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Development of Sulfonated Aromatic Proton Exchange Membranes Containing Biphenyl Moieties for Water Electrolysers

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Abstract. Hydrogen is the most efficient energy carrier that can be obtained from various feedstock sources, including water. One environmentally friendly method for producing high-purity hydrogen is water electrolysis. Polymer electrolyte membranes, or proton exchange membranes (PEMs), are semipermeable membranes that conduct ions while preventing the mixing of reactant materials across the membrane. This study proposes a method for synthesizing proton exchange membranes through post-sulfonation polymer synthesis. The aromatic compound biphenyl is used as the monomer in this synthesis. The advantages of this method are its simplicity, low production cost, and performance equivalent to Nafion® membranes at room temperature. The biphenyl membranes are characterized through FTIR, NMR, Fenton Test, Water uptake, Swelling ratio, IEC, and conductivity analysis. The resulting sulfonated biphenyl membranes exhibit good mechanical strength and oxidation stability. The Weight Loss in the Fenton Test of the sulfonated biphenyl membranes shows a value of 10%, similar to Nafion 212 based on previous studies. Furthermore, the sulfonated biphenyl membranes demonstrate a water uptake of 60%, swelling ratio of 7.5%, Ion Exchange Capacity of 3.31 meq/g, and 40 mS/cm conductivity.

Keywords: *polymer; membrane; water electrolysis; biphenyl; sulfonation.*

1 Introduction

Electrochemical reactions are considered a promising solution for clean and environmentally friendly renewable energy [1]. Recently, the application of electrochemistry in PEM water electrolysis (PEMWE) has been widely discussed. Water electrolysis is one of the many methods of hydrogen production that yields high-purity hydrogen in an environmentally friendly manner. Regarding sustainability and environmental impact, proton exchange membrane

(PEM) water electrolysis is believed to be the most promising approach for efficient and high-quality hydrogen production from renewable energy sources. This technique only generates oxygen as a byproduct, with no carbon emissions. Additionally, the hydrogen (H_2) and oxygen (O_2) produced can be readily utilized for fuel cell and industrial applications [2]. The electrochemical application for producing environmentally friendly renewable energy hydrogen has various important components, including the membrane. PEM water electrolysis technology uses a membrane as an electrolyte [3].

The role of the polymer in PEMWE, as depicted in Figure 1, is to serve as a charge carrier for protons, to separate reactant gases, and to act as an electronic insulator. The proton conductivity level significantly affects the performance of the proton exchange membrane. Additionally, the PEM should possess good oxidation stability and high-temperature resistance and not generate environmentally hazardous waste [4].

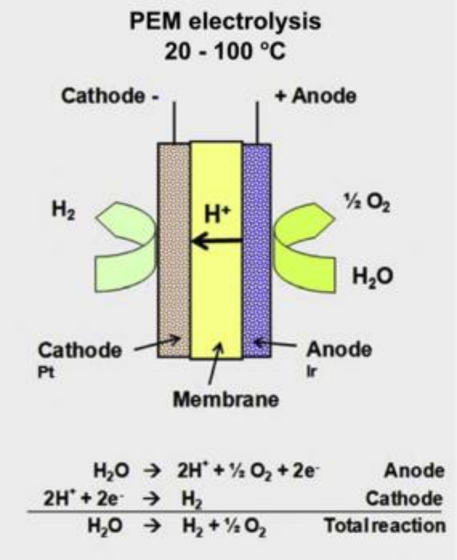

Figure 1 Proton Exchange Membrane Water Electrolysis (PEMWE) Scheme [4].

Solid polysulfonated membranes such as Nafion® and fumapem® are among the most commonly used commercial membranes for electrochemical applications due to their high chemical stability and excellent electrochemical properties. However, these membranes still have several drawbacks, such as expensive production costs, non-environmentally friendly due to the presence of Fluor after use [5], and difficult synthesis processes. Therefore, developing polymer membranes with more affordable costs, easier synthesis mechanisms, environmental friendliness, and similar characteristics and structures to Nafion are essential. Generally, the selected ionomer is an amphiphilic copolymer initiated by free radicals, consisting of a hydrophobic polytetrafluoroethylene (PTFE) backbone and a regularly spaced long pendant perfluoro vinyl ether side chain terminated by hydrophilic sulfonate ionic groups [6].

