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Review Paper

Review on the Proton Exchange Membrane Fuel Cell (PEMFC) in Benin Republic (West Africa)

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Abstract

Energy is fundamental to the socio-economic development of all nations. But the use of fossil fuels causes problems for life on earth because of poorly controlled emissions of greenhouse gases, responsible of global warming. It is therefore necessary to move towards green renewable energy, more promising sources of energy, "clean" and respectful of our environment. Hydrogen seems more reassuring because of its abundance in nature and no Carbone emission through fuel cells technology. The Proton Exchange Member Fuel Cells (PEMFC) use hydrogen as a fuel to generate electricity, but it remains very underdeveloped in West Africa, mainly in Benin Republic. The membrane, one of the fuel cell's components is the core material of the fuel cells device, not only because it allows the exchange of protons, transferred through the electrodes of the fuel cells, but also because of the rarity of Nafion, the best material for manufacturing the existent composite membrane. The main objective of our study is to build literature review on proton exchange membranes which can lead us to manufacture local composite membrane with improved properties, compared to Nafion membrane and expand the use of fuel cells in our region. The Results show that several authors propose chemical protocol to obtain chitosane and chitin, which properties fit those of composite membrane proton exchange. The membranes of composite fuel cells can be made using certain crustaceans' shells, such as crabs, shrimps, and over material like coconut husks, clays and snails' shells. The authors also present the advantages, the limitations of fuel cells functioning and the social economic aspect of fuel cells in general.

Keywords: Renewable energy, dihydrogen, fuel cells, PEMFC, chitosane, Nafion.

Introduction

Energy is fundamental for the development of all nations because of its necessity in industrial and daily activities[1]. But, the dominating use of crude oil and coal as main source of energy negatively impacts environment because of the massive rejection of carbone dioxide (40% of all energy emissions with 34% from transportation only)[1-3], one of the main greenhouse gases, responsible of global warming[2]. It is therefore necessary to promote research for the use of renewable energy as fundamental issue to improved energy transition and carbon-free power production[4]. Let's remind that renewable energy contribute for around 20% of the worldwide energy consumption and hydrogen's contribution is less than 4%. The use of hydrogen through fuel cells is more reassuring as green power because of its high density and abundance in atmosphere[5]. Fuel cells devices use hydrogen to generate electricity in several domain for functioning[2,6], but the devices are not yet well developed in West Africa, mainly in Benin Republic. Authors like Fopah-Lele et al.[7]; Jumare et al.[8] and Towanou et al.[9] have recently carried out studies related to the storage of energy and the production of hydrogen for fuel cells in West Africa (Benin Republic and in Nigeria). Their studies show how necessary is the development of hydrogen storage for the energetic mix and autonomation. But, deep researches for improving knowledge on fuel cells are needed in West Africa. Fuel cells are an electrical energy generator that directly transforms the chemical energy of the fuel into electrical energy[10]. Fuel cells are one of the great solutions to avoid the rejection of greenhouse gases and to overcome the problems related to the intermittent energy storage[11]**.** According to Franck Lacaze et al.[12], fuel cells are not only necessary in the improvement of economy but also a promising solution in the chain of energy conversion[13]. Several types of fuel cells are found from research[14,15]. Among them, one can cite: the alkaline fuel cells (AFC), the Proton Exchange Membrane Fuel Cells (PEMFC), Polymer Electrolyte Fuel Cells (PEFC), Solid Oxide fuel Cells[29,45], Direct Methanol Fuel cells (DMFC) and Phosphoric Acid Fuel Cells (PAFC)[14,15].

The current study focuses on the Proton Exchange Membrane Fuel Cells because of many advantages: i. First, PEMFC can operate at low values of temperatures, facilitating the rapid start of big systems like vehicles, ii. Secondly, PEMFC are equipped with membrane, made of thin sheets of high mechanical resistance, which keeps them strong and allowing to obtain high density power[16]. For this category of fuel cells, an electrolyte made of *"Nafion",* core material of the fuel cells is used**.** The membrane plays a key role, not only because it allows the exchange of protons generated from the anode to the cathode, but also because of its high cost, excessively expensive, costing thousand times more expensive than gold[2]. The study of the membrane within the PEMFC is the subject of this work through the National Fund for Scientific Research and Technological Innovation project in Benin Republic. The main objective is to develop a literature review which setting up local materials capable to stand in the membrane for *Nafion*, with similar characteristics as those of the *Nafion*. These materials could better fit the properties of the *Nafion* membrane in the PEMFC type. From this literature review, we define future research orientations and challenges for making a local PEMFC for the local energy transition. This article is organised as follows: section 2 presents the general information's related to fuel cells, section 3 describes the functioning of the existent fuel cells in Abomey-Calavi University, section 4 presents the probable local material which can be used to make composite membrane, section 5 presents the basic reagent and the chemical protocol for composite membrane. The paper ends with the conclusion section for future studies.

General information on fuel cells

Historical description of fuel cells: According to Zhang[14], a fuel cell is an electrical energy generator that directly transforms the chemical energy of fuel into electrical energy. The electric current is continuously produced as long as the cell is supplied jointly with fuel (hydrogen) and oxidizer (oxygen from the air), making fuel cells different from batteries, accumulators and other cells, where a limited quantity of electrical energy is stored in chemical form and which must be recharged when possible (vehicle battery) or replaced.

The first idea of research related to fuel cell was taken in 1806 by the English chemist and physicist, Sir Humphry Davy who, by carrying out the electrolysis of pure water, obtained distinctly hydrogen and oxygen as the only products[17]. Then, the use of electricity for the decomposition of water into hydrogen and oxygen leads some scientists to perform the inverse process in order to generate electric current from hydrogen and oxygen[18]. Thus, Sir William Robert Grove carried out in 1839, the experiment by assuming that the reverse study of water electrolysis might be possible[19], leading to the first gas battery and later became a fuel cell[17]. The author generated current using a hydrogen-oxygen cell with porous platinum electrodes and sulfuric acid as electrolyte. The figure 1 presents the earlier experimental protocol, constituted with a tube in U-shape, two porous platinum electrodes and sulfuric acid as the electrolyte[18].

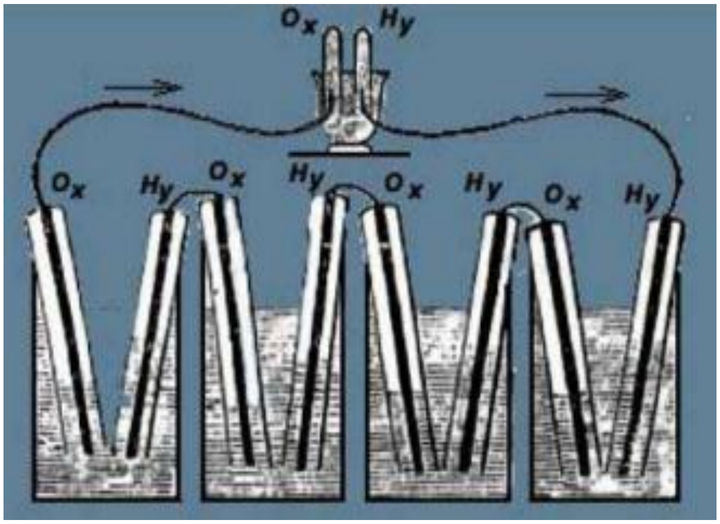


Figure-1: The Experiment System of Sir W. Grove in 1839 from[20].

Sir William Grove's experiment is a crucial historical experiment in the field of electrochemistry that played a key role in the later development of the fuel cell, also known as the Grove cell. Sir William Robert Grove, a Welsh lawyer and inventor, performed this experiment in 1839, making him one of the first researchers to explore the fundamentals of producing electricity from chemical reactions.

Grove designed a primitive fuel cell for his experiment. The fuel cell was composed of two electrodes, a platinum electrode (cathode) and a hydrogen electrode (anode), immersed in a diluted sulfuric acid (H_2SO_4) solution. The sulfuric acid solution was used as an electrolyte. In this experiment, Grove injected hydrogen gas (H_y) into the anode of the cell. Hydrogen is a fuel that reacts with oxygen (O_x) from air in the presence of the electrolyte (sulfuric acid) to produce water. When hydrogen is introduced in the anode, it undergoes a chemical oxidation reaction to form hydrogen ions (H^+). The H^+ protons migrate through the electrolyte towards the cathode. Along the way, they carry positive electrical charges (cations) and generate an electric current in the external circuit that connects the electrodes. At the cathode, hydrogen ions (H^+) capture electrons from the chemical reaction of reducing oxygen (O_2) present in the air. This reduction allows water (H_2O) to be formed. The hydrogen oxidation reaction at the anode and the oxygen reduction reaction at the cathode generate water (H_2O) and electricity simultaneously. Water was collected at the cathode in the form of condensation. Grove was able to observe that his device actually produced electricity continuously by exploiting the chemical reaction between hydrogen and oxygen.

During 1889, Mond and Langer improved Grove's system by introducing a platinum catalyst[21]. In 1945, studies on the technological improvement, described by Liebhavsky HA[22], for an industrial development of fuel cells was carried out[23]. The first applications of fuel cells were made in the space programs of the National Aeronautics and Space Administration (NASA) during the APOLLO mission in 196824. In 1970, DuPont developed the Nafion membrane, which serves as the electrolyte for PEMFC fuel cell type[22]. In 1977, a 1-Megawatt installation of fuel cells was set up in New York[20]. In 1993, the Canadian company Ballard brought technical advances with the introduction of the first hydrogen fuel electric vehicles[23]. This company has strongly contributed to the development of the Proton Exchange Membrane Cells. Today, several cars manufacturers in Europe, America, Asia are gradually developing and improving the fuel cells adventure[25]. The Figure-2 below illustrates the chronological evolution of the development of the fuel cells:

Principles of fuel cells functioning: A fuel cell is an assembly of elementary cells, comprising two electrodes (anodes and cathodes) loaded with catalyst (usually platinum), separated by an electrolyte, which role is to allow the transfer of ions from one electrode to another, under the effect of the created electric field[26]. Let's remind that the principle of the fuel cell was demonstrated by Sir William Grove[19] in 1839. Indeed, the electrical generator of fuel cells is a device, capable of supplying a large quantity of free electrons to the negative (–) electrode and a large quantity of positive ions to the positive (+) electrode[27]. It is a controlled electrochemical combustion of hydrogen and oxygen with simultaneous production of electricity, water and heat[10]. The following reactions are observed from one electrode to another:

-At the anode, the oxidation reaction occurs:

$$2H_2 \rightarrow 4H^+ + 4e^- \qquad (1)$$

-At the cathode, the reduction reaction occurs:

$$\mathrm{O_2 + 4H^+ + 4e^- \rightarrow 2H_2O + Q(heat)} \qquad (2)$$

The global equation of the reaction is written:

$$\mathrm{2H_2 + O_2 \rightarrow 2H_2O + electricity + heat} \qquad (3)$$

The Figure-3 below schematically presents the operating principle of a fuel cell. Air flows to the cathode through channels on the other side of the cell. At the cathode, the electrons returning after doing work react with oxygen in the air and the protons, which have moved through the membrane inside the cell to form water. This reaction is exothermic, generating heat that can be used outside the fuel cell.

