OPTIMIZING THE PERFORMANCE OF NAFION MEMBRANES IN HUMIDIFIERS TO INCREASE THE EFFICIENCY OF HYDROGEN FUEL CELLS IN REALIZING CLEAN ENERGY SOLUTIONS

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Abstract: Proton Exchange Membrane Fuel Cells (PEMFCs) are a key technology in the hydrogen revolution, offering efficiencies of up to 60% and ultra-low emissions. The Antasena ITS Team has integrated an open-cathode PEMFC system into its hydrogen vehicle innovation to optimize performance. However, humidity and temperature significantly impact the performance of PEMFC systems, as the water content in the polymer electrolyte membrane plays a crucial role in enhancing proton conductivity. To address this, humidifiers are employed to maintain membrane hydration, ensuring proton conductivity and system efficiency. By adding moisture to the air entering the cathode, humidifiers prevent membrane dehydration, improving stability and fuel cell performance. Humidifiers typically utilize Nafion membranes due to their exceptional ability to retain moisture under operating conditions. Nafion, a perfluorosulfonic acid ionomer, is renowned for its high ionic conductivity and excellent chemical and mechanical stability. This study investigates the performance of Nafion 117 and Nafion 115 membranes in humidifier applications, focusing on proton conductivity, efficiency, thermal resistance, and chemical stability. Prior to testing, the membranes were cleaned with a 0.5 M sulfuric acid (H_2SO_4) solution at 80°C for 1 hour to remove metal contaminants that could impair conductivity. This cleaning process enhanced membrane conductivity by up to 50%. Following cleaning, the membranes were assembled with protective cover plates to withstand mechanical stress and positioned between bipolar plates featuring reactant gas channels for hydrogen and oxygen distribution. The results demonstrate that Nafion 115 exhibited a higher proton conductivity of 0.33 S/cm at 130°C and 100% relative humidity (RH) compared to Nafion 117, which reached 0.21 S/cm under the same conditions. However, Nafion 117 showed superior resistance to dehydration and greater thermal stability due to its 180 µm thickness. Conversely, Nafion 115 proved more efficient for proton transport at high temperatures but was more sensitive to low-humidity environments.

I. INTRODUCTION

Global CO2 emissions continue to rise, with an increase of 1.9% in 2019 compared to 2018. Total global greenhouse gas (GHG) emissions in 2018 grew by 2%, reaching 55.6 Gt CO2, with an annual growth rate of approximately 1.3% (Cahyono et al., 2022). In 2020, the transportation sector contributed 33 % of total CO2 emissions, making it the largest contributor compared to other sectors. The increase in emissions from transportation continues, raising concerns about its impact on global warming. The type and amount of fuel used in transportation are the main factors driving this rise in emissions.

Hydrogen is considered a sustainable and environmentally friendly energy source for the future, capable of replacing fossil fuels. Shell plans to use green hydrogen to decarbonize the transportation sector and increase the capacity of the Refhyne electrolyzer to 100 MW as part of its Net Zero 2050 target. Hydrogen has advantages such as high energy density, being non-toxic, and the ability to generate electricity, heat, and fuel across various sectors (Alsaba et al., 2023). The Antasena ITS team is currently developing innovative vehicles in the form of hydrogen-based cars and motorcycles utilizing proton exchange membrane fuel cell (PEMFC) technology.

Figure 1. Antasena Hydrogen Motorcycle

Figure 2. Antasena Falcon

Fuel cells, particularly Proton Exchange Membrane Fuel Cells (PEMFCs), are a key technology in the hydrogen revolution, achieving efficiencies of up to 60%. PEMFCs are gaining attention as an environmentally friendly alternative to replace fossil fuels by converting hydrogen into electrical energy. During the electrochemical reaction, PEMFCs produce water and heat; however, improper water management can degrade performance by either drying out or flooding the membrane. Effective water management is essential to enhance the durability and efficiency of PEMFCs in various applications, ranging from energy storage to transportation (Ferraris et al., 2019).

