DETERMINATION OF PREPARATION CONDITIONS FOR MEMBRANE ELECTRODE ASSEMBLY OF PEM ELECTROLYZER

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ABSTRACT

DETERMINATION OF PREPARATION CONDITIONS FOR MEMBRANE ELECTRODE ASSEMBLY OF PEM ELECTROLYZER

The aim of this thesis is to investigate the effect of preparation conditions of Membrane Electrode Assembly (MEA) on the hydrogen production of a single cell Proton Exchange Membrane (PEM) electrolyzer operated at room temperature and atmospheric pressure.

In the first part of the thesis, the catalyst ink, without the metal catalysts, coated membrane (MEA), with the 16 cm^2 active area, were produced. For the proton exchange membrane Nafion-117 membrane was used. An experimental design (Small Central Composite Design) was done in order to investigate the optimum preparation conditions (such as temperature, pressure and holding time in the hot press) for MEA of PEM electrolyzer. The responses were water vapor permeability and the surface resistance of the catalyst ink coating. The optimum conditions that gave maximum permeability and lowest surface resistance were found at 135°C of the hot press temperature, 5000 pound of pressure and 3 minute of holding time.

In the second part, Membrane Electrode Assembly containing Pt and Pt/Ru metals in the catalyst ink was produced using the optimum conditions found in the first part. Then the prepared MEA was compared with the commercial MEA containing Pt and Pt/Ru metals using our home made single PEM electrolyzer.

ÖZET

PEM ELEKTROLİZÖRÜNÜN MEMBRAN ELEKTROT AKSAMININ HAZIRLANMA ŞARTLARININ BELİRLENMESİ

Bu çalışmanın amacı tek hücreli PEM elektolizörünün oda sıcaklığında ve atmosfer basıncında membran elektrot aksamının hazırlanma koşullarının hidrojen üretimi üzerindeki etkisinin incelenmesidir. Bu tez iki kısımda incelenmiştir.

İlk aşamada, 16 cm^2 lik aktif alana sahip katalizör içermeyen katalizör mürekkeple kaplanan membran elektrot aksamı hazırlandı. Nafion-117 elektrolizör membran kullanıldı. İdeal koşulların (sıcaklık, basınç ve sıcak hidrolik preste kalma süresi) belirlenmesi için deneysel tasarım yapıldı. Deneysel tasarım sonucunda yapılan MEA'lar su buharı geçirgenliği ve elektriksel dirençlerine göre incelendi. En ideal koşul 135°C, 5000 pound, 3 dakika olarak bulundu.

İkinci aşamada, katalizör ilaveli membrane elektrot aksamı, ideal koşullarda hazırlandı. Hazırlanan MEA pem elektrolizöründe kullanıldı. En son olarak hazır MEA ile hazırlanan MEA karşılaştırıldı.

dedicated to

my mother; Semra DÜZGÖREN

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CHAPTER 1

INTRODUCTION

Today, energy is the most important concern for developed and developing countries. Energy consumption of the world is increasing day by day due the rapid growth of world population and industrialization. For instane, world primary energy consumption grew by 1.8% in 2012. Energy demand in the world is supplied by different energy sources. Energy sources could be categorized into two main group renewable and nonrenewable energy sources. Currently, the most of the consumed energy has been supplied by fossil sources, such as coal and petroleum (Figure 1.1) (BP-WSR 2013).However, it is estimated that these resources will finish within 100 years. In 1956, Huppert A. King proposed a theory showing that the fossil fuel would eventually come to an end in future due to the energy demand increase and, limited reserves of the fossil fuels. Accordingly to diminishing of the fossil fuel reserves will be reflected on the fuel prices (King 1956). Furthermore, the use of the fossil fuel causes environmental pollutions. Since the fossil fuels contain carbon and other chemicals. In the processes using fossil fuels, CO_2 is released into the atmosphere; in turn CO_2 causes global warming. As a result of increased usage of the fossil fuels, the global warming increases (Bockris et al. 1991).

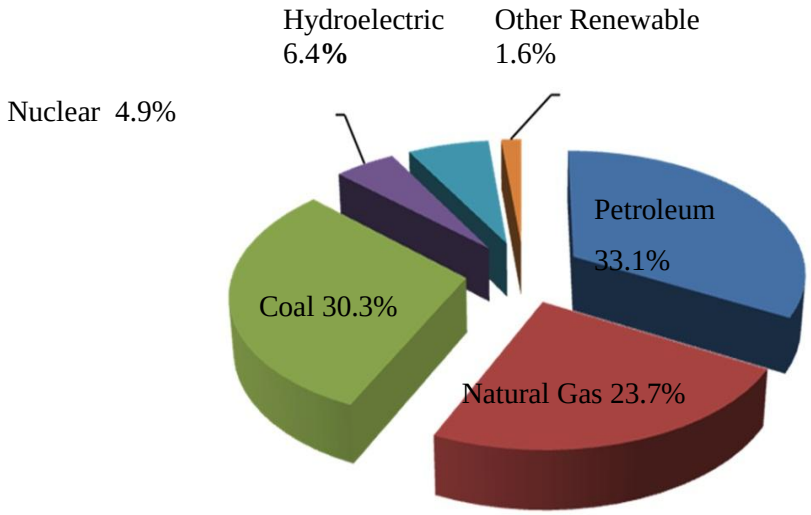


Figure 1.1. World Energy Consumption
(Source: BP 2013)

To meet the growing energy demand, alternative energy production processes, such as nuclear reactors, thermonuclear reactors, solar energy, wind energy, ocean thermal energy and new energy sources such as geothermal energy, have been investigated in recent years. Unfortunately, the alternative processes have disadvantages, such as nuclear wastes, unpredictable nature of the solar and wind energy, too (BP 2013).

This has led to the increased research studies to novel energy conversion systems using "a green fuel" in such as a way that this type of energy systems and the green fuel, should be economical, clean and inexhaustible. Indeed these features could be achieved by using hydrogen as a green fuel and hydrogen energy conversion systems.

Hydrogen is the first element in the periodic table and it is the lightest element in the world. Although hydrogen is the most abundant element in the universe it is hard to find freely available in Nature. So, hydrogen needs to be produced using other sources. In fact, hydrogen is not the energy source but it is an energy carrier. Besides, hydrogen is the only fuel that is clean and renewable. Hydrogen energy has both advantages and disadvantages, too. Harmful emissions, NO_x and SO_x to the atmosphere are eliminated using hydrogen and hydrogen can be transported safely in the pipelines. For hydrogen and its conversion systems to be economically viable alternative to the fossil fuels and their conversion systems, the existing fuel infrastructure and the internal combustion engines must be used in the same way as using natural gas. Unfortunately, the current fuel infrastructure and the fuel storage tanks are not suitable for hydrogen although the internal combustion engines could be modified to directly use hydrogen has wide range of usage. In addition, although hydrogen has notorious reputation, it is much safer than the fossil fuels because it dissipates rapidly in air when it is accidently released; hence this reduces the explosion risk (Bockris, Veziroğlu 1991, Crabtree 2010).

Hydrogen is produced by many methods; for example; steam methane reforming, coal gasification, the partial oxidation of hydrocarbons, biomass gasification, biomass pyrolysis, thermochemical, photochemical and electrolysis (Veziroğlu 1991). Steam methane reforming is the most common way to produce hydrogen in the industry. However, this is not clean way to produce hydrogen since methane is fossil fuel and carbon dioxide is released to the atmosphere during this process(Nieva 2014). Similarly, coal gasification causes air and soil pollutions. These kinds of hydrogen

production methods are not a clean way to produce hydrogen since they could release CO_2 and other compounds, such as NO_x and SO_x to the atmosphere. However, the clean ways to produce hydrogen are with the usage of renewable sources, such as solar and wind energy, and the water electrolysis (Shi 2013).

Electrolyzer dissociates water into hydrogen and oxygen gasses by passing an electric current through the water. There are two types of the electrolyzer, alkaline and acid water electrolyzers Proton exchange membrane electrolyzer is a solid acid membrane electrolyzer.

This thesis was the continuation of the previous project carried out in our group. Briefly, Can AKSAKAL manufactured a single and also five cell PEM electrolyzers using a commercial Membrane Electrode Assembly (MEA). Then, the electrolyzers, powered by using solar panels, were tested under varying atmospheric conditions to study hydrogen and oxygen production efficiency of the electrolyzers. So, in this thesis, membrane electrode assembly (MEA), having similar metal catalyst content as that of the commercial MEA, was prepared. Since the preparation conditions of MEA is known to have direct impact on the performance of the electrolyzer, the effect of preparation conditions of MEA on hydrogen production and V-I characteristics of a single cell Proton Exchange Membrane (PEM) was systematically investigated using an experimental design approach.

The thesis contains five chapters. Following with this introduction, in Chapter 2, a literature review on hydrogen production methods and PEM electrolyzers are given in details. In Chapter 3, the specifications of the materials and methods that were used in this thesis are explained. Chapter 4 gives water permeability and resistivity test results and experimental design analysis. The characterization result of the prepared MEA was also explained in this chapter. Finally, in Chapter 5 the conclusions are given with the research recommendations.

CHAPTER 2

LITERATURE SURVEY

2.1. Hydrogen Production Methods

Hydrogen is the most abundant element in the universe but it is not freely available Nature. Hence, hydrogen must be produced steam methane reforming, coal gasification, the partial oxidation of hydrocarbons, biomass gasification, biomass pyrolysis, thermochemical, photochemical and electrolysis.

2.1.1. Steam Methane Reforming

Steam methane reforming for the production of hydrogen is the most effective, the most economical method and also has the widest range of treatment. The method is mainly composed of three steps; synthesis (syn-gas) production, water-gas shift and the gas purification. (Nieva et al. 2014)

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (2.1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2.2)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (2.3)$$

As seen from the reactions, CO_2 emission occurs in this method. This is the problem for fossil fuel depended hydrogen production (Bockris 1991).

2.1.2. Coal Gasification

Coal gasification also called Koppers Totzek process, has a common usage instead of being economical and efficient way of hydrogen production. The process uses pulverized coal and partly oxidizes the pulverized coal by oxygen. Unfortunately, it is not the clean way of producing hydrogen (Monterroso et al. 2014).

2.1.3. Partial Oxidation of Hydrocarbons

Hydrocarbon converted into hydrogen and carbon monoxide (syn-gas). This procedure is less complex, more compact and effective cost. Reactions of this procedure is given below (Wang et al. 2012) and (Bockris et al. 1991).

$$C_nH_m + n/2\ O_2 \rightarrow n\ CO + m/2\ H_2 + ısı \quad (2.4)$$

$$C_nH_m + n\ H_2O + ısı \rightarrow n\ CO + (n + m/2)\ H_2 \quad (2.5)$$

$$CO + H_2O \rightarrow CO_2 + H_2 + ısı \quad (2.6)$$

2.1.4. Biomass Gasification

Biomass gasification procedure has three step; gasification to produce syn-gas, syngas conversion into hydrogen and finally the purification (Crabtree 2010). When biological waste material is used as a feedstock, this process becomes a completely renewable and sustainable method of hydrogen generation.

2.1.5. Thermo Chemical

When water is heated above 2500ºC, it separates into oxygen and hydrogen in thermo chemical process. But there is a problem because in that temperature hydrogen and oxygen can be converted into water again. The efficiency of the hydrogen production process is 30%.

2.2. Water Electrolysis

Electrolyzer dissociates water into hydrogen and oxygen gasses by passing an electrical current through the water. Electrolysis is not a renewable method because it depends on the source of the electricity used in the electrolysis. If electricity can be provided by any renewable energy source such as, geothermal, solar, wind energy sources, the electrolysis generates renewable hydrogen and oxygen.

In electrolysis ionic reactions occur. Current is applied between to the anode and cathode electrodes. Electrodes attract which are of the opposite charge. Anode electrode is electron donating electrode while cathode electrode is electron accepting electrode.

There are two main types electrolyzer alkaline and acid water electrolyzers. Among acid electrolyzers, proton exchange membrane (PEM) electrolyzer being the solid acid membranes is mostly preferred due to ease of handling and safety. Types of electrolyzers are shown in Table 2.1.

Table 2.1. Types of Electrolyzers

	Anode material	Cathode material	Separation media	Electrolyte	Working temperature
Conventional alkaline Electrolyzer	Nickel	Steel or nickel	Asbestos	25-35% KOH	50-60°C
Advanced Alkaline Electrolyzer	Activated nickel	Activated nickel	Polymer reinforced asbestos	25-35% KOH	80-100°C
Solid oxide electrolyzer	Platinum spots	Nickel or zirconium	-	Solid ceramic electrolyte	800-1000°C
PEM electrolyzer	Pt coating	Pt, Ir, Ru coating	Proton exchange membrane	Separation media acts as an solid electrolyte	70-90°C

Alkaline electrolyzers are the most commonly used electrolyzers in the industry. By using alkaline electrolyzer 99% purity hydrogen can be obtained, but only with usage of another purification unit. This because of high electrolyte vapor alkaline electrolyzer suffers from corrosion .mostly, 25-30 weight percent KOH solution isused as an electrolyte. The efficiency of hydrogen production reaches up to ~80%. Alkaline electrolyzer is the most effective on low current densities; i.e.ca. 0.3 Amp/cm^2. On the other hand, the lifetime of the electrolyzer is short and is not durable at high temperatures due to highly corrosive electrolyte (Barbir 2005).

Proton exchange membrane is much suitable for producing hydrogen. PEM electrolyzer is easy to use because it can operate with a wide range of current densities. Different kinds of electricity source can be used. PEM electrolyzers are the same devices as PEM fuel cells being operates in reverse. However, the catalyst type and coatings on the membrane surfaces that both sides use are different from each other. Also, the optimum operation conditions are significantly different. PEM electrolyzer produces high purity hydrogen and oxygen (~99.999%) among the other electrolyzer types (Grigoriev et al. 2006). There is no need of another purification step in producing hydrogen in PEM fuel cells. This is an important property for some applications like submarines and space shuttles. In addition, PEM electrolyzer can operate at high pressures up to 300 bars. Furthermore, PEM electrolyzer can operate in a wide range of temperatures, pressures and current densities. It is possible to integrate PEM electrolyzer with renewable energy sources.

On the other hand, the cost of the PEM electrolyzer is the most important problem. The high cost of membrane, electrocataylsts (Pt, Ir) and the high cost of constructional materials can reduce the usage in a wide range of area (Grigoriev, Porembsky et al. 2006). Besides, the operation of PEM electrolyzer depends on the electricity .For reducing the operating cost of the electrolyzer cheaper energy source for the electricity must be found. In literature there are many works on reducing the electricity cost by using renewable energy sources. Theoretical electricity equivalent of 1kg hydrogen is about 40 kWh (Grigoriev et al.2006). Another way of reducing the electricity usage is to increase efficiency of electrolyzers by improving the membrane electrode assembly material.

2.2.1. Proton Exchange Membrane (PEM) Electrolyzer

Basically water is a reactant and products are hydrogen and oxygen. PEM electrolyzer consists of membrane electrode assembly (MEA) which is composite material containing solid electrolyte coated with catalysts on each side (it is the medium where the electrolysis reaction occurs), gas diffusion layer and electric current collectors.

The reaction medium is the surfaces of the MEA of the electrolyzer. The electrolyte of PEM is a solid perfluorinated membrane (Nafion membrane) which is the electrically nonconductive and also physical barrier to both hydrogen and oxygen gases but protons pass through the membrane. Both sides of the membrane is coated with noble metals. In anode side, the membrane is coated with Pt and in cathode side it is coated with Ru and Pt. The overall reaction is shown below

$$H_2O \rightarrow H_2 + 1/2\ O_2 \qquad (2.7)$$

The mechanism of the electrolysis reaction has two parts; anode reaction and cathode reaction under the applied potential across the MEA. Anode side reaction is the decomposition of the water shown below.

$$H_2O \rightarrow 2\ H^+ + 1/2\ O_2 + 2e^- \qquad (2.8)$$

After water dissociate into the oxygen, protons and electrons, protons go through PEM electrolyte to the cathode side while the electrons comes from an external power supply to complete the electrical circuit. Cathode side reaction is shown below.

$$2H^+ + 2e^- \rightarrow H_2 \qquad (2.9)$$

Schematic representation of the parts of a single cell is given in Figure 2.1.

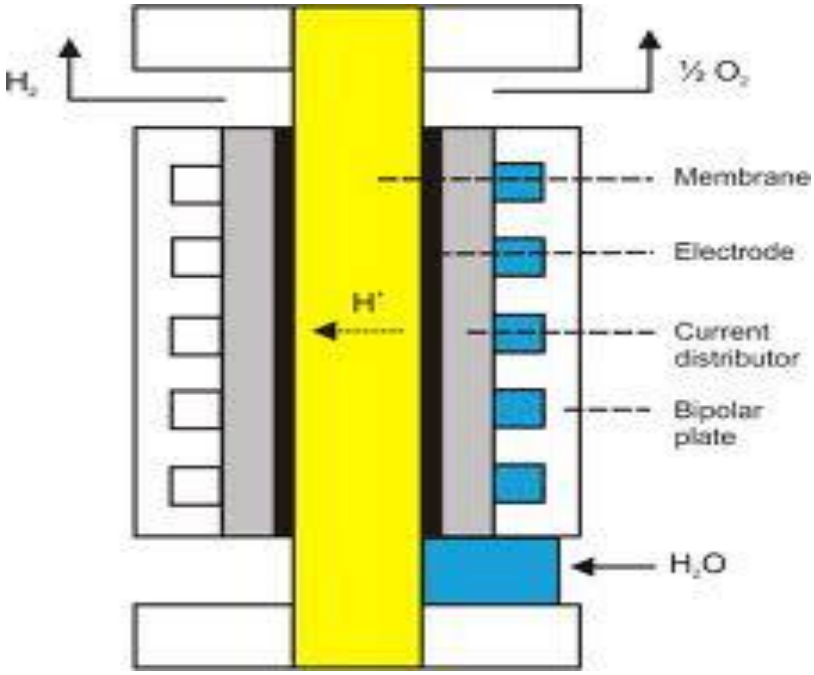


Figure 2.1. Schematic representation of PEM electrolysis cell

2.2.1.1. Proton Exchange Membrane of an Electrolyzer Cell

Proton exchange membrane of an electrolyzer cell is a proton conductive material. It is a polymer based membrane which is called Nafion (perfluorinated membrane). PEM is used for both fuel cell and electrolyzer but its properties are different from each other.