Applications-Advantages and Disadvantages of fuel cells: Fuel cells have many applications in several domains: In the stationary domain[29,30] fuel cells are used to produce electrical power which later can be injected in the grid through the electrical network. There are generally two applications: (a) collective production which power varies from 200kW to few Megawatts and (b) domestic production[31], where power varies from 2 kW to 7kW. A large number of little installations with power varying between 1 kW for individual houses to a few hundreds of kilowatts for residences, have been installed in several countries[32]. The most commonly used fuel cells are those that have a high operating temperature (Solid Oxide Cell and Molten Carbonate Cell), where the use of the heat released for heating and the production of water vapor provides maximum energy efficiency[29].

In the domain of transportation[31], the origins of the development of the fuel cells begin since the early 90s[33] for equipping vehicles with fuel cells[33]. In that domain, the conditions required that fuel cells must be used for a short period of time, suitable for fuel cells operating in low temperature, especially PEMFC fuel cells type.

In portable applications[30], the fuel cell concerns mobile phones and laptops. The user recharges his laptop as one recharges a lighter or an ink pen, in a few seconds and each recharge gives 3 to 5 times more autonomy than a current battery[34]. The batteries mostly used in this field are the DMFC type.

Although fuel cells are not yet competitive compared to other energy sources (solar or wind energy, etc.), they have the advantage of being more efficient, causing less pollution and considerably reducing noise pollution.

Among the advantages of fuel cells as solution of the future in the fields of electrical energy and automotive, fuel cells have a good energy efficiency[13]; they have low noise, low thermal and vibration emissions[16]. Fuel cells can operate easily at low temperatures and require little maintenance process, reducing sometimes the costs[34,35]. Fuel cells have also the advantage of no carbon dioxide emissions in atmosphere; it is a compact, light and silent device[36]. They have a solid electrolyte which makes assembly easier and cheaper[37].

If fuel cells are so interesting, why are they inaccessible in the market? The lack of fuel cells' availability is due mainly to: i. the high cost of the membrane's technologies, which require a large budget before get it. Their substitution to fossil fuel technology also encounters the problem of the management of the water in the membrane electrolyte, which remains a crucial point to be controlled for improving their efficiency[30]; ii. The lack of companies worldwide, capable of hydrogen safe production and dispatching for the functioning of fuel cells[38]; iii. The limited lifetime of certain type of fuel cells[39] (about 5000 hours). iv. The difficulties to compress adequately an appropriate quantity of hydrogen in small containers for the functioning in the low temperature fuel cells for the automotive market[32,40].

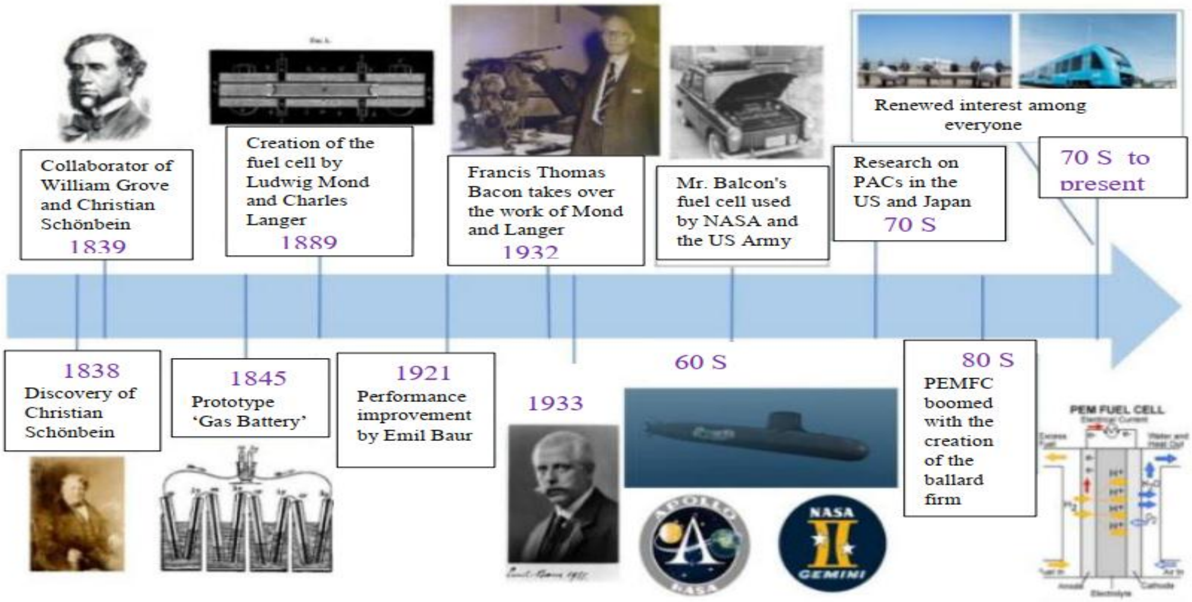


Figure-2: Chronological arrow of the evolution of the fuel cells[10].

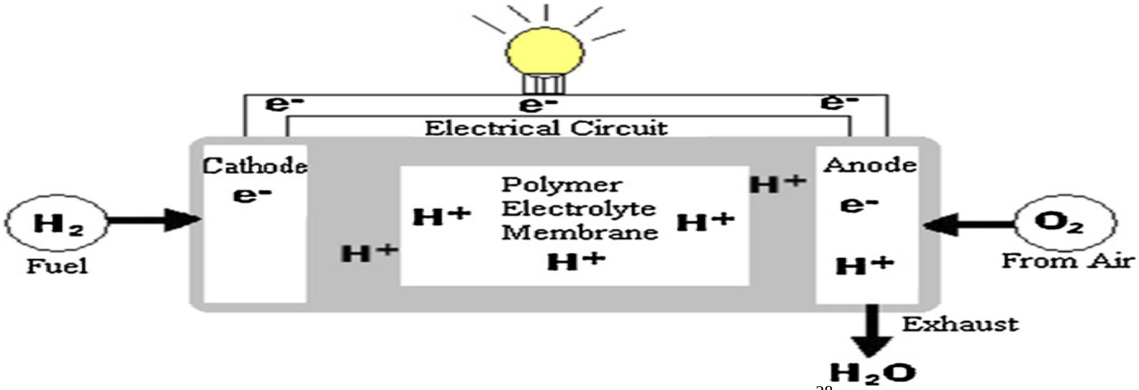


Figure-3: Operating principle of a fuel cell from[28].

Classification of fuel cells: There are several types of fuel cells, generally differentiated by the nature of the electrolyte used and by the operating temperature[34]. One can cite: i. Proton Exchange Membrane Fuel Cell (PEMFC)[41]; ii. Direct Methanol Fuel Cell (DMFC)[42]; iii. Alkaline Fuel Cell (AFC)[43]; iv. Phosphoric Acid Fuel Cell (PAFC)[44]; v. Solid Oxide Fuel Cell (SOFC)[45]; vi. Molten-Carbonate Fuel Cell (MCFC)[15].

Proton exchange membrane fuel cell (PEMFC): PEM fuel cells use a proton exchange membrane as the electrolyte. In PEMFCs, hydrogen is activated by a catalyst to form proton ion and eject an electron at the anode. The proton passes through the membrane while the electron is forced to flow to the external circuit and its motion generates electricity. The electron then returns to the cathode and interacts with the oxygen and the proton ion to form water. Chemicals are as follows:

Anode: $H_2(g) \rightarrow 2H^+ + 2e^-$ (4)
Cathode: $(1/2)O_2\,(g) + 2H^+ + 2e^- \rightarrow H_2O$ (5)

Generally, PEMFC is composed of bipolar plates and a Membrane-Electrode Assembly (MEA). The MEA is composed of a dispersed catalyst layer, a carbon cloth or a gas diffusion layer, and a membrane[46]. PEMFCs are low temperature fuel cells operating between 60°C and 100°C. They are compact and lightweight systems with a quick start-up process. They have a longer lifespan and are cheaper to manufacture[47]. The total cost of a car equipped with the PEMFC system is $500-600/kW, which is 10 times higher than that of cars using an internal combustion engine (IEC)[48]. From an efficiency perspective, the higher the operating temperature, the higher the efficiency can be. The electrical efficiency of PEMFCs is between 40% and 50%, the output power of which can reach 250 kW. PEMFC systems are typically used in portable and stationary applications requiring minimal maintenance because there are no moving parts in fuel cells. Fuel cell vehicles constitute the most promising application of PEMFC systems.

Direct Methanol Fuel Cell (DMFC): Due to its low temperature operation, long life and rapid refueling system characteristics, direct methanol fuel cell (DMFC) is a cell whose power source is suitable for portable energy needs. Like PEMFCs, DMFCs are considered environmentally friendly since there is no production of sulfuric or nitrogen oxides (only carbon dioxide) [49]. The energy source for DMFC systems is methanol. As shown in the equations, at the anode, methanol is reformed into carbon dioxide (CO_2) while at the cathode, steam or water is formed using the oxygen available in the air. The reactions are presented in the equations:

Anode:$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ (6)

Cathode:$(3/2)O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ (7)

Methanol is used in DMFCs in vapor or liquid form but does not work perfectly for mass transfer and requires high localized cooling at the anode. Likewise, the passage of methanol from the anode to the cathode and the release of gas at the surface of the electrocatalyst lead to a reduction in the performance of liquid-fed cells[50]. Proton exchange membrane (PEM) is considered as the main element of DMFCs to provide low penetrability and high proton conductivity. Additionally, it provides high thermal and chemical stability for smooth operation of the DMFC. Asahi Chemical's Flemion and Dupont's Nafion are the most commonly used perfluorinated ion exchange polymers for DMFC[51].

