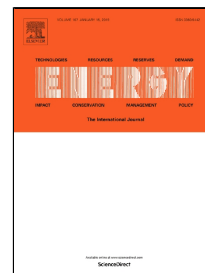


# Accepted Manuscript

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**FUEL CELL MEMBRANES – PROS AND CONS**

Emmanuel Ogungbemi<sup>1</sup>, Oluwatosin Ijaodola<sup>1</sup>, F. N. Khatib<sup>1</sup>, Tabbi Wilberforce<sup>1</sup>, Zaki El Hassan<sup>1</sup>, James Thompson<sup>1</sup>, Mohamad Ramadan<sup>2,3</sup>, A G Olabi<sup>4,5</sup>

1. Institute of Engineering and Energy Technologies, University of the West of Scotland, Paisley, UK.

2. Department of mechanical engineering, International University of Beirut, Beirut, Lebanon;

3 Associate Member at FCLAB, CNRS, Université Bourgogne Franche-Comté, Belfort CEDEX, France

4. Department of Sustainable and Renewable Energy Engineering, University of Sharjah, Sharjah, United Arab Emirates

5. Mechanical Engineering and Design, School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham B4 7ET, UK

**Abstract**

This investigation provides a critical analysis of the development of PEM fuel cells and related research with specific focus on the membrane material. The catalytic membrane is the most important component of the PEMFC giving rise to the need for the use of efficient, durable and cheap material to reduce the overall cost of the fuel cell. In this work, the need for materials other than Nafion to be used as PEM membranes is established and a case for the use of composite membranes material in fuel cells is made. Composite membranes increase the cell voltage by up to 11% even at high cell operating temperature of 95°C. They also increase the overall performance of the cell by up to 17% when dry hydrogen is utilised.

Non-fluorinated membranes are also suitable for use in fuel cells for portable applications but they are very expensive and less conductive. Partially fluorinated membranes have good mechanical stability but expensive. The fluorinated membrane has high stability under oxidation and reduction conditions. Unfortunately, they only reach their optimum performance at

temperatures below 100°C which makes them of limited use in PEM fuel cells application at higher temperatures.

*Keywords:* PEM fuel cells, electro-catalyst layer, proton electron membrane (PEM), bipolar plate (BP) and gas diffusion layer (GDL), Composite membrane

## 1. Introduction

Energy is one of the driving factors that determine the overall sustainability of humanity. It was one of the critical issues that led to several political debates in recent elections (United States, 2016 and France, 2017). The high rate of depletion of the ozone layer and climatic changes continue to be a key determiner for the need for cleaner and environmentally friendly mode of energy generation[1–3]. Fossil commodities remain the highest form of energy generation but in the last decade have seen a sharp decline. This is because of the harmful effect they have on the environment which has been scientifically proven. The prices of fossil fuel are unstable and vary from time to time. In the political terrain, regions where these fossil products are harnessed have experienced serious unrest often leading to the loss of lives and properties. All these issues are some of the binding reasons for scientist around the world to consider alternative form of energy generation[4–6]. PEM fuel cell is regarded as an alternative because it gives near zero emission, high efficiency and near zero noise pollution. It offers all these possibilities by using hydrogen as a fuel to generate electrical energy through a chemical reaction which can also be used with other clean energy sources like solar energy [7].

PEM fuel cells have many advantages compared to other sources of power. Some of these benefits comprise of factors include burning in reduced temperature. Fuel produced from PEM fuel cells is said to be clean and stable when compared to other energy generating mediums. PEM fuel cells are very reliable for a broad range of portable and stationary power applications. This include their utilization in the transport industry as a replacement for engines that functions using fossil commodity like diesel and petrol. Besides using PEM fuel cell as a standalone power generator, the PEM fuel cell can also be implemented with a renewable energy system for energy storage application. It can be used as a single cell for small power requirement or as a cell stack where many cells are combined to achieve higher voltage and electricity[4,5,8,9].

Despite all the notable achievement in the development of the PEM fuel cell and it excellent feature as a power source, commercialization is still a major concern. It faces serious challenges

regarding cost, durability, and performance. Fuel cell technology (particularly PEM type) use platinum as a catalyst. Platinum catalyst form one of the largest cost components in the fuel cells. Fuel cell design with an efficient utilization of platinum catalyst could contribute directly to cost reduction. Also, finding a Platinum-alternative catalyst will cause further cost reduction of the fuel cell. In general, Fuel cells are slightly bigger than batteries with the same capacity. However, to meet the full requirements of portable applications, manufacturers and researchers of PEM fuel cells have in recent times performed many experiments aimed at reducing the size and weight of fuel cells. As a power source, the mechanical durability of the fuel cell is considered as a key performance factor particularly for transport applications[10].

However, it is strongly believed that discovering the right material can be a lasting solution to the problem. Improving PEM components like the membrane, bipolar flow plate, gas diffusion layer, electro-catalyst layers, etc. has shown over time to have direct influence on performance and durability. High cost and low durability of the PEM fuel cell are the main barriers to commercialization of this technology. An insight into the materials used for manufacturing the main components of the PEM fuel cell and their status of development may contribute directly to solve the problems related to the main challenges of the PEM fuel cell (i.e., high cost and low durability) which should lead subsequently to the world-wide commercialization of the technology[10–12]. Research work conducted in the last few decades are aimed at investigating the performance of membrane with respect to proton conductivity, electrical conductivity and mechanical stability. Most membranes used in fuels functions effectively only when they are humidified at higher cell operating temperature and they often come as perfluorinated proton exchange membrane. Other investigators are considering on expanding the operating parameters of the fuel cell beyond 80°C for instance. The performance of the fuel cell will increase appreciable if the membranes used were designed to function without any form of humidification at varying operating cell temperature. This will in effect reduce the cost of the fuel cell because the platinum used at higher cell operating conditions is less compared to that used when the fuel cell is operating at low cell temperature. This work therefore intends to establish more facts on the requirements needed for membranes to function effectively and clearly define the impact that the types of membranes will have on the overall performance of the fuel cell. Different types of membranes are thoroughly discussed. An up to date material used in the production of membranes are also carefully presented in this report. The types of membranes used in proton exchange

membrane fuel cell classified as fluorinated membranes, partially fluorinated membranes, non – fluorinated membranes and acid-based composite membranes are also presented in this paper. Other properties of the membrane like protonic conductivity, ion exchange capacity and permeability of the reactive substances are also presented.

## 2. The PEM fuel cells

Fuel cells are defined as a device which electrochemically converts chemical energy into electrical energy. They are made up of an electrolyte, anode (negative electrode) and the cathode (positive electrode). The  $H_2$  gas is transmitted to the fuel cell through the anode. The fuel on reaching the catalyst layer at the anodic region of the fuel cell split into two ions (Protons and electrons). The proton ions then go through the membrane but the membrane electrode assembly (MEA) is not permeable to electrons. Hence, the electrons flow through the circuit connected to the cell externally to produce electricity. This is because the electrolyte is made up of a proton conductive material. The protons then meet the air/oxygen at the cathode to produced water[13,14]. The half reaction of acid and basic electrolyte for PEM fuel cells can be found in the Table 1 [4].

Table 1: PEM fuel cells half reactions [4]

| Reactions        | Acid electrolyte   | Basic electrolyte   |
|------------------|--|---|
| Anode reaction   | $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$                                 | $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$           |
| Cathode reaction | $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ | $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$ |
| Overall reaction | $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$                | $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$                 |

Generally, fuel cells develop their names according to the type of electrolyte and reacting substances as shown in Table 2. Table 3 also shows the types of fuel cell characteristics. In a PEM fuel cell, the electrolyte used is proton exchange membrane (PEM) or polymer electrolyte membrane (PEM). The equation for the reaction is hydrogen combining with oxygen to give water, electricity and waste heat. Fig. 1 shows a schematic diagram of a 2-stack PEM fuel cell connected by a bipolar plate [15] and Fig. 2 shows PEM fuel cell planar diagrams at UWS fuel cell laboratory [16][6]. In Fig. 1, the two-membrane electrode assembly (MEA) were connected by the bipolar plate. The materials used to make up the system included bulb for electricity, hydrogen, oxygen, bipolar flow plate and the membrane and a more comprehensive view of all components of the proton membrane fuel cell is shown in Fig. 2.

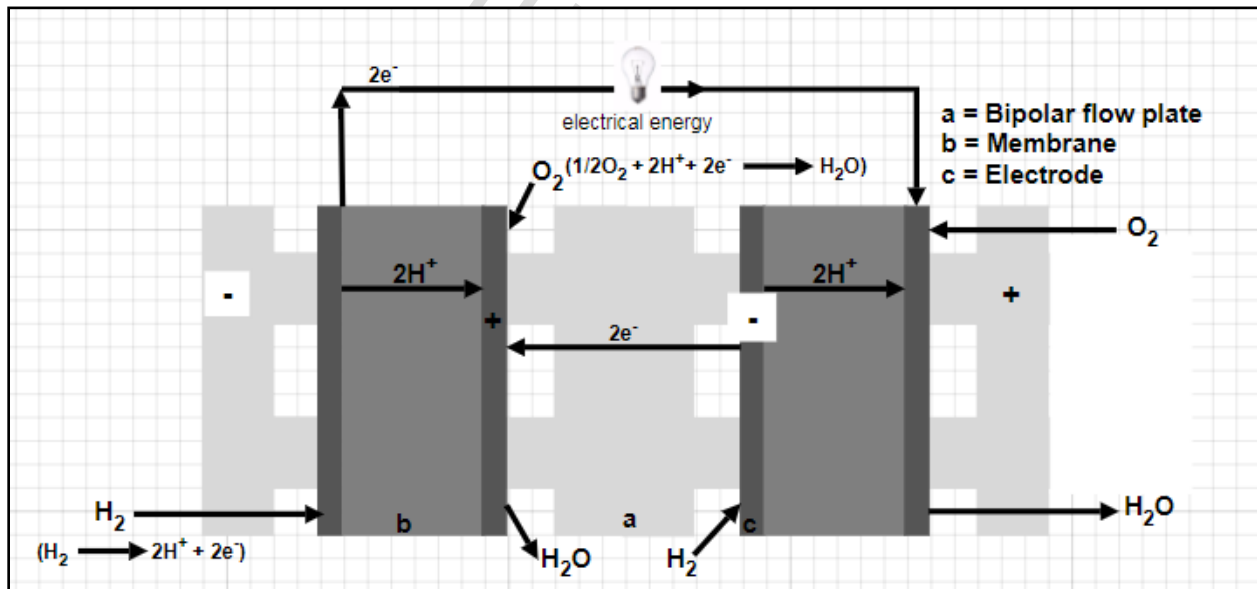


Fig.1: Detailed analysis of 2-stack PEM fuel cell connected by polar cell

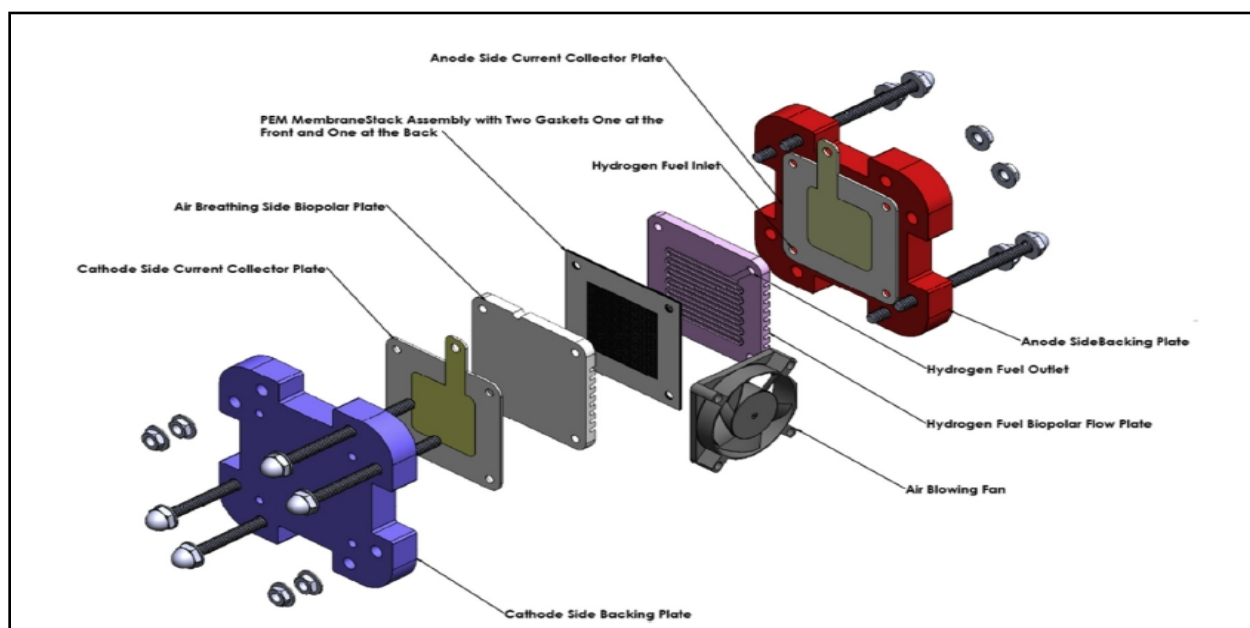


Fig.2: PEM fuel cell planar diagrams at UWS fuel cell laboratory [16]

