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A survey on factors affecting performance and durability of PEM Fuel Cells in Automotive applications

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ABSTRACT

Fuel cell converts chemical energy stored in reactant gases into an electric energy. Fuel cells are used for stationary as well as mobile power supply. Fuel cells are classified in various types. Fuel cell types are classified by the type of electrolyte used in it. Among them, Proton Exchange Membrane Fuel Cell (PEMFC) is most suitable for automotive application. Hydrogen and oxygen are used as fuel in the PEMFC. It is a zero emission power generator as byproduct of the process is water and heat. Moreover, it is compact, lightweight, efficient, high power density, quick startup ability and no corrosive fluid. Hence, PEMFC has attracted automotive industry since a decade. However, it is not yet commercialized due to several issues related to its performance, durability and high cost. Key factors affecting the PEMFC such as water flooding, dehydration, corrosion, degradation of membrane, contamination of cell and reactant gas starvation are studied in this literature survey. This paper consolidates issues affecting performance and durability along with key causes, detection techniques and possible measures for improvement. It also points out to areas for further research and development in this area.

Keywords: PEM Fuel Cell, Automobile

1. INTRODUCTION

A fuel cell converts chemical energy from reactants into electricity. It is an electrochemical reaction at two electrodes, anode and cathode. Output of the reaction is heat and water. Thus, there is no environmental or noise pollution. Hence, it is an excellent power generation source. Hydrogen and Oxygen molecules react and generate electricity and water as a byproduct. Due to its high power density, it is suitable for movable as well as stationary power source applications. Many car makers have already demonstrated fuel cell based vehicles, though not commercially available in many parts of the world. It will be a future power source for automobiles as it does not depend on fossil fuels [10]. Fuel cells have very important role to play in hybrid and electric vehicles. Energy generated by fuel cells will be stored in batteries and motor will be driven [4]. Use of fuel cells in such electric architectures will help in extending range.

Figure 1.1 shows a typical PEM fuel cell. In the fuel cell electric energy is generated through direct conversion of the chemical energy. Hydrogen and Oxygen are separated by the electrolyte. Chemical reaction in the fuel cell is split into two electrochemical reactions. One reaction occurs at anode andanother at cathode. These electrochemical reactions are called as two half cell reactions:

$$H_2 = 2H^+ + 2e^-$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- = H_2O$$

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The overall reaction by combining two half cells is:

$$H_2 + \frac{1}{2}O_2 = H_2O$$

Electrolyte is electrically insulated between the two half-cells. However, it shall allow protons to exchange from anode to cathode. The electrolyte shall be good proton conductor and electrical insulator to facilitate proton exchange and electrical insulation. Also, the electrolyte has to be chemically resistant. The exchanged protons form a water molecule after combining.

