Lappeenranta-Lahti University of Technology
LUT School of Energy Systems
Degree Programme in Electrical Engineering

Ricky Cherian Bijoy

Analysis of Electrochemical Impedance Spectra in the context of Polymer Electrolyte Membrane Water Electrolysis

Master Thesis

Examiners : Prof. Dr.-Ing. Jero Ahola

Prof. Dr.-Ing. Richard Hanke-Rauschenbach

ABSTRACT

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The working of a Polymer Electrolyte Membrane (PEM) electrolysis cell is discussed and a graphical representation analysis of the equivalent circuit impedance is carried out. This helps to provide a comprehensive grasp on the fundamentals and on the factors affecting the changes in the electrochemical impedance spectra. The polarization curve of an electrolysis cell is essential for understanding these variations. Furthermore, an experiment is done on a PEM electrolysis cell at 80°C with a Nafion 117 membrane and data was collected after 50 h and after 500 h of operation for different current densities. The knowledge gained from the initial analysis of the electrolysis cell is employed to explain the impedance spectra obtained from the experiment. The conclusions derived are then used for the formulation of correction factors to obtain the modified parameters of the electrolysis cell equivalent circuit which could prove useful in the long run in reducing the challenges faced while working with PEM electrolysis cells.

PREFACE

This thesis was completed in the Department of Electrical Energy Storage Systems in Leibniz University Hannover (LUH). I would like to thank my examiners Professor Jero Ahola and Professor Richard Hanke-Rauschenbach for the intriguing topic and feedback on this work. I would also like to thank my supervisor Agate Martin for all the help I received during my thesis work. My third and final thanks is to my colleagues, friends, and family.

Hannover, October, 2020

Ricky Cherian Bijoy

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Nomenclature

H_2	Hydrogen molecule
O_2	Oxygen molecule
e^-	eléctron
Pt	Platinum
Ir	Iridium
V	Cell voltage
E	Cell emf
R, R_1, R_2, R_3	Resistance
C, C_2, C_3	Capacitance
L, L_4	Inductance
R_m	Polymer membrane resistance
R_a	Anode transfer charge resistance
R_c	Cathode transfer charge resistance
C_a	Anode double layer capacitance
C_c	Cathode double layer capacitance
Z, Z_R, Z_L, Z_C	Complex Impedance
Z_{Re}	Real part of complex impedance
Z_{Im}	Imaginary part of complex impedance
ω	Frequency
θ	Phase angle of complex impedance
τ	Time constant of RC unit

f	Characteristic frequency
H/A	Heat evolution per unit area
I/A	Current density
t	Time

List of Acronyms

PEM	Polymer Electrolyte Membrane or Proton Exchange Membrane
EIS	Electrochemical Impedance Spectroscopy
OER	Oxygen Evolution Reaction
HER	Hydrogen Evolution Reaction
OCV	Open Circuit Voltage
AC	Alternating current
DC	Direct current
CD	Current Density

1. Introduction

Nowadays, with the increasing acceptance and eventual demand of green renewable energy around the world, it is not enough to depend on one source of energy. Solar panels, wind turbines, tidal farms, hydroelectric power dams are some of the ways to harvest the renewable energy that is available. Since most of these sources are dynamic in nature, it is important to have a more reliable source as a backup. This means there is still some dependence on conventional forms of energy. The aim of researchers is to reduce this dependence over time.

PEM (Polymer Electrolyte Membrane or Proton Exchange Membrane) water electrolysis is the topic of discussion in this thesis. A molecule of water can be split into its individual hydrogen and oxygen molecules with the introduction of electric current. These hydrogen and oxygen gases can then be separately stored for future use. The stored hydrogen is mainly used in hydrogen fuel cells that could ultimately revolutionize the automobile industry. Hydrogen is also used as a source of power supply for areas not connected to the grid and plays a major role in rocket fuel owing to the fact it has more concentrated energy [5]. The PEM is used to divide the anode and the cathode half cells and acts as insulation for the electrodes. It allows for the transport of hydrogen ions or protons while an external circuit carries the electrons. The main advantages of this form of water electrolysis are gas purity owing to the low crossover of gases which depends on a number of factors, and functionality at high current densities. However as the research done on this topic is believed to be less, many of the challenges related to its use are yet to be determined.

Such electrochemical systems can be characterized by a method called electrochemical impedance spectroscopy (EIS) for interpretation. Basically, an electrical equivalent circuit is used to determine the electrochemical impedance which can be further subjected to interpretation based on different parameters. This, however, is sensitive to errors as different electrochemical processes with the same time constant parameters could overlap. Observing the variations in the impedance spectra and understanding the reasons for its behavior could help in eliminating any similar errors in the future.

When considering an equivalent electrical circuit for the electrochemical process, some of the elements used are resistors, capacitors, Warburg diffusion elements and constant phase elements. The impedance of an electrode can be represented by a resistance (charge transfer resistance) and capacitor (double layer capacitance) connected in parallel while the polymer membrane is represented by another resistance. The real and the imaginary parts of the resulting impedance could be calculated for a particular range of frequency. There are two plots associated with EIS – Nyquist and Bode plots. The Nyquist plot is the variation of the imaginary part of the impedance with the real part over a frequency range while the Bode plot shows the variation of the magnitude and the phase of the impedance over the same frequency range.

The aims of this thesis include simulation of electrochemical impedance spectra of PEM electrolysis cells using simple equivalent circuits to get an idea of the working of these systems; variation of parameters to investigate interferences and understand the causes behind the changes; identification of interpretation errors and their causes by comparing simulated spectra with experimental spectra and the measurement of “correction factor” to reduce interpretation errors in future. The measurement of this correction factor could not however be carried out due to limitations brought about by the CoVid-19 outbreak. Achieving these aims leads to a better understanding of a PEM WE cell and greater knowledge on results obtained from an EIS analysis of the aforementioned cell which could be exploited in the future in the development of an improved PEM WE cell with reduced losses and improved production of both hydrogen and oxygen.

2. Theoretical Fundamentals

The theoretical fundamentals of a PEM WE (water electrolysis) cell and EIS are discussed in this chapter. First, the working of the cell is studied along with the reactions that take place in the cell. Then the basics of EIS are described to give a clear idea going forward in the report.

2.1 Fundamentals of PEM WE

2.1.1. PEM WE cell

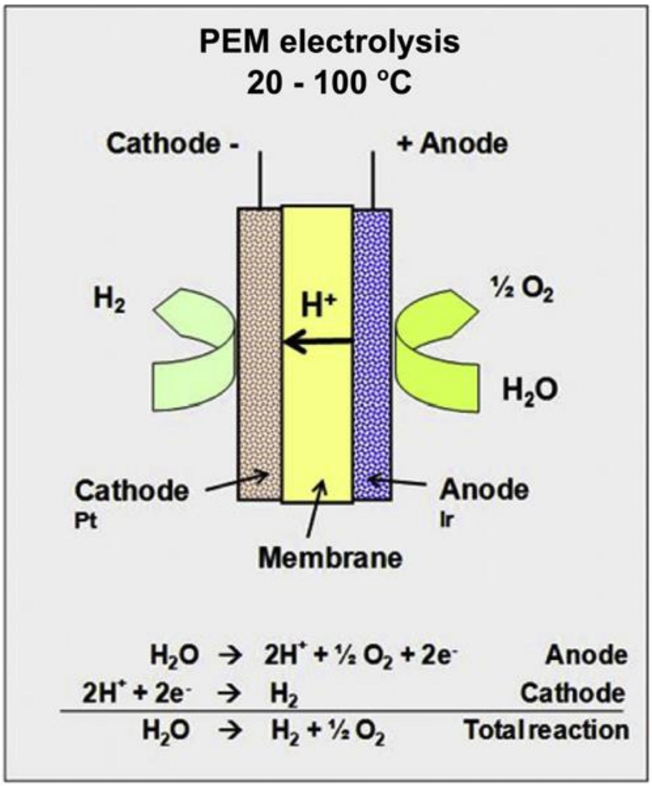


Figure 1: PEM Electrolysis cell [1]

Figure 1 shows the working of a PEM water electrolysis cell. When electricity is passed, the water molecule splits into protons, oxygen and electrons at the anode, while the protons crossover the membrane to the cathode to combine with electrons, through an external connection and form gaseous hydrogen. The reactions taking place at the anode and the cathode are called Oxygen Evolution Reaction (OER) and Hydrogen Evolution Reaction (HER) respectively. The overall cell reaction can be represented as follows

$$2H_2O \rightarrow 2H_2 + O_2 \quad (1)$$

The OCV (open circuit voltage) of the model is calculated to be between 1.75 V and 2.2 V for a temperature range of 50℃ to 80℃ and a pressure less than 30 bar [1].

