

**THE INFLUENCE OF FUNCTIONALIZED BORON NITRIDE  
ADDITION ON THE PROPERTIES OF SPEEK/PBI ELECTROLYTE  
MEMBRANE FOR PEM FUEL CELL APPLICATIONS**

**A THESIS SUBMITTED TO  
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES  
OF  
KOCAELI UNIVERSITY**

**BY  
HUZAIFA MOHAMMED ADAM HARAMEEN**

**IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
FOR  
THE DEGREE OF MASTER OF SCIENCE  
IN  
CHEMICAL ENGINEERING**

**KOCAELI 2023**

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**Asst. Prof. RAMİZ GÜLTEKİN AKAY**

**Supervisor, Kocaeli Univ.**

.....

**Assoc. Prof. MEHMET KODAL**

**Jury member, Kocaeli Univ.**

.....

**Asst. Prof. BERKER FIÇICILAR**

**Jury member, Ondokuz Mayıs Univ.**

.....

**Thesis Defense Date: 19.06.2023**

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June 2023

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## CONTENTS

ETHICAL STATEMENT AND RESEARCH FUND SUPPORT .....	i
PUBLISHING AND INTELLECTUAL PROPERTY RIGHTS .....	ii
PREFACE AND ACKNOWLEDGEMENTS .....	iii
CONTENTS .....	iv
LIST OF FIGURES .....	vi
LIST OF TABLES .....	viii
INDEX OF SYMBOLS AND ABBREVIATION .....	ix
Abbreviations .....	ix
ABSTRACT .....	xi
ÖZET .....	xii
GENİŞLETİLMİŞ TÜRKÇE ÖZET .....	xiii
1.INTRODUCTION .....	1
2. THEORETİCAL BACKGROUND.....	3
2.1. Introduction: .....	3
2.2. Types of Fuel Cells:.....	4
2.2.1. Proton Exchange Membrane Fuel Cells (PEMFC): .....	4
2.2.2. Direct Alcohol Fuel Cells:.....	4
2.2.3. Solid Oxide Fuel Cells (SOFCs): .....	6
2.3. Principle of Operation of PEMFC:.....	7
2.4. PEMFC Membrane Electron Assembly: .....	8
2.5. Ion Exchange Membranes For Fuel Cell: .....	10
2.5.1. Mechanism Of Proton Exchanging Through The İon Exchange.....	11
2.5.2. Proton Exchange Membranes Used In Fuel Cells Applications:.....	12
2.6. Recent Studies On Membrane Materials For Fuel Cells: .....	17
2.7. SPEEK-based Membranes For Fuel Cells:.....	19
2.8. Boron Nitride: .....	22
2.9. Main Properties and Characterization of Ion Exchange Membrane:.....	23
2.10. Electro-catalyst Layer .....	24
3.MATERIAL AND METHODs .....	25
3.1. Materials: .....	25
3.2. Membrane Preparation.....	25
3.3. Membrane And Material Characterizations: .....	29
3.3.1 FTIR Identifying The Samples: .....	29
3.3.2 Degree of Sulfonation (DS): .....	29
3.3.3 Ion Exchange Capacity of The Membrane: .....	30
3.3.4 Water Uptake: .....	30
3.3.5 Mechanical Tests: .....	31
3.3.6 Proton Conductivity Measurement: .....	31
3.3.8 Thermal Characterization (Thermogravometer Analysis TGA): .....	34
3.3.9 Chemical Stability (Fenton Reagent Test):.....	34
3.3.10. X-ray Diffraction Analysis For The Optimum Membrane:.....	34
3.3.11. Homogeneity Test ( Scanning Electron Microscopy) : .....	35
4. RESULTS AND DISCUSSION .....	36
4.1. Verifying The Sulfonating Process Using FTIR Test:.....	36
4.2. SPEEK-BN/PBI Composite Membrane .....	38
4.2.1. Preparation of SPEEK/BN Preparation: .....	38

4.2.2. Membrane And Material Characterizations: .....	39
4.2.2.1. Ion exchange capacity .....	39
4.2.2.2. Water uptake .....	41
4.2.2.3. Mechanical tests .....	42
4.2.2.4. Proton conductivity measurement:.....	43
4.2.2.5. The Thermal Stability of the Membrane:.....	44
4.2.2.6. Chemical stability: .....	45
4.2.2.7. X-ray diffraction analysis for the optimum membrane:.....	45
4.2.2.8. Scanning electron microscopy analysis (SEM): .....	47
4.2.2.9. Comparision with other membranes: .....	50
5. CONCLUSION .....	51
REFERENCES .....	52
PUBLICATIONS AND WORKS .....	56
BIOGRAPHY .....	56



## LIST OF FIGURES

Figure 2.1.	Types of fuel cells .....	3
Figure 2.2.	PEMFC system components .....	4
Figure 2.3.	Scheme for A Typical DAFC.....	5
Figure 2.4.	DAFC system components.....	6
Figure 2.5.	Typical PEMFC components.....	7
Figure 2.6.	Typical MEA components.....	8
Figure 2.7.	Effect of thickness and water content on the characterization of the membrane.....	9
Figure 2.8.	a ) Proton exchange membrane b) Anion exchange membrane.....	10
Figure 2.9	Scheme for proton movement by mean of diffusion: a) Pristine membrane b) Nano particles membrane diffusion .....	11
Figure 2.10.	Proton hopping mechanism.....	11
Figure 2.11.	Perfluorinated materials general structure .....	13
Figure 2.12.	Chemical structure of: (a) Perfluorinated sulfonic acid-based membranes like Nafion (b)Sulfonated trifluorostyrene co- olymer membranes (Partially perfluorinated). .....	14
Figure 2.13.	Some of the materials used as non-fluorinated membranes .....	15
Figure 2.15.	SPEEK/PBI Blend membrane characterization .....	21
Figure 2.16.	Boron Nitride .....	22
Figure 3.1.	Preparing BN (functionalization and sulfonation) .....	26
Figure 3.2.	Preparing SPEEK/BPI membrane.....	27
Figure 3.3.	Preparing SPEEK-BN/PBI composite membrane: A- Casual Blend membrane B- Thin film PBI on SPEEK-BN membrane.....	28
Figure 3.4.	Back titration reaction for SPEEK using NaOH aqueous solution.....	29
Figure 3.5.	Instron 3367 tensile machine and a representative apparatus	31
Figure 3.6.	A 4 probe electrode conductivity cell for measuring the protonic conductivity ( device setup interior part).....	32
Figure 3.7.	EIS conductivity cell that was built specially by Erdes Kimya ve eknoloji company .....	33
Figure 3.8.	Setup used for measuring the thermalstability for the membrane .....	34
Figure 4.2.	FTIR spectra for BN and BN-OH.....	36
Figure 4.1.	FTIR spectra for PEEK and sPEEK.....	37
Figure 4.3.	a) PBI, B) SPEEK@PBI/BN-20, C) SPEEK-PBI/BN-15, D) SPEEK-PBI/BN-10, E) SPEEK/PBI 12hrs stirring and ultrasonic , F) SPEEK/PBI 24hrs stirring.....	39
Figure 4.4.	Ion Exchange Capacity of SPEEK/PBI/BN membrane .....	40
Figure 4.5.	Degree of sulfonation for SPEEK/SBN membrane .....	40
Figure 4.6.	Water uptake of SPEEK/PBI/BN membrane .....	41
Figure 4.7.	Mechanical stability for SPEEK/PBI/BN membrane at maximum loads .....	42
Figure 4.8.	Ionic conductivities for SPEEK/PBI/BN membrane at A) standard temperature B) various temperatures C) Thickness of the membrane.....	43

