Modeling and Analysis of Flow and Heat Transfer in a Large PEM Fuel Cell Suitable for Automotive Applications

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Modeling and Analysis of Flow and Heat Transfer in a Large PEM Fuel Cell Suitable for Automotive Applications

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ABSTRACT

Based on the Zero Emission Vehicle (ZEV) targets, automotive manufacturers realize the necessities to develop new technologies that replace the Internal Combustion Engine (ICE). Nowadays there are two major trends in the automotive industry; First, hybrid vehicles which combine hydrogen energy with combustion energy, and second there is a down-sizing trend. By using hybrid technologies auto makers can obtain a significant drop in emission levels and the efficiencies increase up to 80%. Reaching 80% efficiency is not only achieved by using hybrid technologies. Automotive manufacturers also use different technologies such as the second mega trend: down-sizing. Engine volumes start to decrease but the horse powers of the engines keep increasing. 20 years ago a 2.0lt engine could create up to 120hp. However today, Original Equipment Manufacturers (OEM) could build an engine which can generate 150hp with a1.0lt engine volume. These are great results, but still this technology needs fuel to consume and by using ICE it is not possible to obtain ZEV. In long term this raw material requirement can cause rise in fuel costs. On the other hand, there is still ICE which means there is emission.

Fuel cells (FC) can be the shining star of ZEV targets. There are several types of fuel cells that can be applicable to transportation. The most convenient type is Proton Exchange Membrane (PEM) fuel cell due to its start up time, cold performance and working temperature.

PEMFC systems can be a great displacement for internal combustion engines in transportation industry [84]. FC technologies have high efficiency and when they used in automotive industry they can reduce the CO_x emissions. This makes them a potential candidates for European auto companies to meet their voluntary carbon dioxide emission limits in the European Union [85],[86].

The objective of this work is to find a way to decrease the cost of the fuel cells. Time is necessary to obtain deep knowledge on design principles of proton exchange membrane fuel cell (PEMFC) which could be used in automotive applications. Fuel cells are continuous clean energy converters which run on hydrogen or conventional hydrocarbons. They produce energy much more efficiently and they process quieter than ICE systems with higher power densities. For improved design and control of FCs, better understanding of fuel cell systems and components by means of developing and simulating accurate model FC is necessary.

In this thesis; combinations of simulations were carried out and the results analyzed for enhancing the understanding of distribution of flow and temperature for a 400 cm^2 flow field PEMFC. A three-dimensional (3D) computational fluid dynamics (CFD) based model was used to predict heat and mass distributions of this design. The effect of flow direction and the cooling pattern on this design were also taken into account to enhance the understanding for this selected flow field design.

ÖZET

Sıfır emisyon hedefleri göz önünde bulundurulduğunda otomotiv üreticilerinin içten yanmalı motor teknolojilerinden bir adım öteye ilerlemesi gerekmektedir. Günümüz otomotiv sanayinde bu doğrultuda oluşmuş iki akım mevcuttur. Bunlar hidrojen enerjisi ile içten yanmalı motor teknolojisi birleştiren hibrit araç teknolojileri ve düşük hacimli motor akımlarıdır. Hibrit teknolojiler sayesinde araç üreticileri emisyon seviyelerini ciddi miktarda düşürmüş ve yüzde 80 seviyelerine kadar verimlilik sağlamayı başarmıştır. Tabii ki bu yüzde 80 verimlilik sadece hibrit teknoloji kullanılarak sağlanmamıştır. Günümüzün büyük akımlarından olan düşük hacimli motor teknolojilerinin de payı vardır. Bu düşük hacim akımı, motor hacimlerinin düşerken motor güçlerinin yükseltilmesi üzerine kuruludur. Yaklaşıl 20 yıl önce 2.0 litre hacimli bir motordan 120 beygire kadar güç üretilebilirken günümüzde otomotiv üreticileri 1.0 litre hacimli bir motordan 150 beygire kadar güç üretebilmektedirler. Gelişime bakıldığında bunlar çok iyi sonuçlar olmak ile beraber halen yakıt tüketimine ihtiyaç duyan içten yanmalı motor teknolojileri kullanıldığından sıfır emisyon hedefini sağlamak mümkün değildir. Uzun dönemde ise yakıt için hammadde gereksinimi sebebi ile yakıt fiyatlarında artışlar gözlenmesi de kaçınılmazdır. Yani içten yanmalı motor var ise, emisyon da var olacaktır.

Yakıt pilleri sıfır emisyon hedeflerinin en önemli aracı olabilirler. Ulaşım amacı ile kullanılabilecek birkaç farklı yakıt pili tipi bulunmaktadır. Bunlarda ulaşım için en uygunu; hızlı çalışma süresi, çalışma sıcaklığı ve soğuk koşullarda çalışma performansına bağlı olarak Proton Değişim Membranlı yakıt hücresidir.

Proton değişim membranlı yakıt hücresi sistemleri otomobiller için içten yanmalı motorlara potansiyel rakip olarak kabul edilmektedir [84]. Yakıt pilli araçlar; yüksek verimliği ve düşük karbondioksit salınımı sayesinde Avrupa otomobil şirketlerinin Avrupa

Birliği emisyon sınırlarını karşılamaları adına büyük bir potansiyeli bulunmaktadır [85],[86].

Bu çalışmanın amacı, yakıt pillerinin maliyetlerini düşürmek için bir yol bulmaktır. Bunun için otomotiv uygulamalarında kullanılabilecek proton değişim membranlı yakıt hücresi tasarım ilkelerini öğrenmek de şarttır. Yakıt hücreleri; hidrojen yada konvansiyonel hidrokarbonları ile çalışan sürekli temiz enerji kaynaklarıdır. Onlar geleneksel yakıtlara göre çok daha verimli ve sessizce ; daha yüksek güç yoğunlukları ile elektirik üretirler. Yakıt pillerinin gelişmiş tasarım ve kontrolü için yakıt pili sistemlerini ve bileşenlerini daha iyi anlamak gerekmektedir bu ise ancak gerçekci yakıt pili modelleri ve analizleri gereklidir.

Bu tezde 400 cm2 akış alanlı proton değişim membranlı yakıt hücresi modeli kullanılarak akışkanların ve ısı dağılımınnın durumu değerlendirilmiştir. Bu tasarımlarda ısı ve kütle dağılımları tahmin etmek için üç boyutlu, hesaplamalı akışkanlar dinamiğine dayalı bir metodoloji kullanılmıştır. Akış yönünü ve soğutma kanallarının etkisi de bu çalışmada seçilen akım kanallarının tasarımlarında dikkate alınmıştır.

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LIST OF SYMBOLS AND ABBREVIATIONS

ATS   : After Treatment System

AFC   : Alkaline Fuel Cell

Al   : Aluminum

C   : Carbon

cm   : centimeter

Co   : Cobalt

CAD   : Computer aided design

CAE   : Computer aided engineering

CFD   : Computational Fluid Dynamics

c   : concentration

σ   : Conductivity

I   : current

DI   : De Ionized

DMAc   : Di Methyl Acetamide

DC   : Direct Current

DMFC   : Direct Methanol Fuel Cell

DPG   : Distributed Power Generation

D   : drag coefficient

ϵ : efficiency

e   : Electron

h   : enthalpy

F   : Faraday's constant

FC   : Fuel Cell

g   : Gibbs' free energy

ρ   : Density

H   : Hydrogen

K	: Permeability
R	: Ideal gas constant
ICE	: Internal Combustion Engine
L	: Length of a single channel
La	: Lanthanum
l	: liter
Li	: Lithium
Mn	: Manganese
MEA	: Membrane Electrode Assembly
m	: meter
M	: Molar mass
MCFC	: Molten Carbonate Fuel Cell
µ	: Dynamic viscosity
Nf	: Nafion
PC-25	: Name of a stationary power system
Ni	: Nickel
OEM	: Original Equipment Manufacturer
O	: Oxygen
PFSA	: Per Fluoro Sulphonic Acid
P	: Permeability
PAFC	: Phosphoric Acid Fuel Cell
Pt	: Platinum
PTFE	: Poly Tetra Fluoro Ethylene
K	: Potassium
P	: pressure
PEMFC	: Proton Exchange Membrane Fuel Cell
R&D	: Research and Development
R	: resistance
SOFC	: Solid Oxide Fuel Cell
Sr	: Strontium
S	: Sulfur

T	: temperature
t	: thickness
3D	: Three Dimensional
t	: time
u	: Velocity
V	: voltage
v	: Kinematic viscosity
W	: watt
Y	: Yttrium
ZEV	: Zero Emission Vehicle
Zr	: Zirconium

1.   INTRODUCTION

In many different fields owned by automotive, energy, fuel cell, etc. sectors, zero emission vehicle targets have emerged. Most of the vehicles in traffic produce their energy by internal combustion engine and most of the automotive manufacturers try to improve their ICE technologies over hundred years, to figure out how to produce a ZEV. Regulations force car makers to decrease their vehicles' emission levels. If they are going to use ICE, they can do it two ways; they can improve their engines' efficiency or they can improve their after treatment system (ATS). One should not forget that, ICE systems are limited with the Carnot principle that disables to have a zero emission level. For medium duty or heavy duty vehicles improving ATS system is logical but for passenger cars there is no space for a complicate ATS system. Decreasing the energy output is also an option but this is not feasible due to the market competition.
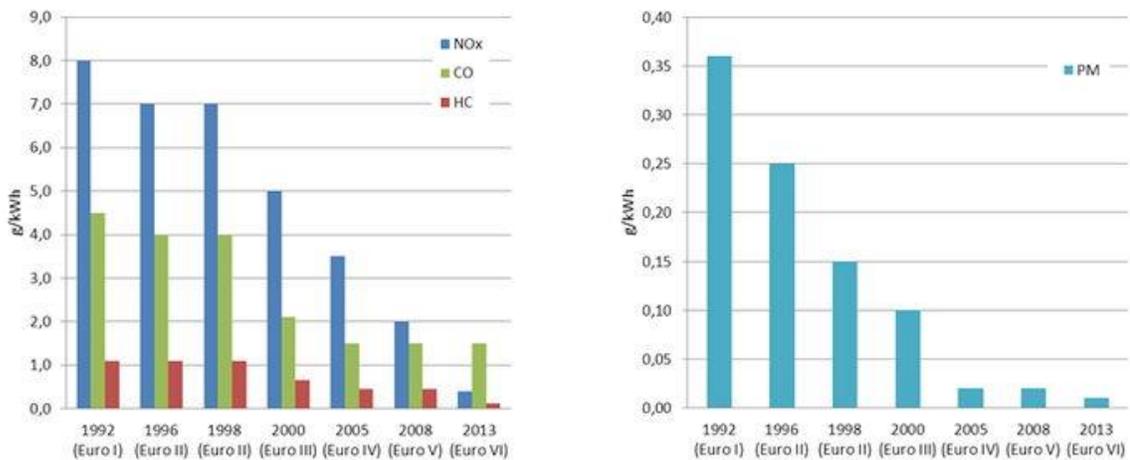
Graph 1 Emission levels based on regulations

Nowadays there are two major trends in automotive. The first one is the hybrid vehicle which combines hydrogen energy with combustion energy. So the vehicle's acceleration is supported by more than one energy system. Due to the hybrid vehicle trend there is a fast growing market based on liquid petroleum gasses (LPG), liquid natural gasses (LNG) and

compressed natural gasses (CNG). On the other hand, vehicles with electric engines enjoy a high popularity in nowadays markets. By using hybrid technologies automakers can obtain a significant emission drop and the efficiency increases up to 80%. While decreasing the emission levels they also benefit from some of the advantages of the downsizing trend. They use smaller volume engines with higher strength material super charges, turbo charges, etc. They increase engine cylinder pressures, so they can have much better combustion efficiency. It is obvious, that they need to use different systems to cool down the system such as intercoolers, etc. These are great results, however car makes spend billions of dollars for the research and development process and still use ICE technology. The problem is, there is pollution. If they really aim to reach zero emission level they need to use a system based on a different energy source, such as electricity.

Fuel cells (FC) can be the shining star of ZEV targets. There are some different types of fuel cells that can be use for transportation applications. The most convenient type is Proton Exchange Membrane (PEM) fuel cell due to its star up time, cold performance and working temperature.
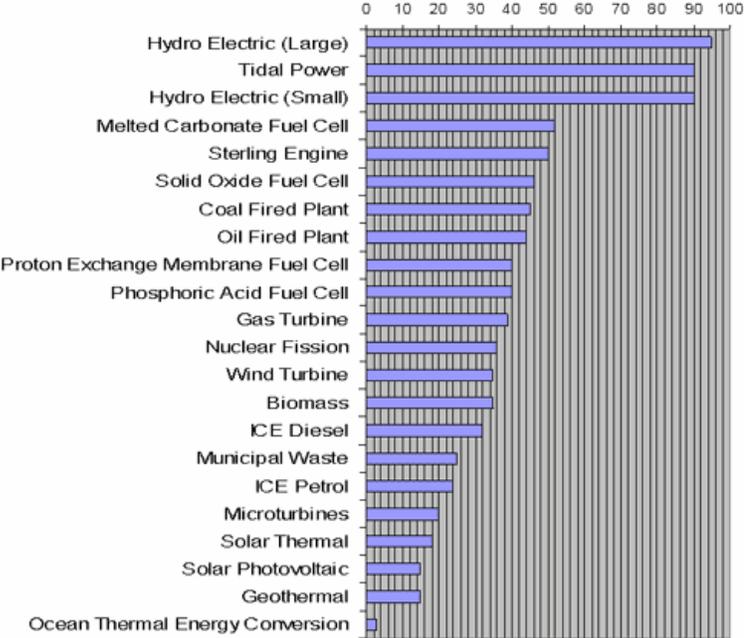
Graph 2 Energy production efficiency comparison

PEMFC systems have a great potential to be the replacement of internal combustion engines in passenger vehicles [84]. FC have a high efficiency with almost no pollution makes them a potential candidate for European auto companies to meet required regulations in the European Union [85],[86].

Proton Exchange Membrane Fuel Cell (PEMFC) is the most used fuel cell type in a variety of applications. Compared to the PEMFC applications; transportation is the most competitive and promising one due to startup time, low sensitivity to orientation, and favorable W/kg ratio. People started to care about the environment and prefer clean energy sources which routes to promising potential of this alternative technology. Also governments force car makers to use clean sources. Car makes need to reach lower emission levels year after year due to homologation requirements. There are many expensive ongoing Research and Development (R&D) studies in this field . Fuel cells have no emissions.