Without water PEM is poor proton conductor. Some amount of water must be kept during PEM electrolysis otherwise the performance of the cell decreases.

Nafion membranes have good film formation, high proton conductivity in water, low electrical conductivity, effective reactant/product separator and mechanical durability at high temperatures (80-140ºC).Another property that affects the conductivity is the thickness of the membrane; in fact, the increased thickness decreases hydration.

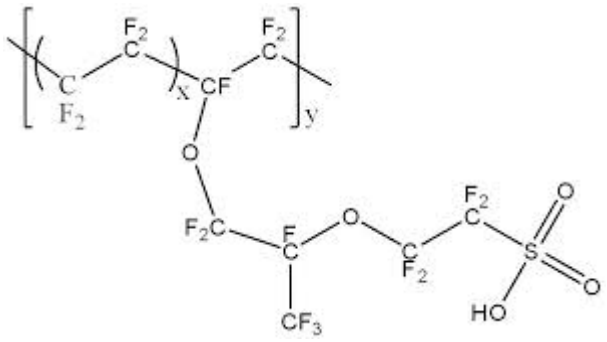


Figure 2.2. Molecular formula of Nafion

The Nafion both have hydrophilic and hydrophobic regions. Sulphonated side chains are hydrophilic region. Nafion adsorbs water with the hydrophilic part. The main principle is that hydrogen ions are weakly attracted to the sulphone groups and easily moved in hydrated regions of the membrane (Larminie 2003).

2.2.1.2. Membrane Electrode Assembly and Preparation conditions of MEA

Catalyst coated membrane is called membrane electrode assembly. MEA contains membrane, anode catalyst and cathode catalyst. The function of the membrane electrode assembly is to separate anode and cathode by membrane. Also, it must provide optimal electrochemical activity furthermore; it must provide proton transfer between anode and cathode reactions because it affects the electrical and proton transfer resistance between the anode and cathode electrodes. For that reason, Nafion membrane is coated by catalyst ink to reduce activation barrier and also, thin Nafion membrane is needed to lower the ohmic resistance to the passage of protons between anode and cathode electrodes. Overall electrolysis reaction occurs in both side of the MEA.

Membrane electrode assembly fabrication is different from PEM fuel cell in a way that PEM electrolyzer has different catalyst loadings, different support material and fabrication methods.

There are two different ways for electrode fabrication used in PEM electrolyzer. First method is the separate electrode method which catalyst ink is fixed to a porous and conductive material, such as carbon cloth or carbon paper (Larminie 2003). The electrodes are then fixed to each side of the membrane by hot press (Thangamuthu 2005). The second method is to build electrodes directly onto the membrane these fabrication approaches are used to achieve a good conduction of the catalyst surface with the PEM which increases the effectiveness of the cell per unit mass of the catalyst(Ioroi et al. 2002).

Membrane Electrode Assembly preparation conditions varies in the literature. There is no systematic investigation about the preparation conditions for MEA used in PEM electrolyzer. For example, Prasana et al. investigated the effect of MEA fabrication method on durability of PEM fuel cell. They used hot press conditions 140°C, 2000 kg/cm^2 pressure for 1.5 min (Prasana et al.). In another literature study, the optimization and modeling of electrode structure and composition was investigated for novel PEM electrolyzer. Zavieh, prepared MEA at 130ºC and 2MPa of pressure for 1 min (Zavieh). Besides, in order to investigate the effect of ionomer content, the preparation conditions were 130ºC and 100 MPa of pressure for 3 min for MEA (Xu et al.). Song et al. investigated the electrocatalysts for the oxygen evolution reaction. They produced the MEA at 140°C and 10 MPa. So, in this study , MEA was prepared using an experimental design method to systematically investigate the effect of the preparation parameters, such as temperature, pressure and holding time of the hot press, on the hydrogen evolution and V-I characteristics of the PEM electrolyzer.

CHAPTER 3

MATERIAL AND METHODS

Catalyst coated membrane electrode assembly was prepared. The preparation conditions, such as temperature, pressure and hot press holding time used in hydraulic press, were varied using the experimental design in order to find optimum water permeability and surface resistance for MEA. Then, the MEA, having optimum water permeability and conductivity, were used in the single cell electrolyzer to compare its hydrogen production to that of commercial MEA.

3.1. Materials and Equipment

All the chemicals, such as hydrogen peroxide (Sigma, H_2O_2, 50%) and sulfuric acid (Fluka, H_2SO_4, 95-98 %), were analytical grade and used without further purification throughout this study.

The specifications of the materials used in the preparation of the membrane electrode assembly are given in Table 3.1.

Table 3.1. Properties of Materials used in membrane electrode assembly

Materials	Specifications
Nafion membrane	N-117 membrane (Ion power) size 70*70 mm
Activated carbon	Carbon powder, activated, ash 4% max (Alfa Aesar)
Nafion ion so lution	Perfluorosulfonic acid-PTFE copolymer 5% w/w solution (Alfa Aesar)
Iso-propanol	Merck
Water	Deionized water
Membrane electrode assembly	Catalyst coated N-117 membrane (Ion Power) (70*70)mm total area
Platinum	Alfa Aesar
Iridium	Alfa Aesar

In this study, the single cell PEM electrolyzer prepared by Can Z. Aksakal was used. Materials and their specifications used to prepare the electrolyzer cell are given in Table 3.2. Regulated DC power supply GP1305TP of EZ electronics, was used to supply the required electrical energy for the electrolysis cell

Table 3.2. Properties of Materials used in Electrolysis Cell

Materials	Specifications
Gas diffusion layer (GDL)	1 micron Pt coated 1.5 mm Titanium screen (45x45)mm
Bipolar Plate	Carbone Lorraine 1940PT graphite Layer
Gaskets	Temperature resistant 1 mm thick silicon gaskets
Endplates	8mm thick stainless steel plates (70x70)mm
Compression Bolts	5mm diameter 8 steel bolts covered with plastic insulators
Electric Conduction Plates	1mm thick TSE 554 copper plates

3.2. Methods

The experiments in this study can be categorized into 5 groups.

- Carbon ball milling.
- Membrane treatment.
- Catalyst ink preparation.
- Manufacture of catalyst coated membrane electrode assembly.
- Investigation of the water permeable and conductivity of the prepared MEA.
- The MEA prepared with the optimum conditions was used in single cell electrolyzer to test its hydrogen production and V-I characteristics.

3.2.1. Carbon Ball milling

Active carbon particle size was not small enough to prevent from precipitating out of the catalyst ink solution. Also, it is known that carbon particle size affects the conductivity of the MEA; in fact the smallest particle gives the most conductive membrane. That's why small particle size of activated carbon was needed. Therefore,

activated carbon was ball milled. The operation was conducted using RETCSH, planetary ball milling RT 100 at a rotation speed of 600 rpm for 1 h.

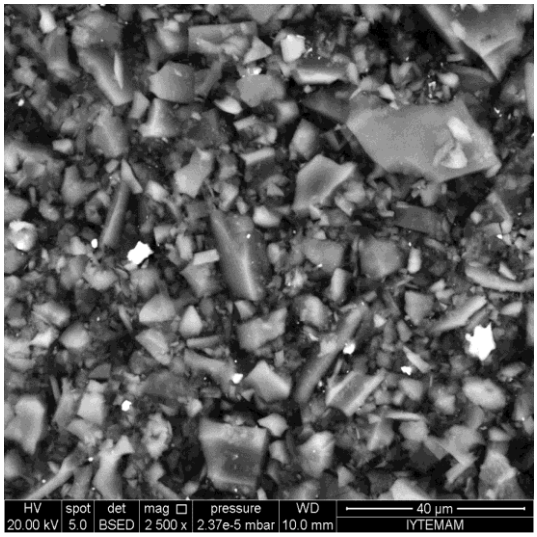


Figure 3.1. SEM image of activated carbon after ball milling

After ball milling particle was not well distributed and not small enough (as seen in Figure 3.1.). In order to overcome to this problem mechanical milling was used and after this treatment, there was no precipitation in catalyst ink.

3.2.2. Membrane Treatment

Nafion membrane must be treated before being used. (Xu 2010) Sulphone groups were inactive before the treatment. After the treatment, the membrane became active. Nafion 117 membrane was first put into 3% H_2O_2 solution at 80ºC for 1 h to remove organic impurities. After that, the membranes were boiled at 80ºC for 1 h at 5M H_2SO_4 solution to change the ions to protons and also by this way the inorganic impurities were removed. After these steps, the membranes were washed by deionized water twice at 80ºC for 1h, as seen in Figure 3.2.

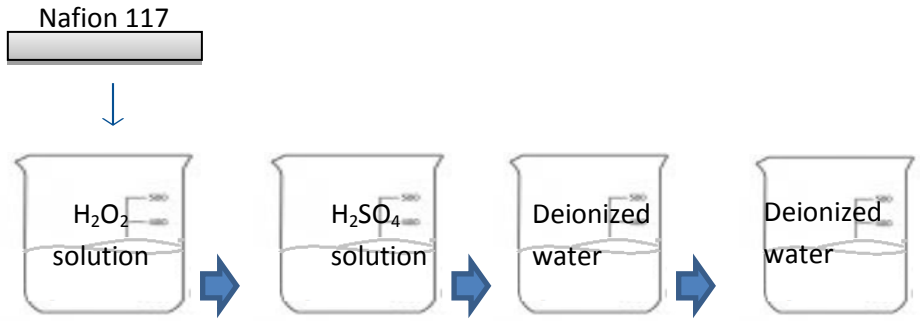


Figure 3.2. Nafion membrane treatment procedure

3.2.3. Catalyst Loading

First, the catalyst ink solution was prepared without Pt or Ru to find out the optimum conductivity and water permeability. Then, the membrane prepared with the optimum conditions was loaded with Pt and Ru to obtain MEA.

In the second part of the thesis membrane electrode assembly was prepared with the catalyst loading. For PEM electrolyzer Pt for anode side and Pt/Ru for cathode side in preparing MEA was used as the metal catalysts. For both anode and cathode sides, 1 mg/cm^2 metal were added. Catalyst was loaded to active carbon using impregnation method and the metal precursor. Briefly, in the impregnation Metal precursor solution having the necessary amount of metal was added to active carbon while being mixed and then put take the oven at 60°C for an hour.

3.2.4. Catalyst Ink Preparation

Catalyst ink was prepared for coating the membrane. For anode and cathode 0.15g of ground active carbon, 0.5ml of water, 0.5ml of isopropanol and 0.17g Nafion of the ion solution were mixed. Prepared ink was ultrasonicated for half an hour.

3.2.5. Catalyst Reduction

A catalyst metal precursor needs to be reduced to obtain metal catalysts on the active carbon. So, $NaBH_4$ was used for reduction of the metal precursors. The procedure of the reduction was. Catalyst loaded active carbon was treated with 0.5M $NaBH_4$ for 2

hours at room temperature. After that the powder washed with deionized water at 60-70°C until no Cl ion detected in washed water. After the washing, the powder was dried at 110°C for 4.

3.2.6. Membrane Electrode Assembly (MEA) preparation and Analyses

The treated membrane was coated with the catalyst ink by using a paint brush. In order to prevent the formation of deformation, such as surface wrinkles, of the membrane during coating, wet membrane was used. The wet membrane was compressed using the rubber gasket (as shown in Figure 3.3.) .The catalyst ink was applied to membrane using the paint brush while membrane was kept wet. Then, the prepared nafion membrane was dried at room temperature.

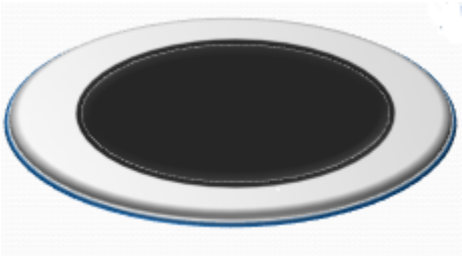


Figure 3.3. Coating Equipment (rubber gasket)

Hot press was used after this step. Hot press conditions changed during the preparation are; temperature, pressure and holding time. Experimental design (Small Central Composite Design) was constructed using the design expert 7software. In the design were water vapor permeability and the surface resistance were the responses while the temperature, pressure and the holding time were the design factors with 3 levels as seen in Table 3.3.

Table 3.3. Experimental design factors and levels

Factors/Levels	Low level	Central	High level
Temperature (ºC)	110	122.5	135
Pressure (pound)	5000	10000	15000
Time (minute)	3	6.5	10

Central composite design was used with 3 levels and 3 factors. Experimental design gave 15 experiments. In the design, there were 4 fact points, 5 central points and 6 axial points. Planned design was given in Table 3.4.

Table 3.4. Experimental Design

Std.order	Run order	Pt type	blocks	temperature	pressure	time
8	1	1	1	122.5	15000	6.5
12	2	0	1	122.5	10000	6.5
7	3	1	1	122.5	5000	6.5
2	4	0	1	135	5000	10.0
11	5	1	1	122.5	10000	6.5
15	6	1	1	122.5	10000	6.5
13	7	1	1	122.5	10000	6.5
14	8	1	1	122.5	10000	6.5
10	9	0	1	122.5	10000	10.0
9	10	0	1	122.5	10000	3.0
6	11	1	1	135	10000	6.5
4	12	1	1	110	5000	3.0
5	13	0	2	110	10000	6.5
3	14	-1	2	110	15000	10.0
1	15	-1	2	135	15000	3.0

3.3.7. Single Cell PEM Electrolyzer Setup

After optimum conditions were obtained using small central composite design, the MEA wasprepared with the optimum conditions, i.e.135°C , 5000 pound of press pressureand 3 min of holding time to be tested in the single cell PEM Electrolyzer at room temperature and atmospheric pressure. In Figure 3.4. single cell PEM Electrolyzer experimental setup isshown.

After the assembly of the cell, the deionized water was fed to the water inlet using peristaltic pump. To make sure that water filled up the inside of cell,filling process was continued until water came out from oxygen output side. The oxygen

output was connected to the inlet water reservoir to recirculate the water back to the inlet . Hydrogen output was connected to a gas liquid seperator to seperate the water and hydrogen.Positive terminal of the power supply was connected to the anode side and its, negative terminal was connected to the cathode side to apply the electricity to the cell.

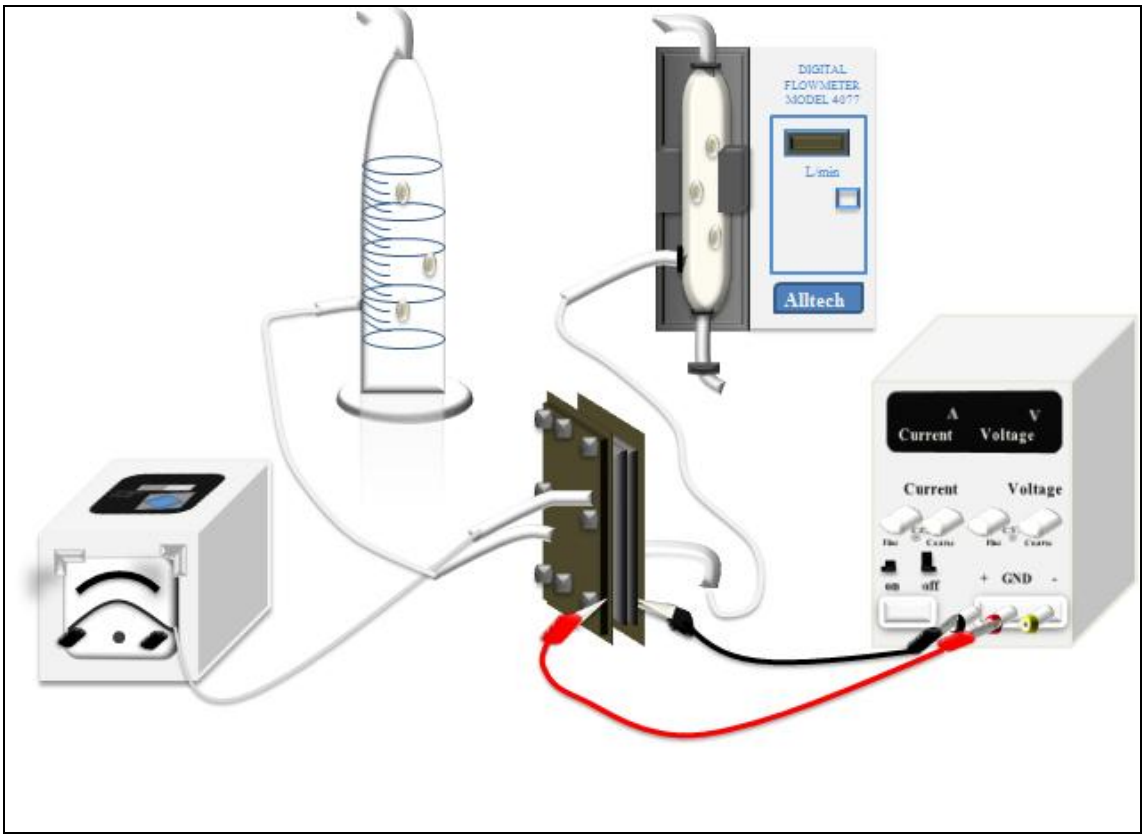


Figure 3.4. Single Cell PEM Electrolyzer Experimental Setup

3.3. Characterization Studies

3.3.1. Scanning Electron Microscope with Energy Dispersive X-Ray (EDX)

Scanning Electron Microscope (Quanta 250FEG) was used to determine the surface elemental analysis and also the structure of the active carbon on the MEA surface using back scattering detectors.