Table 2: Types of fuel cells and their characteristics

|  | Fuel                       | Catalyst                                 | Electrolyte   |
|--|----------------------------|--|---|
| Low-Temperature Proton Exchange Membrane Fuel Cells (LT-PEMFCs)  | Hydrogen (H <sub>2</sub> ) | Platinum supported on carbon             | Solid polymer membrane (Nafion)   |
| High-Temperature Proton Exchange Membrane Fuel Cells (HT-PEMFCs) |                            | Platinum-Ruthenium supported on carbon   | Nafion/PBI doped in phosphoric acid   |
| Phosphoric Acid Fuel Cells (PAFCs)                               | Hydrogen (H <sub>2</sub> ) | Platinum supported on carbon             | Liquid phosphoric acid (H <sub>3</sub> PO <sub>4</sub> ) in silicon carbide (SiC) |
| Direct Methanol  | Liquid methanol-           | Platinum/Platinum-Ruthenium supported on | Solid polymer membrane  |

|  |   |  |  |
|--|---|--|--|
| <b>Fuel Cells (DMFCs)</b>                    | water solution                          | carbon   | (Nafion)   |
| <b>Direct Ethanol Fuel Cells (DEFCs)</b>     | Liquid ethanol-water solution           | Platinum/Platinum-Ruthenium supported on carbon                      | Solid Nafion/Alkaline media/Alkaline-acid media  |
| <b>Alkaline Fuel Cells (AFCs)</b>            | Hydrogen (H <sub>2</sub> )              | Nickel/Silver supported on carbon                                    | Potassium hydroxide (KOH) in water solution/Anion exchange membrane (AEM)  |
| <b>Molten Carbonate Fuel Cells (MCFCs)</b>   | Methane                                 | Nickel Chromium (NiCr)/Lithiated nickel (NiO)                        | Liquid alkali carbonate (Li <sub>2</sub> CO <sub>3</sub> /Na <sub>2</sub> CO <sub>3</sub> /K <sub>2</sub> CO <sub>3</sub> ) in Lithium aluminate (LiAlO <sub>2</sub> ) |
| <b>Solid Oxide Fuel Cells (SOFCs)</b>        | Methane                                 | Nickel-YSZ composite/Strontium-doped lanthanum manganite (LSM)       | Solid yttria-stabilized zirconia (YSZ)   |
| <b>Proton Ceramic Fuel Cells (PCFCs)</b>     | Methane                                 | Nickel   | Protonic/Zirconia  |
| <b>Zinc-Air Fuel Cells (ZAFCs)</b>           | Zinc                                    | Non-noble metal oxides (such as manganese oxide - MnO <sub>2</sub> ) | Liquid alkalines   |
| <b>Direct Borohydride Fuel Cells (DBFCs)</b> | Sodium borohydride (NaBH <sub>4</sub> ) | Gold/Silver/Nickel/Platinum supported on carbon                      | Solid Nafion/Anion exchange membrane (AEM)   |



|   |  |   |  |
|---|--|---|--|
| <b>Direct Formic Acid Fuel Cells (DFAFCs)</b> | Liquid formic acid (HCOOH)                         | Palladium/Platinum supported on carbon                                      | Solid Nafion   |
| <b>Direct Carbon Fuel Cells (DCFCs)</b>       | Solid carbon (coal, coke, biomass)                 | Graphite or carbon-based material/Strontium-doped lanthanum manganite (LSM) | Solid yttria-stabilized zirconia (YSZ)/Molten carbonate/Molten hydroxide |
| <b>Enzymatic Fuel Cells (BFCs)</b>            | Organic matters (glucose)                          | Biocatalyst supported on carbon   | Ion exchange Membrane/Membrane-less                                      |
| <b>Microbial Fuel Cells (BFCs)</b>            | Any organic matter (glucose, acetate, waste-water) | Biocatalyst supported on carbon/Platinum supported on carbon                | Ion exchange Membrane  |

Table 3: Operating characteristics of the types of fuel cells

|  | Electrical efficiency              | Operating Temperature | Charge carrier                                 |
|--|------------------------------------|-----------------------|--|
| Low-Temperature Proton Exchange Membrane Fuel Cells (LT-PEMFCs)  | 40% - 60%                          | 60°C - 80°C           | Hydrogen Ion (H <sup>+</sup> ) (proton)        |
| High-Temperature Proton Exchange Membrane Fuel Cells (HT-PEMFCs) | 50% - 60%                          | 110°C-180°C           |  |
| Phosphoric Acid Fuel Cells (PAFCs)                               | 36% - 45 % (85% with cogeneration) | 160°C - 220°C         | Hydrogen ion (H <sup>+</sup> ) (proton)        |
| Direct Methanol Fuel Cells (DMFCs)                               | 35% - 60%                          | Ambient - 110°C       | Hydrogen Ion (H <sup>+</sup> ) (proton)        |
| Direct Ethanol Fuel Cells (DEFCs)                                | 20% - 40%                          | Ambient - 120°C       | Hydrogen ion (H <sup>+</sup> ) (proton)        |
| Alkaline Fuel Cells (AFCs)                                       | 60-70 %                            | Below zero - 230°C    | Hydroxyl ion (OH <sup>-</sup> )                |
| Molten Carbonate Fuel Cells (MCFCs)                              | 55% - 65% (85% with cogeneration)  | 600°C-700°C           | Carbonate ion (CO <sub>3</sub> ) <sup>2-</sup> |
| Solid Oxide Fuel Cells (SOFCs)                                   | 55% - 65% (85 % with cogeneration) | 800°C – 1000°C        | Oxygen Ion (O <sup>2-</sup> )                  |
| Proton Ceramic Fuel Cells (PCFCs)                                | 55% - 65%                          | 700°C – 750°C         | Hydrogen ion (H <sup>+</sup> ) (proton)        |
| Zinc-Air Fuel Cells (ZAFCs)                                      | 30% - 50 %                         | Below zero –          | Hydroxyl ion                                   |

|   |           |                |   |
|---|-----------|----------------|---|
|   |           | 60°C           | (OH)-                                   |
| <b>Direct Borohydride Fuel Cells (DBFCs)</b>  | 40% - 50% | 20°C – 85°C    | Sodium ion (Na <sup>+</sup> )           |
| <b>Direct Formic Acid Fuel Cells (DFAFCs)</b> | 30% - 50% | 30°C – 60°C    | Hydrogen ion (H <sup>+</sup> ) (proton) |
| <b>Direct Carbon Fuel Cells (DCFCs)</b>       | 70% - 90% | 600°C – 1000°C | Oxygen Ion (O <sub>2</sub> -)           |
| <b>Enzymatic Fuel Cells (BFCs)</b>            | 30%       | 20°C – 40°C    | Hydrogen ion                            |
| <b>Microbial Fuel Cells (BFCs)</b>            | 15% - 65% | 20°C – 60°C    | (H <sup>+</sup> ) (proton)              |

It is established according to research that PEM fuel cell has a lot of advantages which includes low operating temperature, high efficiency, quick start-up and low CO<sub>2</sub> emission. A good knowledge of the overall fuel cell operating conditions will in effect reduce the possibility of the fuel cell being damaged. Performance of a PEMFC can be determined by identifying the losses. Fig. 3 below shows the 3-major type of losses in the fuel cell. They are; activation losses (kinetics losses), ohmic losses, concentration losses (mass transport losses which are due to the water generated from the reaction blocking the channels and leading to the limited diffusion of reactant gases) [17][18]. This is as shown in Fig. 3 and could also be referred to as polarization curve [19]. These losses occur in the fuel cell because not all the protons are able to go through the membrane and some of the hydrogen forcefully flows through the membrane indicating that not all electrons can be captured from the quantity of fuel supplied to the cell through the anode bipolar channels. Again, for the electrons to flow through the external circuit, they must be in an excitation state and for this to occur, the electrons use existing energy already in the cell. These are some of the reasons why there are losses in the fuel cell [20].

During the operation of fuel cells, so many reactions occur at the same time. Therefore, a slight change in any parameter causes a shift in at least two other parameters and therefore has an overall effect on the fuel cell. The factors listed below influence the performance of the PEM

fuel cell considerably that is; Change in the operating parameters [21], types of electrolyte used [22], and catalyst used [23,24]. Performance of a fuel cell can be described by a characteristic curve which plot the voltage output as a function of electrical current density, called as (I–V) curve, as shown in Fig. 3. The ideal the theoretical cell voltage is 1.23V but this is not the case as there are losses for practical fuel cells operating under thermodynamic conditions. These losses have been mentioned above.

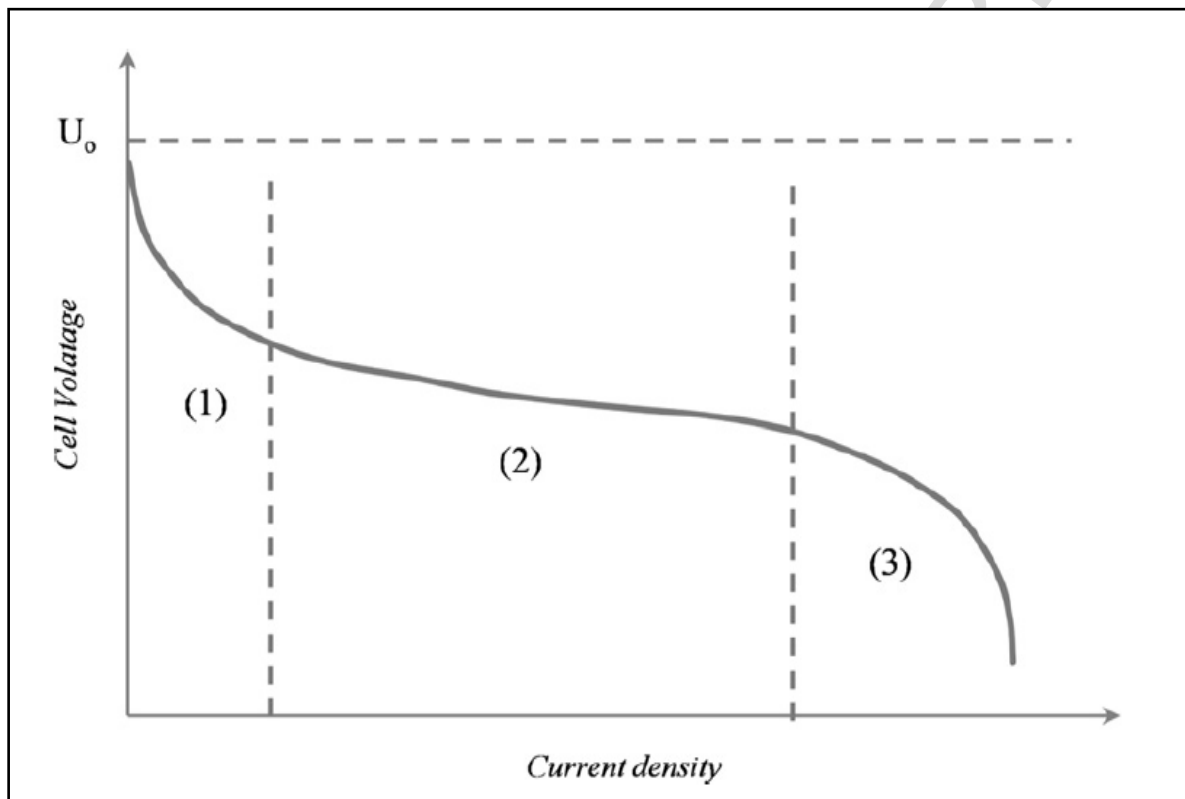


Fig.3: Showing PEM fuel cell losses[25]

Normal salt used for cooking and domestic purposes (sodium chloride, NaCl) is normally obtained through electrodialytic concentration of sea water. Ion exchange membranes are used in this process to obtain the edible salt. It functions as a separator during the electrolytic process in desalination of water that is saline by means of electrodialysis. Ion exchange membrane is also used when separating material that is ionic from other materials that are not ionic through electrodialysis. During diffusion dialysis in order to recover acid and alkali from waste solution that is acid or basic in nature, ion exchange membrane is used as well. It is also used in the dehydration of water by means of pervaporation. The membranes used in proton exchange

membranes are polymeric in nature and are designed mainly to allow the easy transfer of protons through them [26]. Ionic polymers used for membranes in fuel cells are gel – like in nature. Protonic conductivity through these membranes is reduced during low humidification conditions. It implies that well humidified membranes used for PEM fuel cells allow easy flow of protons. Nafion membranes were developed by DuPont in 1970 and they were developed to be chemically stable. Nafion membranes are manufactured from sulfonated polytetrafluoroethylene [27,28]. Today, Nafion is also used in the chlor–alkali production companies. Nafion has now become a brand and standard used for PEM fuel cell membranes [29]. The ion exchange membrane and the period there were developed is captured in Fig. 4. They are categorised depending on the specific kind of ionic group fused to the matrix of the membrane. Ionic exchange membranes are grouped into cation exchange membranes and anion exchange membrane.  $-\text{SO}_3^-$ ,  $-\text{COO}^-$ ,  $-\text{PO}_3^{2-}$ ,  $-\text{PO}_3\text{H}^-$ ,  $-\text{C}_6\text{H}_4\text{O}^-$  are the main composition for cation exchange membranes attached to the backbone of the membrane. Cations are permeable to these membranes, but anions are blocked. Exchange membranes purposely for anions also allow the passage of only anions but reject cations. Anion exchange membranes are also often made up of  $-\text{NH}_3^+$ ,  $-\text{NRH}_2^+$ ,  $-\text{NR}_3^+$ ,  $-\text{PR}_3^+$ ,  $-\text{SR}_3^+$  and they are attached to the membrane for easy rejections of cation [30]. Ion exchange membranes are also categorised as homogenous and heterogeneous membranes. For the homogenous ion exchange membranes, the charge groups are bonded together chemically but that of the heterogeneous membranes are done physically. The strength of the homogenous ion exchange membranes is low, but they have excellent electrochemical characteristics [31]. On the other hand, the electrical characteristics of the heterogeneous ion exchange membrane are low, but they have good strength mechanically. The dimensional stability for the heterogeneous ion exchange membrane is also good compared to that of the homogenous ion exchange membrane [30].