Polymers with an aromatic backbone structure (Backbone Aromatic) can replace Nafion because of their excellent thermal and mechanical strength, adjustable ion conductivity, lower vanadium permeability, and potentially lower cost. Based on these advantages, aromatic backbone polymers have the potential to be developed with an easier synthesis process [7]. Polymer without ether groups is an alternative material for ion exchange membrane composition. Choosing the simplest polymer structure would be beneficial in terms of cost and scalability. One example of a polymer without ether groups is polyphenylene. Combining p-phenylene and m-phenylene monomers in the polyphenylene backbone provides high membrane flexibility in this ionomer. The polymer structure's separate hydrophilic and hydrophobic portions result in proton conductivity. This type of polymer membrane exhibits high oxidative stability. When subjected to oxidative testing, the membrane retains its original molecular structure and properties, such as proton conductivity, mechanical stability, and fuel cell performance. High thermal stability is another advantage of this membrane [8]. This study focuses on synthesizing a proton exchange membrane using a simple direct polymerization method that can be applied in electrochemistry. The selected direct polymerization method is post-sulfonation, a relatively short and uncomplicated process, making it suitable for laboratory-scale experiments [9].

2 Materials and Methods

2.1 Materials

The materials used as raw materials in this study are Trifluoromethyl Keton, Biphenyl (C12H10), Trifluoromethanesulfonic Acid (TFSA), Dichloromethane (CH2Cl2), Trichloromethane (CHCl3), Oleum (H2SO4.xSO3), Fenton reagent (FeSO4.7H2O/H2O2), Dimethyl Sulfoxide ((CH3)2SO), Sulfuric Acid (H2SO4), Sodium Hydroxide (NaOH), Phenolphthalein, Methanol, and Aquades.

2.2 Method

2.2.1 Polymerization

Figure 2 illustrates the polymer synthesis reaction involving the monomer trifluoromethyl ketone and the aromatic hydrocarbon biphenyl. The trifluoromethyl ketone solution is carefully introduced into a round-bottom flask equipped with a magnetic stirrer, followed by the addition of the aromatic solution, dichloromethane (CH_2Cl_2), and the TFSA catalyst at a concentration of 31.25% v/v.

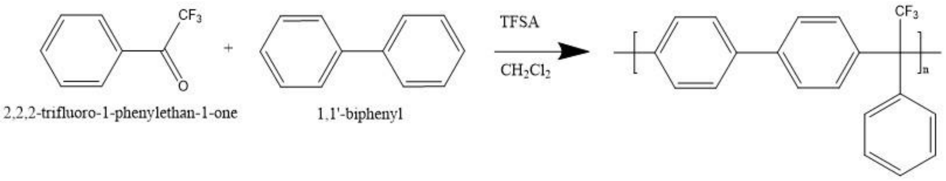

Figure 2 Polymerization reaction of Trifluoromethyl Ketone with Biphenyl

The polymerization reaction is conducted within the temperature range of 3°C to room temperature for 42 hours. An ice bath system is implemented within the polymerization scheme to lower the reaction temperature. Once the solution has thickened, it is poured into hot methanol, and the resulting precipitate is filtered using a vacuum filtration setup. The obtained precipitate is subsequently dried using an oven at a temperature of 60°C until the formation of the solid aromatic polymer. The resulting aromatic polymer will be characterized through FTIR, NMR, and TGA analysis before Sulfonation.

2.2.2 Sulfonation

In this experiment, the Sulfonation of the aromatic polymer shown in Figure 3 is carried out by substituting SO_3 into the polymer chain. A total of 50 mg of polymer is required for each concentration of the sulfonating agent. The solvents used are CH_2Cl_2 and $CHCl_3$. The sulfonating agent employed in this experiment is $H_2SO_4.xSO_3$.

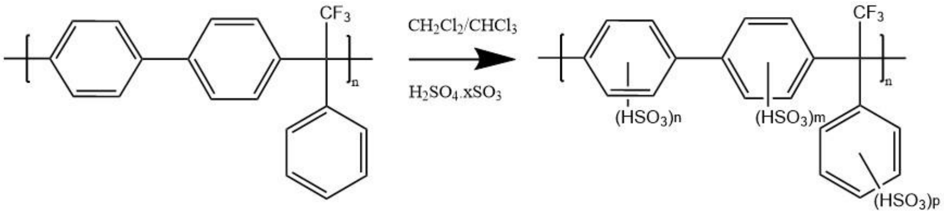

Figure 3 Sulfonation of aromatic polymer with biphenyl

The obtained polymer solution is dissolved in a polar aprotic solvent such as DMSO, poured onto a glass plate, and evenly spread across the surface. The casted polymer solution is then allowed to stand for a certain period of time and heated to evaporate the solvent, forming a polymer membrane. The characteristics of the produced membrane are determined by conducting Fenton Test, Conductivity Test, Swelling ratio and water uptake, IEC, and SEM analyses.