Figure 4.9.	a) Thermal stability for SPEEK/PBI/BN membranes (derivative mass decomposition in respect to temperature). b) Thermal stability for SPEEK/PBI/BN membranes (Mass decomposition).....	44
Figure 4.10:	Chemical stability for the proposed membrane .....	45
Figure 4.11.	XRD analysis for the optimum membrane (i.e. SPEEK/PBI/ BN-10). A) The front side B) The back side C) Comparison .....	46
Figure 4.12.	SEM surface images for a) SPEEK/PBI , b)SPEEK/PBI/ BN-10%, c) SPEEK/PBI/BN-15%, d) SPEEK/PBI/BN-20.....	47
Figure 4.13.	SEM cross sectional images for a) SPEEK/PBI , b)SPEEK/PBI/BN-10%, c) SPEEK/PBI/BN-15%, d) SPEEK/PBI/BN-20 .....	48
Figure 4.14.	Microscopy image at 2.5 micrometer zooming for both sides.....	49
Figure 4.15.	Ionic conductivity of SPEEK/PBI/BN compared to other developed membranes. ....	50



## LIST OF TABLES

Table 2.2.	Commonly used Material for PEMFC Membrane .....	16
Table 2.3.	Commonly used electrolyte membranes. ....	18
Table 2.4.	Most commonly used fillers for electrolyes membranes.....	19
Table 3.1.	Currently Membrane Used In Proton Exchange Fuel Cell .....	28
Table 4.1.	Calculations for degree of sulfonation and IEC for SPEEK membrane .....	38
Table 4.2.	Degree of sulfonation and IEC for SPEEK membrane .....	38
Table 4.3.	Contents of the membrane.....	38
Table 4.4.	Degree of sulfonation and IEC for SPEEK/PBI/BN membrane .....	40
Table 4.5.	Water uptake of SPEEK/PBI/BN membrane .....	41
Table 4.6.	Mechanical stability for SPEEK/PBI/BN membrane at maximum loads .....	42
Table 4.7.	Thermal stability for SPEEK/PBI/BN membranes .....	45
Table 4.8.	Ionic conductivity of SPEEK/PBI/BN compared to other developed membranes. ....	49
Table 5.1.	Physicochemical properties for SPEEK/PBI/BN membranes.....	50

## INDEX OF SYMBOLS AND ABBREVIATIONS

T <sub>g</sub>	: Glass transition temperature
TGA	: Thermo Gravimetric Analysis
W <sub>PA</sub>	: Weight of acid doped membrane
W <sub>dry</sub>	: Weight of dry membrane
ΔG	: Change of Gibbs free energy
ΔH	: Change in Enthalpy
ΔL	: Change of Length
μCHP	: Micro generation
η <sub>theo</sub>	: Efficiency of Fuel Cell

### Abbreviations

AF	: Alkaline Fuel Cell
ADL	: Acid Doping Level
AL	: Acid Leaching
BN	: Boron Nitride
B-PEI	: Branched Polyethyleneimine
CaTiO <sub>3</sub>	: Calcium Titanate
CL	: Catalyst Layer
CO	: Carbone Monoxide
CCM	: Catalyst Coated membrane
DMFC	: Direct Methanol Fuel Cells
DMAc	: N,N-dimethylacetamide
E <sub>a</sub>	: Activation Energy
EIS	: Electrochemical Impedance Spectroscopy
Fe <sub>2</sub> TiO <sub>5</sub>	: Iron Titanium Oxide
GDE	: Gas Diffusion Electrode
GDL	: Gas Diffusion Layer
HT-PEMFC	: High temperature PEMFC
LT-PEMFC	: Low temperature PEMFC
MCFC	: Molten Carbonate Fuel Cells
MEA	: Membrane Electrode Assembly
MWCNT	: Multi walled carbon nanotubes
PAFC	: Phosphoric Acid Fuel Cells
PAAM	: Polyacrylamide
PEM	: Polymer Electrolyte Membrane
PEMFC	: Proton Exchange Membrane Fuel Cell
PFA	: Perflorosulfonic Acid
PPA	: Polyphosphoric Acid
PTFE	: Polytetrafluoroethylene
PBI	: Polybenzimidazole
PC	: Proton Conductivity

PVA : Polyvinyl  
SOFC : Solid Oxide Fuel Cells  
SEM : Scanning Electron Microscopy



# **THE INFLUENCE OF FUNCTIONALIZED BORON NITRIDE ADDITION ON THE PROPERTIES OF SPEEK/PBI ELECTROLYTE MEMBRANE FOR PEM FUEL CELL APPLICATIONS**

## **ABSTRACT**

To overcome the limitations of SPEEK/PBI membranes, BN was incorporated into membranes in varying proportions. First, boron nitride was functionalized by introducing hydroxyl groups using KMNO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> as oxidizing agents. Simultaneously, SPEEK was prepared by sulfonating PEEK with sulfonic acid at 80°C. Additionally, a SPEEK/PBI/BN mixture was prepared by dissolving SPEEK/BN in DMC and mixing with the heated PBI solution. The BN percentages were 10%, 15 and 20%. The properties of the prepared membranes were investigated and SPEEK/PBI/BN-10% showed the best physicochemical properties. where the degree of sulfonation, ion exchange capacity, water absorption, tensile stress, ionic conductivity and thermal stability are 80.53%, 2.18 meq.g<sup>-1</sup>, 6.13%, 8.61 MPa, 245 mS/cm, 316 at 6°C. bottom. The results show that the addition of BN had a significant positive effect on the membrane properties, as the proton conductivity increased significantly from 170 mS/cm to 245 mS/cm. In addition, the thermal stability and ionic conductivity were also significantly improved.

**Keywords:** Boron Nitride, Fuel Cells, Membrane, PEM.

# PEM YAKIT PİLİ UYGULAMALARI İÇİN SPEEK/PBI ELEKTROLİT MEMBRANININ ÖZELLİKLERİ ÜZERİNDE FONKSİYONEL BOR NİTRÜR İLAVE ETKİSİ

## ÖZET

SPEEK/PBI membranlarının sınırlamalarının üstesinden gelmek için BN, değişen oranlarda membranlara dahil edildi. İlk olarak bor nitrür, oksitleyici maddeler olarak KMNO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> kullanılarak hidroksil gruplarının eklenmesiyle işlevselleştirildi. Eşzamanlı olarak, SPEEK, PEEK'in 80°C'de sülfonik asit ile sülfonlanmasıyla hazırlandı. Ek olarak, SPEEK/BN'nin DMC içinde çözülmesi ve ısıtılmış PBI çözeltisi ile karıştırılmasıyla bir SPEEK/PBI/BN karışımı hazırlandı. BN yüzdeleri %10, %15 ve %20 idi. Hazırlanan membranların özellikleri araştırılmış ve SPEEK/PBI/BN-%10 en iyi fizikokimyasal özellikleri göstermiştir. burada sülfonasyon derecesi, iyon değiştirme kapasitesi, su emme, çekme gerilimi, iyonik iletkenlik ve termal kararlılık 6°C'de %80,53, 2,18 meq.g-1, %6,13, 8,61 MPa, 245 mS/cm, 316'dır. alt. Sonuçlar, proton iletkenliği 170 mS/cm'den 245 mS/cm'ye önemli ölçüde arttığından, BN ilavesinin membran özellikleri üzerinde önemli bir pozitif etkiye sahip olduğunu göstermektedir. Ek olarak, termal kararlılık ve iyonik iletkenlik de önemli ölçüde iyileştirildi.

**Anahtar Kelimeler:** Bor Nitrür, Yakıt Pilleri, Membran, PEM.

# PEM YAKIT PİLİ UYGULAMALARI İÇİN SPEEK/PBI ELEKTROLİT MEMBRANININ ÖZELLİKLERİ ÜZERİNDE FONKSİYONEL BOR NİTRÜR İLAVE ETKİSİ

## GENİŞLETİLMİŞ TÜRKÇE ÖZET

Dünya neredeyse tüm ihtiyaçlarda elektriğe bağımlı hale geldi. Böylece, fosil yakıtla ekonomik olarak karşılanamayan elektrik talebi çok büyük hale geldi. Öte yandan, elektrik üretimi ile ilgili çevre sorunları, geleceğin ve gelecek nesillerin en büyük endişelerinden biri haline geldi. Sonuç olarak, hepsi değilse de çoğu ülke, yenilenebilir enerji ve yakıt alternatiflerinin ana konulardan biri olduğu, dünyanın 2035 yılına kadar 800 GW yenilenebilir enerji hedeflediği bir vizyon hazırlamıştır (Van de Graaf ve diğerleri, 2000).