Competing with the Internal Combustion Engine (ICE), incorporation of the PEMFC in transportation applications comes along with different challenges. This thesis is dedicated to give a perceptive about the design and operation of PEMFCs that is applicable to automotive industry. Fuel Cell Vehicle (FCV) development requires a proper energy management system which can be obtained by the integration of a FC system with electric energy storage devices. Major carmakers in the world are engaged in developing prototype FCVs for reaching to the future transportation goals.
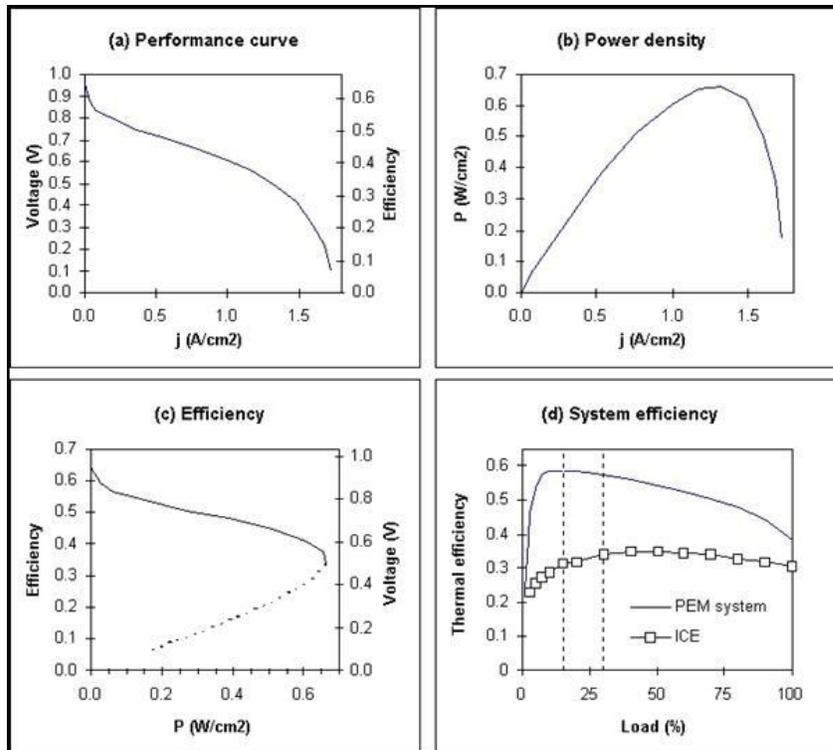
Graph 3 PEMFC performance graphs

The future and present specifications of PEMFC for FCV can be explained by the technology roadmaps and there are many different FCV roadmaps present. All of them focus on similar points. Those major similar four points are critical for the commercial adaptation of FC in automotive. They are cost, durability, start up (warm up) time and volumetric power density. When we look a bit more detailed at the targets of the lifetime of FC, it aims to reach freeze-start capability down to 1C for 5000 hours, reaching 50% of the rated power in 30 seconds with a 2500Wnet/l volumetric power density which targeted to be cost of US$ 30/kW net at a volume of 500,000 units.

In these road maps FC manufacturers are not the only responsible ones. There are also some roles for government and the automakers. Policy makers need to force automakers to use electricity based systems in their vehicles by regulations. For example if there is no emission requirements it will not be possible to reach euro 6 emission limits; every automotive manufacturer spend billions of dollars every year. On the other hand policy

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makers must support their regulations too, by creating new funding for fuel cell technologies. Also car makers need to provide vehicle volume commitments. There is a strong duty distribution here. The energy industry must support this process too by building hydrogen stations in the cities. By doing this it can be possible to reach lower emission or zero emission targets.
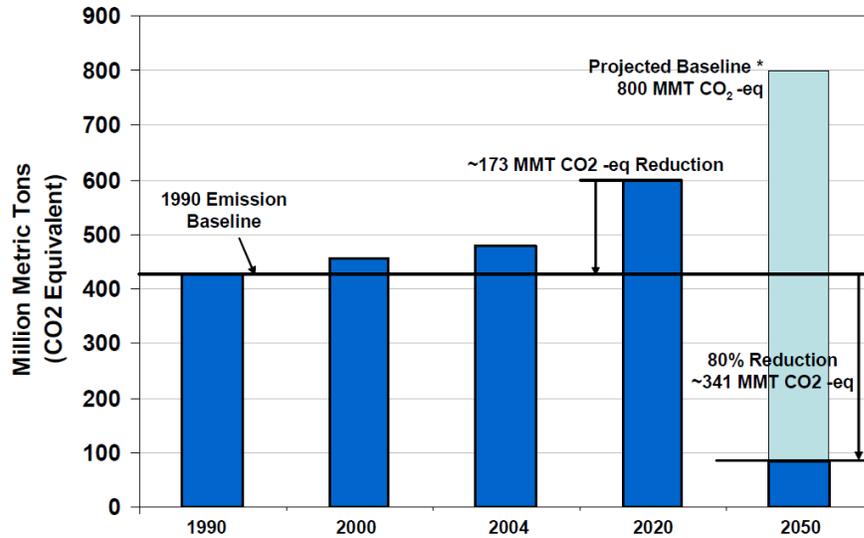
Graph 4 California's 2020 emission regulation targets

The success of PEMFC in the automotive industry can be a very important opportunity for applications in other fields. Due to the usage volume of FC in the automotive industry, the costs decrease. It begins to be feasible for application in different field's cause decreased costs.

Due to the ZEV targets, homologation requirements, increase of green house gases and the advantages of FCs emerges; PEMFCs are feasible to be used in automotive industry. For using a FC system in automotive applications, there are many challenges. Due to the bigger size of the FC, cost is the most important challenge. At the beginning, FCs matter of platinum have the highest effect on cost. However, in the early days they used $28gr/cm^2$ platinum, nowadays it is just $0,2gr/cm^2$. To do the decrease they had to simplify the FC system. Less complexity means less devices. Concerning the complexity decrease; for

example to eliminate the recovery pump in anode side the flow needed to be studied. So that heat and flow distributions start to be a challenge due to components with very large surface area. In this thesis flow through FC model is developed and its anode side, cathode side and water channels studied.

In the anode side, due to continuous flow; uniform mass transfer tried to be obtained. The fuel pumped in the FC is optimized to almost the same amount with the required fuel. The aim is to operate all the H_2 into the reaction; due to the chemical reaction, supply needs to be equal to demand. By doing this, it is possible to have a dead-end anode site.

In the cathode side; the challenging point is to optimize the inlet pressure of the fuel. The pressure difference between the outlet and the inlet needs to be minimum; otherwise based on irregular pressure distribution, it is not possible to obtain from all channels. Lower pressure drop results with homogeneous pressure distribution. By homogeneous pressure distribution it is also possible to reach uniformity in temperature management.

In water channels; the water flow should be optimized for having an uniform flow distributing among the channels. Out of that the uniform heat distributions is also necessary. All the het needed to be removed from the membrane with a maximum efficiency to keep the efficiency on higher levels

2.   BACKGROUND INFORMATION

FC is an electrochemical energy conversion device which produces electricity by using chemical energy. As a result of the chemical reaction occurring inside the membrane, electricity is generated. Side reactants flow into the fuel cell without interruption and the electricity is generated as the supply continues without recharging the cell.
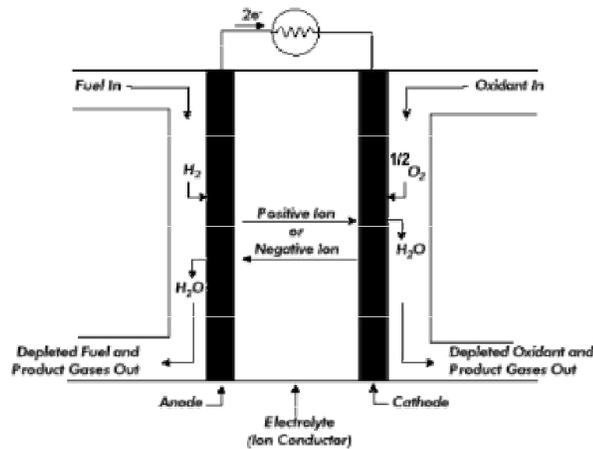
Figure 1 Schematic of a fuel cell

A general view of a fuel cell is showed in Figure 1 above. Fuel enters the cell from anode (negative electrode) and oxidant enters the cell from cathode (positive electrode). In many types of FCs electrodes are platinum (Pt) and this is where the high cost comes from. Pt is a very expensive material. The chemical reactions occur at the electrolyte. The reaction occurring inside the cell produces a potential of about 1 Volt. To obtain a higher voltage and current output, FC stacks created by combining the cells parallel and serial.
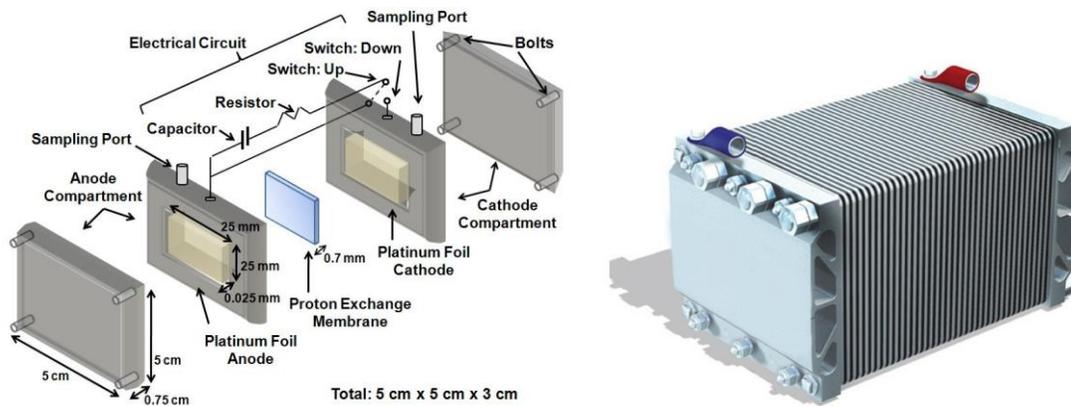
Figure 2 Example of a FC Stack

With respect to the electrolyte material different chemical reactions take place so different products are released in addition to heat. Types of fuel cells are defined by the electrolyte material, fuel and the conducting ions. Energy conversion process from chemical reaction is common for all of them. Finally, each type of fuel cell stack generates direct current (DC) electricity.

2.1.   History of Fuel Cells

In 1838, Christian Friedrich Schoenbein was discovered the first fuel cell whom is a German-Swiss Professor from the University of Basel. Grove's apparatus consisting of a platinum electrode immersed in nitric acid and a zinc electrode immersed in zinc sulphate took in hydrogen and oxygen to generate electricity and water. It generated 12 amperes current at about 1.8 volts [2].
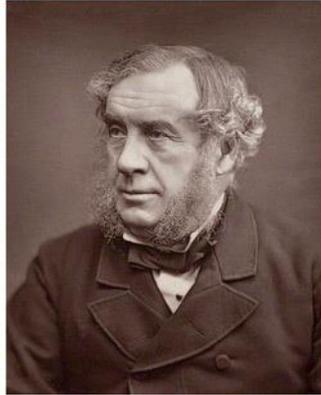
Figure 3 William Grove

The term "Fuel-Cell" was first used in literature in 1889 by Ludwig Mond and Charles Langer. They attempted to build the first practical device using air and industrial coal gas. Chronologically milestones of the FC technology can be stated as:

- William Jacques invented first FC for household use in 1886.
- Walther Nernst first solid electrolyte, zirconium for FCs in 1900.
- Emil Baur invented the first molten carbonate fuel cell in 1932.
- NASA began experiments for obtaining a FC powered power source for spacecrafts in the late 1950's.
- Allis-Chalmers Manufacturing Company demonstrated a 20 hp Solid oxide FC powered tractor in 1962.

Figure 4 An Allis-Chalmers D21 series II tractor

The first FCs were very expensive for commercial success when compared with today's conditions. In the early twentieth century with the development of the internal combustion engines which was a lower cost power source, fuel cells cannot be popular. FCs were developed just for space or military technology until nowadays. After this initiative, the automotive industry recognized the potential of fuel cells for commercial use with the support from governments, research and development (R&D). Fuel cell technology has been encouraged and many companies and research centers around the world are engaged with the technology. The government of Turkey also has R&D foundations for FC researches.

Due to the environmental and economical concerns based on oil, coal and nuclear energy resources, sustainable energy sources such as fuel cells are seen as promising alternatives for many different applications. FCs have many potential benefits although the commercial deployment of fuel cells still faces many challenges such as high cost.

2.2. Energy Variations of Fuel Cells

The characteristics of fuel cells make them preferable between conventional energy

converters in many different applications. These characteristics which vary in different types of fuel cells determine the applications area. The most effective decision of where to use which type of fuel cell is to check operating temperature, start up time and power density. For example it is not logical to use a fuel cell operating in 800 degree Celsius to generate electricity for a passenger car but you can use it in buildings (stationary applications) so you can also use it as a heat source to heat a building or for hot water.

Type	PEMFC	AFC	PAFC	MCFC	SOFC	DMFC
Electrolyte	Ion exchange membrane	Mobilized or Immobilized Potassium Hydroxide	Immobilized Liquid Phosphoric Acid	Immobilized Liquid Molten Carbonate	Ceramic	Ion exchange membrane
Mobile ion	H^+	OH^-	H^+	CO_3^{-2}	$O-2$	H^+
Fuel	H_2, reformate	$H2$	H_2, reformate	H_2, CO, CH_4	H_2, CO, CH_4	methanol, ethanol
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskites	Platinum
Operating temperature	$60 - 80^0C$	$65 - 225^0C$	$\sim 200^0C$	$\sim 650^0C$	$800 - 1000^0C$	$\sim 80^0C$
Efficiency	25 - 35%	32 - 40%	35 - 45%	40 - 60%	45 - 55%	~20%
Power density	$3.8 - 2.6 \, W/cm^2$	$0.7 - 8.1 \, W/cm^2$	$0.8 - 1.9 \, W/cm^2$	$0.1 - 1.5 \, W/cm^2$	$1.5 - 2.6 \, W/cm^2$	$\sim 0.6 \, W/cm^2$
Startup times	sec-min	Min	hours	hours	hours	sec-min
Applications	Electric utility Portable power Transportation	Military Space	Electric utility Transportation	Electric utility	Electric utility	Portable power Transportation
Stage of development	Commercially available	In use since 1960s	Commercially available	Demonstration	Prototype	Prototype
Advantages	Low corrosion Low temperature Quick startups	Cathode reaction is faster in alkaline electrolyte	Impure H_2 acceptable Less Pt needed	No noble metals needed Efficiency is improved	Less Pt needed Low corrosion Fuel flexibility High eff.	Direct feed of fuel Zero emission
Dis-advantages	Cost of catalyst Sensitivity to fuel impurities	Expensive removal of CO2 from fuel	Cost of catalyst Low power Large size	Thermal effects on cell component Corrosion Low power	Thermal effects on cell component	Higher system complexity

Table 1 Comparison of FC types

2.2.1. Efficiency

Direct conversion of the chemical energy to electrical energy is not limited by Carnot Cycle like what happened in ICEs. The FC stack efficiencies are greater than are combustion type energy converters. Depending on the FCs type, stack efficiencies up to 60% are available with a wide range. Ideally it is possible to obtain up to 90% overall system efficiencies. FCs can reach to very high efficiency levels but the problem is obtaining the suitable environment for FC. There is always a chemical reaction going on so it requires its fuel, hydrogen. The amount that you delivered is to important; if you supply less hydrogen, efficiency decreases. If you provide to much hydrogen pressure can increase significantly and to much material could cause slowdown in reaction rate. Similar to this all the material must have a balance. On the other hand there is heat that appears by result

of chemical reaction. The heat must be removed from membrane to keep the efficiency in high level so water management systems is required to decrease the temperature which can work with all other systems in a harmony. Every single thing can affect the efficiency.

2.2.2. Power Density

It is possible to obtain a higher power from a FC which has the same size with conventional energy converter but as mentioned before the suitable environment must be obtained to keep the efficiency on high levels. If the efficiency decreases, depending on that power density decreases.

