



THERMO-ELECTROCHEMICAL PROPERTIES OF POLYMER ELECTROLYTE MEMBRANE DERIVED FROM POLYISOPRENE/POLYSTYRENE BLEND

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ABSTRACT

Apart from the very high cost of the state-of-the-art Nafion® membranes that are derived from polytetrafluoroethylene, another serious factor that hinders their full commercialization is the loss of conductivity at elevated temperature (above 120°C) under fuel cell operation. These factors have challenged researchers to seek alternative membranes from other polymeric materials. On this premise, this study seeks to derive a possible alternative from polyisoprene and polystyrene (PIPS) blend via sulfonation process, and to investigate its thermo-electrochemical properties. The PIPS blend (70:30) was sulfonated with chlorosulfonic acid for 1–18 h, and the ion exchange capacity (IEC) and degree of sulfonation (DS) were determined from the sulfur content. Thermal properties were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), proton conductivity by AC impedance spectroscopy, and the open circuit voltage and power density in a single fuel cell at catalyst loadings of 15, 30 and 40 wt%. From the study carried out, results show that the membrane derived from the sulfonated PIPS (SPIPS) demonstrates thermal stability with a glass transition temperature of 150°C and a degradation temperature of 400 °C, making it suitable for fuel cell application, particularly proton exchange membrane fuel cell and direct methanol fuel cell that operate up to 120°C. An optimum proton conductivity of 4.09×10^{-2} S/cm is achieved with the membrane of optimum degree of sulfonation (3.969%), which is of the same order as that of Nafion®. Other electrochemical testing shows that the synthesized membrane achieves an optimum open circuit voltage (OCV) of 645.91 mV and power density of 62.0 mW/cm² using 40% catalyst loading. These characteristics, therefore, place the PIPS blend as a viable alternative polymer electrolyte membrane material for fuel cell applications.

Keywords: Conductivity, current density, degree of sulfonation, power density, thermo-electrochemical, voltage.

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INTRODUCTION

Besides the very high cost, one of the serious limitations of the state-of-the-art polymer electrolyte membrane, being the perfluorinated Nafion® is the loss of conductivity at high temperature (> 120°C) [1-4]. To address the high production cost and limited durability of the conventional commercial membranes of Nafion®, researchers have focused on developing alternative cation exchange membranes (CEMs) using different structural and compositional strategies, which include modification of organic polymers, formation of organic-inorganic hybrid membranes, blending of compatible polymers, and chemical cross-linking to improve mechanical and thermal stability [5, 6]. Apart from Nafion® membranes that have maintained the center stage, other known perfluorinated membranes include Aciplex (Asahi Chemical), Flemion (Asahi Glass), and Gore-Select (Gore & Associates). These materials are known to

share a similar structural framework composed of perfluorinated backbones with ionic side chains that facilitate proton transport [7]. Nafion®, introduced by DuPont in the 1960s, was initially deployed to serve as a separator in chlor-alkali cells before being adapted for PEM fuel cells in NASA's space program. Its superior oxidative stability and ionic conductivity established it as the benchmark for electrochemical systems. Early versions such as N-115 and N-117 exhibited outstanding lifetimes exceeding 57,000 hours, which underscores their reliability for industrial and defense applications [2, 8].

It should be noted that polymer electrolyte membranes (PEMs) are central components in fuel cell technology, which uses the principle of the electrochemical cell to produce electrical energy from chemical energy [9]. Ionic conductivity is an important factor that determines the electrical output of fuel cells using PEMs. The relationship between ionic conductivity and electrical output is one of direct proportionality, as low ionic conductivity produces

low electrical output while high ionic conductivity produces high electrical output [10, 11]. However, any PEM that exhibits excellent electrical output but suffers loss of conductivity due to elevated temperature becomes a serious problem, and this is one of the reasons why efforts are being made in research and development of alternative PEMs to Nafion® membranes, which not only suffer from this major drawback but are also very expensive, thus impeding their full-scale commercialization [10-12]. These are the reasons that propelled this study, in the bid to derive an alternative PEM from the blend of polyisoprene and polystyrene. Blending both polymers stems from the fact that blends of materials show superior properties over single materials [5, 6, 10, 13].