Amerika Birleşik Devletleri, AB ülkeleri, Birleşik Krallık ve bu tür diğer bazı gelişmiş ülkeler şimdiden yenilenebilir enerji potansiyellerini yönetmeye başladılar ve 2019 yılı sonunda küresel elektrik üretiminin %29'undan fazlasına ulaşan optimum yenilenebilir potansiyelden yararlanmak için teknolojilerini geliştiriyorlar (Van de Graaf ve diğerleri, 2020). Bu arada Orta Doğu ülkeleri şimdiden en büyük fosil yakıt potansiyeline, su kıtlığına ve tarım ikilemine sahip ülkeler. Tarım ürünlerinin yüzde 80'inin komşu ülkelere ithal edilmesi, petrolerini ihraç amacıyla biriktirmeleri konusunda üzerlerinde daha fazla baskı yaratıyor.

Hidrojen teknolojisi, Hidrojenin üretilmesinde ve kullanılmasında kullanılan teknolojileri ifade eden bir terimdir. Son zamanlarda, hidrojen teknolojisi dünya çapında büyük ilgi gördü. Örneğin, Suudi Arabistan sadece güneş enerjisi kullanarak sudan hidrojen üretmek için 4 milyar dolarlık devasa bir proje başlattı (Gherboudj ve diğerleri, 2021). Ayrıca, yakıt pili teknolojisi, pek çok uygulamada uygulanabilir olması ve dünyanın yıllardır beklediği elektrik ve kirlilik için nihai çözüm haline gelmesi nedeniyle en ilginç araştırma alanlarından biri haline gelmiştir. Dönüşüm işleminin tek çıktısı su olduğu için hidrojen, büyük bir ısı değerine ve tamamen temiz bir yakıtı sahiptir. Hidrojen birçok farklı şekilde üretilir, ancak hidrojen ekonomisi hidrojenin karbondioksit içermeyen kaynaktan üretilen alternatif yakıt olarak kullanılmasıdır.

Yakıt pili teknolojisi son birkaç yılda yükseldi, ancak yakıt pilini ticari olarak kullanmanın ana zorluğu, malzemesinin yüksek maliyetidir. Ancak son yıllarda yapılan çalışmalar katalizör tabakasında kullanılan platin miktarının azaltılmasına ve elektrolitte düşük maliyetli malzemelerin kullanılmasına odaklanmaktadır. Şu anda, Nafion ve diğer bazı kısmen per-florlu malzemeler, per-florlu materyallerin yüksek protonik iletkenliği için yakıt hücresi üreticileri tarafından ticari olarak kullanılmaktadır. Bununla birlikte, perflorlu malzemeler son derece pahalıdır ve çevre dostu değildir, bu da alternatif arayışlarını gerekli kılar. Bu nedenle, perflorlu olmayan zarlar oldu. Bununla birlikte, perflorlu olmayan membranlar, kabul edilebilir protonik iletkenlik elde edemedi.

Yakıt hücreleri, doğrudan kimyasal reaksiyonlardan elektrik üreten cihazlardır. Yakıt hücresi 1839'da icat edildi (resimde). "Yakıt hücresi" adı, 1889. yüzyılda Charles Langer tarafından tanıtıldı. İlk proton değişim yakıt hücreleri, NASA tarafından 1950'lerde

insanlı uzay görevleri için bir astronota güç ve içme suyu sağlamak için geliştirildi. Bununla birlikte, yakıt hücreleri arasında proton değişim membranlı yakıt hücresi (PEMFC), alkalın yakıt hücresi (AFC), katı oksit yakıt hücresi (SOFC), erimiş karbonat yakıt hücresi (MCFC), fosforik asit yakıt hücresi (PAFC) ve diğerleri bulunur.

Tez cümlesi: 2021 yılında PBI'ya bor nitrürün eklenmesiyle bu sınırlamanın üstesinden gelmek için bir çalışma yapıldı (Hussin ve diğerleri, 2021), çalışma başarılı oldu ve zarın protonik iletkenliği 240 mS/cm'ye sıçradı ve en önemlisi BN, zar üzerinde herhangi bir olumsuz etki göstermedi. Öte yandan 2020'de, BN'nin tanıtılmasıyla SPEEK zarının protonik iletkenliğini en üst düzeye çıkarmak için bir çalışma yürütüldü; bu, BN'nin her iki SPEEK'i de modifiye etmek için başarıyla eklenebileceğini gösteriyor (Yogarathinamve diğerleri, 2021). AKAY ve arkadaşları tarafından SPEEK'in mekanik ve termal sınırlamasının üstesinden gelmek için SPEEK/PBI karışımı üzerinde başka bir çalışma yürütülmüştür; burada PBI dolgu maddesinin %10'u en iyi özellikleri göstermiştir; ancak PBI sonucunda protonik iletkenlik azalmıştır (Akay ve diğerleri, , 2018). Bu nedenle, BN yüksek protonik iletkenliğe ve iyi termomekanik özelliklere sahip olduğundan, bu çalışmada SPEEK, zarın mekanik kararlılığını, termal kararlılığını ve protonik iletkenliğini arttırmak için PBI ve BN ile modifiye edilmiştir.

Polieter eter keton (PEEK), yaygın olarak kullanılan düşük maliyetli bir termoplastik malzemedir. Ticarileşme 1980'lerin başında başladı. Sülfonlanmış poli-eter-keton, düşük metanol geçirgenliği ve nispeten yüksek elektrik iletkenliği nedeniyle PEM'e rekabetçi bir alternatif iyon değiştirici membran malzemesidir. Bununla birlikte, SPEEK'in proton değişim kapasitesi, metanol direnci, mekanik özellikler ve termal kararlılık gibi bazı özellikleri, SPEEK'in sülfonasyon derecesi (DS) ile doğrudan ilişkilidir. SPEEK membranları üzerinde çok araştırma ve geliştirme yapılmıştır. Bu çalışmaların sonuçları, SPEEK/PES-C zarının 10 cm<sup>2</sup>/s ile 7 cm<sup>2</sup>/s metanol geçirgenliğine sahip olduğunu göstermektedir. SPPEK/SPEEK membranın proton iletkenliği, 80 °C sıcaklıkta maksimum 0,212 S cm<sup>-1</sup>'e ulaşır. Çapraz bağlı Her SPEEK membranları, gelişmiş termal ve boyutsal kararlılığa sahiptir. Solvent eksikliği, SPEEK saçan radikallerin birikmesine yol açar. SPEEK/BMIMPF/PA membranının proton iletkenliği de 160 °C'de 600 saatlik testin ardından 2,0 × 10<sup>-2</sup> S cm<sup>-1</sup>'de sabit kalır. Uyumlu karbon nanotüplerin SPEEK'e dahil edilmesinin, kompozit zarın proton iletkenliğini iyileştirdiğini ve metanol geçirgenliğini azalttığını bulduk. PANI hidrotermal etkiyi geliştirir. Önceki çalışmalar, SPEEK membranlarının iyon değişim kapasitesi (IEC), su alımı ve iletkenliğinin yakıt hücresi yapısı, kararlılığı, mekanizması ve metanol geçirgenliği ile yakından ilişkili olduğunu göstermiştir. SPEEK folyolarındaki iyileştirmeler, havacılık, askeri ve diğer sektörlerdeki uygulamalarını iyileştirecektir. Gelecekteki araştırmalar için bazı öneriler ve önerilerde bulunulmuştur (Shachidhara ve diğerleri, , 2010)

Yakıt Hücreleri için SPEEK/PBI Membranları: SPEEK membranlarındaki mekanik ve termal kararlılık sınırlamasının üstesinden gelmek için SPEEK membranına PBI eklenmiştir. Karışım hazırlandı Zar, PEEK'in sülfonlanmasıyla hazırlandı ve PBI ile birlikte DMA çözücüsü Akay RG, et al. Membranın karakterizasyonu şekil 1'de gösterilmektedir. SPEEK/PBI-10 ve SPEEK/PBI-15 karışımları optimum karışım gibi

görülmektedir. Ancak SPEEK/PBI-10, daha yüksek iletkenlik ve mükemmel termal, mekanik ve kimyasal kararlılık gösterir.

