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Article

Investigation and Development of the Modelling of Intermediate Temperature PEM Fuel Cells for Transport Applications

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Abstract: Proton-exchange membrane Fuel Cells (PEMFCs) have garnered significant attention due to their distinct advantages over other fuel cell technologies. These advantages include high efficiency, minimal environmental impact, and robust power generation capabilities, making PEMFCs highly suitable for both stationary and transportation applications. As a promising solution for mitigating climate change, PEMFCs contribute to the sustainability of the transportation sector while ensuring a reliable energy supply, provided that a continuous hydrogen source is maintained. This study presents a comprehensive review of Intermediate-Temperature Proton-Exchange Membrane (IT-PEM) fuel cells, a crucial advancement aimed at enhancing fuel cell performance under elevated operating temperatures. In an ideal scenario, gas crossover across the membrane in PEMFCs should be completely prevented. However, a minimal crossover rate—accounting for approximately 1–3% fuel losses—is observed, necessitating further investigation alongside other critical challenges associated with PEMFCs. To address these concerns, a theoretical model for IT-PEM fuel cells has been developed and remains an ongoing research endeavour. An extensive literature review reveals that a nanocomposite membrane with 15 wt.% additive content exhibits superior reliability for facilitating PEMFC operation at intermediate temperatures. Nevertheless, further research is required to enhance efficiency at both intermediate and high-temperature conditions, thereby improving CO tolerance and other gas interactions, while fully leveraging the benefits of IT-PEM technology for next-generation fuel cell applications.

Keywords: Proton-Exchange Membrane (PEM) fuel cell, Intermediate Temperature (IT-PEMFCs), Nafion Membrane, SPEEK Membrane, COMSOL software, Department of Energy (DoE).

1. Introduction

Proton-exchange membrane Fuel Cells (PEMFCs) have attracted significant attention from researchers and scientists over the past decade due to their numerous advantages, including structural simplicity, high power density, reduced harmful emissions, and superior energy conversion efficiency [1]. The proton-exchange membrane (PEM) serves as the core component of PEMFCs, playing a crucial role in proton transport and overall system performance [2]. Consequently, the development of an alternative membrane to replace the conventional Nafion membrane is imperative. The ideal membrane should be cost-effective, exhibit high proton conductivity, and demonstrate operational stability at intermediate or elevated temperatures while maintaining superior gas permeability properties.

Additionally, as indicated in [3], low methanol permeability is a critical requirement for improving membrane performance, particularly in applications involving direct methanol fuel cells (DMFCs). Addressing these challenges necessitates the exploration of advanced materials, such as nanocomposites and modified polymeric membranes, to enhance thermal and chemical stability, proton conductivity, and fuel crossover resistance. The ongoing pursuit of these advancements is essential for the next generation of high-performance, durable, and economically viable PEMFC membranes.

In terms of the history and definition of PEMFCs, we can briefly describe according to the Department of Energy (DoE) in the United States [4,5], that PEMFCs have been commercialized for stationary applications since 2001 and transport applications since 2003. However, PEMFCs still have several challenges such as issues of crossover, cost and durability besides the challenges of the infrastructure of hydrogen fuel [5-8]. A fuel cell is simply defined as an electrochemical device that converts chemical energy into electrical energy, which can be described in Figure 1.

(A) The reaction of hydrogen and oxygen (B) Schematic of physical PEM fuel cell system

Figure 1. The basic chemical reaction of PEM fuel cell.

There are several methods to assess the mass transport properties of the membrane as presented by several researchers [5, 9-13]. It would be useful in this paper to discuss these methods briefly. These techniques include the volumetric method, gas chromatography techniques, time-large approaches, and electrochemical monitoring methods. The volumetric techniques determine the permeability coefficient of H_2 and O_2 in Nafion membrane as presented by Kocha *et al.* [8], where high pressure is applied to one side of Nafion membrane, and from another side of the membrane, the permeating flux of gas is estimated. But in the time-large approaches, the time to fill up fixed downstream volumes is estimated while the concentration change is measured in gas chromatography techniques. The Membrane Electrode Assemblies (MEA) are assembled and on the one side, are exposed to an acid solution while on another side, the reactive gas is supplied and estimated over time to determine the diffusion factor and solubility coefficient of the membrane.

This paper provides a comprehensive review and critical evaluation of various approaches and techniques related to mass transport properties in PEMFCs. Additionally, it outlines the methodological framework for experimental investigations. The paper is systematically structured into several sections to ensure a logical progression of concepts and findings. Initially, the study presents state-of-the-art advancements in membrane materials, emphasizing their suitability for intermediate-temperature PEMFC (IT-PEMFC) applications. This is followed by an extensive review of related research and theoretical background, providing essential context for the study. Subsequently, the paper delves into the methodology and modelling strategies employed in the development and optimization of IT-PEMFCs, detailing key parameters influencing performance. The discussion further extends to the evaluation of experimental results and the insights derived from ongoing research efforts. Before concluding, the paper outlines key recommendations and unresolved challenges, highlighting future research directions to advance the efficiency, durability, and commercial viability of IT-PEMFCs.

2. State of the Art of Material to Allow PEMFCs to Operate at Intermediate Temperature

In the section above we discuss mass transport. In this section, we will present some previous works and then proton conductivity will be discussed. The conventional Nafion membrane requires an external humidification complex system that will increase the weight and complexity of PEMFCs. These disadvantages can be overcome by adapting the self-humidifying membrane that helps Pt-$Cs_{2.5}$ catalysts in the membrane to combine the permeable H_2 and O_2 to produce water and humidify the membrane [14]. It helps hygroscopic metal oxides [S_1O_2 or T_1O_2] to absorb H_2O and accordingly enhance proton conductivity [14-16], and lastly, it helps to increase the proton conductivity of membrane under dry operation conditions such as Zirconium phosphate [17,18].

It is important in this paper to discuss the framework for the self-humidifying system and preparation procedures. The material and preparation of the Pt.Cs2.5H0.5Pw12O40 catalysts were presented by Peighambardoust *et al.* [2], and also Misono *et al.* [19] described these techniques. The material of $Cs_{2.5}H_{0.5}Pw_{12}O_{40}$ can be varied as presented by Misono *et al.* [19]. The Pt.$Cs_{2.5}H_{0.5}Pw_{12}O_{40}$ was synthesized with platinum in the catalyst surface and then synthesized by titration approach [2]. One alternative membrane is the SPEEK membrane among other types such as Poly Ether Sulfone (PES) [20] Polybenzimidazole (PBI) [21] and others as shown in Figure 2. The SPEEK membrane which is converted from PEEK has good mechanical properties and high thermal stability.

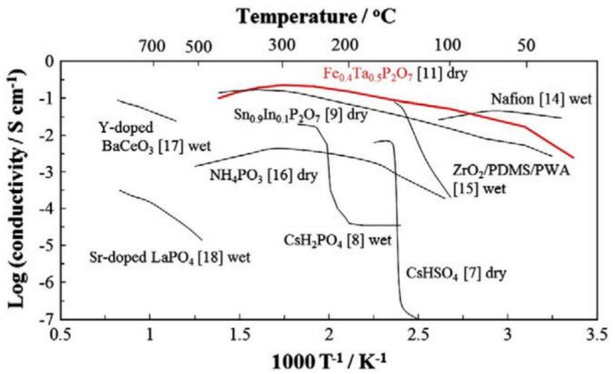


Figure 2. Effective of using $Fe_{0.4}Ta_{0.5}P_2O_7$ at an intermediate temperature and comparing with other materials for MEAs [23].