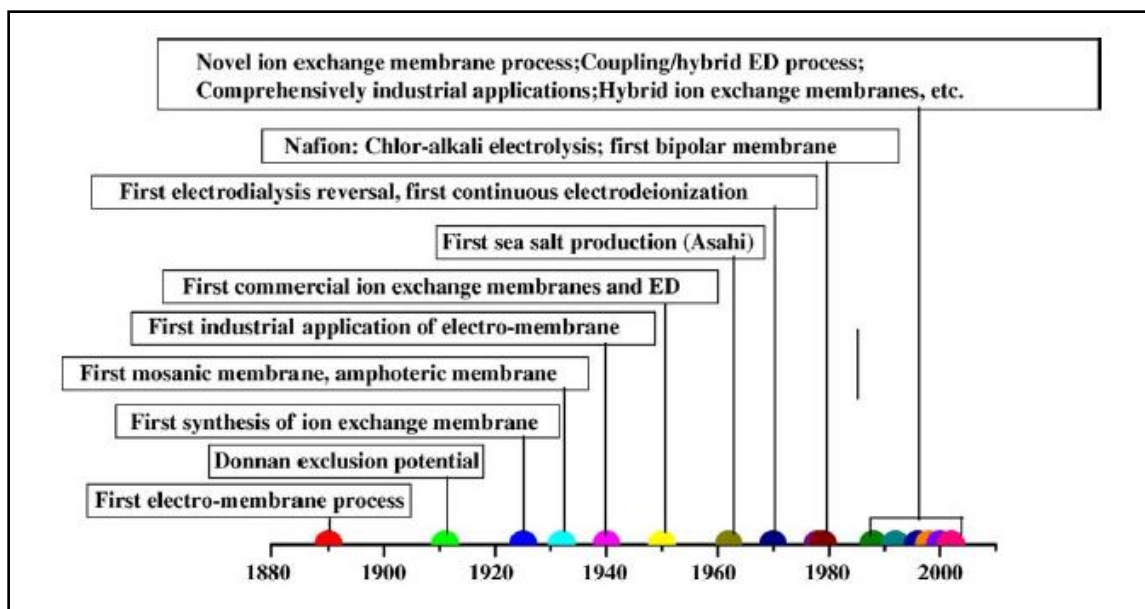


Fig. 4: Various kinds of membranes developed in the last three decades [31].

### 3. Proton Electron Membrane

The fuel cell operates as a single unit therefore each of the material and component should be taken as important. This is because a defect in a material can affect one of the parameters and according to the 1st law of fuel cell, a change in a parameter affects at least two other parameters. The activities taking place is determined both by materials and component with the operating parameters. The major components are the electrolyte, electrodes, gas diffusion layers and bipolar flow plates. The electrolyte, gas diffusion layer and the electrodes are sometimes grouped together and called the Membrane electrode assembly (MEA) [32,33]. Fig. 2 shows the detailed 3D planar image of a PEMFC at University of the West of Scotland fuel cell laboratory.

The membrane is regarded as the most important component in the PEM fuel cell and fuel cells as a whole. It is in the centre of the fuel cell. The membrane is so important that it is used in the classification of fuel cells. The membrane determines the name of the fuel cell. For example, in a PEM fuel cell, the proton electrolyte membrane (PEM) is used. Most research conducted in recent times is related to PEM fuel cells. This is because it is the most promising of all the fuel cells. There are different types of membranes and the differentiation is based on the types of materials used in the production [25].

There are so many different types of membrane and they are made using different types of materials. The choice of materials used as membrane is dependent on the physical and chemical properties needed to ensure efficient performance in the membrane. Irrespective of the type of fuel cells, the following identified properties must be met [34];

- i. The ionic conductivity must be high
- ii. It must be chemically stable
- iii. It must have good mechanical properties
- iv. It must be easy to get or produce and not expensive

Getting a material that meets all these identified criteria may be difficult. Nafion as described earlier can meet all these requirements hence they are the most recommended brand for fuel cell membranes as explained earlier. Polymer membranes used in fuel cells have three crucial functions in the fuel cells. They are responsible for easy transfer of protons, support in effective separation of the fuel and oxygen being supplied to the fuel cell and finally act as barrier to prevent the passage of electrons through it due to the presence of  $\text{SO}_3^-$ . As stated earlier, Nafion<sup>®</sup> being perfluorosulfonic acid was developed by DuPont in 1970. The membranes have high ionic conductivity with very good life time of almost 105 hours. Some companies like Dow chemical company and Asahi chemical company synthesized perfluorosulfonic acid membranes having very short chains but high ratio of  $\text{SO}_3\text{H}$  to  $\text{CF}_2$  [35,36]. Some companies that produce cation exchange membranes are captured in Table 4.

| Table 4: Characteristics of materials used for cation exchange membranes |                        |                 |                |               |   |
|--|------------------------|-----------------|----------------|---------------|---|
| Membrane   | Membrane types         | IEC (mequiv/gr) | Thickness (mm) | Gel water (%) | Conductivity (S/cm) at 30°C and 100% RH |
| Asahi Chemical Industry Company Ltd, Chiyoda-ku, Tokyo, Japan            |                        |                 |                |               |   |
| K101   | Sulfonated polyarylene | 1.4             | 0.24           | 24            | 0.0114                                  |
| Asahi Glass company Ltd., Chiyoda-ku, Tokyo, Japan                       |                        |                 |                |               |   |
| CMV  | Sulfonated polyarylene | 2.4             | 0.15           | 25            | 0.0051                                  |
| DMV  | Sulfonated polyarylene | -               | 0.15           | -             | 0.0071                                  |
| Flemion  | Perfluorinated         | -               | 0.15           | -             | -                                       |

|   |                |     |     |    |         |
|---|----------------|-----|-----|----|---------|
| Ionac Chemical Company, Sybron Corporation, USA |                |     |     |    |         |
| MC 3470   | -              | 1.5 | 0.6 | 35 | 0.0075  |
| MC 3142   | -              | 1.1 | 0.8 | -  | 0.0114  |
| Ionics Inc., Watertown, MA 02172, USA           |                |     |     |    |         |
| 61AZL386  | -              | 2.3 | 0.5 | 46 | 0.0081  |
| 61AZL389  | -              | 2.6 | 1.2 | 48 | -       |
| 61CZL386  | -              | 2.7 | 0.6 | 40 | 0.0067  |
| DuPont Company, Wilmington, DE 19898, USA       |                |     |     |    |         |
| N 117   | Perfluorinated | 0.9 | 0.2 | 16 | 0.0133  |
| N 901   | Perfluorinated | 1.1 | 0.4 | 5  | 0.01053 |
| Pall RAI Inc., Hauppauge, NY 11788, USA         |                |     |     |    |         |
| R-1010  | Perfluorinated | 1.2 | 0.1 | 20 | 0.0333  |

The Nafion membranes have its structure being in the form of copolymer obtained from fluoro-3, 6-dioxo 4, 6-octane sulfonic acid with polytetra-flu-orethylene (PTFE) that Teflon backbone of this structure makes the membrane hydrophobic and at the same time hydrophilic because of the sulfonic acid,  $\text{HSO}_3^-$  attached to the membrane. The ionic nature of the membrane supports good absorption of water making the membrane moist constantly [37]. According to some research conducted on membranes of PEM fuel cells, the thickness of the membranes and hydration of the membranes are the main determiner for the overall performance of the fuel cell [38,39]. The rate of protonic conductivity through the membrane contributes to the increase in performance of the fuel cell but this phenomenon occurs when the membrane is well humidified. Reducing membrane thickness curb the possibility of water cross over or water drag on the membrane and this enhances the performance of the membrane [40]. The resistance of the membrane is also reduced when the thickness of the membrane is reduced as well. This process also increases the performance of the fuel cell and affects the general cost of the fuel cell. Hydration of membrane becomes easy when the thickness of the membrane is small [41,42]. Membranes in general must be cheap, repel electrons and allow easy passage of electrons with little resistance. They must also not allow the passage of fuel to the cathode electrode and oppose the flow of air or oxygen to the anode electrode. Fig. 5 shows the structure of Nafion<sup>®</sup> chemically and other kinds of Perfluorinated electrolyte membranes.



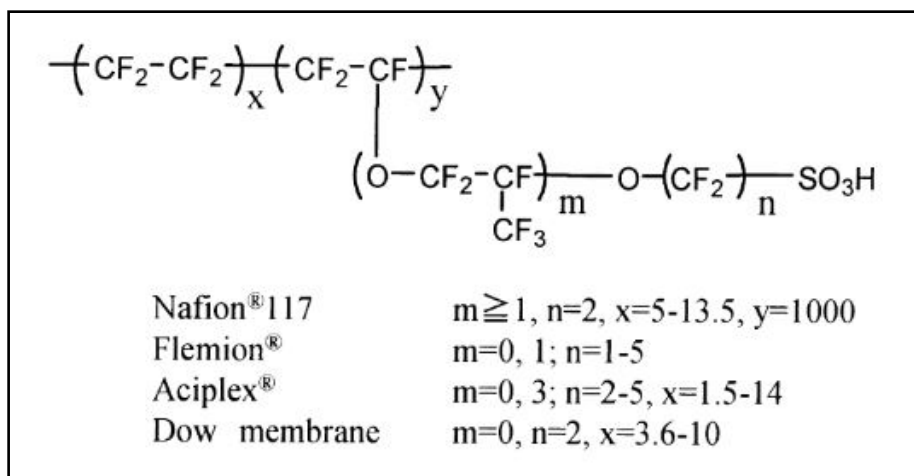


Fig. 5: Chemical composition of Polymer electrolyte membranes for PEM fuel cells [43].

During the evaluation of proton exchange membrane fuel cell, one of the critical issues considered is the easy flow of protons through them. At high current densities, the membrane is expected to allow easy flow of protons and lower loss due to resistivity. The resistivity of the membrane is directly proportional to the surface area of the membrane [44]. The protons flow through the membrane molecularly by two mediums and these are proton hopping or Grotthuss Mechanism and movement by means of diffusion [45,46]. There is movement of the protons from one a specific hydrolysed ionic site ( $\text{SO}_3^- \text{H}_3\text{O}^+$ ) to another specific region on the membrane. As the fuel flow through the flow channels of the bipolar plate on the anodic region of the fuel cell, it breaks into two ions once it reaches the catalyst area. The protons then stick to water molecules present on the membrane and this leads to the formation of hydroxonium ions. Another separate proton from the hydroxonium ions then moves from one water molecule to another. This results in percolation which aids the easy movement of protons and causes swelling of the membrane due to the formation of ionic clusters [30]. The conductivity of the protons is not influenced significantly by the hopping process shown in Fig. 6.

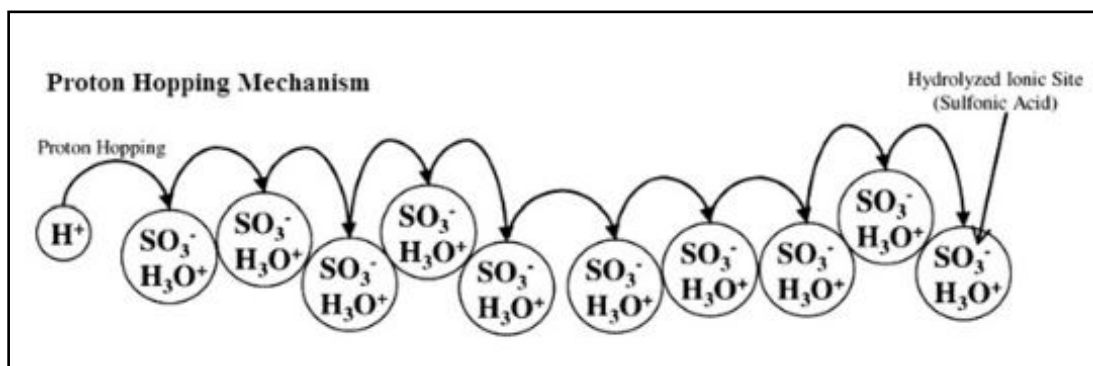


Fig. 6: The hopping process of protons on the membrane of fuel cells [30]

Movement of the protons due to diffusion occurs when protons that carriers water from the surface of the membrane flow through due to electrochemical differences on the membrane surface. Transfer of protons through the membrane occurs because the protons carry one molecule of water through the membrane by means of diffusion ( $H^+(H_2O)_x$ ) or electroosmotic drag. Most proton exchange membranes have unoccupied spaces (volumes) which support the easy movement of the hydroxonium ions. Transfer of protons through pristine and nanocomposite membranes is presented in Fig. 7 (a and b). Transfer of water on the membrane occurs by two mediums. These are electroosmotic drag and concentration gradient due to diffusion. The membranes of PEM fuel cells as described earlier have Teflon backbone which is hydrophobic. This helps in easy movement of water via the membrane because water is repelled because of the nature of the hydrophobic surface [47]. The level at which the membrane is well humidified determines the kind of mechanisms likely to occur on the surface of the membrane.