2.1.2. Performance of the PEM water electrolysis cell

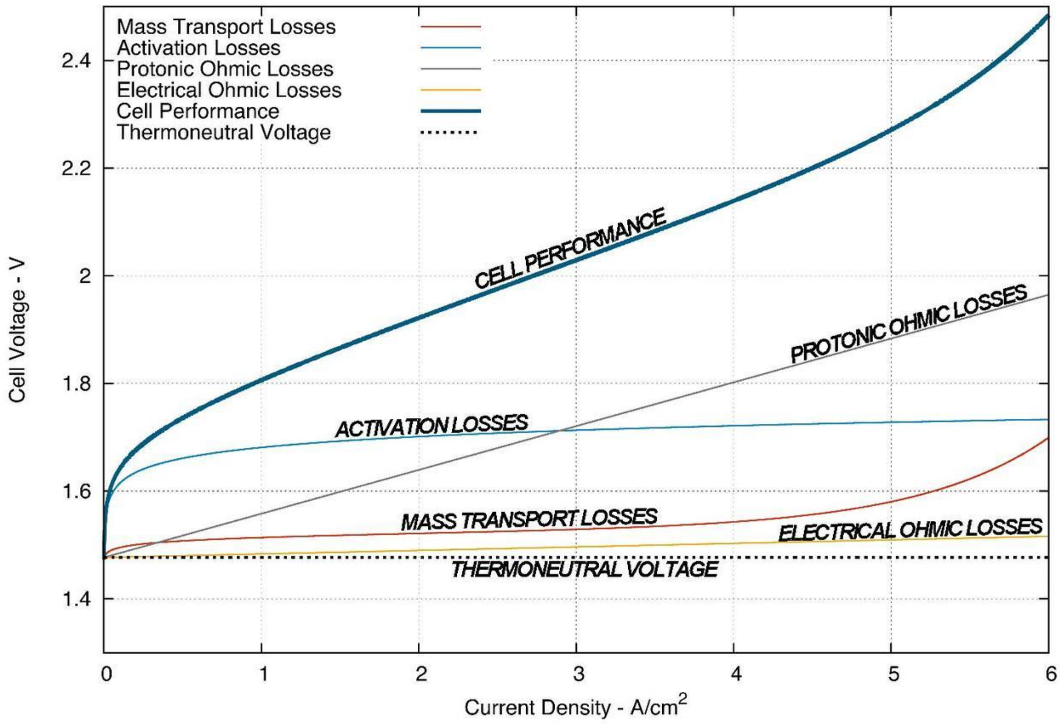


Figure 2: Polarization curve of a PEM WE cell [1]

The polarization behavior of an electrolysis cell can be determined by plotting the cell voltage against the current density. The voltage of the cell is expressed by

$$V_{cell} = E + V_{ohm} + V_{trans} + V_{act} \quad (2)$$

The main losses include ohmic, transport and activation losses. Ohmic losses are due to the internal resistance of the components of the cell and transport of charges through the membrane. Activation losses are due to the activation overpotential that needs to be applied for current flow. The cell performance is divided into three regions. The steepest portion of the curve represents the activation/kinetic polarization. The next linear portion is the dominated by ohmic polarization losses and the last portion falls in the concentration polarization region.

As observed from the graph, the cell voltage that needs to be applied increases with an increase in the current density. This is because as the current density increases, the current through the cell increases and as a result, the voltage losses also increase. The area under the polarization curve shows the power input per square centimeter of the cell.

2.2. Fundamentals of EIS

Electrochemical reactions are chemical reactions that take place in the presence of an electric current. In electrochemical reactions, the transfer of charges occurs at the surface of the electrodes. So, these reactions include transfer of mass to the electrodes from the solution, charge transfer at the surface of the electrodes and resistance of the electrolyte or the membrane in use. These processes can be represented in the form of an electrical circuit. Impedance spectroscopy is a technique in which each component in the circuit can be extracted to give an idea about the characteristics of an electrochemical reaction. By subjecting an AC amplitude signal with varying frequency to a stable DC signal (or at open circuit voltage), the change in the impedance can be noted after scanning the frequency which would lead to the values of the components being obtained.

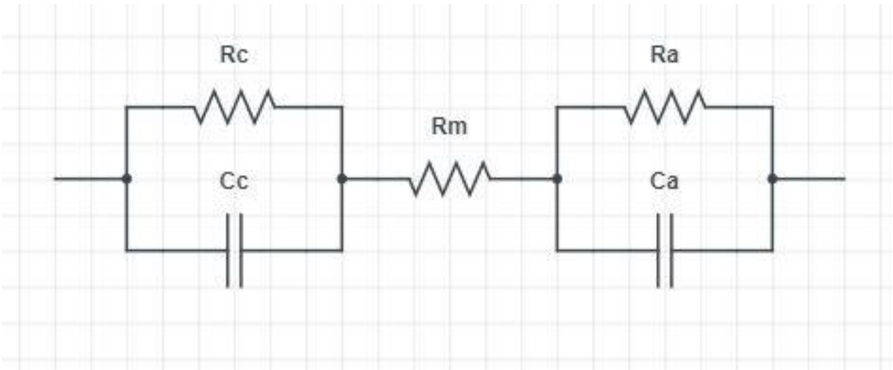


Figure 3: An equivalent circuit representing a PEM WE cell

Figure 3 shows a typical model of a PEM WE cell with the resistance and the capacitance of the cathode being denoted by R_c and C_c, membrane resistance as R_m, and the resistance and the capacitance of the anode being R_a and C_a. The two RC units represent the electrode resistances and the double layer capacitances of the two electrodes of the cell. While considering an experimental setup of a PEM WE cell, the inductance (L) of the cable connections is also considered.

The introduction of an AC signal means the impedance of each component of the circuit has to be taken into account. In an AC circuit, the current and the voltage have the same phase shift for a resistor. The current leads the voltage by a phase angle of 90 degrees for a capacitor and the voltage leads the current by a 90 degree phase angle for an inductor [2]. The equations for the impedance of each component are given in the next section. Impedance is expressed as Z which is a complex unit and represents both the real and the imaginary values of the parameters as the complex plane is a two-dimensional plane with both the real and the imaginary axes.

2.2.1. AC Impedance in the complex plane

The AC Impedance of a resistance (Z_R), capacitance (Z_C) and inductance (Z_L) can be expressed by the following equations respectively,

$$Z_R = R \qquad (3)$$

$$Z_C = \frac{1}{i\omega C} \qquad (4)$$

$$Z_L = i\omega L \qquad (5)$$

where ω is the frequency of the AC signal and i is the imaginary constant.

And the phase angle of the equivalent impedance is given by

$$\theta = \tan^{-1}\left(\frac{Z_{im}}{Z_{re}}\right) \qquad (6)$$

where Z_{im} (imaginary part of the impedance) is the sum of Z_C and Z_L and Z_{Re} (real part of the impedance) is Z_R in a scenario where just these three components are present.

When Figure 3 is considered, we get the following equations by using Eq. (3) and (4),

$$Z_{re} = R_m + \frac{R_c}{1+\omega^2 C_c^2 R_c^2} + \frac{R_a}{1+\omega^2 C_a^2 R_a^2} \qquad (7)$$

$$Z_{im} = i\left(-\frac{\omega C_c R_c}{1+\omega^2 C_c^2 R_c^2} - \frac{\omega C_a R_a}{1+\omega^2 C_a^2 R_a^2}\right) \qquad (8)$$

As evident by the equations (7) and (8), it can be observed that at low frequencies, the imaginary part of the impedance can be neglected and at high frequencies, the imaginary part approaches zero and can again be neglected.

The imaginary impedance is zero at high frequencies which gives the value of effective impedance as R_m. The effective impedance is the sum of R_m and R_{ct} (charge transfer resistance) at low frequencies from which R_{ct} can be obtained. R_{ct} is the sum of R_c and R_c. And the product of R_cC_c is obtained from the frequency which shows the maximum imaginary impedance. By using different combinations, it is possible to obtain all the parameters of the circuit.

2.2.2. Graphical representation of EIS

By using the above equations to calculate the equivalent impedance and the phase angle, they can in turn be used to plot Im(Z) vs Re(Z) and |Z| and θ vs frequency graphs. The following figures show the respective plots of a parallel RC circuit.

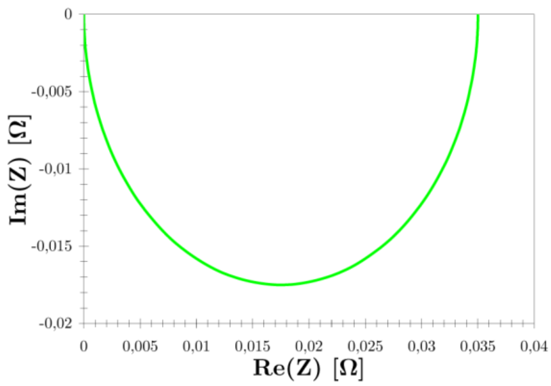


Figure 4.1: Nyquist plot [4]

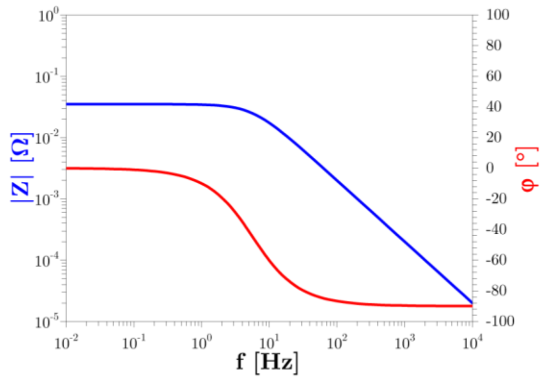


Figure 4.2: Bode plot [4]

Figure 4.1 shows the Nyquist plot of a parallel RC circuit is always a semi-circle. The circuit acts as a resistor at low frequency and as a capacitor at high frequency. The right part of the curve starts at zero frequency ending at high frequency on the left. The width of the semi-circle is equal to the resistance value.

