

Performance and Degradation of a Battery-Free Water Leak Detection Device

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Water waste is one of the major causes of water scarcity, and it has become an alarming issue these days. According to the reports from UNICEF, it is estimated that by early 2025, half of the world's population may be residing in regions facing water scarcity [1]. The main reason for water waste is water leakage which also leads to significant property damage and heavy restoration costs if the leak is not detected at early stages. Currently, one of the solutions to these problems, is to detect the leak before it causes significant damage and water waste. The existing market provide solutions through water leak detectors which can identify leaks immediately after the incident. However, these devices are constrained by their dependency on batteries that contains hazardous chemicals, require high maintenance, and are difficult to access in remote areas.

To address these issues, our team has launched the world's first IoT-based Battery-Free Water Leak Detection device in which wireless signal transmission (via BLE) is powered by the energy harvested from the sensor-water reaction. One example of this type of sensor is the Mg-CNF (carbon nano fiber) system that converts the chemical energy to the electrical energy upon reaction with water [2]. The device made by our research group uses a magnesium-graphite couple that undergoes an electrical change as a sensing mechanism, in the presence of water. This electrical energy is stored and utilized to power the Bluetooth low energy (BLE) module that transmits the signal (sensing) generated by the sensor after contacting water. Although, the prototype has previously been built successfully, further tasks are needed to improve the performance, find failure modes and reduce the cost of the device. Therefore, this thesis focuses on the electrical performance, degradation on repeated uses, and reasons behind the failure of the sensor device.

The thesis will describe the I-V characteristics of the sensor under various conditions. It also discusses the electrical performance of the sensor with respect to charge capacity and internal resistance under variable load applications. Clear demonstration of the number of repeatability of the device under specific parameters is given, and the changes in the behavior of the device in terms of power production and beacon activation is also indicated. The reasons behind the degradation of the device are addressed by using various tools such as SEM/EDX, XPS, XRD and FTIR. Moreover, the surface analysis for measuring the critical thickness and roughness of some compounds is also performed with AFM and profilometer. The recommendations for the future improvements are suggested to enhance the performance and ease the production of the device.

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List of Abbreviations

AFM	Atomic Force Microscopy
BLE	Bluetooth Low Energy
DC	Direct Current
DI	Deionized
DMM	Digital Multimeter
EDL	Electrical Double Layer
EDX	Energy Dispersive X-Ray Spectroscopy
EHB	Energy Harvesting Board
FTIR	Fourier Transform Infrared Spectroscopy
IC	Integrated Circuit
IR	Internal Resistance
LDO	Low Drop-out
LED	Light Emitting Diode
OCV	Open Circuit Voltage
PCB	Printed Circuit Board
SCC	Short Circuit Current
SEM	Scanning Electron Microscopy
SWCNT	Single Walled carbon Nanotubes
UUID	Universally Unique Identifiers
WEG	Water Enabled Electricity Generators
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

Chapter 1: Introduction

1.1 Background

Water leak damage is one of the most destructive and expensive problems that house owners, large manufacturers and building owners deal with. There could be various causes of the water leak such as leakage of water through pipes, under sinks, toilet valves, dripping faucet, clogged lines, leakage from machinery etc [3]. It might not seem very destructive at first but leads to serious damage in long run. The leakage from pipes can cause major damage to the structure of the house/buildings since plumbing pipes are usually behind walls. It can also result in short-circuiting because of the electrical connection/wires, ultimately causing a potential fire threat. Therefore, repairing and cleanup of water damage can be very costly if not detected early enough. A study found that tiny leaks cause the typical North American household to waste about 10,000 gallons of water annually [4]. This figure can enormously increase if the leak is large and not solved immediately. Moreover, the insurance companies also lose \$2.5 billion a year due to water damage and mold, and a residential water damage insurance claim is typically \$6,965 [5]. In addition to the repairing costs, water waste can also lead to a considerable increase in water bills. For example, a toilet leak can waste around 6000 gallons per month and can increase the water bill by hundreds of dollars [6]. Therefore, if the leak is big and is not detected at early stages, it can increase the water bill enormously.

In addition to all these damages, water leaks also cause massive water waste which is one of the reasons for water scarcity. Water scarcity can be very devastating in coming years and according to UNICEF, 2/3 of world's population experience this problem for one month each year. It is also predicted that by 2025, it's possible that half of the world's population would reside in regions with scarce water supplies [1]. Water scarcity restricts the availability of clean water for drinking and performing basic hygiene at home, and in healthcare facilities. It can also cause sewage systems to malfunction and increase the risk of getting diseases like cholera.

All these problems can be minimized by encountering water leaks at initial stages. For instance, if the water leak is resolved immediately when it occurs, it can solve the issue of damaging the property, large repairing costs and water bills. Along with that, it can also reduce the wastage of water which can help to alleviate water scarcity. Many water leak detection devices are available in the market that detects the leak incident. These devices contain a sensor part and a communicating part, which sends an alert to the user when the device comes in contact with water. An alert can be anything i.e. a notification on

phone through email or a text which will give information about the leak by particular device, that has detected a leak. There are few major components that are required for the water leak detection device to function (**Figure 1**). If the system is a sensor device that generate electric signal, most important components will be (1) Materials for chemical reaction to occur, (2) Electronics comprising Bluetooth chipset to send signal, (3) Power source to operate the microcontroller (chipset), (4) Programming of the microcontroller, and (5) An enclosure to package materials and electronics. The thesis will focus mainly on materials and electronics part of the sensor.

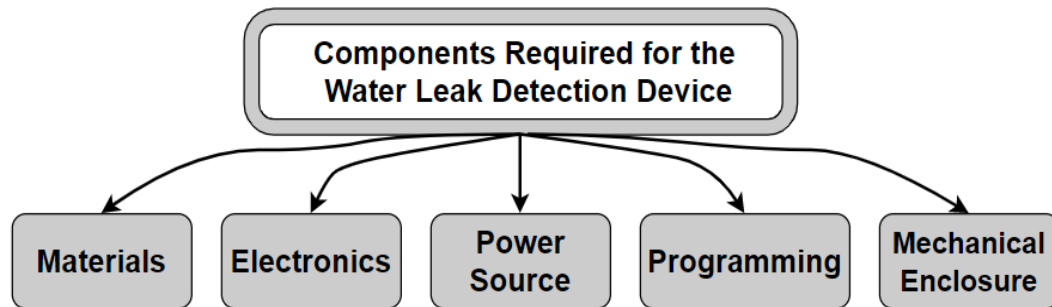


Figure 1: Components required for making water leak detector.

1.2 Problem Statement

There are various types of water leak detection systems available in the market. Few examples are “Ring Alarm Flood and Freeze Sensor”, “D-Link” and “Phyn Wifi Smart Water Sensor” etc. These detectors can be placed near sinks, water heaters, washing machines, basements and other potential leaks; and can detect leaks quickly and send alerts to customer’s phone/email. However, the main problem with these sensors is that they are all based on rechargeable or non-rechargeable batteries. Because the power from batteries is required for communicating the signal obtained from the sensor by using BLE devices. Therefore, frequent battery charging, testing or changing is required which can be very problematic when there are hundreds of sensors installed in a factory or hospital. Additionally, some pipelines/facets are away from the electric supply to charge batteries and therefore, rechargeable battery-powered systems cannot be installed in that area. As a result, it not only increases a step for sensor’s maintenance, but also increases the cost of changing batteries from time to time as well as the labor cost. These problems can be solved by a battery-free water leak detection system. To make such a device, water-induced reactions that undergoes electrical change can be used which is discussed throughout the thesis.

1.3 Objective

A prototype of battery-free water leak detector that works well for leak detection application has previously been developed by our research team. However, various electrical characteristics and sensor's behavior on repeated uses was not investigated, and are required for the further development of the device. Therefore, measuring the performance and the degradation of the battery-free water leak detection device are the two key objectives of the thesis. The device has a sensor unit that senses water and experience an electrical change as a sensing output. This electrical energy is then utilized to power the electronics unit that sends a Bluetooth signal. Therefore, the electrical properties (such as I-V characteristics, charge capacity, internal resistance etc.) of the sensor under various conditions will be measured. Moreover, the sensor device is capable of being used several times once it is dry and therefore the number of successful repetitions of the sensor will also be recorded. Another objective of the thesis is to analyze the reasons behind the degradation and failure of the sensor after being used repeatedly, which will be addressed with different characterization tools.

1.4 Thesis Outline

The chapter 2 presents the literature review about the water leak detection devices currently available in the market, their drawbacks and solutions to solve those limitations. It also gives the brief overview of the background of the battery-free water leak detection device made by our research group. The various test setups and different characterization tools are discussed in chapter 3. Chapter 4 presents the results and discussion for electrical performance and repeated use of sensor for water leak detection. The analysis of materials with different characterization tools is involved in chapter 5. And finally, conclusions and recommendations are proposed in chapter 6.

Chapter 2: Literature Review

To solve the issues of water leaks and meet the demands of fresh water to the world population, different water leak detection technologies are available in the market. Mainly, many companies have developed battery powered and plug socket powered water sensors while battery free devices are still in research phase. This chapter will talk about various currently available devices in the market and their limitations. It also explains the new ongoing research on self-powered water leak systems. Moreover, it will give an overview of the previous work on “Battery-Free Water Leak Detection Device” made by our research group, and it also describes the sensing property and electricity production by the device.

2.1 Water Leak Sensing Technologies

Various water sensing devices are available in the market that can detect water, and notify the user by sending an alert, or beeping an alarm. These can be used in houses, industries, residential buildings, warehouses etc., to detect the water leak at right time and reduce the water waste. Few examples of the companies that make these devices are “Moen”, “D-Link”, “Honeywell”, “Phyn”, and “Orbit”. The **Table 1** comprises the brief information about the sensor devices made by these five companies.

Table 1: Different Water Leak Detection Devices by Different Companies.

Company Name	Power Source	Features Other than Water Leak Detection	Price (CAD \$)	Ref.
Moen	Single CR123A Battery	Temperature and Humidity Sensor	69.95	[7][8][9]
D-Link	Two AA Batteries	-----	100	[10] [11]
Honeywell	Three AA Batteries	Temperature and Humidity Sensor	79.99	[12] [13]
Phyn	Two AA Batteries	Temperature and Humidity Sensor	49.99	[14] [15]
Orbit	Single CR2032 Button Battery + Wall Output	Temperature Sensor	147.29 (3 Sensors + Hub)	[16] [17]

Moen: The system named ‘Flo Smart Water Leak Detector (Moen 920-004)’ is made by Moen corporation and it costs CAD \$69.95 per unit. It connects via Bluetooth technology and sends text, email, and push notifications when detects even a slight amount of water. The device is shaped like a

water droplet, and it comes with additional unit i.e. a sensor cable that helps to cover a larger area of detection. The whole system is powered with a single CR123A (3V) battery. Along with water leak detection, it also helps in monitoring temperature and humidity of the place [7].

D-Link: This company made various systems and one of them for water sensing is called ‘DCH-S161 Wi-Fi Water Sensor’. It uses 2.4GHz Wi-Fi radio to connect to the home network and costs around CAD \$100 per unit. The device consists of two units, a main sensor unit and a cable. The sensor unit is powered by two AA batteries and is hanged at some height; however, the sensor cable is placed at the floor where water will collect to detect the leak. Unlike Moen, it does not have extra feature to detect temperature and humidity but can support google assistance voice service [10].

Honeywell: This company also make ‘Lyric Wi-Fi Water Leak and Freeze Detectors’ useful for the freezing temperature and flood areas. It is bit expensive like D-Link and price around CAD \$79.99. It requires three AA batteries to function and uses Bluetooth circuitry for connection with the mobile phones. This device can itself be used for water detection and does not require any extra cable for sensing. However, the device is big in size and cannot be placed under washing machines or other small appliances, therefore the cable is available for those applications at extra cost. It also has temperature and humidity sensor inside the sensor device [12].

Phyn: The Phyn corporations also make smart water sensors that can sense water and send text and push alerts, along with that it monitors temperature and humidity of the place. It can either be set down on the ground or hung from a wall or cabinet side. Sensor itself costs CAD \$49.99, but cables and extension nodes costs extra around CAD \$25.99 for four feet long cable. The device is powered by two AA batteries that can last for 2 years before replacement. It is Wi-Fi enabled and uses 2.4GHz Wi-Fi radio for connecting the device with the home internet to send text and push alerts [14].

Orbit: The ‘B-Hyve Smart Flood Sensor’ by Orbit Irrigation is a leak detection system that includes three tiny water sensors and a hub that links them to the home Wi-Fi and mobile device. It requires two separate power sources for the sensors and the hub. Each sensor is powered with the single CR2032 button battery and the hub is connected to the wall outlet. It also has built-in temperature sensor but lacks in humidity detection. The sensors can be placed under hot water heaters, washing machines or sinks to detect the leak. The pack of three sensors and a hub costs CAD \$147.29 and any additional sensor can also be purchased for CAD \$34.99 that works with the same hub [16].

2.2 Problems Associated with Existing Technology and Limitation of Current Inventions

The above discussed sensor devices solve many problems and help people to identify water leak immediately after the leakage/situation. However, still there are many developments needed in the existing technologies, and therefore research on improvement of these systems is still in progress.

2.2.1 Important Marketing Requirements [18]

- a) Ensure minimal operating expenses, users require an economic system that uses less energy.
- b) It must be autonomous, requiring no further user input after installation.
- c) The system must operate correctly so that when the user receives a leak notice, it recognizes a genuine leak and does not malfunction the sensor.
- d) The device should be eco-friendly.
- e) Installation must be easy.
- f) It should not be affected with changing weather conditions.
- g) The concept of battery-free sensors can be an asset and result to solve many problems such as labor cost, time consumption etc.

Most of the sensor devices in the market meet almost all the above-mentioned marketing requirements except being environment friendly and battery-free, which causes various problems. All the water sensing devices (explained in section 2.1) available in market are powered either by rechargeable and non-rechargeable batteries or by electric energy from the wall socket. These systems can work well and needs little maintenance at the smaller scale for example houses or apartments. However, replacing batteries for hundreds of battery powered sensor devices installed in a massive factory, hospital or residential buildings can be very challenging. Specially for the sensors mounted behind heavy machinery or tools could be more problematic. It will require high maintenance, labor and battery costs. Moreover, since the devices are battery powered and batteries contains hazardous chemical wastes, the battery powered water leak detection devices are not environmentally safe [19]. In addition to that, the devices powered by electric energy from the wall socket are limited by the number and places of electric sockets available in the room, and using so many extensions does not sound feasible. Even some places, not necessarily have the electricity supply through wall plugs, so in those cases such sensors cannot be

used. Additionally, detecting a leak in the walls and ceilings where the water pipes pass through, is another major challenge [20]. All the above discussed sensor devices lack in usage at these sites since the batteries cannot be replaced after certain period of time. All these problems can be solved with a self-powered water leak detection systems that does not require any outside power source either the rechargeable and non- rechargeable batteries or wall socket to function. Therefore, researchers are working on battery-free water detection devices.

2.2.2 Research on Self-Powered Water Sensors

The research on battery-free, self-powered water leak sensor is attracting a lot of attention from last few years, and researchers have found various technologies of harvesting energy from environment and other means. This section will demonstrate the two research findings by different research teams to make self-powered water sensors.

Zhang et al. worked on making self-powered active sensors for detecting liquid or gases [21]. These sensors can detect water, ethanol, and humidity without the requirement of any power source. The central component of such a device is the triboelectric nanogenerator (TENG) that determines the electric output signal by surface-adsorbed molecules, which has a significant impact on the outcome of surface electrification. For the fabrication of the sensor, firstly an Al foil with large surface area is obtained by etching the foil using electrochemical anodization [22] [23]. After that a thin layer of Al is deposited on the top with physical vapor deposition (PVD) method. This acts as one of the electrodes in the system. Subsequently, another electrode is prepared by depositing Cu thin foil on polyamide 6,6 (PA) film.

According to the triboelectric series, PA film and Al foil have different abilities to draw and hold onto electrons, leading in preferred output performance [24]. The initial output voltage of the PA TENG is shown in **Figure 2(a)**, which is greater than 70 V. When a drop of water is spread on the bottom electrode, the signal almost completely declined, as depicted in **Figures 2(b)**. This finding suggests that the TENG can function as an active sensor for liquid water detection. The similar experiment is also performed to test the humidity effect on the output. **Figures 3** display the PA TENG's performance under relative humidity (RH) conditions rising from 40% to 80%. The overall trend shows that the output signals logarithmically decline as RH rises.

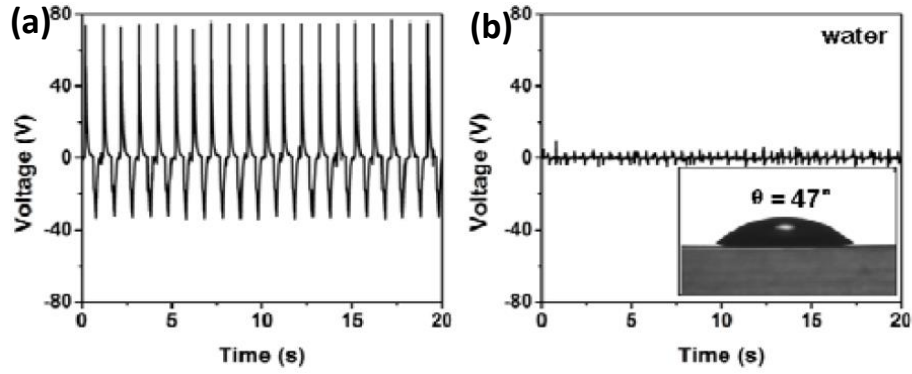


Figure 2: The output of the PA TENG (a) Without solution, (b) With water.

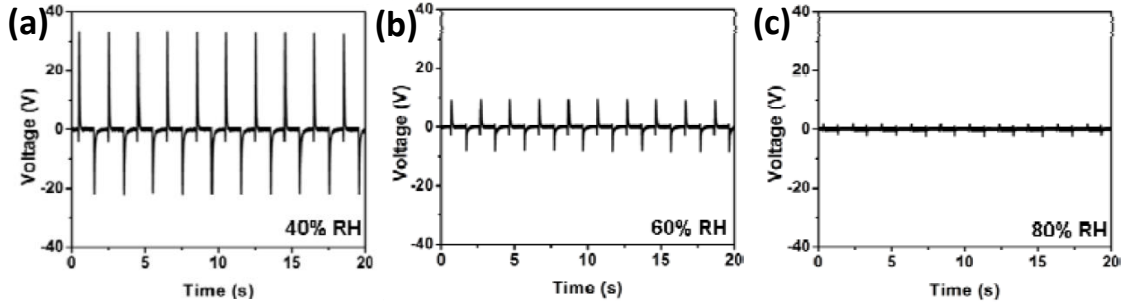


Figure 3: The performance of PA TENG under humidity (a) 40%, (b) 60%, (c) 80% [21].

Song Hao and Garcia developed a digital and battery-free smart flowmeter that detects water without the need of batteries or other external power supply [25]. It is made possible by three key technologies: an ultra-low-power metering system, a highly efficient cog-resistance-free generator, and a successful method to harvest and store its energy. It works on the principle of extracting energy from the fluid to run a generator. The generator comprises a rotor, a stator disc, and a turbine. The rotor and stator are designed in such a way to eliminate copper and iron losses and the turbine is used to convert kinetic energy (K.E) to the electric energy. The system effectively removes portion of the kinetic energy from the fluid, store it in a capacitor, and then use it to power the device. The **Figure 4** shows the design mechanism of the device, from left to right: frame, IC circuit and sensor, casing, blades, magnets, coils and a capacitor. The **Table 2** shows the power consumption of individual components and is measured by attaching a voltmeter and a current meter across them. The system as a whole uses 4.75 μA power at 25 RPS (revolution-per-second) and this amount decreased to 2.0 μA while it is at rest.

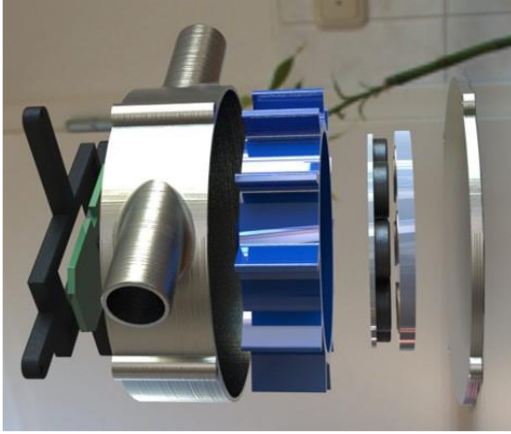


Table 2: Power consumption by individual components of flowmeter

RPS	Sensor	CPU	RTC	LCD	Total (μ A)
5	0.70	0.15	1.2	0.5	2.55
10	1.10	0.30	1.2	0.5	3.10
15	1.50	0.45	1.2	0.5	3.65
20	1.90	0.60	1.2	0.5	4.20
25	2.30	0.75	1.2	0.5	4.75

Figure 4: Design mechanism of the flowmeter [25].

These smart flowmeters can be placed inside pipelines to monitor the fluid/air flow. The flow rate is monitored through turbine speed in RPS and the corresponding total energy. Moreover, for data transmission to a centralized unit, particularly in situations like leakage or backflow, smart flowmeters are fitted with wireless transceivers. The new Bluetooth low energy devices can be utilized for that purpose to consume less power.

2.2.3 Issues Related to Present Inventions

First of all, not much invention has seen in developing self-powering water leak sensors that can be used to detect any type of water leak, either it is inside a pipe and wall or normal leaks at homes such as leaks due to toilet and bathtubs. Moreover, the researchers who invented self-powered water leak detection systems are limited with fabrication complexity or their use for specific applications. For example, the self-powered triboelectric nanogenerators water sensor developed by Zhang et al. have a difficult production procedure. It can be very expensive for large scale production due to some complicated process of etching and deposition (PVD) for preparation. Furthermore, the smart flowmeters fabricated by Song Hao and Garcia, have limitation of only being used at high water flow places such as pipes, since the turbines moves with water flow to generate energy. These kinds of sensors cannot detect normal leak at houses for example, leaks under toilet, bathtub, from the pipes etc. Therefore, this project focuses on a “Battery-Free Water Leak Detection System” that will overcome all the limitations poses by existing devices as well as the devices under research. This system is an example of the water enabled chemical reactions.

2.3 Water-Enabled Electricity Generators (WEG)

These generators are divided into three categories based on the power source of the input water and the power conversion mode: chemical to electric WEG, mechanical to electric WEG, and thermal to electric WEG (**Figure 5**). These types indicate that the driving force is derived from chemical potential variation, mechanical movement, and thermal differences respectively [26].

2.3.1 Chemical to Electric WEG

When water undergoes a chemical transition from a high potential state to a low potential state, energy is released that can be used to power a moist-electric generator (MEG). The MEG typically comprises two electrodes and useful components that can release moveable ions. This type of WEG is the examples of the Mg-water reaction in Mg/graphite couple discussed in next section. Another example of this kind of WEG is a moisture activated reaction to make a moisture battery that formed by contacting magnesium (anode) with foamed polyaniline (cathode) [27].

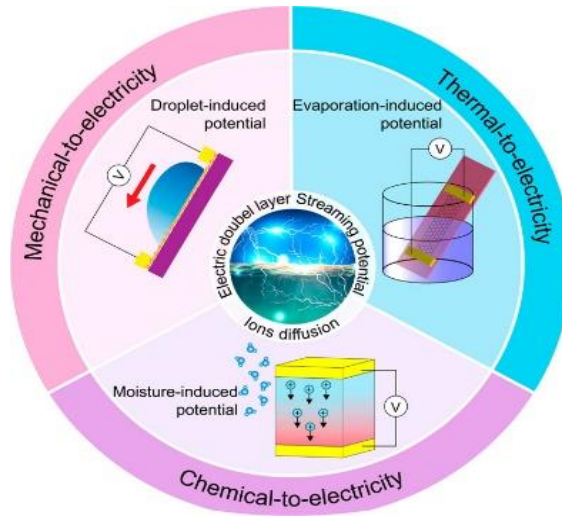


Figure 5: Overview of the water-enabled electricity generation (WEG) techniques [26].