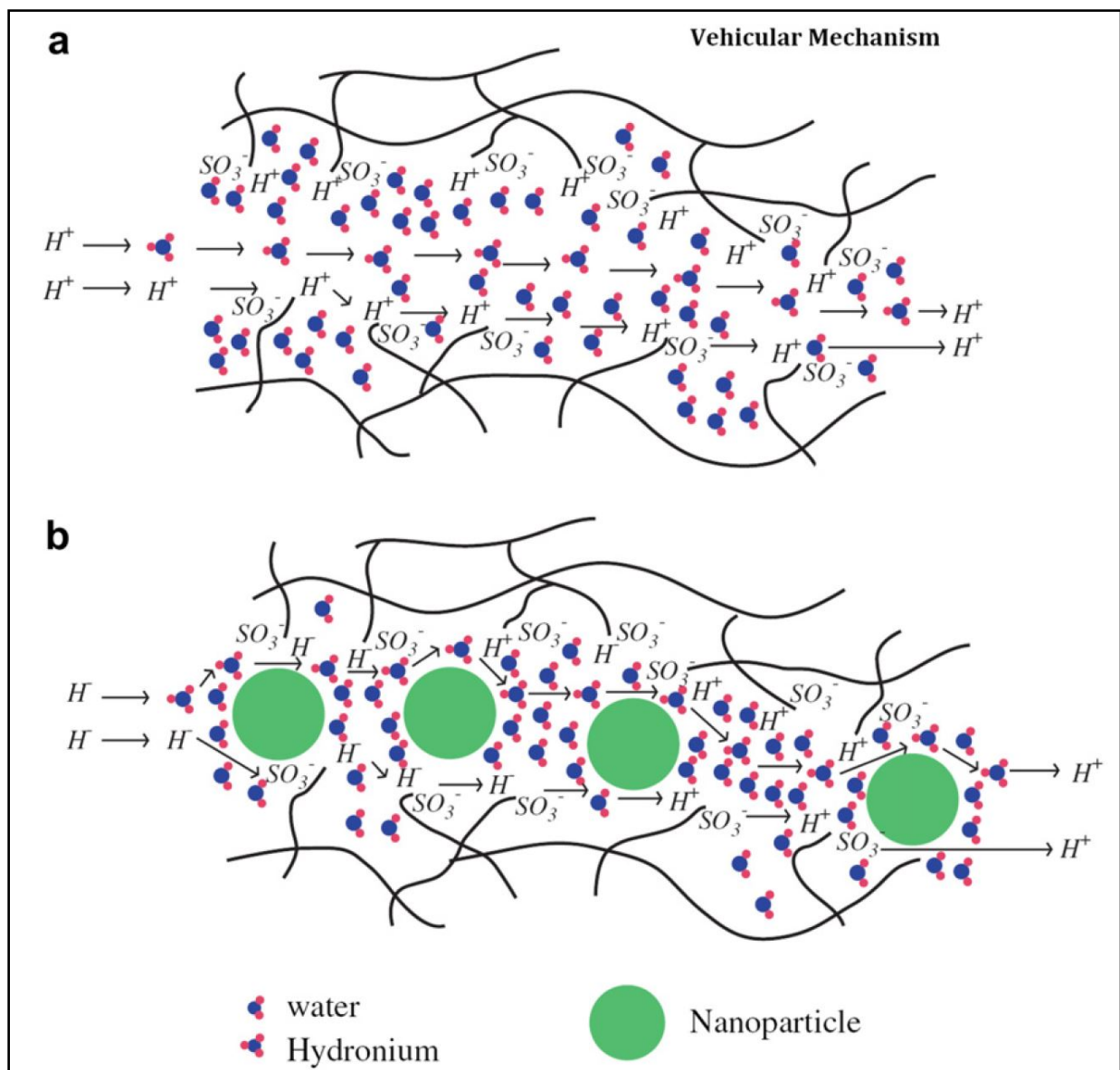


Fig. 7: Diagram of proton movement by means of diffusion in a) pristine membranes b) polymer/ Nano particle membrane [47].

### 3.1 Categories of membranes used in fuel cells

Membranes used in fuel cells are grouped into 3 main categories. These are Perfluorinated, partially fluorinated and non-fluorinated membranes. However, in addition to these we have other membranes derived from these major categories or using additional materials. The various types of membranes used in the fuel cells are shown in Fig. 8.

| Perfluorinated  | Partially fluorinated   | Non-fluorinated   | Acid-base blends   | Others  |
|---|---|---|--|---|
| <ul style="list-style-type: none"> <li>• PFSA</li> <li>• PFCA</li> <li>• PFSI</li> <li>• Gore-select</li> </ul> | <ul style="list-style-type: none"> <li>• PTFE-g-TFS</li> <li>• PVDF-g-PSSA</li> </ul> | <ul style="list-style-type: none"> <li>• NPI</li> <li>• BAM3G</li> <li>• SPEEK</li> <li>• SPPBP</li> <li>• MBS-PBI</li> </ul> | <ul style="list-style-type: none"> <li>• SPEEK/PBI/P4VP</li> <li>• SPEEK/PEI</li> <li>• SPEEK/PSU(NH<sub>2</sub>)<sub>2</sub></li> <li>• SPSU/PBI/P4VP</li> <li>• SPSU/PEI</li> <li>• SPSU/PSU(NH<sub>2</sub>)<sub>2</sub></li> <li>• PVA/H<sub>3</sub>PO<sub>4</sub></li> </ul> | <ul style="list-style-type: none"> <li>• Supported composite membrane</li> <li>• Poly-AMPS</li> </ul> |

Fig. 8: Categorises of membranes used in PEM fuel cells [48]

### 3.1.1 Fluorinated membrane

Fluorinated membranes are the most popular membranes used in PEM fuel cells. The most common type used is the perfluorosulfonic polymers called Nafion membranes made by Dow Chemical Company developed with patent in 1966 (Connolly and Gresham 1966) and 1982 [39]. In the material, a sulfonic acid group is bonded with the fluoropolymer which is the backbone as explained earlier.

Sulfonated polymers comprising of Perfluorinated back bones and sulfonated side-chains such as Nafion are the most popularly used membrane for PEM cells because they function properly within operating temperatures below 100°C. They are only used when operating at low temperature. This type of membrane has a lot of problem with water (Swelling). All the alternatives to Nafion membranes have failed to achieve an acceptable level of conductivity. Therefore, a lot of work is ongoing to determine a low cost and high proton conductive membrane [50]. Sulfonated side-chains aggregate and facilitate hydration while perfluoroether are responsible for chemical stability. The Nafion membrane is manufactured by DuPont and has the chemical formula stated in Fig. 9 below.

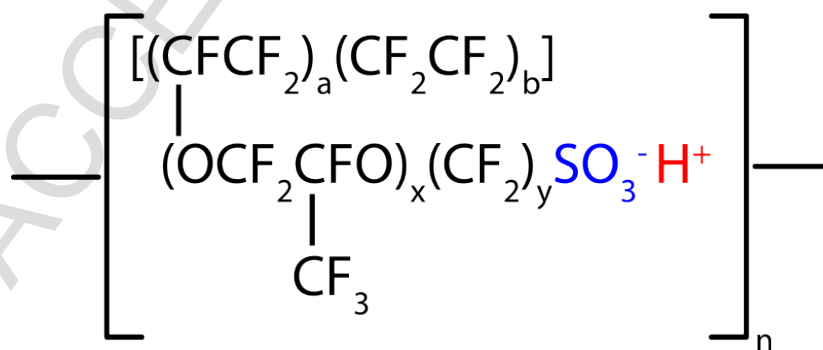


Fig.9. Showing Chemical formulae for Nafion membrane [43]

The use of Nafion as a membrane is often recommended by researchers around the world and it is also used commercially in industrial applications. Being a fluorinated membrane, it has a high stability in both oxidation and reduction environment. It also has a high proton conductivity which is the most important properties for a material to be used as membrane. Increasing the hydration level of polymer increases the efficiency in ion conduction. The Nafion membrane has several challenges. This is its high cost and inability to cope at high temperature. At high temperature, it has low proton conductivity, low mechanical stability and low swelling properties [41]. The Nafion membrane structure is as shown in Fig. 10. Challenges for using Perfluorinated membrane include:

- Inoperability at high temperatures.
- High cost of materials.
- Need humidification equipment to reach the required level of humidity.
- Produces wastes that are harmful to the environment.
- Swelling and shrinking due to changes in water uptake during thermal and humidity cycling.
- Chemical degradation.

In other to cover for its deficiencies at high temperature, there is the need to use other materials alongside the Nafion. That is why the use of partially fluorinated membrane is very important. Despite all the challenges being faced by the Nafion membrane, it still produces the most acceptable properties and usually used as a benchmark when considering new membranes for PEM fuel cells. These types of membranes are produced when monomers are polymerized, and this is capable of being made anion or cation if it undergoes other chemical and physical treatment. Some researchers also describe them as being fluorocarbon based ion exchange membranes. The various steps that were used in producing Nafion by DuPont are as shown in Fig. 9.

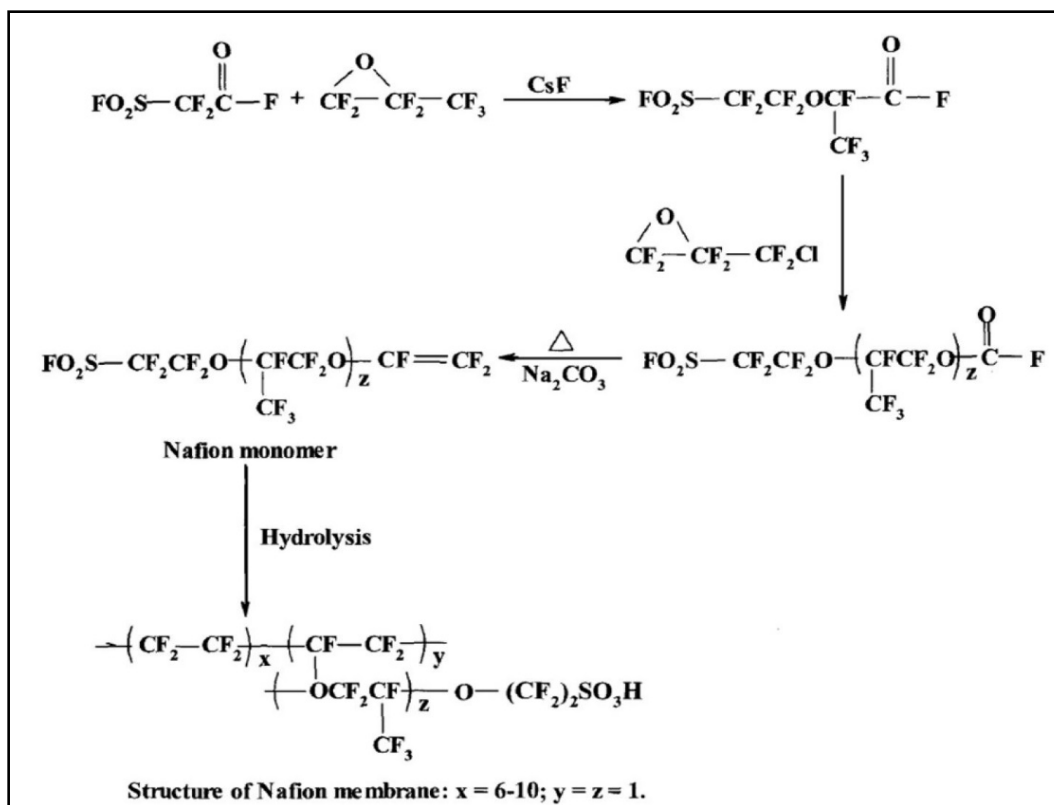


Fig. 10: Step wise approach leading to the production of Nafion membrane [40].

These types of membranes in recent times have seen a sharp decline in their usage in fuel cells because they require high power density and are also described as high equivalent weight fluorinated membranes. Companies like Asahi and Aciplex - S® produces flemion® which has the same characteristics as Perfluorinated ionomeric membranes, but DuPont continue to dominate the production of membranes for fuel cells because of the high protonic conductivity of Nafion as well as excellent chemical and mechanical strength.