In Figure 4.2, the phase angle decreases with increasing frequency which shows how the behavior of the circuit becomes more capacitive in nature over time. The magnitude remains constant for a while after which it goes down and then again becomes constant with increasing frequency.

The graphical representation varies with a change in the value of the parameters in the circuit and also with the different combinations of the components used in the circuit. By observing these changes among the different variations gives an idea of how each variation affects the respective characteristics. This knowledge can then be utilized in an experimental set-up to understand the change in the characteristics and the circuit can be modified to counter the effects of the variations.

3. Simple Equivalent Circuit

A typical electrolysis model with two electrodes and a membrane in between can be broken down into simple electrical elements and formed into an equivalent circuit.

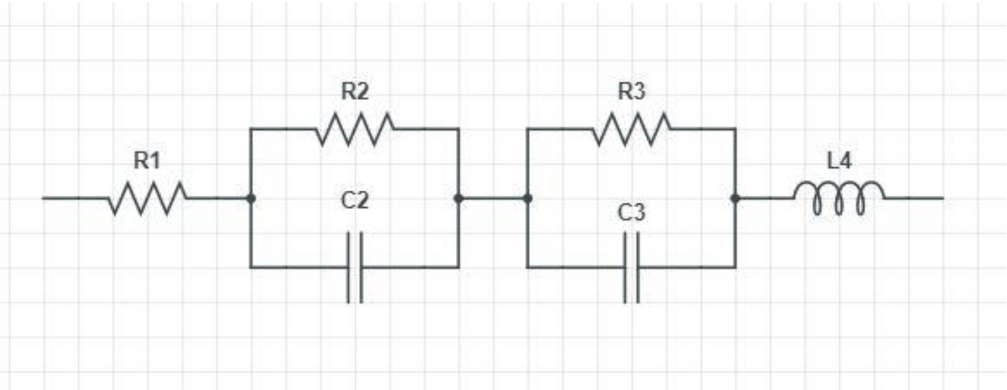


Figure 5: Electrolysis model circuit

As seen in Figure 5, the parallel RC couplings represent the electrodes and the other resistance and inductance represent the membrane and the cable (for the measurement setup) respectively.

The equivalent impedance of this circuit can be obtained by using the AC impedance equations.

$$Z = Z_{re} + Z_{im} \tag{9}$$

$$Z_{re} = R_1 + \frac{R_2}{1+ \omega^2 C_2^2 R_2^2} + \frac{R_3}{1+ \omega^2 C_3^2 R_3^2} \tag{10}$$

$$Z_{im} = i\left(- \frac{\omega C_2 R_2}{1+ \omega^2 C_2^2 R_2^2} - \frac{\omega C_3 R_3}{1+ \omega^2 C_3^2 R_3^2} + \omega L_4\right) \tag{11}$$

$$|Z| = \sqrt[2]{{Z_{re}}^2 + {Z_{im}}^2} \quad (12)$$

$$\theta = \tan^{-1}\left(\frac{Z_{im}}{Z_{re}}\right) \quad (13)$$

$$\tau = RC \quad (14)$$

$$f = \frac{1}{2\pi\tau} \quad (15)$$

A mathematical analysis of Eq. (9) to Eq. (13) is done. The equivalent impedance in Eq. (9) is the sum of the real and the imaginary parts of the impedance in the complex plane. The real part of the impedance depends on the parameters R_1, R_2, R_3, C_2, C_3 as seen in Eq. (10) and ω while the imaginary part of the impedance depends on R_2, R_3, C_2, C_3, L_4 and ω as seen in Eq. (11). A change in the ohmic resistance R_1 has no effect on the imaginary part of the impedance while a change in the inductance L_4 has no effect on the real part of the impedance. At low frequencies, the terms with a capacitance parameter dominate, while at high frequencies, they become negligible. The magnitude of the complex impedance is calculated by taking the square root of the sum of squares of the real and imaginary parts of the impedance as showed in Eq. (12). This value has a maxima and a minima depending on the frequency. The phase angle of the impedance is calculated in Eq. (13). An increase in the imaginary part or a decrease in the real part of the impedance leads to an increase in the phase shift and vice-versa. Eq. (14) and Eq. (15) are used to calculate the time constant 'τ' and the characteristic frequency 'f' of an RC unit which are useful in the EIS analysis of the PEM WE cell. A variation in either the resistance or the capacitance of the RC unit affects the time constant and furthermore the characteristic frequency of the RC unit. An increase in either parameters leads to an increase in the time constant and a decrease in the characteristic frequency and vice-versa.

4. MATLAB model of the equivalent circuit

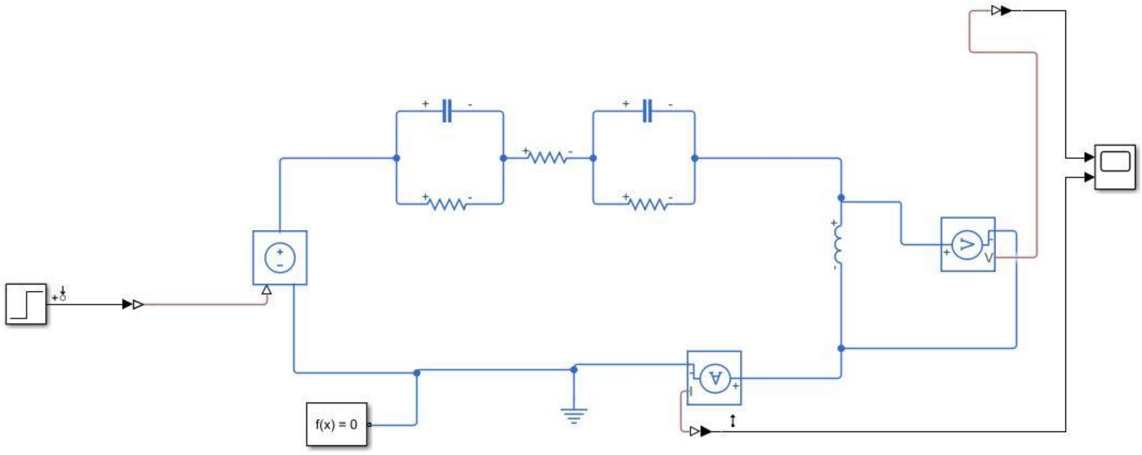


Figure 6: MATLAB model of an equivalent circuit of a PEM WE cell

The above figure shows the MATLAB model of the simple equivalent circuit. A MATLAB model is required to calculate the impedance of the circuit and plot the respective EIS curves from which datasets are extracted for further analysis. A controlled voltage source is connected to the circuit to which a step signal can be given to obtain the impedance characteristics. An ammeter and a voltmeter are connected to measure the current and the voltage respectively (at a given time) which are in turn connected to a scope to show the measured values. As the frequency cannot be changed during simulation, the step response of the model is plotted initially following which a frequency range is set to obtain the model transfer function. This transfer function is then used to plot the Nyquist and Bode graphs using a specific set of commands. The following commands are used to plot the respective graphs and export the data.

```
w1=logspace(6,-4,501);
nyquist(sys1,w1)
[re1,im1,wout1]= nyquist(sys1,w1);
writematrix(re1,'nyrel.dat','Delimiter',';');
writematrix(im1,'nyim1.dat','Delimiter',';');
```

Nyquist plot MATLAB commands

```
w=logspace(-4,6,501);
P=bodeoptions;
P.PhaseUnits='rad';
sys1=tf(linsys1);
[mag,phase,wout] = bode(sys1,w,P);
writematrix(phase,'bodephase1.dat','Delimiter',';')
```

Bode plot MATLAB commands

5. Circuit Analysis

5.1. Analysis with base parameters

In this section, an analysis of the circuit is done with a fixed set of parameters. The results then obtained are considered as the benchmark against which future results would be compared. Some circuit parameters from an appropriate range are selected to be analysed.

$R_1 = 0.15\ \Omega$	$C_2 = 0.1\ \text{F}$
$R_2 = 0.04\ \Omega$	$C_3 = 0.1\ \text{F}$
$R_3 = 0.16\ \Omega$	$L_4 = 0.1\ \mu\text{H}$

A frequency range of 0.001 – 100000 Hz is set to plot the graphs.

5.1.1. Nyquist plot

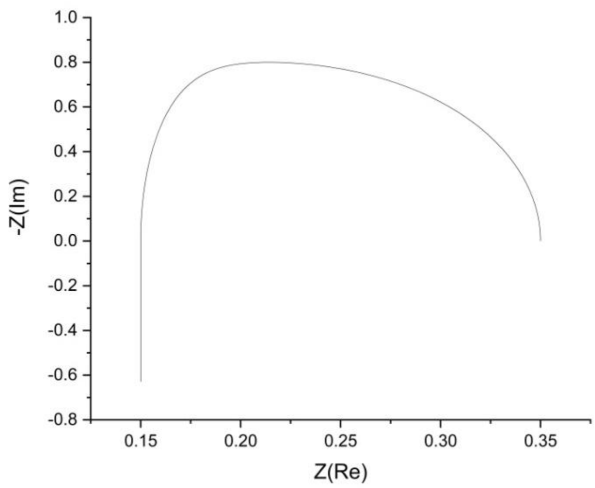


Figure 7: Imaginary vs Real Impedance (in ohms)

The above figure shows the variation of the imaginary part of impedance with the real part with an increase in frequency from right to left. The initial shift in the curve on the x-axis is because of the lone resistance component in the electrical circuit. The part of the curve in the negative y-axis represents the inductance in the circuit. The semi-circle part of the curve is due to the RC couplings. Since the time constants of the two couplings are almost similar, there are no distinct semi-circles. The width of the semi-circle is the sum of the electrode resistances.