Alkaline fuel cell (AFC): The alkaline fuel cell generates electrical energy using the alkaline electrolyte potassium hydroxide (KOH) in a water-based solution. The presence of hydroxyl ions passing through the electrolyte makes it possible to create a circuit and extract electrical energy[52]: The different reactions that occur are written (Figure-6):

Oxidation:$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$ (8)

Reduction:$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (9)

AFCs are classified as low operating temperature fuel cells with low-cost catalysts. The most used catalyst is nickel. NASA first used AFCs to provide potable water and electricity to shuttle missions for space applications where they are currently employed in submarines, boats, forklifts and applications niche transport[53].

Phosphoric Acid Fuel Cell (PAFC): Although AFC was the first type of cell to be used in electrical applications, phosphoric acid (PA) fuel cells were the first type of cell to be commercialized after their first development in the mid-1960s. Phosphoric acid fuel cells (PAFC) use carbon paper electrodes and liquid phosphoric acid (H_3PO_4) as the electrolyte. The charge carrier in this type of fuel cell is the hydrogen ion (H+ or proton). They pass from the anode to the cathode through the electrolyte and the expelled electrons return to the cathode through the external circuit and generate the electric current. At the cathode, water is formed as a result of the reaction between electrons, protons, and oxygen in the presence of a platinum catalyst to accelerate the reactions. The expelled water is typically used in heating applications. The redox reaction that takes place in the anode is oxidation and a reduction reaction at the cathode[54]. The reaction equations are written:

Oxidation:$2H_2 \rightarrow 4H^+ + 4e^-$ (10)

Reduction:$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (11)

The PAFC does not require pure oxygen for its operation since CO_2 does not affect the performance of the electrolyte or the cell. They run on air and can easily be operated with reformed fossil fuels. Currently, PAFC systems are at the commercial stage with a capacity of up to 200 kW and systems with higher capacities (11 MW). PAFCs are expensive to manufacture due to the need for a finely dispersed platinum catalyst covering the electrodes.

Solid Oxide Fuel Cell (SOFC): Solid oxide fuel cells (SOFCs) are high temperature fuel cells with solid metal oxide ceramic electrolyte. SOFCs typically use a mixture of hydrogen and carbon monoxide formed by the internal reforming of hydrocarbons and air as the oxidant in the fuel cell[55]. Yttria-stabilized zirconia (YSZ) is the most commonly used electrolyte for SOFCs due to its high chemical and thermal stability and pure ionic conductivity[56]. Oxygen is oxidized in a reduction reaction at the cathode and fuel oxidation occurs at the anode. The reaction equation is written:

Oxidation: $(1/2)O_2(g) + 2e^- \rightarrow 2O^{2-}(s)$ (12)

Reduction:$O^{2-}(s) + H_2(g) \rightarrow H_2O\ (g) + 2e^-$ (13)

SOFCs are well adopted with distributed power generation systems large-scale with a capacity of several hundred MW. SOFC systems are reliable, modular and fuel adaptable with low harmful gas (NOx) emissions. They can be considered as local electricity production systems for rural areas without access to public networks.

Alkaline fuel cell (AFC): The alkaline fuel cell generates electrical energy using the alkaline electrolyte potassium hydroxide (KOH) in a water-based solution. The presence of hydroxyl ions passing through the electrolyte makes it possible to create a circuit and extract electrical energy[52]: The different reactions that occur are written:

Oxidation:$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$ (14)

Reduction:$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (15)

AFCs are classified as low operating temperature fuel cells with low-cost catalysts. The most used catalyst is nickel. NASA first used AFCs to provide potable water and electricity to shuttle missions for space applications where they are currently employed in submarines, boats, forklifts and applications niche transport[53].

The Table-1 shows an overview of Membrane/electrolyte, combustible, Oxidant, Ion used, Power Range, Electrical Cell, Efficiency for system/stack., Optimum operating temperature, Advantages, Disadvantages and the applications of each type of fuel cell.

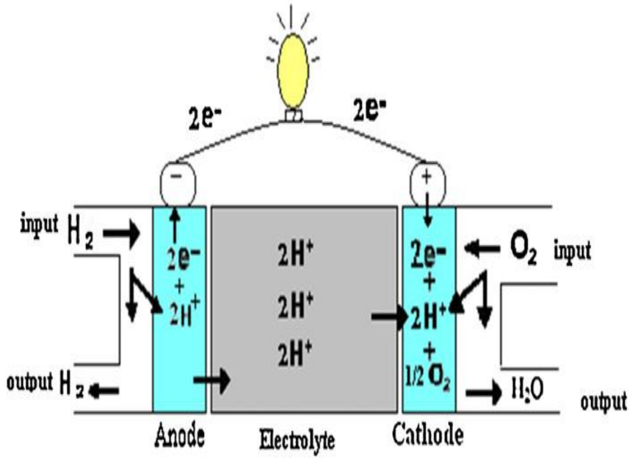


Figure-4: Proton exchange membrane fuel cell (PEMFC)[57].

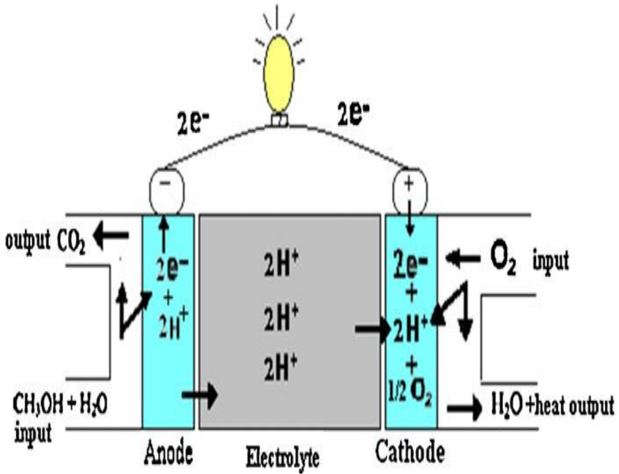


Figure-5: Direct methanol fuel cell (DMFC)[57].

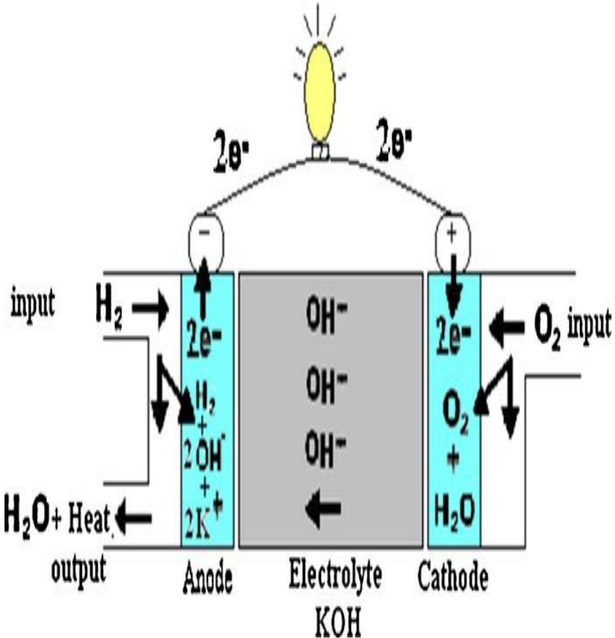


Figure-6: Alkaline fuel cell (AFC)[57].

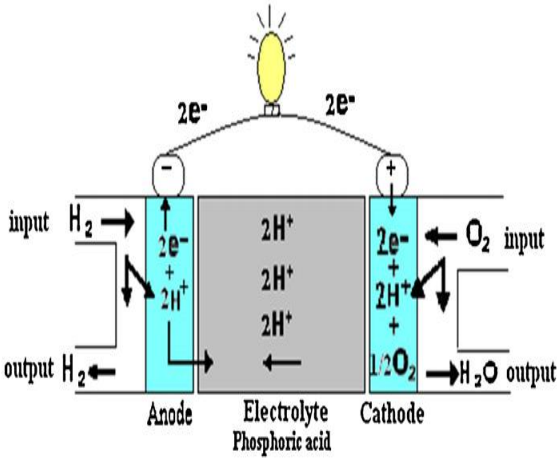


Figure-7: Phosphoric acid fuel cell (PAFC)[57].

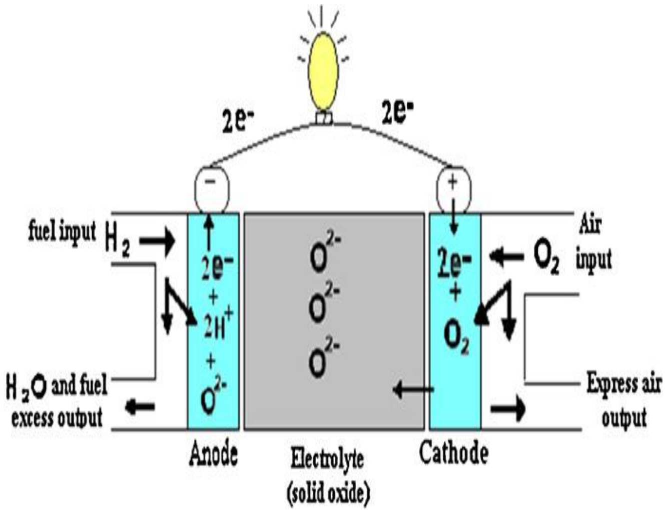


Figure-8: Solid–oxide fuel cell (SOFC)[57].