Therefore, a proper humidifier for reactant gases before entering the fuel cell plays a crucial role in the performance and lifespan of the cell. A humidifier is used to maintain the moisture of the PEMFC membrane, which is essential for proton conductivity and system efficiency. Current fuel cell humidification methods can be divided into internal and external humidifiers, depending on how water is introduced into the system. One example of an external humidifier design is the membrane humidifier. In this type of humidifier, humidified exhaust gas from the fuel cell stack is passed through a selective membrane to moisten the incoming dry air. The membrane in the humidifier must have high water permeability while being impermeable to other air components. Additionally, the membrane material must withstand the operational conditions of the fuel cell over long periods and remain mechanically stable. Most modern membranes for fuel cell humidification use perfluorosulfonic acid (PFSA) polymers, with Nafion® being the most commonly employed. However, studies involving Nafion® membranes of different thicknesses have shown varied results.

The objective of this study is to compare the performance of Nafion® 115 and Nafion® 117 membranes, which differ in thickness, and to analyze the impact of membrane thickness on proton conductivity, efficiency, thermal resistance, and chemical stability. The research aims to understand how variations in membrane thickness influence the performance and durability of fuel cells under diverse operational conditions, as well as to evaluate the potential application of these two types of membranes in hydrogen-based fuel cell systems. This study is expected to provide valuable insights for selecting the optimal membrane to enhance the performance and durability of fuel cells under various operating conditions.

RESEARCH METHODS

A. Writing Method

The preparation of this scientific paper follows a systematic literature review approach, involving a critical examination of various scientific journals. The stages of writing align with the workflow illustrated in the research flow diagram below:

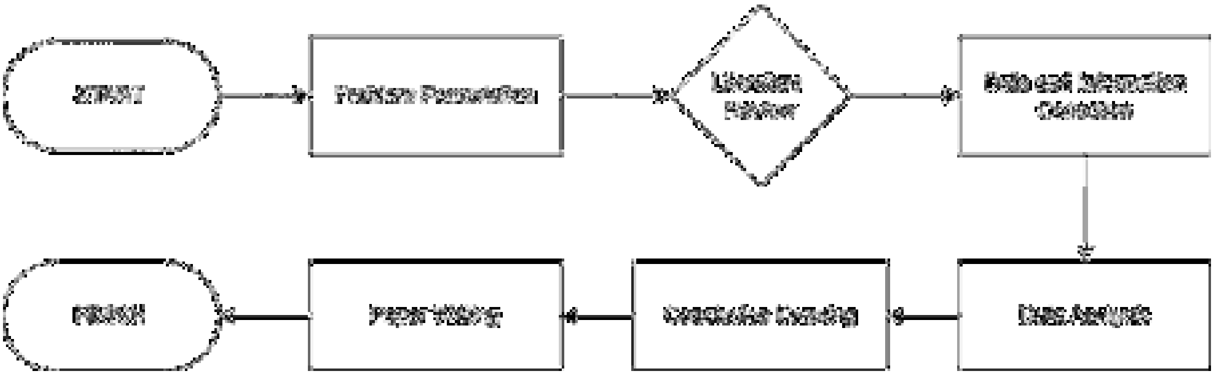


Figure 3. Research Process Flow

Source: Private Document, 2024

The materials considered in this study, namely Nafion 115 and 117 membranes, are applied as components within the humidifier of a Proton Exchange Membrane Fuel Cell (PEMFC).

B. Data Sources and Collection Techniques

This paper integrates both qualitative and quantitative data types. Qualitative methods are used to describe the data obtained and required by comparing various studies, both nationally and internationally. The sources for the paper are derived from journals published by reputable publishers. The quantitative method involves calculations of the conductivity produced by Nafion 115 and 117 membranes. The results are then compared with existing studies. The data collected are compiled, processed, and analyzed to derive conclusions regarding the findings of the literature review.