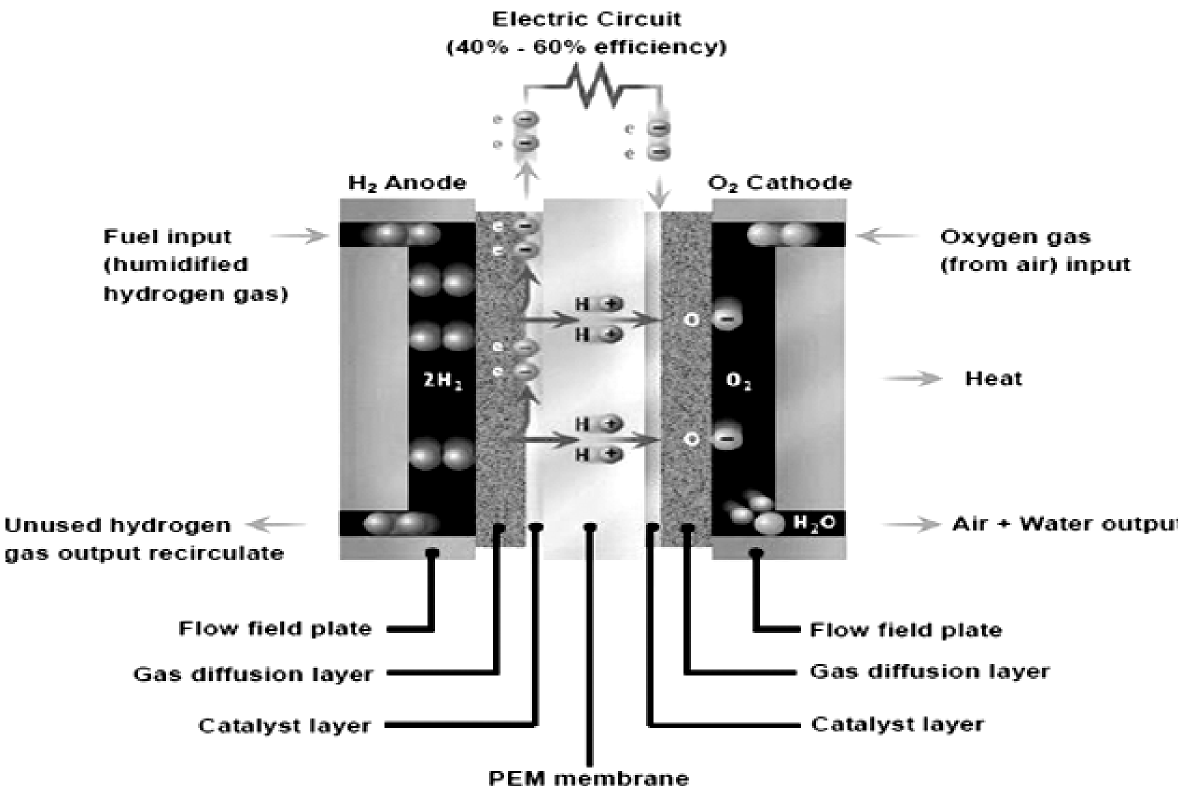

Figure 1: Basics of PEM fuel cell [10]

Electrodes are connected to an electric circuit. Since the electrolyte is electrically insulated, electrons are forced to flow through the electric circuit. Whereas, protons pass through the electrolyte as it is good conductor for protons. The membrane has to be hydrated to improve proton conductivity.This allows electric current to flow through the external circuit.

The complete reaction in fuel cell is:

$$2H_2 + O_2 = H_2O + Energy$$

Hydrogen ions and electrons are separated at anode due to reaction. The reaction is:

$$2H_2 = 4H^+ + 4e^-$$

The hydrogen ions are exchanged from anode to cathode. They combine with oxygen ions to form water molecules and free electrons. The reaction is:

$$O_2 + 4H^+ + 4e^- = 2H_2O$$

Fuel cells are classifiedbased on electrolyte type. Six types of Fuel Cells are defined in literature [3].

1. PEM (Proton Exchange Membrane)
2. DMFC (Direct Methanol Fuel Cell)
3. AFC (Alkaline Fuel Cell)
4. PAFC (Phosphorous Acid Fuel Cell)
5. MCFC (Molten Carbonic Fuel Cell)
6. SOFC (Solid Oxide Fuel Cell)

Fuel cells are compared with respect to various parameters as shown in Table 1.1.

Table 1
Features of Fuel cell types [12]

	PEM water-cooled	PEM air cooled	DMFC	AFC	HT PEM	PAFC	MCFC	SOFC
Typical output range	1 - 100 kW	mW - 1 kW	mW - 1 kW	1 - 5 kW	100W - 10kW	25 kW - 125 kW	50 kW - 125kW	mW - 125 kW
State of development	Pr	Pr	Pr	Pr	D	Pr	Pr	D
Scalability	E	Li	Li	P	U	Li	P	P
Turndown dynamics	E	Mo	Mo	P	Mo	Mo	P	P
Power density	E	Mo	P	P	Mo	P	P	Mo
Quality of heat	L	N	L	L	M	M	H	H
Variety of fuels	P	P	P	P	Mo	Mo	Mo	G
Sensitivity to contaminants	H	H	H	H	M	M	L	L
Start-up time	F	F	F	F	M	M	S	S
Robustness	E	E	Mo	Mo	U	E	P	P
Lifetime	G	Mo	Mo	Mo	U	E	G	P

Pr=Proven; D=Development; E=Excellent; Li=Limited; P=Poor; U=Unknown; Mo=Moderate; L=Low; N=Nil; M=Medium; H=High; G=Good; F=Fast; S=Slow

From Table 1.1, PEM fuel cell has excellent for scalability, turndown dynamics, power density, robustness and fast start-up time. Furthermore, it is lightweight, compact, high power, low cost [2] and operates at lower temperature (40-80 °C). Moreover, the PEM fuel cell has good transient response, high efficiency and absence of corrosive electrolyte [5]. These characteristics are highly desirable in automotive application. Hence, it is the most appropriate power generating device in future automobiles [2], [5].

Besides all the benefits of being efficient and zero emission power source it is not commonly used in automobile. Few of the reasons are: fuel cells are expensive, their durability and efficiency needs to be improved to make it commercially practical.

This paper presents a literature survey on the following topics:

1. Factors affecting fuel cell performance and durability.
2. Detection techniques of the factors
3. Measures to improve performance and durability.