5.1.2. Bode plot

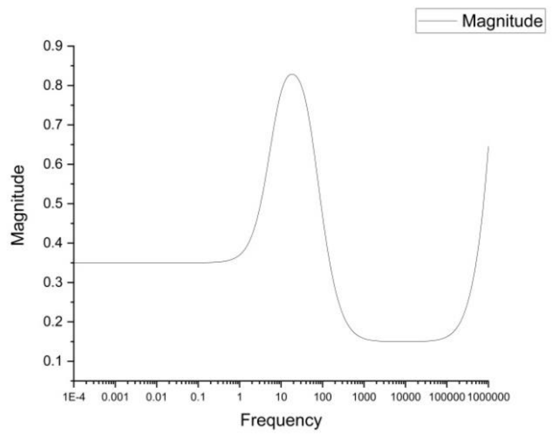


Figure 8.1: Magnitude vs Frequency (Hz)

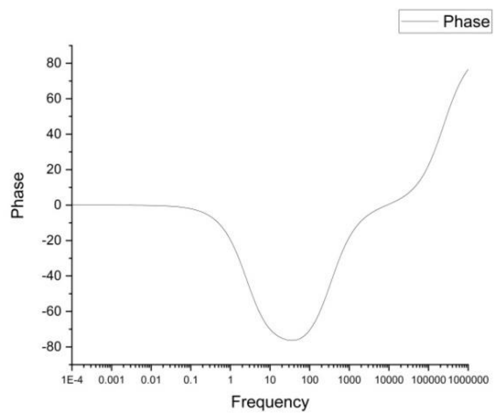


Figure 8.2: Phase vs Frequency (Hz)

In Fig.7.1, the magnitude remains constant before 1 Hz, peaking between 10 and 100 Hz after which it remains the same again before increasing at very high frequencies. From Eq. (10) and (11), it can be observed that at low frequencies, the variables with ω can be neglected, thus resulting in a constant magnitude followed by a sudden rise with an increase in the frequency. After reaching the peak, the curve decreases suddenly with further increase in frequency and reaching a lower stable magnitude value as the imaginary part of the capacitances cancel out that of the inductance. The curve then again attains a steep rise at very high frequencies as the imaginary part of the inductance impedance becomes significantly larger than that of the capacitances.

In Fig.7.2, phase remains constant before 1 Hz after which there is a peak minima mirroring the effect of the capacitances on the model. The curve then goes up at very high frequencies because of the inductance. As the curve moves away towards a negative value from a phase angle of zero, the circuit becomes more and more capacitive in nature and vice-versa. This is evident from the Eq. (12) and (13). The imaginary part of the impedance has a much lower value than the real part initially which leads to a negative phase angle which increases after the minima as the increase in frequency leads to a much larger imaginary part.

Both figures have the maxima and the minima at approximately the same frequency.

5.2. Analysis with single parameter variation

In this section, different parameters of the components of the circuit are varied randomly to ascertain their effects on the circuit which is visible in the graphical representation. The changes observed with the variation of the parameters are compared to the results obtained with the base parameters. Initially, parameters are varied individually and the characteristics are compared followed by the variation of more than one parameter at a time.

5.2.1. Variation in R_1

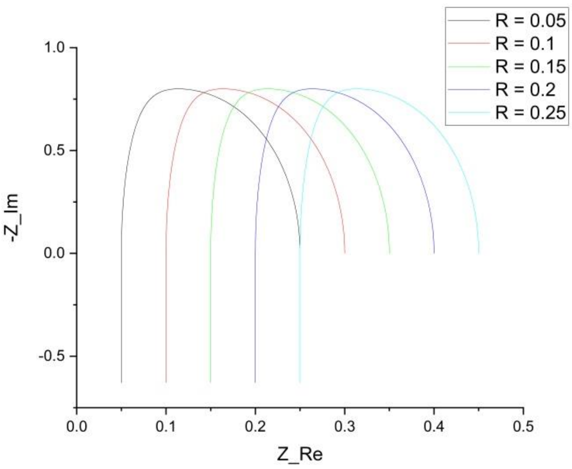
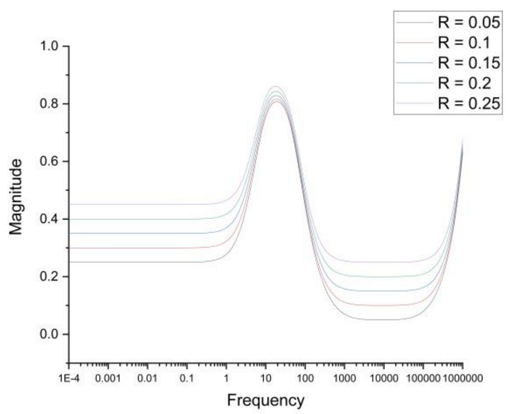


Figure 9: Imaginary vs real impedance (in ohms)

The Nyquist curve in Fig.9 shifts to the right with an increase in the resistance. From Eq. (10) and (11), it can be seen that an increase in R_1 only affects the real part of the impedance while the imaginary part remains unchanged. The shape of the curve remains unchanged.



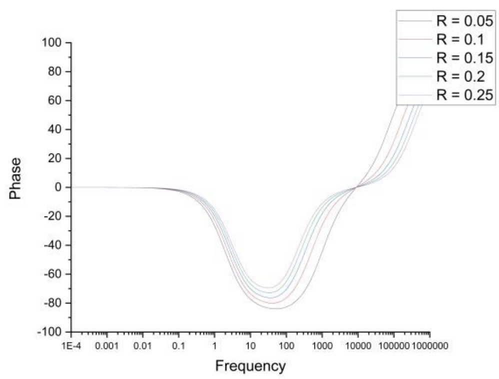


Figure 10.1: Impedance magnitude vs Frequency

Figure 10.2: Phase vs Frequency

In Fig.10.1, the curve shifts upwards with an increase in the resistance. From Eq. (12), it is clear that the impedance magnitude increases as the resistance increases. The curve in

Fig.10.2 also shifts upwards towards a positive phase angle with an increase in the resistance and can be seen from Eq. (13) as the phase shift decreases with an increase in Z_{Re}. There is a frequency shift of the minima towards the left and the curves are more separated at mid and high frequency regions as the capacitance terms in Eq. (10) and Eq. (11) become smaller.

5.2.2. Variation of R_2

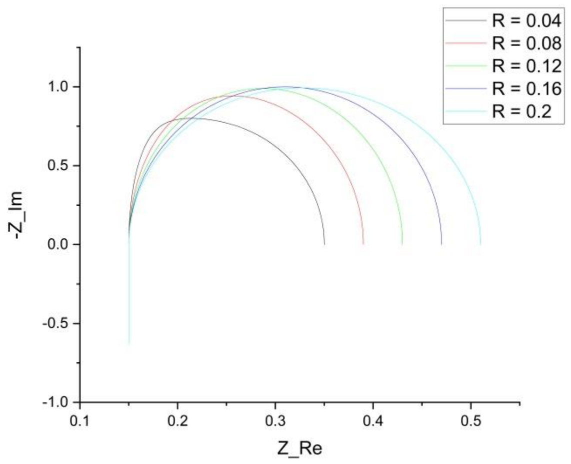


Figure 11: Imaginary vs real impedance (in ohms)

The increase in R_2 leads to an increase in the real part of the impedance while the change in the imaginary part is negligible. In Fig.11, the curve gets bigger with an increase in the resistance.

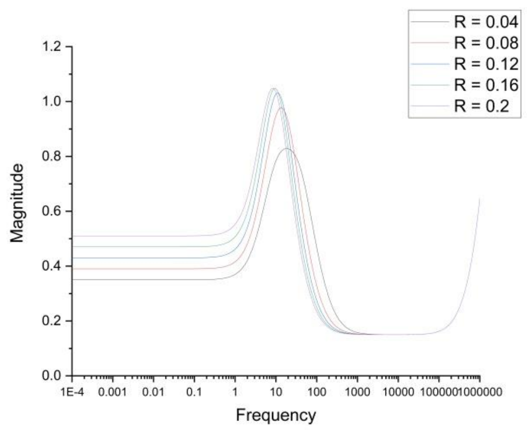


Figure 12.1: Impedance magnitude vs Frequency

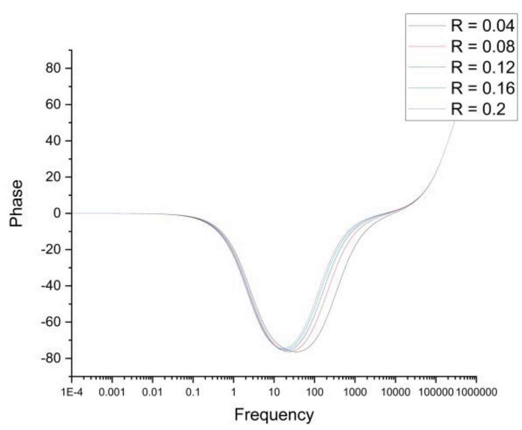


Figure 12.2: Phase vs Frequency

There is a shift in the curve upwards in the low and mid frequency region in Fig.12.1 with an increase in R_2. As the resistance increases the overall magnitude also increases but there is no change in the curve in the high frequency region. In Fig.12.2, the curve shifts upwards as the negative phase shift decreases along with a minima shift with an increase in the resistance.