2.3.2 Mechanical to Electric WEG

The mechanical flow of water over materials has the potential to produce electricity based on the changes in the electrical double layer (EDL). Therefore, this concept can be used to make a water based electric generators [28]. Example of such a WEG is the movement of electrolyte droplet on the surface

of a monolayer graphene in forward and backward direction. Since 2D graphene has large surface area and excellent carrier mobility, it has impact on the strength of EDL when coupled with water droplet. Therefore, when the droplet of water moves on the graphene layer, it produces electricity due to changes in ELD [29].

2.3.3 Thermal to Electric WEG

The natural evaporation of water is prevalent, spontaneous phenomenon that can extract thermal energy from the environment. And this energy can be utilized to produce electricity. For example, a surface tension-driven directed flow of ethanol over the single-walled carbon nanotubes (SWCNTs) in ethanol solution results in hundreds of microvolts when the SWCNTs are simply positioned in the solution at an angle of inclination of 40°. The performance of such a device is determined by the evaporation kinetics and liquid characteristics [30].

The system made by our research team is an example of “Chemical to Electric WEG” and the material’s concept of Mg-graphite couple device is detailed in next section.

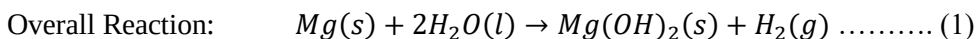
2.4 Concept Behind Battery-Free Water Leak Detection Device

The water induced chemical reaction system is utilized to make a self-powered water leak detection device. The magnesium metal is used to carry out this work since it undergoes oxidation reaction when reacts with water. Magnesium is an alkaline earth metal of the group 2 of the periodic table and is an element represented with a symbol Mg [31]. It is a shiny silvery-white metal present in the earth’s crust and is the eight most abundant element on earth [32]. The magnesium element is highly reactive and therefore does not find in its elemental form, and the most common Mg containing minerals are the magnesite, carnallite, and dolomite [33]. The atomic number of Mg is 12 and has an atomic mass equal to 24.305 u. The Mg metal has two valence electrons in its valence shell and the electronic configuration of Mg is written as: $1s^2 2s^2 2p^6 3s^2$ [34]. Therefore, it mainly exhibits +2 oxidation state by losing or sharing the two electrons in its 3s orbital, to acquire a stable noble gas configuration [35]. Moreover, the pure Mg has low structural strength and therefore is usually used in the form of alloy. This water leak detection device uses AZ-31 alloy of Mg which have various elements with different approximate minimum and maximum ratios as mentioned in **Table 3** [36].

Table 3: Percentage of various elements present in AZ-31 alloy of Mg.

Elements	Max. (%)	Min. (%)
Magnesium (Mg)	97	94.5
Aluminum (Al)	3.5	2.5
Zinc (Zn)	1.4	0.6
Manganese (Mn)	0.2	0
Silicon (Si)	0.3	0

It is found in the literature that the Mg metal reacts readily with water and encounters an oxidation reaction [37]. The oxidation reaction with respect to electron transfer is defined as loss of electrons [38]. And since Mg has two valence electrons, it loses those electrons and forms a Mg^{2+} ion or a stable compound upon reaction with oxygen and hydrogen present in water. The reactions between Mg and water are presented below:



The flow of ions and electrons caused by the various redox mechanisms in these reactions causes this Mg-water reaction to generate electricity. This indicates that when Mg metal reacts with water, it undergoes a change, in the form of electricity production. This demonstrates that it can be used as a water sensing system and since it produces electricity as a sensing mechanism, it can also serve as a power source, making it a self-powered system.

Moreover, the Mg metal can also react with oxygen and CO_2 in air to form MgO and $MgCO_3$ [42][43][44]. All these magnesium compounds are insoluble in water, therefore when Mg metal reacts with water, O and CO_2 (in air), a thin coating of $Mg(OH)_2$, MgO and $MgCO_3$ on Mg metal surface is

formed respectively. These protective coatings formed on the surface of the Mg slows down the further reaction of water with Mg and therefore reduces the efficiency of the reaction over time.

The standard reduction potential of Mg is -2.37V according to standard reduction potential table [45]. If the right combination of materials are selected, high voltage can be obtained from the Mg-water reaction. In this case, a Mg-graphite couple is used which produces voltage around 2.0V when reacts with water. More information on the fabrication of the device is presented in section 2.5 and **Appendix A and Appendix B**.

Requirements for making a water leak detection device:

1. Need materials/components that undergo any change when reacts with water.
2. A microcontroller or Bluetooth module to process data about the change, and send it to the cloud which will alert the user through an email or text notification.
3. Programming of the microcontroller.
4. A power source to power the microcontroller.
5. A housing to place materials and electronics, and to make electrical connection between both.

According to these requirements, the concept discussed above for Mg-water reaction can be used to make a water leak sensor. Since this chemical reaction produces power, there is no need of any external source to power the electronics circuit to process the Bluetooth signal. The electricity produced from the chemical reaction will be transferred to the electronics circuit to power the microcontroller which makes it a self-powered system. This means, the signal will only be sent when the reaction will happen (when water contacts Mg electrode) and then the user will receive notification on the phone. The programming of the microcontroller was done by the software team and the plastic housing was made by the mechanical team. Making this kind of system will solve all the problems mentioned in section 2.2.3.

Similar to this water induced electricity production system, the above explained water-enabled electricity generators (WEG) that works on different principles can also be used for similar purposes [26]. However, there are limitations of amount of energy production, difficult fabrication techniques and cost of these devices.

2.5 Brief Overview of the Previous Work on Fabrication of the Battery-Free Water Leak Detection Device

The powdered graphite is pressed into a pellet shape and is used to make one of the components in the device. Then an anode electrode is prepared by punching the Mg sheet into circular disks and subsequently sanded with a sandpaper to remove the protective coating. A circular filter paper that acts as a separating layer is placed between both electrodes to prevent short circuiting since the electrons must only pass through the external circuit of metallic wire. Another filter paper is placed beneath the whole setup to absorb water. Then all these layers are placed in plastic enclosure (sensor unit).

Another enclosure (electronics unit) is placed on the top of the sensor unit which comprises electronics components. It includes a BLE (Bluetooth low energy) board required to process the signal. Other than that, one more board is required to amplify the energy produced by the chemical reaction since this energy is not sufficient to activate the beacon (BLE board). To do that, an energy harvesting board (EHB) is installed which includes a boost converter and a LDO to boost up and regulate the energy produced by chemical reaction (more in **Chapter 4**). More information about the synthesis of each component of the device, can be seen from the thesis and publications written by prior students [46][2].

2.6 Summary

The chapter explains the existing water leak sensor technologies and their benefits and drawbacks. It summarizes the current research on self-powered water sensors from two publications. Moreover, it describes the major limitations of the sensor devices which included the problem of changing batteries or using external power source to power the device. In the second half of the chapter, it discusses about the self-powered water leak sensor and its reaction with water. It further gives a brief overview of the other water enabled electricity generation technologies. At the end, brief overview on the background of previous work of device fabrication is reviewed.

Chapter 3: Test Set-ups Procedures and Characterization Methods

The chapter 3 talks about various instrumentations used and their test set-ups for measuring electrical characteristics of the sensor device. This also includes different characterization tools for analyzing the surface properties of the anode electrode (center of the reaction) such as surface particle's morphology, elemental information, and thickness of the oxide structures.

3.1 Test Set-up Procedures for Electrical Measurements

Various electrical specifications of the sensor device such as open circuit voltage (OCV), short circuit current (SCC), power, voltage trend in several electrical components and resistance are measured with different instruments. The instruments used are digital multimeter (DMM) (Agilent 3411A), source meter (Agilent B2911A) and an oscilloscope (RIGOL DS1104).

3.1.1 Instrumentation Setup for OCV and SCC Measurement

The OCV and SCC are measured with the DMM in different modes. The OCV analysis measures the electrical potential difference between two terminals of the device when no current passes through it. However, the SCC analysis measures the current through the device when the voltage across it is zero. The DMM is used in voltmeter mode for OCV measurement and an ammeter mode while measuring SCC.

During voltmeter mode, the DMM is connected in parallel with the sensor enclosure and it has very high impedance so that very little current goes through it **Figure 6(a)**. The positive and negative pins of the sensor unit are connected to the high and low of the voltmeter in DC voltage mode. On the other hand, in ammeter mode, the DMM is connected in series with the sensor enclosure and in this mode, the DMM has very low impedance so that no voltage drop occurs. Similar to the voltmeter mode, the positive and negative from the sensor are connected to the high and low of the ammeter **Figure 6(b)**.

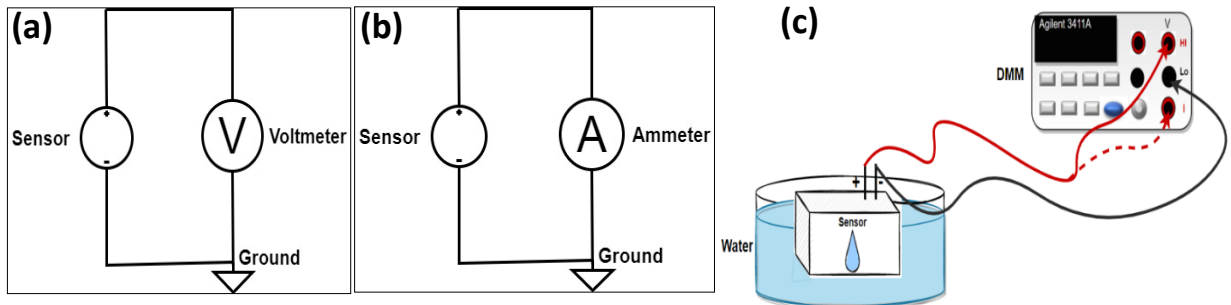


Figure 6: Electrical schematics for the (a) OCV and (b) SCC measurements; (c) Test setup for voltmeter and ammeter mode.

3.1.2 Instrumentation Setup for Load Test

This test setup is used to analyze the voltage trend from the sensor unit under variable loads. Therefore, different load values are applied through the source meter and the voltage is measured with DMM in voltmeter mode. To do so, the source meter is used in the current drawing mode and varying values of the current are entered in the settings on machine with negative sign. The connections are made such that the DMM and source meter are connected in parallel to the sensor unit. Therefore, positive and negative pins from the sensor are connected with the positives and negatives of both instruments **Figure 7**.

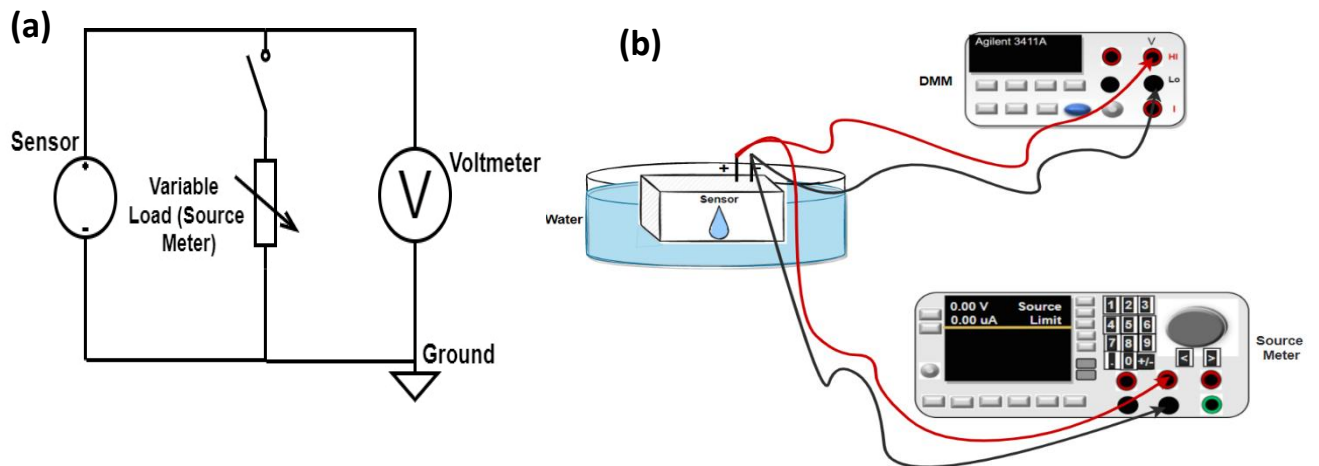


Figure 7: (a) Schematic for the load test; (b) Test setup for the applying variable load from the source meter and measuring voltage with DMM.

3.1.3 Instrumentation Setup for Voltage Measurement in the Device (Sensor + Electronics Unit)

This instrumentation setup is used to measure the voltage from different components inside the device all at once. Therefore, a four-channel oscilloscope is used to analyze the voltage trend with time from sensor unit, bulk capacitor and output of the EHB. A breadboard is also utilized to make the connection from various parts. As seen from **Figure 8**, the sensor's output goes in breadboard from which it transfers to the input of the EHB, and at the same time it is measured through channel 1 of oscilloscope. The trend of bulk capacitor's voltage is also measured through the channel 2. After that, to measure the output of the EHB, the connections are made to the breadboard and from here it is connected to the input of the BLE boards and to the channel 3 of the oscilloscope. The measurements from all the channels are discussed in the next chapter.

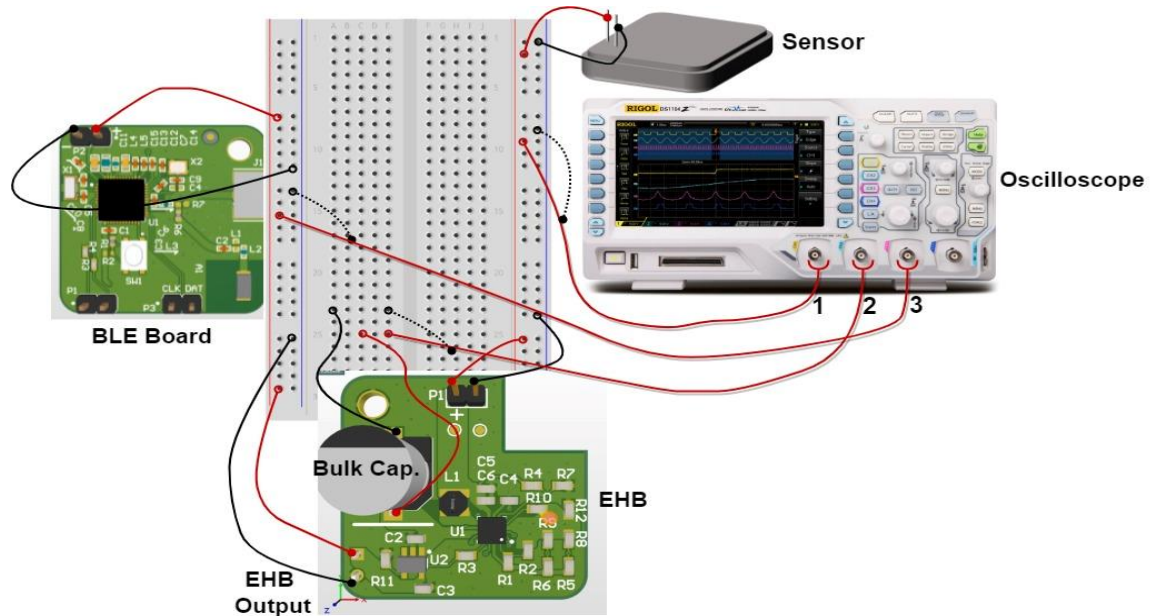


Figure 8: Test setup for measuring voltage from sensor, bulk capacitor and output of EHB at the same time with 4 channel oscilloscope.

3.1.4 Instrumentation Setup for Resistance Measurement

This test setup is made to measure the resistance of the anode electrode inside the sensor unit. The DMM is set to resistance measurement mode during this analysis. It can be done in two ways, 2-wire measurement (2W) or 4-wire measurement (4W). During 2W mode, only two wires are connected from

the DMM to the sensor unit (**Figure 9(a)**), however, four wires are required to do the 4W measurement (**Figure 9(b)**). The difference between two modes is that in 2W measurement, the DMM measures the resistance of the leads along with the electrode (since the current flows through the leads as well). However, in 4W measurement, the voltmeter is directly connected with the electrode and therefore only measures the resistance from the anode electrode. The 4W measurement is used in this case since the resistance of the electrode is very low and therefore can be measured correctly with this setup.

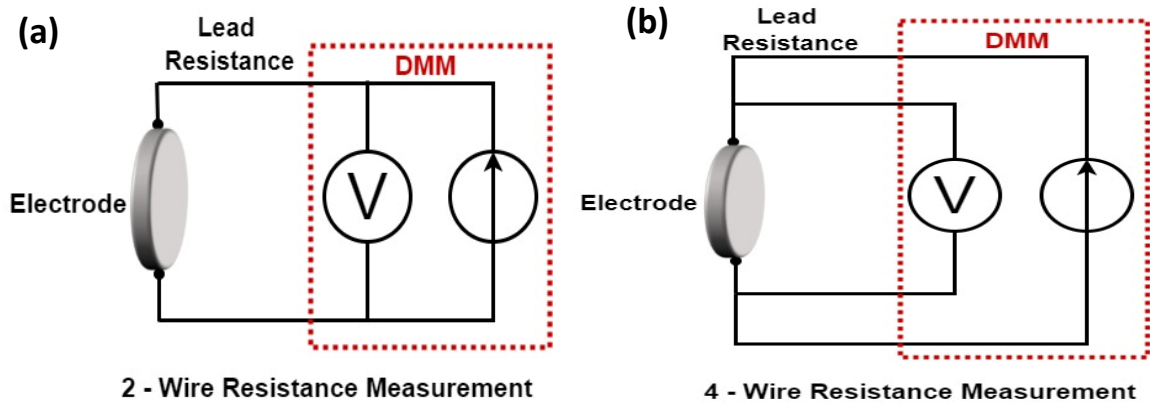


Figure 9: Resistance measurement with DMM (a) 2-wire mode, (b) 4-wire mode.

The connections are made from the DMM to the electrode with 4 wires in which 2 positive and 2 negative leads from both sides of the electrode are connected to the high and low on the voltage and resistance measuring sites as shown in the **Figure 10**.

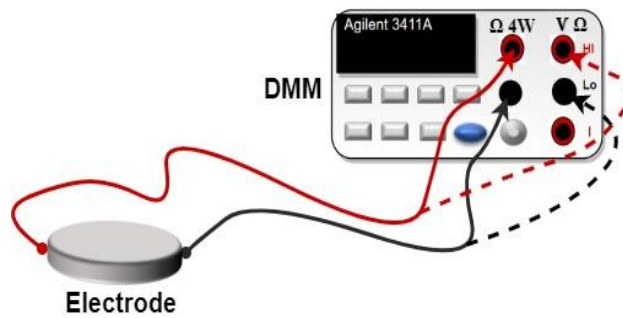


Figure 10: Test setup for 4W resistance measurement of the electrode (anode).

3.2 Characterization Tools for Analyzing Surface Properties of Anode Electrode

Several characterization instruments are used to investigate various properties of anode electrode (Mg disk) in the sensor unit. These tools give information about the structural morphology, elemental and chemical information about the surface, and thickness of layers grown on top of anode electrode after repeated use of the sensor unit. The instruments in G2N lab and WATLAB at the University of Waterloo are used for characterization and are listed as: SEM (Scanning Electron Microscopy) (Hitachi, SU5000), EDX (Energy Dispersive X-Ray Spectroscopy) (Oxford Instruments), XPS (X-Ray photoelectron spectroscopy), XRD (X-Ray diffraction) (X'Pert), FTIR (Fourier Transform Infrared Spectroscopy) (Bruker, Tensor 27), AFM (Atomic Force Microscopy) (Digital Instruments, VEECO Metrology Group) and profilometer (Dektak 8).

3.2.1 SEM and EDX

The SEM instrument is used to image the surface of Mg disks, and compare them with the Mg sheets inside the repeatedly used sensor devices. The freshly sanded Mg is very shiny and has almost the whole area available for reaction with water. However, literature shows that MgO and Mg(OH)₂ builds up on Mg metal when it contacts with air and water respectively. Therefore, the structure of the layers grown after the reaction, is imaged with the SEM to see the porosity of the layers. The EDX is used to identify different elements and their percentage on the surface of Mg disk. The elements i.e. Mg, Al and Zn are expected to be observed since the metal is AZ-31 alloy of Mg. Moreover, the O is also anticipated due to the reaction of Mg with air and water. Therefore, the EDX measurement is done on various samples that has been repeatedly used in the sensor device, to see the variation in O and Mg content (due to oxidation of Mg disk). This instrument is equipped with the SEM (**Figure 11(a)**) and the measurements from both the machines are done together at the same time with different software. For the sample preparation, the Mg disk is removed from the sensor device and then the gold coating is done on the top surface, since the sample must be conductive for the SEM measurement. The gold coating is done with the sputter coater (Denton Vacuum Desk II) shown in **Figure 11(b)**.

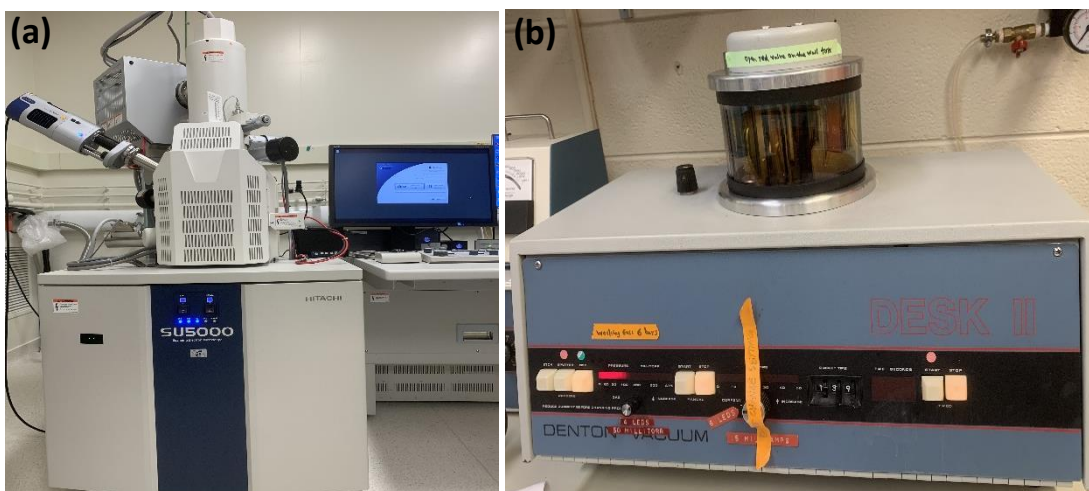


Figure 11: (a) SEM and EDX Instrument; (b) Sputter Coater (pictures taken while doing the measurement).

3.2.2 XPS, XRD and FTIR

To confirm different compounds present on the Mg disk used inside the device, the characterizations are done with XPS, XRD and FTIR.

The XPS (**Figure 12(a)**) is surface sensitive and therefore reveals information about the top surface layers only. The sample is taken from the sensor device that has been used for one time for water leak detection. The analysis of this sample with XPS confirms the type of oxide and few other compounds present on the sample surface. Moreover, other than the surface, inner layers are also examined by using “Depth Profile” feature in XPS. During depth profiling, the argon (Ar) sputtering is done for 20 min. which removed the surface layers and exposed the inner layers for measurement. The XPS requires the sample to be conductive, and since the Mg disk (after used in the device) is not very conductive, the flood gun is used for ion compensation. The differences in the results of surface and inner layer are then examined and are discussed in **chapter 5**.

The XRD is used to confirm the results received from XPS. During this measurement, two different scans: 2Theta and 2Theta-Omega scan are done for analyzing the surface and inner layers respectively. The Mg disk used for this analysis is taken from the sensor that has been used for 12 times (wetted 12 times after drying at each use). This analysis also confirms the type of oxides and other compounds that are grown on the surface of Mg disk. The **Figure 12(b)** shows the XRD instrument used for the analysis.