### 3.1.2 Partially fluorinated membrane

To resolve the hydration problem of Nafion membrane, Nanocomposite membranes were proposed which were just a modification of the Nafion membrane to increase water retention capability by including micron/submicron organic or inorganic additives like  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{TiSiO}_4$ , and Silica. This move improves the chemical and physical properties (elastic modulus, tensile strength, hydrophobicity) of the membrane without affecting its proton conductivity. In place of Nafion membrane were the hydrocarbon polymers e.g. sulfonated hydrocarbons, that enabled

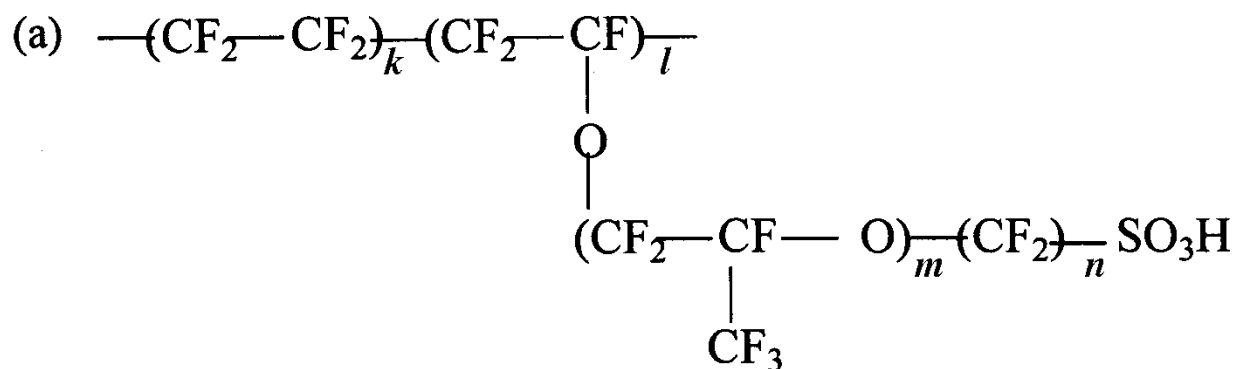
manufacturing of non-fluorinated membrane for PEM fuel cell applications though bringing with it advantages and disadvantages. Fullerene based membrane enabled operation of PEMFC at temperatures greater than 150°C while increasing the kinetic rate and reducing use of costly catalyst to cause overall improvement in fuel cell performance.

Some other materials are used for the membranes in addition to fluorinated membranes. This is done to reduce cost compared to when only fluorinated materials were used. Some of these partially fluorinated membranes has been discovered to produce membranes which have a stability which is higher and better mechanical properties. Some popular Perfluorinated material include the following as listed [42].

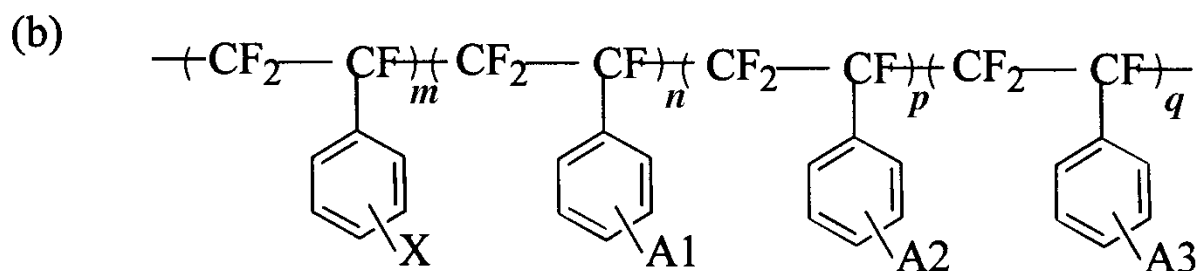
- a. Sulphonated  $\alpha,\beta,\beta$ -trifluorostyrene and m-trifluoromethyl- $\alpha,\beta,\beta$ -trifluorostyrene
- b. Sulphonated polymer of  $\alpha,\beta,\beta$ -trifluorostyrene
- c. Copolymer of  $\alpha,\beta,\beta$ -trifluorostyrene, m-trifluoromethyl- $\alpha,\beta,\beta$ -trifluorostyrene and p-sulfonyl fluoride- $\alpha,\beta,\beta$ -trifluorostyrene
- d. Sulphonated copolymer of  $\alpha,\beta,\beta$ -trifluorostyrene and p-fluro- $\alpha,\beta,\beta$ -trifluorostyrene
- e. Copolymer of  $\alpha,\beta,\beta$ -trifluorostyrene, p-fluoro- $\alpha,\beta,\beta$ -trifluorostyrene and p-sulfonyl fluoride- $\alpha,\beta,\beta$ -trifluorostyrene

Just like fluorinated membrane, partially fluorinated membranes have succeeded in showing a high proton conductivity however it is expensive and cannot be referred to as low cost because expensive fluorinated materials are used. Additionally, commercialisation of these materials has not been visible due to cost and because the trifluorostyrene monomer is limited in availability.

The most popular partially fluorinated membrane is sulfonated copolymer incorporating  $\alpha,\beta,\beta$ -trifluorostyrene monomer (Basic Advanced Materials 3rd Generation, BAM3G) made by the company Ballard Advanced Materials. The structure of BAM3G is as shown in Fig. 11 [42]. This work [43] shows that the cost of BAM3G is low compared to the fluorinated membrane materials however more work still needs to be done to ascertain their properties and make possible recommendations for commercialisation.



where  $k = 6-10$ ,  $l = 1$ ,  $m = 0-1$ , and  $n = 2-4$



where at least 2 of  $m, n, p, q$  are integers  $>0$ ,  $X = \text{SO}_3\text{H}$ , and  $A1, A2, A3 = \text{alkyls, halogens, O-R, CF=CF}_2, \text{CN, NO}_2, \text{OH}$

Fig. 11: Chemical structure of (a) Perfluorinated sulfonic acid-based membranes like Nafion, Dow and Aciplex (b) Sulfonated trifluorostyrene copolymer membranes (BAM3G) [42].

These types of membranes are also often aliphatic or aromatic polymers made up of benzene rings structures. Using hydrocarbon polymer is currently being recommended by researchers around the world because they produce membranes that have high protonic conductivity [55]. These types of membranes are cheaper, readily available commercially and their general structure allows the usage of polar sites compared to fluorinated membranes. Hydrocarbons made up of polymer groups have high uptake of water when operated within varying temperatures. Their water uptake is dependent on the polar group. Using good molecular design can aid in the easy decomposition hydrocarbon polymers. Using conventional approach can help in the recycling of hydrocarbon polymers. Fig. 12 can also be used to represent the structure of membranes made up of hydrocarbon chemically.



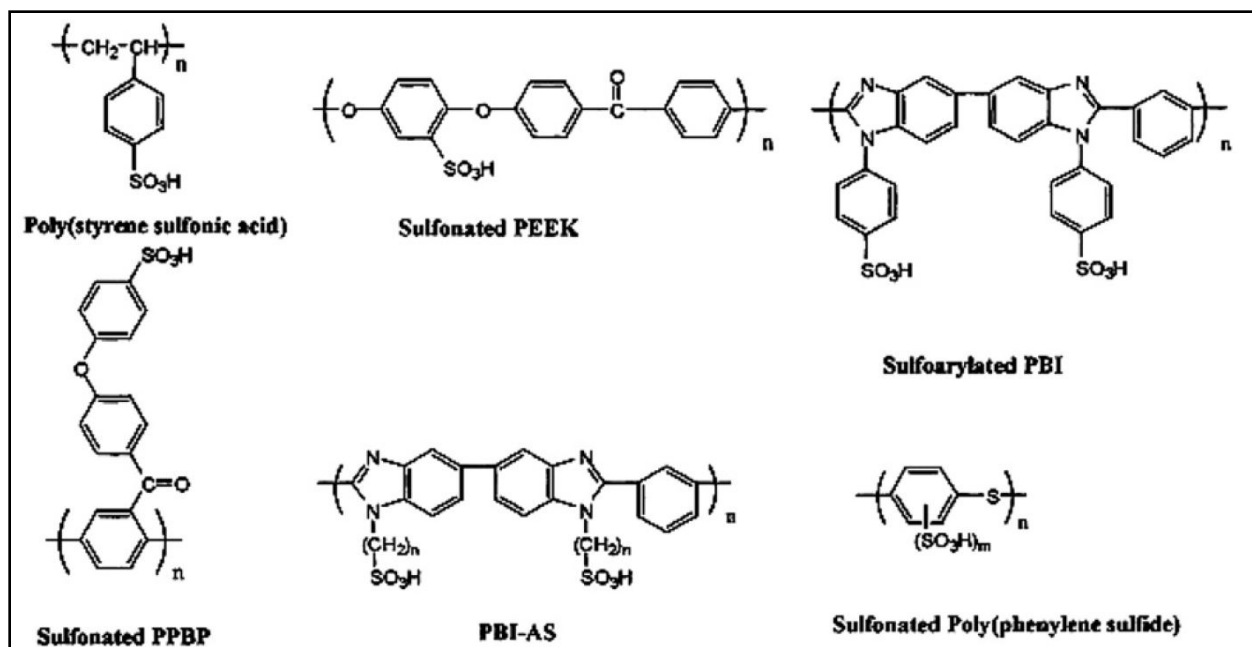


Fig. 12: Hydrocarbon based membrane structure for PEM fuel cells [30]

### 3.1.3 Non-Fluorinated membrane

Efforts were being made to produce low cost membrane. The focus of the effort is on the total replacement of the fluorinated membrane materials in the PEM fuel cells. Non-fluorinated membranes are used as replacement. Evidence from other research shows that reducing cost associated with the membranes also have significant effects on the overall cost of production.

Non-fluorinated membranes are made from polymer materials which are functional. These are materials which are not only cheap but also highly available.

The following are some of the materials used as non-fluorinated membranes [56];

- Polystyrene membrane materials
- Poly (arylene ether sulfone) membranes
- Poly (arylene ether ketone) membranes
- Acid-doped polybenzimidazole membranes
- Poly (vinyl chloride) membranes

Even though the use of polymer materials is promising, it currently shows lesser conductivity, reduced thermal and chemical properties. Some authors [43] believe that manufacturers should be ready to sacrifice some of the properties in favour of cost. This will help to encourage research and development. Studies on polymeric membrane were done by Fathima et al [57]. The

low-cost membrane has been tested and has shown very good performance. It has recorded most success in the water industry where it is being used for purification and in the treatment system. This is an industry where the margin of profit is low so also the need for a very good method that saves cost.

Non-fluorinated membranes are also made using other materials different from polymer. PEM membrane with nanoporous hematite ceramic materials was prepared by Colomer et al [58]. It was shown that the membrane developed have lower cost, friendly with the environment, shows a good proton transport, high water uptake and high hydrogen permeability. In another work by Makinouchi et al [59], it was observed that the nanofiber composite showed proton conductivities higher than Nafion and also a better mechanical stability. A water permeability which is good was also indicated.

#### **3.1.4 Composite membranes**

Compared to the other types of membranes, the composite membrane is cheaper, has a higher water uptake, has a high temperature range and can be recycled [60]. This is very good for the environment. However, there are problems associated with it thermal conductivity, chemical stability and proton conductivity because they are low compared to the other types of PEM membranes. They are recommended by scientist because they keep a constant protonic conductivity at higher temperatures without any form of dehydration. It involves fusing an acid component with a polymer that is alkaline in nature to enhance the protonic conductivity. Fig. 13 depicts the structure of these types of membranes chemically.

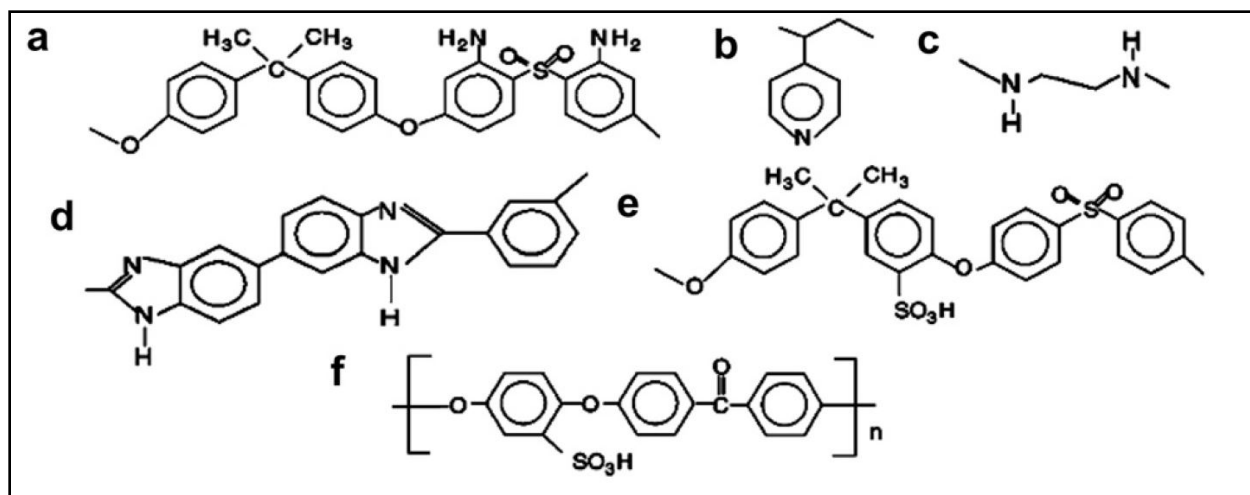


Fig. 13: Basic polymer structure (a-d) and acid polymer (e,f) [48]

By using composites, many other types of membranes can be made. Researchers continue to carry out investigations aimed at studying the material composition of the membrane in order to increase its overall performance and this resulted in considerable advances in the formulation of catalytic membranes for PEMFCs. For example, in an investigation conducted by Tu et al [61] using composite membranes made of ePTFE matrix and short chain perfluorinated sulfonated ionomers, they concluded that the performance of the fuel cell increased at 95°C even under unfavourable relative humidity conditions. The investigation also showed an increase in the stack voltage by 11% when the inlet gas temperature was varied between 75 – 80°C. Their results also indicated that using dry hydrogen and air also increased the voltage output by 17%. The investigation buttresses the future of these novel types of membranes in fuel cells for their application in the automobile industry.

Table 5 shows the current uses of composite membranes in fuel cell applications including the materials used in the preparation, with many of these materials showing good performance. Composites of silica and graphite are also promising and they outperformed some Nafion membranes under some conditions. Although a lot of work needs to be done in research and development, the use of composite membranes should be encouraged especially in light applications where performance constraints are not demanding.