Meanwhile, styrene-based polymers have emerged as promising candidates for PEMs and AEMs in fuel cell applications. This is as a result of their tunable chemical structure, cost effectiveness, and ease of functionalization [14]. Their hydrophobic backbone combined with the ability to introduce hydrophilic sulfonic acid groups allows these materials to achieve the critical balance between proton conductivity, mechanical stability, and fuel barrier properties [14, 15]. In the light of the foregoing, a previous study on the assessment of the properties of proton exchange membrane in formulated polyisoprene/polystyrene (PIPS) blend for fuel cell application shows that the PEM derived from this blend of material achieves an excellent ionic conductivity (10^{-2} S/cm) that compares well with Nafion® [12]. The hydrodynamic properties were equally very promising in terms of water uptake and water desorption [12]. These are superior results demonstrated over a single polymeric material in polyisoprene that was also investigated in the past [16]. Hence, this study becomes an extension of the previous one, and seeks to investigate the thermo-electrochemical properties of the PEM derived from PIPS blend in order to understand its behaviour under heat as well as its electrochemical outputs in terms of voltage and power densities in a single fuel cell operation.

MATERIALS AND METHODS

Materials

Analytical grade chemicals (> 97%) were used in this study, which include ethanol, toluene, 1,2-dichloroethane, chlorosulfonic acid, (Charlec Laboratories, Nigeria), commercial polyisoprene, polystyrene (Karbochem RSA). A fabricated four-neck round-bottom flask reactor and a multimeter were also used.

Chemical modification of PIPS blend

The chemical modification of PIPS blend was carried out through a sulfonation process using a predetermined (70:30%) 20 g blend of polyisoprene

and polystyrene, following a prescribed procedure [10, 16]. This involved the polymer blend that was initially dissolved in 1,2-dichloroethane in a four-neck round-bottom flask reactor with a gradual addition of previously chilled chlorosulfonic acid of 0.0023 mol/L. The chilling was done in an iced bath. The reaction was stirred vigorously in the reactor to prevent formation of lumps, and was carried out under an argon atmosphere at room temperature. The reaction was then allowed to run at different times of 1, 3, 6, 9, 12, 15 and 18 hours, respectively with a termination at the end of each reaction using ethanol. The precipitated sulfonated polyisoprene/polystyrene (SPIPS) was recovered and washed with deionized water until the wash attained almost a neutral pH (6-7). The precipitated and washed SPIPS was immediately dried in an oven at 80°C for 2 hours. Thereafter, the ion exchange capacity (IEC) and degree of sulfonation (DS) of the chemically modified PIPS were obtained using equations 1 [10, 15-17] and 2 below:

$$IEC = \frac{1000 \times S_c}{MW_s} \quad (1)$$

where: S_c = sulfur content expressed as a mass fraction (g S per g polymer) from elemental analysis, MW_s depicts the molecular weight of sulfur (32.06 g/mol), and where 1000 is the multiplication factor to obtain IEC values in mmol/g; if S_c is expressed in wt%, the multiplication factor is 10 instead of 1000 (1000 mmol/mol ÷ 100 g).

$$DS = \frac{MW_{SPIPS} \times IEC}{MW_{PIPS} \times MW_{SO_3H}} \times 100 \quad (2)$$

where: MW_{SPIPS} = molecular weight of the sulfonated blend of polyisoprene and polystyrene, MW_{PIPS} = molecular weight of the unsulfonated PIPS blend, and MW_{SO_3H} = molar mass of the sulfonic acid group = 81.07 g/mol.