5.2.3. Variation of R_3

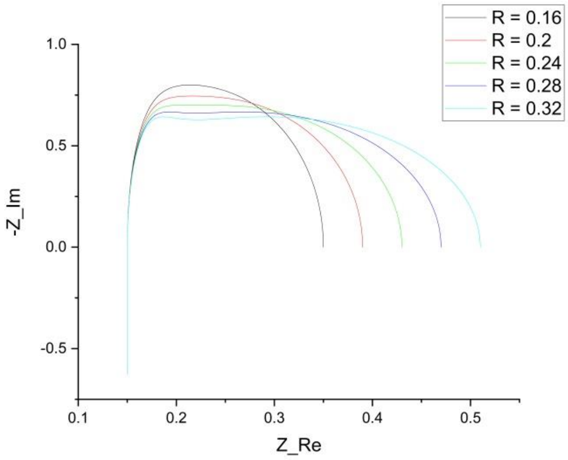


Figure 13: Imaginary vs real impedance (in ohms)

In Fig.13, the Nyquist curve gets flattened and more distorted with an increase in the resistance. Since the time constants are more or less the same with the base parameters, there is just one visible maxima. As the resistance increases though, the difference in the time constants gets bigger and this results in the beginning of the formation of two maxima.

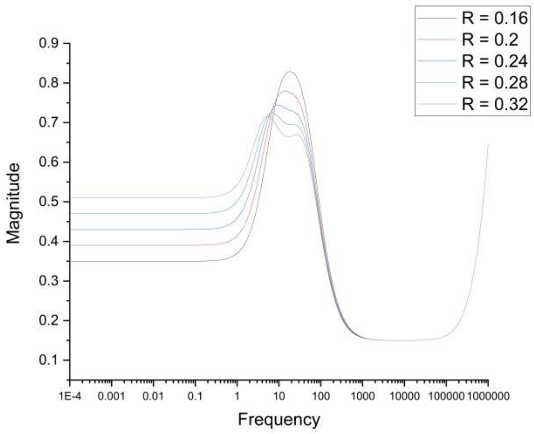


Figure 14.1: Impedance magnitude vs Frequency

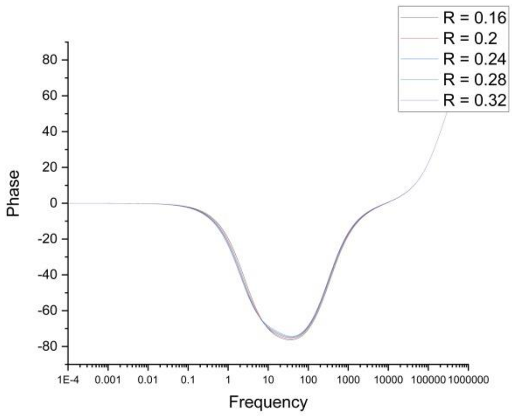


Figure 14.2: Phase vs Frequency

The increase in the resistance leads to the shifting of the curve upwards at low frequencies in Fig.14.1 along with the formation of two peaks that is consistent with the observations made from the Nyquist plot. This is because the terms with R_3 in Eq. (10) and Eq. (11) only affect the overall equation at low frequencies. There is also a slight shift of the curve in Fig.14.2 upwards as the negative phase shift decreases with an increase in the resistance.

5.2.4. Variation of C_2

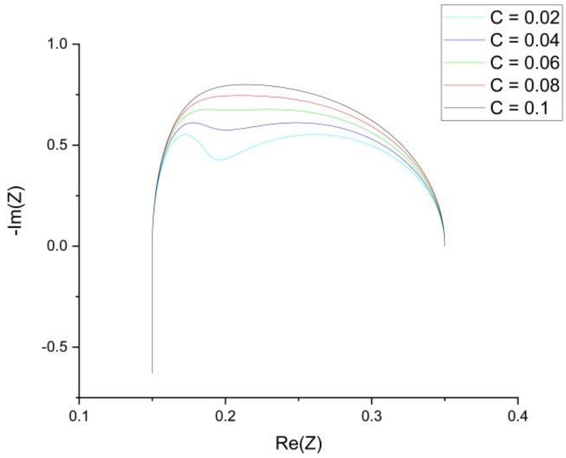
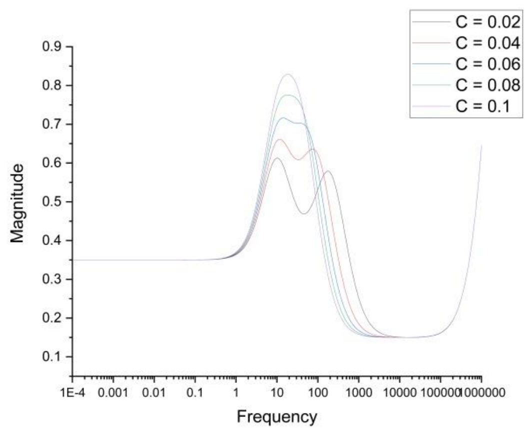


Figure 15: Imaginary vs real impedance (in ohms)

The decrease in the capacitance in Fig.15 results in a lower time constant as seen from Eq. (14) and the difference between the two time constants increases which leads to the formation of two maxima. The curve shifts downwards with a decrease in the capacitance.



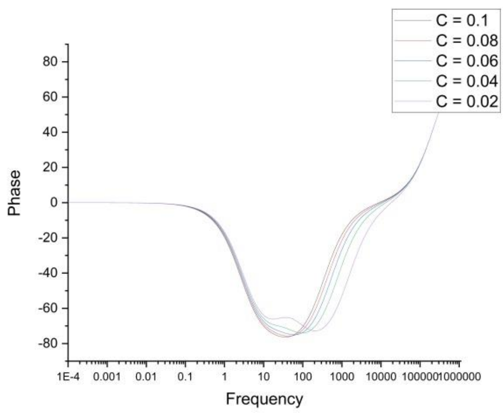


Figure 16.1: Impedance magnitude vs Frequency

Figure 16.2: Phase vs Frequency

In Fig.16.1, there is a formation of two maxima with the decrease in the capacitance. The curve remains unchanged in the low frequency region while the change occurs in the mid and high frequency region. This can be attributed to the terms with C_2 in Eq. (10) and Eq. (11) that affect the Eq. (12) at high frequencies. A similar observation can be derived from the Bode plot in Fig.16.2. There is also a shift of the curve upwards and to the right as the negative phase shift decreases with the decrease in capacitance. From Eq. (15) it can be deduced that this decrease causes a shift of the minima to the right due to an increase in the characteristic frequency.

5.2.5. Variation of C_3

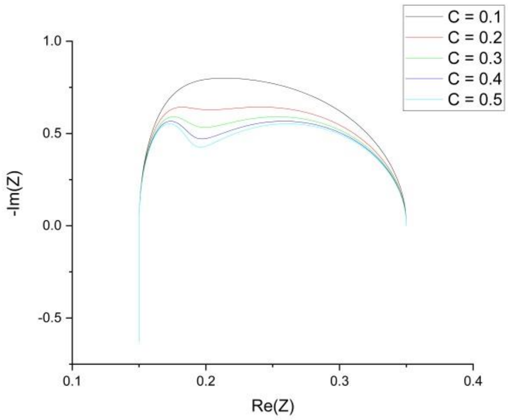


Figure 17: Imaginary vs real impedance (in ohms)

The increase in capacitance leads to an increase in the time constant which differs from that of the other RC unit and there is a two maxima formation in the Nyquist plot in Fig. 17. The curve also shifts downwards with an increase in the capacitance.