The SPEEK is made by electrophilic substitution of the sulfonic acid groups in the polymer backbone through sulfonation chemical reaction as presented by authors in ref. [2, 24] and other authors in references [25,26]. It is important here to clarify that the proton conductivity of SPEEK is enhanced by expanding the Degree of Sulfonation (DS). However, the increase in DS causes the deterioration of mechanical strength because the water content becomes high and the membrane will have high swelling [27]. Therefore, we have to increase the DS until the optimal value where good proton conductivity and favourable membrane strength should be accomplished. According to Shao [28], the DS is controlled by varying temperature reaction time and acid concentration.

The SPEEK/Pt.$Cs_{2.5}H_{0.5}Pw_{12}O_{40}$ non-fluorinate self-humidifying nanocomposite membranes were developed and fabricated by Peighambardoust *et al*. [2] to use with dry reactant gases. Several tools were used (e.g. X-ray diffraction (XRD) was performed using a PHILIPS PW-1800 diffractometer to determine the particle size of catalyst samples, while X-ray fluorescence (XRF) analysis beside other Fourier Transforms Infrared Spectroscopy (FT-IS) analysis and Scanning Electron Microscopy (SEM) were utilized to find the quantity of minimizing platinum on the $Cs_{2.5}H_{0.5}Pw_{12}O_{40}$ catalyst supports). Transmission Electron Microscope (TEM) can be adapted to show whether the catalyst particles are uniform or not. These are all testing and analysis tools used to study membrane characterization.

Figure 3 shows the changes in the weight of the sPEEK/$H_3PW_{12}O_{40}$ and sPEEK/Pt-$Cs_{2.5}$ nanocomposite membranes as a function of immersion time.

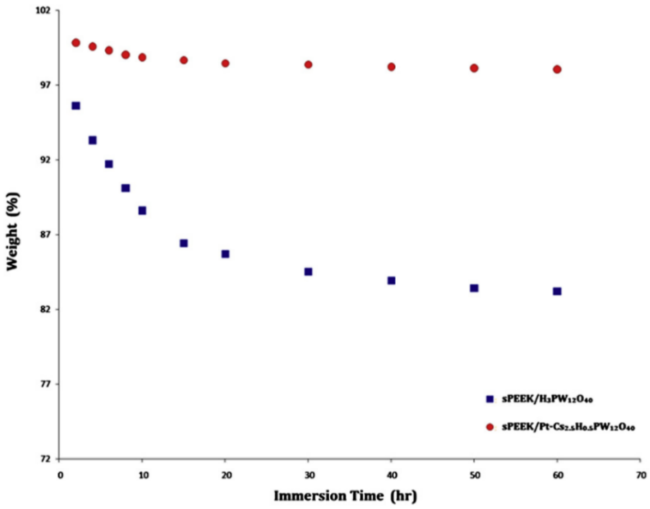


Figure 3. Variation of the weight of the sPEEK/$H_3PW_{12}O_{40}$ and sPEEK/Pt-$Cs_{2.5}$ nanocomposite membranes against immersion time [2].

The analysis of steady-state and transient PEMFCs with analysis of internal humidification and water management by node-side modulation was presented by Bao and Bessler [29]. However, there are several assumptions and phase changes of water that are not taken into consideration by the authors. There is a great matching between the model and the experimental results and several mathematical equations that could be useful in designing a numerical model.

3. Related Works and Background

This section has several subsections that are varied to increase understanding of PEMFCs. Then we can improve the performance of PEMFCs. Recently, PEMFCs have become very important due to their advantages over other types of fuel cells. These advantages of PEMFCs are high efficiency, low pollution power generator stationary and transportation applications [30]. The membrane accounts for approximately 6%-30% of the cost of PEMFCs [5, 13, 31,32] claimed that "*the inorganic proton conductors could be silica, Heteropolyacids (HPAs), layered zirconium phosphates, and liquid phosphoric acid*". The silica needs a high pressure to sustain 100% Relative Humidity (RH) for high proton conductivity above 100°C. The use of HPAs an example Phosphotungstic Acid (PTA) into polyelectrolyte membranes that can improve both proton conductivity and effectiveness of PEMFCs above 100°C; could cause flooding for the membrane. However, to prevent HPA leaching, amine-functionalized mesoporous silica can be utilised to immobilize PTA in Nafion membranes as presented by authors in ref. [13, 32]. The composites of SPEEK with HPAs show increased proton conductivity at elevated temperatures when fully hydrated and excellent thermal and electrochemical stability, however, the cost of the material is very high. We can extend the discussion by focusing on organic/inorganic hybrid membranes from acid-doped PBIs and other polymers as part of future work.

a. *Basic Background in Chemistry*

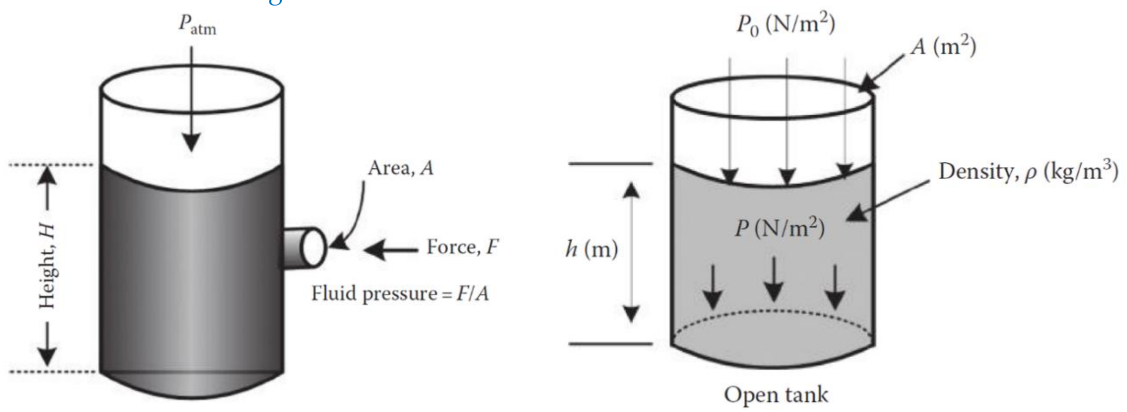
Since we study IT-PEMFCs and conventional PEMFCs operating at low temperatures, it is important to highlight the conversion in the temperature in this paper where some academic works are presented in Kelvin while others are in Celsius. Hence it would be useful to study the conversion relation. To convert the temperature from Celsius to kelvin, the following formula is used and vice versa [33]:

$$T(K) = T(°C) + 273.15 \qquad \text{Eq. 1}$$

Density (ρ) is well-defined as mass (m) per unit volume (v) of material which is given by [33]:

$$\rho = \frac{m}{v} \qquad \text{Eq. 2}$$

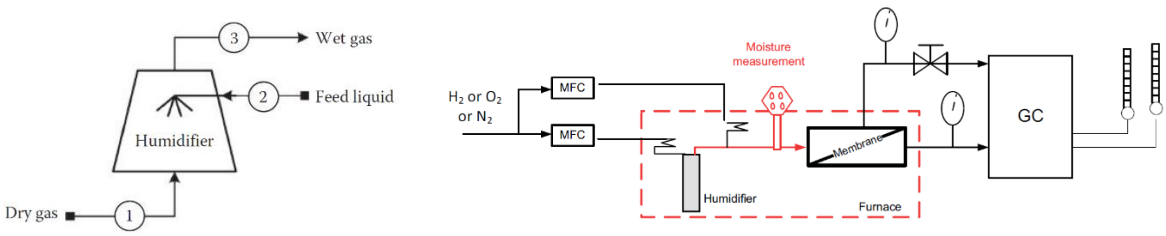
While the concentration is expressed by weight per volume and the best description for the density can be presented as shown in Figure 4.