3.3.2. X-Ray Diffraction (XRD)

Philips X'Pert diffractometer was used to investigate crystalline phases present and also the crystallite size of carbon, Pt and Ru on the MEA. The operating conditions of the diffractometer were 45kV and 45mA.The range for the X-ray scan was 2Ɵ values of 5-80°. XP'pert plus software was used to record the XRD patterns of the metals and their locations.

3.3.3. Water Vapor Permeability

Water vapor permeability was measured with a vessel consisting of a three seperable parts. In the bottom part, there was a small bath filled with water. At the middle part of the vessel there was a hole. MEA were cut into the same diameter as that ofthe hole so that thearea of the hole was covered. The upper part of vessil consists of a probe to read the humidity of the upper section. When the solvent trasnport through the MEA, an increase in relative humidity of the upper part is read by the probe and the relative humidity, time and temperature data were collected and stored in the internal memory of the probe (Datalogger SK-L 200 TH).

The upper part of the vessel wasexposed to dry air during 3 hours. After drying procedure, the computer program was started to record while increasing relative humidity values. Time interval to collect the relative humidity and temperature data was selected as 10 second.

3.3.4. Resistance

Keithley 6517A Electrometer/High Resistance meter was used in the determination of the electrical resistance of the membrane electrode assemblies. Constant voltage method was used for measuring current and the resistance of the MEA was calculated. Two probes were put around the MEA with the same distance. A total of 4 measurements were made at the surface of the MEA samples. The average of these readings and the error of the measurement were calculated.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Fabrication of Membrane Electrode Assembly

In the literature there are many methods for fabricating the membrane electrode assembly (MEA) for PEM fuel cells but there are a few studies on the preparation of MEA for PEM electrolyzer. In fact, there are no systematic studies on the preparation of MEA for PEM electrolyzer. In this work, the catalyst coated membrane method was used for fabricating the membrane electrode assembly. In catalyst coated membrane method, the catalyst ink is directly applied onto the membrane. The values of the preparation parameters, such as temperature, pressure and holding time, were set using small central composite design. In this experimental design, the water permeability and the surface resistance were response of the MEA since water permeability and surface resistance affect the V-I performance and hydrogen generation rate of the PEM electrolyzer.

4.1.1. Catalyst ink preparation

Although the catalyst materials are different in anode and cathode sides, the active carbon, nafion solution, isopropanol and water contents are the same. In the first part of the study, the catalyst ink was prepared without the metal catalyst in order to find the optimum preparation conditions at which water permeability and conductivity were high.

First issue was to determine the suitable catalyst ink composition because the activated carbon and PTFE (Nafion ion solution) percentages affect the physicochemical properties, such as colloidal stability of the catalyst ink and the durability of the coating. The concentration of nafion ion solution was first varied. If the Nafion ion solution concentration was low, the coating layer on membrane was observed to peel off after the hot press application Figure 4.1. shows the effect of the

different concentrations of Nafion ion solution on physical appearance of the MEA. As can be seen from the figure, when the PTFE percentage was 52% the durable coating was obtained.

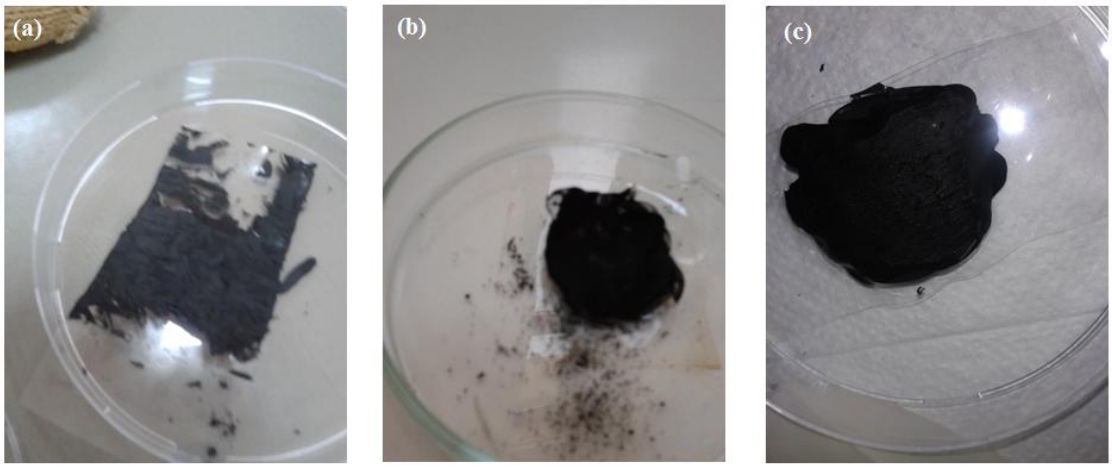


Figure 4.1. Effects of PTFE percentage on to a physical appearance (a) PTFE % is 5%,(b) PTFE % is 30% and (c) PTFE % is 52%

4.1.2. Membrane Coating

It was found that Nafion membrane was wrinkled and twisted if membrane was dry during preparation. This was due to the fast and uneven absorption of water in Nafion. In literature, this was the most significant problem for the catalyst coated membrane method. In this study rubber gaskets were used as a template during coating to coat the ink. The membrane was clamped between two gaskets before applying the catalyst coating on the wet membranes. The visual quality of the MEA prepared using dry and wet membranes is compared as shown in Figure 4.2.

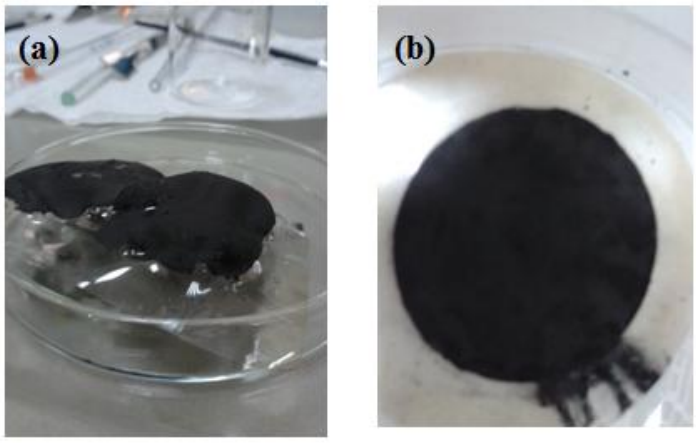


Figure 4.2. Effect of initial state of the membrane on the MEA physical appearance (a) without initial water treatment (dry membrane) (b) with initial water treatment (wet membrane)

4.1.3. Hot press

Hot press was the last part of the fabrication of membrane electrode assembly. In this study, the aim was to determine the effect of the hot press conditions on the physicochemical properties of the MEA. Three factors were selected in the experimental design; temperature, pressure and holding time. It was observed that the catalyst ink coated membrane was wrinkled and folded if the membrane was directly put into hot press at high temperature .This was eliminated by putting the membrane into the press at room temperature before raising the press temperature. Also, it was found that the slow heating rate prevented the membrane from deforming. Figure 4.3. shows the effect of the initial temperature of the press on the physical appearance of the MEA.

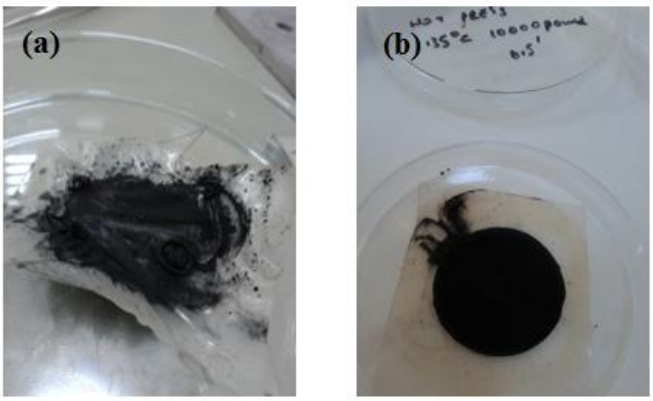


Figure 4.3. Effect of initial temperature of the hot press (a) high temperature (b) room temperature

4.2. Characterization of the MEA

4.2.1. Water Vapor Permeability

All the 15 MEAs were prepared using the parameters generated by small central composite design. After that water vapor permeability tests were performed for all the samples. The thickness of MEA used in the experiments are slightly different from each other, the change of relative humidity in the upper part of the permeability vessel was plotted as a function of time and normalized with the thickness of the films. The permeability of water vapor was calculated from the slope of linear portion of a ln P_{IL}-$P_{ıui}$ / P_{IL}-$P_{ıut}$= (Peff.A.R.T/Vu.L).t and time graph. Results were tabulated in

Table 4.1.

Table 4.1. Water permeability coefficients

No	Temperature(°C)	Pressure(pound)	Time(minute)	water permeability mol/s.cm.kPa
1	122.5	15000	6.5	0.2131
2	122.5	10000	6.5	0.3232
3	122.5	5000	6.5	0.3899
4	135	5000	10	0.0944
5	122.5	10000	6.5	0.3336
6	122.5	10000	6.5	0.3864
7	122.5	10000	6.5	0.4298
8	122.5	10000	6.5	0.276
9	122.5	10000	10	0.2415
10	122.5	10000	13	0.3088
11	135	10000	6.5	0.3194
12	110	5000	3	0.3971
13	110	10000	6.5	0.275
14	110	15000	10	0.3993
15	135	15000	3	0.172

4.2.2. Resistance test

Another issue affecting the efficiency of the water electrolyzer is the resistance of the MEA. The resistance test was repeated 4 times for all the prepared MEAs and the results were given in Table 4.2.

Table 4.2. The resistance test results

No	Experiment 1 (kΩ)	Experiment 2 (kΩ)	Experiment 3 (kΩ)	Experiment 4 (kΩ)	Average(kΩ)
1	5.9	4.3	4.4	4.5	4.77
2	3.7	3.8	4.2	4.5	4.05
3	10.1	8.8	10.2	10.1	9.80
4	3.1	2.98	3.2	3.3	3.14
5	4.6	4.1	4.5	4.6	4.45
6	5.3	4.8	4.3	5.1	4.87
7	2.6	3.3	3.9	2.6	3.10
8	2.16	2.38	2.08	1.77	2.09
9	2.25	2.77	2.25	2.28	2.38
10	2.01	7.3	6.09	4.7	5.02
11	8.5	8.5	6.2	4.28	6.87
12	3.9	4.4	3.9	3.4	3.90
13	2.65	2.65	2.39	2.4	2.52
14	1.8	2.17	1.64	2.35	1.99
15	3.8	3.06	3.11	3.06	3.2575

4.3. Analysis of the Experimental Design Results

In this work, while the hot press conditions, such as temperature, pressure and time were changed, water permeability and resistivity were monitored. A response surface methodology via central composite design was used. The central composite designs for three factors at three levels were used. This design was used to obtain the optimum conditions in the preparation of PEM electrolyzer. 15 different combinations of the factors were obtained through the central composite design by using Design Expert 7 software. The measured responses at each combination of the factors were tabulated in Table 4.3. Water permeability was found to vary from 0.0944 to 0.4298 and the resistance varied from 1.99 to 9.8 kΩ.

Table 4.3. Central composite design matrix with experimental values for resistivity and water permeability

	Std	Run	Block	Factor 1 A:temperature	Factor 2 B:pressure	Factor 3 C:time	Response 1 water permeat	Response 2 resistance
	8	1	Block 1	122.50	15000.00	6.50	0.2131	3.9
	12	2	Block 1	122.50	10000.00	6.50	0.3232	5.025
	7	3	Block 1	122.50	5000.00	6.50	0.3899	1.99
	2	4	Block 1	135.00	5000.00	10.00	0.0944	9.8
	11	5	Block 1	122.50	10000.00	6.50	0.3336	3.1
	15	6	Block 1	122.50	10000.00	6.50	0.3864	4.05
	13	7	Block 1	122.50	10000.00	6.50	0.4298	4.775
	14	8	Block 1	122.50	10000.00	6.50	0.276	4.025
	10	9	Block 1	122.50	10000.00	10.00	0.2415	2.37
	9	10	Block 1	122.50	10000.00	3.00	0.3088	2.5225
	6	11	Block 1	135.00	10000.00	6.50	0.3194	3.2575
	4	12	Block 1	110.00	5000.00	3.00	0.3971	5.475
	5	13	Block 1	110.00	10000.00	6.50	0.275	6.87
	3	14	Block 1	110.00	15000.00	10.00	0.3993	3.145
	1	15	Block 1	135.00	15000.00	3.00	0.172	4.875

The correlation coefficient shows the relationship between two variables numerically. In fact, the correlation coefficient scales from +1 to -1. Positive sign means that the variables acted in the same way. Negative sign means that variables acted in the opposite way. If the correlation coefficient is zero, it means that variables have no relationship with each other. Before the detailed analysis, the interactions correlation coefficients were sought. Figure 4.4. and Figure 4.5. shows the correlation graphs.

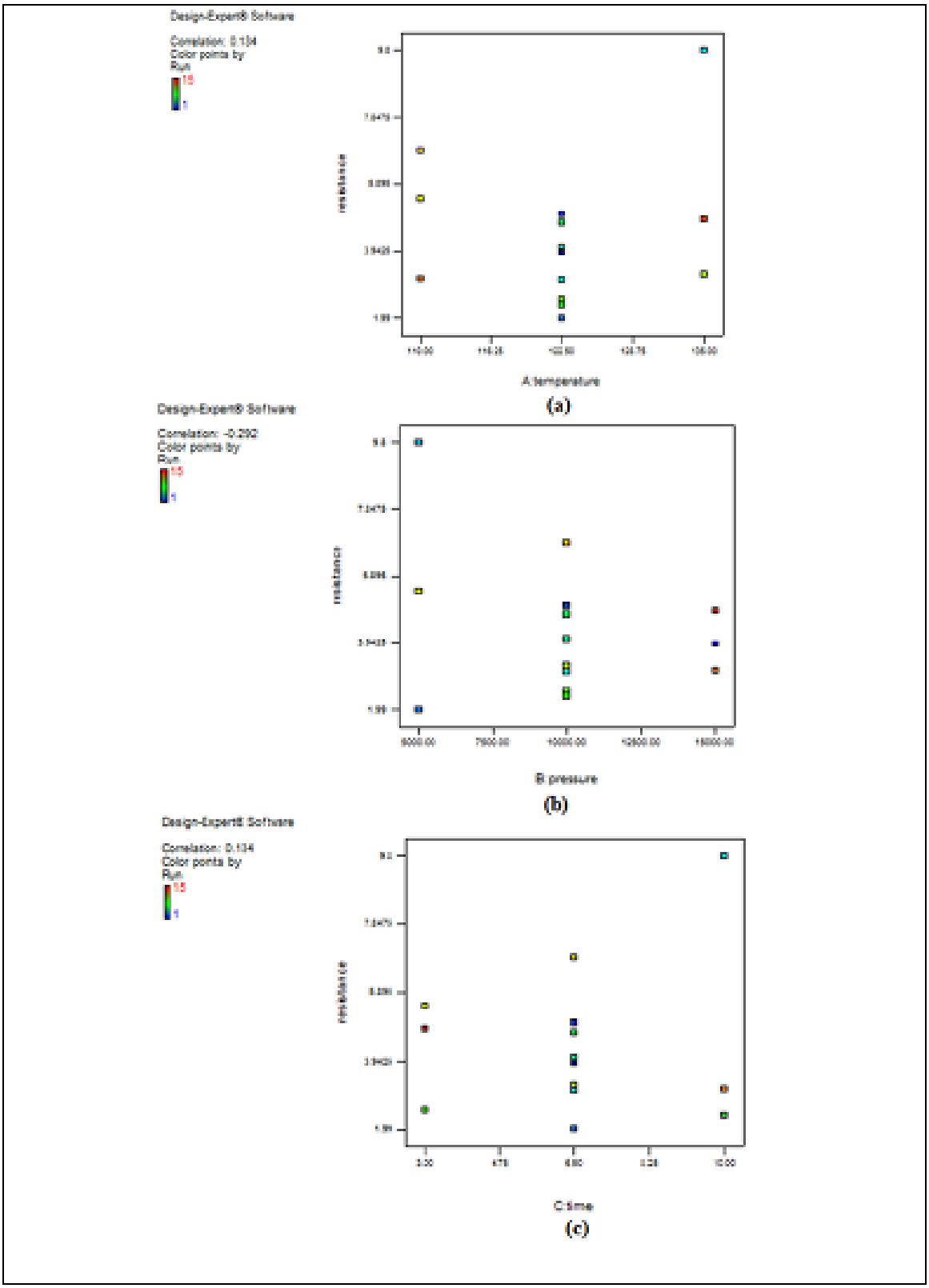


Figure 4.4. Correlation graphs of water permeability via (a) temperature (b) pressure (c) time