Körlüğün tek sınırlaması, PBI'nın zayıf iletkenliği nedeniyle düşük protonik iletkenliktir. Yine de, bu sınırlama, PBI'yi sülfonlayarak ve/veya zarı yüksek protonik iletken bir malzemeyle veya her ikisiyle doldurarak aşılabilir.

Bor nitrür (BN), kafes yönünde bor ve nitrojen atomlarına dayalı bir yapısal formasyona sahiptir. Bu yapılar amorf, altıgen, kübik ve kök şeklindedir.

Bor nitrür ve aerojelden oluşan nano ağ ağı, özellikle biyomedikal alanda (M.W. Smith ve diğerleri., 2009). Başlangıçta, bor nitrür 18. yüzyılın başlarında geliştirildi, ancak 1940'lara kadar uygulanmadı. Günümüzde esas olarak amonyağın (veya bazen ürenin) nitrojen atmosferinde boron trioksit veya borik asit ile reaksiyona girmesiyle oluşur. Bor nitrür, elektronik yapılarda en çeşitli element karbona benzer olduğundan, benzersiz bir dolgu maddesidir, komşu atomlarla aynı sayıda elektronu paylaşırlar. sentetik grafit elmas gibi, kübik bor nitrür çok yüksek basınç ve sıcaklıkta birincil altıgen versiyondan yapılır. Üretilen malzeme neredeyse elmas kadar sağlam taşlardır ve diğer bazı yetenekler karbon kardeşlerine elleriyle vurur (Naresh Muthu ve diğerleri, 2015).

Altıgen bor nitrür, tek tabakalı bir h-BN ile oda sıcaklığında mükemmel bir proton iletkenidir; daha yüksek sıcaklıklarda, h-BN daha iyi performans gösterir (Golberg ve diğerleri. , 2010) Daha fazla araştırma, Arrhenius tipi üstel çizimde h-BN oranlarının artan sıcaklıkla birlikte grafene kıyasla hızla arttığını göstermiştir. Bu sonuçlar, yakıt hücresi performansının iyileştirilmesinde ileriye doğru bir adım olabilir ve hatta belki de parfümlü membranların yerini alabilir, örn. Birkaç dezavantajı olan Nafion. Kovalent olarak bağlı alternatif bor ve nitrojenin bir izoyapısı olan h-BN, sofistike uygulamalara doğru ilerliyor. Genellikle "beyaz grafen" olarak bilinen bor nitrür (BN), h-BN'deki geniş bant aralığı, onu polimer kompozitler için uygun bir dolgu malzemesi haline getiren mükemmel mekanik ve termal özelliklere sahip elektriksel olarak yalıtkan bir malzeme yapar. Makul bir proton iletkeni, elektriksel yalıtkan özelliklere sahip ideal bir polimer elektrolit membran olmalıdır. H-BN, yakıt hücrelerinde kullanılan bir kompozit membran dolgu maddesi olarak henüz başlangıç aşamasındadır. h-BN'nin polimer kompozitlerde kullanımını değerlendirmek için çok az çaba olmuştur (Golberg ve diğerleri. , 2010). H-BN, matrise dahil edildiğinde polimere termal ve mekanik mukavemet sağlar. yüksek yüzey alanı da onu organik kirleticiler, boyalar için iyi bir emici yapar. Hu ve ark. h-BN'nin, oda sıcaklığında en yüksek proton iletkenliğine ve tek tabakalı h-BN ile daha yüksek değerlere atıfta bulunarak mükemmel bir proton iletkeni olduğunu buldu (Smith ve diğerleri. , 2009).

Bu çalışmada inorganik dolgu maddesi olarak işlevselleştirilmiş Bor Nitrür ile SPEEK bazlı kompozit membranlar hazırlanmıştır. Kompozit membranlar solvent döküm yöntemi ile elde edilmiştir.

10 gram PEEK ilk olarak 100 ml sulu sülfürik asit (%97) içinde eritildi ve ardından ortam sıcaklığında yüksek sülfonlaşmaya sahip olması için 170 saat karıştırmaya bırakıldı. Sülfonlama işlemi tamamlandıktan sonra, karışım, sülfonatlama reaksiyonunu durdurmak

için düşük karıştırma altında buz soğukluğunda deiyonize su içine yavaş yavaş döküldü. Karıştırma sırasında, kalan asidin fazlasını uzaklaştırmak için su sürekli değiştiriliyordu. Elde edilen SPEEK daha sonra vakumlu etüvde kurutuldu, küçük parçacıklar halinde ezildi ve daha ileri karakterizasyonlar ve membran hazırlığı için saklandı.

Bu arada boron nitrür işlevselleştirildi ve daha sonra sülfonlandı. İlk olarak 2 gr bor nitrür partikülü 40 ml H<sub>2</sub>SO<sub>4</sub> ve H<sub>2</sub>PO<sub>4</sub> (8:1) karışımında oda sıcaklığında 24 saat karıştırılarak eritildi. Daha sonra reaksiyonu homojenleştirmek ve sülfonasyon işlemini tamamlamak için 15 gm KMNO<sub>4</sub> eklendi. Karışım 12 saat daha 80°C'de karıştırılmaya bırakıldı. Karışımın rengi bir saatten fazla yeşil kaldı, bu da reaksiyonun tamamlandığının bir işaretiydi. Ardından 15 ml peroksit hidrojen H<sub>2</sub>O<sub>2</sub> ve 250 ml deiyonize su ilave edildi. Sülfonlanmış bor nitrür parçacıklarını asidik çözeltiden ayırmak için bir santrifüjli ayırıcı (BIOSAn) kullanıldı. Daha sonra nihai olarak üretilen sülfonatlı bor nitrür kurutuldu ve karakterize edilmek üzere saklandı ve karıştırma amaçları (Rajput ve diğerleri, 2021).

SPEEK/PBI membrane Karışım şu şekilde hazırlandı: Ağırlıkça PBI'yi 20x ml DMAc içinde en az 10 saat güçlü karıştırma altında eritin. 2/0,2 ağırlık SPEEK'i DMAc içinde ayrı bir fırınlayıcıda eritin. İki çözeltiyi karıştırarak 5 dakika karıştırın ve homojenliği sağlamak için bir süre ultrasonik içine koyun. Membranı bir patera kabına dökün ve 80oC'de 24 saat vakumlu bir fırına koyun.

Kompozit Membran SPEEK-BN/PBI Kompozit Membranın Hazırlanması: Adımlar: Ağırlıkça PBI'yi 20x ml DMAc içinde en az 10 saat kuvvetli karıştırma altında eritin. 2/0.2 ağırlık SPEEK'i DMAc içinde eritin. İki çözeltiyi karıştırarak 5 dakika karıştırın ve homojenliği sağlamak için bir süre ultrasonik içine koyun. Membranı bir patera kabına dökün ve 85oC'de 24 saat vakumlu bir fırına koyun.

Hem SPEEK hem de BN, FTIR kullanılarak test edildi ve reaksiyonun ve sülfonatlama işleminin başarıyla gerçekleştirildiğinden emin olmak için sülfonatlanmamış malzemeleriyle karşılaştırıldı. Doruklar, sülfat ve alkolün FTIR spektrumunda gösterilmesinin beklendiğini gösterir.

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Membranların su tutma kapasiteleri, kuru ve ıslak koşullardaki kütle değişimleri kullanılarak hesaplanmıştır. Hazırlanan membranlar 3 cm x 2 cm boyutlarında kesilerek vakumlu etüvde 60 0C de kurutularak tartılmıştır. Kuru membranlar suya daldırılarak bir gün bekletilir ve yağ ağırlıkları tartılır.

Membranın mekanik performansını incelemek için bir çekme testi yapılmıştır. Deneyler ASTM 638 ile yapılmıştır. Instron 3367 evrensel test makinesi kullanılmıştır (Şekil 3.4). Test hızı 10 mm/dk olarak alınmıştır. Test için numuneler özel aparatlar kullanılarak kare şeklinde kesilerek çekme test makinesine hazırlanmıştır. Numune üzerine yük kuvveti (F) uniform olarak uygulanmıştır. Daha sonra, numunenin uzunluğundaki değişimi ( $\Delta l$ ) referans olarak orijinal uzunluk ( $l_0$ ) ile birlikte ölçmek için bir ekstansometre kullanıldı.