2.2.3. Emission

When pure hydrogen is used, the FC maintains zero emission characteristics which make FCs perfectly suitable for using in automotive sector and obtaining long term zero emission level. However, oxides of nitrogen, sulfur and carbon occurs as a result of the chemical reactions when carbon rich fossil fuels used for obtaining hydrogen. The emission values are lower than conventional energy converters. For electrolysis, CO_2 release does not cause any problem.
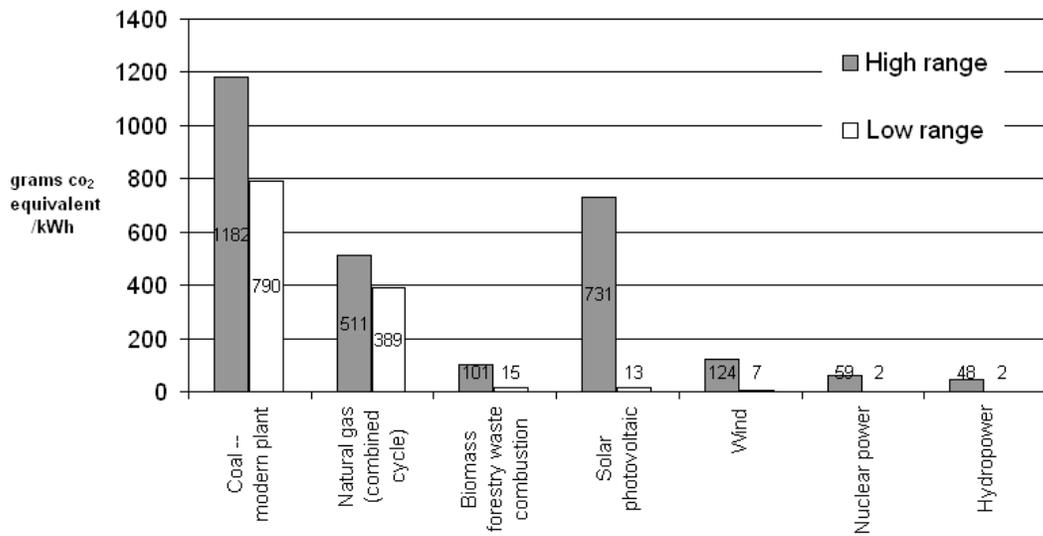
Graph 5 Greenhouse gas emissions from electricity productions

2.2.4. Reliability and Availability

FCs have no moving parts, also the FC systems have almost no moving parts. Only the moving parts in this system are the auxiliary components so the integrity of the FC to a system is simple. Due to the type of the FC thermal management could be a challenge. The maintenance requirements are reduced and the life of the FC increases based on simplicity. It is reported that a PC25 fleet consisting of more than 200 units has demonstrated 90% availability during 4 million operating hours [13]. Also the maximum power is available 99% of the operating time. Most of the time reliability and lifetime of FC is limited by the catalyst performance.

2.2.5. Size Range

The range of output power from a fuel cell of a few watts to some megawatts which results with high application range depending on size and the required power. Also numbers of cells you use in stack have a major effect on your range. By combining the cells, required energy output can be obtained as a FC stack. When compared to ICE the weight of FC system is lower but the volume of the system is higher. For a passenger car it is possible to reach the same ranges of mileages by FCs compared with gasoline engines.

2.2.6. Fuel Flexibility

Direct hydrogen, direct methanol or reformed hydrogen from natural gas, methanol and different hydrocarbons can be used as fuel for different types of cells.

Type	PEMFC	AFC	PAFC	MCFC	SOFC	DMFC
Electrolyte	Ion exchange membrane	Mobilized or Immobilized Potassium Hydroxide	Immobilized Liquid Phosphoric Acid	Immobilized Liquid Molten Carbonate	Ceramic	Ion exchange membrane
Mobile ion	H^+	OH^-	H^+	CO_3^{-2}	O-2	H^+
Fuel	H_2, reformate	$H2$	H_2, reformate	H_2, CO, CH_4	H_2, CO, CH_4	methanol, ethanol

Table 2 Fuels of FCs

2.3.   Fuel Cell Applications

The first application of fuel-cell systems were used to generate electricity in a space shuttle in Apollo and Gemini space programs. There are 3, 12 kW alkaline FCs used in over 87 missions with 65,000 hours working time [9]. Out of that, fuel cells are expected to be used as regenerative power systems for space stations. In today's conditions; commercial usage of FCs are also possible. FC applications can be classified in three groups; stationary applications, portable applications and transportation applications.

Application	Function	Power	Fuel	Comments
Hybrid power bus	Power supply	50 kW	Compressed hydrogen in cylinder	Efficiency: 40%, Mean power consumption: 17–24 kW
Powered bicycle	Power supply	300 W	Hydrogen stored in the metal hydrides	Efficiency: 35%, Distance-to-fuel ratio: 1.35 km/g
Lightweight powered vehicle	Power supply	5 kW	High pressure gaseous hydrogen in cylinder	Drive over a 100 km run at a speed of 18 km/h
Sailing yacht	APU (auxiliary power units)	300 W	Hydrogen produced by LPG via a series of processor on-board system	Used as auxiliary power units using bottled LPG as fuels
Stationary power generator	Power supply	5 kW	Commercially available 15 MPa hydrogen cylinder	Efficiency: more than 30% in fully loaded operation. Operated 3 h at 5 kW with two 50 liter hydrogen cylinders
Uninterrupted power supply	Power supply	2 kW	Hydrogen produced by methanol via fuel processing	Total cost was strongly dependent on the service time.
Portable computer	Power supply	46 W	Hydrogen stored in the metal hydrides	Trouble-free start-up of the portable computer

Table 3 Various application tests of PEMFC

2.3.1. Stationary Applications

Electricity generation for buildings is one of the most common examples of stationary FC

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applications. Especially for inner city buildings, FCs are niche applications due to its clean operations and low noise. The power capacities of stationary plants have a wide range from kilowatts to megawatts. In stationary application most common used fuel cell type is Solid Oxide FCs. SOFCs operates over 800 degree Celsius so in addition to generation electricity; they can be used as heat source for heating the buildings or obtaining hot water.

Figure 5 PC-25 FC Plant

The first commercial fuel cell plant PC-25 consisting of a 200 kW phosphoric acid fuel cell (PAFC) stack has been used for many stationary applications in hospitals, hotels and manufacturing sites.

2.3.2. Portable Applications

FCs have been used since 1960s in military portable applications. There was a significant increase in usage of portable FC applications until 1990s, approximately 1700 operating systems in the power range of 1 W to 1500 W had been built due to a survey of 2002 [3]. Why they only use this technology only for military is because of its cost. FC technologies had been developed for military and space applications for a long time. According to important decrease in its cost, FCs started to be used commercially.

Since FCs are modular devices, they can be used in small portable applications instead of batteries. Compared to batteries; FCs have higher energy density so they have longer

operation time and able to used for higher power requirements of the devices. Many device manufacturers have begun to develop and try the FC technology in their devices in order to use batteries for dealing with short battery life problem.

Nowadays, there are many mobile applications of FCs that shows the usage of FC technology in consumer electronics such as mobile phones and laptops. The commercialization of the systems is not completed due to the high cost of the systems and the regulations relating to the distribution. By the increase of the demand on FCs, the mass production of FCs increases and due to that, costs start to decrease so portable fuel cell applications will be provided to markets.

2.3.3. Transportation Applications

In the long term the biggest pie of the cake is going to be transportation for fuel cells. There are many targets in the automotive industry such as decreasing emissions and making zero emission vehicle in a long term but most of the vehicles in traffic produce its energy by internal combustion engine so for ZEV target they need to move a step forward and start using electricity based technologies in their vehicle. That's where FCs come into play.

Car makes spend millions of dollars for research and development processes to decrease emission levels of their internal combustion engines. Homologation requirements for emissions are getting to strict. Because of this, company research costs are extremely high. Companies can also use the capital for FC researches. This way, they can decrease emission levels and also have better fuel consumptions. Low emission values, high efficiencies and simple mechanical integrities of FCs constitute merits in their use in heavy duty and light duty vehicle propulsion. Also, under today's conditions, Euro 6 emission regulations must be implemented to sell a vehicle in Europe. FC vehicles offer the high power density with a very low CO_x emissions; this makes them potential candidates for European car makers to meet their voluntary carbon dioxide emission limits and regulation limits in the European Union [85],[86].

PEMFCs have been used for transportation applications because of their high power densities, high efficiencies, low corrosion characteristics and cell life time. In a long term PEMFC is considered as a potential replacement systems for internal combustion engines in automobiles [84]. As mentioned before, when compared to internal combustion engine, PEMFC efficiency is higher at partial loads; also efficiency of the FC at nominal speed is two times higher with direct hydrogen supply [4],[6]. In a FC, energy created due to chemical reaction and directly used in an electric motor. In combustion engines, chemical energy is first converted to thermal energy and then converted to usable mechanical energy then the energy transports to wheels. Efficiency of the combustion engine is limited with Carnot cycle.

The present and future specifications of PEMFC for FCV are explained in many different roadmaps so everything is planned. The question is how and when to expand FCs in to the market. All of them focus on similar points. Major items are durability, cost, start up (warm up) time and volumetric power density. When we look a bit more detailed, the targets are the lifetime of FC aims to reach 5000 hours with freeze-start capability down to 1C, reaching 50% of the rated power in 30 seconds with a 2500Wnet/l volumetric power density which targeted to be cost of US$ 30/kW net at a volume of 500,000 units. Now the manufacturers push to reach those limits. The most problematic point is cost for now. The success of PEMFC in automotive industry is very important opportunity for applications in other industries because due to the increase of usage volume, the costs decrease so it begins to be feasible for application in different fields.

3.   PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC)

There is a proton conductor in a PEMFC which is stacked between two electrodes. In order to maintain a good conduction between the ions, the membrane is needed to be humidified. Water and heat becomes the end products of the operation. It is not possible to use the produced heat in cogeneration applications, since the operating temperatures are low because of the limitations that the polymer membrane imposes. PEMFC can operate in low temperate so it allows quick start because of the shorter warming time and better durability. However, high Pt catalyst loadings are required to promote the reactions at the operating temperatures. Catalyst is sensitive to carbon mono oxide poisoning so hydrogen fuel is required to prevent poisoning. The following chemical reactions take place in the electrodes.

Anode   : $H2 \rightarrow 2H + 2e-$

Cathode   : $1/2O2 + 2H + 2e- \rightarrow H2O$
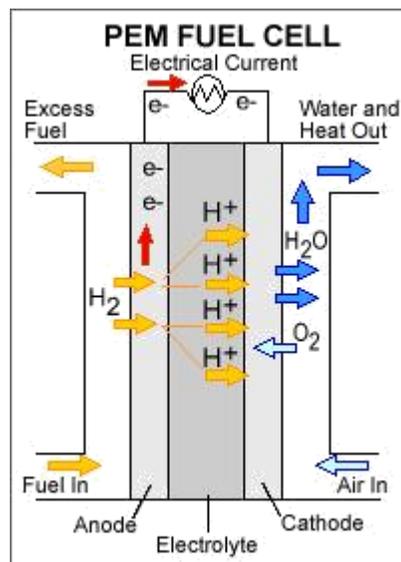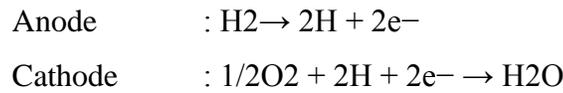
Figure 6 Schematic of PEMFC

For car makes PEMFCs are preferable for use in transportation applications due to the fast startup time, low sensitivity to orientation, and high W/kg ratio. Currently, hydrogen storage is limiting the use of PEMFC passenger cars due to lack of space.

As stated before PEMFC is the most used fuel cell type in a variety of applications. Competing with the ICE, incorporation of the PEMFC in transportation applications comes along with different challenges. Optimization of the operating conditions, transients of the system, robustness of the operation and system integration issues are the main concerns.

3.1. Design of the PEMFC

A PEMFC consists of two electrodes, a polymer electrolyte membrane, current collectors and gas flow fields. The combination of anode, electrode and cathode is referred as membrane electrode assembly (MEA).

3.1.1. Electrodes

All electrochemical reactions consist of two separate reactions, oxidation and reduction. Oxidation reaction occurs in the anode side and reduction reaction occurs in the cathode side. Both of the electrodes are porous. This property increases the surface area and enhances the reaction rate and allows reactants to be transported easily. The electrolyte layer on the electrode surface needs to be thin in order not to block the pores and so there will be more area for transportation of the reactants to active sites. Target is to establish a three phase interface consisting of gas, electrolyte and electrode surface.

The structure of the electrodes is composed of carbon black and Poly Tetra Fluoro Ethylene (PTFE). Platinum (Pt) catalyst is bounded to the high surface area carbon black which is an electronic conductor. PTFE is a hydrophobic material that lets the gases permeate inside the electrode. Due to the material properties, carbon black also acts like a wet proofing agent. This composite structure establishes a stable three phase interface in the electrode, which is regarded as the benchmark of PTFE bonding. An increase in the

PTFE loading results in a decrease in the permeability of the liquid water and an increase in the volume fraction of the gas pores which then enhances the cell performance [1].

The only catalyst that reacts sufficiently with both hydrogen (H) and oxygen (O) intermediates is Pt which has also high performance in releasing these intermediates. As in the anode half reaction, Pt first bond H atoms then release the intermediate as two protons and two electrons.

In the first term of PEMFC development, Pt is used as a catalyst with an amount of 28 mg/cm^2 of Pt [87]. Pt has a major affect on the cost of a PEMFC so higher rate of Pt has a major effect on total cost of FC. In recent years the usage has been reduced to around $0.2 mg/cm^2$, yet with power increasing [87]. The basic structure of the electrode in different designs of PEMFC is similar. The anodes and the cathodes are similar too. The Pt catalyst is formed into very small particles on the surface of larger particles of finely divided carbon powders. The Pt is highly divided and spread out. Only that very high proportion of the surface area will be in contact with the reactants.

3.1.2. Membrane

In PEMFCs, solid polymer membrane is used (as a thin plastic film) as electrolyte.
The membrane of PEMFC is generally poly per fluoro sulfuric asid. Not only the material but also the thickness, which generally derives between 50 to 175 microns, is crucial.

Sulphonic groups, SO3, are attached to side chains and are stationary. The presence of water in the membrane allows protons to move. Protons, that are bond to water molecules, can move from one sulphonic group to another one. By this mechanism, the membrane becomes an ionic conductor in the existence of water.

PEMFCs' operating temperature is restraint by the range when the water is in the liquid form, which means operating temperature of the PEMFC usually does not extend beyond 100 Celsius degree. In order not to limit the membrane by the temperature, new

mechanisms for proton conducting should be suggested.

Despite resembling plastic wrap; due to the Teflon backbone structure, selectively permeable membrane is stronger and makes protons available to move through without mixing the reactants. Due to the membrane's organic nature, it does not conduct electrons, which are vital for the operation of FC.

Based on their material features, numerous different membranes could be used in PEMFCs. PEMs can be made from polymer membranes or composite membranes where other materials are embedded in a polymer matrix. Proton exchange membranes are primarily characterized by thermal stability, methanol permeability (P), and proton conductivity (σ) [17].

Membranes can be generalized under four topics; sulfonated aromatic hydrocarbon polymer membranes, organic - inorganic composite membranes, polymer blend membranes and Polybenzimidazole based acid base membranes.

3.1.2.1. Sulfonated Aromatic Hydrocarbon Polymer Membranes

Sulfonated aromatic hydrocarbon polymer membranes would be used as membranes of PEMFCs. Below, it is possible to see the details of some of these membranes such as sulfonated poly p-phenylene, Sulfonated Polyether Ketone, Sulfonated Polysulfone, etc.