The FTIR is used to find out different functional groups present on the sample, and it indirectly confirms the compounds found in XPS and XRD. In this case, two samples, unoxidized and oxidized are analyzed with the ATR (Attenuated total reflection)-FTIR which basically qualifies samples to be directly characterized in solid state without any sample preparation. The unoxidized sample is refer to the sample that has never used in the sensor device and is sanded with the sandpaper before characterization (it can have a little oxidation from the air), and the oxidized sample is used for 12 times inside the device (wetted with water for 12 uses). The ATR-FTIR used for the measurement is shown in **(Figure 12(c))**.



Figure 12: (a) XPS Instrument; (b) XRD Machine; (c) ATR-FTIR Spectroscopy (pictures taken while doing the measurement).

3.2.3 AFM and Profilometer

The AFM and profilometer are used for the roughness and thickness measurement of the oxide layer grown on the Mg sheet. The AFM requires very smooth surface for analysis, however, the Mg disk used in the device is sanded with sandpaper and consequently the surface is very rough. Therefore, special sample preparation is done for this measurement. The Mg disk is sanded with various sandpapers (from high to low grain size) in different directions to obtain a smooth surface. After that, half of the disk is taped with scotch tape to prevent oxidation, and the other half is left for the reaction to obtain oxide layer. The disk is placed inside the sensor enclosure and the device is used for one time. The Mg disk is then taken out for the AFM analysis and the scotch tape is removed before the measurement. The roughness measurement is done on oxide layer as well as the bare Mg surface (under scotch tape) and the 3D pictures are obtained. Other than that, the thickness measurement is also performed to measure the oxide layer thickness (**discussed in chapter 5**). The **Figure 13(a)** shows the AFM machine used for the measurement.

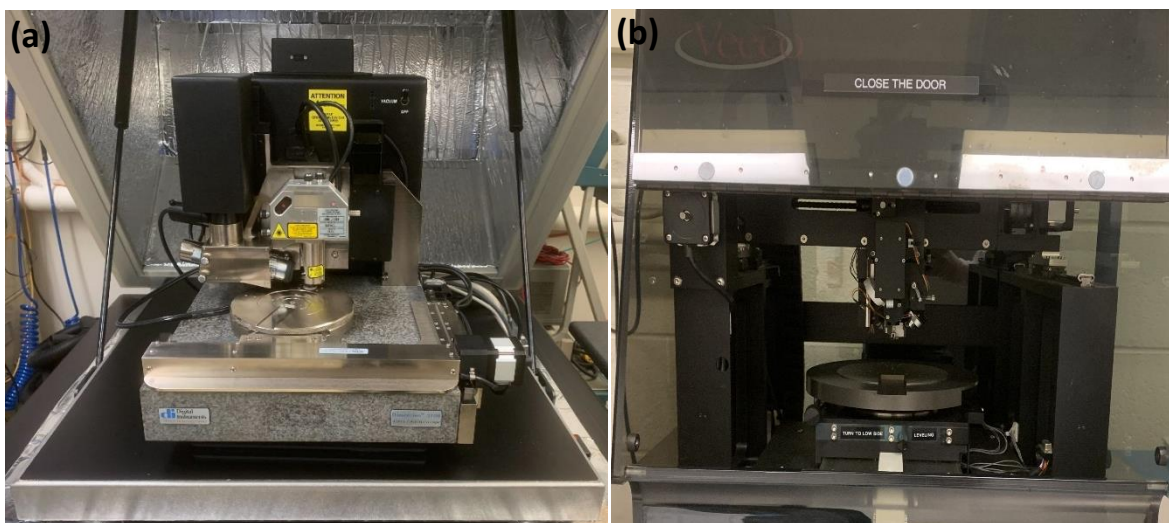


Figure 13: (a) AFM; (b) Profilometer Instrument (pictures taken during the measurement).

Since, the AFM has a limit in measuring height ($6\ \mu\text{m}$), it cannot measure the samples that has been used for more than ~ 2 times (because of thicker oxide layer due to long reaction time). Therefore, another method that can measure larger thickness is used and is called “Profilometer” (**Figure 13(b)**). Similar to AFM, this also requires smooth surfaces, but it has some tolerance for measuring the rough samples. Therefore, this is the best method to analyze the oxidized Mg disks (since oxide layer is non-uniform). The same method as AFM, is used for sample preparation and 8 samples are prepared and

placed inside the sensor units. All the samples are used for a different number of times to see the variations in oxide thickness with increase in number of uses of the device.

3.3 Summary

This chapter describes different instruments used for electrical measurement and their test setup procedures. It shows the electrical connection from the sensor device to various instruments, and also explains the connections through the breadboard for measuring voltage from several electrical components in the water leak detection system. Other than that, in the second half of the chapter, it explains the characterization tools used for analyzing various surface properties, and it also describes the sample preparation required before the measurement with each instrument.

Chapter 4: Electrical Performance and Repeatability of the Sensor Device

This chapter discusses the electrical characteristics of the sensor by describing the energy it can produce under various circumstances such as with and without varying loads applied across the sensor. The sensor is used for sensing water (its actual purpose) as well as an energy source to replace the battery requirement to power up the Bluetooth chipset. Therefore, this also explains the sensor's behavior when connected/loaded with Bluetooth beacon (Nordic) in electronics packaging (shown in chapter 3). The repeatability of the sensor with electronics to send Bluetooth packets and the beacon activation time are also evaluated.

4.1 Electrical Performance of the Sensor

The performance of the sensor is analyzed with different electrical characteristics such as OCV, SCC, charge capacity and internal resistance of the sensor. The OCV and SCC are conducted when no load is applied across the sensor, only the DMM is connected to measure DC voltage and DC current respectively. "Load Test" is performed to measure the charge capacity of the sensor. The measurements are conducted using various test setups (detailed in chapter 3) and all the tests are carried out with sensors packaged inside the plastic housings. The data is plotted with Origin 2021 software and Excel.

4.1.1 OCV and SCC

The sensor's performance is assessed by measuring OCV of seven sensors and the data is recorded until the sensors achieved their maximum voltage. The sensors are placed inside petri dish containing water and as soon as water contacts Mg sheet, the voltage starts increasing gradually. All sensors take separate times to reach to their maximum OCV since the water entrance time can vary from sensor to sensor. The average maximum OCV obtained from the sensors is 2.04 ± 0.04 V. **Figure 14(a)** shows the voltage trend from the sensors and average time (~17 seconds) to reach to the maximum value of OCV.

The SCC of the sensor is also measured for around five sensors with different testing setup than OCV (presented in chapter 3). The sensor's SCC increases to maximum value in about 5-7 seconds when placed inside water. The average maximum SCC recorded is 12.5 ± 1 mA and this value decreases rapidly to half of the maximum (~6 mA) just after about one minute. Following this sudden drop, a slow decline in the SCC is identified for four minutes **Figure 14(b)**.

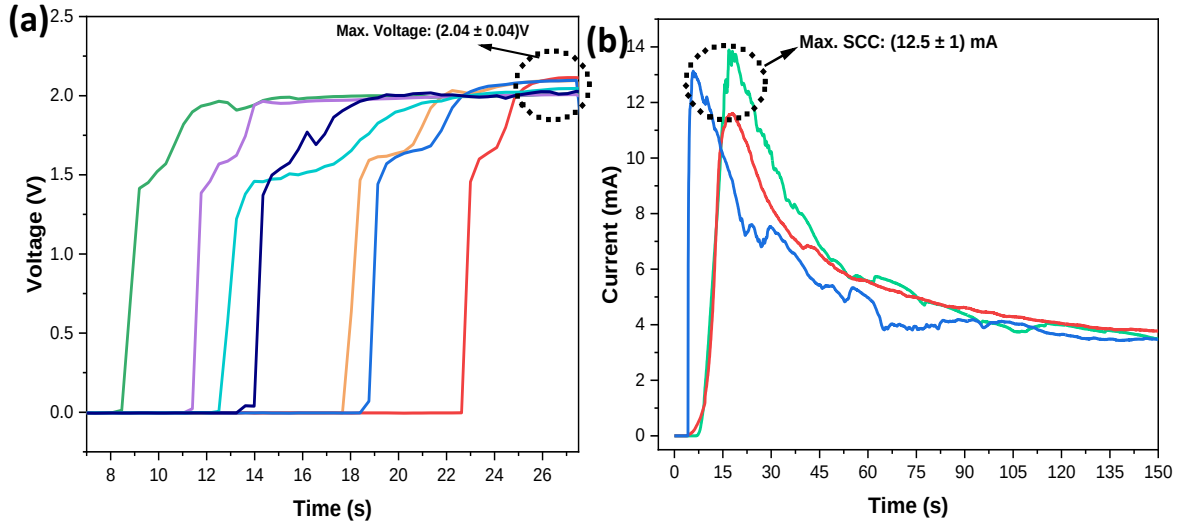


Figure 14: (a) Open circuit voltage; (b) Short circuit current of sensor units.

4.1.2 Load Test

This test is conducted to measure the amount of charge capacity the sensor can have, when different loads are applied across it. During this test, a source meter which acts as a load, is used to apply different load currents. The five fresh sensors that has never been used are prepared for this test and are loaded with various load values. The load values of 50 μ A, 100 μ A, 1mA, 5mA and 10mA are selected according to the sensor's capability of producing power. The source meter as the name suggests is a source of power and is mostly used to supply voltage/current, however in this experiment, it is set to draw current. Therefore, while setting the specifications for source and limit on the source meter, the current is set as source with different values (from 50 μ A to 10mA) with the negative sign (positive sign refers to supply of current instead of drawing current), and the voltage is set as limit (3.0V). The DMM is fixed to measure DC voltage from the sensor under application of specific load.

During the test, the DMM and source meter are connected with the sensor unit in parallel and then the sensor is placed inside petri dish containing water. The measurement with the DMM starts when the sensor is placed inside water while the load from source meter is turned ON once the sensor reaches its maximum voltage around 2.0 V. The **Figure 15** shows the voltage trend from the sensor when various loads are applied across it. The data is recorded for each load until the sensor's voltage drops to 500mV. As expected, for the higher load values, sensor's voltage drops faster as compared to the lower load

currents. Therefore, the voltage from the sensor under 10mA load dropped to less than 0.5 V in just few seconds, however, the sample under 50 μ A sustained for almost 7 hours.

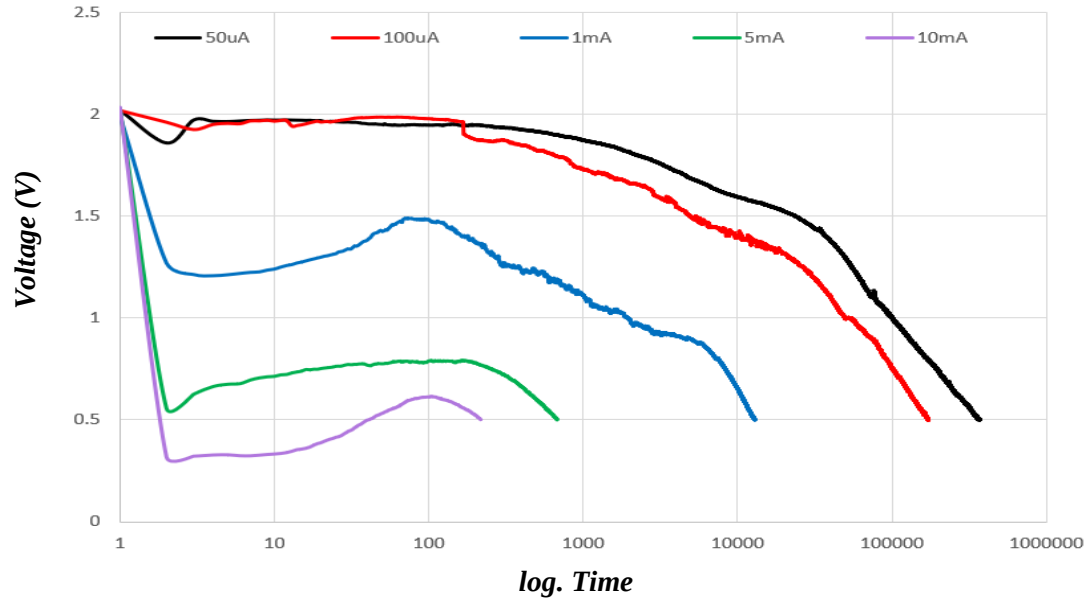


Figure 15: Voltage vs Time graph at different load values.

The measurement/graph (**Figure 15**) is divided in three stages (**Figure 16**) and are named as stage 1, 2 and 3. The sensor's voltage drops rapidly when the load is applied and is named as "Stage 1". This decrease is different for different load currents and is most significant for higher load values (10mA) and least for lower load values (100 μ A, 50 μ A). During the "Stage 2", the voltage from the sensor starts rising again to a particular value less than the maximum voltage of the sensor. This increase in the voltage is more prominent in smaller load values than larger load currents as expected from stage 1. Furthermore, in "Stage 3", the voltage from the sensor starts decreasing gradually and is recorded till 500mV. The sensors under different applied loads take different time to reach to 500mV. For example, the sensor under 50 μ A load, took around 7 hours (417 min.), under 1mA load takes 14.5 min. and the one with 10mA load dropped to 500mV in just 0.24 min.

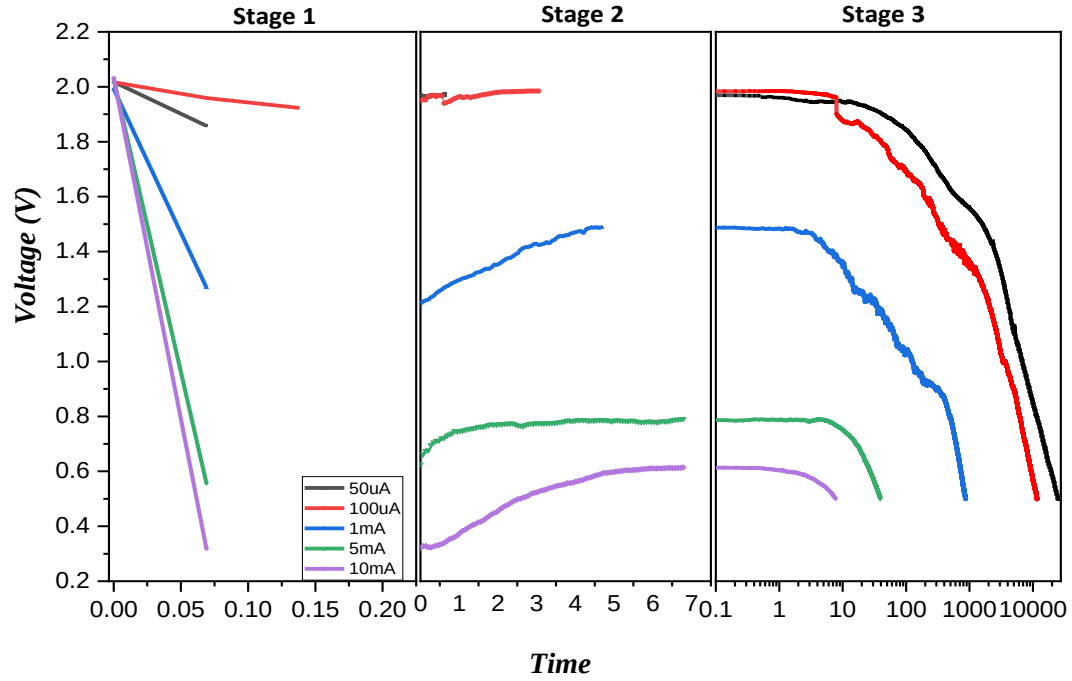


Figure 16: Three stages of the voltage curve when different loads are applied.

The **Table 4** shows the voltage values in all three stages under different loads. This explains the voltage trend in stage 1 and 2, which decreases with increase in load value in stage 1. The voltage starts increasing in stage 2 and the rise is lower for the larger load values. This also summaries the sensor's life under specific load condition. It further describes that the sensor cannot withstand high load values and therefore almost dies under 10mA in just few seconds and can stay longer at lower loads.

Table 4: Voltage values during three stages and sensor's life under applied loads.

	Load Applied	Voltage (V) after Abrupt Decline (Stage 1)	Max. Rise in voltage (V) (Stage 2)	Minimum voltage (V) from Sensor (Stage 3)	Sensor's Life (Min.)
Sample 1	50uA	1.85	1.97	0.50	417.19
Sample 2	100uA	1.95	1.98	0.50	194.4
Sample 3	1mA	1.26	1.48	0.50	14.5
Sample 4	5mA	0.55	0.79	0.50	0.77
Sample 5	10mA	0.31	0.61	0.50	0.24

4.1.2.1 Charge Capacity

The charge capacity is the measure of sensor's capacity to generate electricity due to chemical reaction that occurs when sensor reacts with water. It is calculated from the data obtained from the load test under different load currents. The charge capacity is given by the following formula:

$$\text{Charge Capacity} = \text{Area} * \text{Load}$$

Area under v-t graph can be approximated using the average voltages during particular time period under specific load current and is expressed as:

$$\text{Area} = \text{Total Time} * \text{Average Voltage}$$

The calculated charge capacity with respective loads is presented in **Table 5**. The trend for amount of charge capacity with respect to load applied is shown in **Figure 17**. It is clearly observed that the charge capacity decreases with increase in load value. So, for the load value of 50uA, the maximum charge capacity i.e. 301.2μWh is obtained whereas for 1000μA (10mA) load, 22.3μWh charge capacity is indicated.

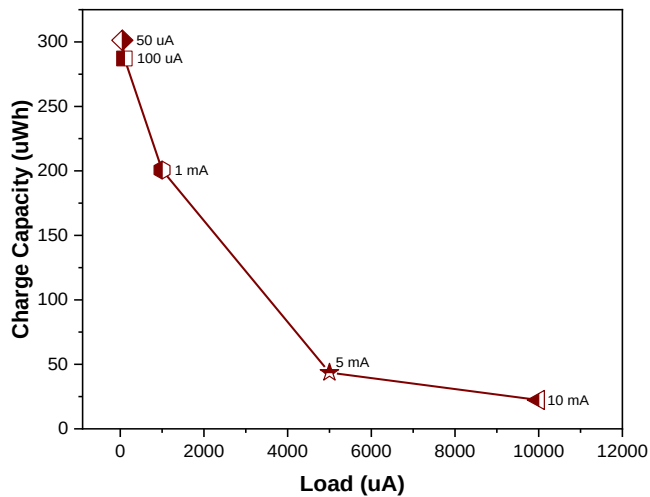


Figure 17: Plot showing the Charge capacity vs Load values.

Table 5: Charge capacity under various loads.

Load (μA)	Charge capacity (μWh)
50	301.2
100	287
1000	200.7
5000	43.6
10000	22.3

4.1.3 Internal Resistance

Internal resistance of the battery (sensor) is the measure of opposition to the current flow inside the battery. It can be affected by two main components inside the device, ionic resistance and electronic resistance. Total effective resistance of the sensor is the collective sum of these two components. The ionic resistance is basically due to several electrochemical factors such as electrolyte, ion mobility and surface area of the electrode, however, electrical resistance is caused by actual materials for example metals/electrodes, metal contacts, wires etc [47].

During the test, the sensor is charged to maximum voltage when placed inside water. After that, the source meter is set to draw a continuous current of 2uA (idle current) till the end of the test. Since the load value is extremely small, the drop in the voltage is negligible. At the same time, another parameter is also set on the source meter to draw high current pulses (1mA) for 20ms during the test. Significant drops are seen during these pulses because the sensor cannot sustain at this high load value. The voltage vs time graph under small continuous load and high pulse load is shown in **Figure 18**. Inset of the **Figure 18** shows the sensor's behavior during high load pulse for 20ms.

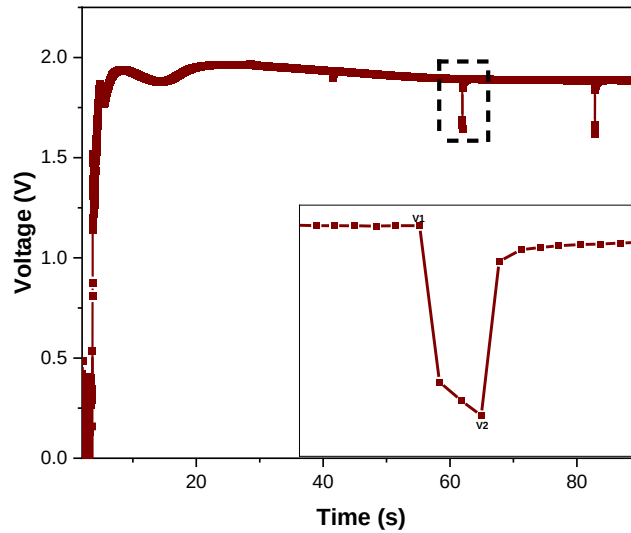


Figure 18: Voltage vs Time graph for sensor under idle and high (inset) loads.

The formula used to calculate the IR is as follows:

$$R_{IR} = \frac{V_1 - V_2}{R_2 - R_1}$$

Where V_1 is the voltage of the sensor under an idle load (2 μ A) and V_2 is voltage under larger load (1mA). R_1 and R_2 are the loads applied i.e. 2 μ A and 1mA respectively. The same test is performed on five sensors and the average internal resistance (IR) is found to be approximately 0.29 ± 0.0035 k Ω .

4.2 Sensor's Integration with Electronics

As described in chapter 2, the electronics packaging has two PCBs, energy harvesting board (EHB) and Nordic beacon board (Bluetooth board). The main purpose is to send the Bluetooth packets when sensor contacts water which are received by the cloud to alert the user about the leak. Therefore, a Bluetooth low energy device (Nordic) is needed which requires low energy to perform its function.

4.2.1 Power Requirements for Nordic Beacon

A Nordic chipset nRF-53832 requires 1.7V - 3.6V input voltage to operate. Moreover, it consumes about 2.4 μ A current during sleep mode and uses high current of ~10mA when advertising. The average current consumption depends on the transmission interval that can be set during programming the chip. In this case, it is set to send Bluetooth packets every 1s and therefore the average current consumption is found around ~20 μ A. **Figure 19** shows the high current consumption (10mA) after every second and low current consumption (few μ A) during sleep mode. The expanded view of the **Figure 19** shows the current consumption during the transmission period (4ms) due to radio transmission and various pre and post processing stages [48].

To accommodate the power requirements of the nRF-53832 chipset, a sufficient power supply is required. As explained in the previous sections, the sensor's maximum OCV is around 2.0V and the voltage under load is less than that value. Furthermore, the results explain that the sensor cannot sustain during high current consumption modes if directly connected with Bluetooth board. This means the sensor alone cannot meet the power requirements of the nRF-53832 chipset. Consequently, an additional unit is needed that can boost up the sensor's power to the required amount and is called the EHB.

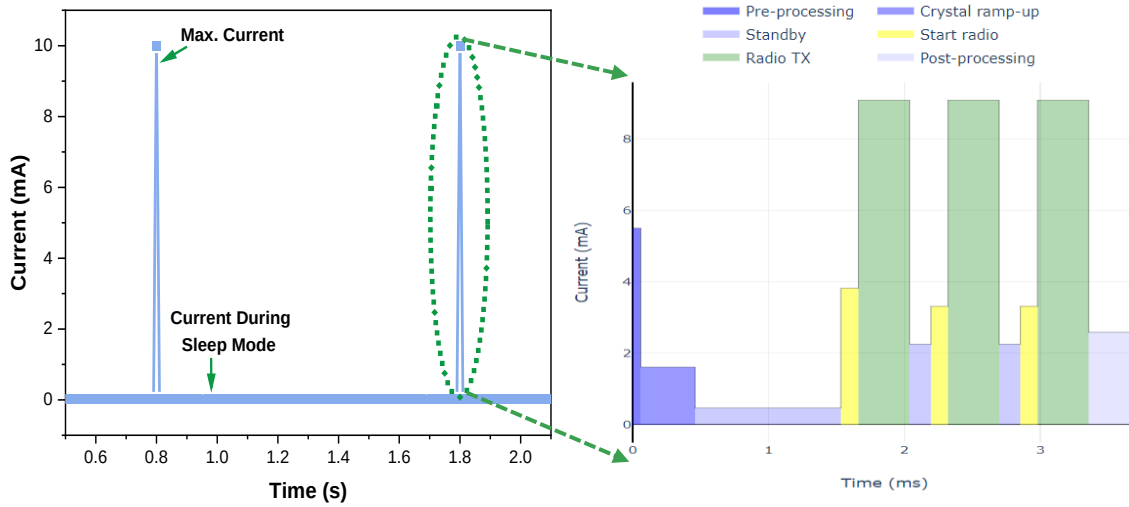


Figure 19: Current consumption by the Nordic chipset (nRF-53832) [48].