Membranların kalınlık yönündeki iletkenlikleri elektrokimyasal empedans spektroskopisi (EIS) yöntemi kullanılarak oda sıcaklığında ölçülmüştür. Bu testi gerçekleştirmek için proje kapsamında satın alınan Gamry potansiyostat/galvanostat ve Erdes Kimya ve eknoloji firması tarafından özel olarak yapılmış 4 prob elektrotlu iletkenlik hücresi kullanılmıştır. Membranlar, iyonik iletkenlik ölçümünden önce bir gün boyunca 1M sitik solüsyonda bekletilerek şartlandırıldı. Membrandan 2cm x 2cm boyutlarında test yapmak için kesilen parça kullanıldı. Daha sonra 4 platin tel elektrotlu bir hücreye yerleştirildi. Elektrotlar, zarın her iki yüzeyi ile temas halinde birbirine zıt iki şekilde konumlandırılmıştır. Ölçümler 1-105 Hz frekans aralığında ve potansiyostatik modda nemli ortamda gerçekleştirilmiştir.

TGA testi, membranın sıcaklık aralığını ve termal kararlılığını test etmek için yapılan termoanalitik bir tekniktir. İlk çalışmalarda, numuneler oda sıcaklığından 300 oC'ye ısıtıldı, soğutuldu, ardından ikinci çalışmada 600 oC'ye ısıtıldı. Isıtma hızı 20 oC/dk idi.

Membranın kimyasal stabilitesi 25 oC sıcaklıkta milyonda 4 kısım Fe tuzu ve yüzde 3 Hidrojen peroksit içeren Fenton reaktifi kullanılarak test edildi. Önce her bir zardan 0,2 gram numune tartılarak sulu demir (+2) sülfat hepta-hidrat (5 ppm, 55 mL) çözeltisine konuldu. Daha sonra çözeltiye 7 mL %3 hidrojen peroksit ilave edildi, kalan ağırlıklar saatte bir kontrol edildi.

Optimal zarlar için, zarı karakterize etmek ve sülfonasyon ve hidroksilasyonun zar üzerindeki etkilerini doğrulamak için XRD analizi yapıldı. Bununla birlikte, XRD sonuçları, film boyunca tekdüzeliği doğrulamak için kullanıldı.

Membran boyunca ve membran yüzeyindeki morfoloji ve homojenlik, Taramalı Elektron Mikroskopu (SEM) ve mikroskop (15-30 milimetre yakınlaştırma aralığı) ile test edilmiştir. Mikroskopi, zardaki SPEEK, PBI ve BN dağılımının üniform olup olmadığını gösterir.

Sülfonlama işlemini doğrulamak için, tekli bağ bölgesinde (sülfonik asidin alkol kısmı) yeni bir geniş tepe noktası görünmelidir (Nandiyanto ve diğerleri., 2019). Öte yandan, SPEEK zincirinde sülfonik asit grubunun varlığı, 1251 – 1000 cm<sup>-1</sup> aralığındaki güçlü karakteristik piklerle doğrulanabilir (Rajput ve diğerleri, 2021)

Ancak hidroksil grubunun yoğun olarak varlığını gösteren 3460 – 1570 cm<sup>-1</sup> dalga sayısı aralığında geniş bir pik gösterdiği dikkat çekmektedir. Yukarıdaki sonuçlara göre, PEEK'te sülfürik asit ve BN'de hidroksil grubunun varlığı doğrulandı.

sülfonatin varlığını gösteren 1300 – 1000 cm<sup>-1</sup> dalga sayısı aralığında yeni piklerin görüldüğü fark edilebilir. Aynı şey görülmektedir. SPEEK spektrumunda simetrik ve asimetrik olmak üzere iki pik tespit edildi. Ayrıca geniş pik 3300 – 3000 gösterir.

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Sülfonasyon dereceleri ve IEC, geri titrasyon kullanılarak bulundu. Sonuçlar, dolgu maddesinin SPEEK/PBI'ye eklenmesinden sonra sülfonasyon derecesinin pristeden daha

yüksek olduğunu göstermektedir; bu, BN'nin asit reaksiyonunun bir sonucu olabilir. Bununla birlikte, PEEK için sülfonasyon işleminin süresi ve sıcaklığı artırılarak daha yüksek bir SPEEK/PBI DS'si elde edilebilir.

Öte yandan IEC, BN ilavesiyle dikkat çekici bir şekilde arttı, ancak doldurucu içeriği arttığında hemen hemen sabit kalıyor. Sonuç olarak, zarin BN ile modifiye edilmesinin, DS ve IEC'yi önemli ölçüde artırdığı, buna karşın dolgu yüzdesinin zardaki dolgu yüzdesinden etkilenmediği doğrulandı.

Speek-PBI'a göre kompozitte BN içeriğinin %10'a kadar artmasıyla iletkenlik arttı. En yüksek iletkenlik 0,0245 S/cm olarak SPEEK-PBI/10BN için elde edilmiştir. Ancak BN içeriğinin daha da artmasıyla %15 ve %20'ye varan iletkenlik azalmıştır. Daha yüksek içeriklerde BN partiküllerinin kendi kendine agregasyonu mümkün olabilir. İyonik iletkenlik, artan sıcaklıkla artar.

Membran, 305-317 oC'ye kadar bir TG ile termal stabilitede büyük gelişme gösterir. Bu, HT-PEM yakıt hücrelerinin çok yüksek sıcaklıklarda çalışmasına izin vererek yüksek verimlilik ve daha az katalizör içeriği sağlar.

SPEEK/PBI/BN-10 filminin X-ışını kırınım modeli, zar tamamen şekilsizdir. 2θ 20° civarındaki geniş bir kırınım tepe noktası, kristalliğin olmadığını gösterir. Filmlerin amorf doğası, orta ve yüksek DS'li SPEEK'i gösterir. SO<sub>3</sub>H ve OH gruplarının PEEK'e dahil edilmesi zincir yapısını ve paketlenmesini değiştirerek kristallik kaybına yol açar.

Membranın morfolojisi ve topografyası SEM ile incelenmiştir. Küçük parçacıkların, özellikle polimerik malzeme içinde iyice karıştırıldıktan sonra, yüksek yüzey enerjisinden bir topaklaşması muhtemeldir. Bu, istenmeyen termal ve mekanik özelliklerle sonuçlanan polimerik kompozit membranların hazırlanmasında büyük bir sorun olabilir (Kumar ve diğerleri, 2009).

Bu çalışmada, membranın dökümü için ileri bir teknoloji bulunmadığından ve sıcaklık dikkatli bir şekilde izlenmediği için solvent buharlaşması, yüzeyde ve membran boyunca bazı küçük gözenekler oluşturmuştur. Bu gözeneklerin metanol geçirgenliğini ve mekanik dayanımı etkilemesi beklenmektedir. Bununla birlikte, tüm zarlar, içinde SPEEK/PBI'nin mükemmel bir şekilde karıştığı ve BN'nin zardaki dağılımının, hiçbir konsantre veya tamamen boş blok olmaksızın neredeyse tekdüze olduğu yüksek homojenlik gösterir.

Homojenlik (membranların yüzeyi üzerinde SPEEK, PBI ve BN'nin muntazam dağılımı) ayrıca Mikroskop (15-30 nano) kullanılarak her iki tarafta da kontrol edildi. Küçük PBI ince parçacıklarının düzgün bir şekilde çözünmemesi dışında zar homojen görünüyor.

BN ilavesi, zarin fizikokimyasal özelliklerini önemli ölçüde artırmıştır, ancak yüzde %10'u geçtiğinde zarı olumsuz etkiler. Ancak optimum dolgu yüzdesi %10 olarak bulunmuştur. Membran, yüksek mekanik basınca (yani 8.61MPa) maruz kaldığında dayanıklılığını kanıtladı. Aynı zamanda, PBI ve BN'nin varlığı nedeniyle yüksek termal kararlılık (yani) gösterir. Bu çalışmada, BN işlevselleştirildi ancak sülfonatlanmadı,

sülfonatlanmış bor nitrürün son derece yüksek protonik iletkenliğe sahip olması bekleniyordu.