Thermal analysis

Both the differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to investigate the thermal properties of the unsulfonated and sulfonated PIPS. The DSC was carried out using an 822E DSC analyzer. Measurements were carried out over the range of 30 – 400°C at 5°C/min heating rate under nitrogen atmosphere (flushed at 70 ml/min). The TGA on the other hand was performed using a Perkin Elmer Pyris 1 TGA/DTA analyzer, where samples were heated to 600°C at 10°C/min, also under nitrogen atmosphere (flushed at 150 mL/min) to ascertain the decomposition temperature of the unsulfonated and sulfonated PIPS blend. The DDSC and DTG curves were obtained as the average rate of change between successive tabulated data points (20–50°C apart).

Fabrication of thin film membranes

Fabrication of thin film polymer electrolyte membranes from SPIPS was carried out in line with the procedure given by Idibie et al. [10]. Accordingly, 10 g SPIPS was dissolved in 250 ml mixture of

toluene/dichloroethane (50:50) at elevated temperature, where a casting solution was formed, and thereafter cast onto a polymer paper support with the use of a laboratory doctor blade casting machine, adjusted to appropriate thickness. The casting was followed through by pulling the casting head of the blade along the length of the substrate, and cured for 4 days. This was followed by drying in the oven below 80°C for a period of 2 hrs, followed by subsequent vacuum drying for extra 2 hrs to ensure residual solvent removal.

Proton conductivity (PC) measurement

Measurement of PC of the synthesized membrane was carried out by AC impedance spectroscopy over 1 Hz–10⁶ Hz with a 10 mV AC perturbation, in 1 M H₂SO₄ as electrolyte at 25 ± 2°C; as the membrane is immersed in liquid electrolyte it is fully hydrated, so external humidity control was not applicable. This involved using membranes of different degrees of sulfonation at constant membrane thickness (120 μm) with the intersection value of the high frequency impedance curve being taken as the membrane resistance. The proton conductivity was calculated using the equation:

$$\sigma = \frac{T}{RS} \quad (3)$$

where: σ represents proton conductivity (S/cm), T (cm) depicts membrane thickness and S (cm²) stands for the surface area of the membrane and R is the resistance obtained from the impedance plane.

Determination of electrochemical properties

The electrochemical properties of the synthesized membrane were investigated in a single fuel cell system, where the fuel (hydrogen gas at the anode) and oxidant (oxygen at the cathode) were allowed to diffuse through the porous backing layer, and at the gas/electrolyte interface the gases dissolved and later diffused to the electrolyte/electrode interface [10].

The membrane electrode assembly (MEA) was initially hydrated in demineralized water for 48 hrs before installing it in the fuel cell testing apparatus. This was to facilitate ionic transport in the polymer electrolyte membrane. The fuel cell testing apparatus was equipped with gas sources, temperature control, and gas flow–rate control rotameters. Other features included were the back pressure regulators for both hydrogen and oxygen as well as a resistance load box.

Thereafter, the electrochemical tests were conducted using Pt/C catalyst in order to determine the distribution of reaction products, which involved passing hydrogen through a humidifier to wet the gas before it entered the anode at a flow rate of 615 mL/min and 20 kPa. Conversely, oxygen was allowed to enter the fuel cell through the cathode at a flow rate of 375 mL/min and 15 kPa. In the course of the test, the electrons produced from the anode were linked to a digital multimeter having an external variable resistance to measure the current and voltage produced by the cell. The polarization tests started when the open circuit voltage (OCV) stabilized. It is important to mention that the electrocatalytic reaction on the catalyst layer followed the gas adsorption at the electrode surface, while the ionic transport and the electronic transport occurred in the electrolyte and the electrode, respectively.

RESULTS AND DISCUSSION

Effect of the sulfonation on the modified PIPS

The styrene group in styrene-based polymers is usually the site of sulfonation, involving an electrophilic substitution reaction. Studies have also shown that the para position, which has the highest electron density (fourth carbon), is favoured for the electrophilic substitution [11, 15, 17, 18]. A close look at Figure 1 shows a sharp band around 1500 cm⁻¹, which reduces due to the effect of the sulfonation.