3.1.2.1.1. Sulfonated Poly P-Phenylene

The polymer that is produced was treated at room temperature with H_2SO_4. The polymer was washed with DI water after sulfonation and was left to dry for 24 hours at 80 Celsius degrees before usage.
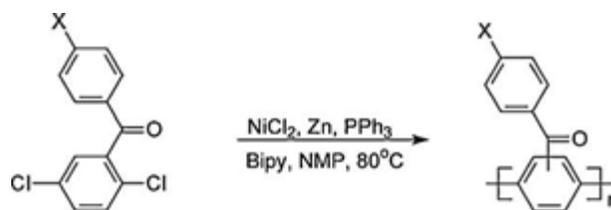
Figure 7 Polymerization technique via nickel-catalyzed coupling polymerization

Membrane fabrication turned out to be difficult since it was a rigid polymer. After placing small piece of a glass cloth over a glass plate, the polymer solution in n-methylpyrrolidone was poured on the plate. Following the coverage of the plate with a dish, it is heated via an infrared lamp at 60 Celsius degrees. The membrane which is produced in the form of glass fibers was 150 μm thick. Kobayashi [25] indicated the sulfonated P-Phenylene membrane's synthesis and features. To be able to synthesize SPPBP, concentrated H2SO4 was used to dissolve PPBP in inert atmosphere. Via filtration, the sediment was collected and first was pulverized and then it was washed properly until a neutral pH was obtained for the solution. After, a cellulose acetate membrane was used to dialyze the SPPBP against DI water.

3.1.2.1.2.　　Sulfonated Polyether Ketone

It is possible to synthesize polyether ketone via nucleophilic aromatic substitution polycondensation [26]. In the existence of K2CO3 in TMS as a solvent, the polymerization occurred at 210 Celsius degrees. High molecular weight polymers were attained in four hours. The attained polymer was spilled into 150 ml of ethyl alcohol and it was heated several times in ethyl alcohol and under reflux in DI water in order to eliminate the salts and solvents. After, it was dried for 24 hours at 120 Celsius degrees. Later on it was washed and left under drying for 24 hours at 120 Celsius degrees. In 5 grams of polymer, 100 ml of concentrated H2SO4 was added. For the fabrication of the membrane, a glass plate is used to pour the sulfonated polymer solution in DMAc under inert atmosphere at 50 Celsius degrees [27]. Later on, the membrane with 100-150 μm thickness was left to dry under vacuum for 24 hours at 120 Celsius degrees.
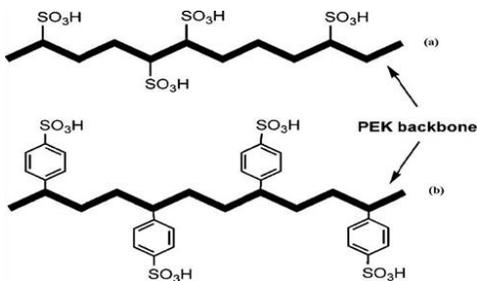
Figure 8 Sulfonated polymer

3.1.2.1.3.   Sulfonated Polysulfone

A technique by using $(CH_3)_3SiO_3Cl$ (TMSCS) as the sulfonating agent was claimed by Genova Dimitrova for the sulfonation of polysulfone [28]. A polymere solution is prepared by mixing di chloro ethane and iso propanol. The phosphate anti monic acid was used just as the aqueous gel. The existing water in the solution was eliminated under vacuum at 80 Celsius degrees. The intense suspension was poured on a glass plate. To eliminate the solvent, high temperature was used for heating the membrane with the ventilation for a few hours. The flat glass was placed at 24 Celsius degrees, where also water was used to peel the polymer film. The membranes had 150-200 μm of thickness.

3.1.2.1.4.   Sulfonated Polyaryleneethersulfone

The most common procedure for polyaryleneethersulfone synthesis is Nucleophilic aromatic polycondensation [29]. Sulfonation of the resultant polymer was done by using chlorosulfonic acid in dichloromethane. The product was washed several times with water and hexane. After that, it dried at 60 Celsius degree under vacuum for 15 hours to obtain a white powder of sulfonated polymer. Sulfonated polymers were added to DMAc. As a next step, it was casted on to a glass plate and waited for 15 hours. At the end in nitric acid; the colorless membranes were then immersed. Colorless membranes washed with DI water several times and placed under vacuum at 60 Celsius degree for 15 more hours.

3.1.2.2.   Organic - Inorganic Composite Membrane

Also there are organic - inorganic mixture based composite membranes that can be used in PEMFCs. You can see some of the materials with details below.

3.1.2.2.1.   Fluorinated Polymer / SiO$_2$

Synthesis of organic polymers involving hexa fluoro iso propyli dene di phenol and deca fluoro bi phenyl in the presence of di methylacetamide followed by the addition of KCO$_3$ and heating to 120 Celsius degree for 2 to 3 hours under an inert atmosphere [34]. Then waited for it to cool down in normal conditions. As a next step washed with CH$_3$COOH - DI water mixture to precipitate the polymer. By using fuming H$_2$SO$_4$, sulfonation of the polymer was done. The sulfonated polymer was precipitated in water and washed for neutoralizing the pH. Using tetra ethoxy silane, DI water and HCl; a silicon oxide solution was prepared and waited for 3 hours. Then silicon oxide solution was added to sulfonated polymer and waited for 24 hours to get dry under 100 Celsius degree.

3.1.2.2.2.   Nafion / Ptfe / Zirconiumphosphate (Zr(HpO$_4$)$_2$)

The thin PTFE film was immersed into the Nafion - ZrOCl$_2$ blend solution for 5 hours. Then it was annealed at 130 Celsius degree for 1 hour. Next step was removing the residual solvent. The residual ZrOCl$_2$ was precipitated on the membrane surface, then the membrane was washed in DI water. The membrane was treated with H$_3$PO$_4$ solution for 4 hours under normal conditions to convert the ZrOCl$_2$ to Zr(HPO$_4$)$_2$.

$$ZrOCl_2 + 2H_3PO_4 \rightarrow Zr(HPO_4)_2 + H_2O + 2HCl$$
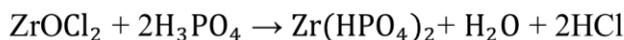
To clean out the residual H$_3$PO$_4$ on the membrane surface, the membrane was washed and dried with DI water several times at ambient temperature. Than the membrane was swollen in DI water for 24 hours at ambient temperature, and then for a further 6 hours in H$_2$SO$_4$ at room temperature. The membrane was subsequently dried at ambient temperature. As a

result you obtain the NF–ZrP composite membrane with a thickness between 20 to 22 μm.

3.1.2.2.3. Nafion / TiO$_2$

Most of the time, the Nafion / TiO$_2$ composite is prepared by solgel process [37]. The solgel incorporation of a catalyst is essential as it can provide an acidic environment for the reaction to initiate. Addition of acid is not needed in the reaction below because the sulfuric acid clusters of Nafion structure act as a catalyst [38].

$$Ti(OC_4H_9)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_4H_9OH_4$$
$$Ti(OH)_4 \rightarrow TiO_2 + H_2O$$
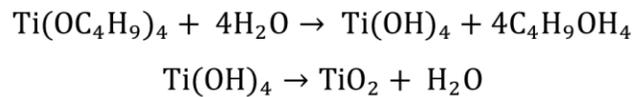
The Nafion membrane was swollen in a CH$_3$OH solution for 20 minutes at 60 Celsius degree. By mixing TBT and CH$_3$OH a precursor solution that had been prepared and the swollen membrane was dipped in to that solution to complete hydrolysis. At the end; the membrane was dried for 12 hours at 60 Celsius degree under vacuum.

3.1.2.2.4. Pva / SiO$_2$ / Silicotungsticacid (Siw)

Using a solgel method, the organic polyvinyl alcohol and inorganic (SiO$_2$) composite was prepared [39]. Tetra ethyl ortho silicate and silicotungstic acid were added to a solution of PVA in water and refluxed for 6 hours at 80 Celcius degree. SiW acted as an acid catalyst for hydrolysis. It was promoted the condensation of tetra ethyl ortho silicate to SiO$_2$. To obtain a membrane between 60 to 100 μm in thickness, transparent gel form was drop casted.

3.1.2.3. Polymer Blend Membrane

Third type of membrane can be used in PEMFC are polymer blended membranes. You can see some of the exact materials can be used with details below.

3.1.2.3.1. Nafion/Poly (1-Vinyl-1, 2, 4-Triazole)

Using AIBN as the initiator, PVTri is produced by the free radical polymerization of 1-vinyl1, 2, 4-triazole in toluene [49]. The reaction mixture was purged with nitrogen. Following to that the polymerization reaction was performed for 2 hours at 85 Celsius degree. The white powder occurred as a result of the reaction was filtered and dried by a vacuum. The resulting polymer was dissolved in DMF. Next step is mixing it with a Nafion solution. The solutions were then cast onto polished Teflon plates. The slow evaporation of the solvent was carried out for at least 24 hours at 40 Celsius degree and at 80 Celsius degree. As a result a hygroscopic and free standing film is obtained with thickness between 150 and 300 μm.

3.1.2.3.2. Sulfonated Pbibi/Poly (Vinylidene Fluoride)

By dissolving SPBIBI and polyvinylidenefluoride in DMSO for 12 hours blends were prepared [50]. The homogeneous blend solutions were filtered through a 0.5 μm PTFE membrane and poured into a glass petri dish at 80 Celsius degree to cast the blended films. The transparent homogeneous thin films between 30 to 50 μm were boiled in water. Then to remove the solvent; sample was dried in a vacuum oven for 48 hours at 100 Celsius degree. The PEMs were washed thoroughly with DI water and dried in a vacuum for 10 hours at 100 Celsius degree.

3.1.2.3.3. Polybenzimidazole/Polyether

As a first step, both polymers were placed in a DMAc solution. The mixture solution was stirred at ambient temperature for 2 hours.
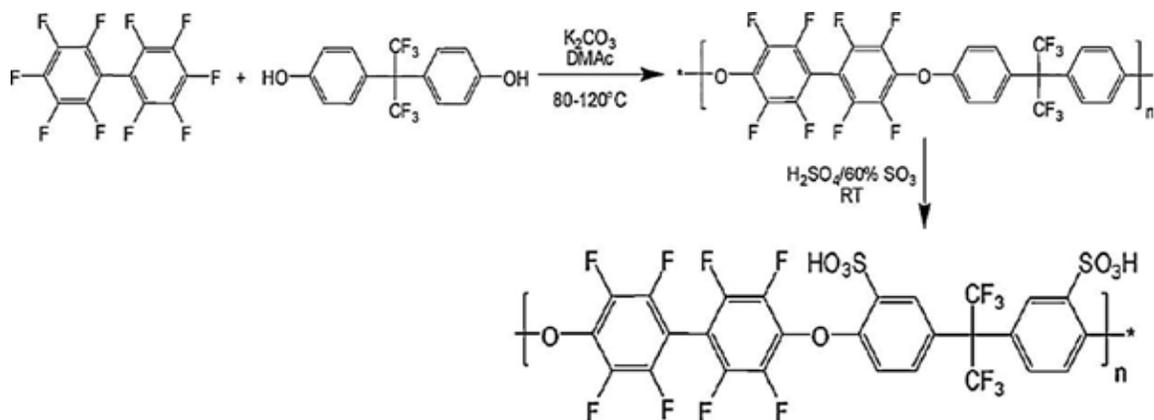
Figure 9 Synthesis of partially fluorinated polyether

By using petri dishes, the resulting PEMs were casted from the mixture solution. The majority of the solvent was evaporated in a ventilated oven at temperatures ranging from 60 to 120 Celsius degree. Then the membranes were peeled off and boiled in water. Then they dried for 2 hours at 200 Celsius degree. The blend membranes were doped with H_3PO_4 in a closed container to avoid changes in the concentration from acid evaporation. As a next step; the blended membranes were removed from the acid solution, blotted with filter paper and dried under vacuum for 120 hours at 110 Celsius degree.

3.1.2.3.4.   Ppo/Poly (Styrene-B-Vinylbenzylphosphonic Acid)

By stable free radical polymerization; Polystyrene-b-vinylbenzylphosphonic acid (PSb-PVBPA) has been prepared [52]. Then by vigorous stirring, PPO and PS-b-PVBPA copolymer were dissolved in NMP at 80 Celsius degree. The obtained solution was filtered rapidly through a 0.45 μm membrane and casted onto a 95 Celsius degree glass plate. NMP was then evaporated for 6 hours at 95 $^{\circ}$C. The resulting film was dried again under vacuum for 24 hours at 95 Celsius degree. The film was treated with an HCl solution for 12 hours at 50 Celsius degree to transform the film into a membrane, and then in boiling DI water for 12 hours. As a final step sample was washed with DI water.

3.1.2.4. Polybenzimidazole (PBI) Based Acid–Base Membrane

For synthesing the PBI there are two types of synthesis is possible; heterogeneous synthesis and homogeneous synthesis.

For heteregeneous synthesis Choe proposed a single stage method to synthesize high molecular PBI using tetra amino bi phenyl and iso phthalic acid as monomers [55].
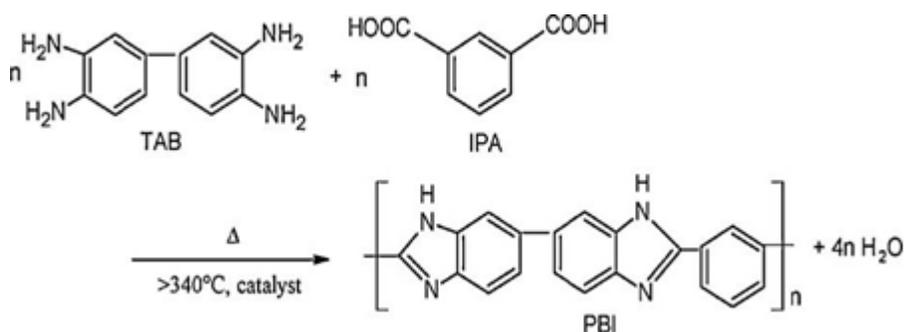
Figure 10 PBI synthesis

Other method is homogeneous synthesis. A liquid with low viscosity such as a mixture of P_2O_5 and methanesulphonic acid were also used as a solvent for the homogeneous synthesis of PBI [58].

After synthesing the PBI next step is modifiying it. Pyridine based PBI was synthesized from the pyridinedi carboxylic acids [58]. Schuster synthesized OO-PBI and OSO_2-PBI. By using tetra amino di phenyl sulphone and oxydibenzoic acid mixtures; the OO-PBI was prepared by a poly condensation reactions and OSO_2-PBI was synthesized [59]. Bhadra synthesized hyperbranched PBIB with a honeycomb structure through the condensation polymerization of trimesic acid and di amino benzidine [60]. Xu synthesized amine-terminated hyperbranched PBI [61]. Bhadra also synthesized Poly(5-aminoisophthalic acid) by the oxidative polymerization of amino iso phthalic acid, which was then subjected to condensation polymerization with di amino benzidine to obtain poly benzimidazole-co-aniline, a self-cross-linked, net-structured, proton conducting PBI type of polymer

membrane for high temperature proton exchange membrane FCs [62].

Poly benzimidazole (AB-PBI) has an uncomplicated structure compared to PBI. The polymerization procedure of ABPBI was carried out using a single monomer (di amino benzoic acid). Recent efforts were made to synthesize AB-PBI in poly phosphoric acid [59] or in a P_2O_5 - MSA mixture [57]. Figure below shows the synthetic route for the fabrication of AB-PBI.
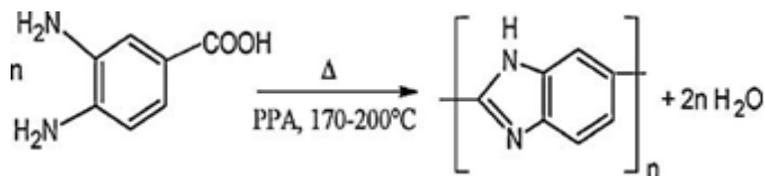
Figure 11 Synthesis of AB-PBI

When these steps are completed, materials for membrane are ready. After preparation part is completed, membrane needed to be cast.

The conductivity of Polybenzimidazole (PBI) generally increases by increasing acid doping level and decreases by the ways of mechanical strength. Different methods have been used to improve the proton conductivity without decreasing the mechanical strength. These methods include ionic and covalent cross linking of the polymeric membranes.