C. Analytical Techniques

The data analysis incorporates both the operational mechanisms and numerical calculations to evaluate the performance and effectiveness of Nafion 115 and 117 membranes, employing a meta-analysis methodology. Following data collection, comparative analysis is conducted against established theories and findings documented in scientific journals. This analytical approach aims to derive a comprehensive and substantiated explanation aligned with the research objectives.

RESULTS AND DISCUSSION

The chemical reactions occurring within a Proton Exchange Membrane Fuel Cell (PEMFC) begin at the anode, where hydrogen gas (H_2) dissociates into two protons (H^+) and two electrons (e^-) under the influence of a catalyst, typically platinum. This reaction is expressed as:

$$H_2 \rightarrow 2H^{+}+2e^{-} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

The resulting protons (H^+) traverse the proton exchange membrane to reach the cathode, while the electrons (e^-) flow through an external circuit, generating an electrical current. At the cathode, oxygen (O_2) from the air reacts with the protons and electrons to form water (H_2O), described by the reaction:

$$\frac{1}{2}O_2 + 2H^{+} + 2e^{-} \rightarrow H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

This continuous process, maintained under constant pressure and temperature, converts the chemical energy of the fuel into usable electrical energy (Paul C. Okonkwo, 2021).

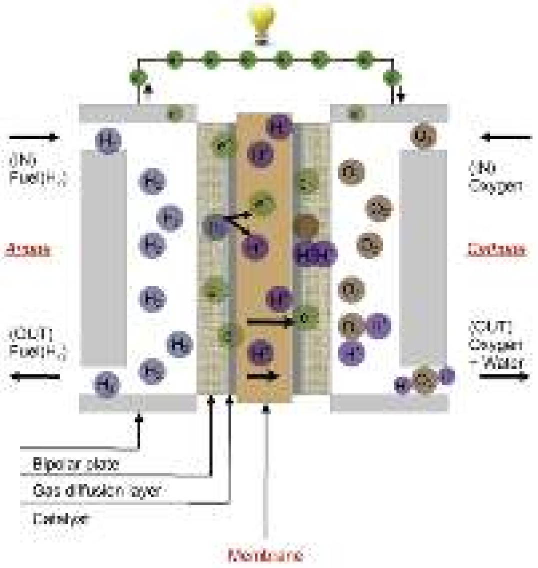


Figure 4. Reactions Occurring in a PEMFC Fuel Cell

Source : (Paul C. Okonkwo., 2021).

The humidifier consists of several key components: a water distribution system, a Nafion membrane, and a cover plate. It is manufactured using a 3D printer with nylon material and is connected to a purge valve located at the anode outlet. During the purge process, unused hydrogen along with water vapor flows into the humidifier and is directed to the membrane surface via channels in the water distribution system. The membrane absorbs water while hydrogen is released into the environment. The absorbed water diffuses to the opposite side of the membrane, increasing the humidity of the air entering the open cathode channel. The humidified air is then delivered to the cathode channel with the help of an electric fan, enhancing the efficiency of PEMFC operation (Phuong-Long Le, 2022).

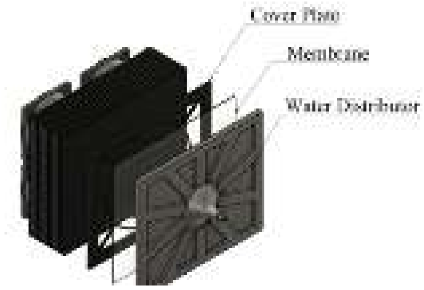


Figure 5. Humidifier

Source: Private Document, 2024

Nafion is a perfluorinated polymer membrane extensively used in hydrogen energy applications. Its exceptional thermal, mechanical, and chemical stability enables its utility beyond hydrogen energy in fields like physics and chemistry. In aqueous environments, Nafion exhibits unique bulk and surface ultrastructural properties. It is synthesized through the copolymerization of perfluorinated vinyl ether monomers with tetrafluoroethylene (Teflon) (Ninham et al., 2023).