Table 5: Fuel cell applications of composite membranes

| Type of fuel cell membrane   | Materials used as composite                       | Comments   | Ref  |
|------------------------------|---|--|------|
| Ion-conducting membrane      | $\text{Al}_2\text{O}_3\text{-NaAlO}_2$            | $\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{CO}_3$ were used to prepare a novel oxide-salt $\text{Al}_2\text{O}_3\text{-nNaAlO}_2$ composite which was characterized using X-ray diffraction (XRD) pattern, scanning electron microscopy (SEM) and impedance spectra to determine the structure, morphology and the electrical properties. The images showed good ion transport and the electrochemical impedance spectroscopy (EIS) indicated a promising future for composite materials. | [62] |
| Polymer electrolyte membrane | Asymmetric silica                                 | Membranes made with asymmetric composites results in increased proton conductivity in a low humidity environment. Due to the presence of silica, analysis of the drain water and electrochemical characterisation showed that the structural arrangement supports efficient water management because the acceleration of water transport is increased.   | [63] |
| Direct methanol fuel cell    | Nafion-mordenite incorporated with graphene oxide | Research on graphene oxide is increasingly popular and in this work it was used to reduce permeability of methanol. In this instance, modification with 0.05% resulted in the highest proton conductivity. When compared with Nafion 117 membrane it recorded power density 4-times higher with a model prediction having a very low error of 0.082%.  | [64] |
| Fuel cells in general        | Graphene oxide                                    | The graphene characteristics of high thermal/electrical conductivity, great mechanical strength, optical transparency, inherent flexibility, huge surface area, and unique two-dimensional structure attracted the interest of many researchers.. Although more development work still needs to be done, its compatibility with many polymers and solvents increases the potential of it being used in the production of graphene-based membranes for fuel cells.                            | [65] |
| High temperature             | Polybenzimidazole-                                | The work shows the fabrication of polybenzimidazole based composite membranes with   | [66] |

|  |   |  |      |
|--|---|--|------|
| polymer electrolyte membrane fuel cells        | Ce <sub>0.9</sub> Gd <sub>0.1</sub> P <sub>2</sub> O <sub>7</sub> and polybenzimidazole-Ce <sub>0.9</sub> Gd <sub>0.1</sub> P <sub>2</sub> O <sub>7</sub> -graphite oxide | polybenzimidazole, Ce <sub>0.9</sub> Gd <sub>0.1</sub> P <sub>2</sub> O <sub>7</sub> and graphite oxide by a procedure called solution casting. Characterisation of the phosphoric acid-doped composite membranes was done for fuel cells applications given the favourable microstructural, mechanical and electrical properties of the material. The material gives better proton conductivity compared to that earlier reported for phosphoric acid-doped polybenzimidazole membranes and that can be attributed to the addition of graphite oxide. The major challenge for this type of material is that above 160°C the maximum power density decreases irrespective of the conductivity value. |      |
| Direct methanol fuel cell                      | Homogeneous polymer/filler  | A comparison between the composite membranes made using a spraying method and a conventional Nafion membrane using solution casting was made when mordenite was used as a filler in both cases. Images from the SEM showed that the spraying method produced a more homogeneous composite membrane. The membrane with 5 wt% mordenite from the spraying method showed greater improvement in DMFC performance and produced better performance than that of commercial membrane with 5 wt % mordenite produced by the solution casting method.  | [67] |
| Nanohybrid proton exchange membrane fuel cells | Highly sulfonated poly(ether ether ketone) grafted on graphene oxide (GO)   | Hydrogenation of highly sulfonated poly(ether ether ketone) (PEEK) polymer is done and grafted with GO to produce nanohybrid material GO-g-SPEEK. Upon testing, the material showed good properties that are needed for preparing the PEM. These results indicated that Nafion might serve only as an enhancer of compatibility between membrane and the Nafion-supported catalyst phase in the membrane electrode assembly, and therefore suggest that the GO-g-SPEEK may be a promising membrane material for application in proton exchange membrane fuel cells.  | [68] |
| Anion exchange                                 | Ionic-liquid-coated   | The performance of anion exchange membranes (AEMs) was enhanced by fixing ionic-   | [69] |

|   |  |  |      |
|---|--|--|------|
| membrane fuel cells                                 | silica/quaternized poly (2,6-dimethyl-1,4-phenylene oxide) | liquid-coated silica in trimethylamine functionalized poly(2,6-dimethyl-1,4-phenylene oxide). The structure of the modified silica and polymer backbone was crosslinked to improve the performance of the AEMs. Improvements were noticed in the hydroxide ion conductivity, mechanical properties, dimensional stability, and chemical stability of the quaternized poly(2,6-dimethyl-1,4-phenylene oxide)/ modified silica composite membranes (designated as QAPPO/IL-SiO <sub>2</sub> ). It showed higher dimensional stability after hot pressing than pristine membrane. Therefore, the QAPPO/IL-SiO <sub>2</sub> composite membranes proved to be a promising AEM material for fuel cells.  |      |
| Fuel cells in general                               | Cross-linked PVA/SSA/GO                                    | PVA/SSA when cross-linked with GO showed improved performance but the performance is affected when GO was in excess so there is a need to optimise the use of GO and other composite material so that they can give the optimum membrane performance.  | [70] |
| Proton exchange membranes for fuel cell application | novel sulfonic acid functionalized zeolites                | Sulfanilic acid functionalized poly(1,4-phenylene ether ether sulfone) (SPEES-SA) membrane was prepared and further modified by the incorporation of different mass % of sulfonic acid functionalized zeolites for the development of the composite membranes. The functionalization of zeolites was confirmed by wide-angle X-ray diffraction and X-ray photoelectron spectroscopy. The resulting SPEES-SA and its composite membranes were subjected to various techniques to investigate their physico-chemical properties. The morphology of the membranes was studied using both atomic force microscopy and scanning electron microscopy. The performance of the membranes was studied in terms of swelling behaviour, water uptake, ion exchange capacity and proton conductivity with respect to the mass % of the functionalized zeolites. The results showed that the data sets were better than | [71] |

|                       |  |   |      |
|-----------------------|--|---|------|
|                       |  | those obtained for a commercially available Nafion® 117 membrane giving potential for their use in fuel cells.  |      |
| fuel cells in general | sulfonated PEEK/sulfonated nanoparticles | PEM fuel cells having varying quantities of sulfonated nanoparticles and different sulfonation reaction times of PEEK polymer were studied. The best performance for different concentrations of PS-SO <sub>3</sub> H particles is determined by measuring proton conductivity, water behaviour in the membrane and mechanical properties. The composite membrane showed higher proton conductivity when compared with pure sPEEK membrane. An increase in the content of PS particles increases proton conductivity because of the presence of hydrophilic nanoparticles which has been incorporated into the membrane material. | [72] |

|  |  |  |      |
|--|--|--|------|
| fuel cells in general                              | sulfonated poly ether ether ketone (sPEEK)/ CNTs | In the evaluation of Sulfonated poly ether ether ketone (sPEEK) membrane after being synthesized for PEM applications. Success in sulphonation of PEEK was confirmed using Fourier transform infra-red (FT-IR) and Ultra-violet (UV) visible spectra. The results showed reduction in water uptake and swelling ratio which are desired qualities of a good membrane. In terms of conductivity, this composite membrane gave values more than twice those obtained from sPEEK (22.44 mS/cm and 9.93 mS/cm).  | [73] |
| Non-humidified Proton Exchange Membrane Fuel Cells | Protic plastic crystal/PVDF                      | The development of composite membranes based on the protic plastic crystal N, N-dimethylethylenediammonium triflate [DMEDAH][TFO] and poly(vinylidene fluoride) (PVDF) nanofibers was done for use in proton exchange membrane fuel cells (PEMFCs) under non-humidified conditions. The researchers reported that the acid-doped plastic crystal produced more than two-times the ionic conductivity of the pure plastic crystal. The application of composite membranes based on PVDF nanofibers and [DMEDAH][TFO] in a single PEMFC confirmed the potential of these composite membranes for use as electrolytes in this electrochemical application without external humidification.  | [74] |
| Fuel cell applications                             | Silica   | Silica is the most common inorganic filler used in membranes destined for use in fuel cells including PEMFC and DMFC. Silica has played an important role in improving the performance of fuel cells by enhancing the membrane properties and it has been used in different membranes such as fluorinated membranes (Nafion), sulfonated membranes (SPEEK, SPS, SPAES, SPI) and other organic polymer matrices. Addition of silica into the membrane matrices has improved their thermal stability, mechanical strength, water retention capacity and proton conductivity. Although there are currently some challenges associated with the use of silica as part of the membranes material, nevertheless it is predictable that | [75] |



|  |   |  |      |
|--|---|--|------|
|  |   | silica has a promising future in membrane-based fuel cell applications.  |      |
| fuel cell in general                                 | Mechanically stable nanofibrous sPEEK/Aquivion®             | The preparation of nanocomposite PEM using fibrous sulfonated poly(ether ether ketone) (sPEEK) and Aquivion® were made using electrospinning and impregnation processes. Although in the reported work the composite membrane has a lower proton conductivity, an improvement in its mechanical properties and stability were noted. Additionally, when crosslinked with sPEEK, its behaviour in terms of swelling ratio and mechanical properties were the best when compared with those with no crosslinking.  | [76] |
| High temperature proton exchange membrane fuel cells | Phosphonate ionic liquid immobilised SBA-15/SPEEK composite | Composite membranes can be used for high temperature PEM fuel cells. A composite membrane was prepared using phosphonate ionic liquid immobilised SBA-15 as filler and SPEEK as matrix. Morphology studies were conducted using characterisation techniques such as SEM and XRD. An increase in the ion exchange capacity, proton conductivity and water uptake were observed and this was attributed to the presence of PIL-SBA-15. The mechanical strength was improved by the filler and a maximum power density of 183 mW/cm <sup>2</sup> was achieved when used at a temperature of 140 °C. | [77] |

### 3.2 Preparation of Membrane

In terms of cost, the material used for the membrane account for the majority therefore materials and component that is cost-effective would go a long way in reducing the total cost of production. At the moment, the raw materials used are Nafion made by DuPont USA, Aciplex and Flemion made by Asahi japan and the composites. These above-mentioned materials are expensive and the need for a material that is cheap with a better performance is becoming very important. Composite Membranes have been made from materials like hydrocarbons [43,54,56,78–82], ceramics [83][22,58,83], graphene [65,84–87] among others. Current research efforts aims to produce catalytic membranes wholly made of composites thus replacing Nafion. The membrane can be prepared using different types of method. The method used usually depends on the type of membrane to be made and the available materials and equipment. The different preparation methods for the membrane are listed below;

#### 3.2.1 Irradiation grafting polymerization method

This method has been used to prepare different types of membranes like anion exchange proton membrane fuel cell [88], proton exchange membrane [89,90] and alkaline proton exchange membrane [82]. Four processes were involved; pre-irradiation, grafting reaction, sulfonation reaction and alkylation reaction. An example of this process is as shown in the Fig. 14 [91] below. Effort to prepare the membrane using this method was intensified because membranes made using this method has shown to have some advantage over those prepared using other methods. As deposited by Zhou et al [82], the composition is well controlled and has a high level of functionality among other advantages. The reaction is simple and highly effective. It is cost effective and the requirements for base polymer is fewer compared to other methods[92].

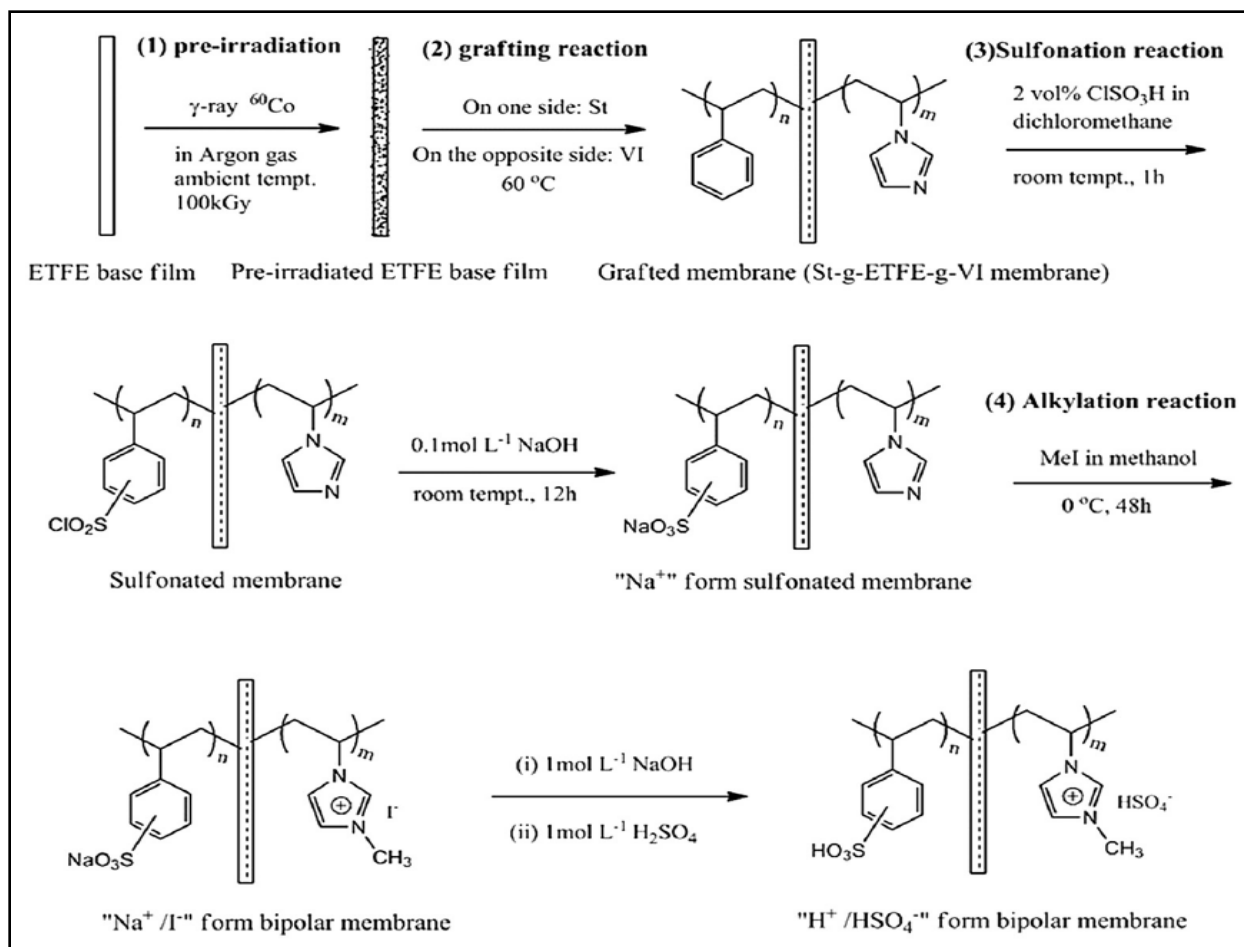


Fig. 14: Stages involved in the preparation of fuel cell membrane using irradiation grafting polymerization method [91].