2. EFFECT OF TEMPERATURE AND HUMIDITY ON FUEL CELL PERFORMANCE

Fuel cell performance varies at different humidity and operating temperature conditions. Figure 1.2 shows graph of fuel cell power output at various humidity and temperature levels. Performance is lower at low humidity and temperatures. It is also low when the humidity and temperature is more than the optimum level for the fuel cell. When the fuel cell is not operating at optimum performance, it degrades its life. Hence, if water and temperature are managed at optimum level then, the fuel cell efficiency and durability will increase [2].

Experimental results conclude following:

1. Fuel cell performance was improved when operating temperature increased from 20ºC to 40ºC in absence of humidity.
2. At higher temperature, the membrane gets dry. It reduces ion conductivity of the membrane. Hence, voltage is decreased. Experimental observation is shown in figure 1.3. Current density is better until 20 ºC to 50 ºC. Current density to stack voltage is poor when temperature is increased to 60 ºC.
3. The membrane is better hydrated at higher humidification temperatures. It helps increasing proton conductivity of the membrane. Hence, better hydration leads to improved performance. But water evaporates at very operating temperature and the membrane start getting dry. It leads lower proton conductivity hence; the fuel cell performance decreases. Therefore, higher humidification temperature is required when the operation temperature is high. However, flooding may occur at lower operation temperature.

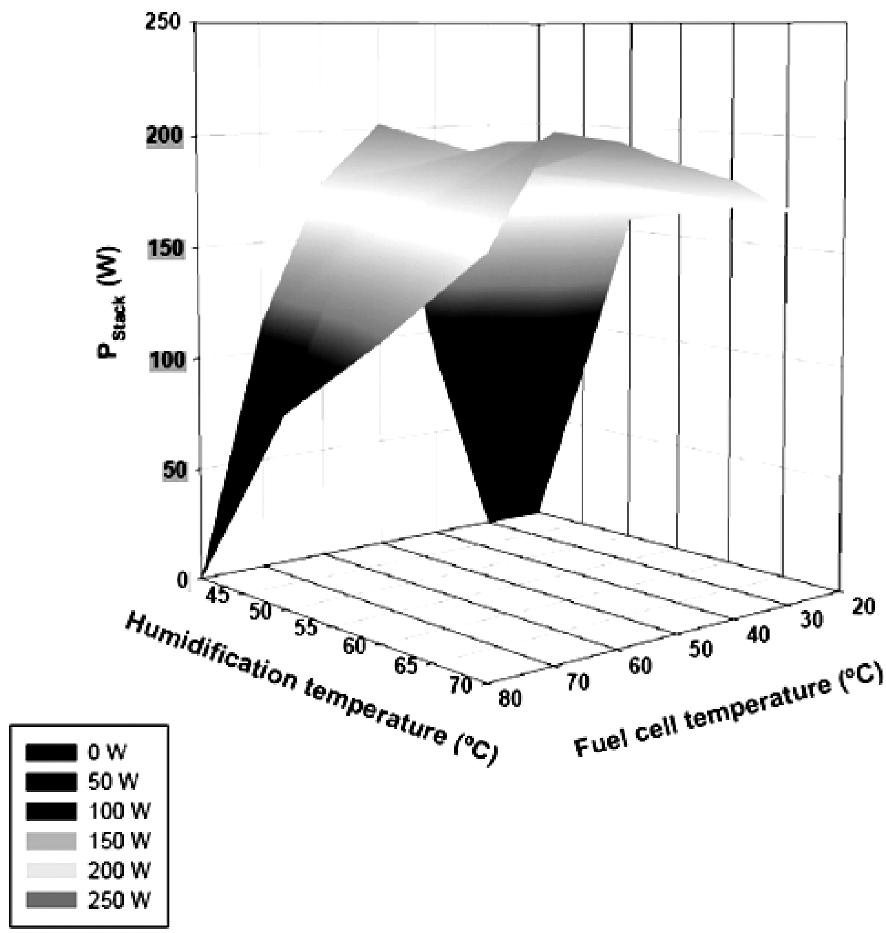

Figure 2: Maximum power generated by the fuel cell stack at different humidification and operation temperatures [2]

4. Figure 1.4 shows the Tafel slope decreases with increasing operation temperature. Figure 1.5 shows relation of membrane humidification and resistance. Resistance decreases when operating temperature is increased.