4.2.2 Function of EHB

The layout presented in **Figure 20(a)**, is the EHB with different components. The EHB is included to meet the power specifications of the Bluetooth device to send an alert to the user after the sensor's activation. The detail about the major components (highlighted) i.e. boost converter, bulk capacitor, and LDO is discussed in this section.

4.2.2.1 Boost Converter

The boost converter is a DC-to-DC converter that is used to step-up an input voltage to some high value on the output. In this case, the sensor unit's output acts as an input for the boost converter and it boosts up the voltage of the sensor from 2.0V to ~3.5V to meet the input voltage requirements of the nRF-53832. This rise in the voltage benefits the device to send Bluetooth signals safely even in the case sensor produces less than 2.0V due to some malfunctioning issues.

4.2.2.2 Bulk Capacitor

The bulk capacitor stores the output voltage coming from the boost converter. It is required to provide the continuous supply of average voltage to the BLE module to ensure the proper functioning of the device. A capacitor of 420 μ F is used which can easily store voltage of more than 3.5V.

4.2.2.3 Low Drop Out (LDO)

Nordic chipset requires a stable power supply for proper performance. Therefore, another component called LDO is recommended that provides a constant output voltage even though the input voltage is unstable. The voltage stored in the bulk capacitor acts as the input voltage for the LDO which gives the

regulated (constant) voltage on its output. This chipset (LDO) has a specific enabling threshold around 0.8V at which it starts performing its function. Therefore, the LDO does not apply load on the sensor until the voltage on the bulk capacitor reaches to 0.8V thus gives time for the sensor to charge. The minimum input voltage requirement for the nRF-53832 chipset is 1.7V, therefore, the LDO is set to provide a constant output voltage supply of 1.8V.

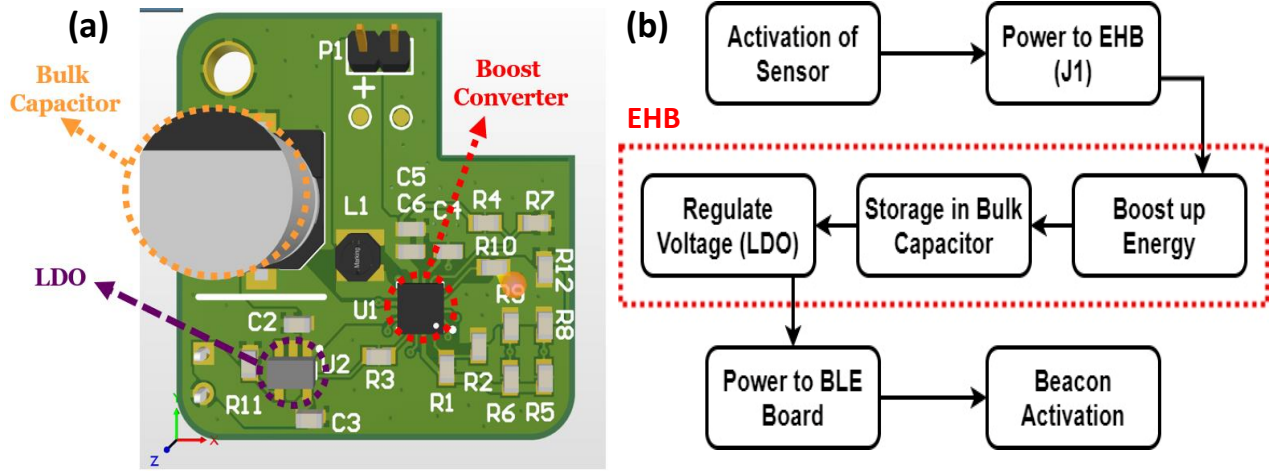


Figure 20: (a) Layout of the EHB; (b) Flowchart shows the flow of power in the circuit

The **Figure 20(b)** explains the power flow through different components inside the device. First of all, the sensor is activated when it comes in contact with water and starts producing power. The voltage from the sensor goes to the boost converter that boosts up the voltage to ~3.5V. Then from here, the voltage is stored inside the bulk capacitor that acts like an input voltage source for the LDO. The regulated voltage (1.8V) from the LDO's output is then transferred to the BLE (beacon) board which sends the Bluetooth signal.

The voltage at different components is measured with 4 channel oscilloscope (setup is shown in chapter 3) to identify the voltage flow throughout the circuit. The **Figure 21(a)** shows the voltage trend from the sensor, bulk capacitor and output of EHB when the sensor packaging is connected with the electronics packaging (EHB + BLE board). It shows that when sensor starts charging, the capacitor also begins charging at the same time. The maximum voltage observed on the sensor is around ~1.8V while capacitor ranges maximum to ~3.5V. As soon as the voltage on the capacitor reaches ~2.0V, the output voltage from the EHB jumps to 1.8V. The voltage stays constant even though the voltage from the

sensor or capacitor is varying and at this voltage, the beacon pops up on the “nRF Connect” app **Figure 21(b).**

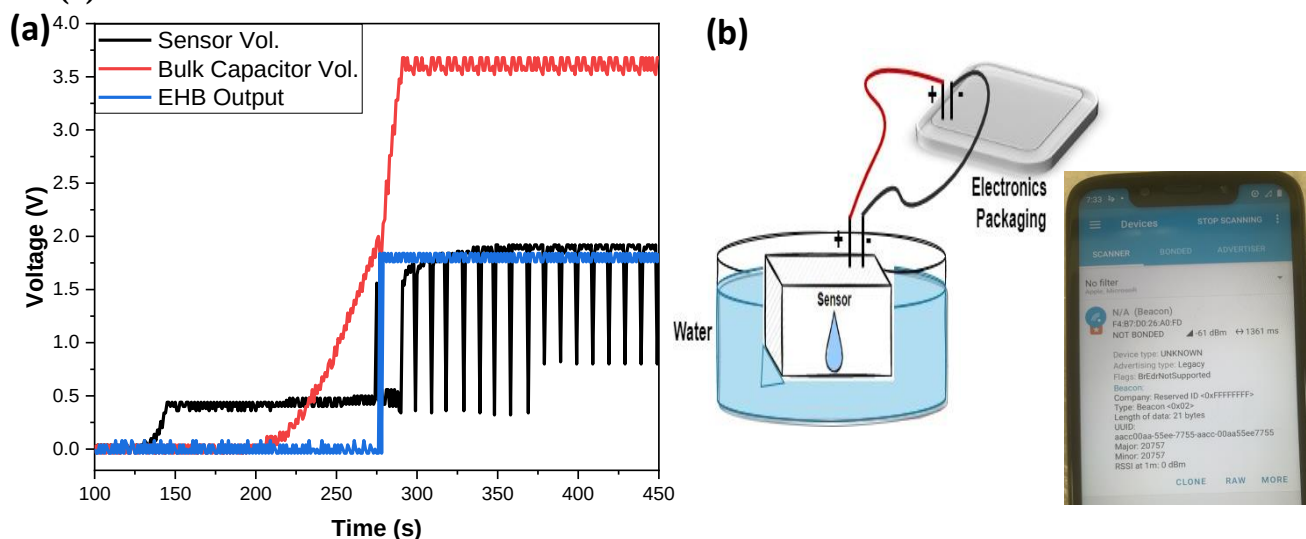


Figure 21: (a) Graph showing the voltages from different components on the EHB at the same time; (b) Beacon activation when sensor contacts water.

4.3 Sensors in Series

One sensor produces power that is enough only for a low energy BLE device to work. However, if more than one sensor is connected in series, the voltage from the sensor can be increased significantly and therefore can be used to power other devices. The **Figure 22** shows the three sensors connected in series and are then connected with the LED strip (originally requires three AA batteries or 4.5V in total), which lights up upon sensor activation.



Figure 22: Three Sensors connected in series with LED.

To make the series connection between sensors, the negative terminal of sensor 1 is connected with the positive terminal of sensor 2 and similarly, the negative pin of sensor 2 is connected with the positive pin of sensor 3. Then the positive and negative terminals of sensor 1 and sensor 3 respectively are left for connection with the device for example LED strip. Other than lighting the LED strip, the voltage from different combinations of sensors in series is also measured with DMM. **Figure 23** shows the OCV from one sensor, two sensors connected in series, and three sensors connected in series. It can clearly be observed from the graph that the voltage from the sensors is doubled ($\sim 4.0\text{V}$) when two sensors are connected and increased by three times ($\sim 6.0\text{V}$) when three sensors are connected in series.

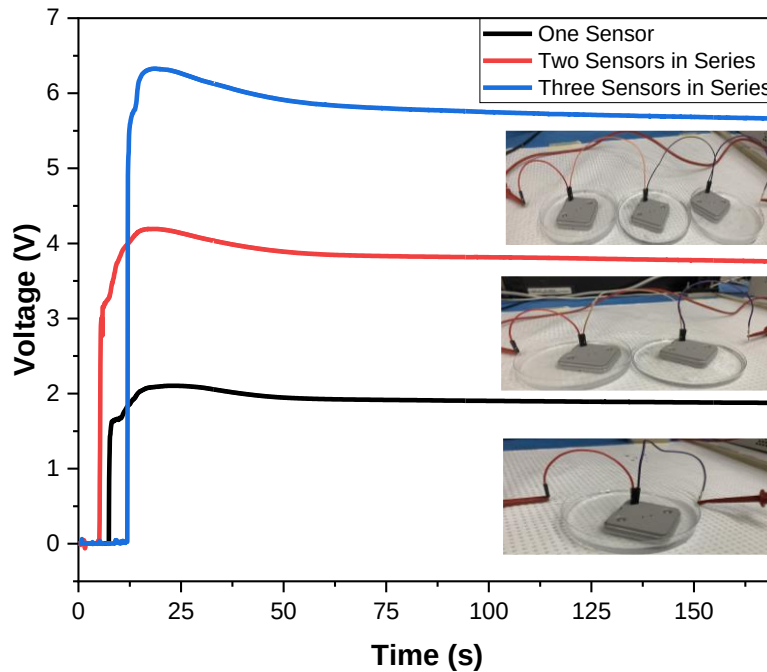


Figure 23: OCV of one sensor, two sensors connected in series and three sensors connected in series.

4.4 Repeatability of Sensor

Repeatability or reusability is a characteristic property of the sensor which gives the measure of the number of times the sensor can be used for leak detection. This section explains the changes which occur on the sensor's performance when used repeatedly. Basically, two different experiments are conducted to know the various properties of the sensor i.e. "Short Time in Water Test" and "Long Time in Water Test". In the first test, the sensor is placed inside water for a short time (~ 10 minutes) at every use. However, for the second test, the sensor remains in water for 3-4 days on each usage. Two different electrical evaluations are done to assess the sensor's performance i.e. beacon activation, and power test.

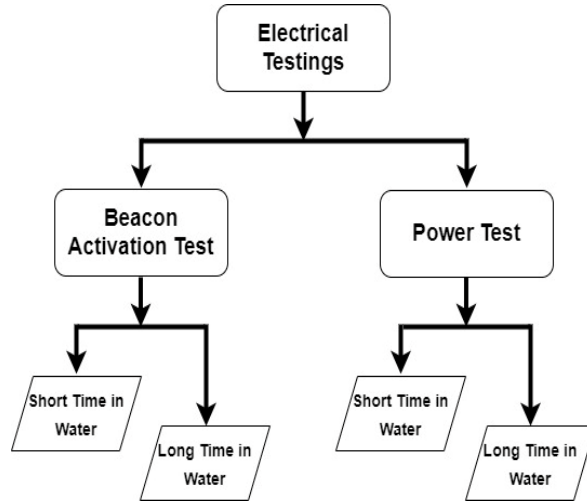


Figure 24: Flow chart showing the different tests performed.

4.4.1 Beacon Activation Test

All the prepared samples are tested for beacon activation at every use. During this test, the device (sensor package connected with electronics package) is placed inside water and the Bluetooth scanner is scanned continuously to check the beacon activation. Once the device starts sending data, the beacon with a specific UUID (universally unique identifiers) number, pops up on the screen of the phone (red started) which confirms the activation of the beacon as shown in the **Figure 21(b)**. This activity is observed for at least one minute after the beacon is activated, and the initial beacon activation time for all sensors is also noted at every trial. The test is performed for both type of sensors i.e. short and long time in water tests.

4.4.1.1 Short Time in Water

It is observed that in this case, the sensors can activate the beacon on average for 12 times when tested repeatedly with controlled conditions. The beacon activation time vary with different test (use) numbers. It can be seen from the **Table 6** that the average time for fresh samples (test 1 & 2) is ~30 seconds and then it starts rising as the number of the tests (uses) increases. The tests 3 & 4 shows a slightly high activation time around ~45 seconds. Similarly, tests from 5 - 8 & 9 -10 take approximately 55 & 62 seconds respectively. On the other hand, higher beacon activation time is observed in case of the last tests (test 11 & 12) around ~70 seconds. There can be various reasons behind this behavior of

the sensors such as oxidation of the Mg surface, manufacturing defects etc. that are discussed further in chapter 5.

4.4.1.2 Long Time in Water

In this case, sensor's performance is not very effective as compared to the previous test. The sensors are able to activate the beacon only for 8 times and they stop working after that. But the performance for these 8 uses is almost as good as the previous test since the beacon stays active for at least one minute after activation in all the cases. The average time for activating the beacon is same for fresh samples i.e. 30 seconds (**Table 6**) and is rising as the number for the tests increasing. It is higher for tests 5 - 8 (61s) as compared to the test in case of the short time in water experiment.

The beacon activation time can vary with different factors such as drying time of the sensors after every use, the time when the load (electronics) is connected to the sensor (before or after sensor activation), and the total time period of the load application. In this experiment, the sensors were dried for varying times (1-3 weeks) at every use and the electronics units were connected after measuring the power from the sensor units. The load from the electronic units was only applied across the sensor during the test (5 minutes) and was removed throughout drying period. Therefore, the beacon activation time can be different if the conditions will be changed.

Table 6: Beacon activation time for Short time and Long time in water tests.

	Short Time in Water			Long Time in Water		
	Beacon Activation	Avg. Activation Time (s)	Stayed Activated	Beacon Activation	Avg. Activation Time (s)	Stayed activated
Test 1 & 2	✓	30	Yes	✓	30	Yes
Test 3 & 4	✓	45	Yes	✓	45	Yes
Test 5 - 8	✓	55	Yes	✓	61	Yes
Test 9 - 10	✓	62	Yes	×	—	—
Test 11 & 12	✓	70	Yes	×	—	—

This difference in the behavior of the sensors, for both the tests can also be seen from **Figure 25**. It clearly depicts that as the number of tests increases, beacon activation time also rises. And it is seen that beacon activation time for sensors that are sitting longer time in water, is higher in almost all the uses (1-8 uses). Moreover, the sensors in this case stop working earlier than the short time in the water test. This shows that length of stay in water affects the number of repeatability, as well as beacon activation time. All the observations from this test confirmed that the sensor's performance is degrading not only with the increase in number of uses but also with increased stay in water.

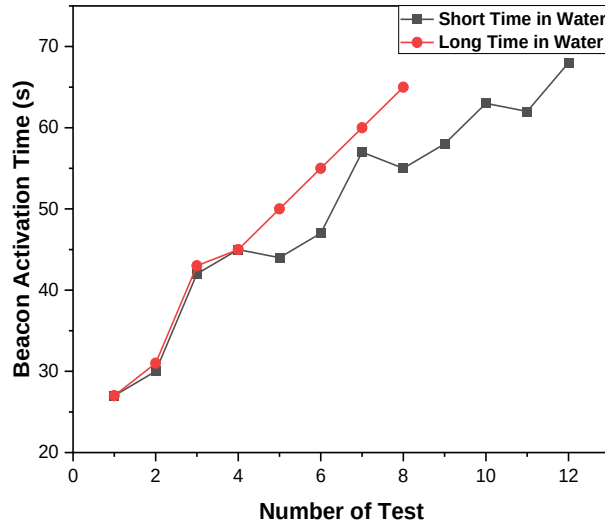


Figure 25: Beacon activation time vs number of tests for Short time and Long time in water tests.

4.4.2 Power Test

Some other electrical specifications such as changes in voltage curve, power values and average voltage are examined in this test.

4.4.2.1 Changes in the Voltage Curve

The test setup for this test is same as load test performed for $50\mu\text{A}$ load current (shown in chapter 3). The same load value is used throughout the experiment for the repeated use of the sensor. This load of $50\mu\text{A}$ is chosen since it is close to the value of average current consumption for the Nordic beacon. The first test/use for the fresh sensors shows the same behavior of the voltage curve as described in Section 4.1.2 with three different stages.

Short Time in Water Test: As shown in the **Figure 26(a)**, with an increase in number of the tests, the drop in the voltage in “Stage 1” also increases. Moreover, the stabilizing voltage in “Stage 3” is also lower in almost every test than its previous test. Only tests 7&8 showed a varying behavior for “Stage 1”, but the stabilization is similar or lower than the previous tests (1-6 tests). Overall, it is seen that the voltage for all three stages is decreasing with an increase in the number of tests.

Long Time in Water Test: During this experiment, some fluctuations in the results are seen **Figure 26(b)**. Not all the tests show decreasing trend in the voltage with increase in the number of the test. However, the overall trend for test numbers 1 and 8 is decreasing. The first use/test shows highest voltage in all three stages, and test 8 shows lowest voltage in all the stages. The other tests from 2-7 show variations but their voltage lie in between test 1 & 8. These differences in the results in this experiment can be due to the longer sitting time in water or some other manufacturing defects while fabrication.

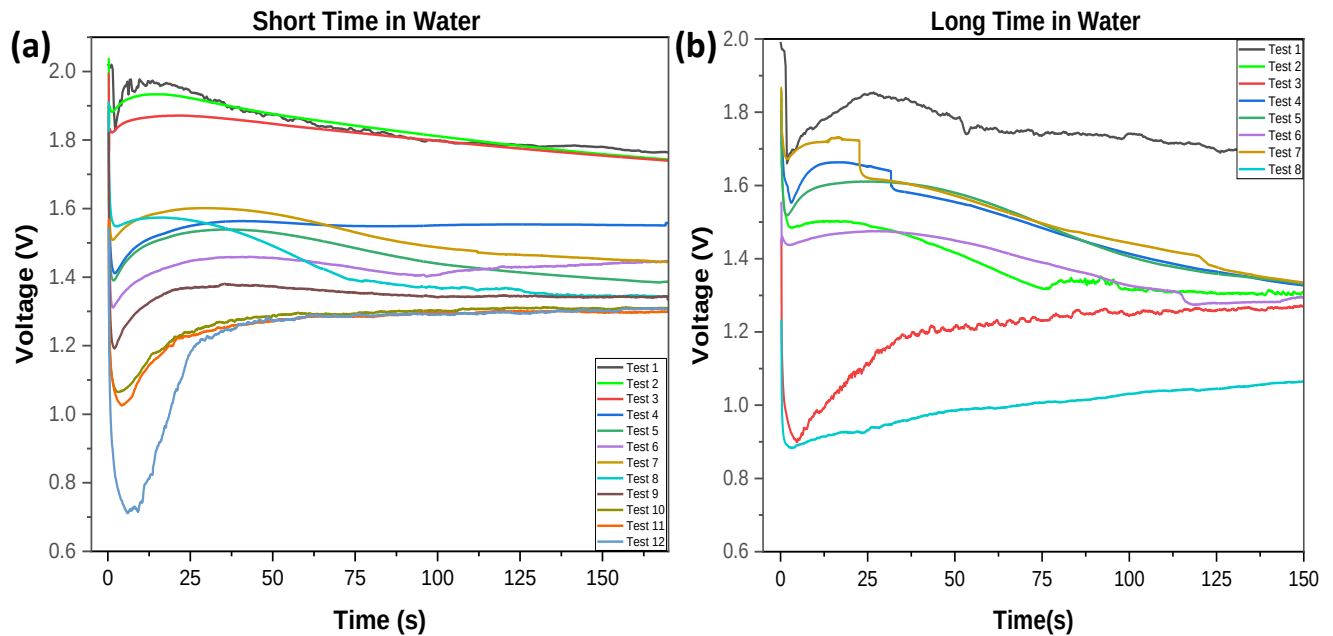


Figure 26: Voltage curve trend with increase in number of tests/uses in (a) Short time in water test; (b) Long time in water tests

Since the voltage in all the stages is decreasing with increase in number of tests, the average voltage for particular time frame is also decreasing. This further affects the overall power production (explained

in detail in section 4.4.2.2) from the sensor unit which results in increase in beacon activation time with increase in number of tests/uses (**Figure 25**).

4.4.2.2 Power and Average Voltage

Since the current applied as load in the power test is constant i.e. 50uA and voltage is also known (from measurement), the power can be calculated by formula given as:

$$Power = Average\ Voltage \times Current$$

To calculate the power for each test, the average voltage is calculated. This average voltage is multiplied with a constant current value (50uA) which then gives the power value (**Table 7**). The **Figure 27** shows the changes in power values from the fresh sensors to the used sensors in both experiments. Although, there were some variations, the general trend shows a decline in the power value as the number of tests are increasing.

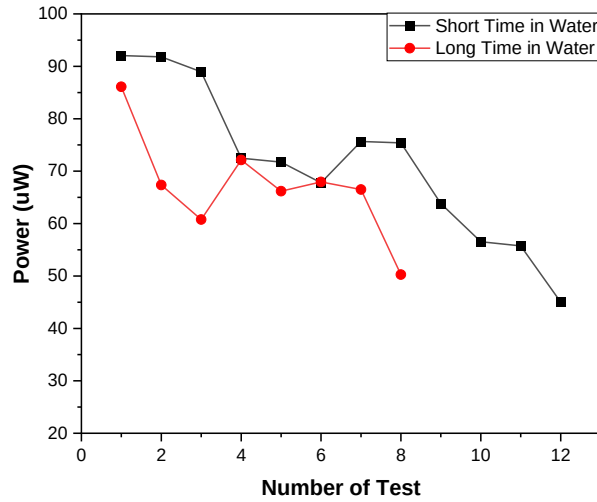


Figure 27: Power vs number of tests

Table 7: Average voltage and power for different tests.

	Short Time in Water		Long Time in Water	
	Average Voltage (V)	Avg. Power (μW)	Average (V)	Avg. Power (μW)
Test 1	1.84	92.05	1.82	91.40
Test 2	1.83	91.81	1.34	67.35
Test 3	1.77	88.94	1.21	60.78
Test 4	1.44	72.46	1.44	72.12
Test 5	1.43	71.73	1.32	66.17
Test 6	1.35	67.79	1.35	67.95
Test 7	1.51	75.65	1.32	66.49
Test 8	1.50	75.40	1.00	50.25
Test 9	1.27	63.82	-	-
Test 10	1.13	56.54	-	-
Test 11	1.11	55.74	-	-
Test 12	0.90	45.00	-	-

The exact values for average voltage and average power are mentioned in the **Table 7**. The maximum average voltage and power for the first test are around 1.8V and 91uW respectively for both cases. It starts decreasing for the next tests and this decrease is more rapid in a long time in water test as compared to the short time in water test. It can be seen from the last test (test 8) for a long time in water experiment, which shows very low power value i.e. 50.25uW, however, the same test number (test 8) in a short time in water exhibited a much higher value of power ~75.40uW. Therefore, this confirms

that the sensor's performance is not only degrading with increase in number of uses of the sensor but also with increase in time for sensor sitting inside water.