For Ionic cross-linking; flexible ionomer networks can be prepared from acid–base polymers by the ionic cross-linking of polymeric acids and polymeric bases [65]. Sulphonated polysulphone [66], sulphonated polyetheretherketone [67], sulphonated poly (2, 6-dimethyl-1, 4-phenylene oxide) and sulphonated poly (arylene thioether) s are the acidic polymers typically used to modify basic PBI through ionic cross-linking [68], [69]. Basically the ionic cross-linked membrane shows poor thermal stability and readily ruptures at elevated temperatures, resulting in unacceptable swelling and mechanical instability.

For covalent cross linking using in FC applications, dibromo-p-xylene is used as a cross linker for PBI membranes [70]. Above 250 $^\circ$C, cross-linked membranes not only show higher proton conductivity but also improved mechanical strength.

3.1.3. Flow Fields

There are two flow field designs commonly used in PEMFCs, conventional and interdigitated. As seen in Figure 13, in conventional flow fields, gases enter from the inlet port of the channel and leave the cell from outlet port. However in the interdigitated flow field design, the grooved channels are dead ended. This dead ended design forces gases to flow from inlet to outlet through the porous electrodes, resulting in a convection dominant mass transport, whereas in the conventional flow field, diffusion was the motive force for mass transport. As reported in the literature, when FC performance is considered interdigitated, flow fields have some advantages over the conventional type.
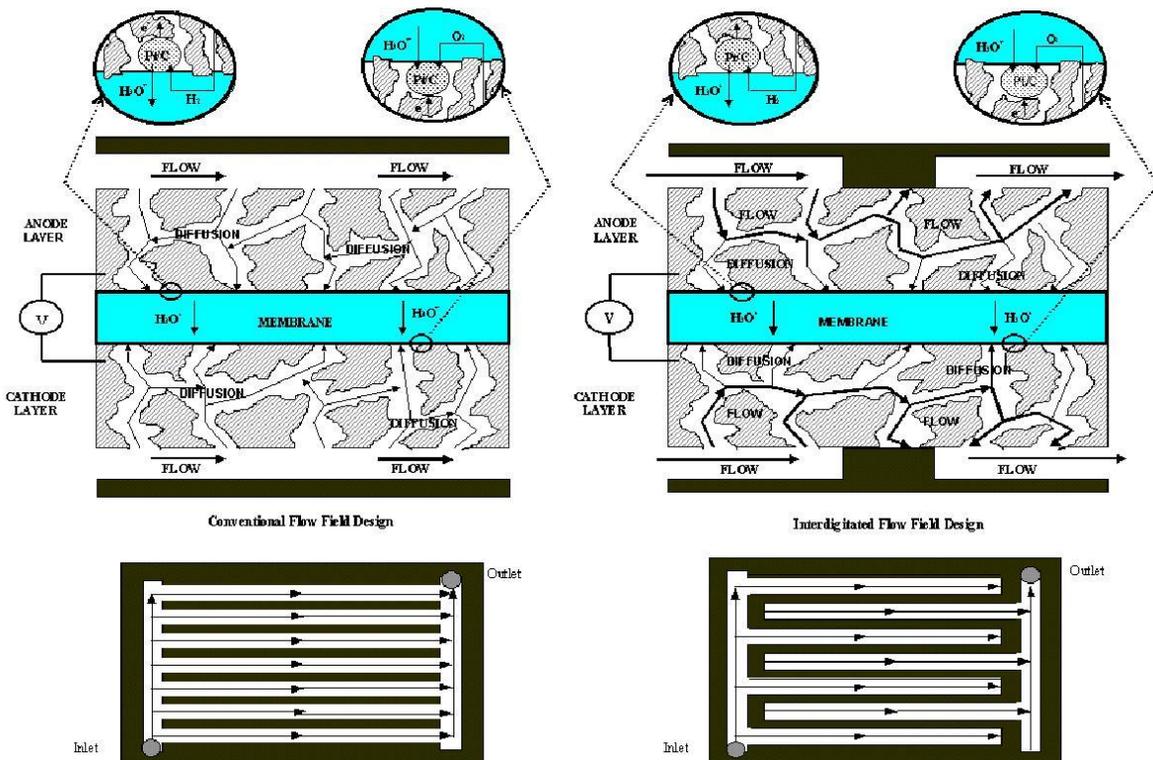
Figure 12 Conventional (left) and interdigitated (right) flow field designs

3.1.4. Current Collector Plates

As a collector plate; graphite or metals commonly used due to light strength. Flow fields on the plate have a significant effect on the performance of the FC. The width of the grooves directly affects the produced current.

3.2. Performance Issues

The performance of the FC dependents on many different parameters and all these parameters interact with each other. These parameters should be optimized in order to obtain high performance which is also high efficiency FC.
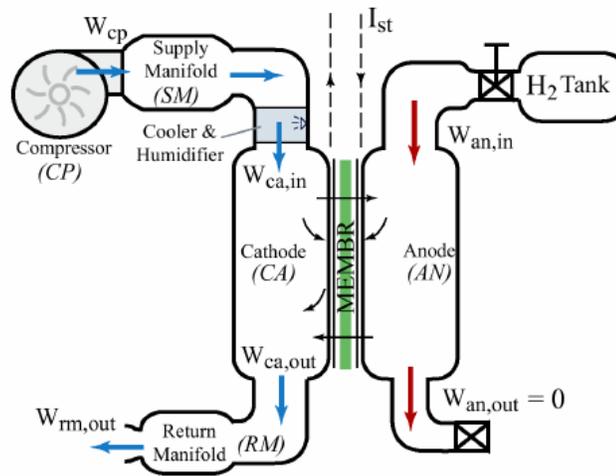
Figure 13 Simplified FC reactant supply system

A FC model developed above contains nine states [102]. The compressor has a state based on speed of rotor, the supply manifold has two states based on air mass and pressure; the return manifold has a state based on air pressure and the FC stack has five states based on O_2, N_2, vapor masses in the cathode side and H_2, vapor masses in the anode side. Combination of these states determines the voltage output of the FC. In this thesis FC is the focus point.

When we talk about performance the first think comes to the mind is produced voltage. Voltage of a FC has a basic formulation based on Gibbs free energy for open circuit voltage for hydrogen based FCs such as PEMFCs. You can see the equation below but there is also many voltage losses that you can see in following pages.

$$V = \frac{-\Delta g_f}{2F}$$

The target is to obtained a high efficiency cell. Simple equation of efficiency based on Gibbs free energy and enthalpy can be seen below.

$$Efficiency = \frac{-\Delta g_f}{-\Delta h_f}$$

In FCs the general equation used for obtaining efficiency is;

$$\epsilon_{fc} = \frac{w_{fc}}{m_{fc} \; x \; LHV}$$

where m_{fc} is mass flow rate, w_{fc} is FC power produced, and LHV is fuel lower heating value. In this equations FC power comes from a basic equation which is;

$$W_{fc} = \frac{V \; x \; I}{1000}$$

3.2.1. Mass Transfer in Cathode Side

Ideally while the calculations air should be investigated in three different steps, as oxygen, as nitrogen and as water vapor. The inlet and outlet mass flow rate of air is calculated from the inlet and outlet cathode flow conditions using thermodynamic properties. You can see the mass flow rate calculations below where m is the mass and, W and dm/dt is the mass flow rate. The mass continuatively is used to balance the mass of air which includes three elements (in this case).

$$\frac{dm_{O_2}}{dt} = W_{O_2,in} - W_{O_2,out} - W_{O_2,reacted}$$

$$\frac{dm_{N_2}}{dt} = W_{N_2,in} - W_{N_2,out}$$

$$\frac{dm_{w,ca}}{dt} = W_{v,ca,in} - W_{v,ca,out} + W_{v,ca,gen} + W_{v,membr}$$

Also it is possible to beneficial from electrochemistry principle while the mass flow rate calculations as it seems below where F is the Faraday's constant, I is current and M is molar mass.

$$W_{O_2,reacted} = M_{O_2} \ x \ {}^{nI_{st}}/_{4F}$$

$$W_{v,ca,gen} = M_v \ x \ {}^{nI_{st}}/_{2F}$$

3.2.2. Mass Transfer in Anode Side

The inlet and outlet mass flow rate of air is calculated from thermodynamic properties using flow properties. Air flow behavior is developed using the mass conservation principle and the thermodynamic and psychometric properties of hydrogen as you can see below.

$$\frac{dm_{H_2}}{dt} = W_{H_2,in} - W_{H_2,out} - W_{H_2,reacted}$$

$$\frac{dm_{w,an}}{dt} = W_{v,an,in} - W_{v,an,out} + W_{v,membr}$$

Also due to the electrochemistry principle you can see the mass flow rate equation below.

$$W_{H_2,reacted} = M_{H_2} \; {^{nI_{st}}}\!/_{2F}$$

3.2.3. Water Management

One of the most important items that can affect FC performance is water management system. Water management is effective in two ways; for humidifying the cell and for removing the heat. Humidity values of entering gases and the liquid water generated during the reaction are the water sources. On the other hand while the chemical reaction occurs in the membrane there is heat as a result of the chemical reaction. The point is, if the heat produced does not disappear from the reaction area, it decreases the reaction rate so efficiency of the FC decreases.

The water transport across the membrane can happen by the help of two forces. First one is the electro osmotic drag. Electro osmotic drag phenomenon is the drag forced cause by the molecular forces. In this case it drags across the membrane from anode side to cathode side. The amount of water transported is proportional to the electro osmotic drag coefficient which is defined as the number of water molecules carried by each proton. Second one, is the gradient of water concentration. The water concentration differs on the membrane linearly. By combining these two calculated methods you can see the final equation below where n_d is drag coefficient, c_v is water concentration, t_m is the membrane thickness and D_w is the water drag coefficient.

$$W_{v,membr} = M_v \; A_{fc} \; n \; \left(\frac{n_d \; I_{st}}{F} - D_w \; \frac{c_{v,ca} - c_{v,an}}{t_m} \right)$$

There are some assumptions while calculating the mass transfer such as water content and mass flow. They are perfectly uniform over the surface area of the membrane, and are functions of stack current and relative humidity of the gas in the anode and cathode.

3.2.4. Heat Management

A chemical reaction taking place inside the FC. As a result of this reaction a heat flux happening form inside the membrane to outside of the cells. It is very important because of two reasons; high temperature causes a decrease in reaction rate so FC efficiency decreases and, high heat can damage the cell. The ideal is having a homogenized distribution of temperature over the cell for decreasing the thermal stresses.

3.2.5. Voltage Losses

Another very important performance issue in FC's is voltage losses. In a FC there is four major voltage loss reasons; activation losses, internal losses, ohmic losses and losses caused by mass transport. When all different type of voltage losses comes together the equation for FC voltage is below. The aim is to decrease losses to develop higher energy. You can see the details of the losses in the following pages.

$$\Delta V = E - r\,(i - i_n) - A\,\ln\left(\frac{i + i_n}{i_o}\right) + B\,\ln\left(1 - \frac{i + i_n}{i_l}\right)$$

3.2.5.1.   Activation Losses

Activation losses are directly connected with activation energy of the chemical reaction. Before reaching the activation energy level, reaction does not start. Activation losses can be calculated with Tafels equation you can see below; where A is a constant based on material properties and i_o is exchange current.

$$V = A\,\ln\left(\frac{i}{i_o}\right)$$

And the constant A can be calculated by the equation below; where T is temperature as Kelvin Degree, R is ideal gas constant, F is the Faradays constant and α is charge transfer coefficient which generally changes between 0,1 and 0,5.

$$A = \frac{R\,T}{2\,\alpha\,F}$$

For having a minimal loss what needed to be done is to prefer a better catalyst with lower i_o. Most common used material is Platinum.

Metal	$i_o \left(\frac{mA}{cm^2}\right)$
Pb	$2.5x10^{-13}$
Zn	$3.0x10^{-11}$
Ag	$4.0x10^{-7}$
Ni	$6.0x10^{-6}$
Pt	$5.0x10^{-4}$
Pd	$4.0x10^{-3}$

Table 4 i_o values of some materials

3.2.5.2. Internal Losses

Second major voltage loss is the internal losses. They are the losses based on leakage problems such as fuel leakage to electrode or electron leakage to electrode. It is very important for low temperature FCs, for high temperature FCs i_n is too small so it is negligible. You can see the equation below.

$$V = A\,\ln\left(\frac{i_n}{i_o}\right)$$

3.2.5.3. Ohmic Losses

Ohmic losses are based on resistance of the components. It is directly affected by the resistance of the electrodes and collector plates to the transfer of electrons and the resistance of the polymer membrane to the transfer of protons.

$$V = I\,R$$

On the other hand, resistance depends on cell temperature and membrane humidity [103]. So as like seen in the equation below, resistance is effected by membrane thickness and conductivity.

$$R = \frac{t_m}{\sigma_m}$$

3.2.5.4. Mass Transfer Losses

The last reason of voltage losses is the losses caused by mass transfer. It is because of the concentration of fuel issues. High concentration of fuel or low concentration of fuel affects the chemical reactions rate. So the rate between supply and demand is very important for the cell.

$$\Delta V = \frac{R\,T}{2\,F} \ln\left(\frac{P_2}{P_1}\right)$$

P_1 is the pressure of fuel so most of the time hydrogen pressure and i_l is the limiting current density.

$$P_2 = P_1 \left(\frac{i_l - i}{i_l}\right)$$

3.2.6. Power Management

The power produced by the stack is used for the auxiliary components like the compressor that is used to increase the pressure. Increase in the pressure affects the power output. The parasitic power due to the compressor demand also increases so it reduces the net power. The pressure should be optimized due to required power output of the system.

3.2.7. Sealing

The sealing function in FCs is can effect reliability, durability and cost of the FC [83]. A small leakage in the cell can result with a major decrease in efficiency.

3.3.   System Integration

Between the application areas of PEMFC; transportation applications have the main attraction. In order to be used in automotive, PEMFC must be combined with many components and systems. Figure 15 shows the automotive FC system prepared by Pukrushpan [5].
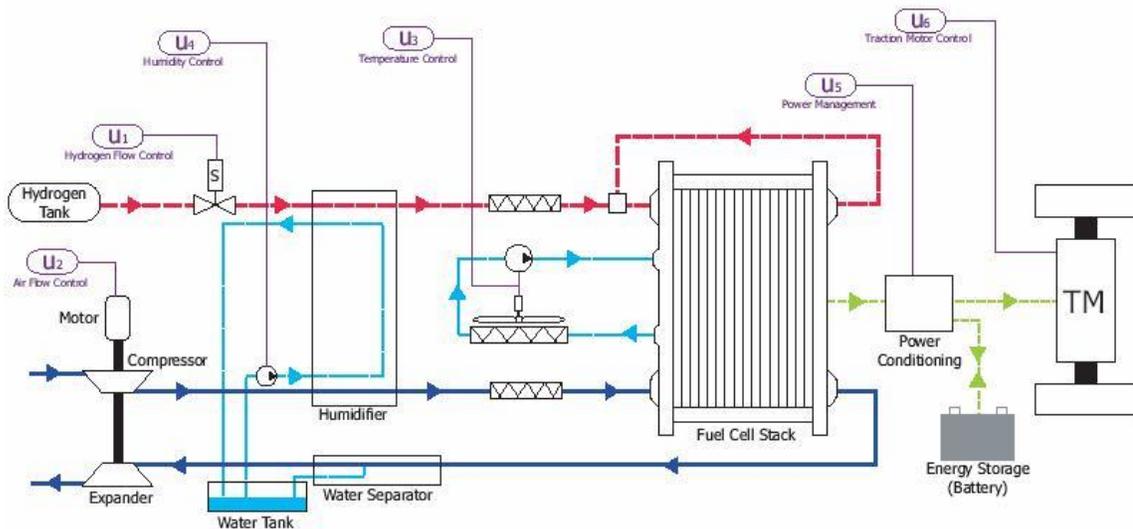
Figure 14 Automotive FC propulsion system

A compressor is used to supply pressurized air to the FC stack. It enhances the power output of the system. The air temperature increases during the compression process so a heat exchanger is used to reduce the temperature. Air entering the stack is humidified for water management purposes. Water produced at the stack is used in humidifiers after it is separated from the exhaust gases. On the other side a valve is used to control the flow of hydrogen from the pressurized tank. The hydrogen entering the stack also humidified by a humidifier. The extra heat formed due to the chemical reaction is removed from the stack

by using a de-ionized water coolant to keep temperature in suitable operation ranges.