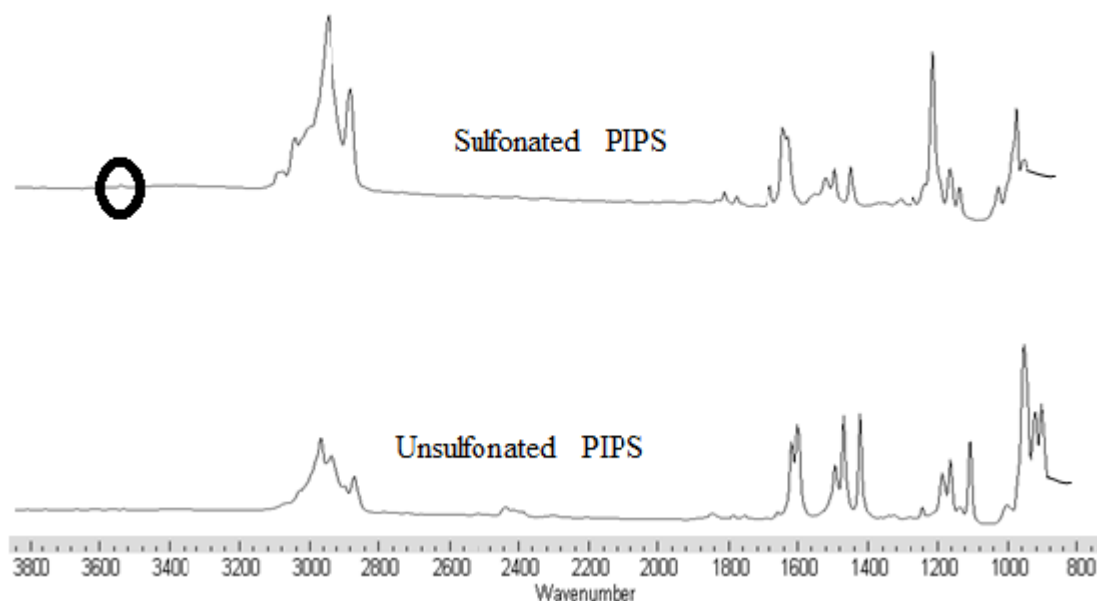


Figure 1: Sulfonated and unsulfonated PIPS.

The weak broad band around 3600 cm^{-1} appearing on the sulfonated being circled can be attributed to the sulfonic group O-H vibration. Asymmetric and symmetric stretching vibrational effect of S=O group can be seen between $1500 - 900\text{ cm}^{-1}$ of the sulfonated with a very weak band of S=O at 1370 cm^{-1} . While the aromatic C=C and C-C bands could be seen around $1650 - 1490\text{ cm}^{-1}$, while that of the non-aromatic are around $2845 - 2985\text{ cm}^{-1}$, respectively. It should also be noted that the single strong peak appearing around 970 cm^{-1} can be assigned to the aromatic H atom of the SO_3H group. All of this confirms a successful chemical modification of PIPS via sulfonation.

Outcome of the sulfonation process on IEC and DS

The concentration of acid in the sulfonation of a polymer impacts directly on both the IEC and DS of the sulfonated polymer, and is associated to the amount of ionic groups in the resulting synthesized

membrane, and thus ascribes as the measure of the degree of sulfonation [3]. However, the ion exchange capacity (IEC) indicates the proton conduction sites. Results as presented in Figure 2 showed that both IECs and DS increased with sulfonation time. A minimum IEC of 0.937 mmol/g was achieved at 1 hr of sulfonation while a maximum IEC of 3.031 mmol/g was achieved at 18 hrs, with their corresponding DS of 1.702 and 5.501%, respectively. It is worth noting that the ease of attachment of the sulfonic group to the substrate, which results in moderately high degree of sulfonation (5.501%) in this process as compared to Nafion® membranes could be attributed to the tunable chemical structure and ease of functionalization of styrene at the para position of the aromatic region. Although membranes with high DS facilitate high ionic mobility and conductivity due to hydration, they also lead to excessive water absorption, which will consequently cause the membrane to soften and break down under fuel cell application.