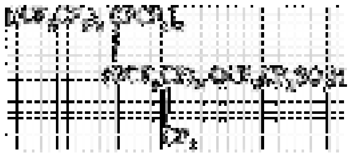


Figure 6. Nafion Chemical Structure

Source: (Daud dkk, 2020).

Figure 7. The hydrophobic and hydrophilic separation sites in the microstructure of Nafion

Source: (Daud dkk, 2020).

Nafion is a type of proton exchange membrane (PEM) commonly used in fuel cells, with variants such as Nafion 115 and Nafion 117. The naming of Nafion membranes reflects their polymer equivalent weight (the first two digits) and membrane thickness (the third digit). For example, Nafion 117 has a thickness of 7 mils and a polymer equivalent weight of approximately 1100 g/mol. The transport and mechanical properties of Nafion are influenced by its equivalent weight, where higher values improve mechanical strength but reduce proton conductivity (Daud et al., 2020).

The degradation of Nafion membranes occurs via two primary mechanisms: main-chain unzipping and side-chain cleavage. Main-chain unzipping degradation begins when fluoroalcohol releases carbon fluoride (CF), forming acyl fluoride that subsequently hydrolyzes into carboxylic acid and additional CF. This process is accelerated by the degradation of acidic hydrogen by hydroxyl radicals, which initiates and propagates further degradation. As a perfluorosulfonic acid (PFSA)-based material, Nafion requires the presence of hydrogen-containing terminal groups to initiate degradation. Without these groups, the material does not degrade even when exposed to similar chemical environments. This degradation process induces both physical and chemical changes in the Nafion membrane, reducing its proton conductivity and structural stability. These changes undermine the membrane's ability to maintain strength and durability, ultimately decreasing its proton conductivity, resistance to operational conditions, and increasing the risk of hydrogen leakage due to structural damage. This, in turn, lowers fuel cell efficiency as the membrane’s ability to facilitate proton transport diminishes (Paul C. Okonkwo, 2021).

Over time, this degradation accelerates membrane deterioration, shortening the fuel cell's lifespan and reducing its overall performance. Side-chain cleavage degradation is more complex and becomes evident only after long-term operation. In this mechanism, the carbon-oxygen-carbon (C-O-C) groups decompose, producing relatively stable radicals. Under low-humidity conditions, which are common in fuel cells, the increased concentration of free radicals attacks C-O-C groups, generating additional stable radicals. In PFSA materials like Nafion, cleavage of the carbon-sulfur (C-S) bond in the side chain produces terminal fluoro radicals, which follow a degradation pathway. Oxygen radicals formed at main-chain junctions trigger further breakdown, generating acyl fluoride and fluorocarbon radicals. Even a small number of side-chain radicals can cause further chain cleavage, accelerating the degradation rate in PFSA materials such as Nafion. This process can begin under extremely dry conditions but accelerates through unzipping mechanisms in moderately humid environments. While initially slow, over time, these mechanisms significantly compromise Nafion's performance in fuel cell applications (Paul C. Okonkwo, 2021).