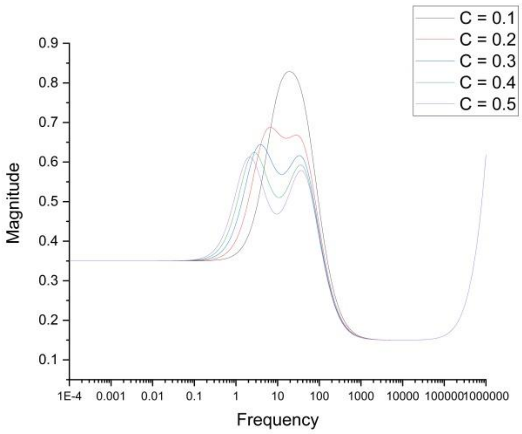


Figure 18.1: Impedance magnitude vs Frequency

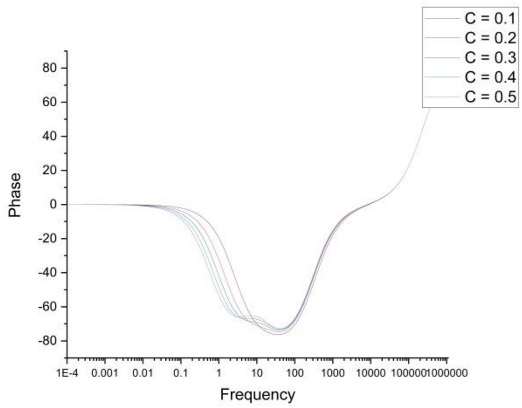


Figure 18.2: Phase vs Frequency

The two peak formation can also be observed from the Bode plot in Fig.18.1. The change occurs in the low and mid frequency region. This can be attributed to the terms with C_3 in Eq. (10) and Eq. (11) that affect the Eq. (12) at low frequencies. In Fig.18.2, there is a shift of the curve upwards and to the left with an increase in the capacitance as there is a decrease in the negative phase shift. Here, an increase in the capacitance causes the minima to shift to the left as the characteristic frequency decreases according to Eq. (15).

5.2.6. Variation of L_4

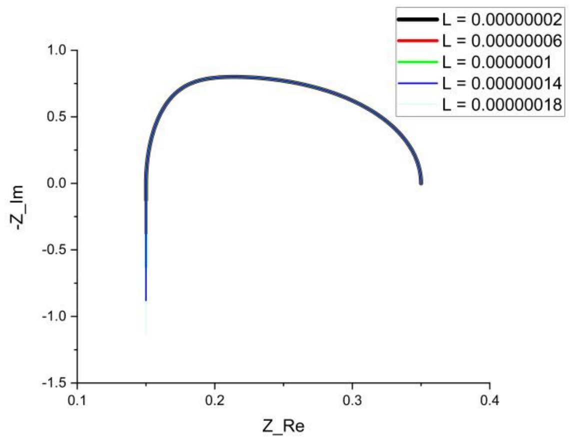


Figure 19: Imaginary vs real impedance (in ohms)

In Fig.19, the left end of the curve extends downwards. From Eq. (11), it can be seen that the imaginary part of the impedance increases with an increase in the inductance. There is no other change in the curve.

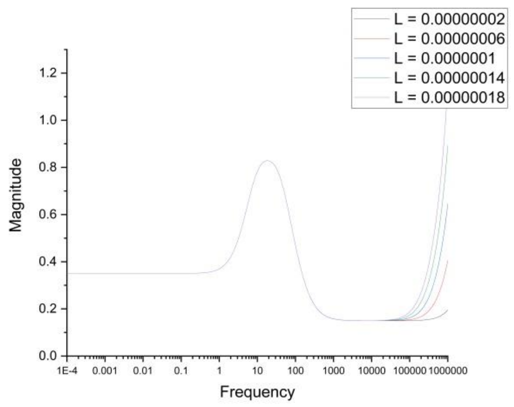


Figure 20.1: Impedance magnitude vs Frequency

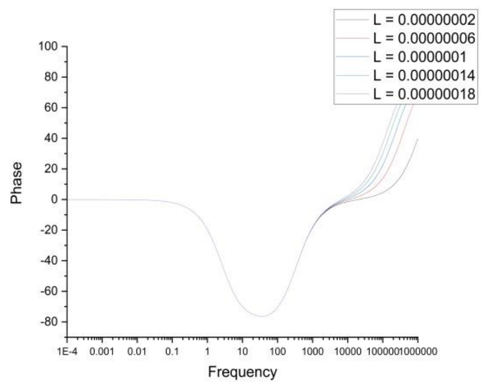


Figure 20.2: Phase vs Frequency

There is an upward shift of the curve in Fig.20.1 in the very high frequency region of the plot. The magnitude increases with an increase in the inductance as can be seen from Eq. (12). There is a similar upward shift in the Bode plot in Fig.20.2 as the phase shift increases with an increase in the inductance. This can be seen from the Eq. (13).

5.3. Analysis with multiple parameter variation

5.3.1. Increase in R_2; Decrease in C_2

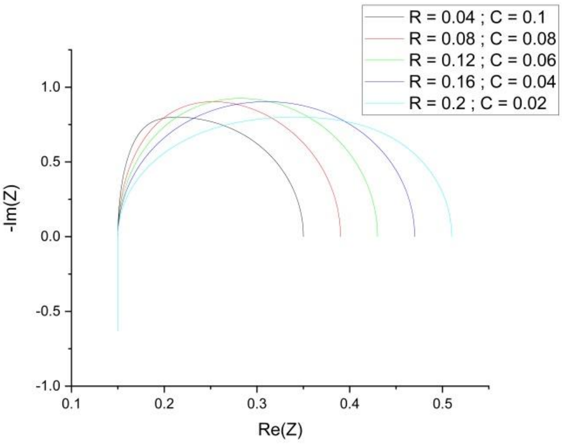


Figure 21: Imaginary vs real impedance (in ohms)

The variation in the resistance and the capacitance values leads to the curve getting flatter and bigger. The time constants of both the RC units from Eq. (14) do not differ much from each other and there exists only one maxima. The shift of the curve on the x-axis reflects the change in the resistance value.

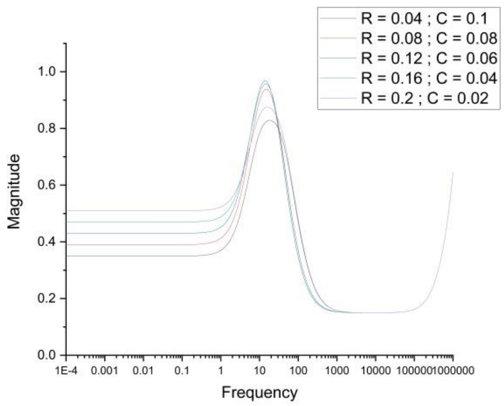


Figure 22.1: Impedance magnitude vs Frequency

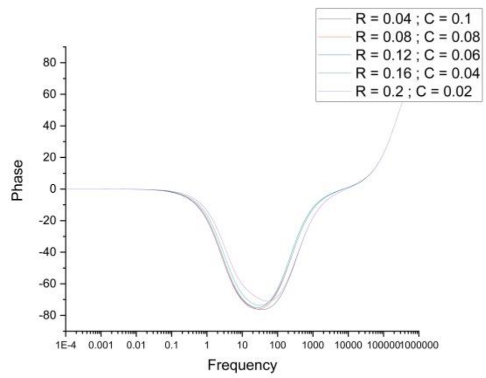


Figure 22.2: Phase vs Frequency

There is a shift in the curve upwards in the low and mid frequency region as there is an increase in the magnitude with the variation of the parameters as seen in the Fig.22.1. There is also an upwards shift in the curve in Fig.22.2 as the negative phase shift decreases with the parameter variation. The shift of the minima can be explained from Eq. (15) as the characteristic frequency changes according to the time constant of the RC unit.

5.3.2. Increase in R_2; Increase in C_2

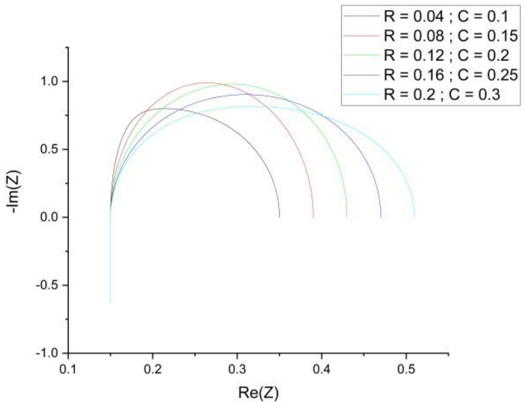


Figure 23: Imaginary vs real impedance (in ohms)

In Fig.23, the curve undergoes the same changes as in the previous case as the curve becomes bigger. The time constants of the RC units still do not differ from each other and so there is only one maxima. This is observed from Eq. (14).

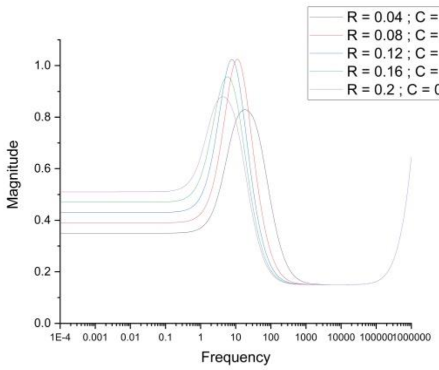


Figure 24.1: Impedance magnitude vs Frequency

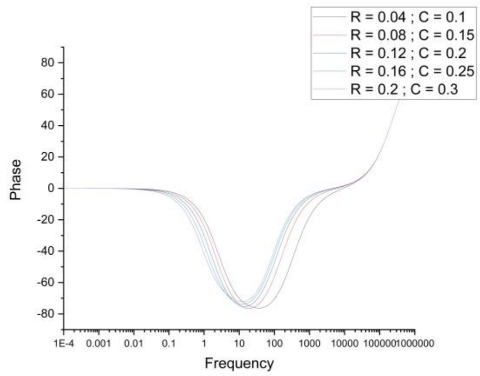


Figure 24.2: Phase vs Frequency

The magnitude increases with the parameter variation as there is an upward shift of the curve in the low and mid frequency region in Fig.24.1. The maximas of the curves shift according to the time constants. The curve also moves upwards as the negative phase shift decreases with an increase in the resistance and the capacitance in the Bode plot in Fig.24.2. The shift in the minima to the left can be explained by the decrease in the characteristic frequency from Eq. (15).