3. FACTORS AFFECTING FUEL CELL PERFORMANCE AND DURABILITY

Power source in automobile encounters various environmental conditions, stop-start cycles and dynamic driving cycles. It makes it difficult to develop durable and highly efficient fuel cell as a power source. Durability of the fuel cell depends on many factors. Less durability is aging of the fuel cell. Fuel cell components degrade due to aging and operating conditions. Degraded components have adverse effect on durability as well as performance of the fuel cell. However, aging or degradation of components is dependent on various factors. The factors shall be understood in order to control them within the acceptable level. Controlling these parameters or conditions will help increasing performance as well as durability of the fuel cell.

Following are the factors affecting performance and durability of PEM fuel cell.

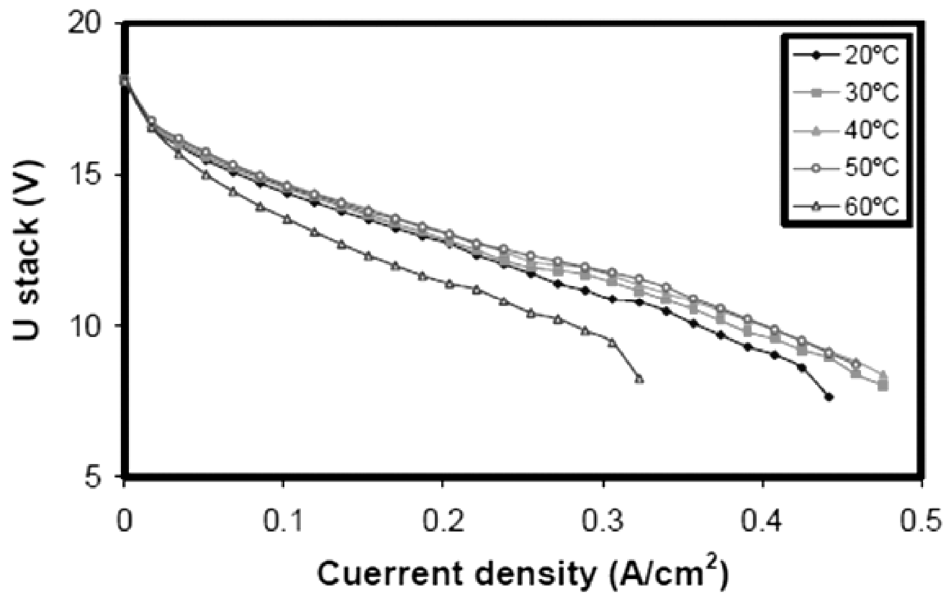

Figure 3: Effect of the operation temperature on in absence of humidification [2]

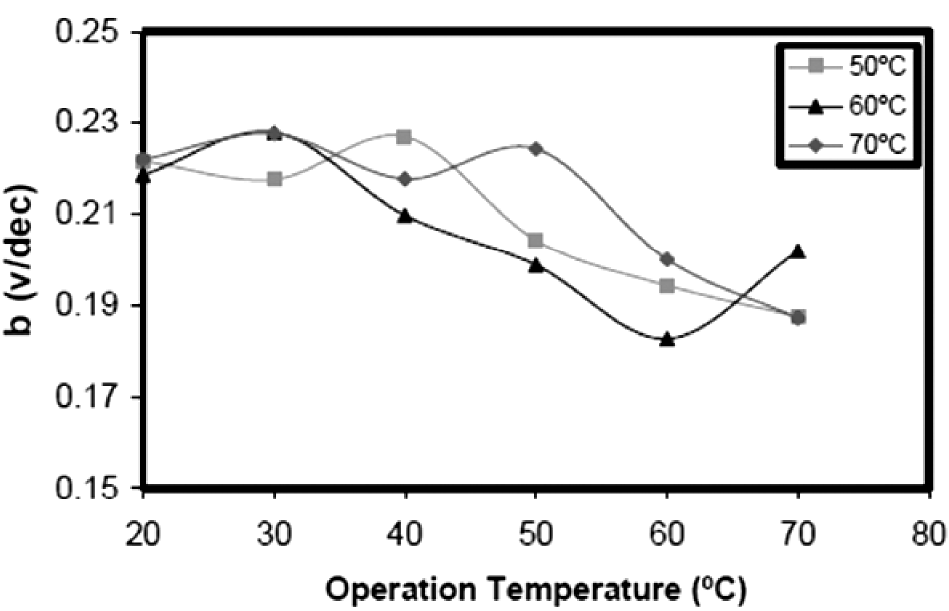

Figure 4: Tafel slope with the operation temperature at different humidification temperatures [2]