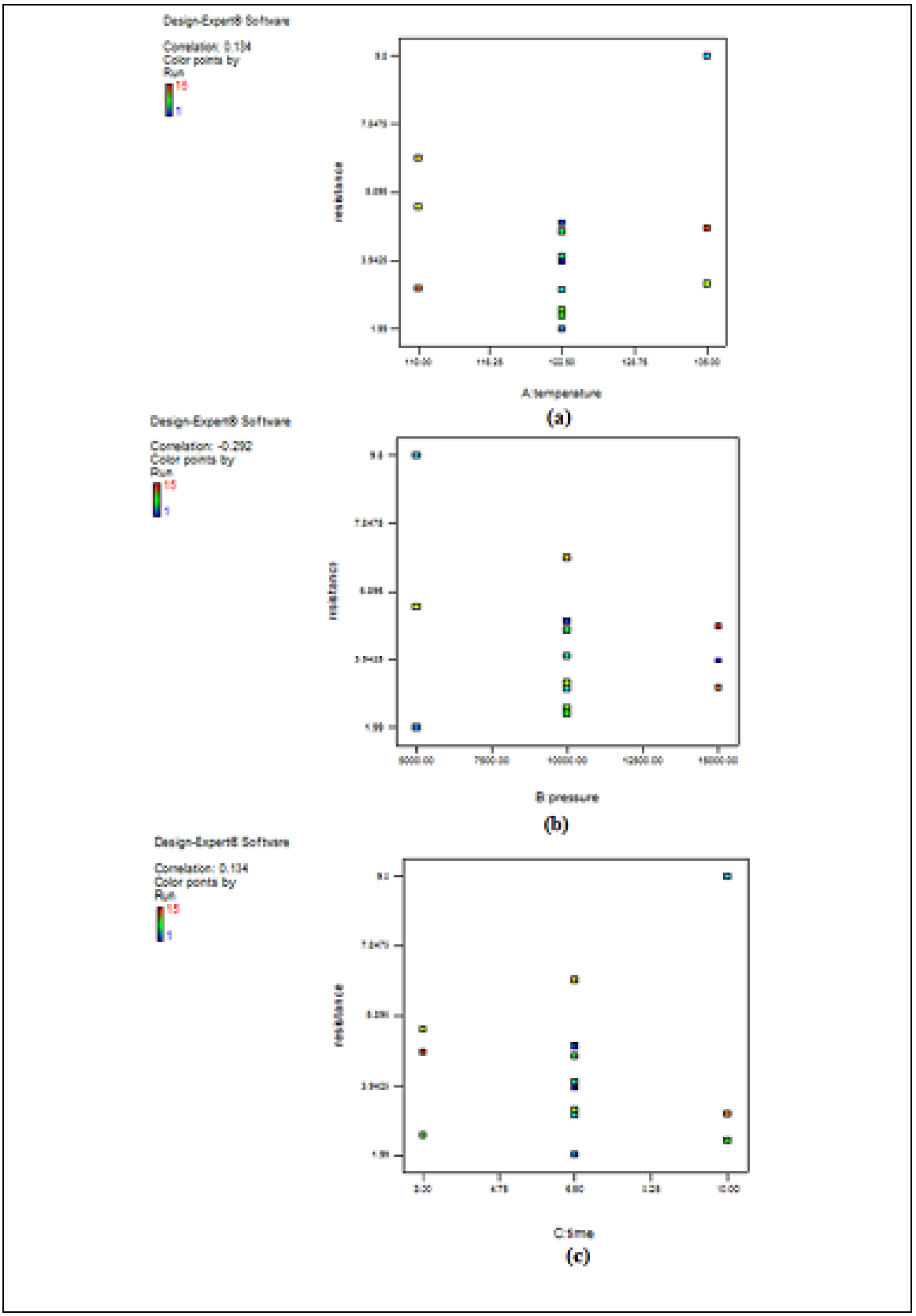


Figure 4.5. Correlation graphs of resistance via (a) temperature (b) pressure (c) time

Table 4.4. shows the correlation coefficients. It is seen from the correlation coefficients that; temperature has the highest and negative effect on the water permeability, while pressure is negative and has small effect on water permeability and also the holding time has small and positive effect on water permeability. On the other hand,temperature has positive and highest effect on resistance while the, pressure is small but as negative effect on the resistance whereas and the holding time has small and positive effect on the resistance.

Table 4.4. Correlation coefficients

	Correlation	
	Relative humidity	Resistance
Temperature	-0.588	0.249
Pressure	-0.030	-0.221
Time	0.034	0.063

4.3.1. Water Permeability Analysis

The results of Anova were shown in Figure 4.6. The Model f-value of 3.80 implies that the model is significant for water permeability. The values of ‘’Prob> F‘’ below 0.05 indicated that the model terms were significant. According to the model, the interaction of pressure and time was significant for the water permeability. The values of the coefficient of the multiple determination (R^2= 0.7445; R^2 adj= 0.5459 and R^2 pred= -0.70 for water permeability). These values are not close to each other. This possibly indicated a large block effect or a possible problem with the model and data. Things to consider were model reduction, response transformation, outliers according to the design expert. However, the model reduction and response transformation did not help to improve model. The model became insignificant. But lower press values of 0.21 could also explain the significance of the model. The lack of fit F value of 0.4082 means lack of fit is not significant. There is only a %40.82 chance that a lack of fit F value this large could occur due to the noise. Insignificant lack of fit is desired values; hence it means that model is fits.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.092	6	0.015	3.80	0.0428	significant
A-temperature	*9.857E-004*	*1*	*9.857E-004*	*0.24*	*0.6344*	
B-pressure	*0.016*	*1*	*0.016*	*3.87*	*0.0846*	
C-time	*2.265E-003*	*1*	*2.265E-003*	*0.56*	*0.4752*	
AB	*2.921E-004*	*1*	*2.921E-004*	*0.072*	*0.7947*	
AC	*0.016*	*1*	*0.016*	*3.88*	*0.0844*	
BC	*0.032*	*1*	*0.032*	*7.91*	*0.0228*	
Residual	0.032	8	4.035E-003			
Lack of Fit	*0.018*	*4*	*4.531E-003*	*1.28*	*0.4082*	*not significant*
Pure Error	*0.014*	*4*	*3.539E-003*			
Cor Total	0.12	14				

Std. Dev.	0.064	R-Squared	0.7405
Mean	0.30	Adj R-Squared	0.5459
C.V. %	20.90	Pred R-Squared	-0.7040
PRESS	0.21	Adeq Precision	7.026

Figure 4.6. Analysis of variance for water permeability

The mathematical regression model for water permeability fitted using the coded factors were as follows:

Water permeability regression model

0.30+0.022*temperature-0.088*pressure-0.034*time – 0.015 temperature*pressure – 0.11 *temperature*time + 0.15 pressure*time

Figure 4.7. (a) normal plot of residuals (b) predicted and actual values graph for water permeability. Normality plot has no unusual appearance so there is no need the transformation the values.

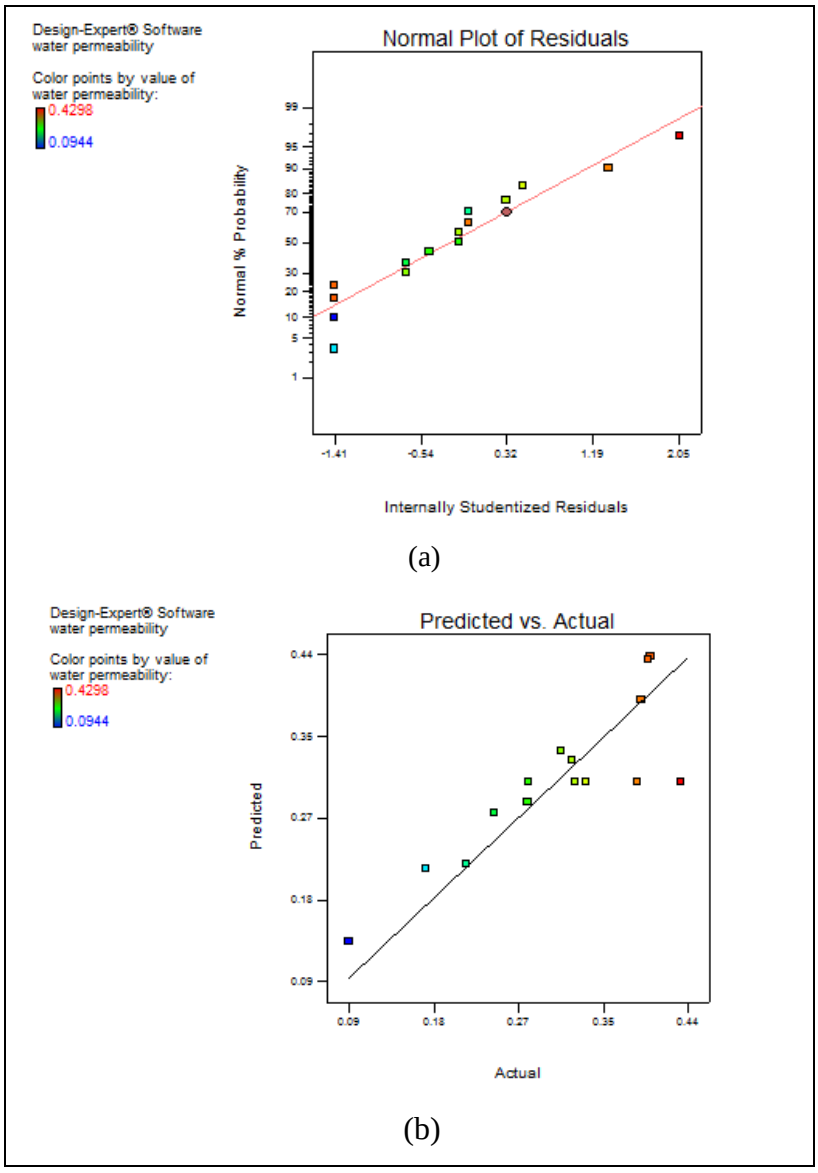


Figure 4.7. (a) normal plot of residuals (b) predicted and actual values graph for water permeability

Figure 4.8. shows that the effect of the one factor on the water permeability. As shown in the figure, the temperature has small influence on water permeability. The water permeability increases with the increase of temperature. With the temperature increase, water permeability increase from 0.281 to 0.3261. However, the pressure has negative effect on the water permeability. The water permeability decreased with the increase of pressure. The pressure has the biggest effect on the water permeability. With the increase of the pressure, water permeability decreased from 0.392 to 0.215. Also, the holding time has negative effect on the water permeability. Water permeability decreases as time increases from 0.3376 to 0.2703.

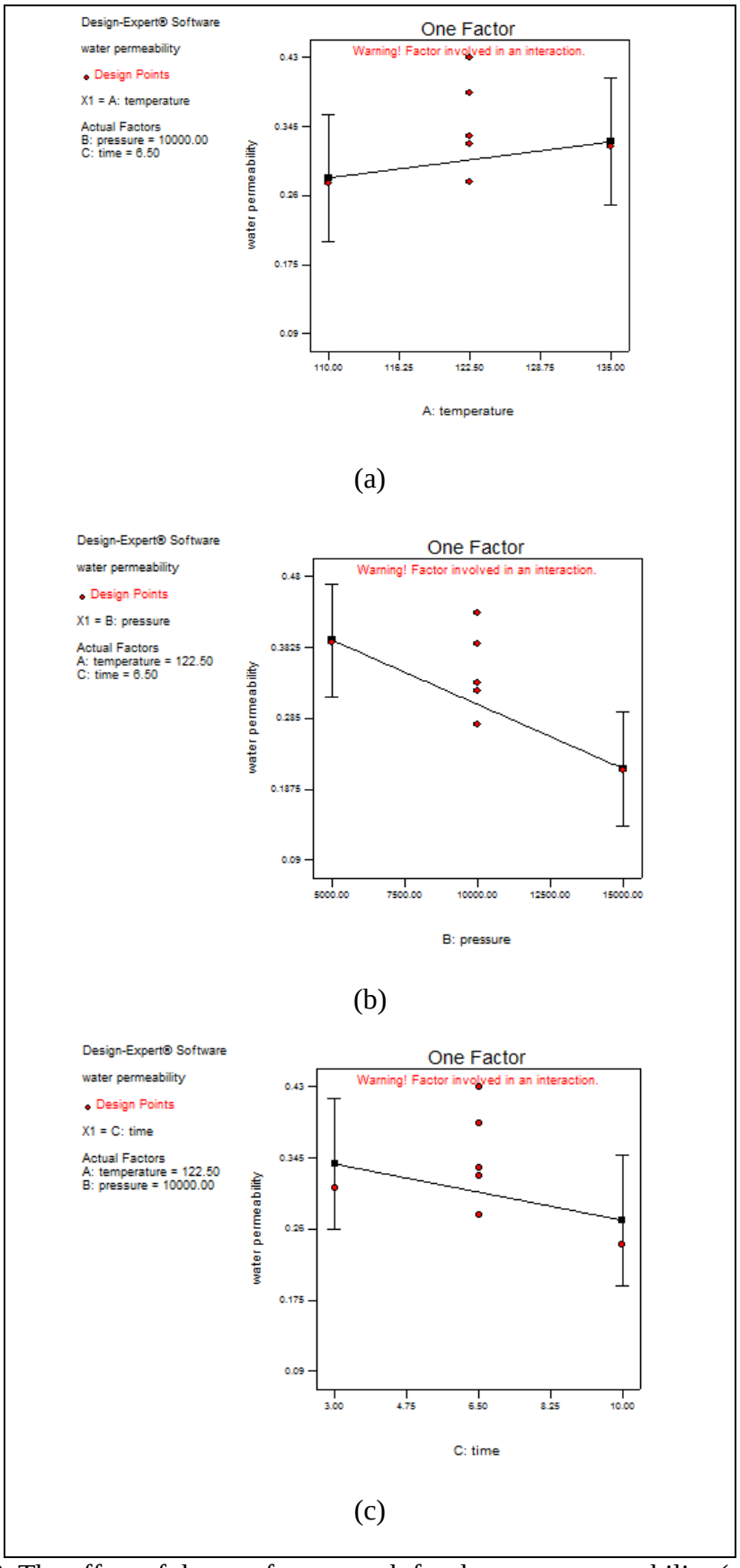


Figure 4.8. The affect of the one factor graph for the water permeability (a) influence of temperature (b) influence of pressure (c) influence of time

Figure 4.9. shows the interaction and 3-D surface plots. As shown in the figure, temperature and pressure has no interaction with each other. The smallest water permeability (0.2450) occurs at the pressure of 12500 pound and the temperature of122.5°C. The highest water permeability (0.3925) occurs at 5000 pound and 122.5°C. However, temperature and time has interaction. The smallest value of water permeability occurs at 3 min and 110°C. The value of water permeability is 0.2315 at that condition. The highest value was obtained at 3 min and 133°C; in fact the value of water permeability was 0.420 at that condition. Time and pressure has the interaction with each other as well. The smallest value of water permeability occurs at 3 min and 13500 pound. The value of water permeability is 0.175. The highest value was obtained at 3 min and 5000 pound that gave 0.4996 of water permeability.