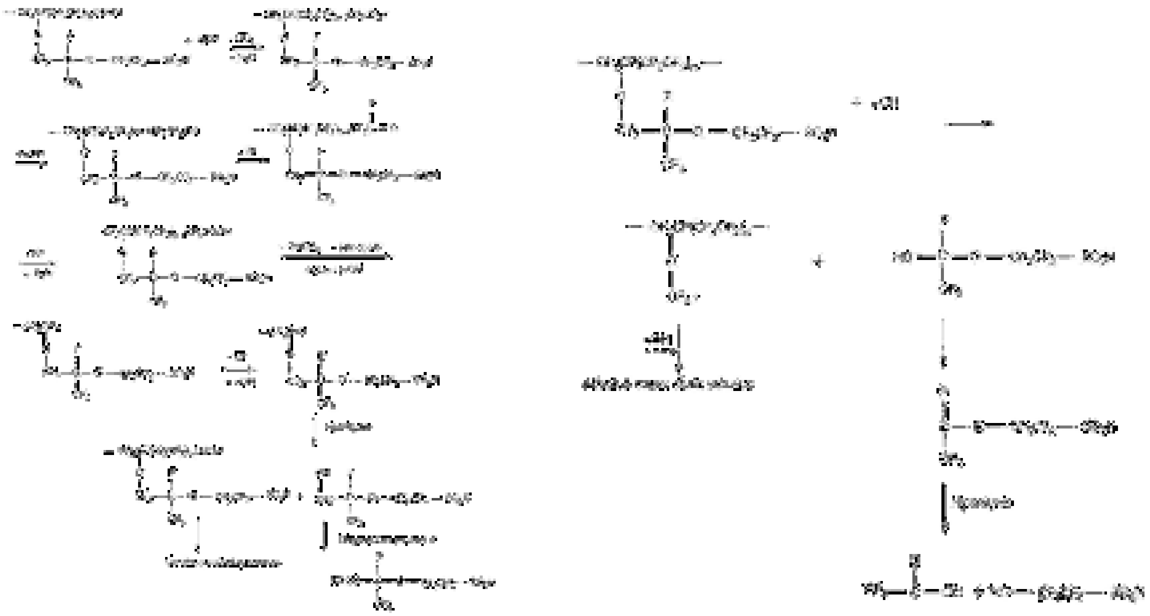


Figure 8. Nafion Ion Degradation Mechanisms

Studies reveal that the conductivity of Nafion membranes decreases following durability testing, which is a primary factor in performance degradation. This decline in conductivity can be attributed to several causes, such as the loss of sulfonic acid groups, proton exchange due to contamination, or the formation of S–O–S cross-links, as identified in FTIR spectra. Conductivity was also measured after treatment with 0.5 M sulfuric acid at 80°C for 1 hour to remove metal contaminants. This treatment resulted in an approximately 50% increase in conductivity in degraded samples, indicating that proton exchange is likely a major contributor to the decline in conductivity. This finding aligns with the understanding that degradation through unzipping of the main polymer chain compromises the overall integrity of the polymer structure. Although the loss of sulfonic acid groups occurs, the reduction in membrane thickness is directly proportional to this loss, suggesting that chain scission in the side chains is a critical factor in the observed decrease in membrane conductivity. Measurements were conducted both ex-situ (in H_2SO_4) and in-situ (within a PEMFC), and results show that Nafion membrane conductivity declines with decreasing membrane thickness (Slade, 2002).

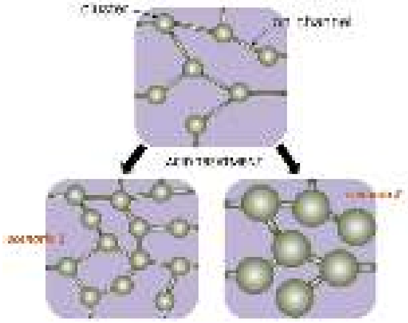


Figure 9. Acid Treatment Process

Source: Iriarte dkk., 2022

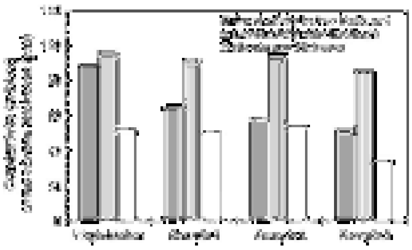


Figure 10. Conductivity Graph

Source: Chen., 2009

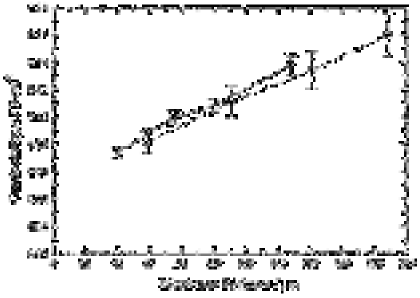


Figure 11. Graph of Conductivity vs. Membrane Thickness

Baseline TGA measurements were conducted on each sample to determine whether the thermal decomposition of the material is influenced by its thickness. Variations in thermal decomposition profiles due to material thickness could affect the sample's response to heating or freezing, which must be considered in the final analysis. Figure 10 presents baseline TGA data from untested dry samples: 115 (blue data), 117 (green data), and 1110 (orange data). These results indicate that all three materials exhibit nearly identical thermal decomposition profiles between 21°C and 700°C, confirming that material thickness does not impact thermal degradation profiles.