(A) Force analysis (B) Pressure analysis

Figure 4. Analysis of pressure and force at the bottom of an open tank [33].

The dehumidification is done with internal or heating coils which help to reduce the level of humidity in the air or gas steam. While the humidifier is to increase the amount of moisture by allowing the water to evaporate. The characteristics of a humidifier are the feed gas is saturated and fluid is vaporized but the exit products may or may not be saturated as illustrated in Figure 5.



(A) A gas humidifier diagram. (B) Schematic of experimental works

Figure 5. A gas humidifier diagram [10,35].

Figure 6 shows the multi-system process and different techniques such as recycling. A recent study by Ghasem and Henda described these processes of purge and others in more detail [33].

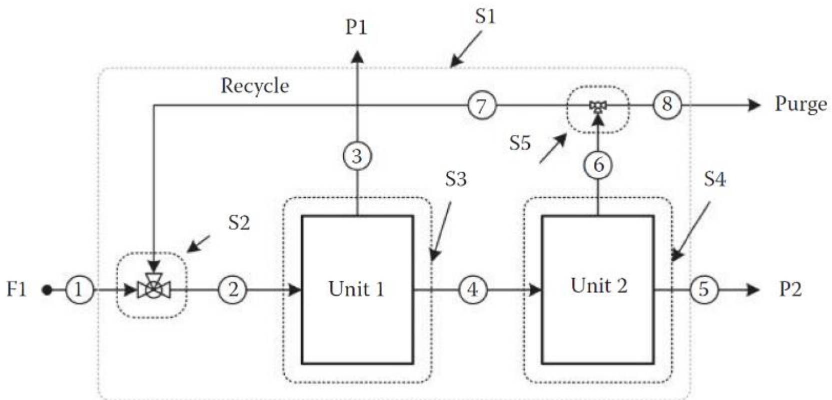


Figure 6. Multi-systems process [33].

b. Stoichiometric Equation, Coefficient, and Ratio

Stoichiometry plays a crucial role in chemical processes, encompassing stoichiometric equations, coefficients, and ratios. While this paper does not delve into stoichiometry, further details can be found in Ref. [35].

c. Study Phase Changes/Phases of Material

Phase changes are utilized in the separation and purification process. Also, the pressure or temperature condition could be used to describe the state of material either solid, gas or liquid, which helps to understand the behaviour of materials. Different names are given for materials when they stay in coexist state such as vapour and liquid coexist. The conventional standard is on the liquid-solid line, the temperature is called the freezing/melting point while on vapour–the liquid line, the temperature is known as the boiling point, and the pressure is the vapour pressure [35]. On the other hand, on the vapour–solid line, the temperature is called the sublimation point, an example is shown in Figure 7.

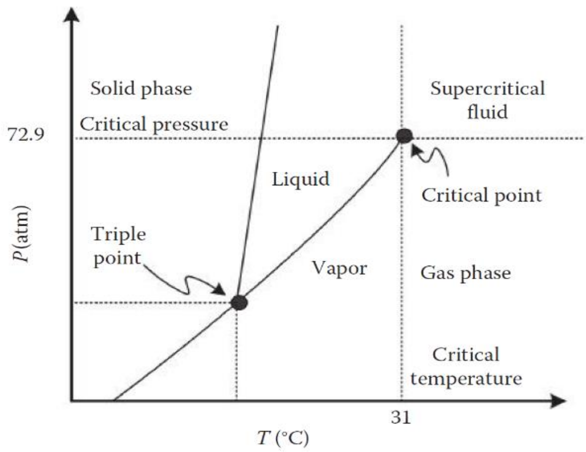


Figure 7. CO_2 phase diagram to understand the material behaviour [35].

d. State of Art of the Mass Transport

The SPEEK membrane was prepared in the laboratory as presented by Brunetti *et al*.[5], the Nafion 117 membrane was obtained from Quintech Company in Germany. The membranes either SPEEK or Nafion 117 were sandwiched between gas diffusion electrodes (Pt-Free ELAT) and pressed. The pressure 58.8 bar and 26 bar were applied to SPEEK and Nafion respectively. Then impedance spectroscopy with a Solartron SI 1260 was used to determine proton conductivity. The RH was determined by calculating the pressure of saturated water vapour (P) at the cold temperature (T_{Cold}) and the hot (T_{hot}) compartment which is given by [5]:

$$RH = \frac{P_{H_2O}(T_{Cold})}{P_{H_2O}(T_{hot})}.100\% \quad \text{Eq. 3}$$

In this direction. It is important to study Stoichiometric PEM fuel cells because we can determine how much power per mass of hydrogen we can get. The stoichiometric of the PEM fuel cell is given by [36]:

$$2H_2 + O_2 \rightarrow 2H_{2o} \quad \text{Eq. 4}$$

Where 2 moles of H_2 would need one mole of O_2 to produce water which requires 4F of charge that is given as:

$$Change = 4F \times amount\ of\ O_2 \qquad \text{Eq. 5}$$

By dividing one the time, we can estimate the usage of O_2 :

$$\mathrm{O_2 usage} = \frac{\mathrm{I}}{4\mathrm{F}} \quad [\frac{\mathrm{moles}}{\mathrm{s}}] \qquad \text{Eq. 6}$$

This result helps to find the relationship between the power of fuel cells and O_2 usages. But the O_2 used is required from the air which is given by Eq. 7.

$$Air\ usage = 3.57 \times 10^{-7} \times \lambda \times \frac{P_c}{V_c} \quad [\frac{kg}{s}] \qquad \text{Eq. 7}$$

Where λ is the stoichiometry and V_c is the voltage of the cell which is 0.65 V is used as a good approximation and the periodic table in chemistry was used to find the molar mass of O_2. Since we focus on the humidity in the PEM fuel cell, the difference between the inlet flow rate of air and the outlet rate will give the exit airflow rate as Eq. 8 [36] :

$$\text{Exit air flow} = \text{rate inlet flow rate} - O_2\text{usage}$$

$$\text{Exit air flow rate} = (3.57 \times 10^{-7} \times \lambda - 8.29 \times 10^{-8})\frac{P_e}{V_c}\ [\frac{kg}{s}] \qquad \text{Eq. 8}$$

While the rate of usage of H_2 by using the molar mass of hydrogen from the periodic table, is given by:

$$H_2 usage = (1.05 \times 10^{-8})\frac{P_e}{V_c}\ [\frac{kg}{s}] \qquad \text{Eq. 9}$$