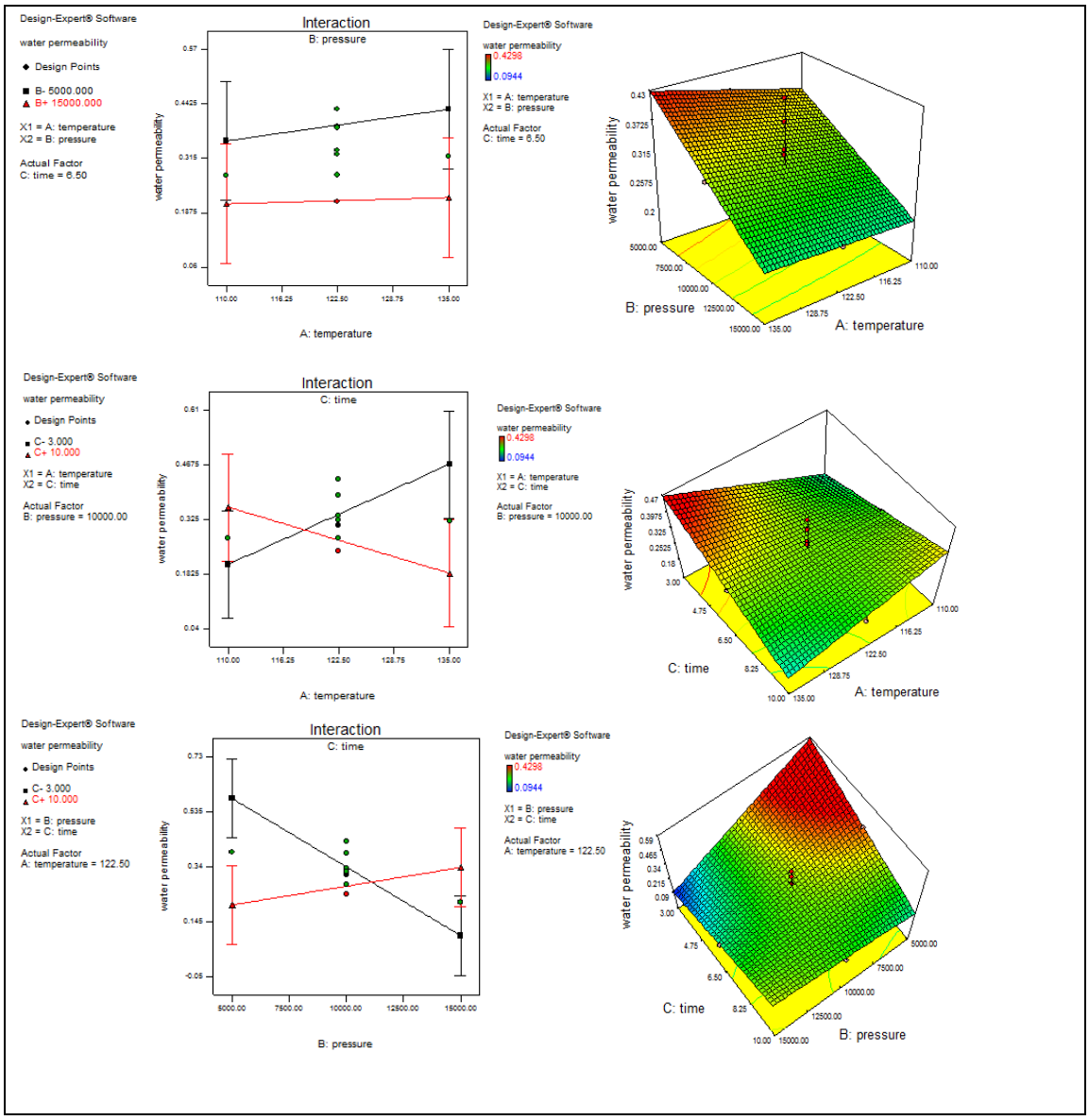


Figure 4.9. Interaction and 3-D surface graphs

Figure 4.10. shows the cube plot of the water permeability. The cube plot shows that all the three conditions affect the water permeability. As shown in the figure, the maximum value of the water permeability was obtained at 3 minute, 135°C and 5000 pound. The value of water permeability was 0.726 under these preparation conditions. The minimum value of the water permeability was obtained at 3 minute 110°C and 15000 pound.

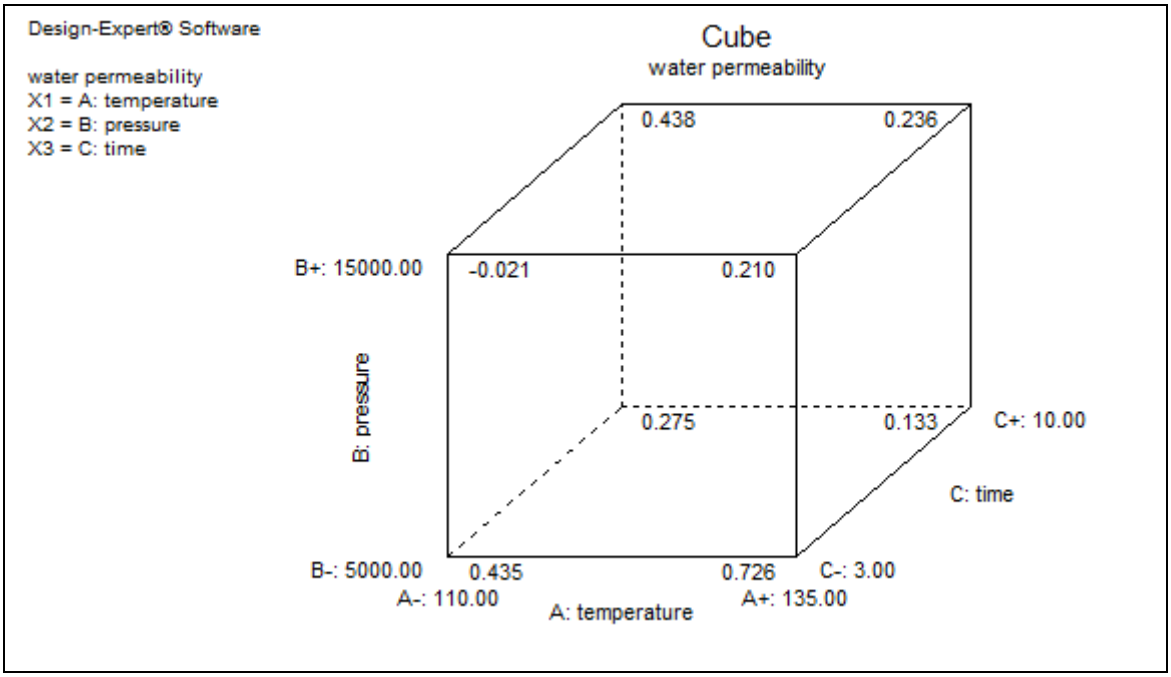


Figure 4.10. Cube plot of water permeability

4.3.2. Resistance –Response Analysis

The results of Anova were shown in Figure 4.11. The Model f-value of 6.92 implies that the model is significant for resistance. The values of '' Prob> F '' below 0.05 indicated that the model terms were significant. According to the model, one factor, temperature, the interaction of temperature and pressure, interaction of pressure and time, also the quadratic effects of temperature were significant for the resistivity. The values of the coefficient of the multiple determination (R^2= 0.8385; R^2 adj= 0.7174 and R^2 pred= 0.32 for resistivity.) are not close to each other. This possibly indicated a large block effect or a possible problem with the model and data. So, model reduction, response transformation, outliers need to be considered according to the design expert software. However, the model reduction and response transformation did not help to

improve the model. In fact the model became insignificant. Lower press values of 37.85 could also explain the significance of the model. The lack of fit F value of 0.1596 means lack of fit is insignificant. There is only a 15.96% chance that a lack of fit F value could occur due to the noise. Insignificant lack of fit is desired values. It means that model fits.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	46.68	6	7.78	6.92	0.0077	significant
A-temperature	*6.53*	*1*	*6.53*	*5.81*	*0.0425*	
B-pressure	*1.82*	*1*	*1.82*	*1.62*	*0.2384*	
C-time	*0.99*	*1*	*0.99*	*0.88*	*0.3744*	
AC	*10.22*	*1*	*10.22*	*9.10*	*0.0167*	
BC	*14.70*	*1*	*14.70*	*13.08*	*0.0068*	
A^2	*15.01*	*1*	*15.01*	*13.36*	*0.0065*	
Residual	8.99	8	1.12			
Lack of Fit	*6.72*	*4*	*1.68*	*2.95*	*0.1596*	*not significant*
Pure Error	*2.27*	*4*	*0.57*			
Cor Total	55.67	14				

Std. Dev.	1.06	R-Squared	0.8385
Mean	4.35	Adj R-Squared	0.7174
C.V. %	24.40	Pred R-Squared	0.3200
PRESS	37.85	Adeq Precision	9.295

Figure 4.11. Analysis of variance for resistance

The mathematical regression model for resistance, fitted using three factors, were as follows:

Resistance regression model

3.53 – 1.81* temperature +0.95 * pressure + 0.41 *time +2.77 *temperature*time -3.32 pressure*time +2.04 $temperature^2$

Figure 4.12. shows the normal plot residuals, the predicted and actual values for the resistance. Normality plot has no unusual issue so there is no need for the transformation of the values.

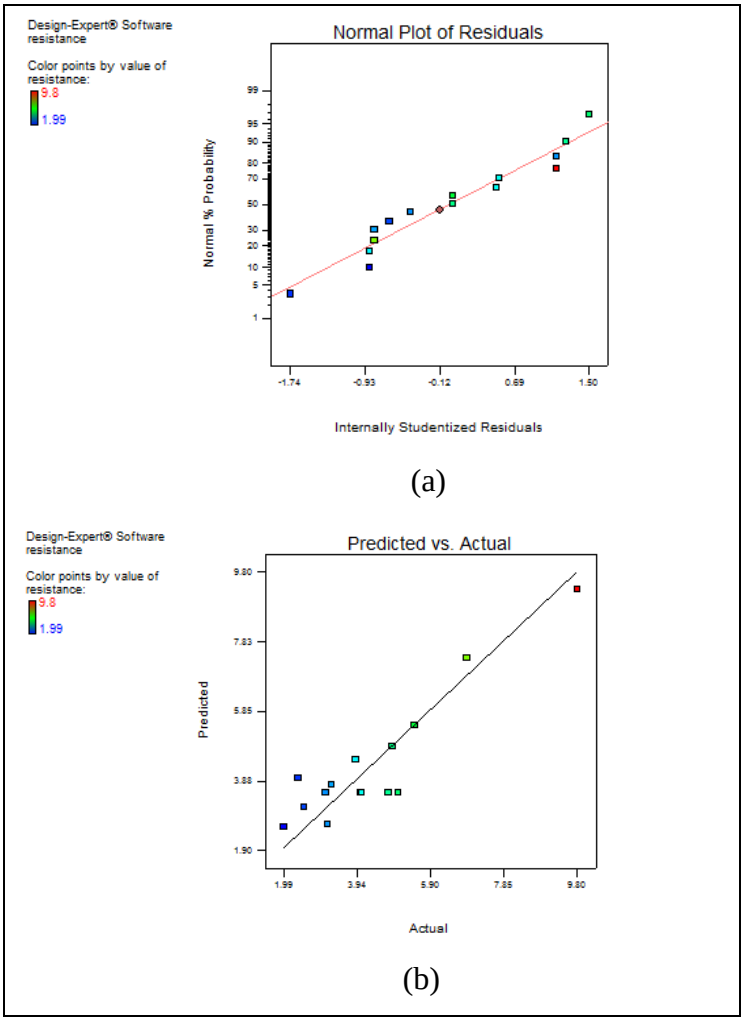


Figure 4.12. (a) normal plot of residuals (b) predicted and actual values graph for resistance

Figure 4.13. shows that the effect of the one factor on the resistance. As shown in the figure, with the temperature increase, the resistance initially increases than it decreases. With the temperature, the resistance decreases from 7.3736 kΩ to 3.68 kΩ. However, pressure has positive effect on the resistance. The resistance increases with the increase of pressure. With the increase of the pressure, the resistance increases from 2.5736 kΩ to 4.4836 kΩ. Also, the holding time has negative and small effect on the resistance. The resistance increases from3.12 kΩ to 3.93 kΩ as time increases.

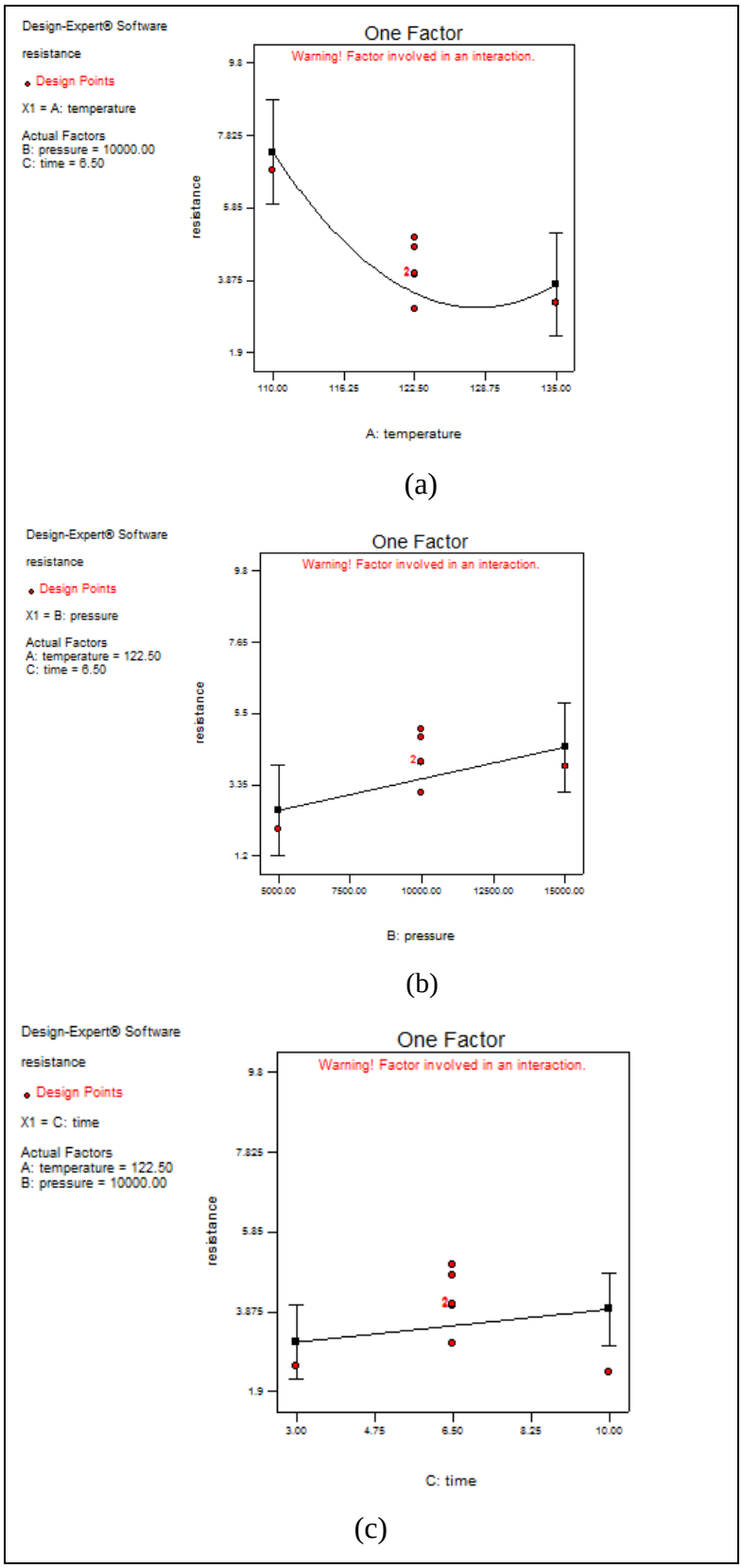


Figure 4.13. The effect of the one factor graph for the resistance (a) influence of temperature (b) influence of pressure (c) influence of time

Figure 4.14. shows the interaction and 3-D surface plots. As shown in the figure, the temperature and time has interaction with each other. The smallest value of the resistance occurs at 4.75 min and 128°C. The value of resistance is 2.11 kΩ under these conditions. The highest value was obtained at 5 min and 110°C. The value of resistance was 8.2123 kΩ under these time and temperature preparation conditions.

Time and pressure has the interaction with each other, as well. The smallest value of the resistance occurs at 4 min and 5000 pound. The value of resistance is 0.2715 kΩ at these conditions. The highest value was obtained at 4 min and 135000 pound. The value of resistance was 5.971 kΩ at these conditions.

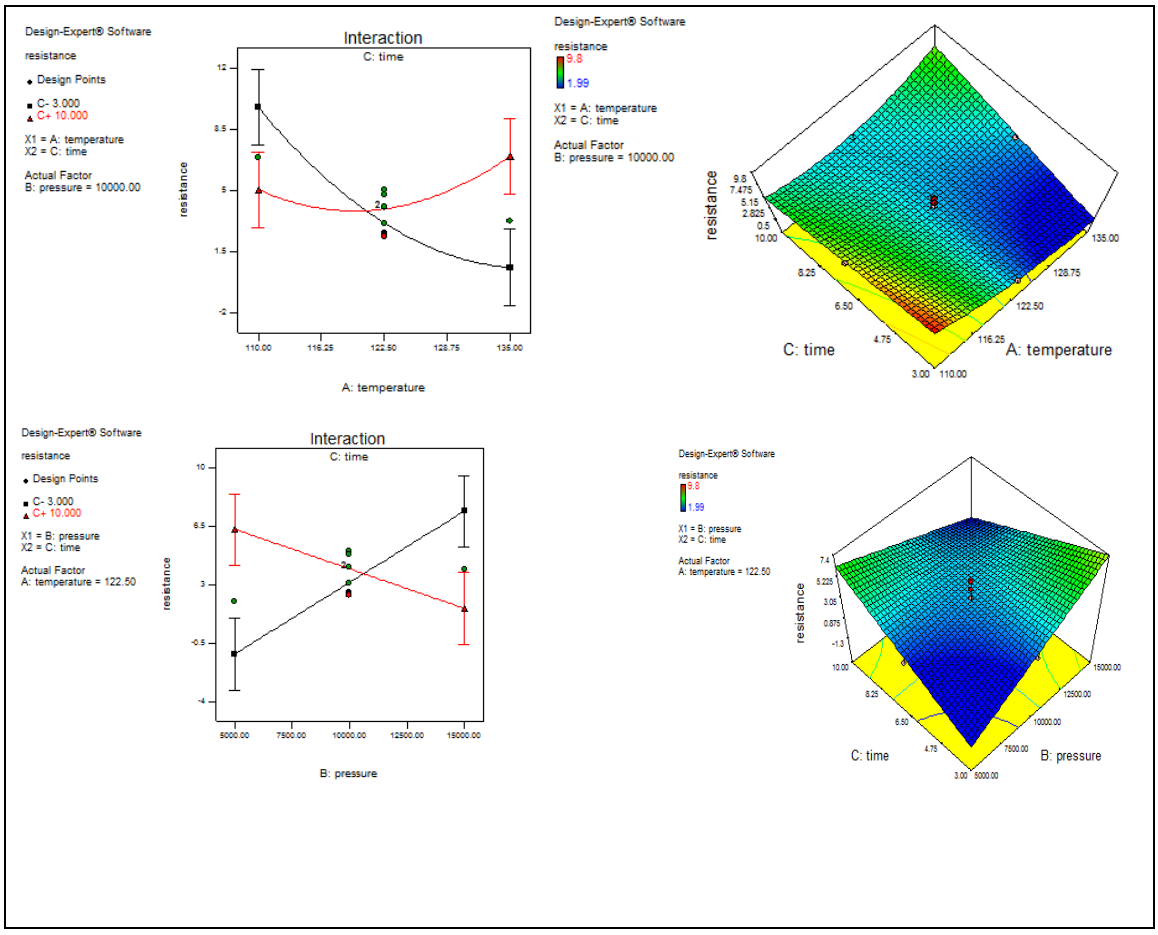


Figure 4.14. Interaction and 3-D surface graphs

Figure 4.15. shows the cube plot of the resistance. The cube plot shows all three conditions affecting the resistance. As shown in the figure, the maximum value of the resistance was obtained at 3 minute, 110°C and 15000 pound. The value of the

resistance was 2.65 kΩ. The minimum value of the resistance was obtained at 10 minute 110°C and 15000 pound at which the value of the resistance was 14.01 kΩ.