Change in one parameter may affect another. For example, change in the pressure of the reactants affects temperature and humidity of the gases entering the stack. The output power directly affected from humidity of the membrane. Also the rate of the chemical reactions affected from the temperature of the stack and it directly affects the energy output.

4.   AUTOMOTIVE APPLICATIONS

When all different types of FCs and their application areas are studied transportation applications are the most promising and competitive application. People are more aware about clean energy sources; they started to care about greenhouse gasses so they prefer to obtain from a clean energy source. This is the reason of promising potential. On the other hand, the success of PEMFC in automotive industry can be a very important opportunity for applications in other fields. When mass production of Fuel Cell Vehicles (FCV) begins, due to the manufacturing rates and mass production the cost of FCs reduces which can also affect all application areas of FCs.

The development of a FCVs require development on many different areas such as thermal management of the cell, transportation of required fuels to the cell, managing size problems due to vehicle size, locating the FC system in the right place of the vehicle due to safety based on crash tests or flammability, etc. As a general view integration of the system is the issue; the onboard integration of the FC system and its energy storage devices with a proper energy management [94]. In order to meet the future transportation needs, most major car makers in the world are engaged in developing prototype FCVs.

The most important factor that supports the growing market for FCV is the success of the hydrogen economy and related technologies to that [94]. FCV system equipped with direct conversion fuel processor can compete with Internal Combustion Engine (ICE) technologies because the performance of hydrogen would exceed the performance of ICE in all aspects out of cost performance [95].

By the technology roadmaps; the present and future specifications of PEMFC for FCV are explained clearly [96]. Those roadmaps were prepared due to required improvement areas and they try to route the developments promising areas for supporting of FC technology. In those roadmaps they focused in four areas that are critical for the commercial adaptation of

FC in automotive industry, which is durability, cost, freeze start time and volumetric power density.

When we make a general overview on those targets;

- As a durability target; 5000 hours lifetime tried to be reached by 2010.
- For decreasing to costs; a 500,000 unit volume tried to be reached of having a stack cost of 30 $/kW.
- A freeze start capability; the target is to obtain 50% of the maximum power in 30 seconds under 1 Celsius degree temperatures.
- And as a volumetric power density target; 2500 W/l tried to be reached.

5.   METHODOLOGY

As stated before the success of PEMFC in automotive industry can be a very important opportunity for many other fields because of mass production opportunity. To increase the usage of FCs the most important problem needed to be solved, which is high cost. In the first years of FCs, most of the costs come from raw materials prices such the price of Pt. Nowadays; it has significantly decreased. Usage of Pt was 28 gr/cm^2 but today it is less than 0,2 gr/cm^2. After this point the cost can decreased by eliminating some components of the system. Simplification of the system can be an opportunity for cost reduction. For elimination some components such as recovery pump of anode flow optimization needed to be developed and due to the large size of automotive applicable FCs, the heat and flow distributions start to be a challenge.

In this thesis a 20x20 cm fuel cell model was designed. Due to the challenges stated above, for optimizing the heat and flow different anode/cathode gas channels and water management system a 3D model of the cell was created by using solid modeling, computer aided design (CAD) and computer aided engineering (CAE) program named Solid Works. After creating few models; they exported to finite element analysis and solver program that can analyze multi-physics named COMSOL for beginning optimization process of this thesis.

Steady state, 3D, single phase, isothermal PEMFC model is developed. The models used for these simulations consists of three different parts; anode, cathode and water channels. A commercial flow solver based on finite element technique COMSOL; solves the complete equations with determined source terms. The stationary nonlinear solver is used since the source terms of the current conservation equation make the problem nonlinear. The impact of various parameters on inlet and outlet studied while optimization process such as flow rates, velocities, pressures and temperatures. After determining the inlet and outlet; boundary conditions needed to be clarified and model needed to be meshed for getting ready for analysis. To accelerate the convergence of the analysis, model is firstly

solved based on the initial settings of Comsols solver and than Navier-Stokes modules and Darcys Law modules are used for analysis that use the results of previous standart solver.

To sum up; at first the behavior of fluid flow and pressure distribution is studied by using solvers. And then a theoretical study of temperature distributions is analyzed. So the simulations are based on two different studies; fluid flow and heat flow.

For fluid flows as a first step flow type is needed to be clarified by calculating Reynolds number because you need this number for determining the flow type such as; creeping, laminar or turbulent. If the Reynolds number is lower than 2300 flow is laminar, if it is higher than 4000, it is turbulent and if it is between 2300 and 4000 it is transient flow. If the Reynolds number is very small so the flow rate is also very slow, it is called creeping flow. You can see the equations below where ρ is density, u is velocity, μ is dynamic viscosity, v is kinematic viscosity and L is the total length of a single channel.

$$Re = \frac{\rho\, u\, L}{\mu};$$

$$Re = \frac{u\, L}{v}.$$

In this equations kinematic viscosity equals to;

$$v = \frac{dm/dt}{\rho\, A}.$$

Than Navier Stokes equations, Darcy's Law, and the Brinkman Equations are used. The flow is solved due to the Newton's second law by using Navier Stokes equations. In the case of a compressible Newtonian fluid, Navier Stokes equation consists of four main parts; inertial forces, pressure forces, viscous forces, and the external forces applied to the fluid.

$$Inertial\ Forces\ = \rho\left(\frac{du}{dt} + u\,.\,\nabla u\right)$$

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$$Pressure\ Forces\ =\ -\nabla p$$

$$Viscous\ Forces\ =\ \nabla.\left[\mu\left(\nabla u+(\nabla u)^T\right)-{}^2\!/_3\ \mu(\nabla.u)I\right]$$

$$External\ Force\ =\ F$$

So the total equation is below where μ is the fluid dynamic viscosity, p is the fluid pressure, u is the fluid velocity and ρ is the fluid density.

$$\rho\left(\frac{du}{dt}+u.\nabla u\right)=-\nabla p+\nabla.\left[\mu\left(\nabla u+(\nabla u)^T\right)-{}^2\!/_3\ \mu(\nabla.u)I\right]+F$$

Navier Stoke equations are solved together with continuity equation as general you can see below. The Navier Stokes equations represent the conservation of momentum, while the continuity equation represents the conservation of mass.

$$\frac{d\rho}{dt}+\nabla.(\rho u)=0$$

In low Reynolds numbers so when the flow type is creeping flow; inertial forces and exteral forces are neglectible. In this condition Navier Stoke equation can be simplified.

Darcy's law is also an approach for solving fluid flows but it is only valid for very slow flows which have Reynolds number smaller than one. Darcy's law was derived from the Navier Stokes equations you can see below where K is the permeability.

$$u=-\frac{K}{\mu}\nabla p$$

Brickman's equation is an approach derived from the Darcy's law. Equation can be seen below where β is an effective viscosity term.

$$B\ \nabla^2q+q=-\frac{K}{\mu}\nabla p$$

After the solvers of the analysis clarified, details of the model needed to be determined. First step is creating the model. It is possible to create the model in Comsol, the same program with the one that can simulate flow analysis. In this thesis models created by a 3D modeling program named Solidworks. Then models were imported to Comsol, which is the multi-physics analysis program. After importing the model to Comsol, it was extracted from a bulk block to obtain channels in it. Then, it was like a cycle; model created than analyzed; if the results were far beyond than expected, new design must be created. If the results are close to expected levels, keep the design but optimize channel sizes. And this process repeated till the desired distribution can observe.

While the analysis other some settings needed to be determined. When the analysis was investigated one by one; for the cathode side; stationary study was developed under laminar flow physics conditions. In the laminar flow physics some other detailed needed to be clarified such as wall conditions, inlets, outlets, etc. The material that flows was chosen as pure air and the fluid properties directly determined based on general properties of air. The air temperature is determined as 333 Kelvin degrees which is the cell temperature under 1,5 atm pressure condition. These values have direct affect on viscosity. Next step is determining the wall conditions. In this analysis it is no-slip. Then inlet and outlet were determined. Inlet is determined as mass flow with a flow rate at 1.10^{-5} kg/s. The outlet is determined as pressure. Initial pressure condition is 1,5 atm and backflow was suppressed. The last step before starting analysis is determining the mesh properties. On the one side of the cathode channel model; free triangular mesh distribution was used with maximum 0,001 m and minimum 0,00004 m particle sizes. Then this distribution swept down as 4 layers (you can see details in appendix 1).

A laminar, continuous flow with uniform mass transfer tried to obtain but the challenging point was optimizing the pressure of the fuel because aim was minimizing the pressure drop. The pressure drop between the inlet and the outlet needs to be too low in all over the channels.

The other part needed to be analyzed is anode channel. For the anode model; stationary study was developed under creeping flow physics conditions. The material that flows was chosen as pure hydrogen and the fluid properties was determined based on that. Initial temperature was determined as 333-Kelvin degree that is the cell temperature and the reference pressure determined 1 atm. Then the wall condition was chosen as no-slip. Next step is determining inlet and outlet. Inlet is determined as pressure and outlet determined as flow. Inlet pressure is 1,5 atm and back flow was neglected. Outlet velocity is $7,6.10^{-4}$ l/min and it is a laminar out flow. On the one side of the anode channel model; free triangular mesh distribution was used with maximum 0,001 m and minimum 0,00004 m particle sizes. Then this distribution swept down as 4 layers (you can see details in appendix 2).

Due to continuous flow, uniform mass transfer tried to be obtained. Significant point is to supply enough H_2 for the cell reaction. If supplied hydrogen is much more than required, H_2 accumulates and due to accumulation reaction rate decreases. What is needed to be done is optimizing the flow rate. The flow type for anode model is used as creeping flow as mentioned above.

The last part that was analyzed is water channels. For the anode model; stationary study was developed. This time physics conditions are a bit more complicated then anode and cathode. Two different physics conditions were used; laminar flow and heat transfer. The material was chosen as water; this time the material of the ribs are also important and they were chosen as graphite. Ribs are important because they also affect the heat distribution. Initial temperature was determined as 333-Kelvin degree that is the cell temperature and the reference pressure determined 1 atm. For the laminar flow study; the walls determined as no-slip. Inlet was a mass flow in 1.10^{-5} kg/s flow rate and outlet is pressure with 0 atm. In this case outer pressure and the back flow is neglected. For the heat transfer study; an extra surface is added to the model for representing the membrane. A heat flux (Q_{in}) was defined to that surface as 6 kW/s. There was also an outflow; it was the same port with the outflow of laminar flow. The flow entering to water channels defined as 293 Kevin degrees, which is room temperature. Mesh was also complicated than cathode and anode

layers due to complication of two physic studies. For membrane side triangular mesh was used and swept to 4 layers. For the water channels side free tetrahedral mesh is used and boundaries of the meshed studied. As a last step for meshing; corner refinement was done. All the mesh sizes were calibrated for fluid dynamics (you can see details in appendix 3).

Uniform flow distribution tried to be obtained in those channels. After that as a second step, uniform heat distribution tired to be obtained. By homogeneous distribution of high flow rate; the heat flux coming from the membrane can be carried out faster. Higher rate of heat removing can increase the efficiency of the FC.

6.   RESULTS, ANALYSIS AND DESIGN

As mentioned in methodology section; three parts of the FC is analyzed during this thesis. There are the flow model of the cathode side, the flow model of the anode side and the heat and mass flow model of the membrane cooling system what was called, water channels.

In the cathode channels; homogeneous distribution and uniform flow is very important. In this case the challenge is optimizing the pressure drop. After trying several designs five-channel parallel serpentine model were used. While optimizing the channels at the end; sizes were chosen as 2 mm depth and 2mm width. When you give a look to the geometry of the cathode side, it is perfectly symmetrical as you can see below.
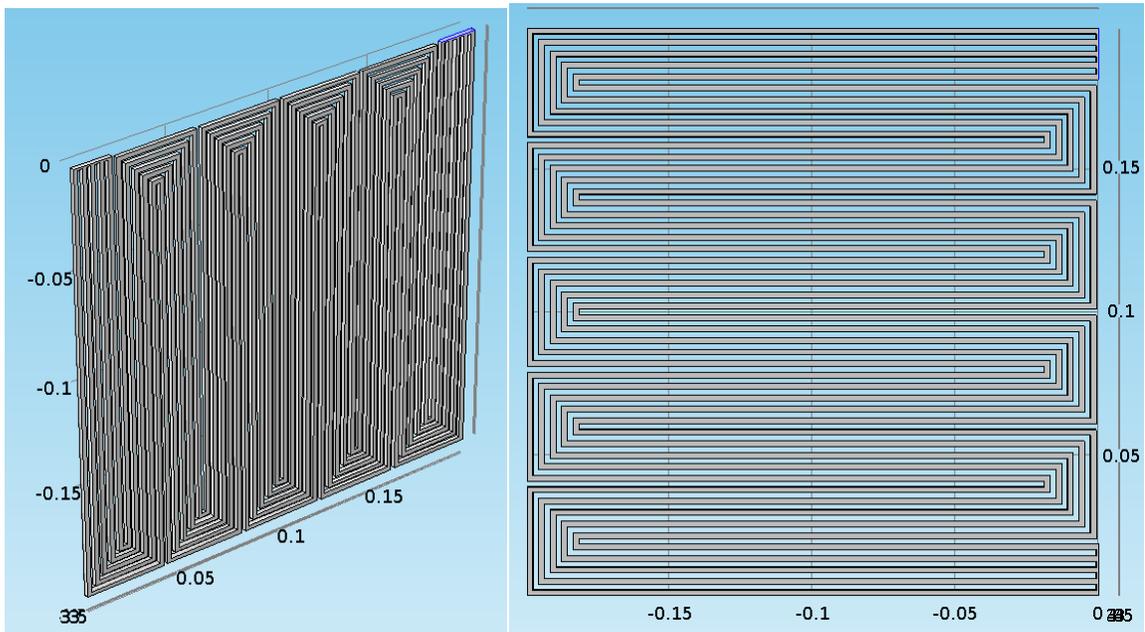
Figure 15 Cathode model channel design

