °C. The fabrication technique used here is the conventional PCB fabrication technique which is associated with significant undercuts. Although, the undercuts are advantageous for this sensor from the fringe field minimization point of view, an effort needs to be made to quantify this effect using FEMLAB. The effects of biofouling have not been studied in this work. This is an important consideration during deployment of the sensor in marine environments. Steps to minimize biofouling need to be incorporated into the system for accurate measurements. Reproducibility can be enhanced by ensuring that the design is coplanar. This is because coplanar arrangement can eliminate the errors due to mechanical placement of the spacers between the electrodes. This will require the use of IDT sensors
over biplanar capacitors. Finally, study needs to be performed to observe the hysterisis properties of the sensor over increasing and decreasing cycles of both salinity and temperature.
REFERENCES


2. “Chapter 6: Temperature, Salinity and Density”, from http://oceanworld.tamu.edu/resources/ocng_textbook/chapter06/chapter06_01.html