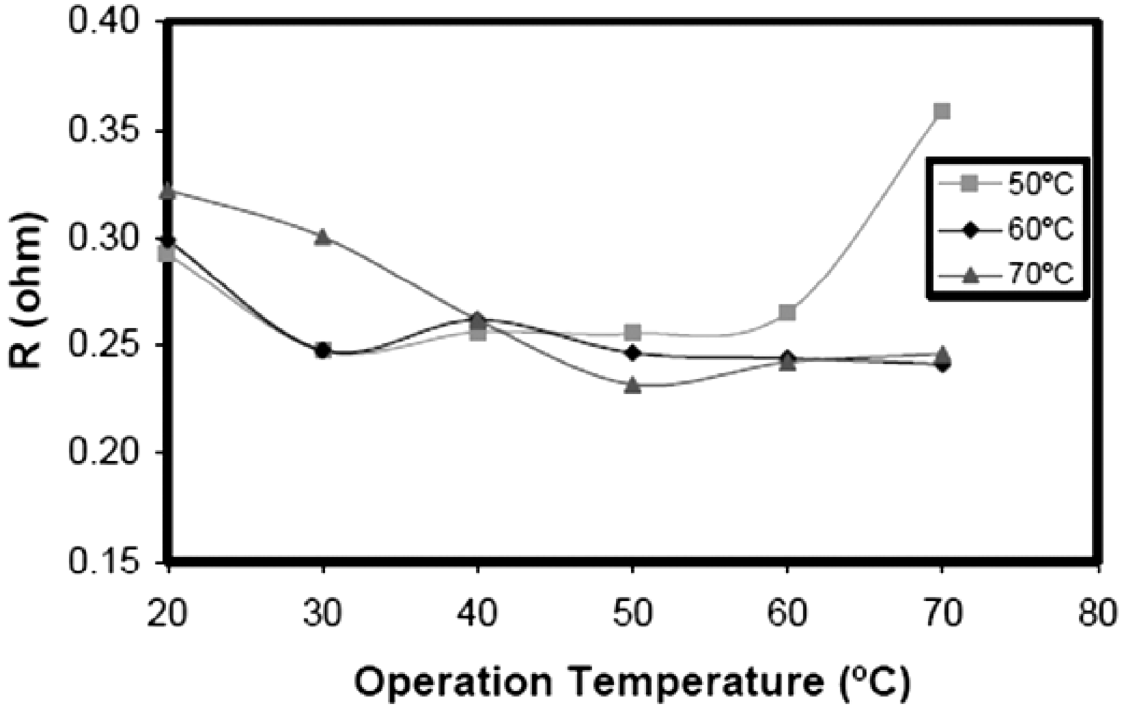

Figure 5: Resistance with the operation temperature at different humidification temperatures [2]

3.1. Water flooding

Hydrated membrane increases proton conductivity. The reactant gases are humidified to keep membrane hydrated. It is directly related to water content. Though, the water content shall be appropriate for the humidification [1]. The water content depends on operating temperature. If the operating temperature is high then, water content for needed humidification is also high and vice versa. Hence, water management is very important to keep membrane hydrated at appropriate level depending on the operating temperature. If the water content is more at lower operating temperature then water is excess in the fuel cell. Moreover, water is produced at cathode side. Poor management of water can lead to flooding due to excess water accumulation. Water accumulation can happen on both, anode and cathode sides of the membrane.

Reasons for flooding are:

1. Water formation in the fuel cell is due to the oxygen reduction reaction. Increasing current density of the fuel cell also forms water.
2. Water molecules are pulled from the anode to the cathode. This phenomenon is called as electro-osmosis. Electro-osmosis rate depends of humidification level and current density of the fuel cell.
3. High humidification of reactant gases.
4. Liquid water injection.

Water flooding has adverse effect on fuel cell performance and durability. Major impacts of water flooding are [1]:

1. Excess water accumulation in fuel cell can block flow channels and the pores of the gas diffusion layer (GDL). It blocks reactant gas flow which lead to reactant starvation condition.
2. Excess water accumulation can lead to corrosion and contamination of components like GDL, membrane, electrodes and catalyst. It has considerable impact on durability of the fuel cell.
3. Ohmic losses increase due to impurities from corroded components. It degrades performance of the electrodes.

4. Dissolved impurities can be transported in the membrane. It can reduce proton conductivity over period of time. It can lead to failure of cell.