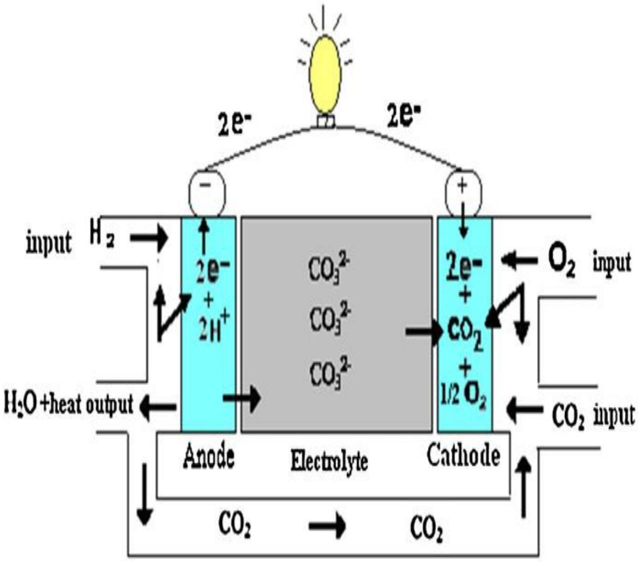


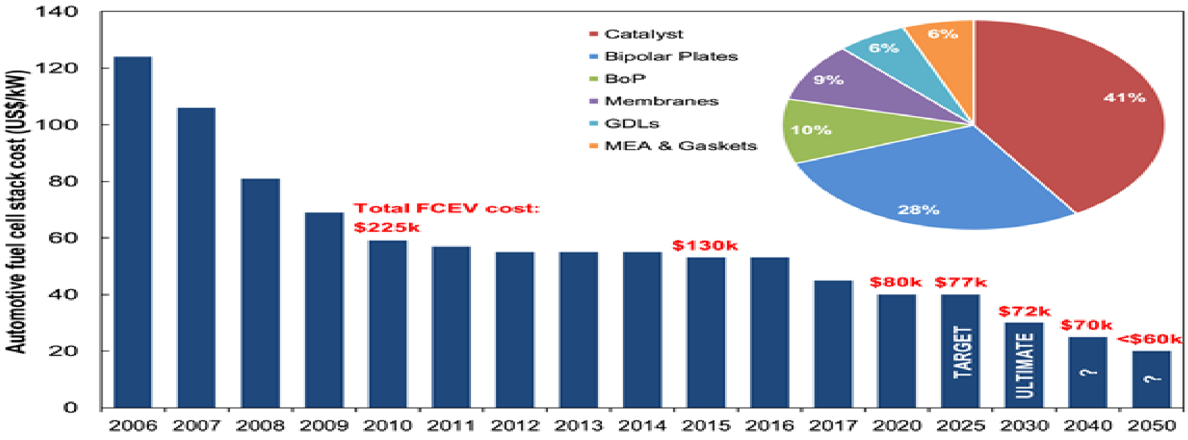
Figure-9: Molten carbonate fuel cell (MCFC)[57].

Analysis of fuel cells prices in the international market: Cost is a crucial factor for the increased commercialization of fuel cells. Today, fuel cell costs vary widely depending on cell type, size, technology and application. However, it is possible to identify some general trends: Thus, proton exchange membrane fuel cells (PEMFCs) often have high costs due to the use of platinum catalysts and expensive membranes like *Nafion*[41]. However, their high energy efficiency makes them attractive for applications requiring high performance[36,41]. Solid oxide fuel cells (SOFCs) have high costs due to their high operating temperatures and the need for expensive thermal support materials[35]. Alkaline fuel cells (AFCs) are less expensive than PEMFCs and SOFCs, but are limited to specific applications due to their alkaline liquid requirements[43]. Molten carbonate fuel cells (MCFCs) are moderately expensive and can be used in some stationary applications[64]. Acid phosphorus fuel cells (PAFC) have high costs and are generally used in stationary applications[44]. Direct Methanol fuel cells (DMFC) use liquid methanol as fuel and are mainly used in portable applications, such as cell phone chargers[42]. DMFC costs are influenced by the cost of methanol, which can be high in some regions. The Table-2 presents the cost of fuel cells[36].

Among these different types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) are considered to be at the forefront of commercialization for portable and transportation applications due to their high energy conversion efficiency and to their low pollutant emissions[65]. Jiao et al. have shown that PEMFC technology prevails on the market, because it meets many applications[66]. But despite this particularity of its domination on over battery categories, two major points are still slowing down its development: i. First, the cost of the system is still relatively high and must be reduced significantly; ii. Secondly, its durability and its reliability in real conditions of use must be significantly increased in order to be able to compete with systems based on thermal motorization[67]. The Figure-10, presents the variation of the cost of the stack and its components on a manufacturing basis of 500,000 units/year[68] from Pollet et al.

According to the US Department of Energy (DOE)[69], the current cost of a PEMFC cell, projected on a production of 500,000 units/year, is approximately US$40/kW while a price of around US$30/kW would be necessary to compete with internal combustion systems[69]. Through the Figure-10; 41%, 28%, 9% and 6% of the total price come from the respective electrodes, bipolar plates, GDL and membrane. The second aspect that hinders the development of PEMFCs is its sustainability. According to the work of Jouin et al., the duration of a PEMFC system in stationary cycles is between 60,000 and 80,000 hours and that obtained in more dynamic usage profiles (automobile profiles) is only approximately 4000 hours[70]. DoE Satyapal estimates that a lifespan of between 5000 and 8000 hours should be achieved to make the system efficient with the solutions currently deployed[71]. For example, a comparison of the cost of the low temperature PEMFC cell shows that it varies from $250/kW to $600/kW while at high temperature, it varies from $600/kW to $1,100/Kw[71]. Furthermore, the price of membranes, which is around 600 euros per m^2, is prohibitive for the marketing of PEMFC batteries intended for the general public[41]. The various research studies over the last few decades aim to contribute to reducing the manufacturing cost of the Nafion membrane of the PEMFC battery due to the high cost of its synthesis. From, the above mention problems, it is necessary to carried out studies which objectives could lead to make popular and cheap the prices of fuel cells for a safe energy transition everywhere. The next section presents the study of one hydrogen fuel cell, which will be used to control and testing future generations of manufacturing fuel cells membranes in Benin Republic.

Study Equipments in Abomey-Calavi University: The Figure-11 presents a 50 watts fuel cell as study material. It is constituted of three main compartments: i. Block 1: Electrolysis compartment; ii. Block 2: Electronic block; iii. Block 3: Fuel cell block. Block 1 is constituted mainly of: 1.a: the demineralised water tank, 1.b: the gas separator, hydrogen from water, 1.c: the proton exchange membrane electrolyser, 1.d: the electrolyser control module.



Current Opinion in Electrochemistry

Figure-10: Evolution of the cost of the stack and its components on a manufacturing basis of 500,000 units/year[68].

Table-1: Comparative table of différent fuel cells technologies.

Type of fuel cell	PEMFC[33,59]	AFC[33,63]	PAFC[33,62]	DMFC[33,58]	MCFC[33,61]	SOFC[33,60]
Membrane/ electrolyte	Nafion	Alkaline	Phosphoric Acid	Nafion	Molten Carbonate	Yttria Stabilized Zirconia (YSZ)
Fuel	H_2	H_2	H_2	Methanol	H_2 produced from hydrocarbon	H_2 and CO produced from hydrocarbon
Oxidant	Air/O_2	O_2	Air/O_2	Air/O_2	Air/O_2	Air/O_2
Ion used	H^+	OH^-	H^+	H^+	CO_3^{2-}	O_2^-
Power Range	1 W-500 kW	10 W-200 kW	50 kW-1 MW, (250 kW Module typical)	100 mW-1 kW	<1 kW-1 MW (250 kW Module Typical)	5 kW-3 MW
Electrical Cell,	50–70%	60–70%	55%	20–30%	55%	60–65%
Efficiency for system/stack	30–50%	62%	40%	10–25%	45–55%	55–60%
Optimum operating temperature	~80 °C	23–70°C	180°C	> 60°C	550–700°C	700–1000°C
Advantages	Vast power range, Easy scale-up, Short start-up time, High power density	Possibility of replacing Pt, Cheaper, High activity, Short start-up time, Simple heat management, Can tolerate a very small Amount of CO, Fast kinetics.	Can tolerate 1–2% CO, Cheaper due to lower of Pt usage, Ability to be used in CHP systems, High stability, Low vapor pressure, Higher tolerance to CO_2.	No CO_2 emissions, Low start-up time, High energy density, Methanol is easy to obtain and store, Resistant to CO, poisoning, Methanol is cheap	High Efficiency, Variety of Fuel, Usable with gas turbines, Cheap, High activity, Supports internal reforming	High efficiency Fuel flexibility Can use a variety of catalysts Solid electrolyte reduces electrolyte management problems Suitable for CHP Hybrid / GT cycle
Disadvantages	Slow oxygen Kinetics, Heat and water management, CO poisoning, Requires high purity H_2	Intolerance to CO_2, Requires pure O_2	Long start-up time, Limitation in material selection, Low membrane ionic Conductivity, Low power density, Intolerant to CO	Fuel Crossover, Expensive (using Ru and Pt), Cathode Poisoning, Methanol is highly flammable, Methanol is toxic	Hardware corrosion, Low power density, Cathode dissolution, Long start-up time, Limitation in material selection, Hard to handle liquid electrolyte	High temperature enhances corrosion and breakdown of cell components Slow start-up Brittleness of ceramic electrolyte with thermal cycling
Applications	Backup power, Portable power, Small distributed Generation, Transportation	Submarines, Military, Spacecraft, Backup power	Distributed generation	Electronic devices (Laptops and Phones)	Auxiliary power, Electric utility, Large distributed generation	Auxiliary power Electric utility Large distributed generation

Table-2: Cost of fuel cells[36].

Fuel cells	PEMFC	AFC	PAFC	DMFC	MCFC	SOFC
Cost ($/W)	50–100	-	4–4.5	125	-	-

Block 2 is the electronic compartment: It is used to measure and display 3 parameters: (a) the current crossing the fuel cell, (b) the voltage of the fuel cell and (c) the generated electrical power. It is constituted of: i. DC current mode, ii. DC voltage mode, iii. DC power mode, iv. DC resistance mode

Block 3 is the fuel cell. It is constituted of: 3.a: the fuel cell control module; 3.b: the proton exchange membrane fuel cell.