The materials were also thermally stable up to approximately 300°C, where major decomposition events began. The observed mass loss between 21°C and 300°C was attributed to water evaporation within the samples, rather than chemical decomposition of the materials themselves. This finding demonstrates that the temperatures used in this study do not induce thermal decomposition of the samples. Additionally, mass change measurements can serve as a secondary decomposition check to assess whether sample mass varies with material thickness after each experiment (Dr. Theodore Burye, 2021).

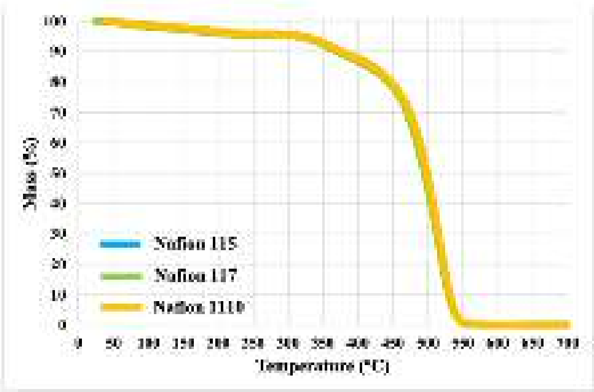
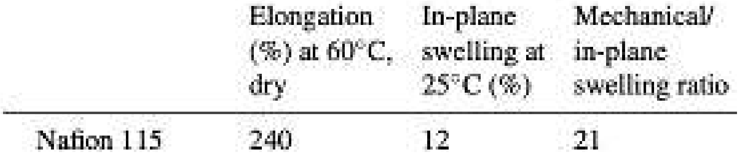


Figure 12. Baseline TGA Measurement Graph

Source: (Dr. Theodore Burye., 2021)

The mechanical properties of Nafion 117 reveal a tensile strength of 21.9 MPa and an elastic modulus of 178 MPa. Its elongation at break reaches 184%, demonstrating that although its mechanical strength is lower compared to SPEEK and S/G, Nafion 117 offers superior flexibility. Despite its lower tensile strength, Nafion 117 performs well mechanically, with a greater ability to stretch before breaking, making it suitable for applications requiring high flexibility (Dai et al., 2014).

Nafion 115, on the other hand, achieves the highest elongation at break at 240%, indicating excellent flexibility. Its in-plane swelling remains stable at 12%, reflecting good dimensional stability. Additionally, its mechanical-to-swelling ratio reaches an impressive value of 21, signifying an optimal balance between mechanical strength and dimensional stability (Caire, 2016).



	Elongation (%) at 60°C, dry	In-plane swelling at 25°C (%)	Mechanical/ in-plane swelling ratio
Nafion 115	240	12	21

Figure 13. Membrane Data 115

Samples	Breaking strength (MPa)	Percentage elongation (%)	Elastic Modulus (MPa)
Nafion117	21.9	184	178