Having continues and symmetric channel design as you can see below it is easier to obtain a uniform flow with homogeneous distribution. And as a result you can see below, a uniform velocity and pressure distribution was obtained.
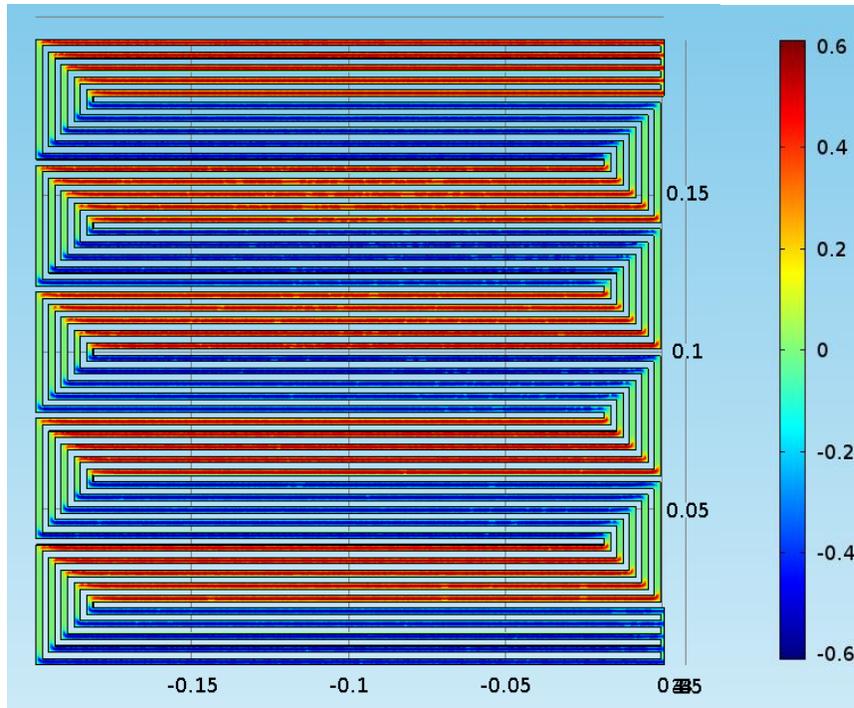
Figure 16 Cathode model velocity distribution

When the color scale was checked it seems like there is a decrease in pressure and velocity but when we checked the values pressure is seem like all the same and the velocities are almost the same in same axis. Pressure seen like the same all over the channels but when calculated manually, we saw that there is only 80Pa pressure drop, which is too low like we try to obtain. On the other hang the velocities above seen like changing but it is almost the same in all over the cell again. The color difference is caused by the way of flow. Red and blue colors are just the same velocity with different ways like +x and −x. And the green part which seen like 0 velocity is zero velocity in x-axis, because in that channel velocity is in y-axis.
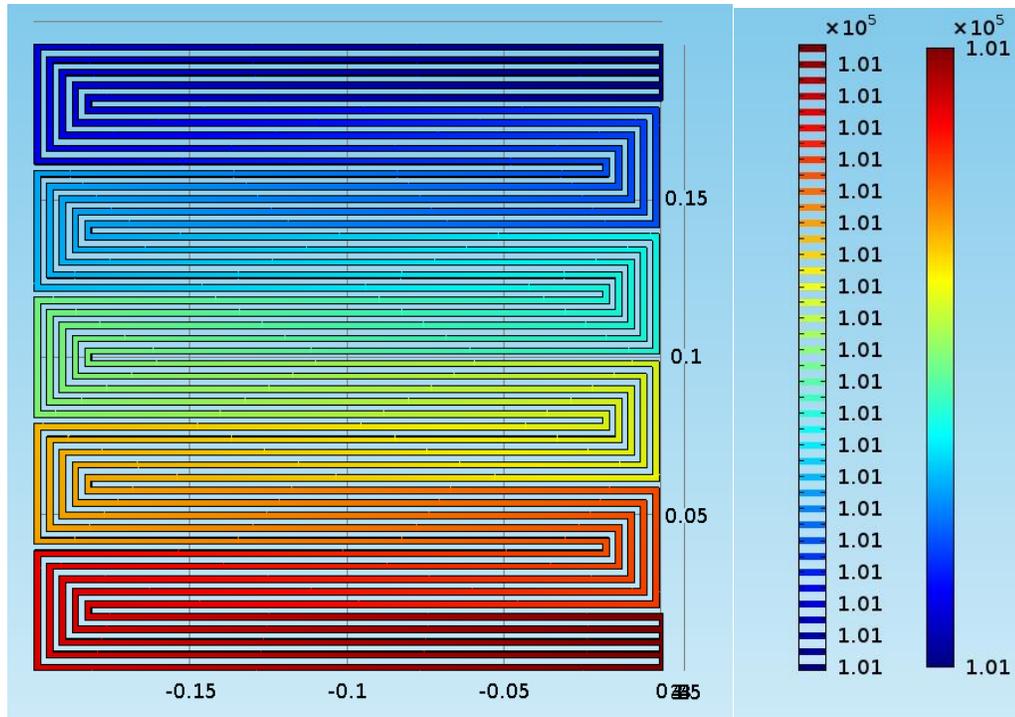
Figure 17 Cathode channel pressure distribution

In anode channels, homogeneous distribution with uniform flow tried to be obtained. Problem is keeping the concentration of the gasses constant in the channels for minimizing its effects on reaction rate. After trying several designs fish bone model with perpendicular entrance side and angular outflow side is used as you can see below. While optimizing the channels, sizes were chosen as 1 mm depth for all the channels. 2mm width is used for main channels perpendicular to sides and 1 mm width for small channels, which is angular to sides. You can see the design below.
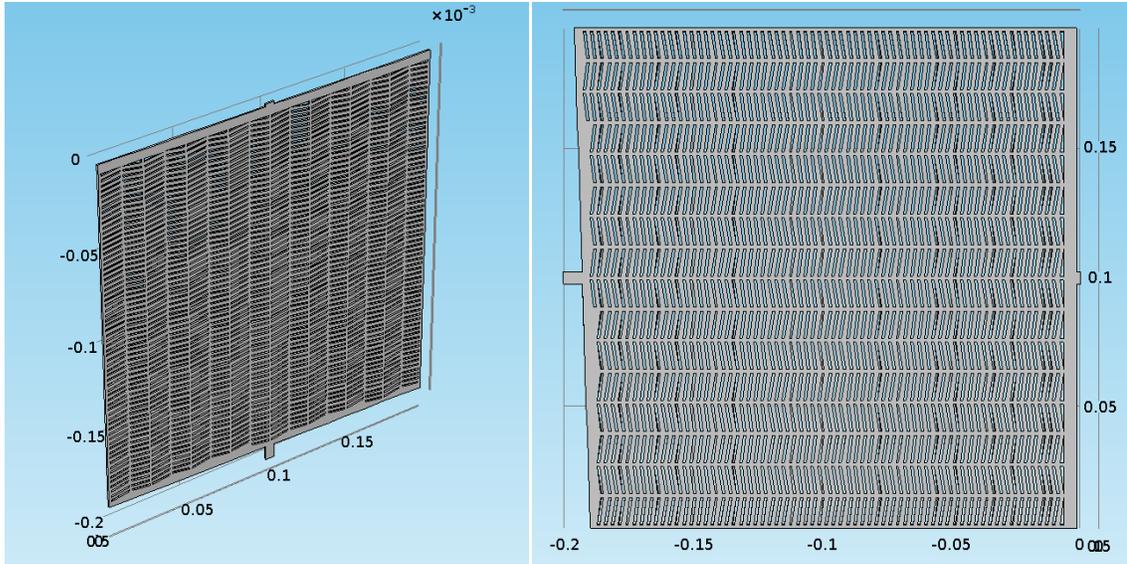
Figure 18 Anode model channel design

By the ways of pressure distribution it reached to the level we expected. It has a uniform pressure distribution in all over the anode surface as you can see below.
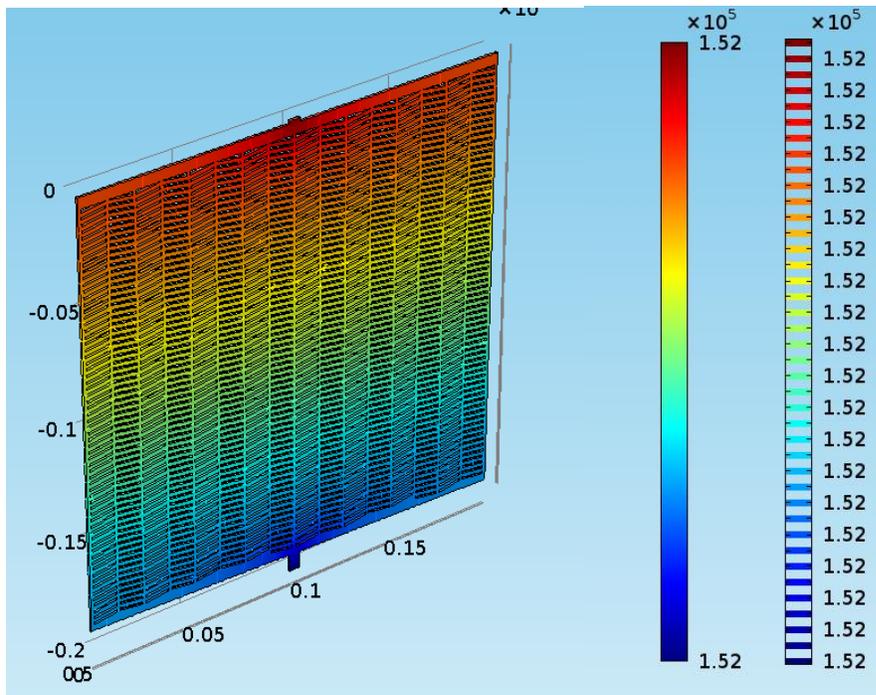
Figure 19 Anode model surface pressure distribution

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The velocity distribution on the surface of the anode was a bit more complicated. Velocity in y-axis is uniform in everywhere. The velocity in x-axis is uniform in the places closer to inlet and outlet; just in to the middle the velocity in x-axis decreases as you can see below.
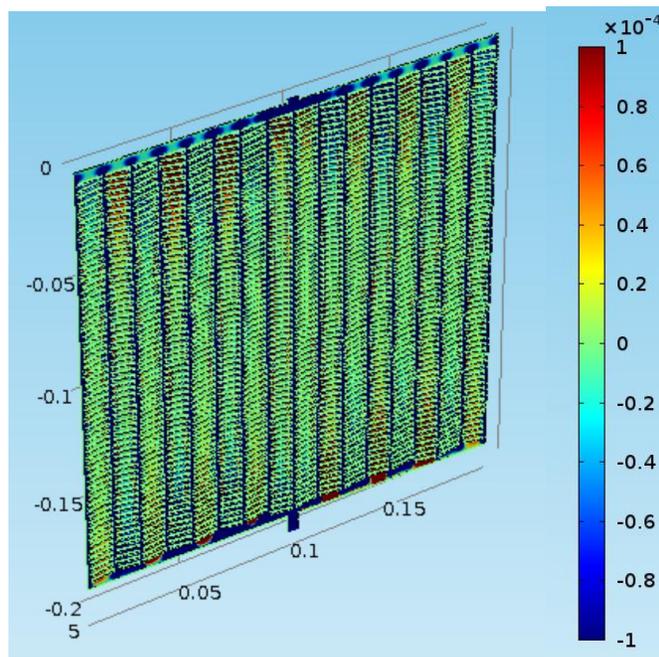
Figure 20 Anode model slice velocity distribution

The last part is water channels. This was the most challenging part of these analyses because both heat flux and mass transfer needed to be analyzed and optimized at the same time. Homogeneous distribution and uniform flow is again very important but the most important part is the heat transfer. These channels remove the heat that is a result of the reaction in the membrane. Three parallel serpentine channel model designs are used. For a single layer of a channel; sizes were optimized as 1 mm depth for all layer, 5mm width for channels and 4mm width for ribs.
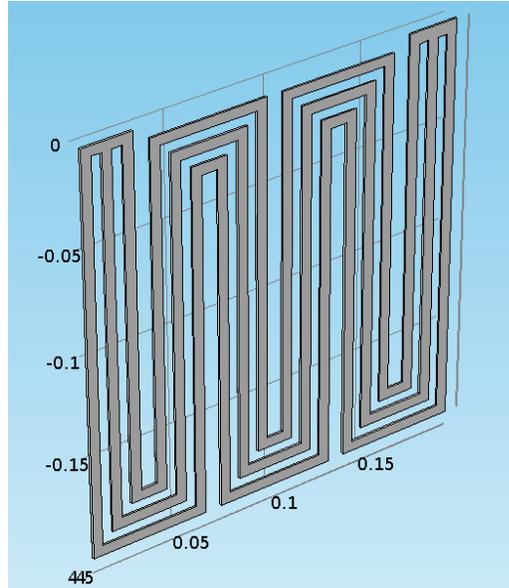
Figure 21 Water channel design

When geometry of the water channels checked, it is perfectly symmetrical as you can see above. This has a major affect on flow distribution. Uniform flow distribution is obtained. You can see the velocity distribution below.
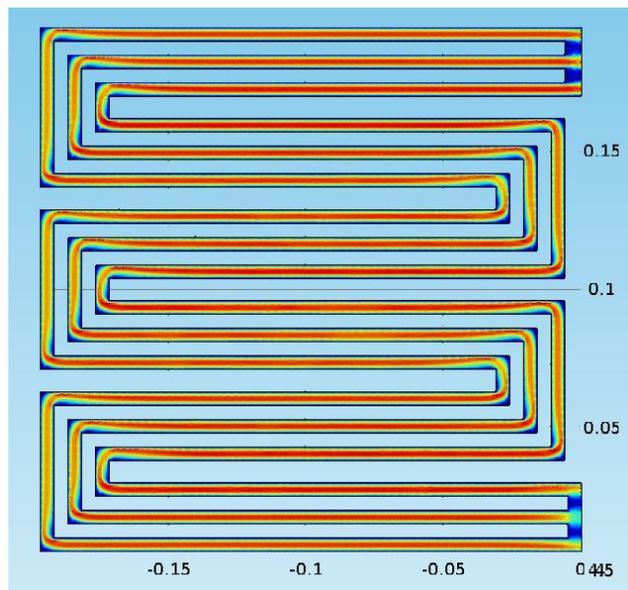
Figure 22 Water channel flow velocity distribution

Additional to mass flows; heat transfer in solids/liquids module is used as mentioned before in methodology section. Due to heat transfer studies; a heat distribution was also obtained. While the studies due to the defined parameters mentioned in methodology part, temperature of the cell kept constant at 333-Kelvin degree as you can see below.
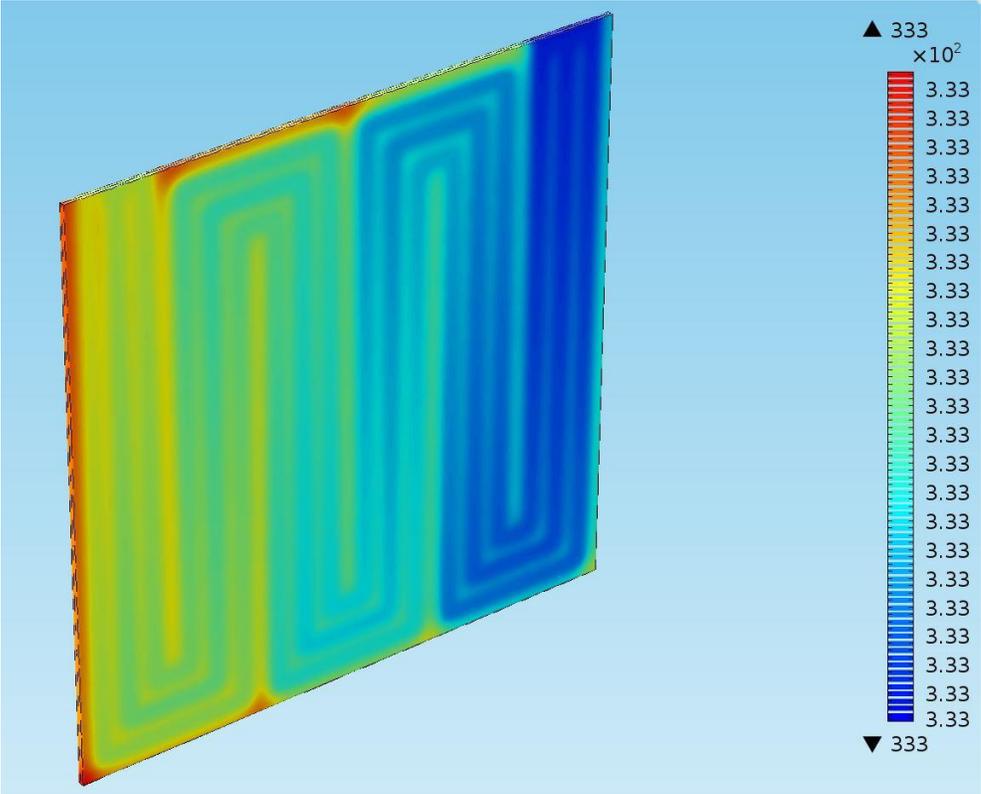
Figure 23 Membranes heat distribution with water channel

7.   CONCLUSION

Due to the high costs of new homologation emission requirements in the automotive industry and increase in costs of raw materials, developing renewable energy sources become feasible. In regulative ways, emission levels based on CO_x, SO_x, particle size, etc. decrease and therefore research costs increase exponentially. These investments can be shifted to renewable energy sources; especially to FC development for the automobile industry.