3 Result and Discussion

3.1 FTIR Test

The synthesis of biphenyl polymer for 42 hours using a TFSA catalyst at a concentration of 31.25% v/v resulted in a yield of 94.2%, which can be dissolved in chloroform without external heating. FTIR analysis was conducted to determine the functional groups present in the synthesized biphenyl polymer. The infrared (IR) spectra used were within the 4000-500 cm-1 wavelength range, as shown in Figure 4.

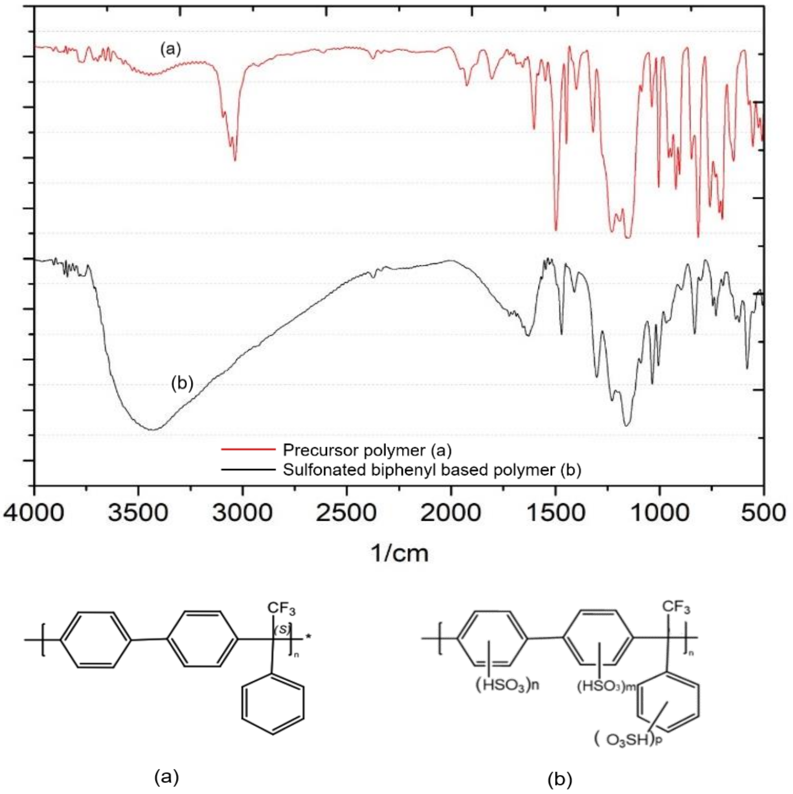

Figure 4 FTIR analysis and structure (a) Precursor polymer; (b) Sulfonated biphenyl-based polymer.

Based on the IR spectrum shown in Figure 4, it can be concluded that before the sulfonation process, the biphenyl polymer contains several main functional groups, including CH (aromatic ring) (~3050 cm-1), C=C (aromatic ring) (~1500 cm-1), and CF3 (~1200 cm-1). On the other hand, after Sulfonation, the biphenyl polymer contains additional main functional groups, namely C-H (~3425 cm-1), C=C (~1629 cm-1), SO3 (~1035 cm-1), and CF3 (~1161 cm-1).

3.2 Nuclear Magnetic Resonance (NMR)

Chloroform and Dimethyl sulfoxide (DMSO) are employed as solvents in (NMR) analysis. Significant differences in the NMR peaks of biphenyl polymer, as shown in Figure 5, are observed between sulfonated biphenyl based polymer and Precursor polymer. The NMR spectrum of the sulfonated biphenyl based polymer exhibits smaller and broader peaks compared to the precursor polymer. This indicates that after the sulfonation process, the aromatic chains of biphenyl have formed bonds with SO_3 groups.