This is very valuable and beneficial to determine the electrical power that can be created from the volume of hydrogen. However, this analysis does not consider the reformed hydrocarbon. Therefore, at high temperatures, the PEM fuel cell will allow and tolerate carbon monoxide which is required to take into consideration with other gases. Lastly, the rate of water production in the PEM fuel cell is produced based on a stoichiometric equation and molecular mass of water by:

$$\text{Rate of water production} = (9.34 \times 10^{-8})\frac{P_e}{V_c}\ [\frac{kg}{s}] \qquad \text{Eq. 10}$$

$$H_2\ usage = \frac{Pe}{2V_cF}\ [\frac{moles}{s}] \qquad \text{Eq. 11}$$

Some water could be used in the internally reformation process such as methane in the internally reformed process. As was pointed out in the introduction of this paper, the techniques of mass transport include the volumetric method, gas chromatography techniques, time-large approaches, and electrochemical monitoring methods. In general, the current in the fuel cell is controlled by the rate of electron transfer and transport of material to and from the electrode surface either the reductions or oxidation processes [37,38]. There are forms of mass transport that are convection, diffusion and migration. The conversion reaction occurs at the electrode surface while diffusion occurs as a random walk model and it is given by Fick laws as follows [39].

$$J_0 = -D_0(\frac{\partial C_0}{\partial x}) \qquad \text{Eq. 12}$$

Where J_0 is the rate of movement or diffusional flux and D_0 is the diffusion factor and $\frac{\partial C_0}{\partial x}$ is the concentration gradient and can be expressed in a function of time as Fick's second law:

$$\frac{\partial C_0}{\partial t} = D_0(\frac{\partial^2 C_0}{\partial x^2}) \quad \text{Eq. 13}$$

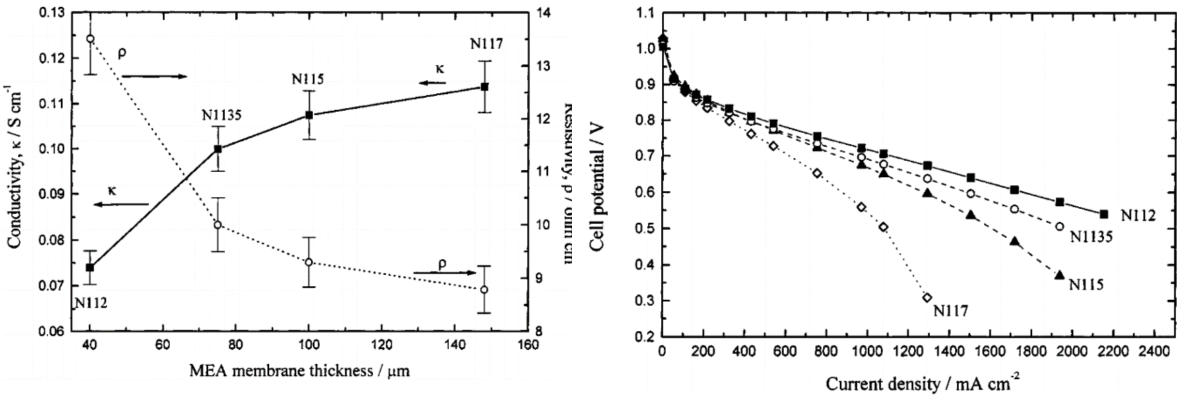
Where x is the distance to an electrode surface. The steeper the change in concentration, it will be the greater the rate of diffusion. Convection is the second approach of mass transport which can be a pump, a flow of gas or even gravity which requires knowledge of turbulent or laminar flow. The migration is the final form of mass transport which is an electrostatic effect that is either attracted or repelled.

e. Review of Ion Conductivity of PEMFCs

The review of ion conductivity is conducted in this section as it is very important in improving the performance of PEMFCs. The comparison between different Nafion membrane materials is presented. Alberti *et al.,*[40] focused on Nafion-1100 annealed at 120 ℃ for 15 h and it was claimed that Nafion 1100 is enough to operate at RH≤ 96% for the range of temperature 100-120℃. The Nafion 117 membranes were studied at a high-temperature range by using the matrix counter-pressure index and by using a factor to determine the density of the inner proton solution. The operating of PEMFCs at 100-120℃ is highly desirable in both automotive and cogeneration applications [41-44]. However, all the ionomer membranes are unable to operate at a temperature above 80-90 ℃ due to the rapid decreasing of performance of PEMFCs at a temperature above 90 ℃ [45, 46]. One study to attempt to overcome the ionomer instability of the membrane was presented by Alberti *et al.,* [40] and some researchers were focused on understanding the thermal instability of ionomers [46,47] and annealing and/or cross-linking techniques [48-50]. The Nafion-117 membranes are treated for an hour each step as follows [40]:

- boiling a 3% solution of hydrogen peroxide
- It was boiled with 0.5 M sulphuric acid
- lastly, it was boiled in the distilled water

The conductivity at the intermediate temperature above 90 ℃ was increased by 0.095 [S/CM] the conductivity at the low temperature of PEMFCs. However, at 100-120 ℃, there is no attempt by Slade *et al.,*[51], although a synopsis of the Nafion membrane was conducted. Also, most tests were in situ, while in *ex-situ* tests the conductivity was significantly scattered. The Nafion 112 Mandarin gave better performance if compared with other commercial Nafion 117, 115, and 1135 as described in Figure 8.



(A) Test conductivity and resistivity of Nafion at 25°C. (B) The MEA performances with the Nafion at 80°C

Figure 8. Different Nafion1100 EW membranes test [51].

According to [52], the Nafion membrane is used in PMFCS and DMFCs which show good thermal stability and high proton conductivity due to perfluorinated polymer materials below 100 ℃ and fall hydrated conditions. But above 100 ℃ these benefits will decline and the fuel will cross over and also the high cost of material will be another issue. Therefore, the Poly Ether-Ether Ketone (PEEK) is presented as the most used alternative for Nafion membrane and we can summarize three modified types that are i)PEEK electrophilic sulfations (SPEEK), ii)S-PEEK and non-formulation polymers blundering and iii) S-PEEK heteropolar compounds and poly-ether mide doping with inorganic acids [52-57].

The iron triangles are used in the fuel cell to describe three important characteristics or properties that are the performance of the fuel cell, cost and durability [52]. This iron triangle should be taken into consideration beside other features or functions such as high proton conductivity (σ) low H_2 crossover and low electronic conductivity and high stability of chemical, thermal and mechanical of the fuel cell.

According to Iulianelli and Basile [52], victrix company produce PEEK polymer that is modified with sulfonic acid groups such as sulfonated PEEK, PEK, PEEK-WC and PEEKK and also SPEEK. These are modified as alternative Nafion membranes. However, some of these are suffering from low proton conductivity. However, S-PEEK has become a really competitive and alternative for the Nafion membrane.

One of the great studies by Peighambardoust *et al.* [2], focused on Self-humidifying nanocomposite membranes. Different tests such as FTIR, XRD, SEM-EDXA and TEM measurements were conducted on the different samples. It was found that the self-humidifying nanocomposite membranes with DS=65.12% and the amount wt.% Pt within catalyst with having 1.25 wt.% Pt within the catalyst is the best PEM for FCs applications even better than the Nafion-117.

The same group research above focused on self-humidifying nanocomposite membranes [58]. The residual weight of the nanocomposite membrane increased to 40 % after Fenton's test and also the oxidative durability was improved [9], presented another great study where the current was set stepwise and the voltage and temperature are observed as shown in Figure 9. One observed and the most interesting point is when the temperature is varied between 16-18 hours, the voltage is dropped at 95. This is required more investigations where other points, when either the current or temperature are varied the voltage, is changed accordingly.