There are too many different fuel cell types. They differ based on the membrane that they use. The working temperature, start up time and the efficiency are the major reasons of the distributing FC to different applications. Compared to other fuel cell types, Proton Exchange Membrane fuel cells are the most suitable for transportation applications because it is the most competitive and promising one due to startup time, low sensitivity to orientation and favorable W/kg ratio.

Determining the right FC type based on application is not enough for having a high efficiency system. The system integration is very important. Water management, heat management, oxygen excess ratio, sealing, etc. all have major effects on the efficiency of the FC system.

FC systems can reach up to 60% efficiency in different applications. However, there is a potential to reach 90%. There is still a long way to go. Next to increasing the efficiency, the cost change is the second major point. This can be changed by two ways: First; most of the cost comes from platinum so replacing Pt with a low cost material significantly decreases the cost of FC. Second; if the usage rate of FC systems increase; price of FC systems decrease due to mass production.

In this thesis a methodology to recognize the various interactions in a fuel cell system is illustrated by the ways of mass flows and heat transfers such as air flow, water flow and thermal management in anode, cathode and water channel layers. By optimizing the flows;

system can be simplified by eliminating some components such as anode recovery pump. The 3D modeling tools like Solid works and a finite element solver program like COMSOL is required for such an analysis are described. While that impacts of varying parameters on fuel cell system operation are studied.

In this study; FC were studied in three parts; flow analysis in anode channel, flow analysis in cathode channel and flow analysis in water channels with heat distribution. In anode channels; homogeneous distribution with uniform flow tried to be obtained. The challenge is keeping the concentration of the gasses constant in the channels to minimize its effects on reaction rate. This obtained by defining creeping flow in anode channels with uniform flow.

In the cathode channels; as like anode homogeneous distribution and uniform flow is very important. In this case the challenge is optimizing the pressure drop. This is also obtained by a laminar flow. It will be good to analyze it by turbulent flow also as a future work.

For the water channels; homogeneous distribution and uniform flow is important but the most important part is the heat transfer. These channels remove the heat which is a result of the reaction in the membrane. Homogeneous distribution with uniform flow obtained by a laminar flow and the heat distribution studied. Analyzing these flows under turbulent condition is important as a future work. A comparison with laminar flow and other channel design is needed to decide the best.

By these studies; it is clarified that obtaining a 20cm x 20cm FC with a well distributed heat and low pressure drops in mass transfer of anode and cathode side is possible. So by the ways of these results it is possible to develop a simplified, low cost FC which is suitable for automotive applications.

As a future work; analyzing the flows in turbulent conditions and studying heat distribution with more details is very important. For studying the heat distribution it is also required to simulate the reaction in the membrane; in the studies belong this thesis, membrane heat

determined as a constant value. For heat distribution, interaction of the material is very important so as a next study it can be simulated and then by combining the FC models; a stack assembly model can be created and analyzed. But before analyzing the stack; sealing of the FC need to be designed and analyzed to be sure there is no leakage under high pressures. Due to the high pressure point bolt locations needed to be determined. A FC model developed above contains nine states so as a last step other components of the FC system can be integrated to energy calculations to reach the net output and efficiency of the system.

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A 1: Cathode Layer Analysis Details

Analysis run by the program COMSOL 5.1. For having a more realistic analysis result we defined most of our parameters. Our analysis done in stationary mode (not time dependent). You can see defined parameters below.

- Study : Stationary

  ∞ Study 1

      Step 1: Stationary

  ▷ Solver Configurations

- Laminar flow

  Laminar Flow *(spf)*

      Fluid Properties 1

      Initial Values 1

      Wall 1

      Inlet 1

      Outlet 1

  - Incompressible
  - Pref=1,5atm

- Material : Air

  Materials

  ▷ Air *(mat3)*

- Fluid properties : T=293,15 K
- Initial values:
  - u= 0.x + 0.y + 0.z
  - P=1atm
- Wall : no slip
- Inlet
  - Mass flow

- o Mass flow rate
- o Mdot=1.e-5 kg/s
- Outlet
  - o Pressure
  - o Po=1,5 atm
  - o Suppress backflow
- Mesh
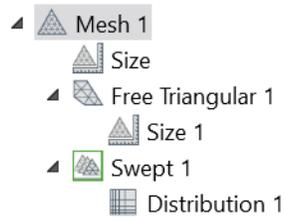
  - o Size
    - Max: 0,02 m
    - Min: 0,0036 m
  - o Free triangular
    - Size
      - Max: 0.001 m
      - Min: 0,00004 m
    - Distribution: 4 layers
  - o Swept
    - Distribution : 4 layers

A 2: Anode Layer Analysis Details

Analysis run by the program COMSOL 5.1. For having a more realistic analysis result we defined most of our parameters. Our analysis done in stationary mode (not time dependent). You can see defined parameters below.

- Study: Stationary

  - Study 1
    - Step 1: Stationary
    - Solver Configurations

- Creeping flow

  - Creeping Flow *(spf)*
    - Fluid Properties 1
    - Initial Values 1
    - Wall 1
    - Inlet 1
    - Outlet 1
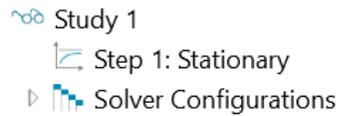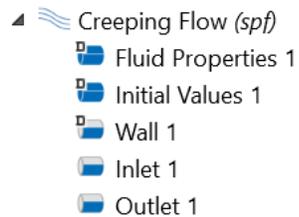
    - Incompressible

    - Neglect inertial term

    - Pref=1atm

- Material : Hydrogen

  - Materials
    - Hydrogen *(mat1)*
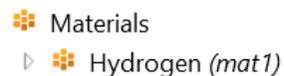
- Fluid properties : T=293K

- Initial values:

    - u= 0.x + 0.y + 0.z

    - P=1atm

- Wall : no slip

- Inlet

    - Pressure

    - Po=1,5 atm

    - Suppres back flow

- - o Normal flow
- Outlet
    - o Laminar out flow
    - o Flow rate
    - o Vo= 7,6e-4 l/min
    - o Lexit= 1m
- Mesh

   - o Size
        - Max: 0.02m
        - Min: 0,0036m
   - o Free triangular
        - Size
            - Max: 0.001m
            - Min: 0,00004m
        - Distribution: 4 layers
   - o Swept
        - Distribution: 4 layers

A 3 :Water Channel Analysis Details

Analysis run by the program COMSOL 5.1. For having a more realistic analysis result we defined most of our parameters. Our analysis done in stationary mode (not time dependent). You can see defined parameters below.

- Study: Stationary

    ∞ Study 1
        ⮢ Step 1: Stationary
        ▷ ⟘ Solver Configurations

    o Study extensions

▼ Study Extensions		
☑ Auxiliary sweep		
Sweep type:	Specified combinations	⌄
►► Parameter name	Parameter value list	Parameter unit
Qin ⌄	1 10 10000	
Mdotin ⌄	.001 .1 1	
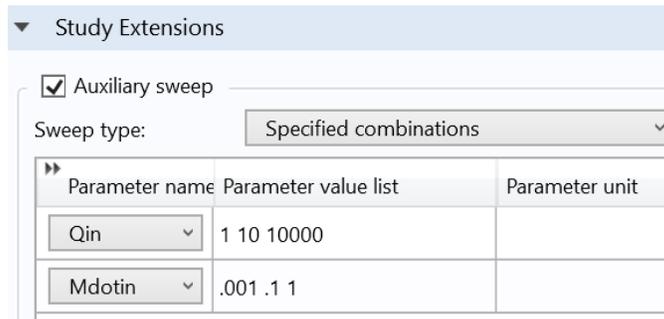
- Material : Water (for flow channels) & Graphite (for membrane)

    ⬓ Materials
    ▷ ⬓ Water *(mat1)*
    ▷ ⬓ Graphite *(mat2)*

- Laminar flow

    ≋ Laminar Flow *(spf)*
        ⬓ Fluid Properties 1
        ⬓ Initial Values 1
        ⬓ Wall 1
        ⬓ Inlet 1
        ⬓ Outlet 1

    o Incompressible

    o Pref=1 atm

    o Fluid properties : T=293,15 K

    o Initial values:

    ▪ u= 0.x + 0.y + 0.z

- P=1000 Pa
  - o Wall : no slip
  - o Inlet
    - Mass flow
    - Mass flow rate
    - Mdot=1.e-5 kg/s
  - o Outlet
    - Pressure
    - Po=0 Pa
    - Suppress backflow
- Global definitions
  - o Parameters

Name	Expression	Value
Pinlet	20	20
Tcell	333	333
Mdotin	1	1
Qin	0	0

- Heat Transfer

  - o Initial values : Tcell
  - o Heat flux (Qin)
  - o Temperature (Tcell)

- Mesh

Mesh 1
    Size
    Size 1
    Corner Refinement 1
    Free Triangular 1
    Swept 1
    Free Tetrahedral 1
    Boundary Layers 1

- o Size (of water channels): Calibrate for fluid dynamics

- o Swept

   - Distribution : 4 layers

A 4: Solid Works Models
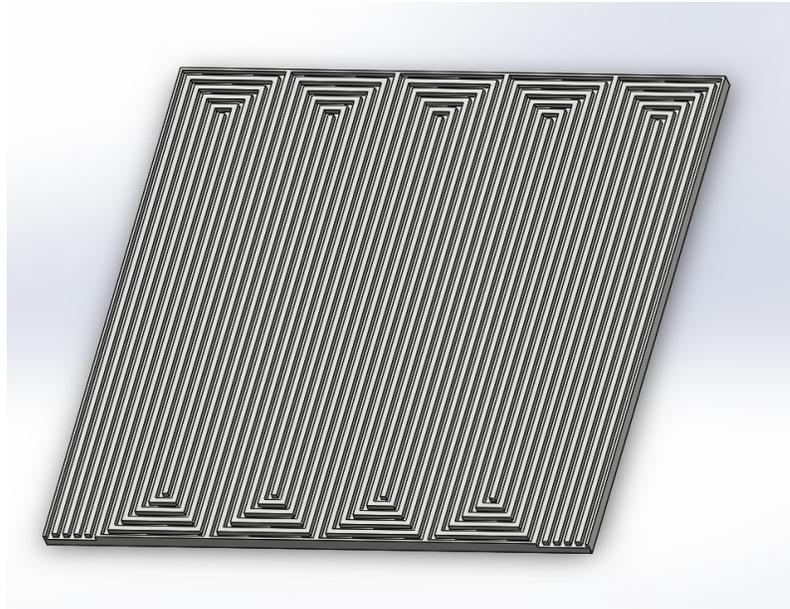
Figure 24 SolidWorks model of anode side
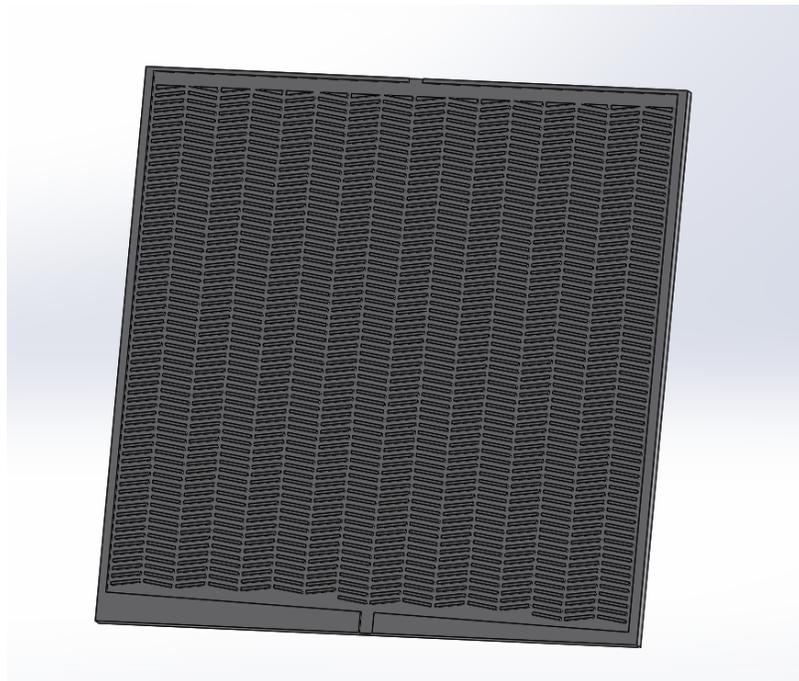
Figure 25 Solid Works model of cathode side
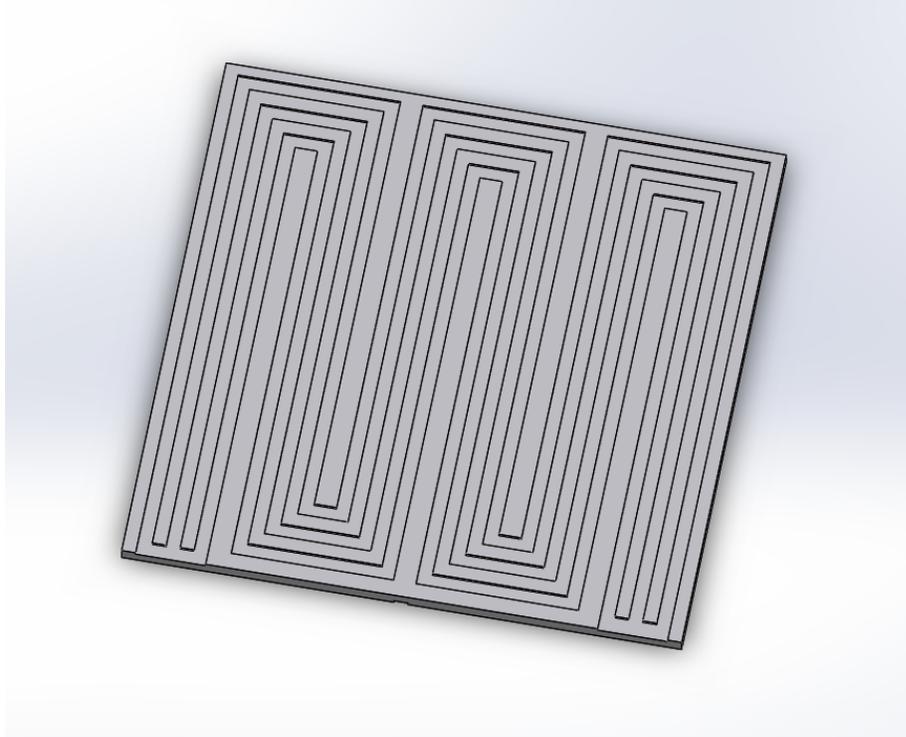
Figure 26 Solid Works model of water channels