4.4.3 Visual Observation

After completing the repeatability series test, the sensor units are visually tested to see the changes on the outer housing of the units. It is observed that the sensor units that are sitting in water for short time looks normal like fresh samples (**Figure 28 (a)**). However, sensor units in long time in water experiment show corrosion on the screws (**Figure 28 (b)**). This indicates that long time in water accelerates the corrosion and there are chances of corrosion inside the package as well. This can be the reason of sensor's failure after 8-time uses only (however the use of sensors till 12 times is successful in short time in water test). Therefore, the next step is to open up all the packages that have been used in both tests for a different number of times and do a visual inspection to see any changes. This test is required to find out the failure of the sensor units after several uses.

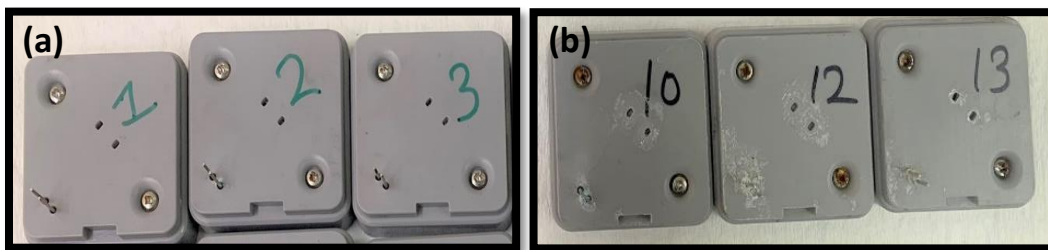


Figure 28: Pictures taken after the test is completed for (a) Short time in water test; (b) Long time in water test.

The **Figure 29 (A0 - A12)** shows the pictures of the interface of Mg disks facing towards graphite pallets used inside the sensor housing from 0-12 times (referred as A1-A12) in short time in water test. Sample named A0 is the control sample (sanded Mg disk) that is never used for the test. It is clearly seen from the images that the Mg sheet is getting corroded/oxidized as expected from the reaction and this corrosion is increasing as the number of repeatability increases. The **Figure 30 (T1)** shows the top surface of Mg disk that touches the spring metal contact to make an electrical connection inside the package. It is not corroded much since it is not in direct contact with water during the reaction. To confirm the reason for the failure, some other parameters need to be characterized. For example, amount of oxidation, porosity of the oxidation layer grown, different elements or compounds present, thickness of the oxide layer etc. These parameters are analyzed with different characterization tools and are discussed in detail in the next chapter.

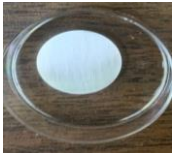
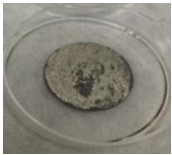
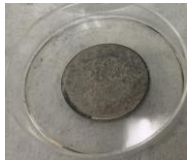
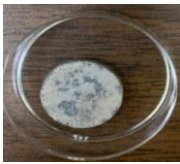
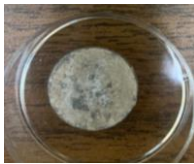
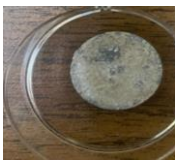
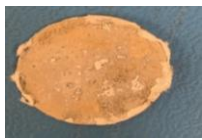
Short Time in Water Test (Interface of Mg Disks from A0-A12)				
A0	A1	A2	A3	A4
				
A5	A6	A7	A8	A9
				
A10	A11	A12	T1 - Top Surface of Mg Disk	
				

Figure 29: Pictures of Mg disks taken from the sensors used from 1-12 time in Short time in water test.

The **Figure 30(a)** shows the pictures of the samples taken from long time in water test that has been used for 8 times (named as B8). The interface of the Mg disk is highly oxidized, and some white patches are also observed on the surface. On the other hand, in this case, not just the interface but also the top surface of Mg disk is also extremely oxidized (**Figure 30(b)**). This can cause very high resistance for the current flow and can result in failure of the sensor unit. These white patches and powder are also examined with various characterization tools that give detailed information about the surface and are discussed in the next chapter.

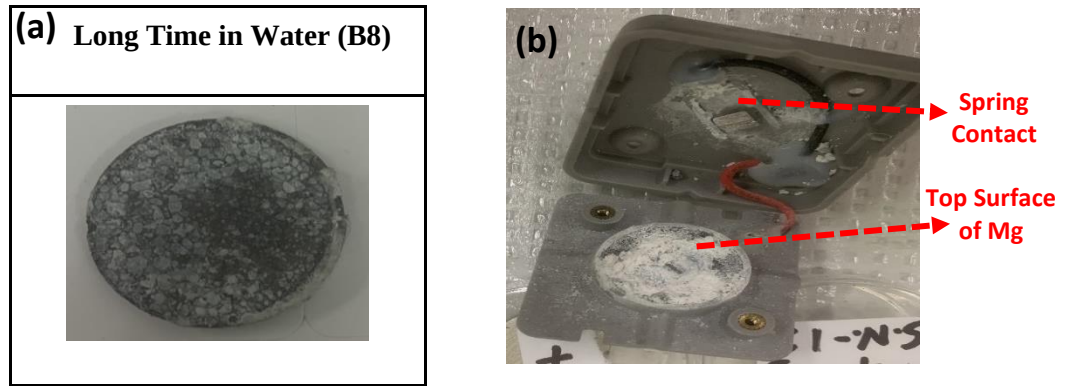


Figure 30: Pictures of Mg disk's (B8) (a) Interface and (b) Top surface for the long time in water test.

4.5 Summary

This chapter explains the electrical specifications of the water sensor that is used for sensing as well as an energy source in the device. This discusses the amount of power produced by the sensor and energy requirements of the Bluetooth chipset. It also discusses the additional components (EHB) that helps the sensor to sustain under applied load from the Bluetooth beacon, and also ensure the reliability and proper functioning of the device for several uses. Furthermore, the repeatability of the sensor is reviewed and is recorded to be minimum of around 8 uses. The degradation of the performance with repeated use is also measured with some electrical measurements. Visual inspection reveals the considerable changes in the sensor's material but more investigation at molecular level on the surface is required that is discussed in next chapter.

Chapter 5: Analysis of the Reasons of Degradation of the Sensor Device

This chapter focuses on the main component of sensor's material which is the center of reaction i.e. "Magnesium (Mg)" electrode. Mg is acting as an anode in the redox reaction when placed inside an electrolyte (water). The chapter discusses about the changes on the surface of Mg disk after undergoing various reactions with water and its impact on sensor's performance. It also explains the critical points where the sensor is at the edge of failure. The chapter will include the characterization of Mg disks (reacted with water under various circumstances) with SEM, EDX, XPS, XRD, FTIR, AFM, and profilometer.

Reaction: As explained in chapter 2, the reaction of Mg with water and air can produce different compounds. The major compounds formed are mainly $\text{Mg}(\text{OH})_2$ (Brucite) and MgO . Since the disks are not pure Mg but AZ-31 alloy of Mg, there are chances that other oxides such as aluminum oxide, zinc oxide, manganese oxide, silicon oxide and other compounds can also be formed on Mg surface. However, the amount of formation of these products will be very less as compared to the Mg compounds since the ratio of Al, Zn, Si, Mn in the alloy is almost negligible (described in section 2.3). Therefore, the major focus is on the Mg compounds formed after reaction with air and water. Additionally, Mg and its compounds will act differently for the chemical reaction and electrical conductivity. The main objective of these characterizations is to identify the reasons behind the changes in the sensor's behavior after the corrosion/oxidation of the Mg metal. It is suspected from the previous tests that the major causes are the changes in surface area for the reaction and the conductivity/resistance of the Mg sheet (will be discussed more in upcoming sections).

5.1 SEM for Surface Analysis

The scanning electron microscopy is performed to investigate the morphology of layers grown on the surface of Mg disks and the differences between the morphological changes under various conditions. The high-resolution SEM images are taken at magnification of $100\mu\text{m}$ for the samples (Mg disks) that has been used inside the "Water Leak Detection Device". The SEM is operated in secondary electron (SE) mode to obtain the clear pictures of the oxide layers. The samples that are characterized, has been used inside the sensor's housing for multiple times and are labelled from A1-A12 (for short time in

water test). A control sample A0 is the sanded pristine Mg alloy (AZ-31) disk that has never been used inside the sensor's packaging and is used as a reference sample. Samples named A1-A12 are the Mg disks from the sensors that has been used repeatedly from 1-12 times respectively. Therefore, to perform the experiment, around 12 sensor units are made. At every use, the sensor is wetted with water for ~5-7 minutes and then dried at normal atmospheric conditions for 7-10 days. Since the graphite remains wet for few days and the Mg disk is in contact with graphite (with a separating layer), therefore the reaction between Mg and water keeps on going until the graphite pellet is dry. After drying period, the sample are wetted again, and this process is repeated for 12 times to obtain the repeatability of sensor for 12 uses. The Mg disks are then taken out of the packages to do the SEM analysis. The pristine Mg disks are electrically conductive however, the oxide growth decreases the conductivity (increases resistivity) of the disks (more in section 5.6). Since the sample used for SEM analysis must be conductive (to inhibit the charging of the sample), a gold coating of 2-5 nm is done on all the samples (**Figure 31**) so that clear pictures can be obtained during measurement.



Figure 31: Gold coated Mg disks used inside sensor unit.

The images shown in **Figure 32**, displays the changes on the surface of Mg disks with repeated use of the sensor unit. The thin lines in pictures A0 and A1 are the grooves/scratches formed during the sanding process. These scratches are not clearly visible in the other samples since the oxide layer covers them during the reaction between Mg and water. As the number of repeatability increases, the time for reaction also increases which results in the formation of thicker oxide layer. A0 and A1 shows almost negligible changes on the surface however, A2 has some small (bright) oxide particles on the surface. These particle's size is becoming bigger and bigger as the number of repeated use (time for reaction) increases. As seen from A3 and A4, some places are covered and some are uncovered with oxide layer, and the grooves are also clearly visible on the uncovered places. After sample number A5, the Mg surface is almost completely covered with oxide layers. The samples A10-A12 looks highly oxidized because of the longer reaction time. The thickness can vary considerably from sample A5-A12, but not any significant differences are visible from the surface of the Mg disks in SEM.

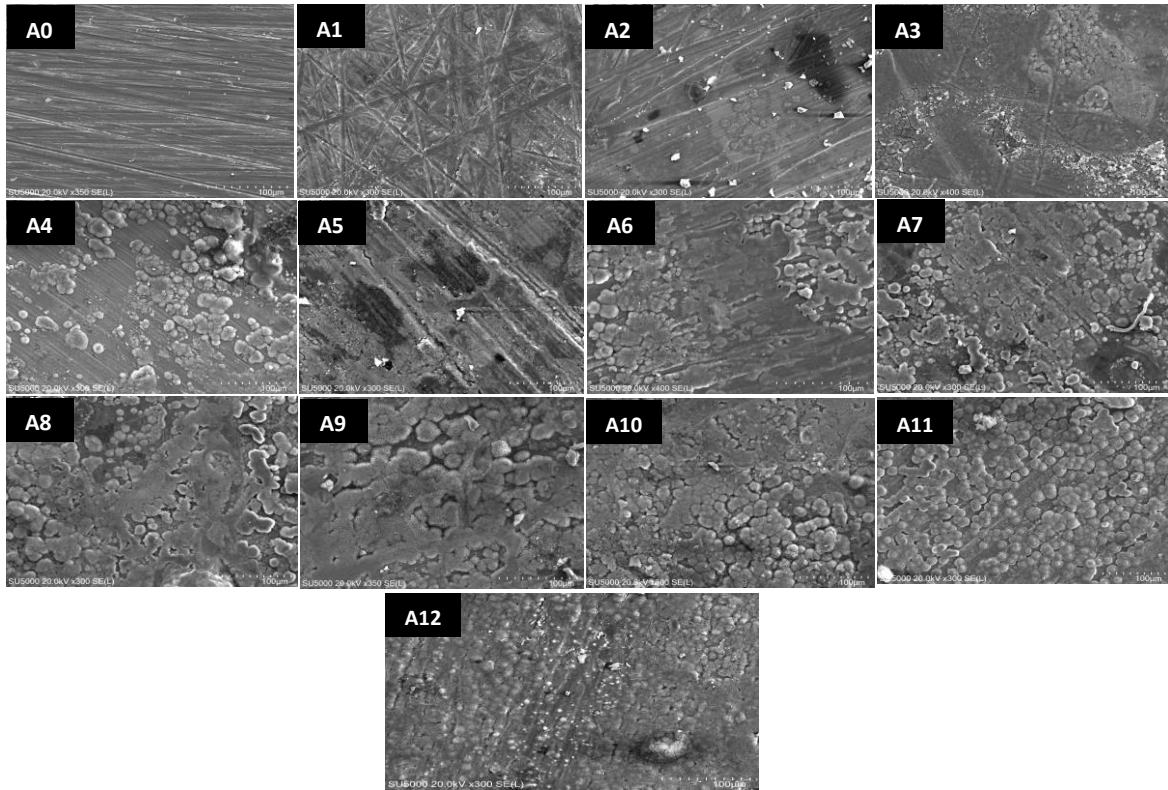


Figure 32: SEM images of Mg disks from sensors used for 0-12 times (A0-A12) in “Short Time in Water Test” at 100um magnification.

The energy is produced due to the chemical reaction between Mg and water therefore, for the reaction to be continuous, the water has to reach the Mg surface. Since the oxide ($\text{MgO}/\text{Mg}(\text{OH})_2$) layer builds up, there are chances that it will block water to reach to the Mg surface. To confirm this, high magnification images are taken to see the porosity of the oxide layer. The **Figure 33** shows the highly oxidized Mg disk (from 12 times used sensor in “Short Time in Water Test”) at different magnifications.

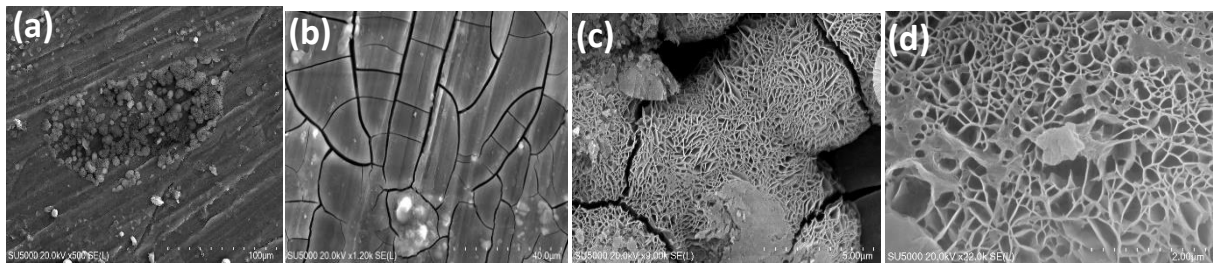


Figure 33: SEM pictures of highly corroded sample (A12) at different magnifications from “Short Time in Water Test”.

Figure 33(b) shows the cracks in surface layer due to flaky nature of oxide film and will allow water to pass through. Moreover, it is clearly observed from **Figure 33(d)** that the oxide layer is porous with average pore size around 2 μm . This means that the water molecules (nm size) can easily pass through the pores and can react with Mg. Therefore, the sensor produces some electricity even if the whole surface is almost covered with the oxide layer (A12). Moreover, the Mg surface available for reaction in case of A1 and A12 is significantly different which results in differences in the amount of power production in both cases (**Figure 32**).

The SEM analysis is also done on a sample with accelerated corrosion from long time in water experiment (labelled as B8). This sample has been used for 8 times in water leak detection device. In this case, the Mg surfaces i.e. interface (facing towards graphite) and top surface (away from graphite) are characterized since both are highly corroded (**Figure 30**). The reason behind high oxidation of the top surface along with interface can be due to the condensation of water molecules inside the package, because the sensor was sitting inside water for about 3 days at every use of the device (in long time in water test). The SEM pictures with different magnifications for both sides of Mg disk are shown in **Figure 34**.

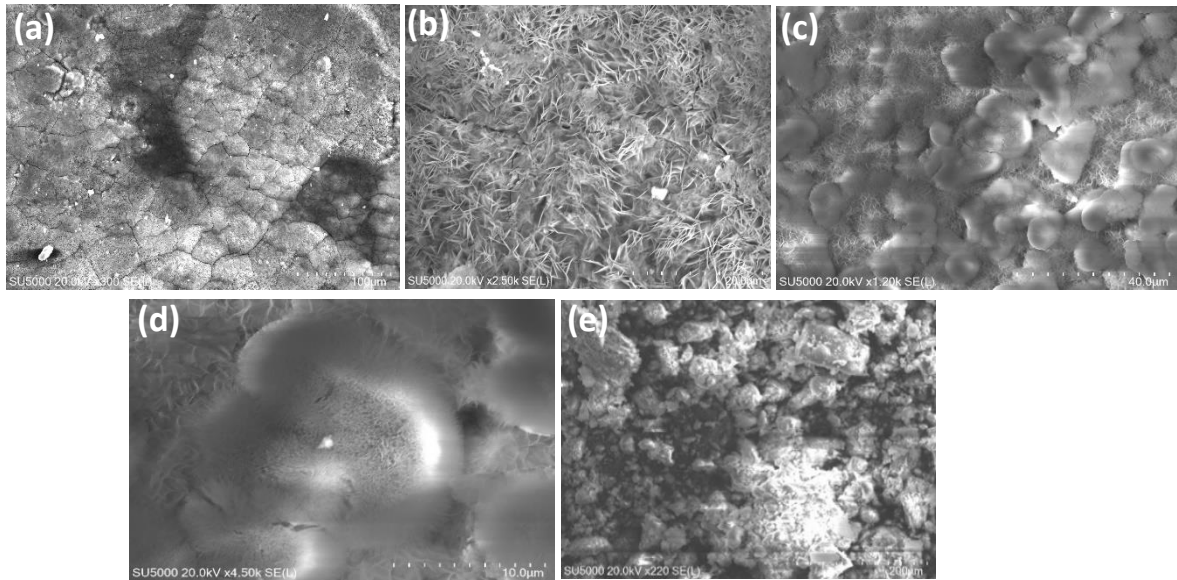


Figure 34: SEM images of sample used for 8 times inside sensor unit (B8) from “Long Time in Water Test” (a) & (b) Interface, (c) & (d) Top surface, (e) Powder collected from top surface.

It can be clearly seen from the **Figure 34(a) & (b)** (interface) that oxide structures are porous and highly dense as compared to the sample A8 (used for 8 times in short time in water test). However, the top surface has oxide content even denser and less porous than interface (**Figure 34(c) & (d)**). Additionally, the whitish powder layer on the top surface is also imaged separately. For that, the powder was scratched from the Mg disk's top surface and was pasted on the conductive carbon tape during measurement. The image for the highly dense particles at magnification 200 μm is shown in **Figure 34(e)**.

5.2 EDX for Elemental Analysis

The EDX analysis is done to measure the elemental composition of the samples for both tests i.e. short time in water (A0-A12) and long time in water (B8) test. Different types of measurements are done with this instrument such as elemental mapping, percentage of elements and elemental spectrum. This analysis reveals the types of elements present and their percentage (wt%) on the surface of Mg disks. The purpose of this test is to observe the change in wt% of elements with repeated use of the sensor.

The **Figure 35** shows the elemental map of the oxidized Mg surface (A4) at 100 μm magnification with different colors showing different elements. As expected from the AZ31 Mg alloy concentration, the major part is Mg that covers the whole surface is shown with purple color **Figure 35(b)**.

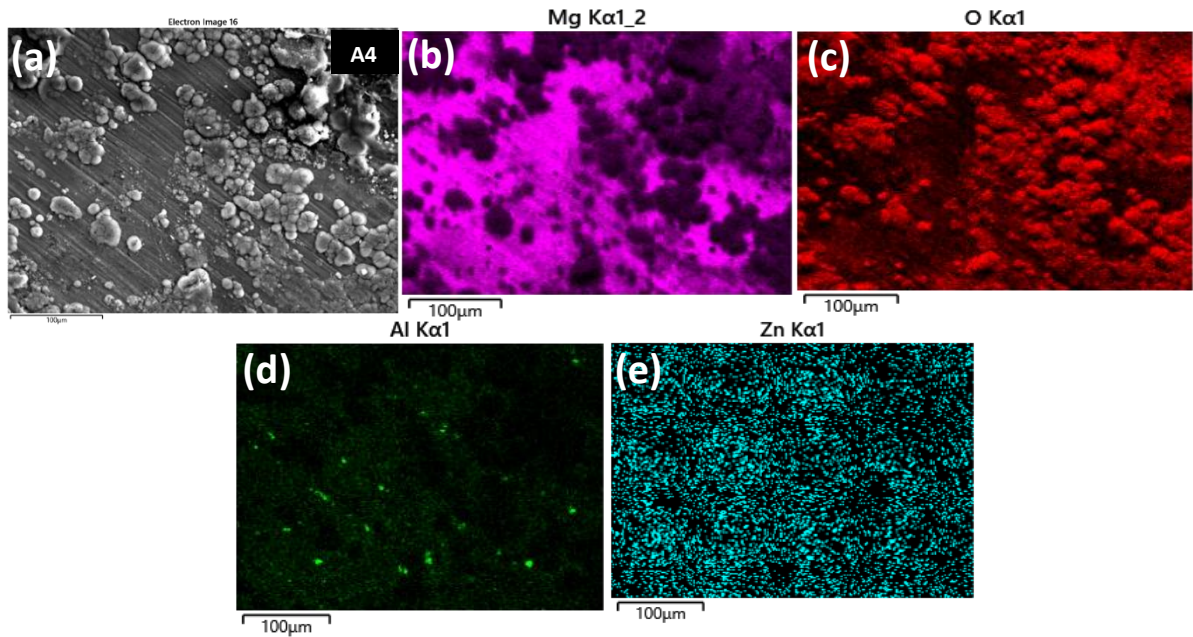


Figure 35: EDX mapping of Mg disk from sensor used for 4 times (A4) from “Short Time in Water Test”.

Since the surface of Mg was in contact with water, the oxygen (present in oxide layer) also covers the surface with varying thickness (**Figure 35(c)**). The raised parts are thicker than the rest of the surface due to the non-uniformity of the oxide layer. Moreover, the Al and Zn are also present in very less ratio in AZ31 alloy, these are distributed less densely throughout the surface.

The graph (**Figure 36(a)**) describes the change in O and Mg content with increase in number of repeated uses of sensor device. The percentage of different elements is calculated from the map spectrum (at 100 μ m) for all samples. The **Table 8** shows the wt% of O, Mg, C, Al and Zn for samples used repeatedly from 0-12 times in the sensor units. As seen from the SEM pictures, the sample A0 has almost the negligible O content (1.7%) due to no oxidation. The percentage of the O element increases continuously until 8 uses (~48%) of the device, and it starts saturating after that point with slight changes. Since the sample's reaction time with water is rising with repeated use, the O content is also increasing, however a reverse trend is seen for the Mg content (because Mg metal is getting covered with oxide layers). The wt% of Mg is decreasing continuously until 8 uses (~32 %) and almost saturated for the later uses. Furthermore, the increase in the O content represents the increase in the oxidation layer. Even though O wt% saturated after several uses, but it is possible that the oxidation layer's thickness is increasing (which cannot be detected with EDX) (discussed more in section 5.8).

The other elements (Al, Zn and C) that are also present in the sample are shown in **Figure 36(b)**. The percentage for Al and Zn stays almost constant through out the whole experiment, but the C content is rising as the number of uses increasing. There could be few reasons for the presence of C on the sample.

The minute C percentage in the control samples (A0) (0.6%) can be the result of the contamination while handling the sample during fabrication or characterization. However, the increase in C percentage can be due to the presence of graphite that is in close contact with Mg with the separating layer (filter paper). Therefore, every time the sensor is wetted, the water reaches to the Mg sheet after passing through graphite, so it is possible that some micrometer particles can also flows through the filter paper to the Mg surface along with water. Therefore, it is possible that more and more C particles can move through the filter paper since the sensor is wetted again and again for the repeated use, which results in the increase in the C content. Another probable reason could be the compounds present in tap water which can have C elements. Therefore, with increase in wetting time, more of these compounds can deposit on Mg surface and can rise the overall C content. Other than that, it is also possible that Mg can react with C in CO₂ (in air) in the presence of water which can result in the formation of magnesium

carbonate (MgCO_3). This can in turn show some C content in the wt% while measurement (more in section 5.4).