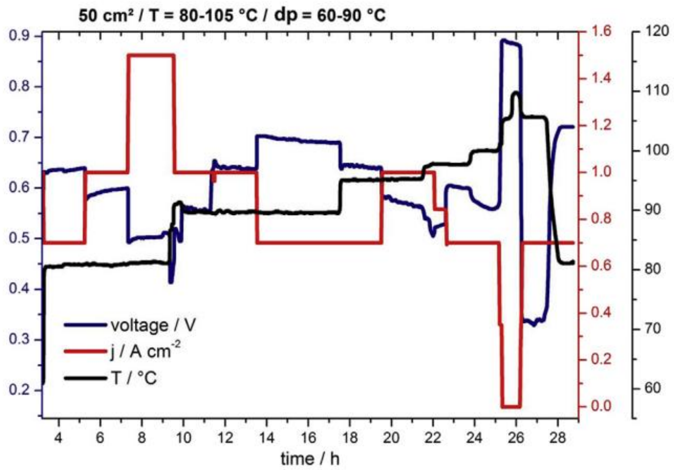


Figure 9. The current setup is stepwise with time, then the voltage responds along with the variation of temperature was varied in-between 80-110 C [9].

4. Methodology and Modelling of the PEM Fuel Cell at Intermediate Temperature

The modelling of gas crossover of PEMFCs with a phosphoric acid-doped polybenzimidazole membrane was developed where operating temperature, current density and gas crossover diffusivity of the membrane were varied [59]. The model of PEM fuel cells to study the effect of relative humidity was developed by Xing *et al.* [11]. The model helps to contribute to the advection and diffusion of liquid water and heat transport [60]. The mathematical equation and interaction are presented in Figure 10.

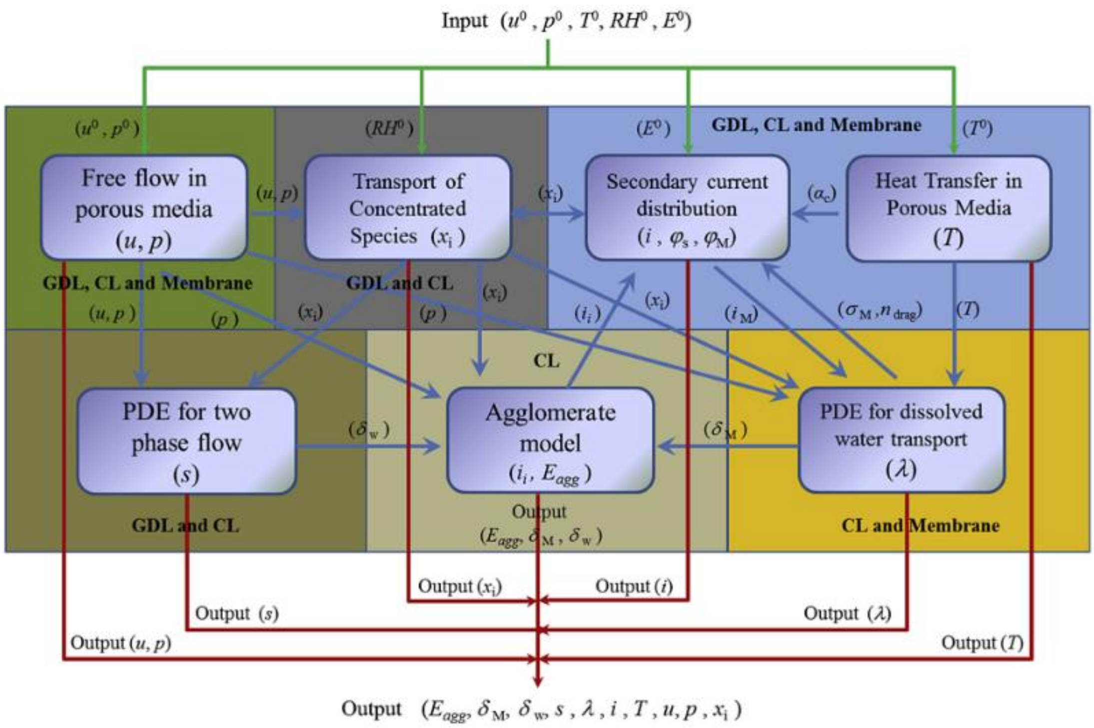
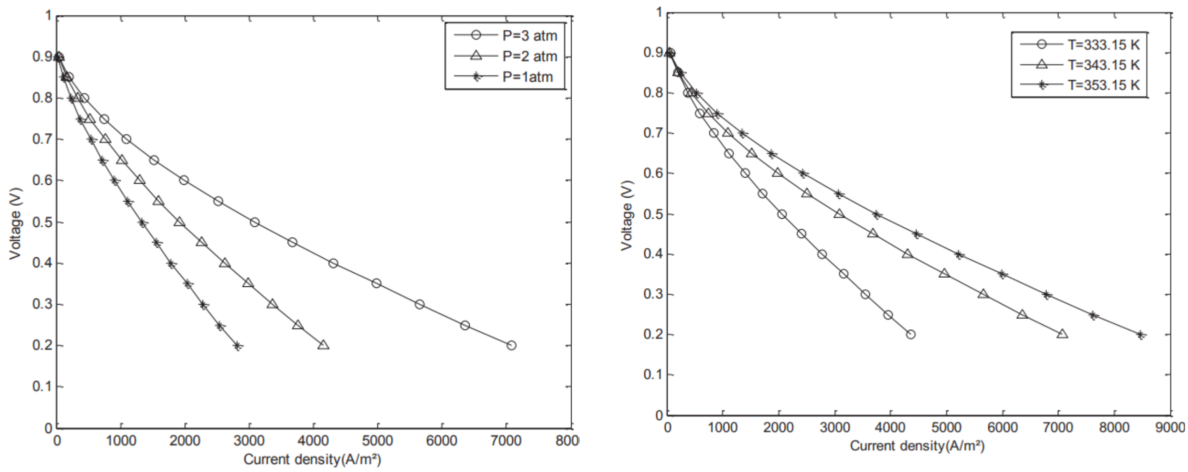


Figure 10. Different factors represent the mathematical model of PEMFCs [60].

Also, the COMSOL Multiphysics software 4.4 was used and most of the results focus on the relative humidity. However, the outcomes show that the Peclet number which demonstrates advection does not affect the liquid water transport in the porous electrode. We could adopt similar techniques of simulation using COMSOL as discussed by Lakshmi *et al.* [61]. The comparative analysis between the 2D and 3D model of PEMFC was presented at 120℃ by Haghayegh *et al.* [62] the study of modelling PEMFCs with the serpentine flow using COMSOL Multiphysics software 4.3. as shown in Figure 11.



(A) The effect of pressure on the polarization curve.

(B) The effect of temperature on the polarization curve.

Figure 11. Effects of changing temperature and pressure in PEMFCs [62].

Thereby, it is shown that pressure and temperature conditions are very important characteristics in PEMFCs. Therefore, we focus on the intermediate temperature. As PEMFCs provide high efficiency and its carbon-free by converting the H_2 through the chemical reaction to electricity, it is important to focus on aspects of PEMFCs in this research. One of the most important aspects is the humidifying system, which allows the PEMFCs to give the greatest performance and increase the water content and chemical reaction. However, this external humidifier causes complexity of PEMFCs and extra cost specifically the transport applications where the space is limited in vehicles. To overcome these problems, the self-humidifying system for PEMFCs is proposed at an intermediate temperature. One of the greatest studies in this field that has been presented recently, the review study by Mirfarsi *et al.* [63], which is classified the material into three types that are proton-conductive materials, inorganic materials and carbon-based additives. Therefore, it is important to present a composition between self-humidifying PEMs and different addictive in terms of performance, and stability, gas crossover, proton conductivity, water uptake and overall durability as presents in Table 1.