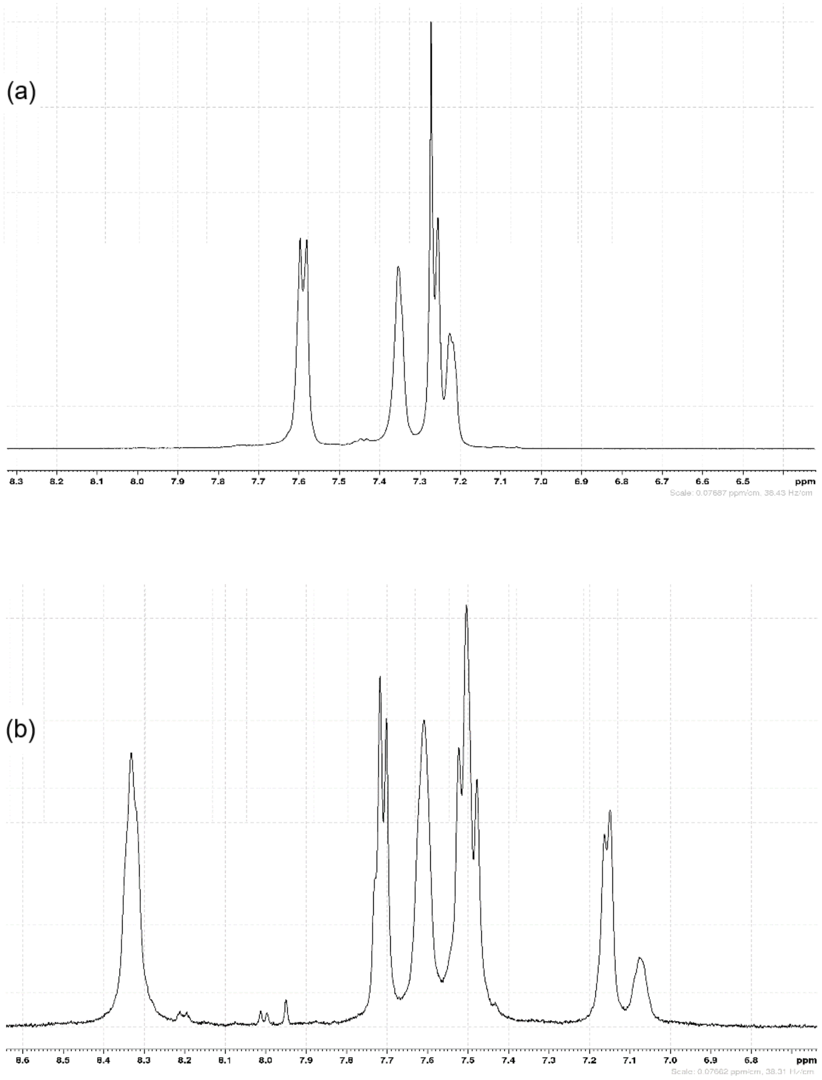

Figure 5 NMR analysis (a) Precursor polymer; (b) Sulfonated biphenyl based polymer.

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3.3 Thermo-gravimetric Analysis (TGA)

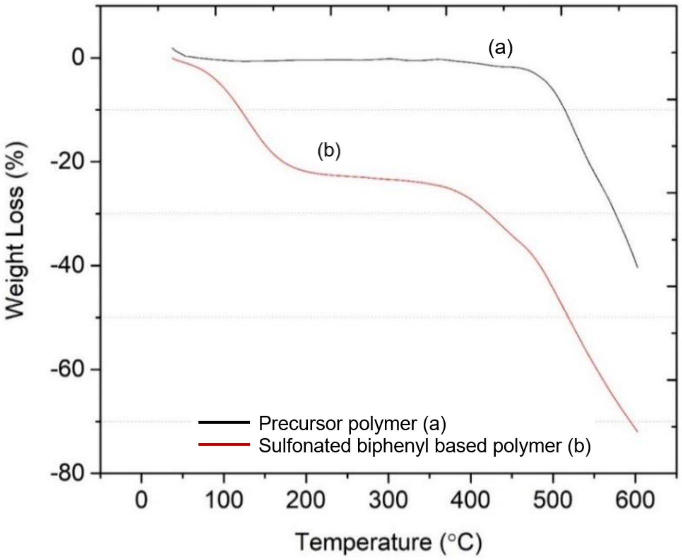


Figure 6 Thermo-gravimetric analysis (TGA) (a) Precursor polymer; (b) Sulfonated biphenyl based polymer.