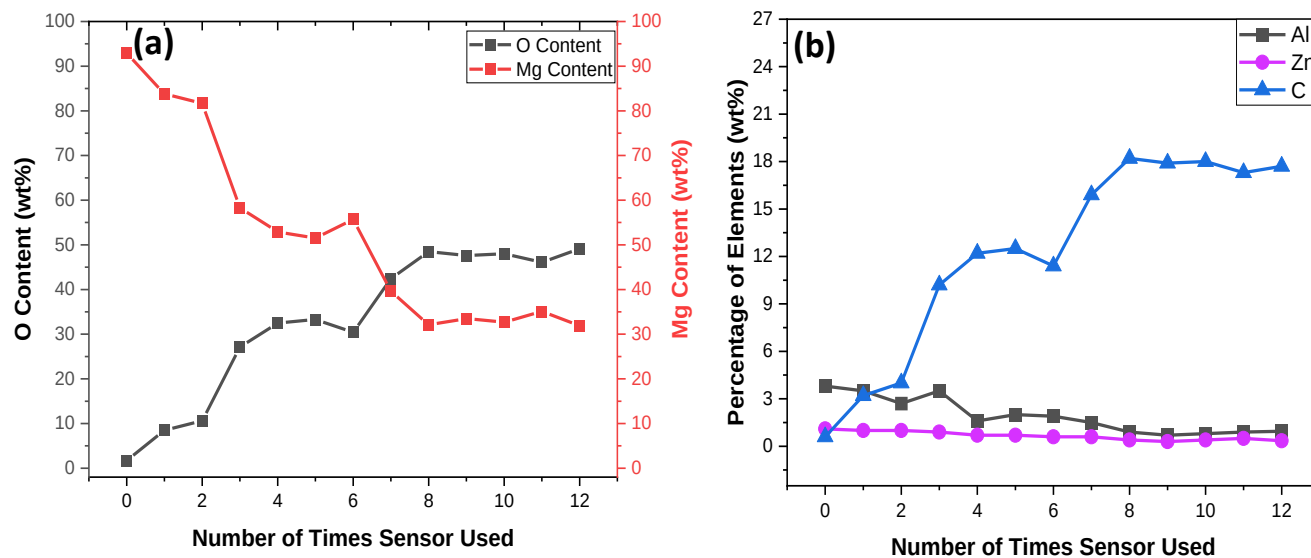


Figure 36: Wt% of different elements on the sample surface with increase in number of uses of the sensor, from “Short Time in Water Test” (a) O, Mg content, (b) Al, Zn, and C.

Table 8: Weight percentage values of O, Mg, C, Al, and Zn with number of times sensor used.

Map Sum Spectrum					
Number of Times Sensor Used	O Content (wt%)	Mg Content (wt%)	C Content (wt%)	Al Content (wt%)	Zn Content (wt%)
0	1.7	92.9	0.6	3.8	1.1
1	8.5	83.8	3.2	3.5	1
2	10.6	81.7	4	2.7	1
3	27.1	58.3	10.2	3.5	0.9
4	32.5	52.9	12.2	1.6	0.7
5	33.3	51.5	12.5	2	0.7
6	30.4	55.7	11.4	1.9	0.6
7	42.4	39.6	15.9	1.5	0.6
8	48.5	32.1	18.2	0.9	0.4
9	47.6	33.5	17.9	0.7	0.3
10	48	32.7	18	0.8	0.4
11	46.1	35.1	17.3	0.9	0.5
12	49.1	31.9	17.7	0.95	0.35

The point spectra of the oxidized sample are also obtained which gives the information about the specific points on the image (unlike map spectrum). A sample that was used for two times (A2) for water leak detection was analyzed at two different points, at normal surface (dark gray) and oxide particles (bright). The points of analysis are highlighted as spectrum 4 & 5 (normal & oxide respectively) in **Figure 37(a)**. The spectrum 4 shows very less O content i.e. ~9% while the spectrum 5 shows high amount of O about ~45%. This explains that the brighter particles are the oxide particles which also confirms the reasoning given in the **Section 5.1**.

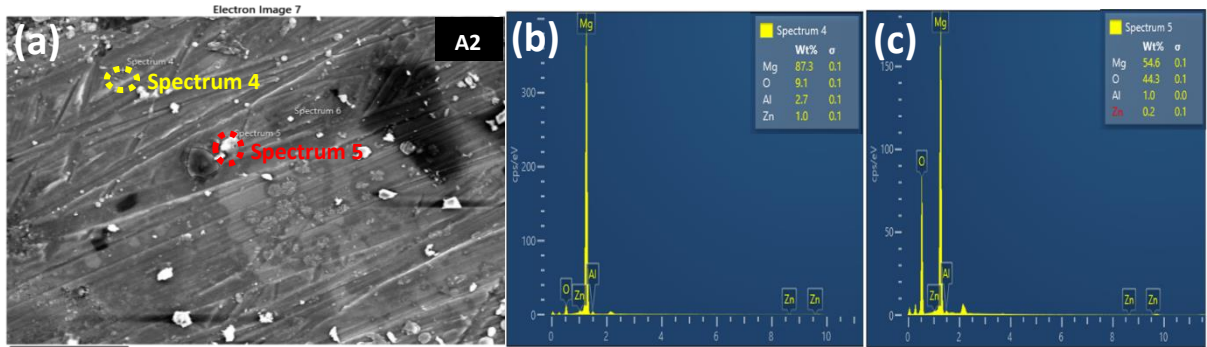


Figure 37: Point spectra to measure the elemental composition at specific points on the sample surface used for 2 times from “Short Time in Water Test” (a) SEM picture of A2 sample at 100 μm magnification, (b) Spectra 4 obtained from bare Mg surface, (c) Spectra 5 obtained from oxide particle.

The EDX analysis is also done on sample used for long time in water test (B8 used for 8 times). Similar to SEM, the analysis is done on both sides of the Mg disk since high oxidation layer is clearly visible at the interface and the top surface of Mg. As expected, this sample showed high oxygen wt% in the EDX spectrum. The results shows that same content for different elements is observed from both surfaces i.e. O - ~60%, Mg - ~23%, C - ~14.7% and negligible amount of Al, Zn and Ca (**Figure 38**).

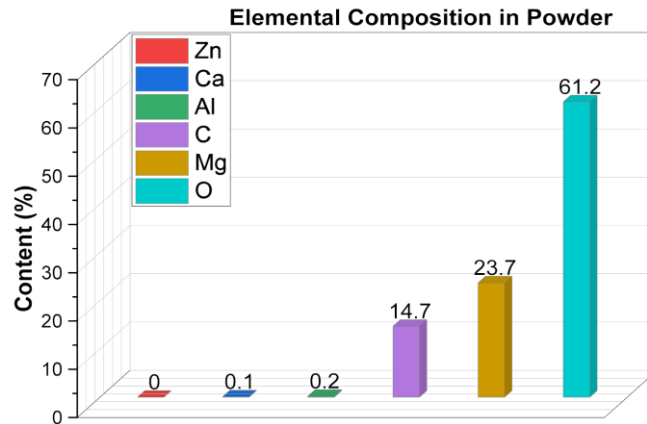


Figure 38: Average percentage of different elements present on the interface, top surface and powder collected from top surface, for sample used for 8 times (B8) from “Long Time in Water Test”.

The small calcium (Ca) content (0.1%) can be due to the presence of CaCO_3 (calcium carbonate) in tap water. These results show that both sides of Mg are highly corroded and therefore the surface area for reaction at the interface as well as resistance of the top surface can be the reason for sensor's failure after 8 uses.

5.3 X-Ray Photoelectron Spectroscopy (XPS)

XPS analysis is done to measure the chemical changes on the surface of Mg disk after reaction with water. The previous characterization results with EDX and SEM confirmed that there is oxygen content present on the Mg metal surface before and after reaction with water, and this oxygen content is rising with increase in reaction time. Moreover, literature shows that this oxygen is due to the oxidation of Mg to form a naturally grown magnesium oxide or magnesium hydroxide films, upon reaction with air and water respectively (detailed in chapter 2). However, above explained results do not specifically explain the type of oxide and composition of the surface and inner layers. Therefore, the purpose of this test is to confirm the type and chemical structure of oxide present in different layers formed onto the Mg surface.

The $\text{MgO}/\text{Mg}(\text{OH})_2$ growth causes two major issues in the energy production of the sensor. The first is the surface area for reaction and second is the conductivity of the Mg metal.

Surface Area for Reaction: The oxide builds up on Mg disk's surface lowers down the power production from the sensor unit. It is because of the difference in surface area available for reaction in both cases, for fresh Mg and oxidized Mg. The Mg metal (AZ31 alloy) freshly sanded has a larger surface area as compared to oxidized metal surfaces, because the former surface has mostly Mg metal (with negligible MgO due to instant reaction with air) while some percent of area is covered with hydroxide in the latter case. Although, $\text{MgO}/\text{Mg}(\text{OH})_2$ has porous structure and the water can transport through the pores for the chemical reaction with Mg, the overall area is still less than freshly sanded Mg sheet because of the area covered with hydroxide other than pores (in case of highly corroded samples). The MgO has very low solubility and $\text{Mg}(\text{OH})_2$ is completely insoluble in water, and these compounds somehow block the reaction of water with Mg metal. This oxide/hydroxide layer is increasing gradually as the reaction time increases which in turn decreases the power produced from the sensor unit.

Conductivity: Another main issue emerged is the drop in conductivity of the Mg sheet with increase in oxide/hydroxide content. Conductivity is the ability of charge carriers to move freely, and it depends on the valence electrons present in the outer shell of atoms. Mg has two valence electrons in its outer shell which helps it to conduct electricity (described in chapter 2) [49]. The magnesium metal has a high conductivity value of $\sim 2.15 \times 10^7$ S/m at 20° C which is comparable to 2nd most conductive metal Cu (5.98×10^7) and higher than iron (1.04×10^7). However, on the other hand, MgO and Mg(OH)₂ have very low conductivity as compared to Mg metal. This is because of the high bond strength in both cases, which means the electrons are tightly bonded in MgO and Mg(OH)₂ while are loosely bonded inside the outer shell of Mg metal. Therefore, the charge transfer of electrons is easy in unoxidized Mg metal than oxidized metal.

The analysis is done on the sample (interface of Mg disk) that has been used for one time inside the sensor package. Two different scans are performed on this sample. The first scan is the XPS scanning on the Mg disk's surface (as obtained) after reaction with water (inside the package). This reveals information about the top layers only, therefore another feature called "Depth Profiling" is used to perform the second scan with XPS to analyze the under layers. During the second scan, an argon (Ar) gun is used to sputter the top layers to expose the bottom (inner) layers. The sputtering is done for around 20 minutes and the new surface layers (under top layers) are then examined with XPS. The comparison between the results obtained from the top and inner layers is further made, to know the type of oxide present in different levels.

The graph plotted (**Figure 39**) shows the survey scan of the top surface (as obtained before sputtering) and the inner layers after 20 minutes sputtering. The top surface exhibits a highly intense O 1s (533.7 eV) peak and low-intensity Mg 1s peak (1302.7 eV) for their respective binding energies. These peaks are obtained from the library function in "CASA XPS" software. The reason behind low-intensity Mg peaks is that the Mg metal is covered with oxide and therefore shows a strong oxygen peak. However, the inner layers after sputtering, indicate that the O 1s is reduced, and Mg 1s peak is enhanced because of the removal of top hydroxide layers. Moreover, the other Mg peaks (Mg 2s and Mg 2p) also intensify in case of inner layers as compared to the surface layers. Additionally, XPS shows some Auger peaks and are labeled as "KLL". The Mg KLL (305.1 eV) auger peak reveals the same information as XPS peaks, that the peak intensity is higher in the case of inner layers after 20 min. sputtering as compared to the surface layers before sputtering (as obtained) [50]. This explains that the oxygen peak diminishes, and Mg peaks strengthens as move from the top to the bottom layers. Additionally, a small peak at

350eV is also observed in both samples which indicates the presence of some calcium (Ca) compounds present on the sample surface. This can be due to the existence of Ca compounds such as CaCO_3 , CaSO_4 etc. in tap water used for reaction.

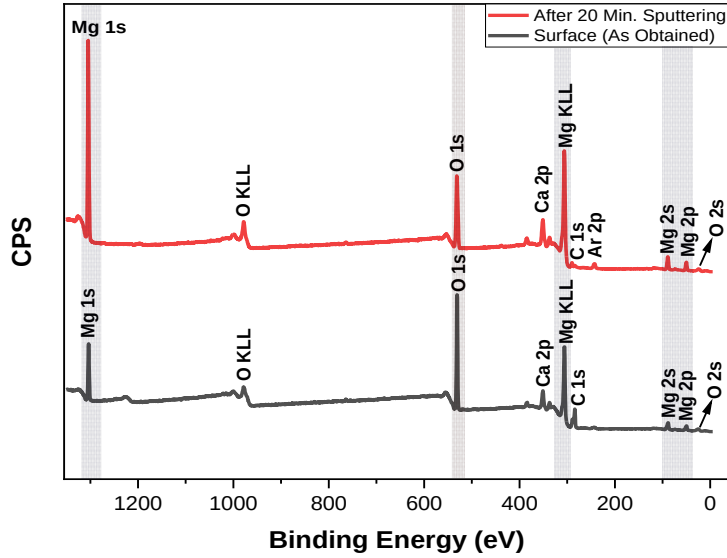


Figure 39: XPS survey scan on the surface (as obtained) and after 20 min. sputtering, for sample used for one time (A1) inside the sensor package for “Short Time in Water Test”.

Furthermore, to find out the type of oxide in top and inner layers, the peak ratio of Mg and O is calculated from the high-resolution peaks of Mg 1s and O 1s as shown in **Table 9**. It is estimated from the chemical structure that the oxygen content should be twice of the Mg content in Mg(OH)_2 since two O atoms present with each Mg atom however, equal amount of oxygen and Mg should be obtained in MgO. This confirms that the O/Mg ratio for Mg(OH)_2 and MgO can be calculated as 2 and 1 respectively [51]. The results indicates that the calculated O/Mg ratio for the surface layers before sputtering is 2.4 and after sputtering is 0.97 which confirms the Mg(OH)_2 presence in top layers and MgO in the inner layers. These results also support the literature findings which says that the freshly sanded Mg metal quickly reacts with O as soon as it comes in contact with air and forms a protective layer of MgO on the surface, therefore the samples has MgO in the inner layers. Moreover, MgO is slightly soluble in water and converts to Mg(OH)_2 immediately after reacting with water which gives rise in the formation of Mg(OH)_2 layer. Porous nature of Mg(OH)_2 helps in continuing the reaction and in energy production. As the time of reaction increases, more and more hydroxide build up and therefore overall surface area for reaction decreases which consequently reduces the power of the sensor unit.

Table 9: Atomic percentage and ratio of Mg and O for surfaces before sputtering and after 20 minutes sputtering (calculated from high resolution scans for Mg 1s and O1s peaks)

	Element	Surface (As Obtained)	Surface After 20 Min.
		Before Sputtering	Sputtering
Atomic %	Mg (1s)	29.60	50.85
	O (1s)	70.94	49.15
Ratio	O/Mg	2.40	0.97

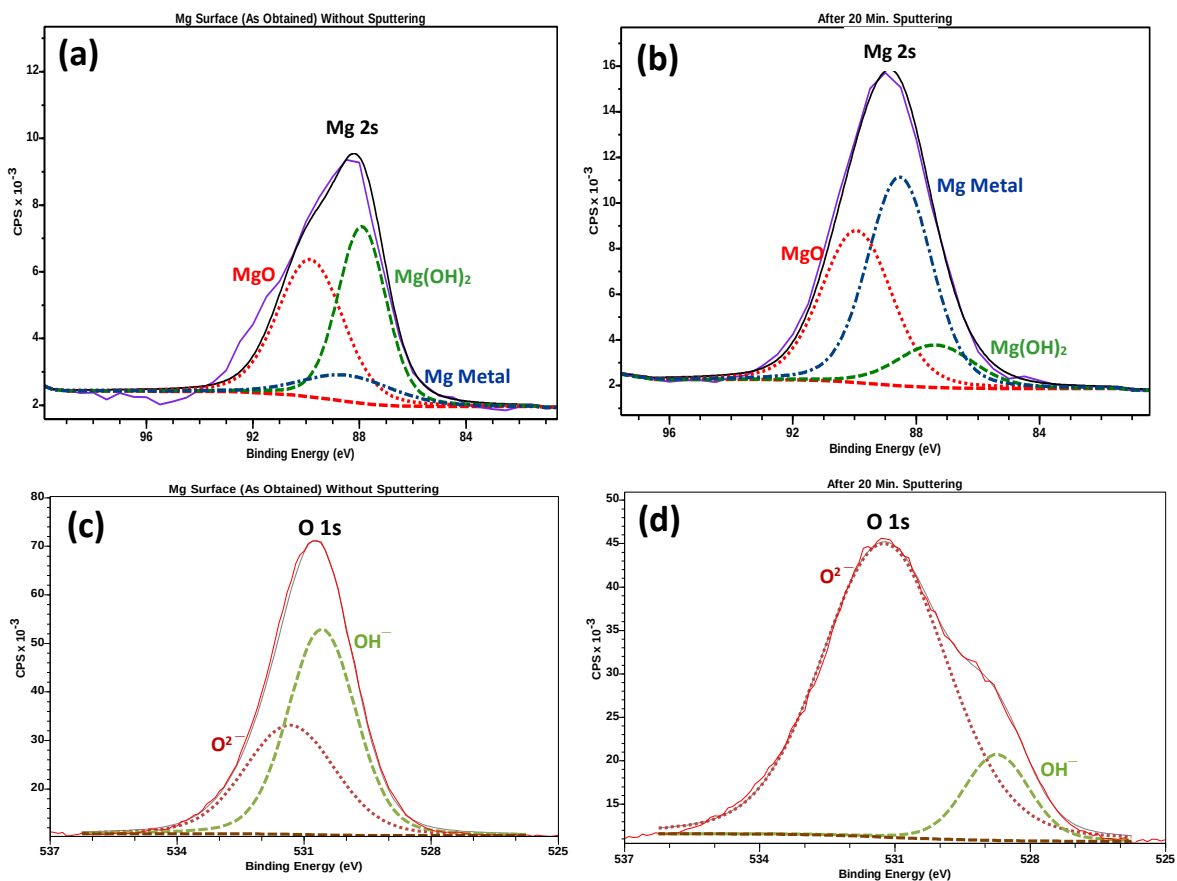


Figure 40: Peak fitting graphs for high resolution (a) Mg 2s peak before sputtering, (b) Mg 2s peak after 20 min. sputtering, (c) O 1s peak before sputtering, (d) O 1s peak after 20 min. sputtering.

The **Figure 40** shows the peak fitting for high resolution Mg 2s and O 1s peaks before and after sputtering, plotted with the same “CASA XPS” software. The Mg 2s plots for before and after

sputtering (**Figure 40(a) & (b)**) comprises three components demonstrated by dotted lines i.e. MgO (red), Mg(OH)₂ (green) and Mg metal (blue). The surface before sputtering indicates more intense Mg(OH)₂ (at 87.8 ± 0.5 eV) and less intense MgO (at 89.7 ± 0.2 eV) peaks, along with very small peak at 88.5 ± 0.1 which corresponds to metallic Mg. However, after sputtering for 20 minutes, the Mg(OH)₂ peak dropped and Mg metal peak intensified significantly, along with a little increase in the intensity of MgO peak. This confirms that top surface layers (as obtained after the reaction) has mostly Mg(OH)₂ and some MgO content, however inner layers after sputtering comprise mostly Mg metal covered with MgO. These measurements are also attained from the high-resolution peak fitting for O 1s (**Figure 40(c) & (d)**) in both cases. Similar to the Mg 2s depth profile plots, the intensity of OH⁻ (in Mg(OH)₂) and O²⁻ (in MgO) peaks in O 1s plot also changes for the surfaces before and after sputtering. The O²⁻ peak enhanced and OH⁻ peak reduced considerably in the inner layers as compared to the top surface layers [52].

5.4 X-Ray Diffraction (XRD)

The X-Ray diffraction analysis is done to find the characteristic peaks and to confirm different compounds in the sample. The sample which used for 12 times for water leak detection (A12), is characterized during this measurement. Dual scans with different incident angles (2Theta and 2Theta-Omega scan) are performed on the same sample to get information from the different layers on the sample surface.

2Theta Scan: This scan is usually implemented to be used for thin film samples since it is advantageous to get diffraction from the top layers only, and not from the substrate. During this measurement, the sample is fixed at a specific position, and the source (x-ray) and detector rotates to collect diffraction data from various angles. The incidence angle is fixed at a small angle (<1 degree) to achieve shallow penetration depth (**Figure 41(a)**) and it also increases the beam coverage area [53][54]. Therefore, when the oxidized sample (A12) is analyzed, this scan gave information only about oxide layer (top layer) not about the Mg metal disc (substrate). The diffraction pattern obtained from that scan is shown in **Figure 42(a)**.

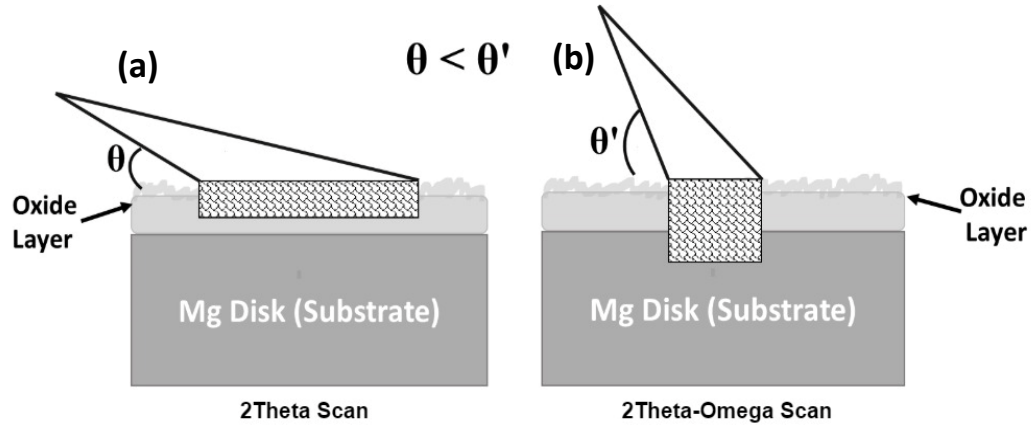


Figure 41: Incidence angle and area coverage by the X-ray beam in case of (a) 2Theta scan, (b) 2Theta-Omega scan [54].

2Theta-Omega Scan: This analysis is different from 2Theta scan in terms of penetration depth of the incident beam. Unlike 2Theta scan, during this scan the source is fixed, and the sample and detector rotates. The incident angle is larger which results in deep penetration depth into the sample. Moreover, the area coverage by the beam is also small in this scan as compared to the 2Theta scan (**Figure 41(b)**) [53]. Due to larger penetration depth, the diffraction signal gives information from the top layers as well as from the substrate (and inner layer). Therefore, during this scan for the same sample A12 (used 12 times) showed information about the oxide surface layers, inner layers and the Mg disk itself (substrate). The diffraction pattern acquired from this scan is indicated in **Figure 42(b)**.

The peaks found from both scans are identified by comparing data with the ICDD files for “Brucite” [55], “Periclase” [55] and “Magnesium Carbonate” [56]. The diffraction peaks are also matched with the literature to know the various compounds present on the sample [57][58][59]. The intense peaks observed at $2\theta = 34.4^\circ, 47.9^\circ$ in both scans confirmed the presence of Mg which is apparently expected since the sample (substrate) is AZ-31 alloy of magnesium. The high intensity peak at $2\theta = 34.4^\circ$ is more prominent in case of 2Theta-Omega scan as compared to 2Theta scan. This is because of the diffraction from the Mg disk substrate in case of higher angle in 2Theta-Omega scan. The existence of different Mg compounds such as MgO, Mg(OH)₂ and MgCO₃ on the sample surface is also confirmed from the peaks present at $2\theta = 36.7^\circ, 41.7^\circ, 32.2^\circ, 34.4^\circ, 59.1^\circ, 63.3^\circ, 70.3^\circ$ in both scans. The peak position are same in both cases regardless of the intensity of diffraction peaks.