Table 1. Some challenges and remedies for self-humidifying of PEM fuel cells [63].

Challenges	Remedies
High ohmic resistance (hygroscopic additives)	▪ The utilization of smaller additives with an enhanced surface area can significantly optimize performance by facilitating improved ionic conductivity. Additionally, integrating a hybrid composition of proton-conductive and hygroscopic materials can effectively enhance the overall electrochemical properties. Furthermore, the functionalization of these materials can augment the density of proton-conductive sites, thereby improving charge transfer efficiency and system stability.
High ohmic resistance (proton conductors)	▪ The effectiveness of the additive or catalyst is highly dependent on its precise concentration, as both insufficient and excessive amounts can detrimentally impact performance. Therefore, an optimal dosage must be carefully determined to achieve the desired electrochemical properties while minimizing inefficiencies.
High ohmic resistance	▪ Regardless of the specific conditions, the use of thinner membranes can enhance proton conductivity by reducing ionic resistance and facilitating more efficient charge transport, thereby improving overall system performance.
Mechanical instability of ultra-thin membranes	▪ Structural integrity can be enhanced through reinforcement with polytetrafluoroethylene (PTFE) support, which improves mechanical stability and durability under operational conditions.
High gas cross-over rate and low OCV value	▪ The implementation of multilayer structures can effectively mitigate the permeation of reactants, thereby enhancing system efficiency and stability. Additionally, ensuring a uniform distribution of catalysts facilitates the availability of abundant recombination-active catalytic sites, optimizing electrochemical performance and reaction kinetics.
Agglomeration or migration of additives	▪ Addressing this issue can be achieved through surface modification or the functionalization of additives, which enhances their dispersion, stability, and interaction within the matrix, thereby improving overall material performance and efficiency.
Mechanical brittleness	▪ Enhancing the dispersion and ensuring optimal compatibility with the polymer matrix can significantly improve the mechanical resilience of proton exchange membranes (PEMs), thereby increasing their durability and operational stability under varying conditions.
Electron short circuit	▪ The implementation of a multilayer design can effectively mitigate this issue by enhancing structural integrity and performance stability. Additionally, functionalization strategies can address electron transfer inefficiencies, facilitating more efficient charge transport. Moreover, platinum (Pt) particles can be stabilized within a polymeric matrix possessing a positive charge, thereby improving their dispersion, catalytic activity, and overall electrochemical performance.

It can be used in the COMSOL Multiphysics software to study all types of fuel cells and physical properties including current distribution in electrodes and electrolytes, gas-phase mass transfer, thermodynamics, multiphase and porous media flow and heat transfer in single, two or multiply phases. In COMSOL, we can model single and two phases of laminar flow. Also, the heat transfer in solids, fluids and porous media can be modelled as shown in Figure 12. At normal pressure and low temperature, the E, A and i_0 are given by 1.2 V, 0.06 and 0.04 [mA/cm2] respectively [36]. Hence, we can draw the polarization curve in theory as follow:

Ohmic losses could be the losses in a fuel cell that are created due to the resistance to the flow of ions in the electrolyte and the electrical resistance of the electrodes. These ohmic losses should be reduced as much as possible which it can be done by manufacturing the electrolyte as thin as possible and avoiding the crossover issue. Also, the electrodes should be designed with the highest possible conductivity material besides the optimal design of BPPs [36].

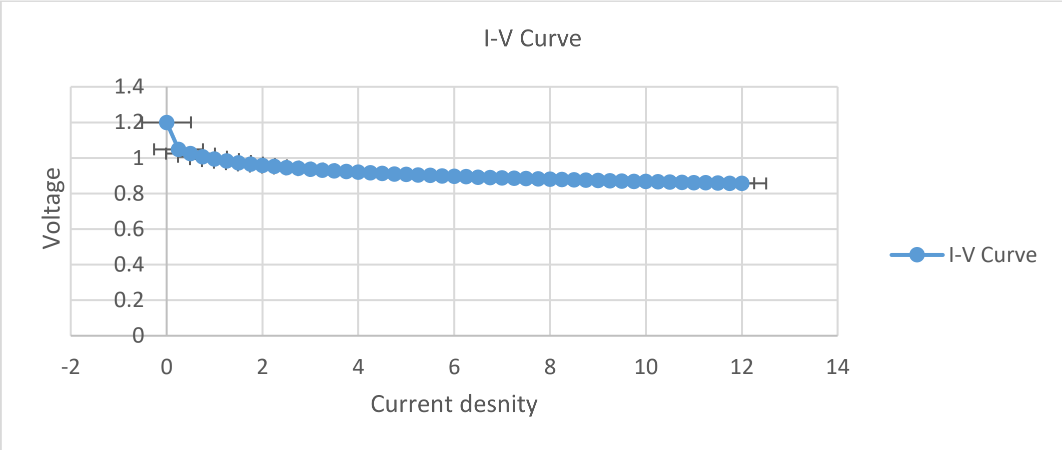


Figure 12. Modelling of PEM fuel cell by varying current and observing voltage numerically.

Figure 13 illustrates the computational modelling of an IT-PEMFCe using COMSOL Multiphysics software. It presents a three-dimensional schematic of the fuel cell structure, highlighting key components:

- Flow Channels: These structures facilitate the transport of reactant gases (hydrogen and oxygen/air) to the electrodes and the removal of byproducts.
- Gas Diffusion Layers (GDLs): Positioned between the flow channels and porous electrodes, these layers ensure uniform gas distribution and effective water management.
- Porous Electrodes: These layers contain the catalysts necessary for the electrochemical reactions that generate electricity.
- Membrane: The central proton-conducting component that enables the transport of hydrogen ions while acting as an electronic insulator to prevent short circuits.
- Inlets and Outlets: These features indicate the entry and exit points of reactant and product gases, facilitating mass transport.

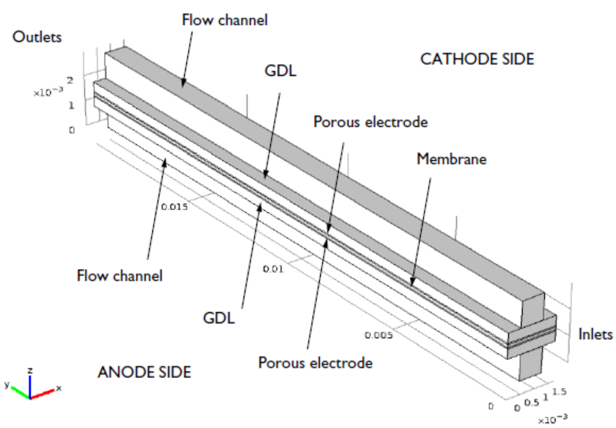


Figure 13. Modelling IT-PEM fuel cell in COMSOL software.

The labelled dimensions in the figure represent various structural aspects of the fuel cell, ensuring accurate modelling of performance characteristics such as mass transport, electrochemical reactions, and thermal management in COMSOL Multiphysics software. The results of the modelling system are shown in Figure 14 to Figure 16.