Figure 14. Membrane Data 117

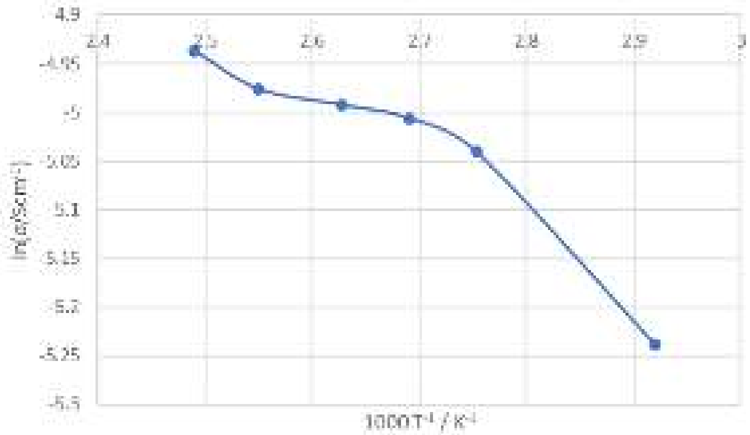


Figure 15. 117 Conductivities

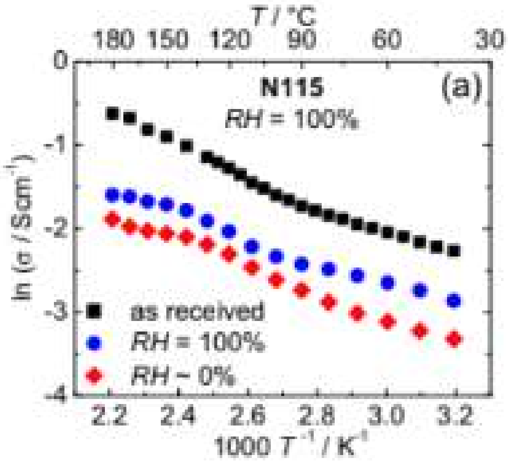


Figure 16. 115 Conductivities

The graph illustrates the conductivity behavior of Nafion 115 and Nafion 117 membranes based on temperature and relative humidity (RH). For Nafion 115, the graph shows significantly higher conductivity at 100% RH compared to lower RH levels, especially as humidity approaches 0% (RH ~ 0%). At 100% RH, conductivity decreases moderately with rising temperature, but this decline becomes much steeper as relative humidity decreases. This indicates that Nafion 115 is highly dependent on humidity to maintain its conductivity performance, with its ion conduction ability declining drastically in drier environments.

In contrast, Nafion 117 exhibits a more stable conductivity pattern, albeit generally lower than that of Nafion 115. Across various temperature ranges, Nafion 117 also experiences a decline in conductivity, but within a narrower range. This decline becomes more pronounced at higher temperatures, reflecting the membrane's sensitivity to temperature increases that impair its ionic performance.

The comparison highlights significant differences in the behavior of the two membranes. Nafion 115 excels under high-humidity conditions, achieving a much higher conductivity of approximately 0.36 S/cm at 100% RH. This makes it more efficient for applications requiring rapid ion transfer in humid environments, especially at low to moderate temperatures. On the other hand, Nafion 117, with a lower conductivity of about 0.00698 S/cm, is less efficient in terms of ionic conductivity but offers greater stability in extreme or high-temperature conditions, albeit with reduced performance under high humidity.

Overall, Nafion 115 is superior in efficiency for ionic processes in moist environments, while Nafion 117 may be better suited for applications involving broader temperature variations, despite its lower ionic performance (Chen, 2009; Bruno R. Matos, 2016).

CONCLUSIONS AND RECOMMENDATION

This study demonstrates that Nafion 115 and Nafion 117 membranes exhibit distinct characteristics in terms of proton conductivity and operational stability. Nafion 115, with its thinner structure, provides higher proton conductivity, particularly under high-humidity conditions, making it a more efficient choice for applications requiring rapid ion transfer in moist environments. Conversely, Nafion 117, being thicker, displays lower conductivity but offers superior stability in environments with more extreme variations in temperature and humidity. Therefore, the selection of membrane type should be tailored to specific operational conditions, where Nafion 115 is optimal for high-humidity environments, and Nafion 117 is better suited for applications demanding stability under fluctuating temperature and humidity conditions. The appropriate membrane selection is highly dependent on the operational environment. Nafion 115 is recommended for applications requiring high conductivity in humid conditions, whereas Nafion 117 is advised for environments with greater variations in temperature and humidity. Furthermore, additional research is necessary to better understand the degradation mechanisms of both membrane types to enhance the durability and efficiency of hydrogen-based fuel cells. The optimal implementation of humidifiers is also critical to maintaining membrane hydration, particularly for Nafion 115, ensuring maximum performance under varying operational conditions.

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