### 3.2.2 Crosslinking method

In this method two compounds combine to form a crosslink. This method has been used in the preparation of PEM [93], alkaline membrane [94], direct methanol fuel cell [95] In a work by An et al [96], the crosslink was formed by Benhydrol and sulfonic acid and this was shown on NMR and FTIR. Crosslinking method is a widely used in the preparation of membrane. This is because it helps to improve the properties of the membrane. It has been reported that it provide solution to the problems associated with conductivity-swelling in anion exchange membranes [97], improves tensile strength [96]. Some cross-linked anion membrane used for alkaline fuel cell application can be recycled and reprocessed for use. In an experiment by Hou et al [98],

some crosslinked membranes after been recycled showed an acceptable conductivity that could be compared to Nafion.

Work by Shin et al [99] showed the effect of crosslinking on durability and electrochemical performance of sulfonated aromatic polymer membranes at high temperatures. It was reported that crosslinked membranes show better thermal and mechanical properties compared Nafion up to 200°C, it also showed improved power densities. The durability of fuel cell were also shown to be enhanced in alkaline anion exchange membrane electrolyte [100].

### 3.2.3 Plasma grafting polymerization method

Plasma grafting polymerization method is used in for preparing proton exchange membranes used for miniaturized fuel cells. The system used to perform plasma polymerization system for preparation of acrylic acid plasma polymerized poly(3-hydroxybutyrate) fuel cell membranes is shown in the Fig. 15 below [101]. Materials needed included two different gases labelled gas 1 and 2, gas mixer, flowmeters, analogue pressure monitor, plasma reactor having substrate, liquid monomer, diffusion pump, rotary vane pump and liquid cold trap. Using plasma grafting, the degree of crosslinkage in the polymerized films is high, making the thickness of the pinhole small. This leads to a decreased resistance and reduced permeability. However, it also shows a reduction in the ionic conductivity. This is because of the limited movement of water. Effort to solve this problem has been made through the development of plasma polymerized electrolyte membranes. It has been used in the preparation of organic/inorganic composite membranes[102]. Plasma graft polymerization was used by Akamatzu et al [103] to prepare low-fouling membranes making use of poly(2-methoxyethylacrylate). The membrane developed showed excellent low-fouling properties when tested using 1000 ppm of aqueous solution of BSA. A review on membranes prepared using plasma-treated phosphoric acid-based material was done by Bassil et al [104]. These membranes after undergoing some preliminary tests shows it can be good for proton exchange membrane fuel cells although accepted more work still needs to be done. They have been used in the synthesis of an hydroxide exchange membrane that is highly stable [105]. This was done by adding the functional group into the PEK-C matrix. Plasma grafted polymerization is believed to have the potential to be applied in direct alcohol fuel cell [106] and also in anion exchange membrane preparation [107]. It has been used to modify existing proton electron membrane fuel cell and this has led to plasma polymerized PEMs which

are sulfonic acid functionalized and other functional groups like phosphoric acid or carboxyl acid groups and the anion exchange membranes [19].

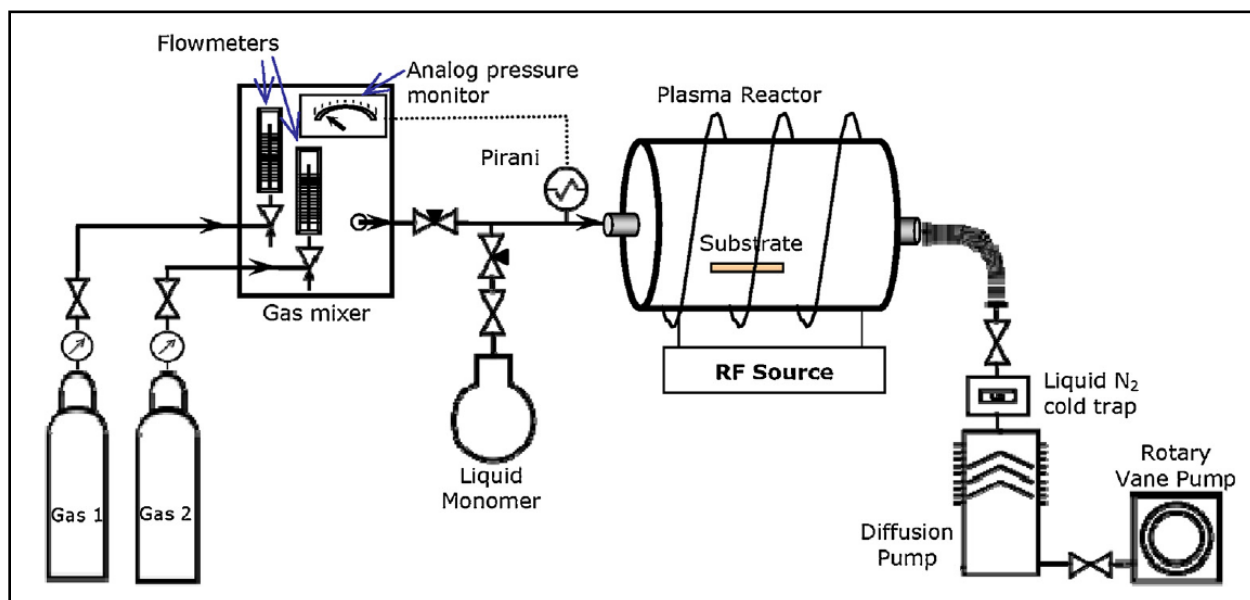
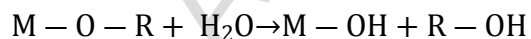


Fig. 15: Plasma polymerization system for preparation of acrylic acid plasma polymerized poly(3-hydroxybutyrate) fuel cell membranes [101]

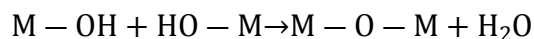
### 3.2.4 Sol-gel method

The sol-gel method is usually used in the preparation of inorganic and composite membranes. In this method, pure inorganic phase combined to form a polymeric matrix. Two materials sols and gels are important and were used. The preparations of the sols were usually made using metallic alkoxides which are dissolved in alcohol. The principle used in this method is the change in the state of the gel with respect to change in properties and a technique used in drying. Two major reactions are involved; hydrolysis and then, condensation. The formation of the polymeric matrix starts with the addition of water to the sol, which is hydrolysis and then condensed. The reaction is as stated below[30].

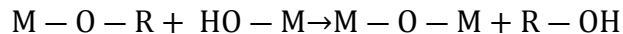
The equation for hydrolysis is



And for condensation reaction, it is



Addition of both reactions gives



In the equation above, M stands for inorganic material and R stands for inorganic member of the alky family. Examples include methyl and ethyl.

This method is a popular method and it has been adopted by many researchers in the field. It was applied during membrane preparation using ceramic materials [108] and preparation of inorganic membrane for direct methanol fuel cell using silica electrodes [109]. Also in the synthesis of polybenzimidazole membrane [110] and in the experiment for preparation and characterization of Nanoporous silica membrane [111]. The sol-gel method has been used in some proton exchange membrane fuel cell applications. An example is when  $40SiO_2-40P_2O_5-20ZrO_2$  sol-gel is infiltrated in sSEBS membranes [112]. When a nanocomposite, Ag-silica is prepared using the sol-gel method, it gives a high electrical conductivity and regularly used for phosphoric acid fuel cells [113]. The chemistry of sol-gel prepared membranes can be optimized. This is done using tools such as atomic force microscopy (AFM) and Raman micro-spectroscopy. This is as shown in the work by Cosas et al [114].

### 3.2.5 Direct polymerisation of monomers

Although this is a new method, it is the popular method used in the preparation of proton electron membrane. It involves two processes; polymerization and sulfonation. Monomers like styrene were polymerized directly and then passed through sulfonation process. When the monomer used is sulfonated, and then there would be no need for additional sulfonation. This method is a popular method and it has been adopted by many researchers in the field. It was used in the preparation of ultrafiltration membranes [115]. In a work done by Kazeroonian et al [116], direct polymerization of monomers improved the diffusivity of hydrogen while studying molecular dynamics simulation involving carboxylated and sulfonated poly(arylene ether sulfone). The carboxylation in the polymer helps to increase the hydrophilicity of the membrane and therefore increase the conductivity [116]. Different monomers of so many polymers have been used. A review into the radical polymerization using monomers of N-vinyl was done. It showed the development achieved in this area reviewing how the properties, structures and architectures of N-vinyl monomers like N-vinylcarbazole, N-vinylpyrrolidone and N-vinylformamide among others has improved the reaction [117]. Stacking of polymer chains has been shown to enhance the performance of the materials used for fuel cell applications. In the

work by Yao et al [118], for perylene-based sulfonated aliphatic polyimides, the hydrophilic interactions shown by the sulfonated group were believed to be responsible for the high performance shown in the membrane. Considering a tetra-ammonium monomer while synthesizing and characterizing imidazole containing PEEK for anion exchange membrane fuel cell, the conductivity of the hydroxide increases as the number of the functional groups increases in the membrane [119]. This shows how effective direct polymerization of monomers method can have on the resulting membrane.

Looking at all the above preparation method discussed, it is observed that almost all the methods are relatively new and requires further work for development. Table 6 below shows a comparison of different membrane preparation methods highlighting the advantages and disadvantages.

**Table 6: Comparison of different membrane preparation methods**

| Method                                     | Advantages  | Disadvantages   | Reference            |
|--|---|---|----------------------|
| Irradiation grafting polymerization method | The composition and functionality of chemicals is well-controlled.<br>Development of strong interaction between the interfacial matrix-nanostructure.<br>The method is versatile and green.     | The chemicals involved in the process is expensive<br>The process is difficult and requires expert knowledge of chemistry<br>Requires improvements in many areas and new. | [82,120]             |
| Crosslinking method                        | Improved chemical, thermal and mechanical properties exhibited compared to non-crosslinked membrane.<br>Conductivity showed by membrane can be compared to Nafion.<br>Prevent over swelling and | Low activation energy<br>Reduce water uptake when crosslinked into s-IPN.<br>More work needed to be commercialized.   | [93,94,96,98,99,121] |

|                                       |  |  |               |
|---------------------------------------|--|--|---------------|
|                                       | <p>improves tensile strength.</p> <p>Can be recycled.</p> <p>Improved durability in the long-term.</p> <p>Best performance observed at 120°C.</p>  |  |               |
| Plasma grafting polymerization method | <p>Helps to preserve the polymer structure and its functional group. Chemical stability of membranes produced is high.</p> <p>PEMs produced using the method shows properties that are superior to other methods.</p> <p>Can be used to modify existing PEMs or synthesis new ones directly.</p> <p>Technology is still new and promising.</p> | <p>Can be used at temperature less than 100°C.</p> <p>Grafting efficiency is low.</p> <p>Further research needed to enhance performance of overall plasma-grafted membranes.</p> | [103,122–125] |
| Sol-gel methods                       | <p>The set-up is flexible and can accommodate different characteristics.</p> <p>It is one of the most popular methods used for catalyst preparation.</p> <p>Produce higher conductivities when used in the preparation of the nanocomposites of Silver-Silica.</p>   | <p>Although appears simple, it is a complex physical and chemical process that needs the knowledge of an expert.</p>   | [126,127]     |



|                                   |  |  |               |
|-----------------------------------|--|--|---------------|
|                                   | It is a versatile method which can be used for spin coating of film, co-polymer-based synthesis of porous silica and electrospinning of fiber.   |  |               |
| Direct polymerization of monomers | Used to produce membrane that shows high proton conductivity and exhibited swelling ratio that is low and acceptable. The performance of fuel cell was excellent when tested for validation. Method is highly versatile and can be used to produce so many new membranes depending on creativity of ideas. | Membrane properties were affected by carboxylation. Needs a comprehensive study of monomer properties before been selected for the reaction. | [116,118,119] |

### 3.3 Membrane properties

During the operation of fuel cells, so many reactions occur at the same time in the membrane. A slight change in any parameter causes a shift in at least two other parameters and therefore has an overall effect on the fuel cell. So many physical and chemical factors have been identified which can affect the performance of the fuel cell[128][129]; they include operating pressure, operating temperature[130], The type of electrolyte in use, The efficiency of the fuel cell, the catalyst used, reactant flow rates, reactants humidity, fuel cell mass balance (inlet flow rates and outlet flow rates), fuel cell energy balance among others. Experimental study of the effect of variable operating parameters on overall PEM fuel cell performance and spatial performance distribution by Zhang et al [131] shows that they have a huge effect. It was shown that when the back pressure is high the fuel cell shows an overall increase in performance, also relative humidity and

air stoichiometry. An increase in these other parameters corresponds to increase performance and improved homogeneity of current distribution of PEM fuel cells. Overtime the performance of fuel cell reduces after a period of time, this is due to decrease in durability often as a result of loading cycle and flooding[132].