The functioning of the three blocks is as follows: the demineralized water contained in the tank is sent to the proton exchange membrane electrolyser using a pump. This produces a reaction of decomposition of water into oxygen and protons at the electrodes (Anode and Cathode).

The first reaction takes place at the anode and separates the water into oxygen and protons according to the following reaction equation:

$$H_2O \to \frac{1}{2}O_2 + 2H^+ + 2e^- \qquad (16)$$

The Figure-12 indicates the schematic principle of a Proton Exchange Membrane Water Electrolyser (PEMWE).

Then, by the mean of the current circulating in the titanium bipolar plates, the protons cross the solid membrane made of *Nafion* 115 and converge towards the cathode. Likewise, the bipolar plates maintain the electrodes and the membrane when the electrons are circulating through the external circuit. The oxygen obtained and the excess of water are sent back to the water tank. The second reaction is produced at the cathode: two electrons circulate in the bipolar plate and recombine with two protons H^+ which come out of the membrane. Finally, hydrogen and water are obtained mixed. The whole is then converged to the gas separator where hydrogen is separated from the water. The equation of the reaction at the cathode is:

$$2H^+ + 2e^- \to H_2 \qquad (17)$$

The obtained hydrogen is sent into the anode of the proton exchange membrane fuel cell. The oxidation within the cathode allows the hydrogen to be separated into two protons H^+ and two electrons according to the following equation:

$$H_2 \to 2H^+ + 2e^- \qquad (18)$$

The electrons generate current flowing in the bipolar plates. These plates play the role of homogeneous distribution of gases on the electrodes and separate the gases between the anode and the cathode[6]. Thus, the protons cross the solid membrane. The final reaction inside the fuel cell occurs at the iridium cathode, where the oxygen from air recombines with electrons and protons to produce water vapor through an exothermal reaction (equation 7) as shown in the Figure-13. The equation of the reaction is:

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \to H_2O + Q(heat) \qquad (19)$$

The device, installed in the UAC campus is used for several local tests related to the membranes' manufacturing.

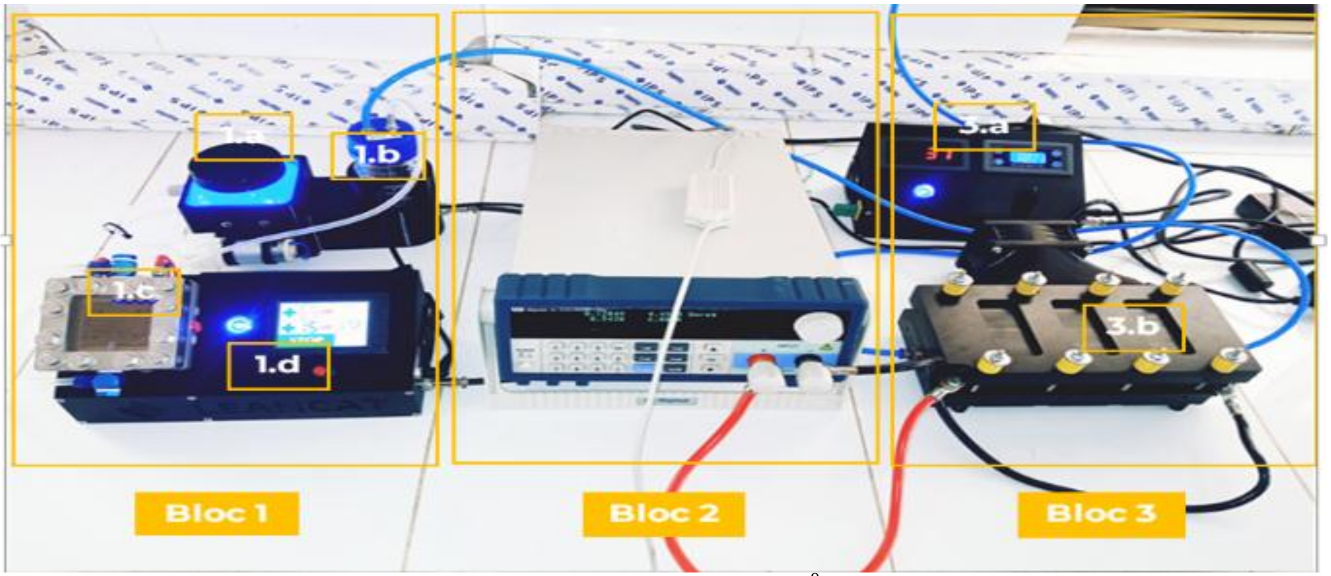


Figure-11: Presentation of the study material at Abomey-Calavi University[9].

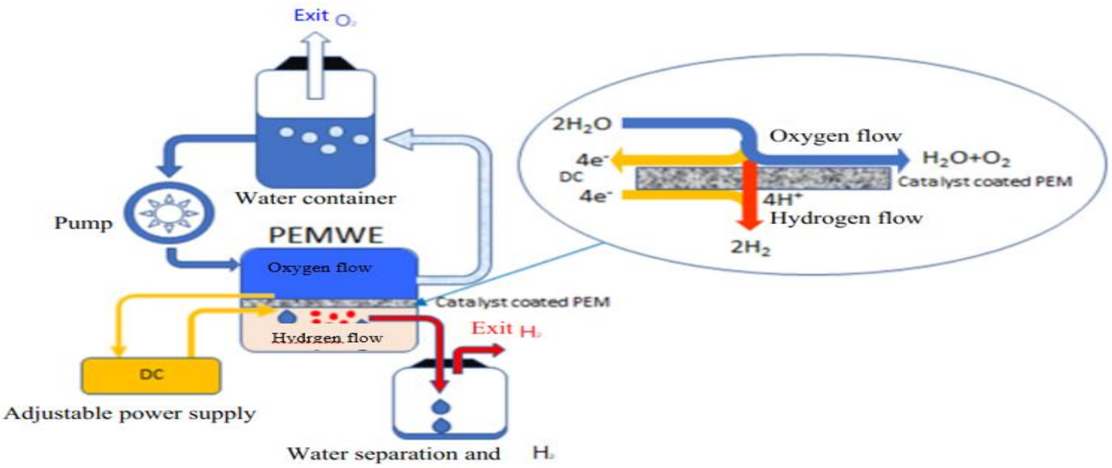


Figure-12: Operating principle of a PEMWE electrolyser **(**info@lean-cat.com**).**

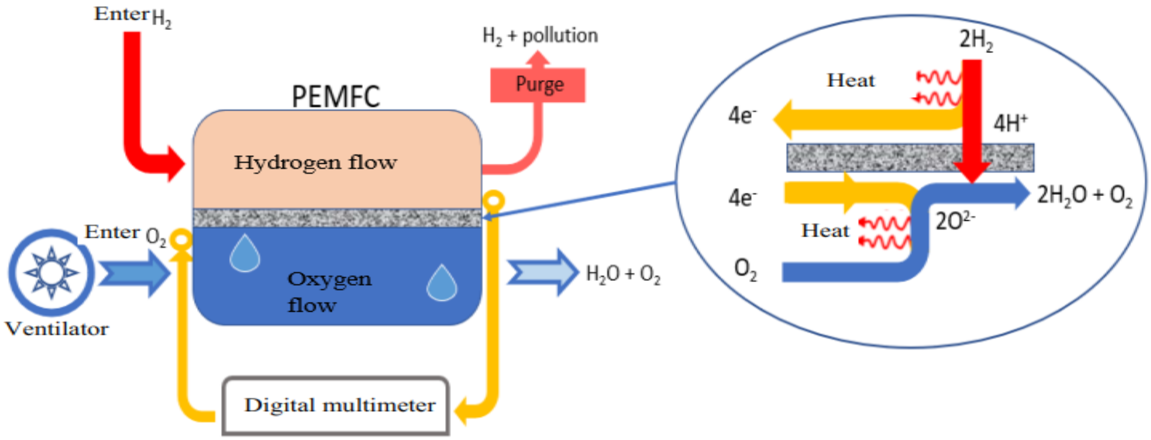


Figure-13: Operating principle of a PEMFC fuel cell (info@lean-cat.com).

Identification of local materials for membrane manufacturing

Reference membrane in PEMFC and its limits: ***Nafion* membrane:** The membrane plays an essential role during the functioning of the fuel cells[35]. It is essential to know the characteristics and properties which must remain intact during the use of the cells. The membrane must perform several functions[72]: i. isolate the two electrodes electrically, ii. ensure ionic conductivity by allowing the transfer of ions from one electrode to the other, iii. have low gas permeability, good chemical, electrochemical and mechanical stability, and iv. stay as thin as possible to reduce the ohmic drop while avoiding permeability to hydrogen and oxygen gases.

The low thickness of the membrane allows the management of the water which must correctly arrive at the anode but must not accumulate at the cathode. Finally, the membrane must withstand acidic environments and functioning temperatures rages around 90°C for several thousands of hours. PEMFC cells membrane is strong and very thin[73]. Generally, the membrane is made of sulfonated polymer which has double characters: (a) a hydrophilic character allowing the membrane to conduct protons between the electrodes and (b) a hydrophobic character allowing the membrane to cope with mechanical resistance[30]. The PEMFC membrane allows ionic species (H^+) to pass from the anode to the cathode, thus facilitates the exchange process within the stack[35].

For optimal functioning of PEMFC cells, membranes based on perfluoro sulfonate acids (PFSA) have been developed[74]. The following examples can be cited: i. *Nafion* manufactured by DuPont de Nemours (USA)[75]; ii. Flemion of Asahi Glass Company (Japan)[76]; iii. Aciplex by Asahi Kasei (Japan)[77]; iv. DOW membrane from DOW Chemical[78]; v. Aquivion from Solvay-Solexis (Belgium-Switzerland)[79]; vi. 3M (USA)[80]; vii. Fumion from FuMAT-Tech[39].etc.