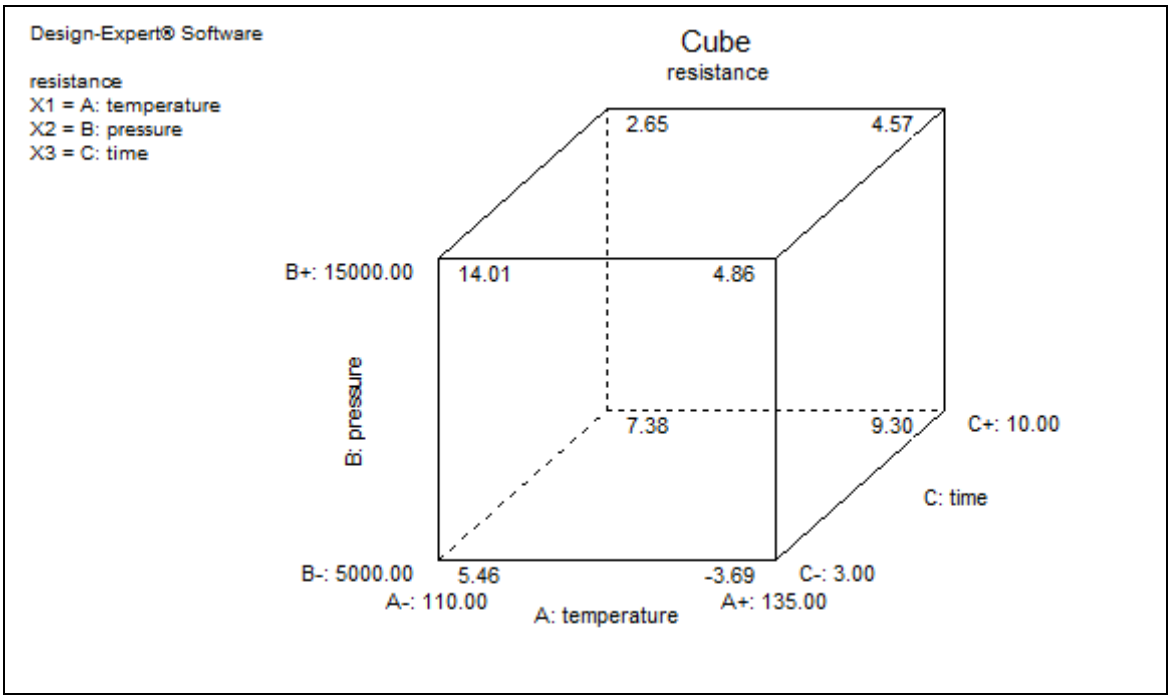


Figure 4.15. Cube plot of resistance

The comparison of water permeability and resistance analysis to find the optimum preparation condition was done using the design expert 7. The optimum conditions were obtained at the maximum water permeability and the minimum resistance. In the Table 4.5., the maximum water permeability and the minimum resistance were attained at the optimum conditions of 129.93°C, 7260.25 pound and 4.60 minute.

Table 4.5. Design Expert optimization output for maximum water permeability and minimum resistance

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
temperature	is in range	110	135	1	1	3
pressure	is in range	5000	15000	1	1	3
time	is in range	3	10	1	1	3
water permeabil	maximize	0.0944	0.4298	1	1	3
resistance	minimize	1.99	9.8	1	1	3

Solutions

Number	temperature	pressure	time	water permeal	resistance	Desirability	
1	129.93	7260.25	4.60	0.469893	0.546568	1.000	Selected

4.3.3. Validation Analysis

Validation of the model (permeability and resistance models) was done at 3 different conditions using the factors selected in such as a way that they are not the same as the factor values used in the construction of the design but within the set of the factor values used in the design. The model prediction and the experimental results are shown in Table 4.6. It is seen that the predicted permeability values using model is within the experimental design. Hence, the model predicts the water permeability of MEA prepared using the factors used in this study.

Table 4.6. Validation Results

Temperature(°C)	Pressure(pound)	Time(min)	Regression model result	Experimental result
115	7000	5	0.3647	0.38
128	12000	8	0.2678	0.23
130	7000	4.5	0.4698	0.48

4.4. Cost Analysis

A cost analysis using the market values for chemicals and the membranes shows that it costs \$3.79/cm^2 to prepare MEA as seen in the Table 4.7. given below.

Table 4.7. Cost Analysis

	Market Value	Cost of 1 cm^2 MEA
Nafion Membrane	10 cm^2 = $ 32	$3.2
PTFE	25 ml= €60	$0.03
Pt	1 g= $94.90	$0.40
Ru	1 g= $ 48.20	$0.15
Activated Carbon	100 g = $21	$0.003
Isopropanol	500 ml =€20.4	$0.003

4.5. Single Cell PEM Electrolyzer

4.5.1. Catalyst Reduction

After having obtained the optimum preparation conditions, the catalyst loaded MEA was prepared using that the optimum conditions (i.e.135°C, 5000 pound and 3 min). The prepared MEA was then tested in the single cell PEM Electrolyzer.

It is known that Pt precursor, such as platonic acid, could be reduced at 80°C in ethanol. So, it seemed that the preparation conditions used in this study would be enough to obtain the metallic catalysts, such as Pt and Pt/Ru on the MEA. But the time, 3 min was not enough for reducing the metal precursor to obtain the metallic catalyst. Therefore, MEA was prepared using slightly different preparation conditions (135°C, 5000 pound and 10 minute) which were different than the optimum conditions found with the model. Indeed, the MEA under this slightly different conditions was found to be active in the electrolyzer but the resistance of the prepared MEA was high which was also predicted by the model; hence, resulting in high over voltages at current densities used in this study. Therefore, $NaBH_4$ was used to reduce the metal precursors on the active carbon to avoid using high holding time or temperature which are not going to be the optimum preparation conditions. In fact, it was found that the catalyst ink solution prepared using $NaBH_4$ treated metal precursor impregnated active

carbons(using a procedure given in Chapter 3) showed almost the same V-I characteristic as that of the commercial MEA as seen Figure 4.16.

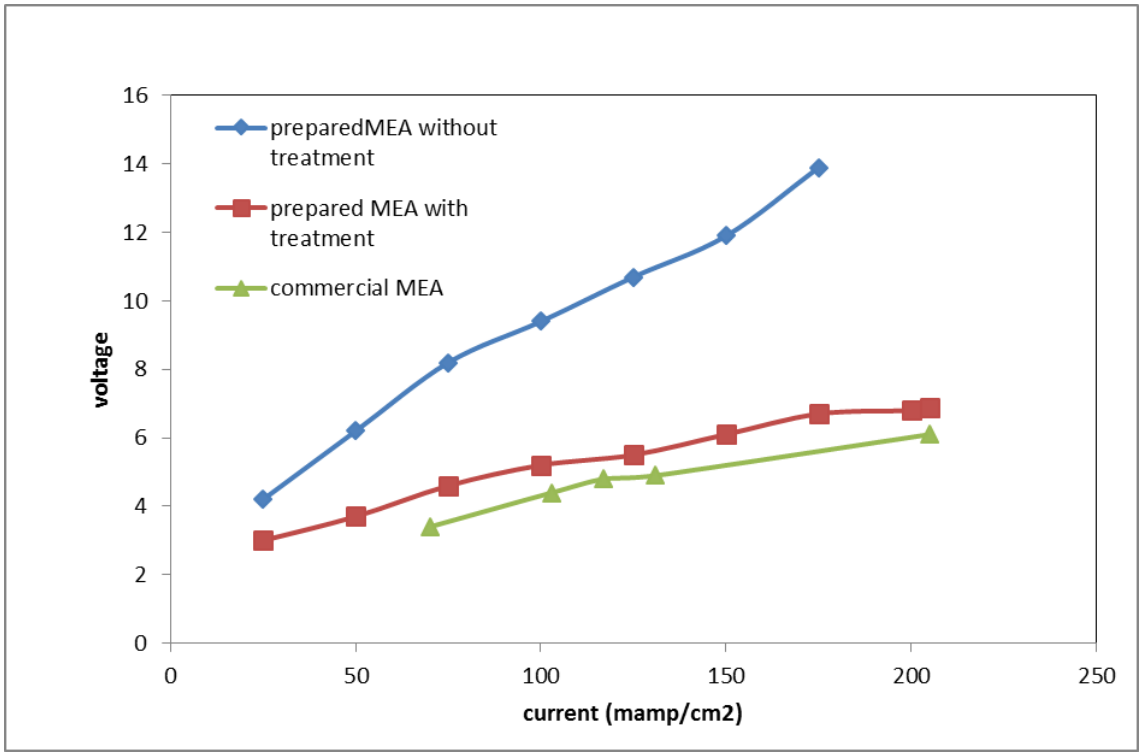


Figure 4.16. Voltage and current graphs of the MEA

In addition, hydrogen flow rate generated as a function of the current density is shown in Figure 4.17. It is seen that $NaBH_4$ treatment of the catalyst ink used to prepare MEA lowered the power consumption during the electrolysis of water without lowering the hydrogen flow rate. The hydrogen flow rates and V-I characteristics of the MEA prepared using the optimum conditions found in this study are the same as that of the commercial MEA within the experimental error of this study.

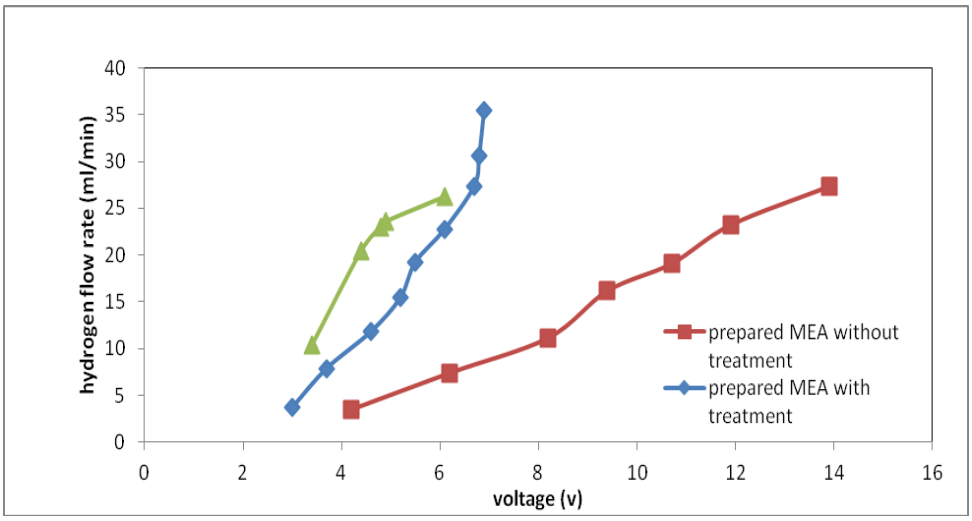
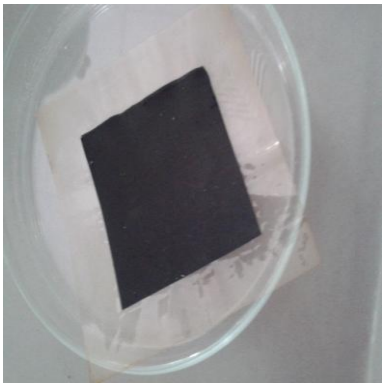
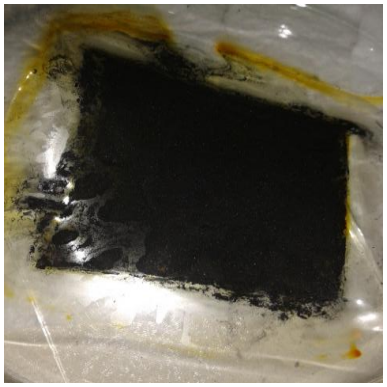


Figure 4.17. Hydrogen flow rate via voltage rate graph

4.5.2. Characterization of MEA

Figure 4.18. shows the picture of the commercial MEA and the prepared Mea in this study. The prepared MEA using the optimum conditions is not as clean as the commercial MEA. This is due to template gasket and securing clamps used for coating MEA with the ink solution. However, The V-I performance and the hydrogen production as a function of current density on the MEA prepared in this study are the same as that of the commercial MEA within the experimental error of the study. The appearance of the MEA could be improved by using other techniques, such as spray coating and better masking of the unused areas, to coat the ink solution.





(a) **(b)**

Figure 4.18. Picture of (a) commercial MEA (b) MEA prepared in this study

4.5.2.1. SEM images of the MEA

The prepared MEA was characterized using SEM. The morphology of the MEA was seen in the SEM micro-graph. The active carbon particles containing metal catalysts were not homogenously distributed. So, milling method of the active carbon needs to further be improved or other types of carbon, such as carbon black or carbon nanotubes need to be considered even though the V-I characteristics and hydrogen flow rate of the MEA prepared using mechanically milled activated carbon are the same as that of the commercial MEA

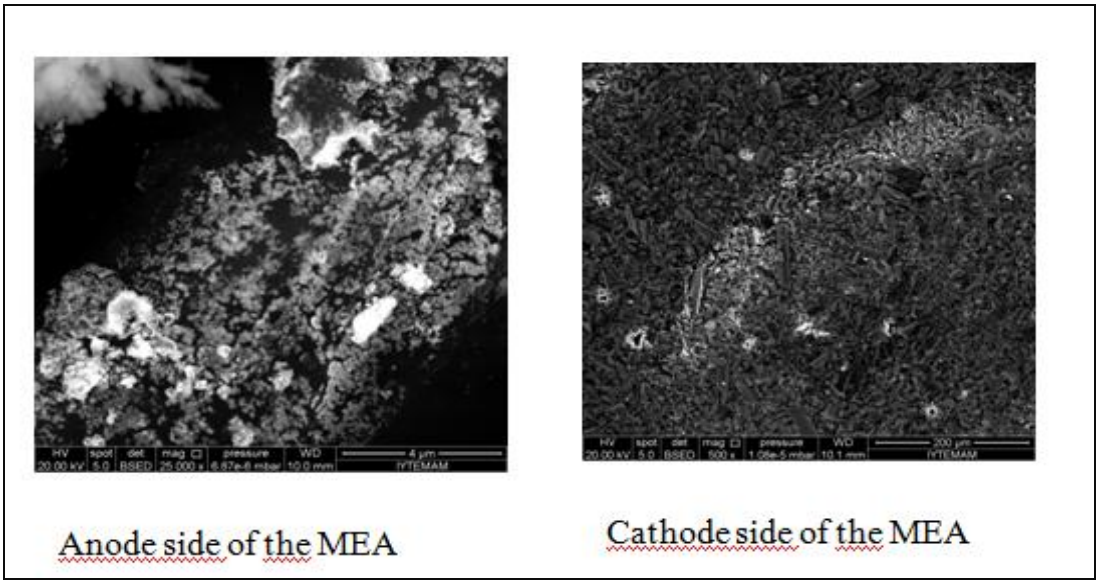
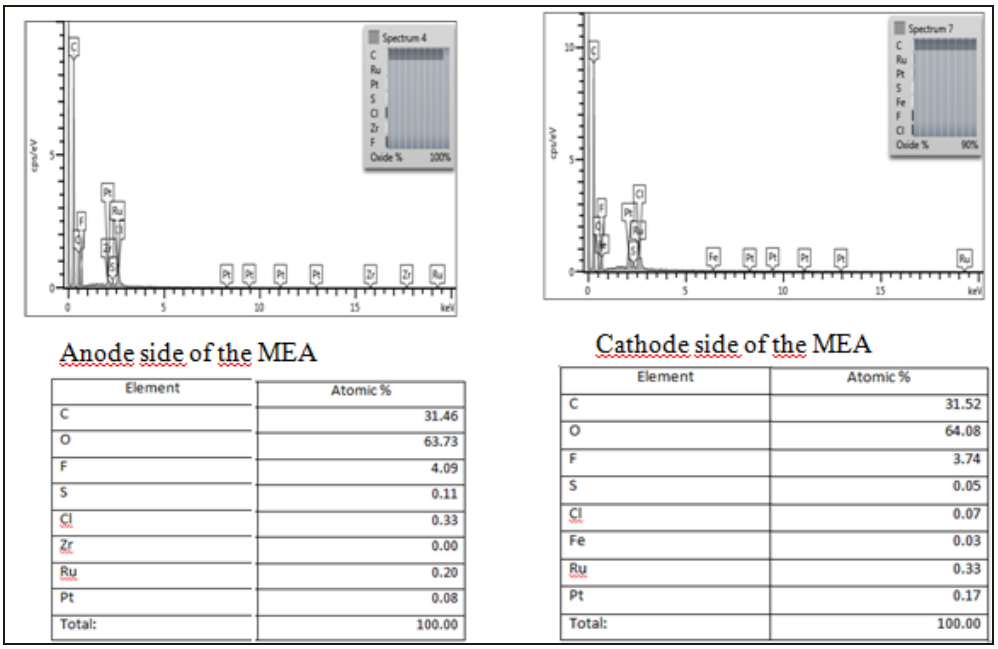


Figure 4.19. SEM image of the anode and cathode side of the MEA

4.5.2.2. EDX results

An EDX result shows the composition and contents of the MEA. Figure 4.20. shows EDX results of the anode and the cathode sides. It is seen that chloride ions are still present on the MEA even though washing was used to remove the chloride ions. This shows that the washing step needs to be improved to remove the chloride ions left during the reduction of the metal precursor using $NaBH_4$.