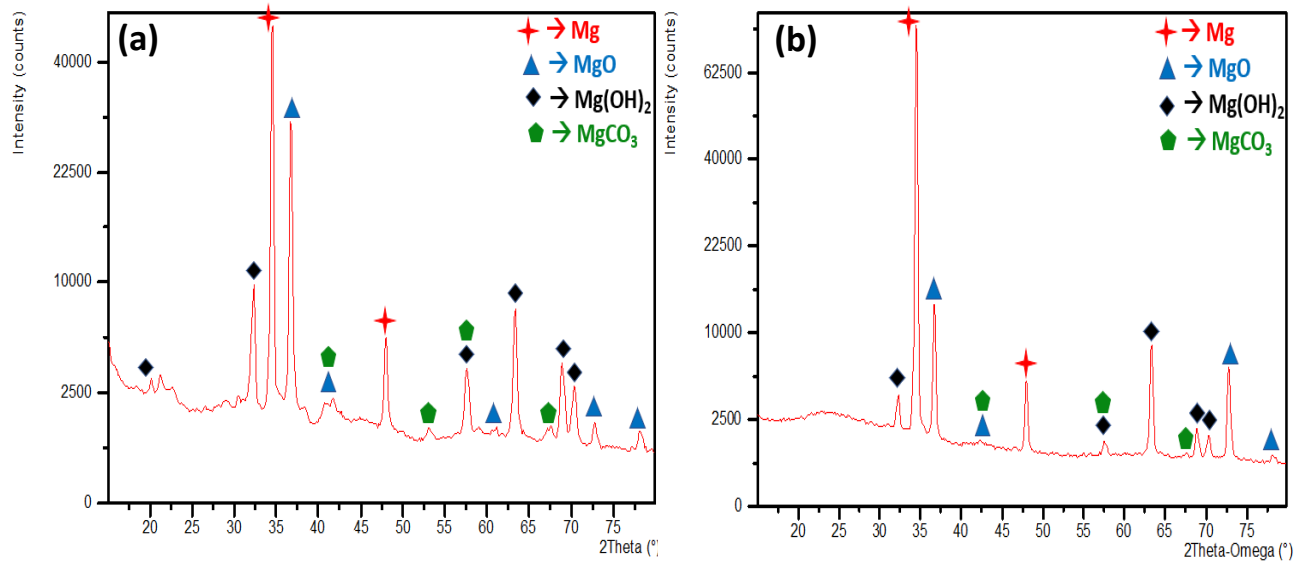


Figure 42: XRD pattern for Mg disk from sample used for 12 times in “Short time in water test” (a) 2Theta scan, (b) 2Theta-Omega scan.

The literature shows that MgO grows spontaneously on the Mg surface in the presence of air. However, the $\text{Mg}(\text{OH})_2$ growth is not that instant, and it grows only when Mg comes in contact with aqueous medium or moist air [60]. This implies that at first, MgO will grow on the Mg disk, and then $\text{Mg}(\text{OH})_2$ will grow on the top. This top layer can be a combination of $\text{Mg}(\text{OH})_2$, MgO and MgCO_3 since there are C and O compounds present in air and water. Therefore, according to these findings, the top layers of the sample (in 2Theta scan) produce most of the diffraction from all three compounds of Mg ($\text{Mg}(\text{OH})_2$, MgO, MgCO_3), and the bottom layer and substrate (2Theta-Omega scan) reveal the information about the Mg substrate covered with MgO along with very little content from $\text{Mg}(\text{OH})_2$ and MgCO_3 . Consequently, for 2Theta scan, the peaks are observed at $2\theta = 32.2^\circ$, 36.7° , 56.5° that corresponds to $\text{Mg}(\text{OH})_2$, MgO, MgCO_3 respectively, have higher intensities than the 2Theta-Omega scans.

5.5 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis is performed to detect different functional groups present on the Mg surface before and after reaction with water. Two samples (a) sanded Mg disk, and (b) Mg disk with corrosion layer (after reaction with water (sample A12)) are characterized for this measurement. The results obtained from both samples are plotted in **Figure 43**. Similar peaks at 562 cm^{-1} and 858 cm^{-1} are observed in

both samples which represents the vibration of the Mg-O stretching bond that indicates the presence of MgO in both samples [51]. Another peak found at 1068 cm^{-1} in sanded Mg disk is ascribed to the C-O stretch which can be from the carbonate group in MgCO_3 [58], and a similar peak at 1066 with more intensity is also seen in other sample with corrosion layer [61]. This confirms that the carbonate group is also present in both samples with varying amounts and can be due to the reaction between Mg and CO_2 (in air).

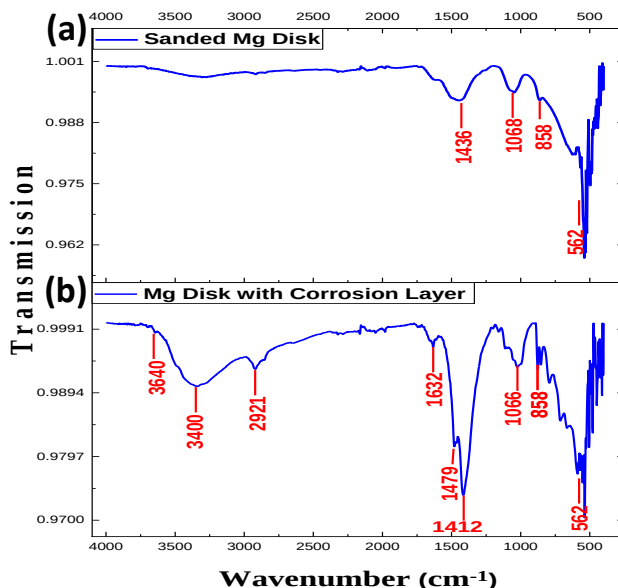


Figure 43: FTIR spectra (a) For sanded Mg disks (b) For Mg disk with corrosion layer taken from sample used for 12 times in “Short Time in Water test”.

Since the sample named “Mg disk with corrosion layer” was in contact with water, hydroxyl groups are seen on this sample only, but not in the other sample. Various peaks at 3400 cm^{-1} , 1632 cm^{-1} , and 1412 cm^{-1} corresponds to -OH stretching and bending due to the hydroxyl group in $\text{Mg}(\text{OH})_2$ [62] [63]. A small peak at 2921 can be attributed to C-H groups due to impurities. The analysis of the results from both samples also resembles the data from literature and the data conducted from the XPS and XRD analysis. It confirms that Mg metal reacts with O and CO_2 in air to form a protective coating of MgO and MgCO_3 on the surface of the Mg disk (in case of sanded Mg disk before reaction with water). Moreover, when the Mg sheet reacts with water, it forms hydroxide on the metal surface (with protective coatings). This means the corroded samples comprise $\text{Mg}(\text{OH})_2$ along with MgO and MgCO_3 in the surface layers.

5.6 Resistance of Mg Disks

This test is conducted to measure the change in resistance of Mg disks upon repeated use inside the sensor unit. The measurement is performed with 4 wire resistance measurement setup with DMM (chapter 3), to eliminate the resistance value from the wires itself. Four alligator clips, 2 for positive and 2 for negative connection are used. Since the clips have jaw like shape, therefore they were making contacts from both sides of the Mg disk (interface and top surface). The test is conducted on two types of samples i.e., from short and long time in water test.

Firstly, the measurement is performed on the samples used for 0-12 times in short time in water test. It is noticed from the results that all the samples have very low resistance values in the range of milliohms **Table 10**. It is seen from the inset of **Figure 44** that the corrosion layer on the top surface of Mg disk (used for 12 times inside sensor package) is almost negligible, however the interface of the same sample is highly corroded (chapter 4, section 4.4.3). Furthermore, it is said that “current takes the path of least resistance to flow” and therefore in this case it can flow from the top surface regardless of the corrosion amount on the interface. Eventually, this can be the reason behind the negligible difference in the resistance for different samples. This confirms that the resistance of the Mg sheet might not be the major reason for sensor failure in specifically “short time in water test”.

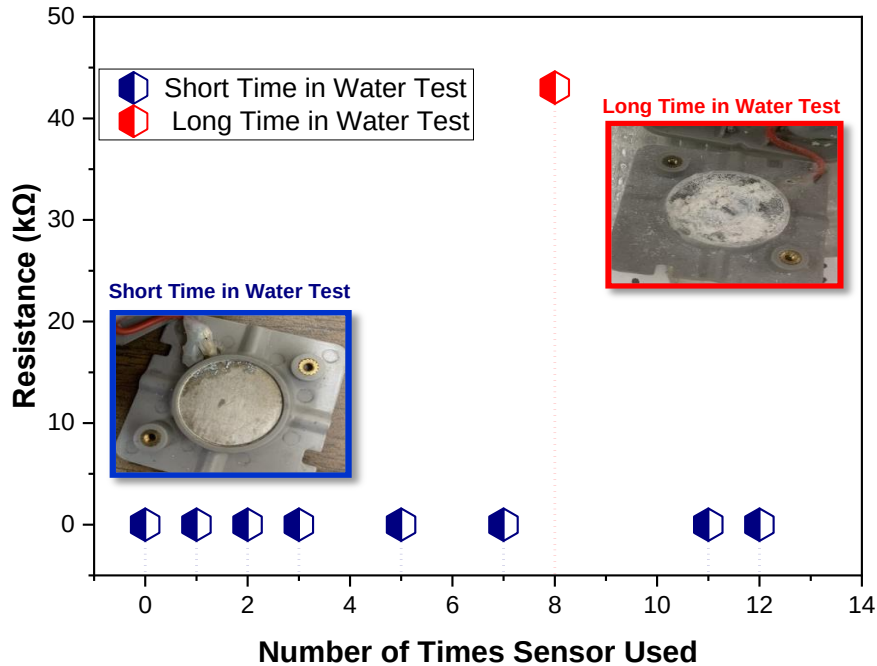


Figure 44: Resistance vs number of times the sensor used in short time and long time in water test.

The same test is also performed on the sample used for 8 time in long time in water test (named as B8). It is seen from the inset of **Figure 44** that unlike short time in water test, this sample's top surface is highly corroded (along with the interface (chapter 4, section 4.4.3)). Therefore, it is expected that this sample can have high overall resistance which is confirmed from the resistance measurement shown in the graph. The results indicate that this sample has very high resistance $\sim 45 \text{ k}\Omega$ and this can definitely be one of the reasons for sensor failure in case of long time in water test.

Table 10: Changes in the resistance values for both tests, with increase in number of times the sensor used.

Number of Times Sample Used	Test Type	
	Short Time in Water (milliohm)	Long Time in Water (milliohm)
0	1.59	-
1	5.54	-
2	6.38	-
3	4.77	-
5	3.13	-
7	4.73	-
8	-	43040107 or 43 k Ω
11	4.28	-
12	3.62	-

5.7 Atomic Force Microscopy (AFM)

All the above discussed results/measurements do not reveal the information about the thickness and roughness of the oxide layers. Moreover, EDX gives the wt% of elements from the surface layers only but not from the inner layers. Therefore, after a point, EDX analysis showed a saturation in the oxide content (**Figure 36(a)**), however there are chances that the thickness of the oxide layer can be increased with increase in reaction time. Consequently, another characterization tool AFM is used for thickness measurement. The purpose of measuring oxide layer thickness is to know the critical thickness at which the sensor stops working or in other words, produces very less power at which it stops activating the beacon. The AFM has high vertical resolution ($<1\text{nm}$) and can measure the height up to $6\mu\text{m}$. To obtain accurate results with AFM, the surface of the sample should be very smooth.

A Mg disk from the sample used for a single time (less oxide thickness) was taken for characterization since the height measurement range is limited. During the sample preparation, the Mg disk was sanded with very fine sandpaper (2500 grains) to obtain a smooth surface. The disk was half covered with scotch tape to prevent the oxidation and other half was left for reaction with water to produce oxide

layer. During the measurement, the tip moved from the bare Mg metal surface (after removing scotch tape) to the oxide surface, to calculate the step/height at the interface. The results (**Appendix D**) didn't show a noticeable difference in the height of the oxide layer due to the roughness of the overall surface i.e. the height of scratches/grooves (due to sanding) and the height of oxide layer grown was almost the same. The samples with thicker oxide layer (from 10-12 times used sensor) was also analyzed and it did not show detectable results since the height of oxide layer was out of the range of AFM ($6\mu\text{m}$). Therefore, another method that can measure the samples with little tolerance on roughness and can also detect height more than $6\mu\text{m}$ (for extremely oxidized samples) was used ("Profilometer") and is discussed in next section.

Despite inapplicable results from the thickness measurement, this technique (AFM) gave some other interesting data related to "Roughness Analysis". The roughness of both the surfaces i.e. bare Mg (**Figure 45(a)**) and oxide surface (**Figure 45(b)**) is measured with AFM. As expected, the Mg surface (protected from oxidation) has more roughness (54.24 nm) than the oxide layer surface (15.98 nm).

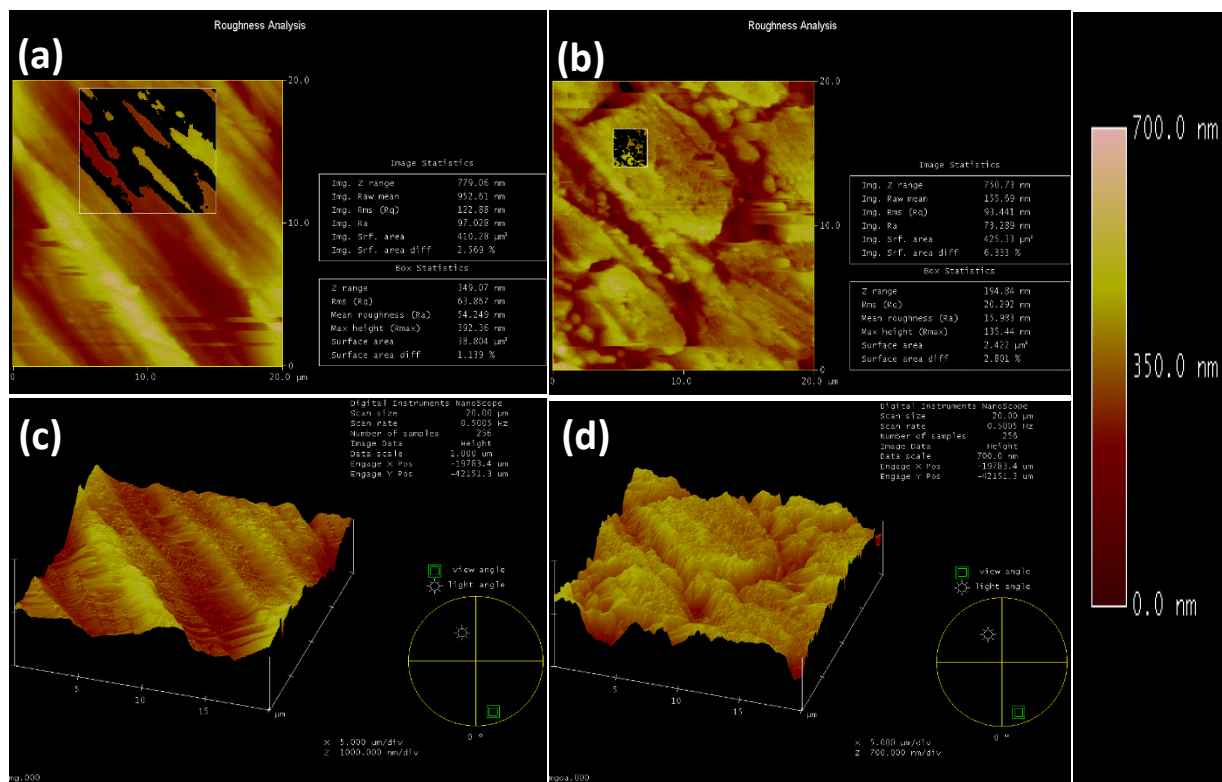


Figure 45: Roughness Analysis of (a) Bare Mg surface, and (b) Oxide layer and 3D view of (c) Bare Mg surface and (d) Oxide layer.

It is because the oxide grows on the rough surface after reaction with water and fills the gaps in thin grooves. This makes the surface smoother and therefore lowers down the overall roughness of the film. However, the surface that was protected from reaction, did not undergo any oxidation and the grooves (due to sanding) remain unfilled which makes this surface rougher than the oxidized surface. This can also clearly be seen from the 3D view of both the surfaces in **(Figure 45(c) & (d))**.

The interpretation of the results is done by using the scale on the right side of the **Figure 45** that provides information about the height of surfaces. Bright surfaces are taller while the dark surfaces are smaller. The sanded Mg surface displays some bright and darks surfaces and on the other hand, the oxide layer shows almost all the surfaces with the same brightness (means same height). This confirms that the oxide layer has less roughness than Mg surface. This test also indicated that the changes in the roughness of the surface can lead to changes in the oxide layer thickness.

5.8 Profilometer for Measurement of Oxide Thickness

This technique is used to measure the thickness of the oxide layer, grows after reaction between Mg and water inside the sensor unit. Special sample preparation is done for this measurement to make the surfaces very smooth. Normally, the Mg disk is sanded with the one sandpaper (can be rough or smooth) and then assembled inside the sensor unit (the reaction occurs on whole Mg surface). However, for this analysis, the sample surface needs to be very smooth to eliminate the effect of height due to grooves formed from the rough sandpaper. Therefore, the Mg disks are sanded with various sandpapers starting from rough, smooth and very smooth sandpapers to make the surface even and polished. After that the sample is half covered with scotch tape to avoid oxidation reaction and rest of the surface is left for reaction. This Mg sheets are then placed inside the sensor packages. Total of 10 sensor units are prepared in the same way, to be utilized for repeated use to see the difference in oxide layer thickness. All the sensor units are wetted for specific number of times and are opened up to take out the Mg sheets. The scotch tape half covering the surface is then removed which reveals the shiny Mg surface (left) and other half is covered with oxide layer (right) **(Figure 46(a))**. The surface layers are also confirmed with SEM/EDX and the results are discussed more in **Appendix C**. This measurement is done with a very sharp tip which moves from bare Mg surface (acts as a reference surface) towards the oxide layer. As shown in the x-axis of **(Figure 46(b))**, the total length of measurement is 4500 μm , out which the tip covers the distance from 0 - 1500 μm on Mg surface and from 1500 – 4500 μm on oxide layer.

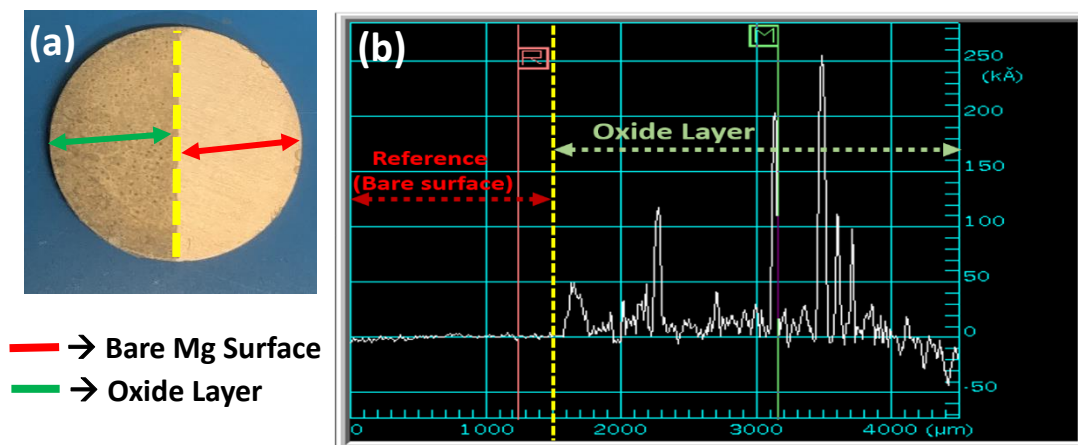


Figure 46: (a) Picture of the Mg disk taken with camera after the reaction, (b) Graph (length vs thickness) obtained during the measurement.

The measurement is performed on the sample wetted for 6 times. It can be seen from this graph that very small vibrations are visible on the bare Mg surface which are due to small grooves left from the sanding procedure. However, large fluctuations in the thickness (y axis) of oxide layer are noticed which confirms that the oxide layer is not uniform. It can also be seen visually that the oxide layer has some smooth and some uneven parts, due to which few peaks are very large in height (251 kiloAngstroms) and other have very less thickness. Therefore, an average value for the thickness is calculated for all the samples and are plotted in **Figure 47**. The graph demonstrates that the average thickness of the oxide layer is rising with increase in number of times the sensor used/wetted. The sensor that has never been used (just sanded Mg disk) has 0 μm oxide thickness and it is increased to 1.1 μm after wetting the sensor for 2 times. Likewise, the oxide thickness grows to $\sim 5.5 \mu\text{m}$ after using the sensor for 6 times. The thickness of the oxide layer is almost saturated after 6 uses and it stays around $5.5 \mu\text{m}$ till 12 uses of the sensor. The **Table 11** displays the maximum as well as the average oxide thickness of the samples wetted for various number of times.

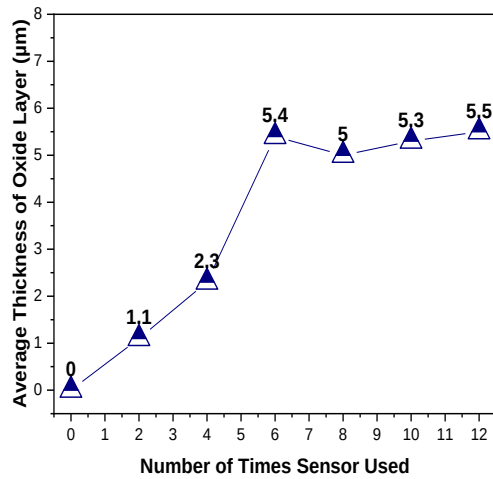


Figure 47: Average thickness of oxide layer vs number of times sensor used.

Table 11: Maximum and average thickness of oxide layer with wetting time of sensor unit.

Number of Times Sensor Wetted	Maximum Oxide Thickness (μm)	Average Oxide Thickness (μm)
0	0.4	0
2	3.8	1.1
4	6.2	2.3
6	25.1	5.4
8	14.2	5.0
10	12.3	5.3
12	25.3	5.5

5.9 Summary

This chapter concluded the surface analysis of Mg electrode (anode) inside the sensor unit used for water leak detection. The analysis represented the changes occurred on the surface of Mg disks with repeated use of the sensor. It is observed that a thin MgO layer forms instantly on Mg metal after reaction with oxygen in air, and a thick $\text{Mg}(\text{OH})_2$ layer along with small portions of MgO and MgCO_3 grows after reaction with water. The thickness of this oxide layer is growing with increase in reaction time or in other words with repeated use. It is also suspected that the surface area for the reaction is decreasing with increase in oxide thickness which impacts the power production of the sensor. Another reason for the sensor failure can be the resistance of the oxide layer building up on the Mg disk's top surface which makes the electrical connection inside the sensor unit.

Chapter 6: Conclusion and Recommendations

6.1 Conclusion

1. The thesis explains, how a battery free device can overcome the drawbacks of the currently available water leak detection systems in the market and even the systems under research. It is the first water sensing device which works on the principle of water enabled chemical reaction and does not require batteries to operate.
2. The performance of the sensor in terms of electricity production was analyzed with various instruments. Different electrical specifications such as OCV, SCC, voltage trend under various loads and internal resistance of the sensor unit were evaluated. The sensor can produce reasonably high voltage of 2.04 ± 0.04 V (under no load) and can generate $\sim 12.5 \pm 1$ mA current. It can also generate charge capacity of $\sim 300\mu\text{Wh}$ under $50\mu\text{A}$ load. All these results concluded that the sensor is capable of activating a low energy Bluetooth device (BLE). It is also analyzed that the device can send the Bluetooth packets in $\sim 30\text{s}$ after it comes in contact with water.
3. Additionally, the repeatability of the sensor was also observed which was found to be 12 times. However, this number can vary with the testing conditions and sensor's stay time in water. The repeatability rounds were decreased to 8 times when sensor's reaction time was increased, and it was placed in water for 2-3 days at every use. Along with the beacon activation, voltage curves were also obtained which concluded that the sensor's performance is degrading with repeated uses, as well as with the sensor's reaction time with water.
4. Therefore, the reasons behind the degradation and failure of the device were analyzed with various characterization tools. The SEM and EDX data shows that a non-uniform oxide layer is forming on the Mg surface, and it is increasing with increase in number of uses of the sensor. The type of compounds i.e. MgO , $\text{Mg}(\text{OH})_2$ and MgCO_3 and their orientation at various levels on the Mg surface were confirmed with XPS, XRD and FTIR. The AFM technique confirmed that the oxide layer is non-uniform and the profilometer was used to measure the exact thickness of that layer. Overall, it was confirmed that the oxide layer is playing an important role in degrading the sensor's performance and is the major reason of sensor's failure.