5.3.3. Increase in R_3; Decrease in C_3

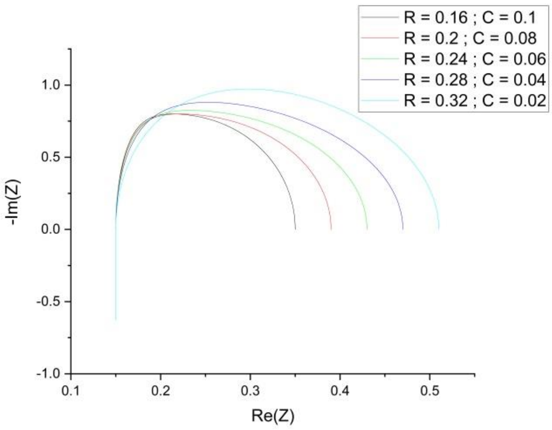


Figure 25: Imaginary vs real impedance (in ohms)

The curve in the Nyquist plot gets bigger with the variation of the respective parameters. There is not much difference in the time constants of the RC units and there is only one maxima as seen from Eq. (14).

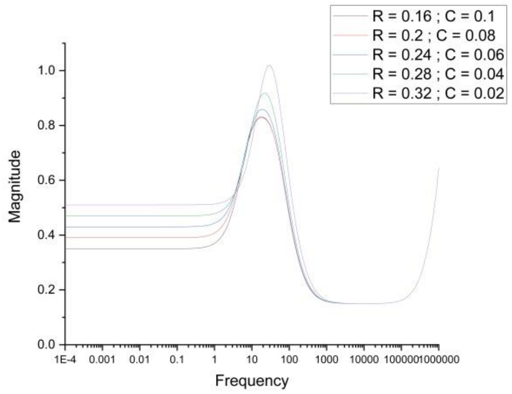


Figure 26.1: Impedance magnitude vs Frequency

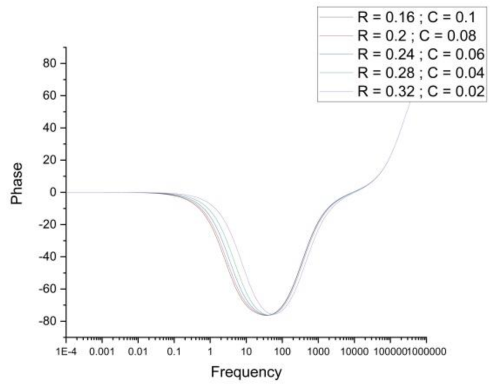


Figure 26.2: Phase vs Frequency

The magnitude of the impedance increases with an increase in the frequency as seen in Fig.26.1. The curve shifts upwards in the low and mid frequency region. The variations in the resistance and the capacitance are insignificant at high frequencies. The negative phase shift decreases with a frequency increase in Fig.26.2. The curve shifts upwards with the variation of resistance and capacitance. The minima shift can again be explained by Eq. (15).

5.3.4. Increase in R_3; Increase in C_3

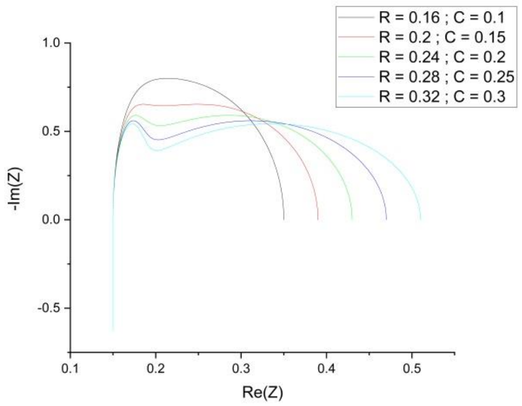


Figure 27: Imaginary vs real impedance (in ohms)

The variation in the parameters leads to the formation of two maxima as the time constants of the two RC units differ from one another as calculated from Eq. (14). The curve also gets flatter and bigger as seen from the Fig.27.

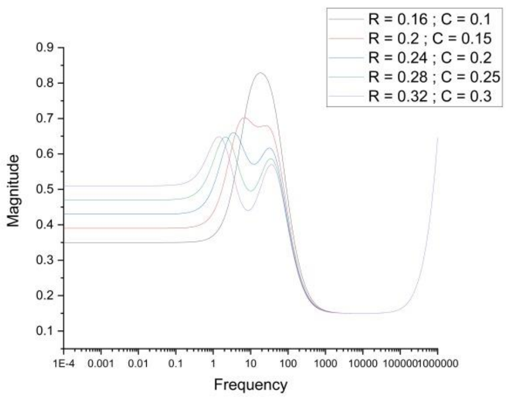


Figure 28.1: Impedance magnitude vs Frequency

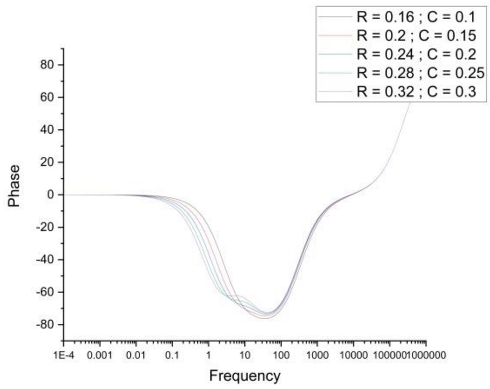


Figure 28.2: Phase vs Frequency

In Fig.28.1, it can be observed that there is a two maxima formation as the magnitude increases with an increase in the frequency. The variations in the resistance and capacitance lead to different time constants and different maximas. The curve shifts upwards with the variation in parameters in the low and mid frequency region. There is a decrease in the negative phase shift as the curve shifts upwards along with a two minima formation in the Bode plot in Fig.28.2. There is a minima shift to the left due to the decrease in the characteristic frequency of the RC unit.

6. Experimental Analysis

An experiment was conducted on a PEM electrolysis cell at 80°C with a Nafion 117 membrane and data was collected after 50 h of operation and after 500 h of operation for current densities (C.D.) of 0.1, 0.2, 0.4 and 0.8 A/cm^2. The real and imaginary parts of the impedance were recorded along with the phase shift of the impedance between frequencies of 0.1 and 10^5 Hz. A graphical representation was carried out to compare the Nyquist and Bode plots for the different current densities. The knowledge gained from the parameter variation in circuit analysis and theoretical fundamentals are used to understand the changes in the graphical plots with an increase in the current density.

6.1. Analysis after 50 hours of operation

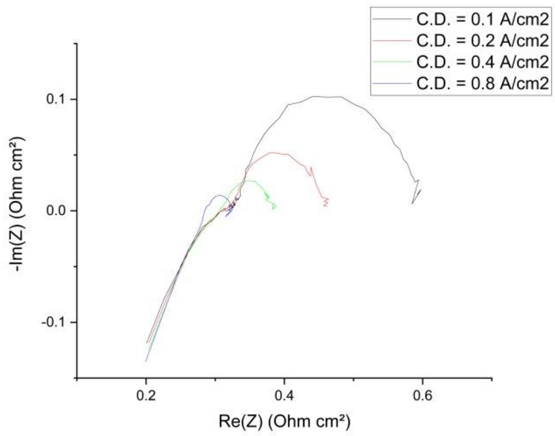


Figure 29: Imaginary vs real impedance

In Fig.29, there is a shift of the curve towards the left which indicates a decrease in the resistance R_1 (from Fig.5). This resistance which is assumed as the ohmic resistance in a PEM cell should be independent of the applied current density. One reason might be that the heat evolution caused by the electrochemical processes increases with increase in the current density, which may result in a decrease of the resistance.

$$\frac{H}{A} = \frac{I^2}{A} Rt \qquad (16)$$

In Eq. 16, the heat produced per unit area is represented by H/A while the current density is I^2/A, R is the resistance and t is the time that has elapsed. From this equation, it is clear that the increase in current density leads to an increase in the heat evolution. This leads to an increase in the conductance which in turn results in a decrease in the resistance.

The curve also gets smaller with an increase in the current density which indicates a decrease in the resistances R_2 or R_3 which stand for the transfer charge resistances of the electrodes. The slope of the polarization curve in Fig.2 is large at low current densities as more energy is required to overcome the transfer charge resistances. As the current density increases, the slope gets smaller as less energy is required to overcome the resistances followed by a decrease in the resistances as activation processes that take place at the anode and the cathode control the electrochemical reactions taking place.