Element	Atomic %
C	31.46
O	63.73
F	4.09
S	0.11
Cl	0.33
Zr	0.00
Ru	0.20
Pt	0.08
Total:	100.00

Element	Atomic %
C	31.52
O	64.08
F	3.74
S	0.05
Cl	0.07
Fe	0.03
Ru	0.33
Pt	0.17
Total:	100.00

Figure 4.20. EDX results of anode and cathode side of the MEA

4.5.2.3. XRD results

XRD patterns of the MEA show that carbon is present in the form of graphite and amorphous carbon at the peaks located at 2Ɵ angles of 40°and10° respectively. Besides, platinum must have the peak located at 39° and also the other peaks of the Pt located at 36,46,85° must be seen. So, this could be due to that Pt crystallites are smaller than 5 nm (since the XRD is sensitive to the crystallites larger than 5 nm). In fact EDX results show that ME contains Pt metal on both sides. Figure 4.21. shows the XRD patterns of the prepared MEA.

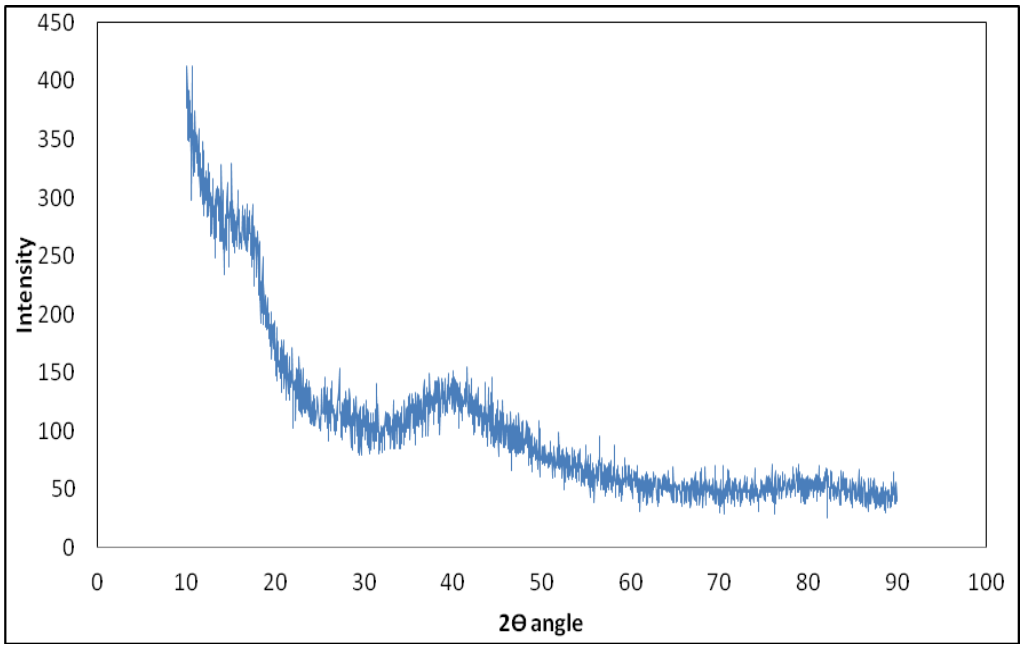


Figure 4.21. XRD patterns of the MEA

CHAPTER 5

CONCLUSION

In the first part of the thesis the preparation conditions of the membrane electrode assembly was investigated using water permeability and resistance as the response of the MEA. The small center composite experimental design was done to find the optimum preparation conditions. The optimum conditions were found to be135°C, 5000 pound and 3 minute of press holding time.

In the second part of the thesis, the MEA loaded with the metal catalyst was prepared at optimum conditions. The V-I performance and the hydrogen production of the prepared MEAs and commercial membranes were compared in the single cell PEM Electrolyzer. The optimum conditions did not yield the MEA with metal catalysts because of the insufficient reduction condition for the metal precursors. However, the catalyst ink prepared using the metal precursor impregnated active carbon treated with the $NaBH_4$ yielded highly active MEA for water electrolysis. In fact, the resistance of the prepared MEA was almost the same as that of the commercial MEA but the hydrogen production was slightly higher than of the commercial MEA.

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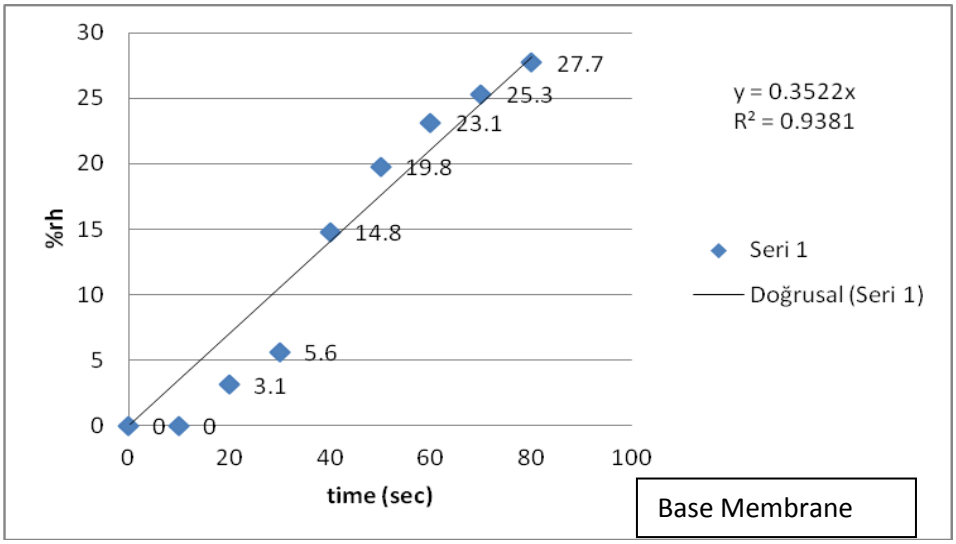
British Petrol World Statistical Rewiews 2013 Energy Outlook.

APPENDIX A

RAW DATA FOR EXPERIMENTAL STUDY



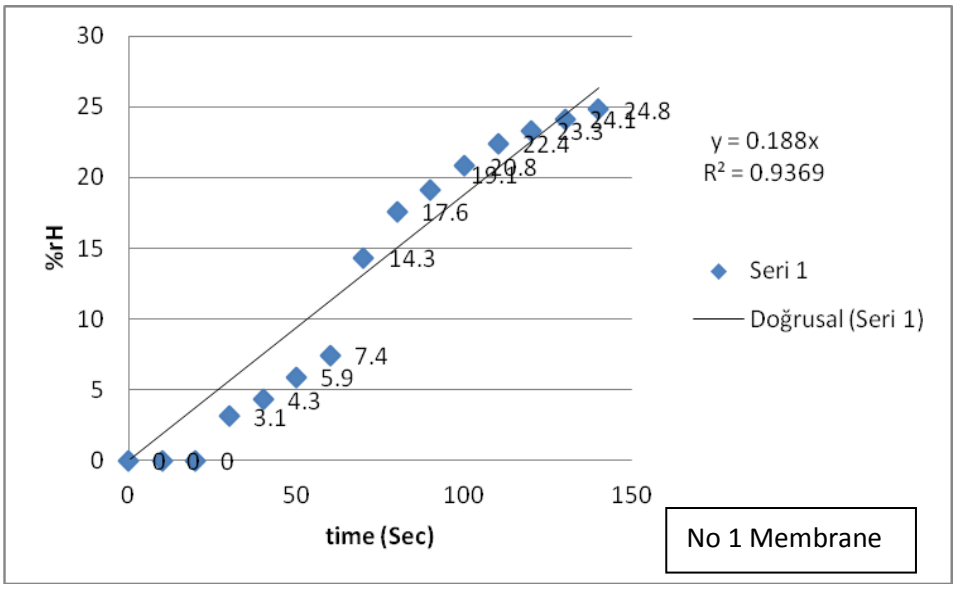


Figure F.1. Relative Humidty versus Time Graphs

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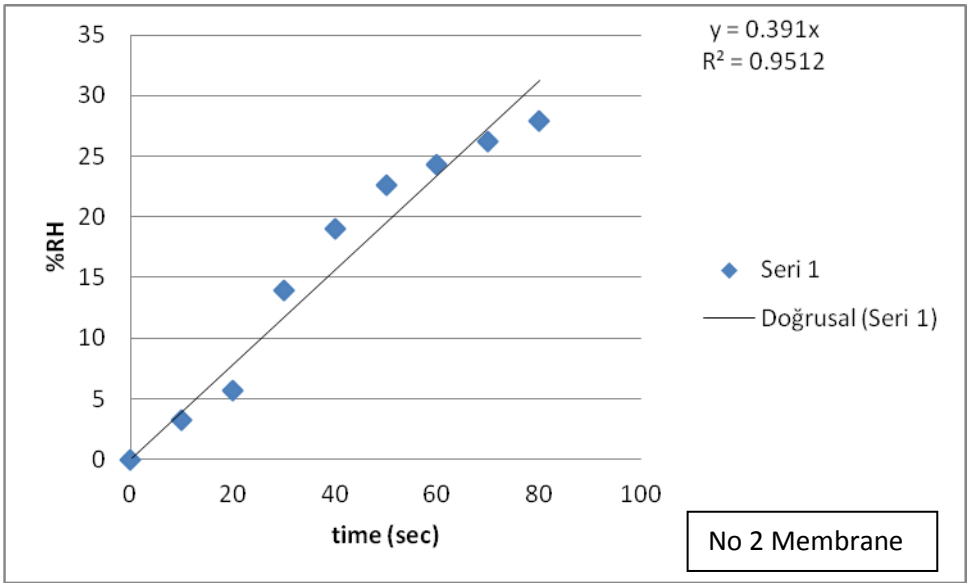

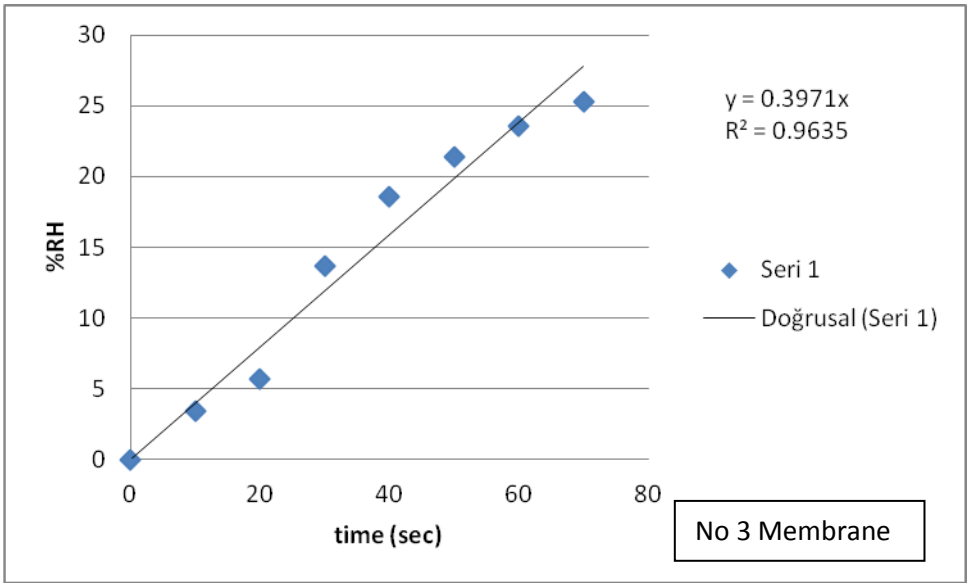

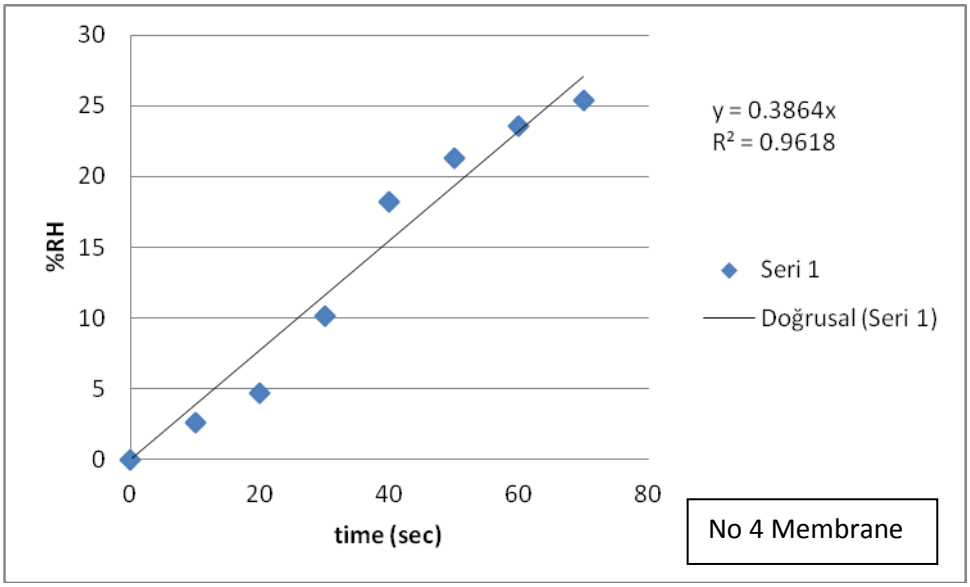

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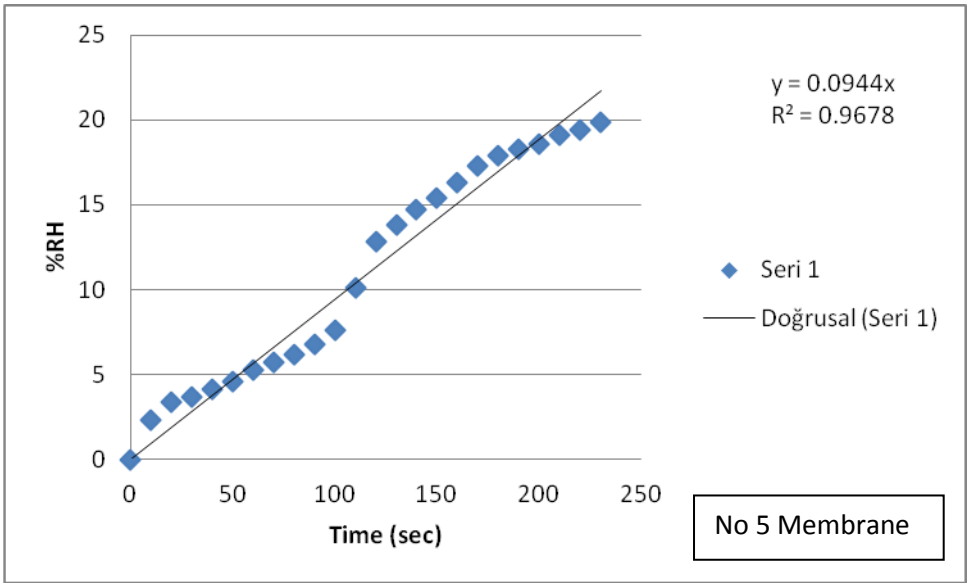