Membranlar, optimum zar için IEC değerinin 2.18 meq/g bulunduğu iyi iyonik değişim kapasitesi gösterdi. Öte yandan, membranlar, küçük kütle kaybı ile 305oC'ye kadar mükemmel termal stabilite göstermiştir. Bununla birlikte, çekme gerilimi 8.61 MPa'yı aşmadığından membran zayıf mekanik stabilite göstermiştir. Membran, oda sıcaklığında (245 mS/m<sup>2</sup>'ye kadar) ve 120oC'ye kadar yüksek sıcaklıklarda mükemmel iyonik iletkenlik göstermiştir. Zar amorf ve homojendir.

BN'nin SPEEK/PBI karışımının sınırlamasını aştığı ve diğer perflunize edilmemiş zarlara kıyasla harika fizikokimyasal özellikler ve yüksek protonik iletkenlik gösterdiği için Yakıt hücreleri ve Hidrojen depolama uygulamaları için çok umut verici bir zar olduğu bulundu.

Yazar, zarı bir yakıt hücresi deneyine uygulamayı ve performansı gözlemlemeyi öneriyor. Ayrıca, BN işlevselleştirme için farklı yollar denemek muhtemelen ilginç bir çalışma olacaktır.

## 1. INTRODUCTION

World has become dependent on electricity in nearly all of the necessities. Thus, the demand of electricity has become tremendously huge, which cannot be satisfied economically with fossil fuel. On the other hand, the environmental issues related to the electricity generation has become one of the biggest concerns of the future and the next generations. As a result, most of the countries if not all of them have prepared a vision in which renewable energy and fuel alternatives are one of its main subjects, in which world has target 800 GW of renewable power by 2035 (Van de Graaf et.al, 2000) .

United States, EU countries, United Kingdom, and some other such developed countries have already started to manage their renewable energy potential, and they are developing their technologies to exploit the optimum renewable potential which has reached to more than 29% of global electricity generation at the end of 2019 (Van de Graaf et.al, 2020). Meanwhile Middle east countries are already having the largest fossil fuel potential, water scarcity, and agriculture dilemma. 80% of their agricultural products are being imported from neighbour countries, the thing that puts more pressure over them to save their petroleum for exporting purpose.

Hydrogen technology is a term refers to the technologies that are used in producing and utilizing of Hydrogen. Recently, hydrogen technology has gotten a huge attention worldwide. For instance, Saudi Arabia only has started an enormous project of 4 billion dollars to produce hydrogen from water using solar energy (Gherboudj et.al, 2021). Moreover, fuel cell technology has become one of the most interesting researching area as it is applicable in so many application and may become the ultimate solution for electricity and pollution that the world have been waiting for ages. Hydrogen has a great heating value and completely clean fuel since the only output of the conversion process is water. Hydrogen can be produced by many different ways, however, hydrogen economy is when hydrogen is produced from carbon dioxide free source and use it as alternative fuel.

Fuel cells technology has taken off in the last few years, yet, the main challenge of using fuel cell commercially is the high cost of its material. However, the recent studies focus on reducing the amount of the platinum used in the catalyst layer and using low cost

materials in the electrolyte. Currently, Nafion and some other partially per-fluorinated materials are commercially used by fuel cells manufacturers for the high protonic conductivity of per-fluorinated materials. However, perfluorinated materials are extremely expensive and environmentally unfriendly, that necessitates the search for alternatives. Therefore, non-perfluorinated membranes became. Nevertheless, non-perfluorinated membranes failed to achieve acceptable protonic conductivity.

Thesis statement: In 2021, a study was conducted to overcome this limitation by introducing boron nitride to PBI (Hussin et.al, 2021), the study was successful and the protonic conductivity of the membrane has jumped to 240 mS/cm, and most importantly the BN didn't show any negative effect on the membrane. On the other hand in 2020 a study was conducted to maximize the protonic conductivity of SPEEK membrane by introducing BN, that shows that BN can successfully be added to modify both SPEEK (Yogarathinamet.al, 2021). Another study was conducted by AKAY et.al on SPEEK/PBI blend to overcome the mechanical and thermal limitation of SPEEK, in which 10% of PBI filler showed the best properties; however, the protonic conductivity had decreased as a result of PBI (Akay et.al, 2018). Therefore, since BN has high protonic conductivity and good thermomechanical properties, in this study, SPEEK was modified with PBI and BN to enhance the mechanical stability, thermal stability, and the protonic conductivity of the membrane.

## 2. LITERATURE REVIEW

### 2.1. Introduction

Fuel cells are devices that generate electricity directly from chemical reactions. The fuel cell was invented in 1839 (pictured). The name "fuel cell" was introduced by Charles Langer in the 1889th century. The first proton exchange fuel cells were developed by NASA for his manned space missions in the 1950s to provide an astronaut with power and drinking water. However, fuel cells include proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC), solid oxide fuel cell (SOFC), molten carbonate fuel cell (MCFC), phosphoric acid fuel cell (PAFC) and many others.

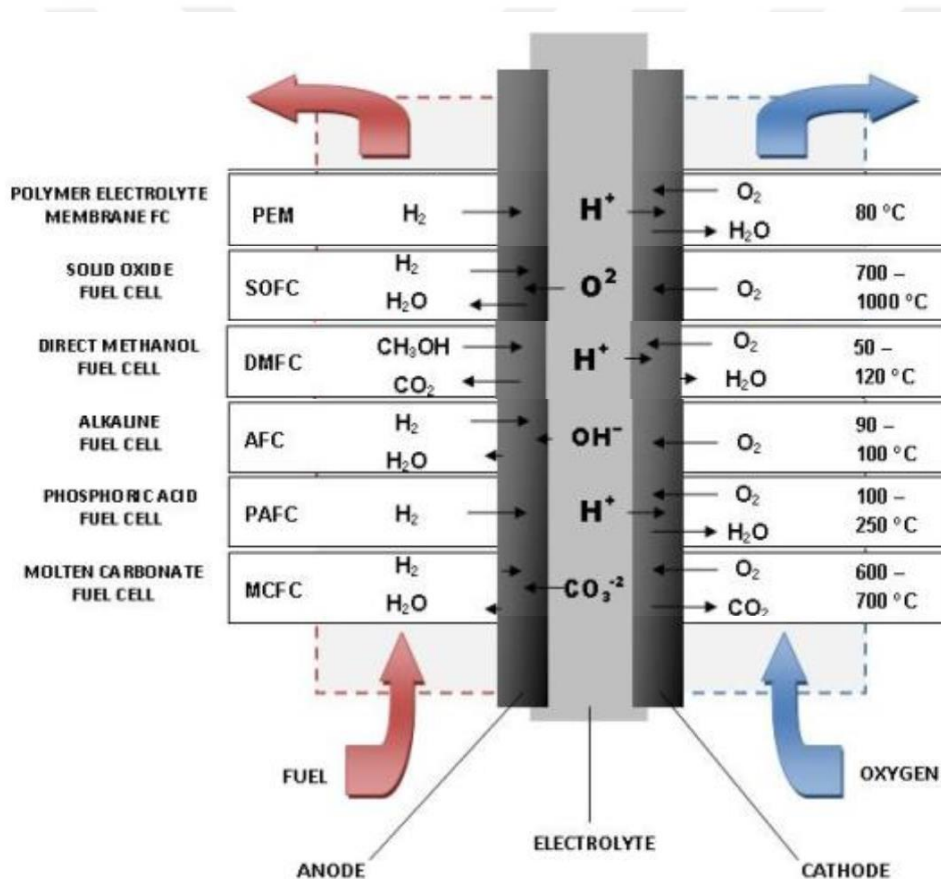


Figure 2.1. Types of fuel cells . (MOHMAD et.al, 2018)

Fuel cells have got a huge attention in the 2000s due to their unique properties such as being a very clean electricity generator with no noises and great efficiency. However, the commercial value of fuel cells is still a challenge due to the high cost of the fuel cell

materials and their testing method and the durability. Thus, current studies are focusing on developing new materials that are cheaper and more stable chemically.