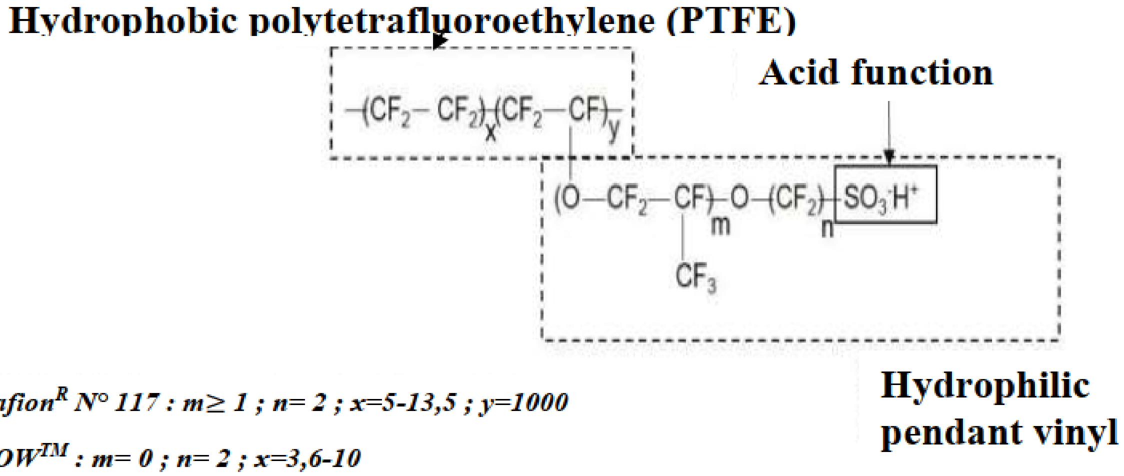
Figure-14 shows the chemical structure of a perfluoro sulfonated membrane. The chemical structure of a perfluoro sulfonated membrane is designed to combine hydrophilic and hydrophobic parts to achieve specific properties necessary for its operation in applications such as fuel cells.

The basic structure of the membrane consists of a perfluorinated polymer chain which is hydrophobic. This means that the hydrogen atoms in this polymer chain are all substituted with fluorine atoms. This characteristic makes the membrane impermeable to polar liquids such as water. Interspersed in the hydrophobic base structure are sulfonate groups (SO_3H) which are hydrophilic. These sulfonate groups make the membrane functional for electrochemical applications, because they allow the conduction of proton ions (H^+) into the electrolyte, which is usually an aqueous solution of dilute sulfuric acid (H_2SO_4).

Today, the membranes with the best performance and the most used is the *Nafion* membranes[81]. These membranes are composed of a perfluorinated skeleton based on polytetrafluoro ethylene (PTFE) which is extremely hydrophobic because of the CF_2 groups on which are bind the perfluoro sulfonated chains, ends by a highly hydrophilic sulfonic acid (SO_3H) group[39]. Indeed, the acid functions create the specific electrical and physicochemical properties of the membranes[82]. The electrical conductivity (the highest one) and the swelling (the lowest one) are essential characteristics for proper functioning of the Proton Exchange Membrane Fuel Cell[83]. Let's remind that there are several types of *Nafion* membranes. They are often designated by a number allowing to indicate their technical characteristics[34] (e.g. Nafion 112, Nafion 117). The first and the second digits indicate the equivalent weight of the membrane and the last digit (2 or 7 in the example) indicates the thickness of the membrane in milli inches (e.g. 50µm and 180 µm respectively for 2 and 7 milli inches)[28]. Indeed, the equivalent mass (mass of polymer which contains one mole of ionic group) and the ion exchange capacity (IEC) (number of ionic groups contained in one gram of polymer) represent the parameters for quantifying the concentration of ionic group in the polymer[84]. The membrane material must therefore have a high ionic conductivity, good mechanical resistance to heat, pressure or hydration stresses and be water proof Mabrouk et al.[34].

Despite all these remarkable properties, the *Nafion* membrane has drawbacks that slow down the development of the cells[85]. Among the disadvantages of this membrane, we can cite for example (a) the high cost due to the complexity of the synthesis of a perfluorinated chain, (b) the difficulties related to the recycling of fluorinated polymers, (c) the losses of gas permeability of the Nafion membrane, (d) the poor performance of the membrane at temperatures above 100°C and at low relative humidity[86]. To overcome these problems, alternative membranes have been developed[87], the main purpose of which is to reduce the cost of synthesis and manufacturing. Among these alternative membranes, we can cite the aromatic membranes listed in the Table-3.

In addition to the aromatic membranes cited in the literature[88], composite membranes are also widely discussed in order to overcome the problems posed by the manufacture of the *Nafion* membrane. As manufacturing materials, we can cite for example: cerium oxide nanoparticles, carbon nanotubes, nanofibers, yttrium-stabilized zirconium oxide (YSZ), cerium oxide, polyether ether ketone sulfonates (SPEEK)[89].



Nafion^R N° 117 : m≥ 1 ; n= 2 ; x=5-13,5 ; y=1000

DOW^{TM} : m= 0 ; n= 2 ; x=3,6-10

Flemion^{TM} : m= 0, 1 ; n= 1-5

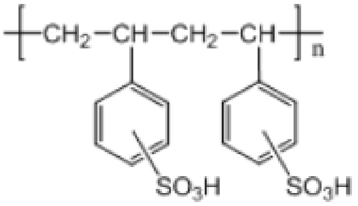
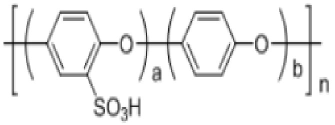
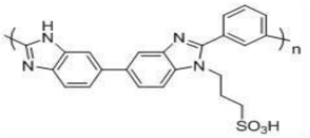
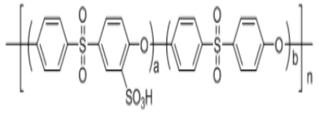
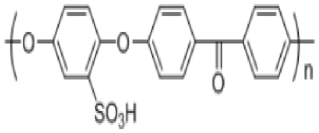
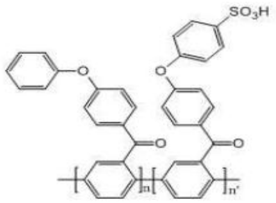
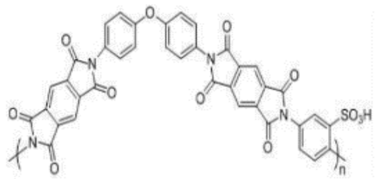
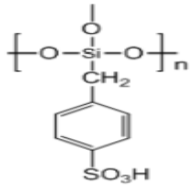
Aciplex^{TM} : m= 0,3 ; n=2-5 ; x=1,5-14

Aquivion^R : m=0 ; n= 2 ; x=3-7

3M^{TM} : m= 0 ; n= 4

Figure-14: Chemical structure of perfluoro sulfonated membranes[39].

Table-3: Example of alternative membranes[34] from Mabrouk et al.

Sulfonated polystyrene (S-PS)	
Sulfonated polyphenylenoxide (S-PPO)	
Sulfonated polybenzimidazole (S-PBI)	
Sulfonated polyethersulfone (S-PES)	
Sulfonated polyetheretherketone (S-PEEK)	
Poly(p-phenoxybenzoyl-1,4-phenylene) sulfonated (S-PPBP)	
Sulfonated polyimide (S-PI)	
Sulfonated silicate (S-Si)	

Identification of alternate materials for the proton exchange membrane: Composite membranes, known as hybrid membranes are essentially based on the assembly of at least two materials allowing the improvement of certain properties such as thermal resistance, mechanical resistance, water retention or proton conductivity values[90] in the membrane. Several reasons justify the development of composite membranes, among which we can cite:

Improved performance: Composite membranes make it possible to combine different classes of materials to improve the overall performance of the membrane. For example, by incorporating proton conductive nanoparticles, the proton conductivity of the membrane can be improved compared to an alternative polymer-alone membrane[91].

Design flexibility: Composite membranes offer significant design flexibility. Researchers and engineers can, for example, adjust the composition and structure of composite membranes to meet the specific requirements of their application, which may be more difficult to achieve with alternative membranes[92].

Improved durability: by using appropriate reinforcing materials or additives, composite membranes can be mechanically reinforced, making them more durable and resistant to mechanical stress, chemical degradation, or contamination[91].

Compatibility with various operating conditions: Composite membranes can be designed to be more robust and better suited to different operating conditions, such as high temperatures or aggressive environments. Likewise, composite membranes can be manufactured more economically than alternatives, using less expensive materials[93].

The studies of Knauth et al.[94] and Grondin-Perez et al.[95] showed that the development of composite membranes is generally based on the dispersion of inorganic materials such as the *chitosan*[82,83]. The *chitosan* is a compound derived from *chitin*, the second most abundant natural polysaccharide[96]. This compound is found generally in crustaceans' shells, shrimps and crabs[97]. *Chitosan* is a material that has a hydrophilic character.

Photos (a), (b), (c) and (d) in Figure-15 illustrate some of the species used in the development of composite proton exchange membranes possessing hydrophobicity.

Chitosan, generally contains three polar functional groups[98]: (a) the hydroxyl group (-OH), (b) the primary amine (-NH_2) and (c) the ether function (-COC-). It is soluble in water at neutral and basic pH due to the numerous hydrogen bonds between the hydroxyl, amine, acetamide and ether functions. Due to the presence of these functional groups, *chitosan* has a strong capacity for attractive interactions with water molecules[98].

The use of *chitosan* as a polymer electrolyte membrane has several advantages: (a) chitosan is an inexpensive and environmentally friendly material; (b) the hydrophilicity of chitosan is a desirable property for fuel cells for use at high temperatures and low relative humidity; (c) chitosan has low permeability to methanol and; (d) chitosan has certain functional groups that allow chemical modifications to adapt its properties[41]. Figure-16 below shows the chemical structure of *chitin* and *chitosan*. In this structure, "*n*" represents the repetition of glucosamine residues along the polymer chain. The number "*n*" can vary from one molecule to another depending on the source and degree of polymerization:


(a) (b) (c) (d)

Figure-15: Some species of materials containing Chitosan: (a) Snail's shells; (b) Shrimps; (c) Crabs; (d) Mushrooms[97].