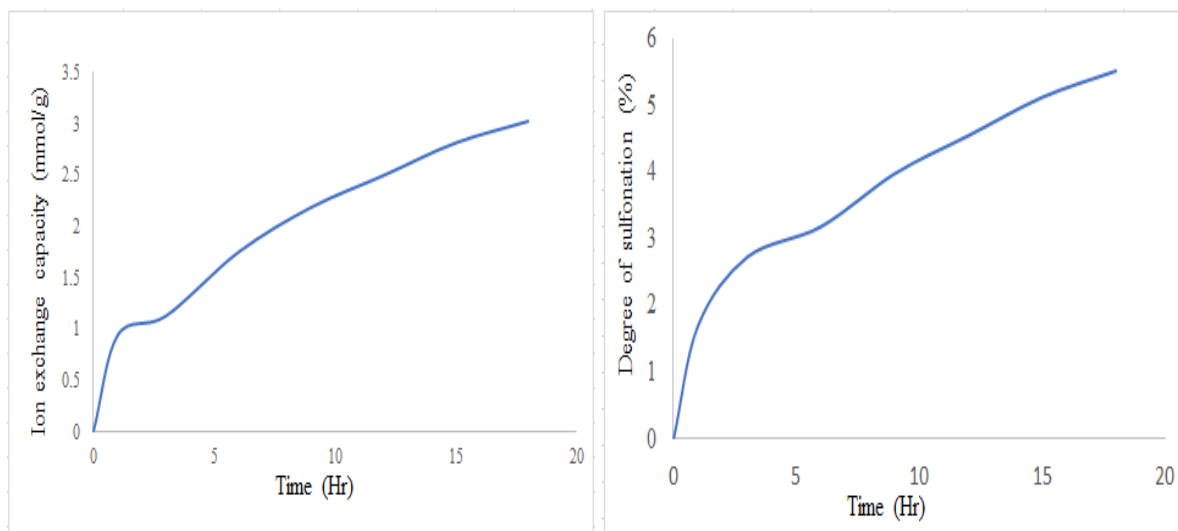


Figure 2: [a] Ion exchange capacity and [b] degree of sulfonation.

The diffusion behaviour of water uptake in the synthesized membranes was further analysed using the power-law model (Figure 3). The log-log plots of $\log(M_t/M_\infty)$ versus $\log(t)$ exhibit good linearity for all samples, confirming that the transport mechanism follows Fickian-type diffusion. The diffusion exponent n varies with degree of sulfonation (DS), with values of 0.227 (DS = 3.969%), 0.287 (DS = 4.537%), and 0.400 (DS = 5.501%), all below 0.5, indicating predominantly Fickian diffusion behavior. Notably, the membrane with DS = 3.969% shows the lowest diffusion exponent and the highest correlation coefficient ($R^2 = 0.9923$), suggesting a more controlled and uniform diffusion process. In contrast,

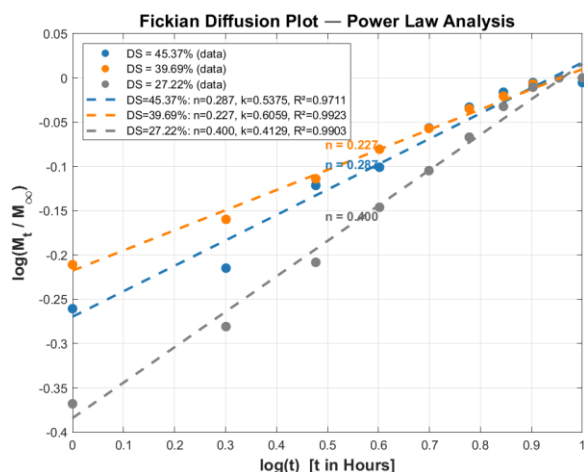


Figure 3: Fickian diffusion analysis of water uptake in SPIPS membranes using the power law model.