Fuel cell flooding is detected by various methods. Key flooding detections methods explored in literature are:

1. Pressure drop across the flow fields is directly related to the flooding level [5]. Figure 1.6 shows effect of cathode flooding on fuel cell performance. Partial pressure drop at the cathode results in a cell voltage drop.
2. Direct Visualization: visual inspection through a transparent cell plate is used. Cameras can be used for monitoring the flooding. The technique provides qualitative data. However, quantitative measurement not possible with the technique [6].
3. Nuclear Magnetic Resonance (NMR) Imaging or Magnetic Resonance Imaging (MRI) technique. It can visualize water in opaque structures [6].
4. Neutron Imaging: the technique can visualize water distribution in channels of cathode, anode and GDL. However, the technique is expensive. Use of the technique is limited due to use of radioactive material [6].
5. Electron Microscopy: It is useful in observing vapor condensation, liquid water [6].
6. X-Rays: the technique can give higher resolution with high signal to noise ratios [6].
7. Fluorescence microscopy: It is used in conjunction with optical photography [6].
8. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS): CV is useful investigating processes occurring in an electrochemical system. It helps to detect change in performance of the systems. EIS is useful in investigation of materials [5].

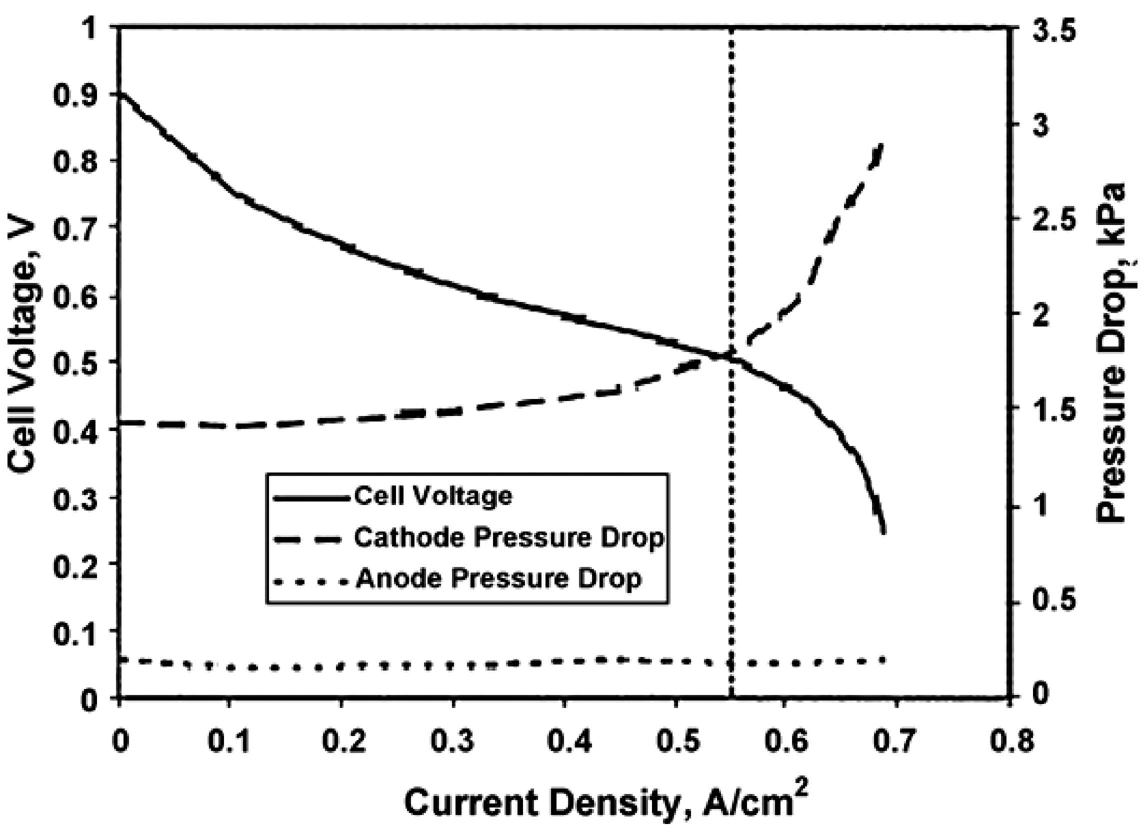

Figure 6: Effect of cathode flooding on fuel cell performance [5]

9. Theoretical Models: Various theoretical models like, Computational fluid dynamics (CFD) have been evolved for water management. The models are used to analyze water saturation, transport and distribution in the fuel cell [7], [8].

Excess accumulated water needs to be removed from the cell to avoid its adverse effects. Excess water removal mechanisms discussed in the literature are:

1. Water back-diffusion to the anode: it takes place when water content at cathode side exceeds that of the anode side [5].
2. Evaporation and higher air flow: Higher cell temperature evaporates water. Higher air flow rate carry water out of the cell [5].
3. Capillary transport of water through the porous cathode helps reducing the water level [5].