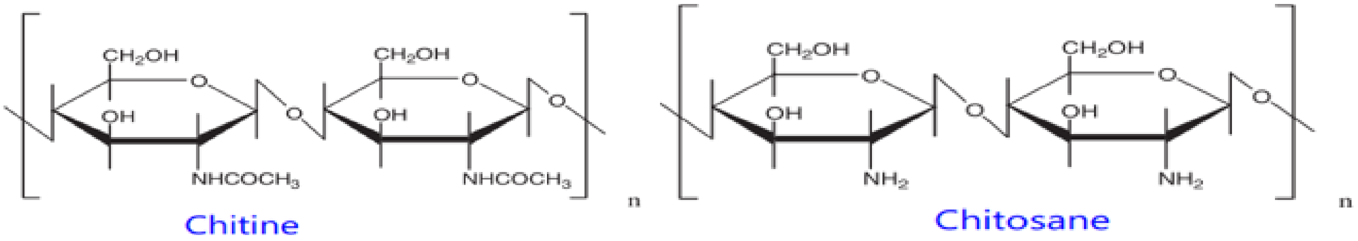


Figure-16: Chemical structure of *Chitin* and *Chitosan*[99].

In addition to *chitosan*, clays of hydrophilic character and *coconut* husks hydrophobic in nature are also used in the development of composite membranes[97]. *Clay* is a natural material which is generally composed of hydrated aluminium silicates[100]. The use of clay in the development of composite membranes for fuel cells has been explored in various research studies (references). Clay-based composite membranes are often considered to improve the performance of proton exchange membranes (PEMs) used in fuel cells due to their properties such as:

Improvement of proton conductivity: One of the main reasons for using clay in composite membranes is to improve proton conductivity. Clay nanoparticles, particularly montmorillonite, have a large specific surface area and can provide proton-conducting channels. The hydrophilic properties of clay also promote proton conduction[41].

Mechanical reinforcement: Clay can act as a reinforcement in the polymer matrix of the composite membrane, thereby improving its mechanical strength. This can contribute to the durability of the membrane under demanding operating conditions[101].

Improved thermal stability: Clay-based composite membranes showed improved thermal stability compared to pure polymer membranes. This increased thermal stability can expand the operating temperature range of fuel cells[102].

Decreased gas permeability: Incorporation of clay into the polymer matrix can reduce the permeability of unwanted gases, such as oxygen or hydrogen, through the membrane. This can help improve the overall efficiency of the fuel cell[103].

Potential applications: Clay-based composite membranes have been investigated for various fuel cell applications, including hydrogen fuel cells, direct methanol fuel cells (DMFC)[41].

The classification of *clays* has been the subject of several publications[104] based on parameters such as porosity, swelling, etc. The types of *clays* discussed in the literature are: Montmorillonite (MMT), Sepiolite, Halloysite Nanotubes (HNTs), oxides (TiO_2, SnO_2, ZrO_2). Thus, clays are classified into three groups: i. Clays of type 1: They are clays with a *tetrahedral* “T” layer juxtaposed with another octahedral “O” layer (kaolinite, antigorite, halloysite). ii. Clays of type 2: they are *clays* belonging to the group of *smectites*; characterized by a layer consisting of an octahedral layer (pyrophyllite, montmorillonite, beidellite)[105]. iii. Clays of type 3: They are *clays* made up of two tetrahedral layers and two octahedral layers (true chlorites and swelling chlorites)[106]. The Photo (e) in Figure-17 shows some samples of *clays* from[99]. Photo (f) shows coconut husks from Cotonou (Benin Republic).

Reagents and chemical protocols of composite membrane based on *Chitosan* and *Clay*

Reagents for making composite membrane: The development of a composite membrane based on *Chitosan* and *Clay* requires the knowledge of some basic reagents. Table-3 presents the physicochemical characteristics of *Nafion*, *Chitosan*, *clays***,** solvents used and some chemical modifying agents for the synthesis of composite membranes[41]. On retient quoi du tableau. Veuille le commenter.

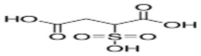
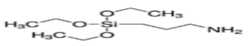
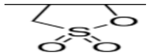
For the establishment of a chemical research prototype on the development of a proton exchange membrane, knowledge of some previous work on this theme is essential. Thus, the next section will focus on some previous works on the synthesis of a proton exchange membrane, with particular emphasis on the composite membrane.

Previous works on the synthesis of a proton exchange membrane: As shown in Figure-18[107], Liu et al. prepared nanohybrid membranes by embedding in a *Chitosan* (CS) matrix, Sulfonated Graphene Oxide (SGO) nanosheets with a controlled sulfonic acid group charge. The authors showed that the incorporation of 2.0% of SGO can provide the nanohybrid membrane with a 122.5% increase in hydrated conductivity and a 90.7% increase in anhydrous conductivity compared to the *chitosan* control membrane. In addition, SGO has been shown to contribute to the improvement of proton conduction, thermal and mechanical resistance properties of the CS/SGO membrane[41]. Ressam et al. also worked on the synthesis of this composite membrane, the results of which confirm those of Liu et al.

(e) Hydrophilic character. **(f)** Hydrophobic character.

Figure-17: Some clay samples[99] and coconut [Cotonou].

Table-4: Some reagents used for the synthesis of composites membranes based on Chitosan and Clay[41].

<table>
<tr><td colspan="5">Physicochemical characteristics of *Nafion*</td></tr>
<tr><td colspan="2">Trade name</td><td>Membrane *Nation 112*</td><td colspan="2">Membrane *Nation 117*</td></tr>
<tr><td colspan="2">Chemical formula</td><td>$C_7HF_{13}O_5S.C_2F_4$</td><td colspan="2">$C_7HF_{13}O_5S.C_2F_4$</td></tr>
<tr><td colspan="2">Equivalent weight</td><td>1.1 $g.mol^{-1}$</td><td colspan="2">0.9 $g.mol^{-1}$</td></tr>
<tr><td colspan="2">Density</td><td>----------------------</td><td colspan="2">0.874 $g.cm^{-3}$ at 25°C</td></tr>
<tr><td colspan="2">Concentration</td><td>----------------------</td><td colspan="2">5% by mass in alcohol and water</td></tr>
<tr><td colspan="5">Physicochemical characteristics of two types of *clays*</td></tr>
<tr><td colspan="2">Trade name</td><td>Halloysite Nanotubes</td><td colspan="2">Montmorillonite</td></tr>
<tr><td colspan="2">Category</td><td>Phyllosilicates Kaolinites serpentine</td><td colspan="2">Smectite phyllosilicates</td></tr>
<tr><td colspan="2">Chemical formula</td><td>$Al_2Si_2O_5(OH)_4$</td><td colspan="2">(Na, Ca)0.33(Al, Mg)$_2$(Si$_4$O$_{10}$)(OH)$_2$ nH$_2$O</td></tr>
<tr><td colspan="2">Density</td><td>From 2.55 to 2.57 g.cm-3</td><td colspan="2">0.874 g.cm-3 at 25°C</td></tr>
<tr><td colspan="2">Shape</td><td>From 2 to 2.7 g.cm-3</td><td colspan="2">Sheets type 2/1, TOT (Tetrahedron/Octahedron/Tetrahedron)</td></tr>
<tr><td colspan="5">Physicochemical characteristics of *Chitosan*</td></tr>
<tr><td colspan="2">Trade name</td><td colspan="3">Chitosan</td></tr>
<tr><td colspan="2">Chemical formula</td><td colspan="3">Poly[β-(14)-2-amino-2-deoxy-D-glucopyranose→</td></tr>
<tr><td colspan="2">Degree of deacetylation</td><td colspan="3">~80%</td></tr>
<tr><td colspan="2">Density</td><td colspan="3">0.15-0.3 $g.cm^{-3}$</td></tr>
<tr><td colspan="2">Solubilization</td><td colspan="3">Soluble in 2% v/v acetic acid</td></tr>
<tr><td colspan="5">Physicochemical characteristics of the solvents used</td></tr>
<tr><td>Trade name</td><td>Acetic acid</td><td>Dimethylacetamide</td><td>Dimethylformamide</td><td>Ethanol</td></tr>
<tr><td>Chemical formula</td><td>$C_2H_4O_2$</td><td>C_4H_9NO</td><td>C_3H_7NO</td><td>C_2H_6O</td></tr>
<tr><td>Molar mass</td><td>60.052 $g.mol^{-1}$</td><td>87.12 $g.mol^{-1}$</td><td>73.09 $g.mol^{-1}$</td><td>46.06 $g.mol^{-1}$</td></tr>
<tr><td>Melting temperature</td><td>16.64°C</td><td>-20°C</td><td>-61°C</td><td>-114°C</td></tr>
<tr><td>Boiling temperature</td><td>117.9°C</td><td>164.5°C</td><td>153°C</td><td>78.37°C</td></tr>
<tr><td>Density</td><td>1.0492 $g.cm^{-3}$</td><td>0.937 $g.cm^{-3}$</td><td>0.944$g.cm^{-3}$</td><td>0.789 $g.cm^{-3}$</td></tr>
<tr><td>Appearance at ambient temperature</td><td>Liquid</td><td>Liquid</td><td>Liquid</td><td>Liquid</td></tr>
<tr><td colspan="5">Physicochemical characteristics of some modifying agents</td></tr>
<tr><td colspan="2">Trade name</td><td>Sulfosuccinic acid</td><td>3-aminopropyltriethoxysilane</td><td>1,3-Propane sulfone</td></tr>
<tr><td colspan="2">Chemical formula</td><td>$HOOCCH_2CH(SO_3H)COOH$</td><td>C9$H_{23}NO_3Si$</td><td>(CH2)$_3$SO$_3$</td></tr>
<tr><td colspan="2">Chemical compound</td><td></td><td></td><td></td></tr>
<tr><td colspan="2">Molar mass</td><td>198.15 $g.mol^{-1}$</td><td>221.37 $g.mol^{-1}$</td><td>122.14 $g.mol^{-1}$</td></tr>
<tr><td colspan="2">Density</td><td>1.438 $g.cm^{-3}$</td><td>0.946 $g.cm^{-3}$</td><td>1.392 $g.cm^{-3}$</td></tr>
<tr><td colspan="2">Solubilization</td><td>water soluble</td><td>-----------------------</td><td>water soluble</td></tr>
</table>