Thermogravimetric analysis (TGA) was conducted in air atmosphere with a heating rate of 10°C/min from room temperature to 600°C, as shown in Figure 6. The TGA results of the precursor polymer indicate its stability at room temperature up to 450°C. Polymer degradation occurs within the temperature range of 450-600°C, as evidenced by the weight loss observed in the thermogram. On the other hand, the sulfonated biphenyl based polymer shows a decrease in mass from room temperature to 100°C and from 400°C to 500°C. The weight loss observed at the range of 100°C indicates the presence of water content in the sample. Furthermore, the mass loss in the range of 200°C to 400°C corresponds to the degradation of sulfonate groups. The degradation of sulfonate groups exhibits a small gradient slope. Lastly, the degradation observed in the range of 400°C to 500°C corresponds to the degradation of the polymer backbone [10].

3.4 Fenton Test

Using 16.6% v/v oleum ($H_2SO_4.SO_3$) as a sulfonating agent with a sulfonation time of 24 hours resulted in forming of a small amount of sticky solid, making filtration challenging. The obtained solid material could be dissolved in DMSO with external heating. However, when oleum was employed as the sulfonating agent, the membrane's casting process was more convenient, as the resulting membrane exhibited improved tear resistance. Additionally, the membranes exhibited good mechanical strength. The oxidation stability of the membranes was evaluated through Fenton testing, wherein the membrane samples were immersed in a Fenton solution containing a mixture of H_2O_2 and $FeSO_4$ with a composition of 3% H_2O_2 dan 3-4 ppm Fe^{2+}. The results from the Fenton test compared the sulfonated biphenyl membranes with Nafion 212, as shown in Table 1.

Tabel 1 The weight loss results based on the Fenton test.

Sample	Weight Loss (%)
Sulfonated Biphenyl	10
Nafion 212	10

The Fenton test is conducted to assess the oxidation stability of membranes used in proton exchange membrane water electrolysis (PEMWE). These membranes require excellent oxidation stability. The Fenton solution used in the test generates hydroxyl (OH•) free radicals that can attack C-F bonds, potentially leading to membrane decomposition. A significant weight loss indicates low oxidation stability. Commercially used 212 membrane exhibit weight losses of 10%, respectively [11]. Based on Table 1, the sulfonated biphenyl sample demonstrates similar oxidation stability to the Nafion 212 membrane.

3.5 Swelling Ratio and Water Uptake

Tabel 2 The results of the Swelling Ratio test.

Sample	Swelling Ratio (%)
Sulfonated Biphenyl	7,5
Nafion 212	28,4 [12]

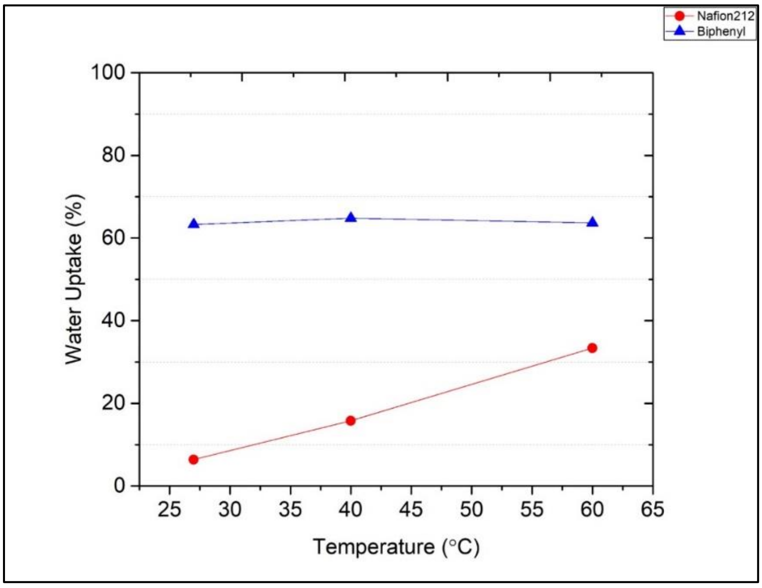


Figure 7 Water Uptake testing of Sulfonated biphenyl and Nafion 212.