Thermal property of the chemically modified PIPS

Thermal stability of the sulfonated and unsulfonated PIPS membranes was evaluated using derivative DSC (DDSC) and DTG analyses (Figures 4 and 5).

the membrane with DS = 4.537% exhibits slightly higher diffusivity ($k = 0.5375$), which corresponds to faster water uptake, while the DS = 5.501% membrane shows a higher n value, indicating relatively slower and less efficient diffusion. These results imply that although all membranes follow Fickian diffusion, the DS = 3.969% membrane demonstrates the most optimal balance between diffusion rate and transport uniformity. This controlled water transport behavior is desirable for proton exchange membrane (PEM) applications, as it supports sufficient hydration without excessive swelling. Consequently, the membrane with DS = 3.969% was selected for further thermo-electrochemical characterization in this study.

The DDSC curves show distinct thermal transitions, with the glass transition temperature (T_g) occurring around 150°C for sulfonated samples and slightly higher (~170°C) for the unsulfonated polymer, indicating reduced chain mobility upon sulfonation. At higher temperatures, a prominent degradation region is observed. The DTG curves reveal an initial minor weight loss below ~150°C, attributed to moisture removal, followed by a gradual early degradation stage. The main decomposition occurs between ~350–400°C, with sulfonated samples showing a characteristic transition with an onset of ~330°C, associated with the breakdown of sulfonic acid groups. In contrast, the unsulfonated polymer does not exhibit this feature and decomposes at slightly higher temperatures (350°C), indicating marginally greater intrinsic thermal stability. The final sharp mass loss, complete by about 400°C, corresponds to backbone degradation of the polymer matrix. Despite the slight reduction in thermal stability due to sulfonation, all membranes remain thermally stable well above typical operating temperatures (~120°C) for proton exchange and direct methanol fuel cells, confirming their suitability for such applications.

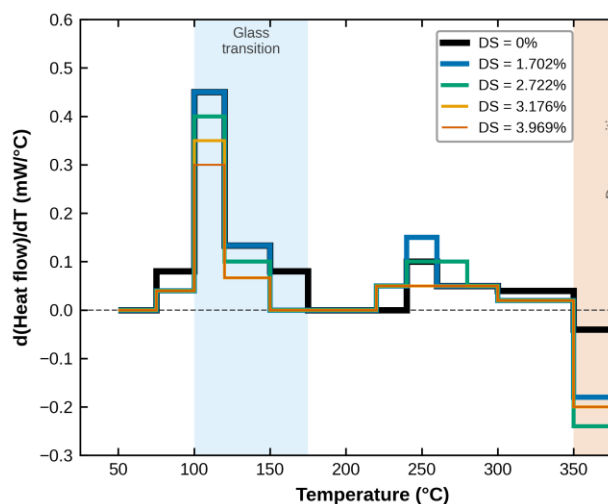


Figure 4: Derivative differential scanning calorimetry (DDSC) curves of SPIPS membranes at varying degrees of sulfonation.

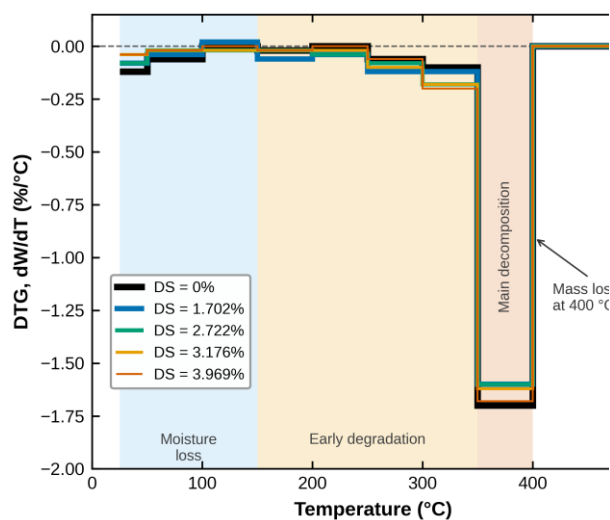


Figure 5: Derivative thermogravimetric (DTG) curves of SPIPS membranes at different degrees of sulfonation.