## 2.2. Types Of Fuel Cells

### 2.2.1. Proton Exchange Membrane Fuel Cells (PEMFC)

Proton exchange membrane fuel cells or polymer electrolyte membrane fuel cells convert the chemical energy from the reaction into electricity directly. However, pure hydrogen and fuel that contains hydrogen are used to fuel the fuel cells, to produce electricity, heat, and water. That is happens when hydrogen reduced into proton and electron, the electron move to generate electrical current, while the proton passed through the membrane and react with oxidant to produce water and heat. Proton exchange fuel cell consists mainly from membrane electrode assembly in which oxidant and fuel diffuse to the catalyst and then to the electrolyte (the membrane). Attractive advantages like its large power density,

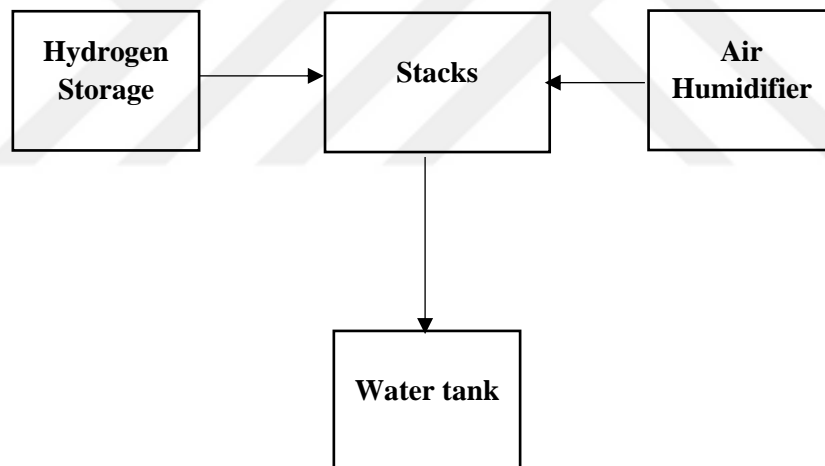


Figure 2.2. PEMFC system components

incredible performance, instance startup run, low sensitivity to orientation, all along with and environmental friendliness make PEMFC so favorable than the other types of fuel cells Mark (Williams et.al., 2011).

### 2.2.2. Direct Alcohol Fuel Cells

Direct alcohol fuel cells (DAFC) utilize the direct electrochemical conversion of alcohol fuel chemical energy into electrical energy, which is environmentally friendly and energy

efficient. However, before this technology is widely adopted, several limitations related to weak electro-chemical performance, the expensive components of the cell, and limited durability of fuel cells need to be addressed. High investment costs in direct alcohol fuel cell systems are mainly to reduce the content of precious metal catalysts, electrolyte medium and the costly bipolar plates. Thus, the development of cheap and high-efficient polymer electrolyte membranes is likely to improve electrocatalysts and low-cost bipolar plates that meet the standards of high performance and fair durability is a major challenge. As new hydrocarbon membranes and low-cost metal-loaded electrodes for DAFC system applications. Various applications can be found, such as mobile power generation systems, distributed power generation systems, and stationary power generation systems. Articles directly addressing cost, crossover, performance, components, systems, reaction mechanisms, and durability analysis of alcohol fuel cells are recommended. We welcome technical surveys, feature articles, analyzes of the latest technology, and future prospects for this technology.

#### Principle of operation

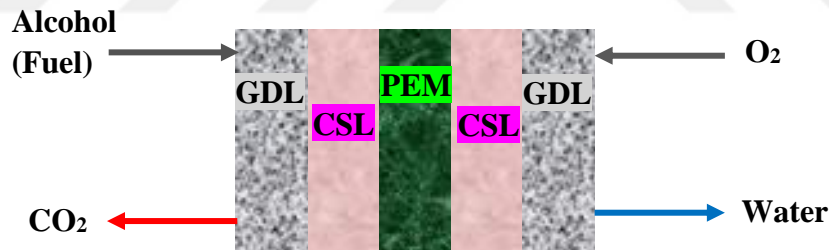
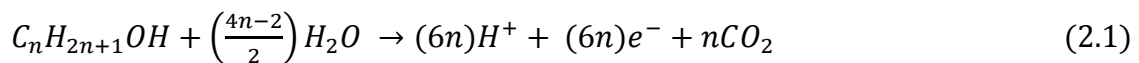


Figure 2.3. Scheme for A Typical DAFC

Direct alcohol fuel cells directly convert chemical energy to electrical energy, so the typical reactions for direct alcohol fuel cells can be expressed as following:

- In anode:



- In cathode:



Not like PEMFC the liquid alcohol is mixed with water (the water is recycled from the reaction) and then it is distributed through the diffusion layer (GDL). Subsequently, reach to the catalyst layer in which the redox reactions take place. At the same time carbon dioxide is come out through the GDL. The free ions then transport to the other electrode through the electrolyte membrane.

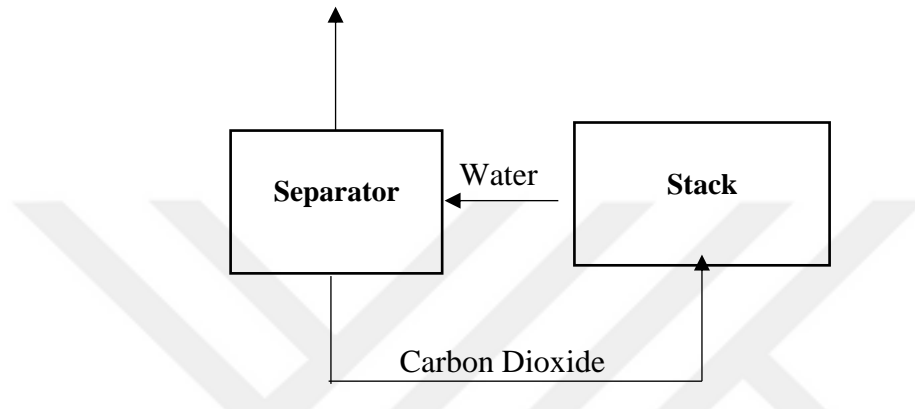


Figure 2.4. DAFC system components

### 2.2.3. Solid Oxide Fuel Cells (SOFCs)

The electrolyte in solid oxide fuel cell is normally a solid metal oxide like yttrium oxide (Y2O3) with Zirconium oxide (ZrO). This type of fuel cells are also called ceramic fuel cells, since such metal oxides are called ceramics.

The anode is made of zirconium ceramic with nickel mixed which provides electrical activation. At the cathode;  $LaCo_{1-x}Mn_xO_3$ ,  $x=0.2-0.3$  or; It consists of ceramic structures such as  $LaSrMnO_3$ . The electrodes are applied to the ceramic surface either by applying them in the form of ink and baking them at high temperatures, or by spraying them in the form of a plasma (fourth state of very high temperature substance) spray. In this fuel cell, unlike the PEM type fuel cell, the oxygen ion (negatively charged) passes through the electrolyte. Therefore, any hydrocarbon fuel can be used on the anode side. At the cathode, the oxygen is ionized by the electron from the external circuit.