Figure 7 shows the water uptake results for sulfonated biphenyl membrane at room temperature up to 60°C, which measured 65%. The graph indicates that increasing the temperature affects the water absorption capability of Nafion membranes. Temperature increases enhance polymer chain mobility, accelerating water diffusion into the membrane. However, due to its higher water uptake, sulfonated biphenyl membrane is unaffected by temperature variations in the experiment, indicating its consistent water absorption capacity. Comparatively, studies by [13], demonstrate lower water uptake levels for Nafion 212 membrane than the experimental findings. Nafion 212 exhibits a water uptake ranging from 5-35%. Nevertheless, despite its high water uptake, sulfonated biphenyl membranes' swelling ratio is smaller compared to Nafion 212, as shown in Table 2. Considering the swelling ratio values, sulfonated biphenyl membranes have a potential for a longer lifetime compared to Nafion 212.

3.6 Ion Exchange Capacity & Conductivity

The Ion Exchange Capacity (IEC) aims to determine the ability of each gram of polymer to exchange ions within a solution. Based on the IEC test results presented in Table 3, it is observed that the sulfonated biphenyl membrane exhibits a higher IEC compared to Nafion 212. A higher IEC value indicates the presence of a greater number of ion exchange groups within the polymer; however, this does not necessarily imply that the ion exchange process will be more effective.

Tabel 3 The results of the IEC test.

Sample	IEC (meq/g)
Sulfonated Biphenyl	3,31
Nafion 212	0,95 [14]

In addition to IEC, conductivity tests were also conducted to determine the membrane's ability to conduct ions. PEM conductivity is a crucial aspect that must be considered in water electrolysis. A higher membrane conductivity indicates a more effective ion conductor, facilitating the movement of ions from the anode to the cathode within the electrolysis cell.

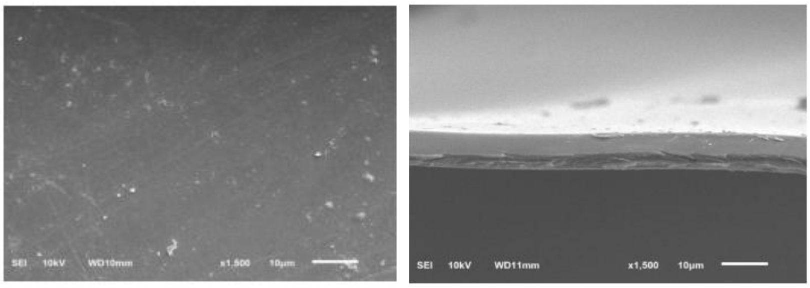
Tabel 4 The conductivity of Sulfonated biphenyl and Nafion at 30°C

Sample	Conductivity (mS/cm)
Sulfonated Biphenyl	40
Nafion 212	103,83 [15]

The conductivity of Nafion 212 shows a conductivity value of 103.83 mS/cm at 30°C [15]. The conductivity of biphenyl-based sulfonated PEM exhibits a lower value than Nafion 212, which is 40 mS/cm. An increase in temperature leads to an increase in conductivity. The rate of conductivity increase with temperature is higher for Nafion 212 compared to biphenyl, as shown in Table 4.

3.7 Scanning Electron Microscope (SEM)

Morphological analysis of the sulfonated biphenyl membrane via SEM examination at 1500x magnification, as Evidenced in Figure 8, Reveals the Presence of a Dense Membrane Structure. A dense membrane enables it to select specific molecular and ion sizes selectively. However, as the pore size decreases, the membrane's permeability also tends to decrease.



(a) (b)

Figure 8 Scanning Electron Microscope of Sulfonated Biphenyl (a) membrane surface; (b) cross section

4 Conclusions

The synthesis of precursor polymer using 31.25% v/v TFSA catalyst for 24 hours yielded 94.2%. Using oleum as a sulfonation agent produced aromatic membranes with good mechanical properties and easy casting. Scanning Electron Microscope analysis revealed that the formed membranes exhibited a dense structure. Based on the Fenton test, it is known that the weight loss of sulfonated biphenyls is 10%. The Fenton test results are the similar as Nafion 212.The Swelling ratio test indicated a value of 7.5% for the sulfonated biphenyl membrane, with a water uptake of 60%, demonstrating its ability to absorb water with good resistance, enabling faster water diffusion within the membrane. FTIR and NMR analysis confirmed that the CF3 and SO3 functional groups successfully formed bonds in the sulfonated biphenyl based polymer. The glass transition temperature of the sulfonated biphenyl based polymer was determined to be 40°C through TGA analysis. Therefore, it is suggested that the sulfonated biphenyl PEM can be used at temperatures below 40°C for water electrolysis applications. The Ion Exchange Capacity obtained was significantly higher at 3.31 meq/g compared to Nafion 212, with a value of 0.93 meq/g. Conductivity testing was crucial in evaluating the sulfonated biphenyl membrane's applicability for water electrolysis, with a conductivity value of 40 mS/cm at 30°C.