Proton conductivity measurement of the synthesized polymer electrolyte membrane

The proton conductivity of the synthesized membranes was measured using membranes of different degrees of sulfonation with constant thickness (120 μm). The results, as shown in Figure 6, show that membranes of DS 1.702, 2.722, 3.176 and 3.969% achieved proton conductivities of 7.7×10^{-3} , 1.67×10^{-2} , 1.81×10^{-2} and 4.09×10^{-2} S/cm, respectively. This is an impressive result, especially for the membranes of 2.722, 3.176 and 3.969%, which benchmark favourably against Nafion® membranes (10^{-2} S/cm) [8, 13]. However, and very importantly, the high-water uptake of the membranes above 3.969% could lead to swelling, degradation and performance counterproductive under fuel cell operation, and thus, discouraged their further consideration.

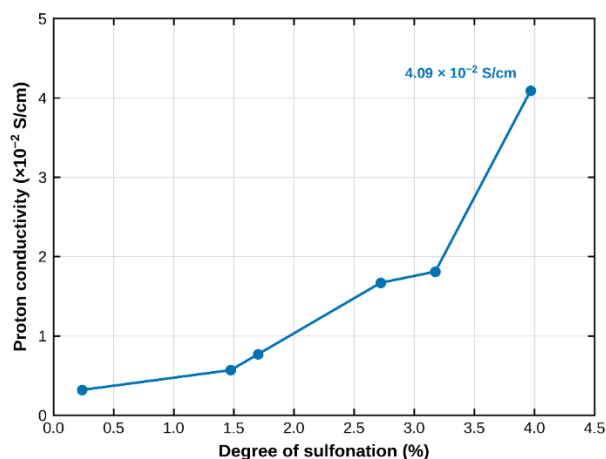


Figure 6: Proton conductivity vs degree of sulfonation with membranes of constant thickness (120 μm).

Performance testing of synthesized electrolyte membrane

The electrochemical performance of the synthesized membranes was evaluated using polarization and power density measurements after stabilization of the open circuit voltage (OCV) (Figures 7 and 8). The membranes (DS = 3.969%, thickness = 120 μm) exhibited OCV values of 645.91, 591.08, and 469.91 mV for catalyst loadings of 40, 30, and 15 wt%, respectively, indicating improved cell potential with increasing catalyst content. As expected, the polarization behavior shows a gradual decrease in voltage with increasing current density, reflecting activation and ohmic losses within the cell. Correspondingly, the power density curves reveal a clear dependence on catalyst loading. The maximum power densities achieved were 62.0 mW/cm² at 200 mA/cm² (40 wt%), 45.0 mW/cm² at 300 mA/cm² (30 wt%), and 35.3 mW/cm² at 190 mA/cm² (15 wt%). For the 30 wt% loading, the power density was still rising at 300 mA/cm², the highest current density measured. Collectively, higher catalyst loading enhances electrochemical performance by facilitating improved reaction kinetics and charge transport, leading to higher power output. The 40 wt% catalyst membrane therefore demonstrates the best performance among the samples studied.