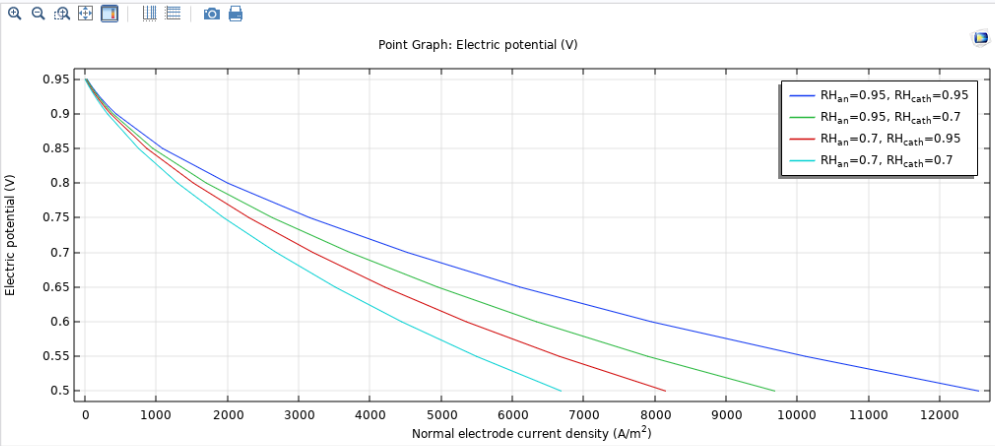


Figure 14. Performance of modelling PEM fuel cell at 80 °C.

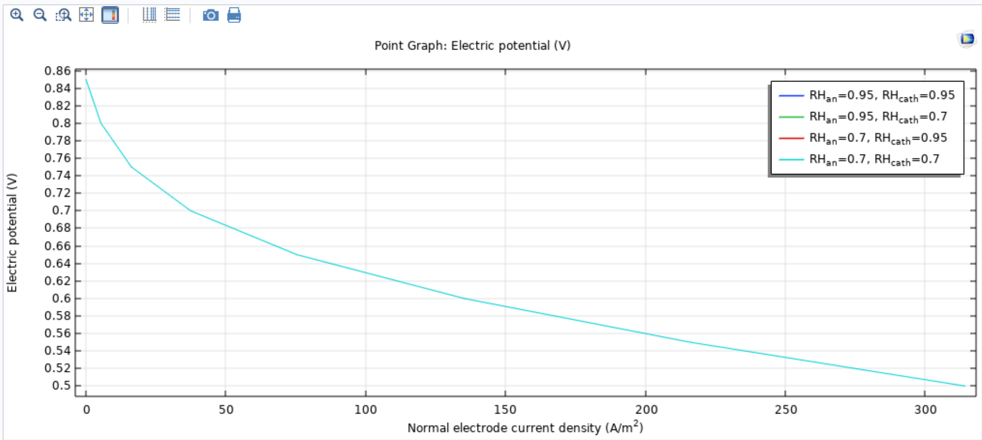


Figure 15. Response of IT-PEM fuel cell at 110 °C.

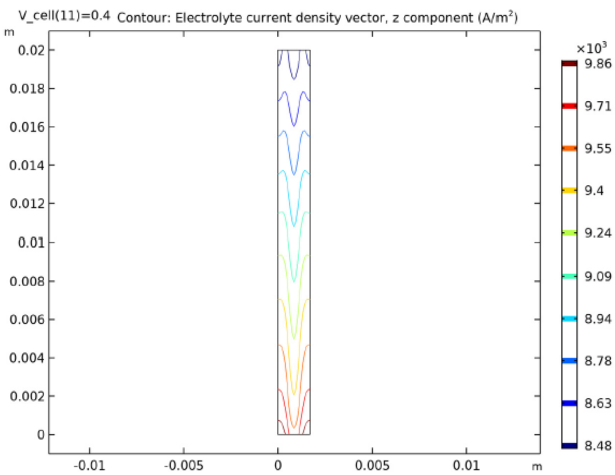


Figure 16. Modelling of ionic current in PEM fuel cell.

This model explores the transport of reactants and water at a high-temperature PEMFC. The model incorporates mass and momentum transport phenomena in the Bipolar Plates, porous electrodes, and GDLs. In addition to electrochemical currents in the GDLs, the porous electrodes, and the PEM [64,65].

5. Evaluation and Finding Outcomes

While, the membranes of SPEEK were tested at a temperature between 120-180 ℃ by Beyraghi *et al.* [66], where FTIR, TGA and AFM were used. Also, chemical stability, hydrogen permeability proton conductivity and water uptake were investigated where annealing-dominated samples were more stable and more homogenous and had better proton conductivity than the samples of cross-linking dominated. SPEEK membrane was treated with a higher Residual Solvent (RS) value which was determined by Eq. 14 and 15 [66,67]:

$$m_{SPEEK\ in\ cast\ solution} = m_{SPEEK\ in\ original\ solution} X \frac{m_{Cast\ solution}}{m_{Original\ solution}} \quad \text{Eq. 14}$$

$$RS(\%) = \frac{m_{Cast\ membrane} - m_{SPEEK\ in\ cast\ solution}}{m_{\ cast\ membrane}} X100 \quad \text{Eq. 15}$$

Where $m_{Original\ solution}$ is the mass of prepared SPEEK solution, $m_{Cast\ solution}$ is the mass of the SPEEK solution in the petri dish, $m_{SPEEK\ in\ original\ solution}$ and $m_{SPEEK\ in\ cast\ solution}$ are the mass of SPEEK in the original and cast solution, respectively while $m_{Cast\ membrane}$ is the mass of the final prepared membrane with the desired amount of RS [66]. Three articles are recommended, which could be worth investigating in this research. These are self-humidifying nanocomposite membranes based on SPEEK, durable sulfonated partially fluorinated polysulfones as the membrane for PEMFCs [68] and the effect of $Pt-Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst addition on the durability of self-humidifying nanocomposite membrane based on SPEEK [58].

Although nanocomposite 15 %wt. (1.25%pt) at temperature 60℃, humidified reactants better than Nafion -117 and SPEEK (DS=65.12%) even nanocomposite at dry reactants better than both Nafion-117 and SPEEK membranes [2], it is only the test at 60 ℃ as shown in Figure 17, and other studies by Sun *et al.*, [69] show C-SPEEK/HPW/GO is better than C-SPEEK while we are interested in the operation of PEMFCs at an intermediate temperature between (80-120℃). The article [2], approved that "*In single cells that employed the sPEEK/Pt-$Cs_{2.5}$ self-humidifying nanocomposite membranes exhibited higher cell OCV values and cell performances than those of plain SPEEK membrane and Nafion-117 membrane under dry or wet conditions and showed good water stability in the aqueous medium*". It would be useful to investigate and test SPEEK/Pt-$Cs_{2.5}$ self-humidifying nanocomposite membranes at an intermediate temperature and compare them with other Nafion membranes.

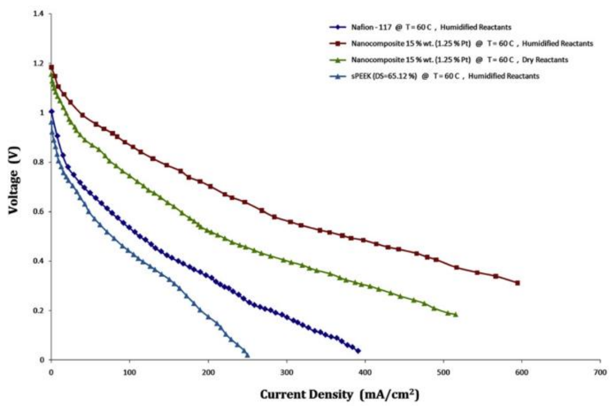


Figure 17. Different membrane materials and testing performance.