References

[1] K. Jiao et al., “Designing the next generation of proton-exchange membrane fuel cells,” Nature, vol. 595, no. 7867. Nature Research, pp. 361–369, Jul. 15, 2021. doi: 10.1038/s41586-021-03482-7.

[2] S. Shiva Kumar and V. Himabindu, “Hydrogen production by PEM water electrolysis – A review,” Materials Science for Energy Technologies, vol. 2, no. 3. KeAi Communications Co., pp. 442–454, Dec. 01, 2019. doi: 10.1016/j.mset.2019.03.002.

[3] L. Gubler, “Membranes and separators for redox flow batteries,” Current Opinion in Electrochemistry, vol. 18. Elsevier B.V., pp. 31–36, Dec. 01, 2019. doi: 10.1016/j.coelec.2019.08.007.

[4] S. J. Peighambardoust, S. Rowshanzamir, and M. Amjadi, “Review of the proton exchange membranes for fuel cell applications,” in International Journal of Hydrogen Energy, Sep. 2010, pp. 9349–9384. doi: 10.1016/j.ijhydene.2010.05.017.

[5] J. Bender et al., “H+-conducting aromatic multiblock copolymer and blend membranes and their application in pem electrolysis,” Polymers (Basel), vol. 13, no. 20, Oct. 2021, doi: 10.3390/polym13203467.

[6] J. Walkowiak-Kulikowska, J. Wolska, and H. Koroniak, “Polymers application in proton exchange membranes for fuel cells (PEMFCs),”

Physical Sciences Reviews, vol. 2, no. 8. De Gruyter, Aug. 01, 2017. doi: 10.1515/psr-2017-0018.
[7] R. S. Raja Rafidah, W. Rashmi, M. Khalid, W. Y. Wong, and J. Priyanka, “Recent progress in the development of aromatic polymer-based proton exchange membranes for fuel cell applications,” Polymers (Basel), vol. 12, no. 5, May 2020, doi: 10.3390/POLYM12051061.
[8] J. Miyake et al., “Design of flexible polyphenylene proton-conducting membrane for next-generation fuel cells,” 2017. [Online]. Available: http://advances.sciencemag.org/
[9] P. Khomein, W. Ketelaars, T. Lap, and G. Liu, “Sulfonated aromatic polymer as a future proton exchange membrane: A review of sulfonation and crosslinking methods,” Renewable and Sustainable Energy Reviews, vol. 137. Elsevier Ltd, Mar. 01, 2021. doi: 10.1016/j.rser.2020.110471.
[10] S. Mollá and V. Compañ, “Polyvinyl alcohol nanofiber reinforced Nafion membranes for fuel cell applications,” J Memb Sci, vol. 372, no. 1–2, pp. 191–200, Apr. 2011, doi: 10.1016/j.memsci.2011.02.001.
[11] O. Lebedeva et al., “Synthesis and characterization of new proton-exchange membranes based on poly-1-vinyl-1,2,4-triazole doped with phenol-2,4-disulfonic acid,” Int J Energy Res, vol. 45, no. 10, pp. 14547–14560, Aug. 2021, doi: 10.1002/er.6686.
[12] S. Shi, A. Z. Weber, and A. Kusoglu, “Structure/property relationship of Nafion XL composite membranes,” J Memb Sci, vol. 516, pp. 123–134, Oct. 2016, doi: 10.1016/j.memsci.2016.06.004.
[13] G. Wang et al., “Durable sulfonated poly(benzothiazole-co-benzimidazole) proton exchange membranes,” Macromolecules, vol. 47, no. 18, pp. 6355–6364, Sep. 2014, doi: 10.1021/ma501409v.
[14] “DuPont Fuel Cells DuPontTM Nafion ® PFSA Membranes NRE-211 and NRE-212.”
[15] C. Wang et al., “A clustered sulfonated poly (ether sulfone) based on a new fluorene-based bisphenol monomer,” J Mater Chem, vol. 22, no. 48, pp. 25093–25101, Dec. 2012, doi: 10.1039/c2jm34414a.