3.2. Dehydration of membrane

Dehydration of membrane is caused due to:

1. less water being supplied to membrane
2. higher operating temperature
3. poor water management
4. poor thermal management.

Dehydrated membrane increases ionic resistance and ohmic losses. Hence, it decreases proton conductivity. It leads to drop in potential of the cell. However, the situation can be recovered if the membrane is kept hydrated at appropriate level. But, prolonged dehydrated operation can lead to irreversible damage to the membrane. The membrane can develop cracks as it becomes brittle. This intern can develop pinhole in the membrane. Pinholes will cause gas crossover and hence, effective reaction cannot take place.

Key reasons for dehydration are:

1. Less humidification of reactant gases.Also, the water formed at cathode is not enough to keep appropriate hydration.
2. Water evaporates due to higher operating temperature.
3. Electro-osmosis force is high when electric field is high at high current density. It can lead to dehydrated condition at the anode.

3.3. Corrosion/degradation

Corrosion is one of the important degradation mechanisms which determine durability of the PEM fuel cell. Corrosion occurs when the fuel cell is:

1. Operated over long time with different operating conditions.
2. Operated in transient or cyclic conditions [5]
3. Flooded with excess water [5].

Corrosion is normally observed on electrodes and Gas Diffusion Layer (GDL). Corrosion of these parts influences both performance and durability [1]. Usually, platinum or platinum alloy is used as catalysts for both anode and cathode. The platinum catalyst is supported on carbon nano particles [1], [5].

Effects of corrosion are:

1. Cell voltage drops
2. Membrane can undergo mechanical, thermal and chemical degradation.
3. Degradation of the electrolyte reduces durability of the fuel cell [5].

3.4. Contamination of the cell

"Contamination is the process when impurities pollute and penetrate into cell components and/or initiate chemical attack and slow down the actual reactions taking place in the cell" [5]. Cell is contaminated due to the contamination products like, metal, alkaline metal and ammonium ions, silicon, catalyst particles and carbon monoxide (CO), nitrogen oxides (NO_x) or sulfur dioxide (SO2).

CO-contamination is also referred as CO poisoning. It affects fuel cell as:

1. It lowers conductivity and water level
2. It will reduce the maximum current in the cells.
3. It has significant effect on fuel cell performance.

Source of CO can be the hydrogen stream if it is obtained from hydrocarbons or alcohol. Hydrogen can also be generated using electrolysis of water [11]. CO will not be present in hydrogen in if the hydrogen is generated through electrolysis of water. However, CO poisoning is a reversible process [5].

CO poisoning effects can be avoided or reduced by techniques like:

1. Pretreatment of reformate: hydrogen stream is pretreated to reduce CO concentration [5], [9].
2. Air bleeding: CO burn in presence with hydrogen when small air is passed [5], [9]. However, air bleed can overheat anode if the air is not controlled [9]. Figure 1.7 shows the cell contamination and recovery after introducing air bleed (2%).
3. Use of CO tolerant catalyst: Pt based alloys like PtRu, Pt-Co, Pt-Mo and Pt-WO_3 have been analyzed to mitigate CO contamination [9].
4. High temperature operation: CO adsorption is high at low temperature while is disfavored at high temperatures [9]. Hence, high operating temperature reduces CO contamination [1], [5], [9].