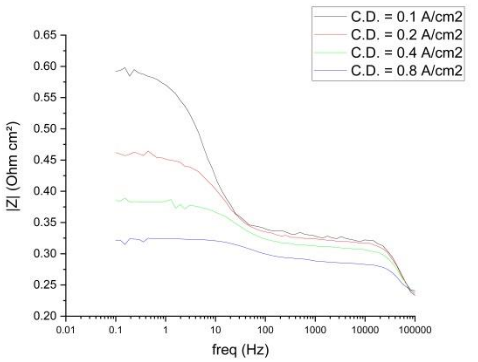


Figure 30.1: Impedance magnitude vs Frequency

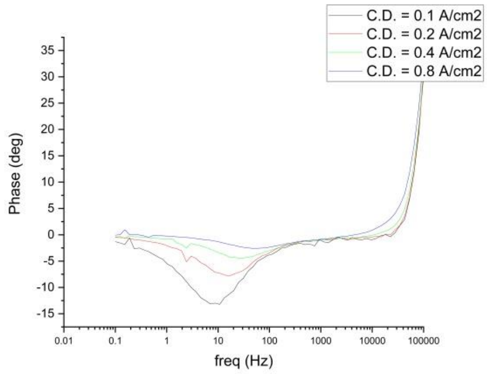


Figure 30.2: Phase vs Frequency

There is a decrease in the magnitude in the impedance with an increase in the frequency in Fig.30.1. The curve shifts downwards with an increase in the current density. The curve in the Bode plot in Fig.30.2 moves towards a phase shift of zero from a negative phase shift which signifies a decrease in the double layer capacitances of the electrodes. This denotes that an increase in the current density which leads to an increased cell potential has an inverse effect on the capacitances of the electrodes. The shift of the minima towards the right denotes an increase in the characteristic frequency from Eq. (15).

6.2. Analysis after 500 hours of operation

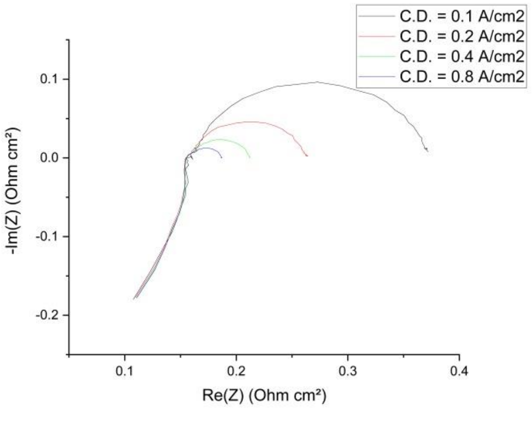


Figure 31: Imaginary vs real impedance

There is no shift of the curve in the Nyquist plot in Fig.31 which means that there is no change in the ohmic resistance. Ohmic losses are negligible with an increase in the current density after a considerable amount of time has passed as evident by the plot. There is however a decrease in the charge-transfer resistances R_2 and R_3 as the activation losses are higher at low current densities which decrease with an increase in the current density leading to a greater driving force and lower resistances.

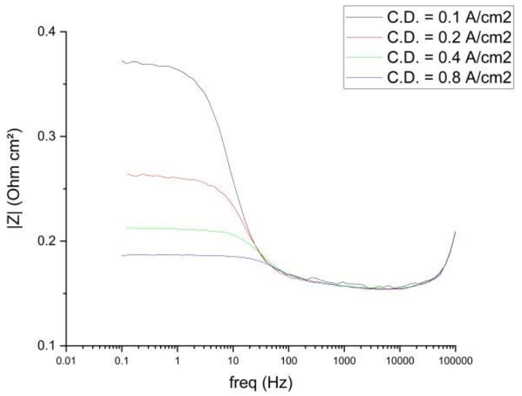


Figure 32.1: Impedance magnitude vs Frequency

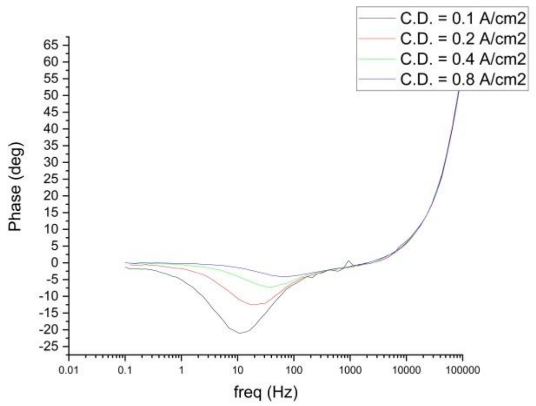


Figure 32.2: Phase vs Frequency

In Fig.32.1, the magnitude of the curve in the Bode plot decreases with an increase in the current density in the low frequency region. This signifies a decrease in the low frequency capacitance C_3 of the equivalent circuit. The curve moves towards a phase shift of zero in the Fig.32.2 with an increase in the current density which also signifies a decrease in the capacitance. The minima shift to the right is explained by Eq. (15).

6.3. Comparison between 50 hour and 500 hour datasets

A comparison and analysis is done between the EIS obtained after 50 hours and 500 hours of operation at the same current density of 0.2 A/cm^2. This helps to understand the dependence of the different parameters on time.

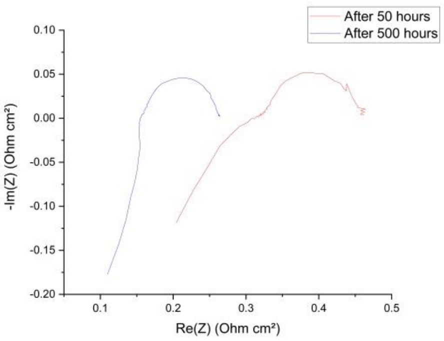


Figure 33: Imaginary vs real impedance

The Nyquist curve obtained after 50 hours of operation is to the right of the curve obtained after 500 hours of operation. There is a large shift of the curve to the left over time. This indicates a decrease in the ohmic resistance R_1. This can further be understood by Eq. (16) which signifies a large decrease in the resistance due to the heat evolution. The shape of the curves are almost the same, (with the blue curve slightly smaller) and so the transfer charge resistances remain the same while the extension of the curve downwards in the blue curve shows an increase in the inductance. The ohmic losses increase over time and this is reflected in the decrease of R_1. The inductance increases with an increase in the temperature.

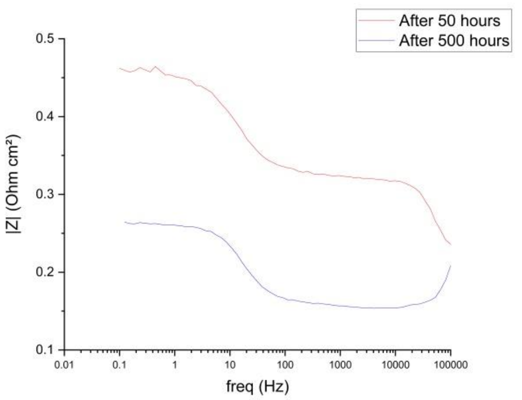


Figure 34.1: Impedance magnitude vs Frequency

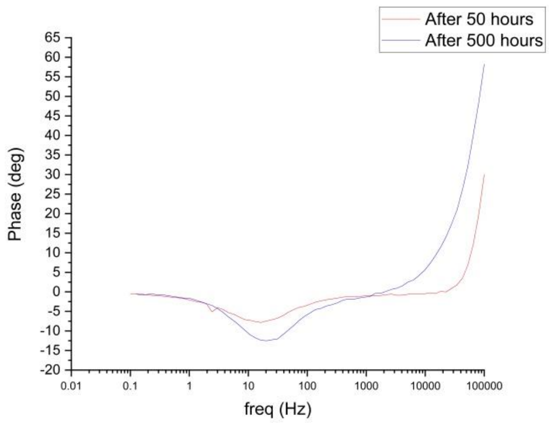


Figure 34.2: Phase vs Frequency

The Bode plot in Fig.34.1 shows that the impedance magnitude of the curve obtained after 500 hours is significantly lower than that obtained after 50 hours which confirms the decrease in the ohmic resistance. The blue curve is at a much lower level than the red curve. There is an increase in the magnitude of the blue curve at high frequencies which reflect the increase in the cable inductance. From Fig.34.2, it can be seen that there is an increase in the capacitance after 500 hours as the blue curve moves away from a phase shift of zero. This increase leads to a minima shift to the left due to a decrease in the characteristic frequency. There is an increase in the capacitance with a temperature increase because of the increased heat evolution.

7. Conclusion

In this thesis, a PEM WE cell was studied and an equivalent circuit of the cell was designed. After studying the working of both the cell and the circuit, a further characterization was done by plotting the EIS curves using data obtained from the circuit. The EIS analysis of the equivalent circuit of the PEM WE cell gave further insight as to the relationship between the different parameters obtained from the circuit. The Nyquist curves gave an idea regarding the ohmic and the transfer charge resistances of the cell and the electrodes respectively while the Bode plots gave an idea regarding the double layer capacitances of the electrodes and the influence of the cable inductance. The next step was the variation of the different elements of the circuit to understand how it affected the impedance spectra. This was determined with the mathematical analysis of a set of impedance equations (Eq. (9) to Eq. (15)). Finally, the information gained from the variation of different parameters was utilized in an experimental analysis of a PEM electrolysis cell. The electrolysis cell was subjected to different current densities and the changes in the EIS curves were observed after two different time periods. The inference derived from the earlier investigation proved helpful in the breakdown of the EIS curves plotted using the experimental datasets. These steps might help in facing the challenges while dealing with a PEM WE cell and work towards identifying and solving potential problems that might arise in order to pave way for a more efficient PEM WE cell.

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