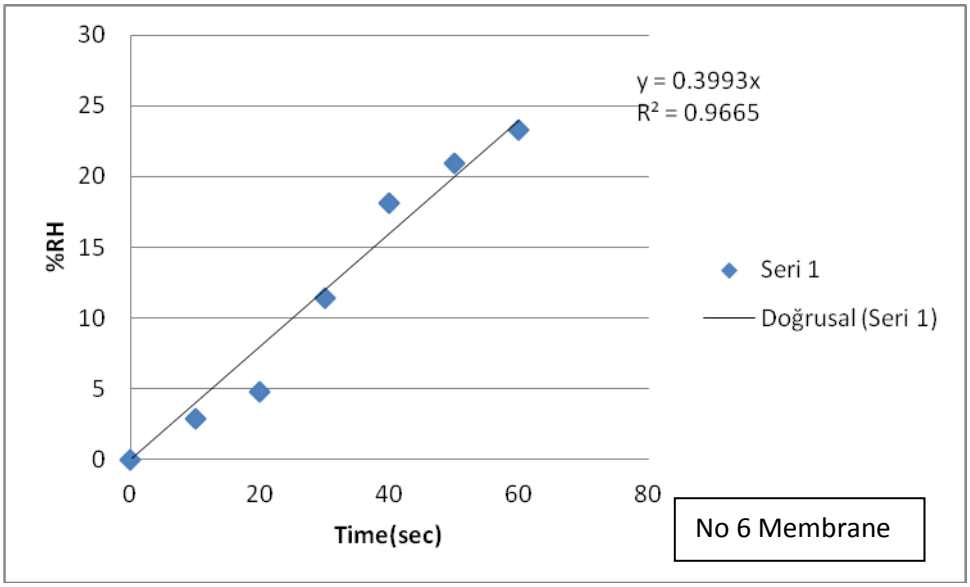

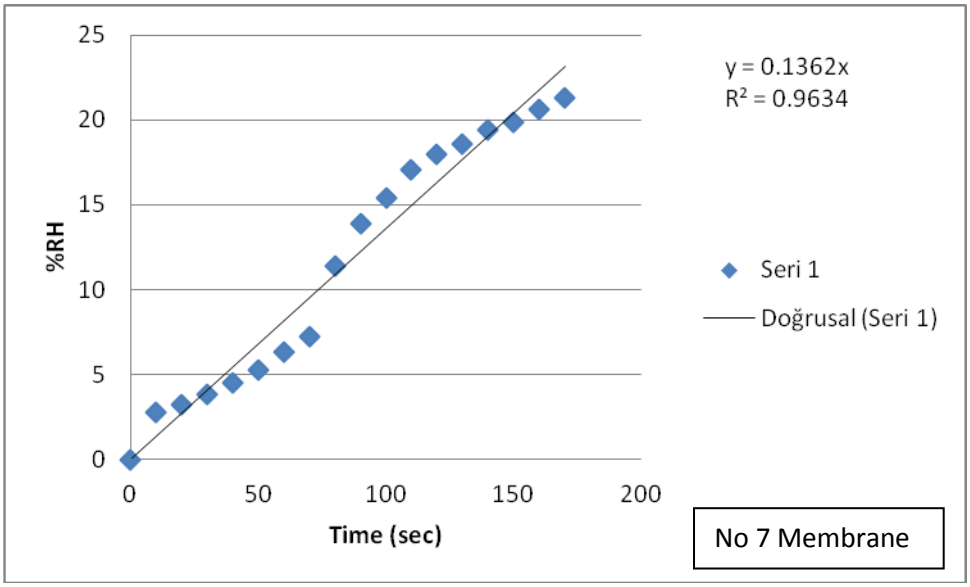

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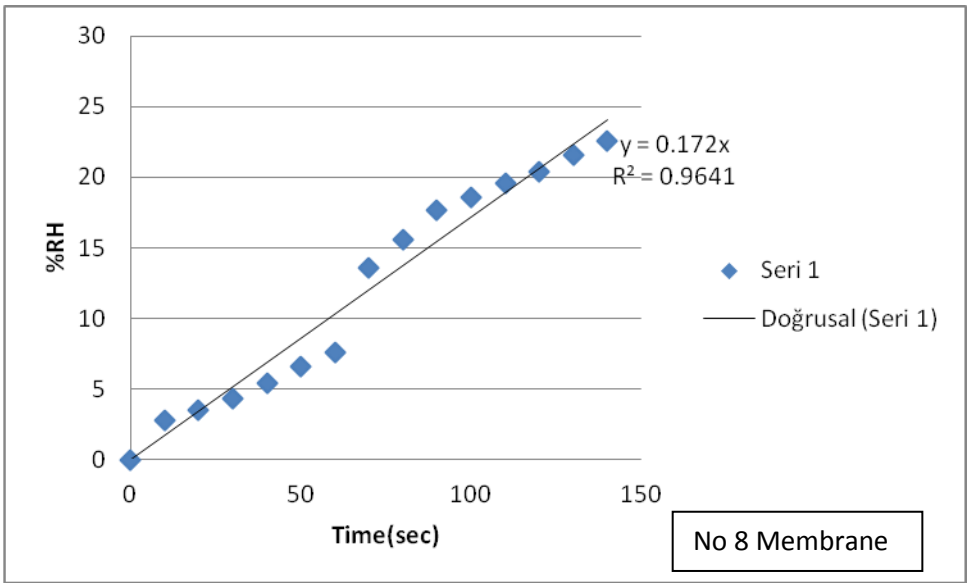

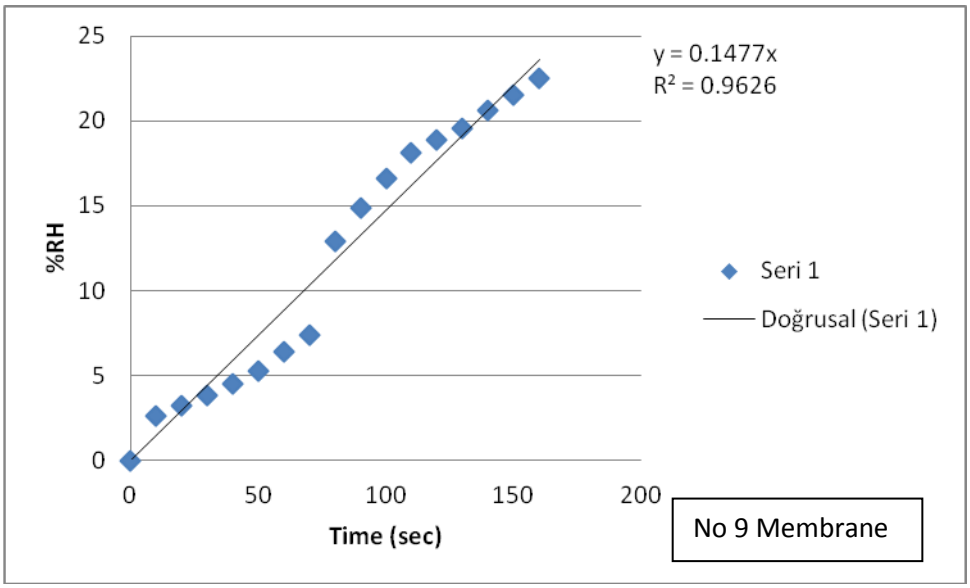

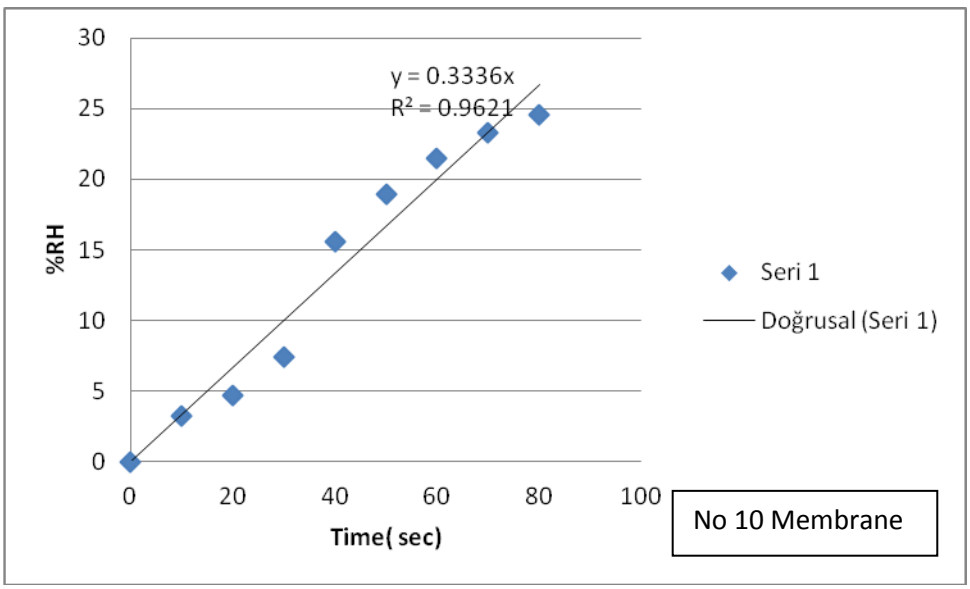

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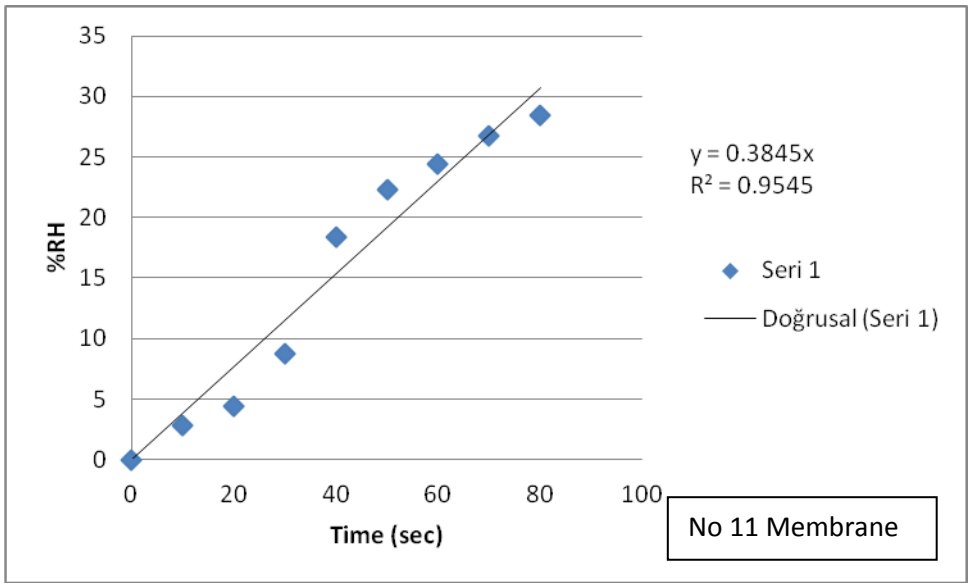

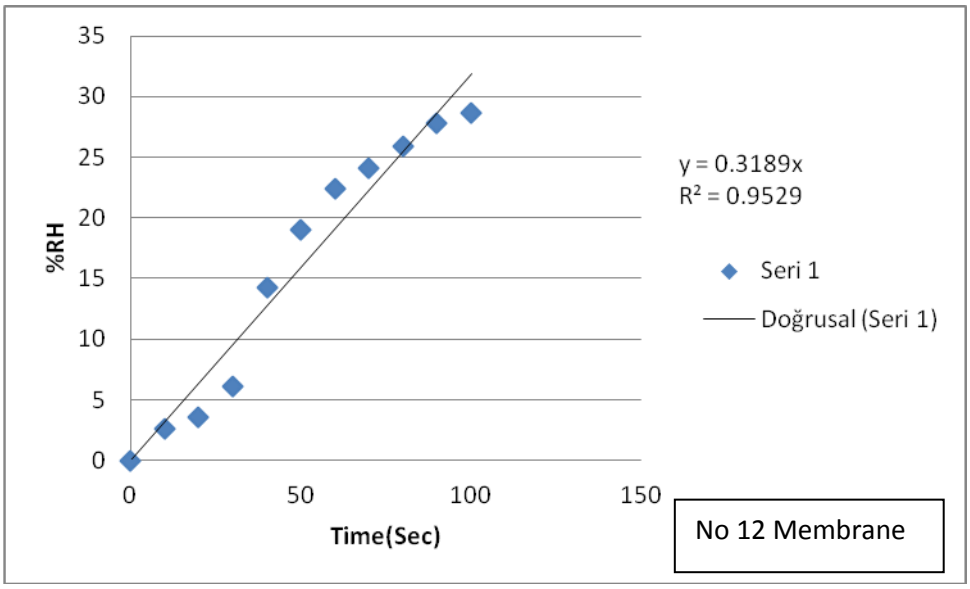

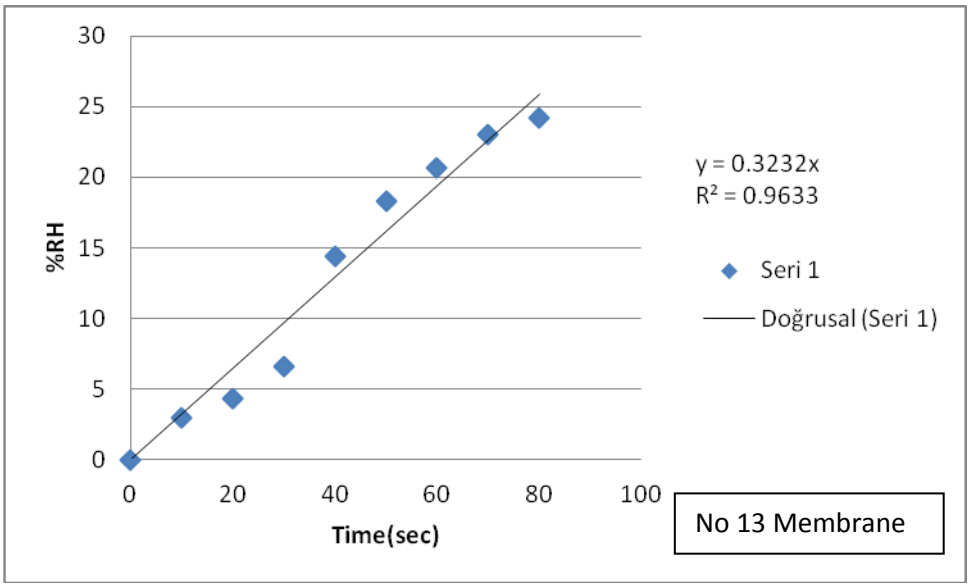

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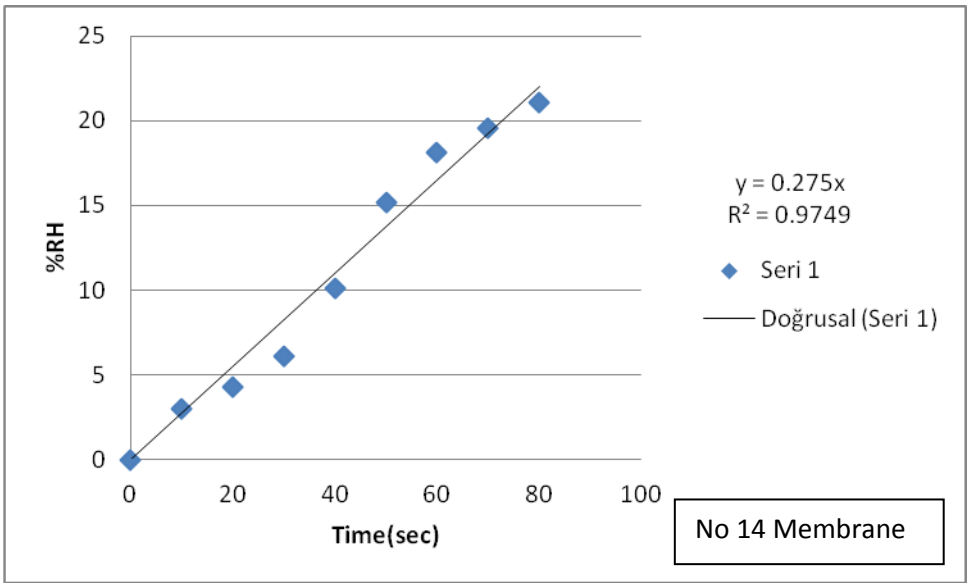

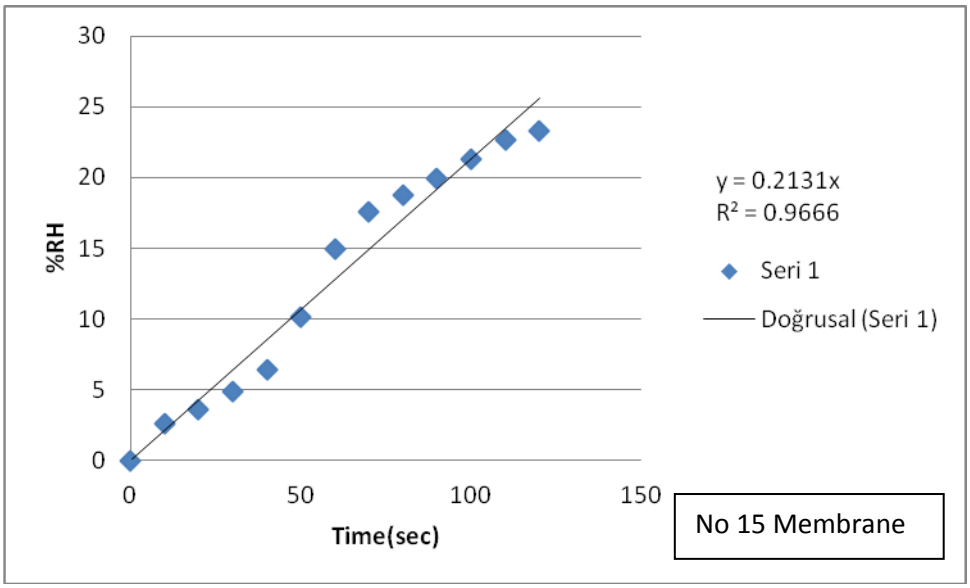

Figure F.1 (cont.)