For these review, some key properties have been identified and would be the focus of the review. They are as listed below; water uptake, physical properties, proton conductivities, gas permeation and water transport. Failure to manage these properties leads to another secondary scenario. For example, poor water transport can lead to poor water management which can result in either drying or flooding.

The properties of the membrane are very important as it determines the performance and durability. Although every property of the membrane is important, it is generally believed that the most important property of a membrane is proton conductivity. For a material to be considered as a membrane, it should have a high affinity for protons. The membrane should as well be durable, robust and resistant to chemical attack. The operating temperature range is an important factor to be considered when choosing the membrane materials thus it should have a wide temperature range about -30 to 200°C. For a material to be developed as a composite membrane, it must show the following properties discussed below.

### 3.3.1 Water uptake

The effect of water uptake on the fuel cell cannot be overestimated. This is because performance increase with increased proton conductivity which is dependent on water content [30]. It is calculated considering the weight of wet sample and the weight of the dry sample of the membrane expressed as a percentage of the dry sample as shown below[133];

$$\text{Water uptake} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \times 100\% \quad (1)$$

Water uptake changes with differences in the temperature therefore it values for water at room temperature is different to that of vapour. Though water uptake is necessary for the normal running of the fuel cell, it however results in swelling. The problem with swelling is that the membrane might not go back to its initial state after experiencing it and it is necessary for a membrane to have good water uptake qualities [28]. Chien et al [134] studied and develop a method to produce activated carbon/Nafion hybrid membrane for proton electron membranes.

The membrane when tested shows having high water-uptake properties improves proton conductivity, gave a better performance than Nafion-211 and also has lower resistance. Furthermore Silva et al [135] went further to identical key parameters to be used in the selection of membrane for PEMFC and DMFC. It is worthy of note that water uptake and pervaporation were also included.

### 3.3.2 Physical properties and operating parameter

A lot of operations within the PEM fuel cell allow it to lose its physical appearance. This is due to a change in physical properties and these affect the performance of the membrane. It either improves it or reduces its performance. Parameters such as operating temperature, operating pressure, membrane thickness can be regarded as physical properties. The effect of the operating temperature on the membrane is highly significant. This is because so many important activities that enable efficient performance are dependent on it. Properties like protonic resistance and gas diffusion which are necessary for mass transport are highly dependent on the operating temperature. Operating temperature also affects the conductivity of the membrane. At higher temperature there will be creation of more protons and increased rate of electrochemical reaction. On the other hand, it leads to increased resistance in the membrane. However, the effect of the increased resistance is reduced because more water molecules which have been formed in the cathode due to increased electrochemical reaction help to keep the membrane hydrated thereby reducing the resistance towards the ions. Experiments by Belkhir et al [136] show a better polarization curve and increased power density at increased temperature with increased hydration. For a material to be a good membrane it needs to have good physical properties. Fathima et al [57] while studying and characterizing polymeric membranes was able to show that they have good physical properties. This includes good thermal stability, good mechanical properties and acceptable level of conductivity with regards to sulphonation level. Increase in temperature usually leads to increased pressure when other conditions remain constant. This is the same with the relationship between operating temperature and operating pressure. Literature has established that the fuel cell performs better with a thinner membrane. Investigations into water profile in PEM fuel show that resistance increases as thickness increases. This was shown in an experiment involving Nafion 112 and 115 (thicker). Also, the tendency of having a drying effect is low with thinner membranes. This is because of the ability

of the back diffusion of water to suppress it [137]. Additionally, because of the reduced resistance, the number of protons which is responsible for conductivity increases and therefore an increase in flux is observed [138].

### 3.3.3 Proton conductivity

Proton conductivity is the most important properties of a membrane to be used in a fuel cell. It increases with increasing temperature and increasing water content. It is also affected by the reaction environment. Work by Chaiwat and Stuart [139] shows that the reaction environment also affects proton conductivity. Proton conductivity was shown to increase with increased acidity. This is supported with experiments by Kuwert et al [140], Zhang et al and Yin et al [71-72]. Hydration also had effects on conductivity. More water shows more  $H^+$  ions and therefore increased concentration. Furthermore, with either hydration or acidity, proton conductivity increases with increasing temperature.

Rikukawa and Sanui [43] in their work on proton-conducting polymer electrolyte membrane established that hydrocarbon polymers can be used to produce membranes with high protonic conductivity. They were able to cover for the deficiencies of the perfluorinated polymers electrolytes; it being expensive and exhibiting low protonic conductivities at low humidity and high temperatures. However further work still needs to be done to improve its durability and also optimization of its performance in the fuel cells. Another work on proton conducting PEM was also done by Rao et al [143].

The Nafion membrane is popularly used because of its proton conductivity which is very good, and attempts were presently being made to develop a membrane of similar properties or better.

### 3.3.4 Water transport

The major problem facing the membrane is the water management. The consequence of not getting this right leads to problems associated with durability, water transport in the stack and thermal management [144]. Too much water can result in flooding and shortage of water can also result in drying. None of these is acceptable as they both have effect on the performance of the PEM fuel cells as usually shown on the polarization curve. It is necessary to know how the properties of different components like gas diffusion layer, bipolar plates etc. affect gas structure

and water transport in a PEM fuel cell. Efficient understanding of water transport will help to solve various issues associated with water management and leads to improvements in stack component design[145].

In a PEM fuel cells, due to the electrochemical reaction, production of water occurred at the cathode side. This is because of the dragging of water by protons passing the electrolyte from the anode to the cathode. This is described as electroosmotic drag. The rate at which water is generated can be calculated. It is dependent on the current density ( $A/cm^2$ ) and Faraday constant (F). Its unit is  $mols^{-1}cm^{-2}$ . Water generation is dependent on the current density and Faraday constant. The electroosmotic drag and water generation has a linear relationship. Water has a great influence on membranes in PEM fuel cells. Roy et al [146] studied the influence of its chemical structure and its composition and revealed a strong relationship existed between morphologies, structures and composition of different types of water. It helps to determine the relationship it has with the other materials and components in the fuel cell.

### 3.3.5 Gas permeation

Theoretically a material used as membrane should be impermeable however due to it having other important characteristics like porosity, water content and hydrogen and oxygen solubility in water, gases were able to permeate through the membrane and these permeations is one of the major causes of membrane poisoning.

Permeability is dependent on properties such as diffusivity and solubility. The relationship that can be expressed as [147]

$$P_m = D \times S$$

Where  $P_m$  = Permeability,  $molcm^{-1}cm^{-2}Pa^{-1}$  called Barrier

$D$  = diffusivity,  $cm^2s^{-1}$

$S$  = solubility,  $molcm^{-3}Pa^{-1}$

Fig. 16 [148] shows a diagrammatical representation of gas transportation in a membrane of proton electron membrane coated with catalyst including all the different activities represented with arrows. These activities are labelled using arrows 1 through 5. Arrow 1 shows reverse diffusion by water from cathode to anode, arrow 2 shows the permeability of hydrogen without electrochemical oxidation from anode to cathode. Permeability of oxygen was shown with arrow 3 and then water generation and nitrogen permeability represented with arrows 4 and 5. It is

worthy of note that gases like Helium, carbon gases, ammonia that can be found in atmospheric air can be present.

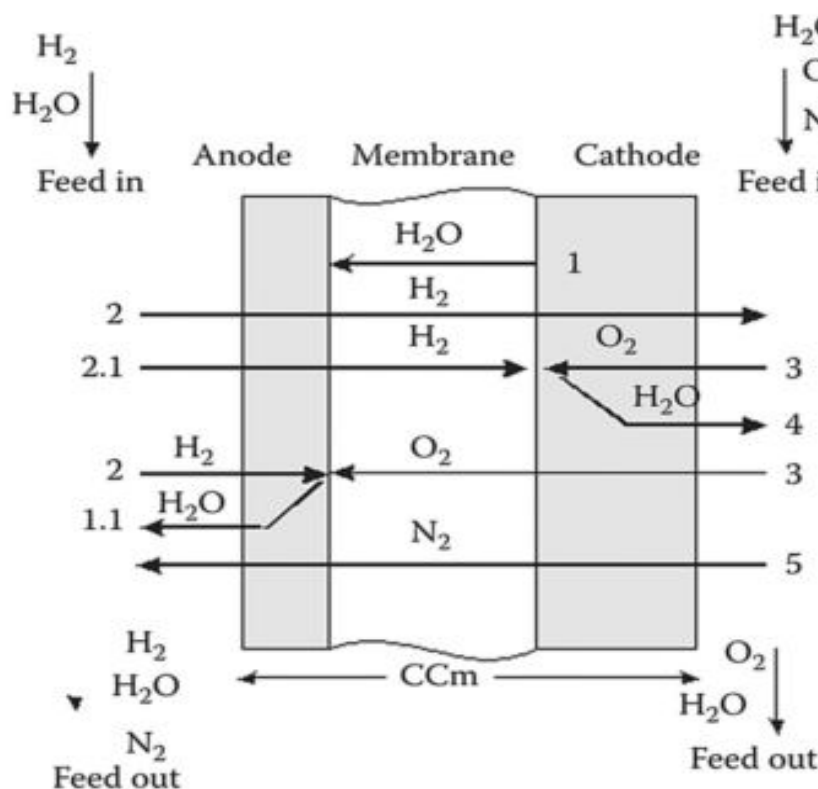


Fig. 16 Gas transport and permeability in a proton electron membrane coated with catalyst [148]

#### 4.1 Future work

All the achievements recorded so far in the fuel cell technology has been due to continued research on PEM fuel cell and renewable energy in general [149–160]. Discussions in this work showed that a comprehensive knowledge of materials and properties is necessary toward choosing the correct preparation method. The preparation method, on the other hand, determines the final product and its quality. It is believed that further work and research in the following area discussed below will help to improve the preparation methods.

In the irradiation grafting polymerization method, there are so many areas that need to be improved. This is because the method is relatively new. It involves a lot of expensive chemicals and a deep understanding of chemistry. More research needs to be focused on stoichiometry and

relationships between different reactants. The process needs to be made simple so that it can be easily reproducible.

The crosslinking method have a potential to be used in high temperature PEM fuel cell. This is noted in membranes whose sulphonation is of higher degree. Further work needs to be done to confirm it suitable and possible upscale. In addition, more work needs to be done to improve the activation energy and increase water uptake especially when it is crosslinked with s-IPN.

The plasma grafting polymerization method is very promising and new. It can be used to modify existing PEMs or produce new ones. More work needs to be done to establish areas of high performance so its advantages can be maximized.

The sol method is popular and have been used. Its physical and chemical process is complex, and efforts can be made to simplify it. It has been confirmed that the properties of the membrane are affected by carboxylation in direct polymerisation of monomers method. Further work could be done to ensure the right sets of monomers is selected for reaction.

#### **4.2 Conclusion**

This work presented a thorough investigation into the state of PEM fuel cell membranes with more emphasis on the methods of preparation and the important properties needed for good performance. PEM fuel cell technology is indeed the future of the renewable energy sector but there is a need for cheaper but effective material that will reduce the overall cost of fuel cells without any limitation to its performance. The membrane performance depending on the preparation approach used is also captured in this investigation. In a nut shell, the work exposes the need for further research to be carried out to increase the overall performance of the fuel cell. For instance, investigations must be carried out on the membrane to increase the protonic conductivity of the membrane and the platinum on the catalyst layer must be reduced further. Composite membranes are suitable for use in fuel cells for the automobile industry due to their wider operating temperature range above 95°C. Fuel cell with composites showed voltages increase by up to 11% when used at 95°C and up to 17% when the reactive substances used are dry hydrogen and air [61]. There is still the need for further research to be carried out to increase the overall characteristic performance of the fuel cell when composite membranes are used. Other types of membranes like the commonly used fluorinated membranes are still undergoing a change in terms of their operating ranges even though they have high stability in oxidising and

reducing environments. Currently fluorinated membranes function best at temperatures well below 100°C [30] and this limits their use in several applications. The conductivity of non-fluorinated membranes is low, and their material cost is high, and more research is needed to reduce the cost and improve their other characteristics. Partially fluorinated membranes have good stability [Ref] but again just like non-fluorinated membranes their cost makes them less favourable and more work is required to achieve reductions in cost.

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