The cost and the durability of PEMFCs under a wide range of operating conditions including RH and temperature were studied by *Brunetti et al.* [5]. These comparisons are very useful in the current research to allow us to focus on the SPEEK membrane rather than the Nafion membrane [70, 30]. Also, the crossover during the low thickness of the membrane is another issue that causes hydrogen and oxygen to pass to the opposite side of the membrane which leads to accelerating degradation of PEMFCs. The Transport Performance Index (TPI) has been defined as the ratio of hydrogen permeability and proton conductivity which is given by Brunetti *et al*. [5] as Eq. 16. TPI has been defined as the ratio of hydrogen permeability and proton conductivity which is given by Brunetti *et al*. [5] as Eq. 16.

$$TPI = \frac{2.H_2\ permeability}{proton\ permeability} \quad [\frac{mols}{Pa * S}] \qquad \text{Eq. 16}$$

It was applied for a Nafion 117 membrane and a cross-linked homemade-SPEEK membrane as a function of pressure, temperature, and RA as shown in Figure 18. Not only this but the mechanical test was conducted as in Figure 19.

With full RH   Variation of RH

Figure 18. Comparison between Nafion-117 and SPEEK membranes performance by using transport performance index [5].

The article can discuss these results where the SPEEK membrane gave better performance even after 200 hours ($\cong 8\ days$). It would be useful to allow SPEEK to operate for a month or even more at 120 °C and determine its durability. For the current as far as I know, there is no measurement for the durability of the SPEEK membrane as the nanocomposite (15 wt.%) shows better mechanical properties and more strength than SPEEK.

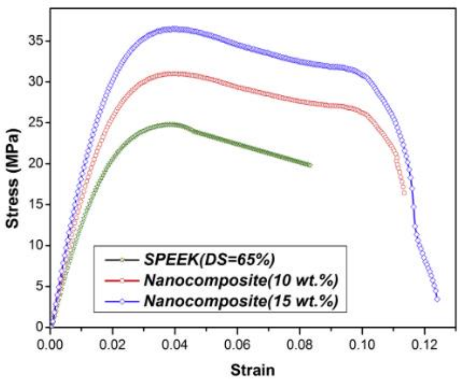


Figure 19. Testing the mechanical strength of different membrane materials [58].

PEMFCs are being developed mainly for transport applications due to the compactness of the PEMFCs. It is considered the prime FCs for vehicles and mobile applications. The membrane must not be electrically conductive to avoid a half-reaction mix [71,72]. When PEMFCs operate at 100 °C or above, the water byproduct becomes steam. The blockage due to condensation could be avoided. The limitations of PEMFCs are:

- Cost.
- Degradation.
- The critical point of water management.

Water management is a very challenging task in PEMFCs due to the slower evaporating water leads to a flood of the membrane and accumulates the water inside the BPPs. On the other hand, the fast-evaporating water causes the drying of the membrane. In both cases, the degradation of the performance of PEMFCs will occur. An electroosmotic pump was used as a solution on the 3D fine mesh of BPP design as a solution adapted by several companies. Once the membrane is made from platinum, it may become sensitive to metal ions and it can be easily poisoned by carbon monoxide. However, with its high temperature, the position of CO could be neglected.

6. Challenging to operate at the intermediate temperature

Nafion is most generally utilized for membranes. The Nafion depends on fluid water to humidify the membrane at low temperatures. It is suitable at low temperatures below 80℃ but at a temperature above 80℃, the membrane becomes dry. The solution for this problem is using Polybenzimidazole (PBI), Phosphoric Acid which allows the membrane to be used without water management and overcomes the problem of no feasibility of using Nafion membrane. According to [73], using PBI for membranes helps to increase power density and efficiency. Not only this but it can overcome water management issues when the Nafion is used. According to authors in references [74-80], the protic ionic liquids and protic organic ionic plastic crystals, allow using membranes at 100-200℃ which are required to operate PEMFCs at intermediate temperatures. The Thermogravimetric Analysis (TGA) curves in Figure 20 illustrate the thermal stability and decomposition behaviour of various membrane materials compared to the benchmark Nafion 117 membrane.

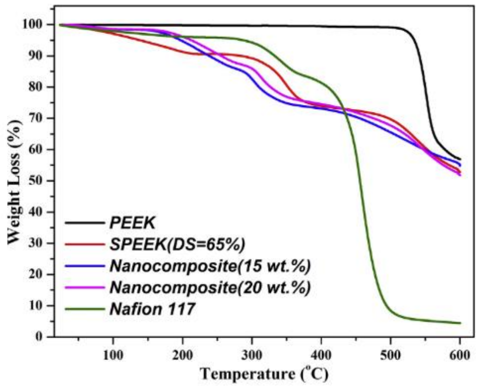


Figure 20. TGA curves of different materials for membranes compared with pure Nafion-117 membrane [58].

The results indicate that PEEK exhibits the highest thermal stability, with negligible weight loss up to 600°C, making it a robust candidate for high-temperature applications. In contrast, SPEEK (DS = 65%) begins to degrade around 300°C, reflecting the influence of sulfonation on its thermal resistance. The nanocomposite membranes (15 wt.% and 20 wt.%) demonstrate improved thermal stability over SPEEK, suggesting that the inclusion of nanomaterials enhances structural integrity and resistance to thermal decomposition. Meanwhile, Nafion 117 undergoes significant weight loss around 400°C, limiting its applicability in high-temperature proton exchange membrane fuel cells (HT-PEMFCs).

These findings underscore the superior thermal properties of PEEK-based membranes, particularly sulfonated and nanocomposite variations, which exhibit enhanced stability compared to Nafion 117. The delayed decomposition of nanocomposite membranes highlights the effectiveness of nanomaterial reinforcement in mitigating thermal degradation, making them promising alternatives for advanced HT-PEM fuel cell applications. By contrast, Nafion 117's lower thermal resistance restricts its use to lower operating temperatures, reinforcing the necessity for alternative membrane materials in next-generation fuel cell technologies. This study emphasizes the critical role of material selection in optimizing PEM performance, particularly for applications demanding high thermal resilience and prolonged operational durability.

7. Conclusion

This study has provided a comprehensive investigation and modelling framework for Intermediate-Temperature Proton-Exchange Membrane Fuel Cells (IT-PEMFCs), emphasizing their potential for transport applications. Through an extensive review of state-of-the-art membrane materials, the research has identified key challenges and opportunities in optimizing fuel cell performance at elevated temperatures. A primary focus has been placed on mitigating gas crossover losses, which, despite being minimal (1–3% fuel losses), remain a critical factor in efficiency. The study has further highlighted the superior reliability of nanocomposite membranes (15 wt.%) in sustaining PEMFC operations under intermediate-temperature conditions. The development of a theoretical IT-PEMFC model, currently an ongoing effort, serves as a foundation for future advancements in this field.

While the findings underscore the viability of IT-PEMFCs in transportation, several technical challenges persist, including enhancing proton conductivity, increasing tolerance to CO and other gas impurities, and improving overall system efficiency. Addressing these issues will require further experimental validation, advanced material engineering, and refined computational modelling techniques. As hydrogen-based energy solutions continue to gain momentum in the push for sustainable transportation, the insights from this research contribute to the advancement of next-generation fuel cell technologies. Future work should focus on bridging the gap between theoretical modelling and real-world applications, ensuring IT-PEMFCs achieve the durability, efficiency, and commercial scalability required for widespread deployment.

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