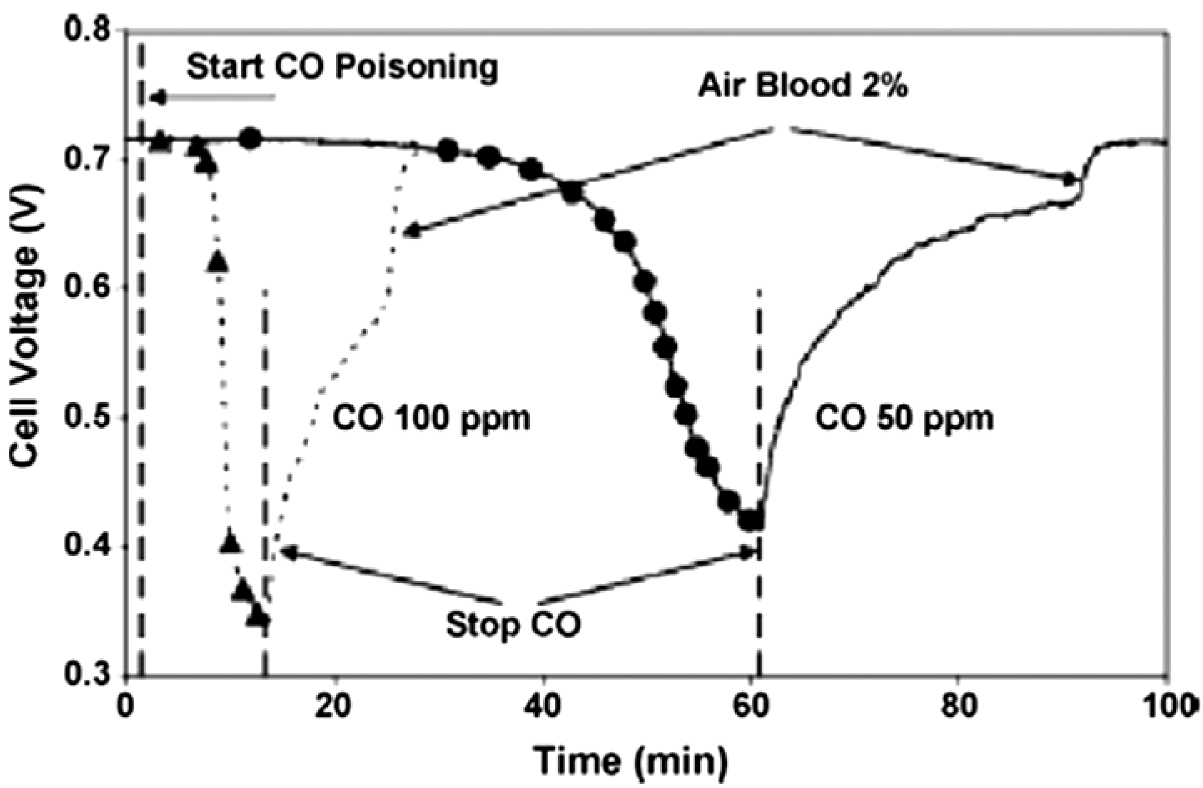

Figure 7: CO contamination of a cell [1]

We can interpret from figure 7 that drastic reduction in cell voltage could be an indication of CO contamination.

3.5. Reactant gas starvation

Reactant gas starvation condition occurs when either of the reactant gases is not supplied in appropriate quantity. Fuel cell performance degrades when the cell is starved.

Reactant gas, oxygen starvation can result in generation of hydrogen in cathode.It will lead to split water in hydrogen and oxygen. It will produce oxygen at anode. The reaction is:

$$2H_2O = O_2 + 4H^+ + 4e^-$$

Due to hydrogen starvation it results oxygen atanode [5]. In the absence of hydrogen, the following anode reaction can take place:

$$C + 2H_2O = CO_2 + 4H^+ + 4e^-$$

Similarly,due to oxygen starvation at cathode, hydrogen is produced. The cathode reaction is:

$$2H^+ + 2e^- = H_2$$

The cell voltage is reversed when oxygen is present at the anode and hydrogen at the cathode. This voltage reverse accelerates corrosion of electro-catalyst. It leads to damage in fuel cell components [5].

Reasons for reactant gas starvation are due to poor management of water,heat, gas feeding andstack assembly.

3.6. Thermal management

Temperature needs to be maintained for efficient operation of the fuel cell. Maintaining temperature is important when the fuel cell is operating in low ambient temperatures. The fuel cell operating in freezing temperature for longer duration will affect life/durability of the fuel cell. Residual water in the fuel cell freezes. It leads to thermal and mechanical stress. Hence, the cell components may damage [1], [5]. Also, fuel can have adverse effect on its durability and efficiency at higher temperatures. High temperature operation can result in dry membrane. It intern may have mechanical damage to the membrane. Hence, combined water and thermal management is a key consideration [9].

4. CONCLUSION

Fuel cell is a clean way of generating power as it does not emit pollutant gases. PEM type fuel cell is most suitable for automotive applications due to its higher power density, robustness and quick start-up time. Despite of its advantages and suitability in automobiles; it is not being widely used. Low durability and lesser efficiency are major reasons to discourage its use. Water and thermal management are most important parameters to operate fuel cell efficiently. Water & temperature management play a key role in efficient operation of fuel cell. Excess water, high temperature as well as low humidity will impact durability and efficiency of the fuel cell. Another reason to reduce efficiency of the cell is physical damage due to storage in freezing temperature, thermal and mechanical stress on the components. Impurities in the reactant gases lead to contamination, which need to be controlled for better efficiency. It is also important to control reactant gas flow to avoid fuel starvation in the cell. In order to have effective control of these parameters, parameter variation needs to be detected. There are several methods worked out so far for detecting flooding and mechanical damages. However, online detection and control would help to increase efficiency and life of fuel cells.

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