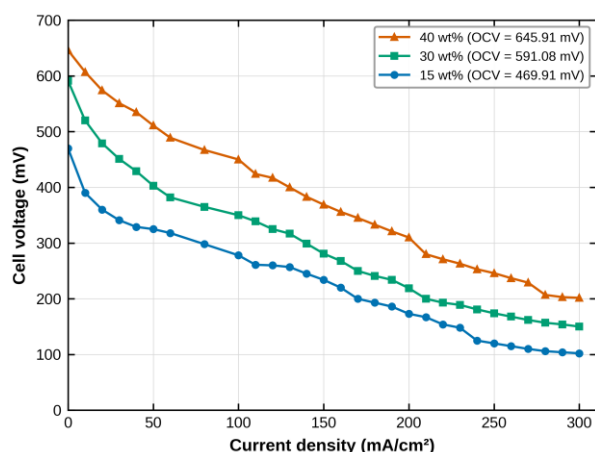


Figure 7: Polarization curves of SPIPS membranes at different catalyst loadings.

Figure 8 further illustrates the relationship between current density and power density for membranes with constant DS (3.969%) and thickness (120 μm). As current density increases, the power density initially rises, reflecting enhanced electrochemical reactions within the cell. The maximum power outputs were observed at 200, 300 and 190 mA/cm^2 , respectively, with peak values of $62.0 \text{ mW}/\text{cm}^2$ (40 wt%), $45.0 \text{ mW}/\text{cm}^2$ (30 wt%), and $35.3 \text{ mW}/\text{cm}^2$ (15 wt%). Beyond these peak points, the power density levelled off or declined despite further increases in current density. This drop in performance can be attributed to limitations such as membrane dehydration, reduced catalyst active surface area, and decreased partial pressures of H_2 and O_2 , which hinder efficient electrochemical reactions [15, 16]. These results indicate that although increasing current density enhances performance up to an optimum point, further increases lead to efficiency losses within the fuel cell system.

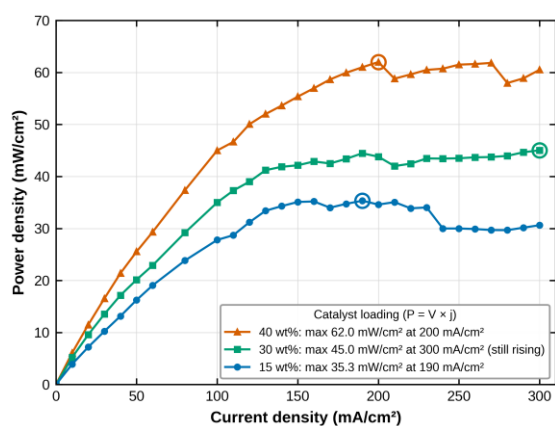


Figure 8: Effect of catalyst loading on power density of SPIPS membranes.

CONCLUSION

Investigation of the thermo-electrochemical properties of the functionalized polyisoprene/polystyrene blend via sulfonation process shows that the polymer electrolyte membrane (PEM) derived from the sulfonated PIPS blend is thermally stable for fuel cell application, especially proton exchange membrane fuel cell and direct methanol fuel cell that are usually operated within 120°C , as the glass transition temperature of SPIPS is 150°C with an onset decomposition temperature of 330°C , but having the main chain degrading finally at $\approx 400^\circ\text{C}$. The membrane displays a competitive proton conductivity in the order of $10^{-3} - 10^{-2} \text{ S}/\text{cm}$, having the membrane with the optimum DS (3.969%) achieving a proton conductivity of $4.09 \times 10^{-2} \text{ S}/\text{cm}$. Other electrochemical properties such as the open circuit voltage (OCV) and power density at different catalyst loadings using the membrane with the optimum DS attained an optimum OCV of 645.91 mV and an optimum power density of $62.0 \text{ mW}/\text{cm}^2$, respectively, using 40% catalyst loading. This therefore places the polyisoprene/polystyrene blend as a viable PEM candidate for fuel cell application. Nevertheless, durability and methanol-permeability tests were not carried out in this study, and the single-cell power density remains below that of Nafion®-based membrane electrode assemblies; these aspects will be addressed in future work.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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