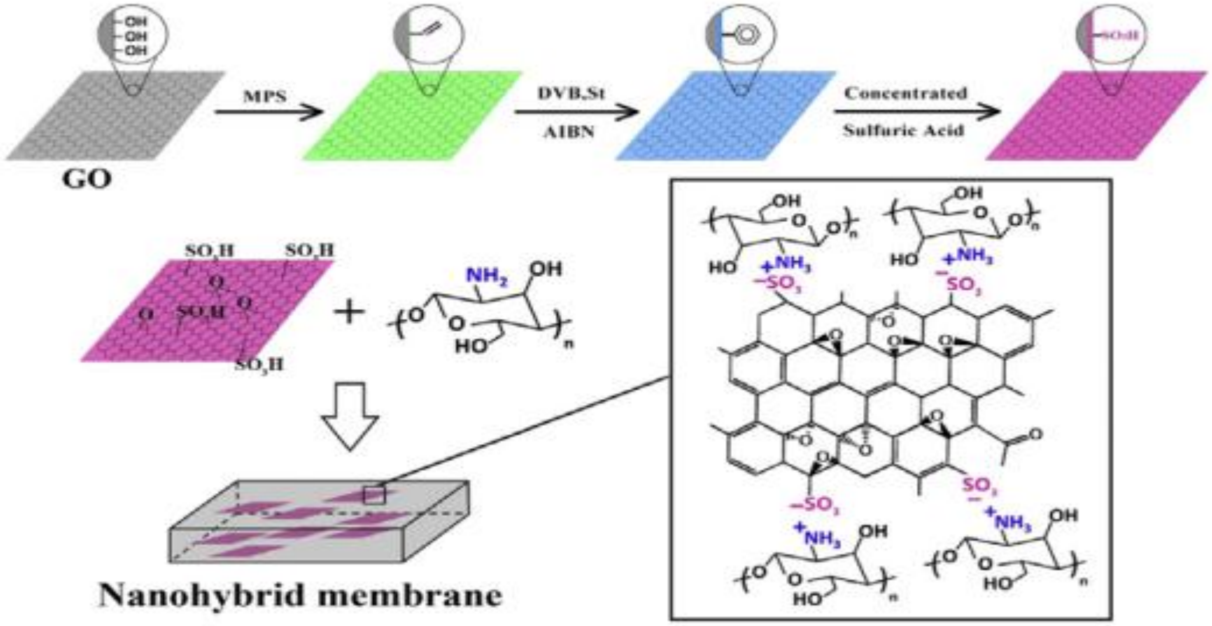


Figure-18: Mode of preparation of SGO and the hybrid membrane CS-SGO[107].

This Figure-18 presents the different methods of preparing a membrane which are as follows: Preparation of SGO (Supported Graphene Oxide): Preparation of Graphene Oxide (GO): The process generally starts with the preparation of graphene oxide (GO) from natural graphite or expanded graphite. GO is obtained by oxidizing graphite, usually using strong oxidants such as sulfuric acid (H_2SO_4) and nitric acid (HNO_3). This step introduces oxygenated functional groups, such as hydroxyl groups (-OH) and carboxyl groups (-COOH), to the graphite surface, thus forming GO.

Exfoliation and Dispersion: The obtained GO can be exfoliated to obtain individual layers or sheets of GO. Exfoliation can be accomplished by ultrasonication or other mechanical methods. Then, the GO is dispersed in a suitable solvent to form a GO suspension. The addition of surfactants or dispersing agents may be necessary to stabilize the dispersion.

Support Material: Support material is prepared. This support can be made of various materials, such as polymers, membranes, or other substrates. The choice of media depends on the specific application.

Deposition of the GO on the Support: the GO suspension is deposited or coated on the support plate. This step allows obtaining the SGO, where the GO is supported by the support material. The deposition can be carried out by methods such as coating, vacuum filtration, or spin-coating.

Preparation of the CS-SGO Hybrid Membrane (Supported Chitosan-Graphene Oxide): Preparation of Chitosan Solution (CS): Chitosan, which is a polysaccharide derived from chitin, is dissolved in a suitable solvent to form a chitosan solution. This solution can be prepared in different concentrations depending on the needs.

Mixing with SGO: the chitosan solution is mixed with the previously prepared SGO. The SGO will act as reinforcement and add specific properties to the membrane, such as proton and mechanical conductivity.

Homogenization: the chitosan-SGO solution is homogenized to obtain a uniform dispersion of SGO in the chitosan matrix. This step is important to ensure homogeneous distribution of reinforcements in the hybrid membrane.

Moulding and Forming of Membrane: The homogeneous solution is moulded or poured into the desired shape of the membrane. This step may include a drying or polymerization process to solidify the membrane.

Kedan et al. synthesized composite membranes by incorporating the *Chitosan* matrix with the montmorillonite clay filler (MMT). The synthesis process is represented in Figure-19. The authors showed that the proton conductivity of composite membranes is increased as the temperature increases[108]. The proton conductivity of the CS/MMT composite membrane increased from 1.75×10^{-2}s.cm^{-1} at 25°C to 3.57×10^{-2}s.cm^{-1} at 80°C. It also exhibits a lower methanol permeability value than virgin CS, namely 1.22×10^{-7}cm^2.s^{-1} and 12.49×10^{-7}cm^2.s^{-1}, respectively[108]. In addition, the synthesized composite membrane has good satisfactory mechanical strength of 39.23 MPa. The results during this study show that the manufactured composite membrane can be used as an alternative polymer electrolyte membrane (PEM) in fuel cells[108].

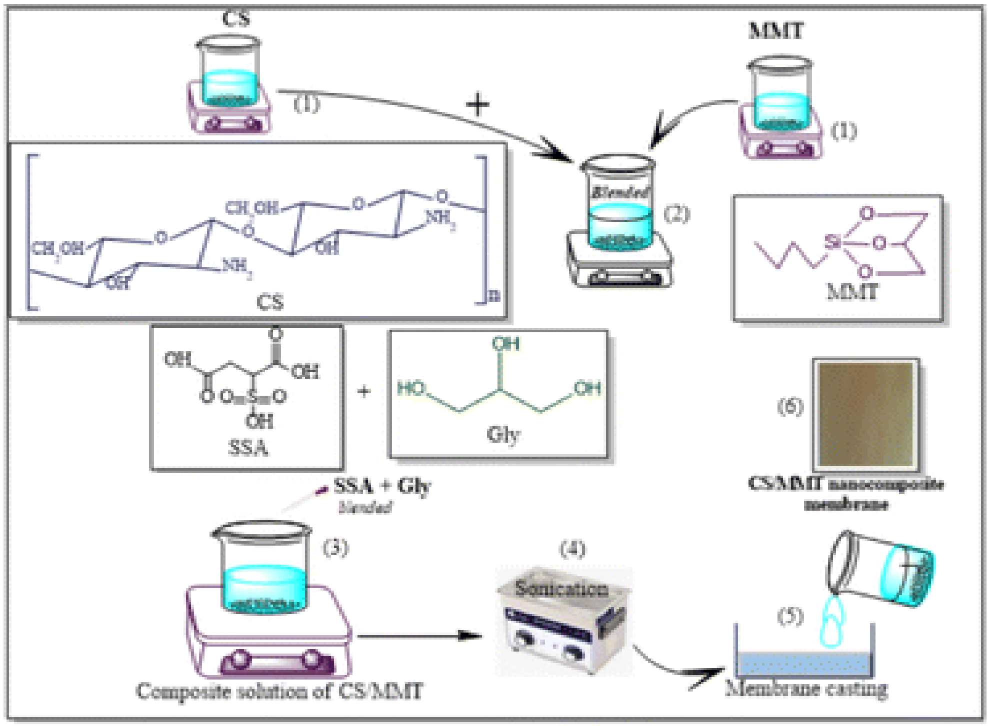


Figure-19: Synthesis process of composite membranes by Chitosan matrix with montmorillonite clay (MMT)[108].

Mabrouk et al[34]. synthesized and characterized new proton conduction membranes for proton exchange membrane fuel cells. The membrane synthesized from octylamine-grafted sulphonated polyether sulfone and mixed membranes were characterized from a physicochemical point of view. The obtained membranes have a good mechanical property, good ionic conductivities and very good chemical stability for use in fuel cells[34].

Neethu et al.[100] worked on the development of a new proton exchange membrane. They have used activated carbon, derived from *coconut* husks (ACCS) mixed with natural *clay* to prepare membrane which cost is approximately \$45/m^2. This is an alternative to the expensive *Nafion 117* membrane. The X-ray diffractogram of the used *clay* in this process showed the presence of different hygroscopic oxides which enhances the hydration property of the obtained membrane. Additionally, the higher surface area of the activated carbon helped to retain water and improve proton transfer. From that work, it appears that the proton diffusion coefficient of the *ACCS/Clay* membrane is higher (36×10^{-6}cm^2/s) than that of the *Nafion* 117 membrane, membrane of reference (4.64×10^{-6}cm^2/s) [88].

Conclusion

Through this study, we note that the proton exchange membrane fuel cells (PEMFC) have many advantages such as the Backup power, portable power, small distributed generation and transportation among the fuel cells that exist. But their prices are still very expensive comparatively to the other types of fuel cells because of the *Nafion* which are rare in nature. Several authors work for manufacturing composite membranes that are shown to be an alternative to overcome the high price of *Nafion* fuel cells, even if the efficiency of composite membrane still needs improvement comparatively to that of *Nafion* membrane. We find that local materials such as shells of crustacean's, crabs, shrimps, and over materials like coconut husks, mushrooms, *clays* and snails' shells are generally use to get the *Chitosan* which characteristics are required to perform a good composite membrane for PEMFC. These materials exist in several regions of Benin Republic. Which of the crustacean's shells used in literature is the richest in *chitosan*? What will be the efficiency of the manufactured composite membrane from these local materials comparatively to the *Nafion* membrane? How can we improve the efficiency of the composite membrane made of local materials? How competitive can be their price according to the fuel cells market? The answers to these questions will be the objectives of the future studies in the context of energy transition in Benin Republic.

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