6.2 Recommendations

1. The manufacturing of some of the components of the device is difficult which can be made easier with few design changes. One of the electrodes is made from the powdered graphite into a pellet shape and therefore is very fragile. It is very time consuming to prepare it and then assemble inside the sensor enclosure. This electrode can be replaced with other type of materials which can also work in a similar way for example: rigid graphite, mesh stainless steel sheets etc.
2. Moreover, the filter paper with legs at the bottom of the device to absorb water is hard to assemble, and it also torn off very easily when wet. The legs of the filter paper can be eliminated for easy assembly and the hole size at the bottom can be increased for increasing the water entrance.
3. The performance of the sensor can also be affected with the oxidation on the top surface of Mg (facing away from graphite) as it is seen from the results in section 5.6. Therefore, to avoid this problem, the top surface of the Mg sheet can be coated with some kind of corrosion-resistant materials to stop oxidation.
4. Various sensor failures are seen which are difficult to access. Some of them are due to the header pin issues in the electronics unit and some are because of the improper gluing of the parts. These problems can be fixed with careful manufacturing. However, some of the issues cannot be found directly by looking at them. It is suspected that maybe graphite thickness is changing after repeated use and therefore is no longer able to wet the filter paper at interface. Therefore, a test with increase in the thickness of the graphite pellet can be done.
5. It is also seen that after repeated uses, the filter paper sticks to the Mg sheet and maybe stopped getting wet on the next uses. Therefore, two filter papers can be placed at the interface to cover the gap, so that after some uses if one filter paper is stucked to Mg sheet then another filter paper can still perform its function to wet Mg disk.
6. The number of repeatability and performance can be enhanced by replacing Nordic BLE with other Bluetooth low energy technologies (for example Inplay nanoBeacon). Even the price of the device can also be reduced by using such a technology.

7. Moreover, one of the expensive parts in the device is the boost converter used to meet the energy requirements of the Beacon. It can be eliminated by producing more power by connecting sensors in series.

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Appendices

Appendix A: Materials Preparation for Sensor Unit

The sensor unit is basically the place where chemical reaction occurs. Therefore, this section of the device is the materials part that contains electrodes and electrolyte for the chemical reaction to produce electrical energy.

The Mg metal is AZ-31 alloy sheet of Mg that is purchased from “Buymetal.com” and graphite (particle size < 20 μ m) is purchased from Sigma Aldrich. The filter paper used are the “Whatman” filter paper. The paper cutting machine is purchased from “Cricut Inspiration” corporation.

A1. Preparation of Different Components

There are five parts of the sensor unit that contains two electrodes, a separating layer, a water absorbing layer and an electrolyte **Figure 48(a)**. The magnesium (Mg) metal sheet is used as an anode and a graphite pellet is utilized another electrode. A filter paper is acting as a separating layer in between both electrodes. Water is acting as an electrolyte for the redox reaction between both electrodes, and therefore another filter paper is used to absorb water to reach to those electrodes inside the packaging. Special preparation requirements for these parts are discussed below:

Anode (Mg): A Mg metal sheet is punched to prepare a specific size of Mg disks i.e. diameter - 19mm and thickness -1.5mm. These disks are then sanded from both sides with a sandpaper (400 grain size) to remove the protective coating for the proper reaction to occur and to maintain a stable electrical connection inside the plastic enclosure. After that, the sanded Mg disks are washed with ethanol and DI water, and then dried with the paper towel.

Graphite: This electrode is made from the graphite powder with micrometer sized particles. It is made in a circular pellet shape that contains 300mg of graphite powder and is compressed at 100N force from the tensile machine. A tri press mold is used to make three pellets at once **Figure 48(b)** with diameter - 17.2mm and thickness - 2.5mm.

Separating layer: This layer is made up of Whatman filter paper in circular shape with the size a little bigger than both electrodes. It is cut in a greater size so that there will not be any contact between both electrodes when placing them inside package to avoid short circuiting.

Water Absorbing Layer: This layer is also cut out of Whatman filter paper in a specific shape with the cricut machine. This layer is threaded out of the sensor unit through holes, so that it can absorb water and take it inside the package to complete the chemical reaction.

Electrolyte (Water): As explained in chapter 2, the sensor acts as a battery to produce electricity and it only works in the presence of water. The water acts as an electrolyte in the electrochemical reaction and therefore this device only produces power when contacts water (which makes it to be used as a water sensor). It can be any water i.e. tap water, DI water, Milli-Q water or sea water.

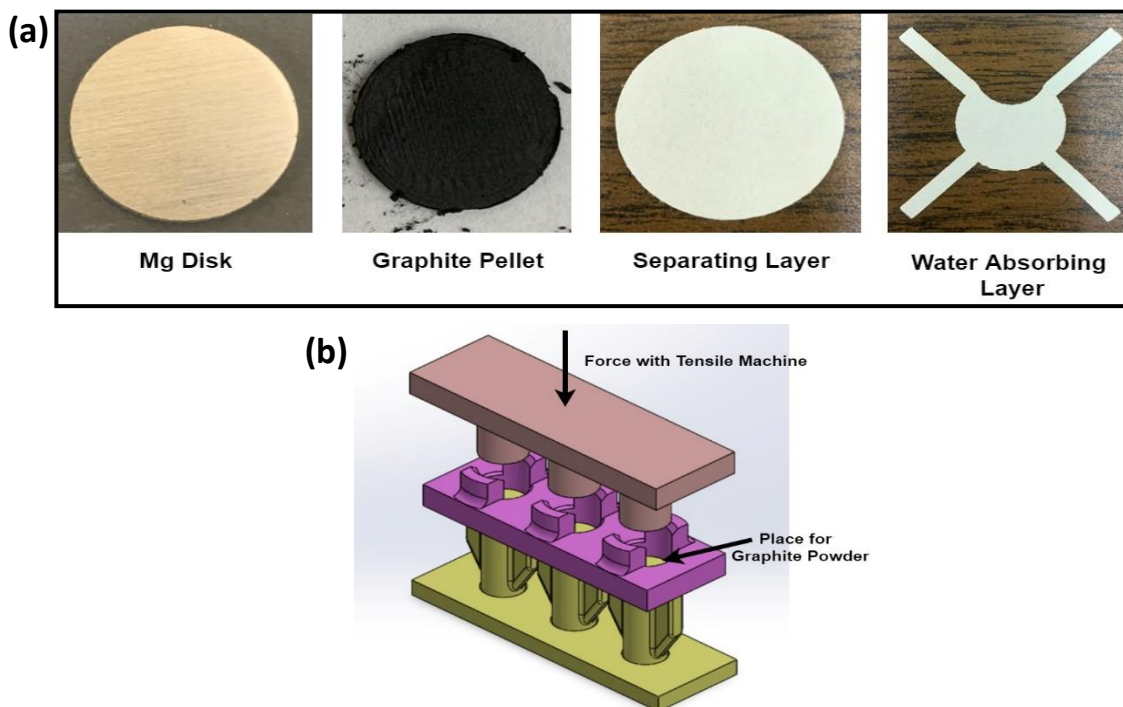


Figure 48: (a) Different materials to make the sensor unit (b) Tri press mold to make graphite pellets.

A2. Packaging of Materials Inside Sensor Enclosure

All the materials are packaged inside a plastic enclosure. The top and bottom of the enclosure has two metal contacts that makes electrical connection with both electrodes, Mg and graphite respectively **Figure 49(a)**. The step-by-step assembly of the sensor unit is shown in the **Figure 49(b)**. At first, the water absorbing layer (filter paper) is placed at the bottom and is threaded through the holes. After that, the graphite pellet is placed on the top of the filter paper very carefully since the pellet is very fragile. In the next step, a separating layer is positioned on graphite pellet and then the sanded Mg disk is

pushed from the top to fit inside the housing. Subsequently, the enclosure is closed with two screws on the top.

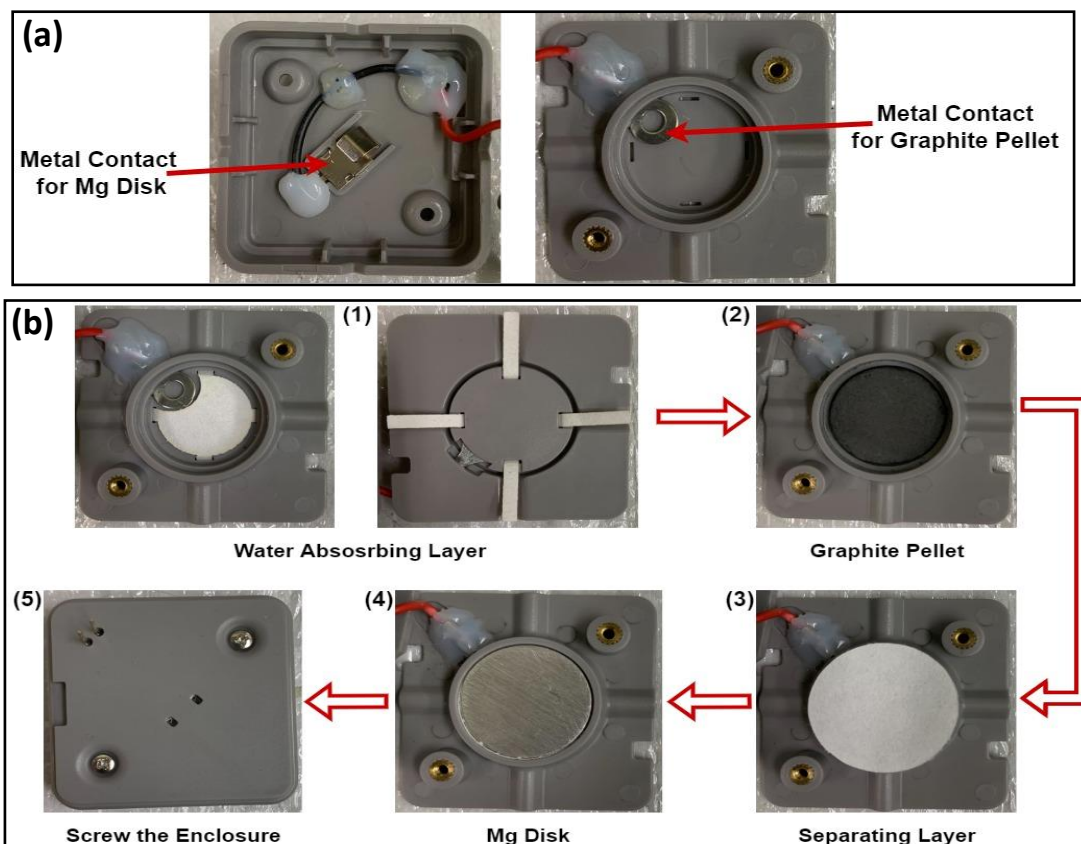


Figure 49: (a) Metal contacts for both electrodes; (b) Step by step assembly of the sensor unit.

Appendix B: Preparation of Electronics Unit

The electronics unit contains different electrical components that processes the power generated by the sensor unit and it also contribute to send the Bluetooth packets through a BLE chipset.

B1. Preparation of Different Components

All the electrical components are purchased from Digi key. The energy produced from the sensor unit is transferred to the electronics unit that has BLE chipset to send out the Bluetooth packets. There are various electrical components that are used to process the sensor's energy to a specific value which is required for the functioning of the BLE chipset. Two printed circuit boards (PCBs) are made to serve

the function of sending Bluetooth signal. The first board is the BLE board that comprises a main component i.e. BLE chipset that functions as sending the signal on activation, along with other small components such as capacitors, resistors, connectors etc. An additional PCB is made since the sensor alone cannot meet the power requirements of the BLE board. That board is named as energy harvesting board (EHB) and is used to enhance and regulate the power produced from the sensor unit. The main components of this board are “Boost Converter”, “Bulk Capacitor” and “Low Drop Out (LDO)”. The boost converter as the name suggests boosts up the sensor’s power. The increased power is then stored inside the bulk capacitor which is then regulated with the LDO.

The **Figure 50** shows the front and the rear view of EHB and BLE board. The EHB has an input connector **Figure 50(a)** and an output connector **Figure 50(b)**. Similarly, the BLE board has an input connector at the front side as well **Figure 50(c)**. The input of the EHB is the output of the sensor unit which is connected to it through a connector. The enhanced and the regulated output of EHB goes to the input of the BLE board.

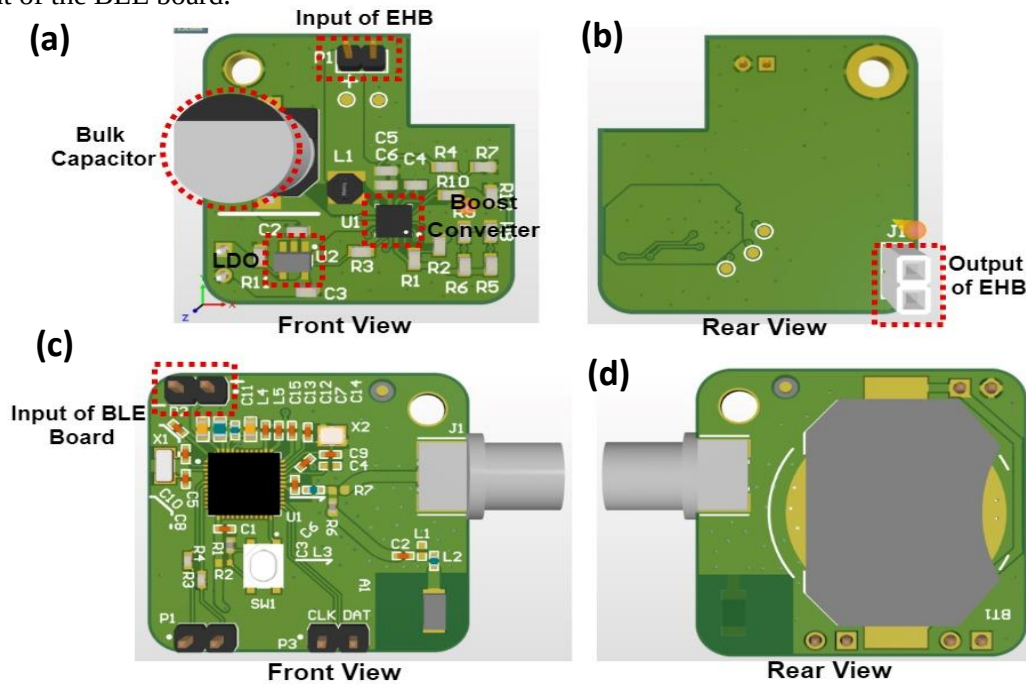


Figure 50: Layout of EHB (a) Front view, (b) Rear view; Layout of beacon board (c) Front view, (d) Rear view.

B2. Assembly of Sensor Unit with Electronics Unit

After preparing the materials and components for both units, they are assembled inside their respective housing and are connected with the connectors (**Figure 51**). Since the chemical reaction will start after

absorption of water, therefore the sensor unit is at the bottom of the device to absorb water through water absorbing layer (filter paper). Once the water reaches to the materials inside the sensor package, the redox reaction starts, and electrical energy is produced. The positive and negative header pins of the male connector in the sensor unit are connected to graphite and Mg respectively. This connector is connected with the female connector in the electronics enclosure to transfer power from the sensor to the electronics unit.

In the electronics unit, the EHB is placed at the bottom and the beacon board is connected with the connector pins from the top. Therefore, according to the orientation of the boards, the power transfer from the sensor to the EHB at first, and then the boosted and regulated power from the EHB transfer to the beacon board that sends the Bluetooth packets on activation (more details in chapter 4). The **Figure 4** shows the zoom in view of both units inside the enclosure.

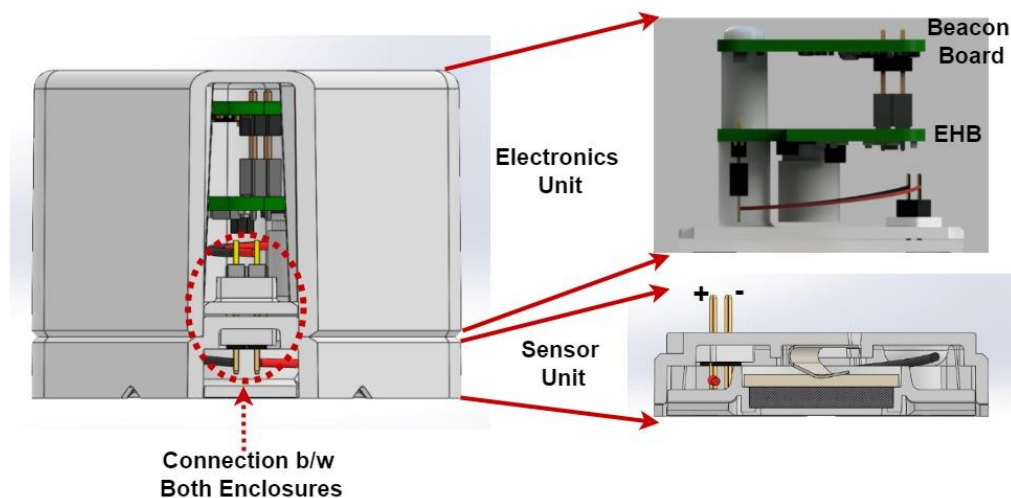


Figure 51: Electrical connection b/w sensor and electronics enclosure, and the zoom in view of the orientation of the components and PCBs inside the plastic housing.

Appendix C: Characterization with SEM/EDX

The Mg disk's surface is half protected from oxidation and other half is exposed to water for oxidation, by covering the protected area with scotch tape. The analysis of the sample is done with SEM and EDX after completing the reaction of the Mg disk with water. Both the surfaces (Mg and MgO) can be clearly distinguished from the SEM pictures **Figure 52(a)**. The line scan with EDX is also performed from the oxide to the Mg surface as shown in **Figure 52(b)**.

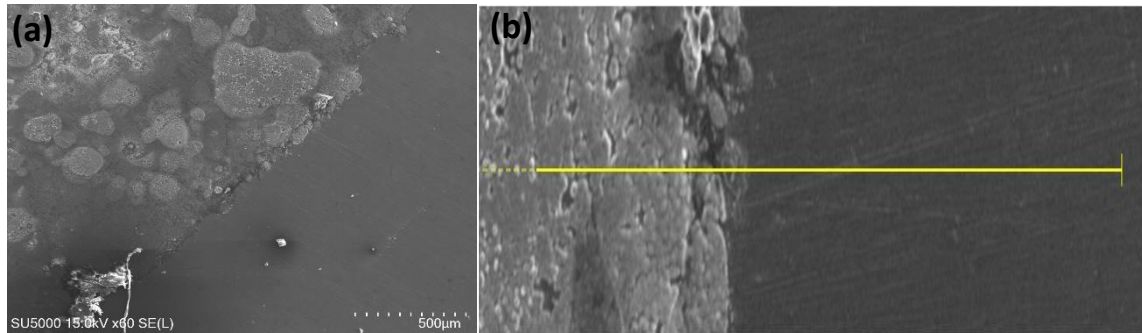


Figure 52: (a) SEM image of the half Mg and half oxide layer; (b) Area for line scan with EDX.

The EDX line analysis shows that the oxide surface has more oxygen content and less Mg content, however, the Mg surface is mostly Mg metal and very minute oxygen percentage **Figure 53**. This also confirms two different layers on the Mg disk's surface.

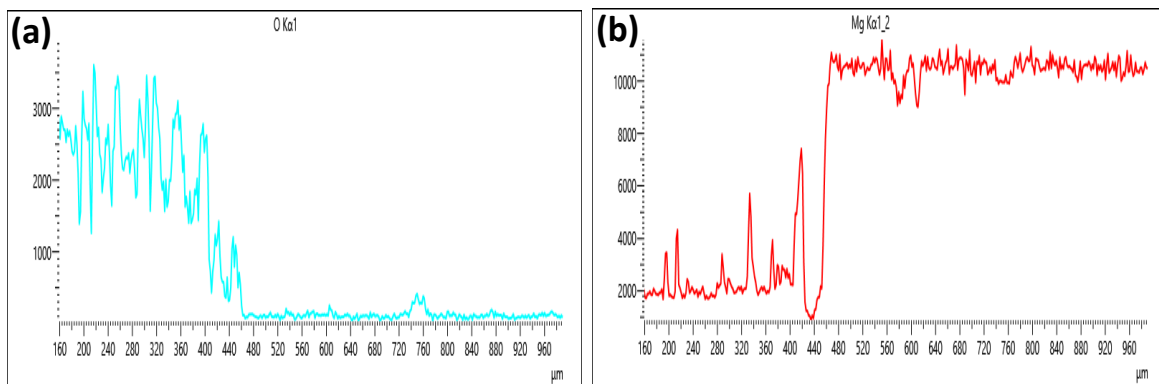


Figure 53: EDX line analysis for (a) O element and (b) Mg element.

Appendix D: Characterization with AFM

The thickness of the oxide layer was measured during this test. Since the sample surface was very rough on both Mg and MgO regions (**Figure 54(b)**), therefore, it was hard to tell the actual thickness of the MgO layer formed on the Mg surface. As shown in the (**Figure 54(a)**), the “Section Analysis” was performed, and two arrows (red) were placed on the darker and brighter surface to approximate the height of the oxide layer. From the vertical distance measurement, it is estimated that the thickness is 379.43 nm which is not entirely true due to the roughness of the surface. Due to the same reason,

3D picture also does not show the step height of the oxide layer and the whole surface looks the same **(Figure 54(c))**.

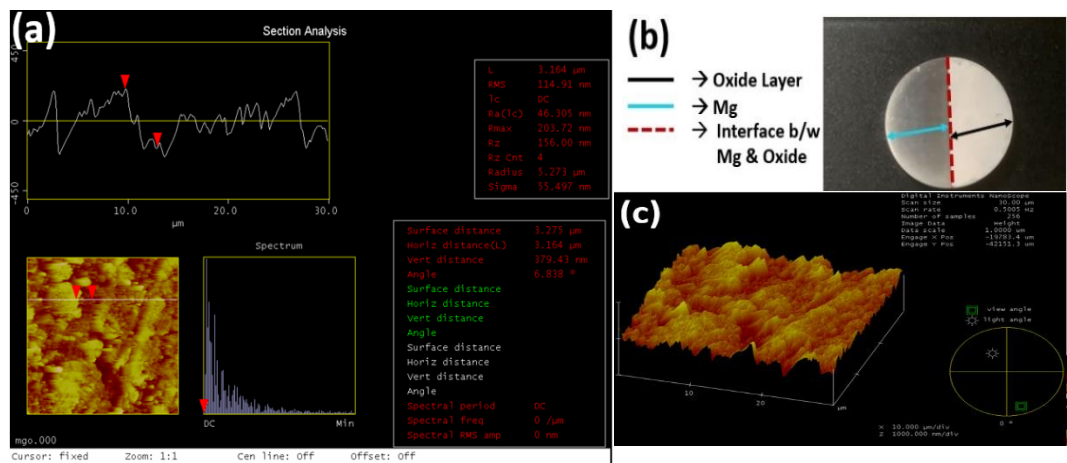


Figure 54: (a) Thickness measurement of the MgO layer; (b) Picture of the sample taken with camera showing two regions (Mg & MgO); (c) 3D picture of the same sample.