### 2.3. Principle Of Operation Of PEMFC

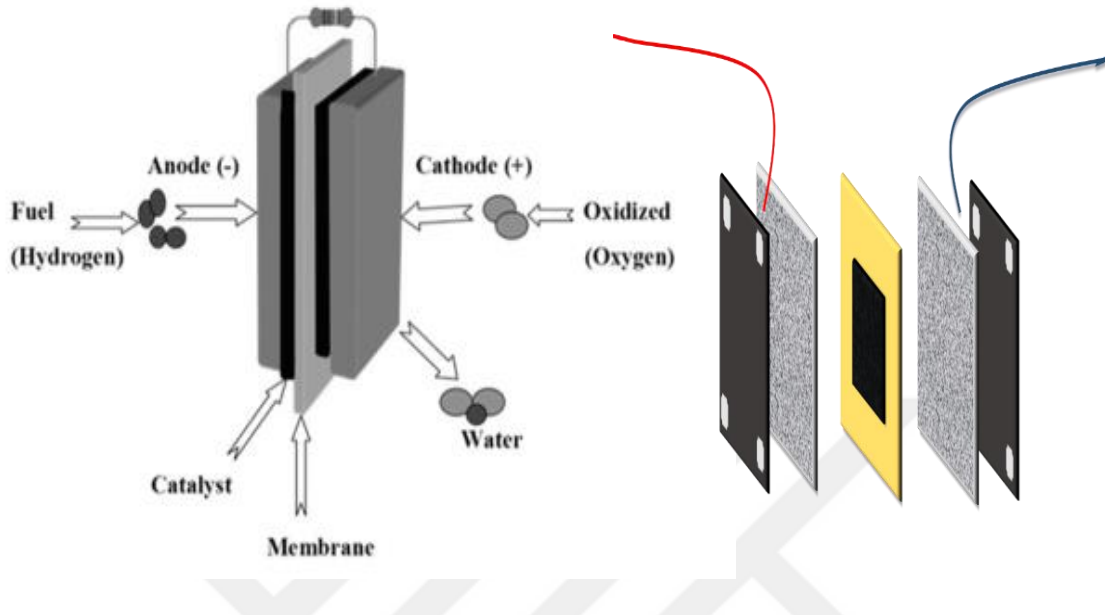


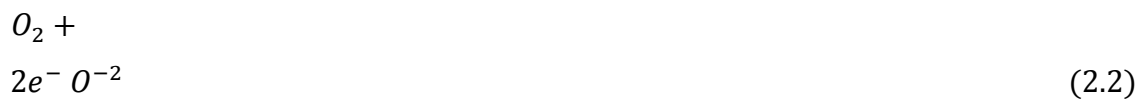
Figure 2.5. Typical PEMFC components.

Proton exchange fuel cells directly convert chemical energy to electrical energy, so the typical reactions for proton exchange fuel cell are:

In anode:



In cathode:



The gas is distributed through a layer called gas diffusion layer (GDL) then reach to the catalyst layer in which the redox reactions take place. The free ions then transport to the other electrode through a membrane which works as an electrolyte.

## 2.4. PEMFC Membrane Electron Assembly

As already mentioned, a reaction occurs at the electrode in which hydrogen is oxidized and oxygen is reduced. They are made up of carbon papers or cloth coated with hydrophobic polymers and platinum carbon particles as an electrocatalyst. The zone where redox reactions take place is called the active zone. The membrane electron assembly

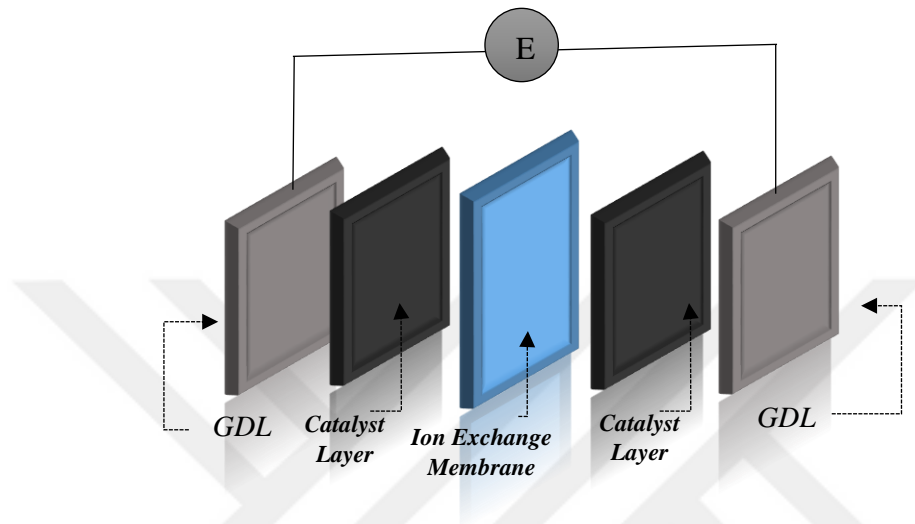


Figure 2.6. Typical MEA components.

consists of three main parts. GDL, catalyst layer, electrolyte (membrane). The function of the porous diffusion layer is to ensure the gas supply to the catalyst and expel the products. The main properties of this layer are porosity, hydrophobicity to repel water, electrical conductivity to carry electricity, and good thermal conductivity to dissipate heat from the reaction sites.

The active zone must have the following characteristics ( MOHMAD et.al, 2018 ) :

- Large active surface.
- Has an acceptable life time.
- Having high electric conductivity to minimize the ohmic losses.
- Having high tolerance to carbon dioxide.

The benefit of using a catalyst in the active zone is to increase the redox reaction, that results in a less fuel cell overpotential and less associated losses. Platinum is the most affective catalyst for fuel cells, however, it is so expensive. The recent researches have

been examining new catalysts or new electrolyte that reduce the amount of platinum used for electrode fabrication (it reduced from 28mg/cm<sup>2</sup> to 0.02mg/cm<sup>2</sup>) (MOHMAD, 2018).

The electrolyte function in the PEMFC is to (Ogungbemi et.al, 2019):

- a. Conduct protons between the electrodes with the least ohmic loss. Thus, its protonic conductivity should be relatively high.
- b. The electrolyte must isolate any electrical between the cathode and anode.
- c. Prohibit mixing of the oxidant with the fuel to avoid any direct reaction which result in low efficiency and system break down.

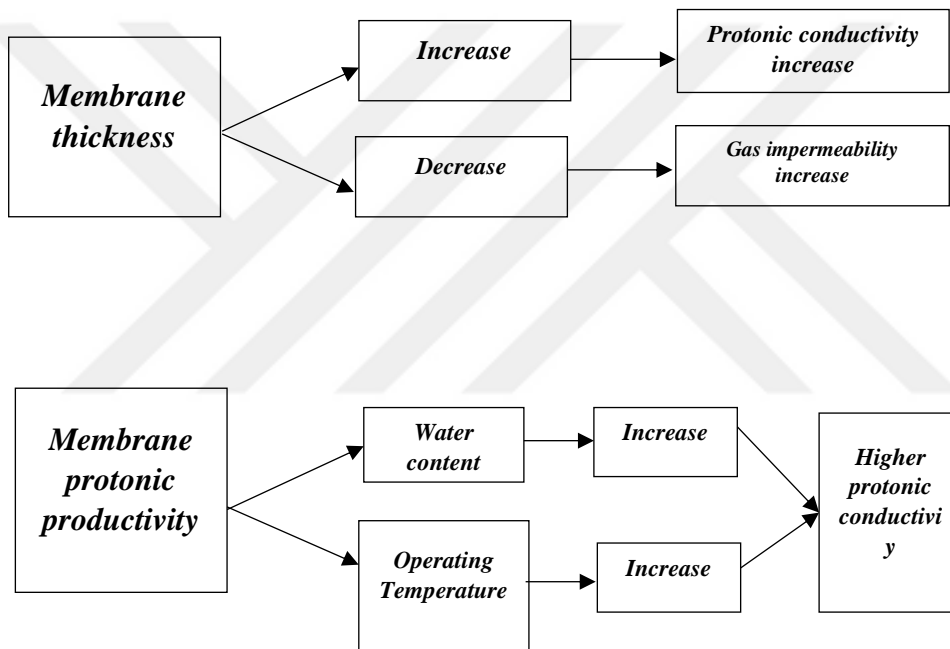


Figure 2.7. Effect of thickness and water content on the characterization of the membrane.

Increasing the operating temperature from 25°C to 80°C doubles the conductivity. However, because of the polymer's stability the operation stability must not exceed 85°C, therefore, currently, the researchers are trying to increase this limit to enhance the efficiency of the PEMFCs.

## 2.5. Ion Exchange Membranes For Fuel Cell

A membrane is a porous or non porous barrier is used to select something from mixture or group of things attached together. This thing can be small particles, molecules, or ions. Membrane can be used as flat sheet, tubes, or hallow fiber. In general membranes are three types:

- Symmetric porous membranes.
- Symmetric nonporous membranes.
- Asymmetric porous membrane.

Symmetric nonporous membranes are usually prepared by solution casting or melt extrusion.

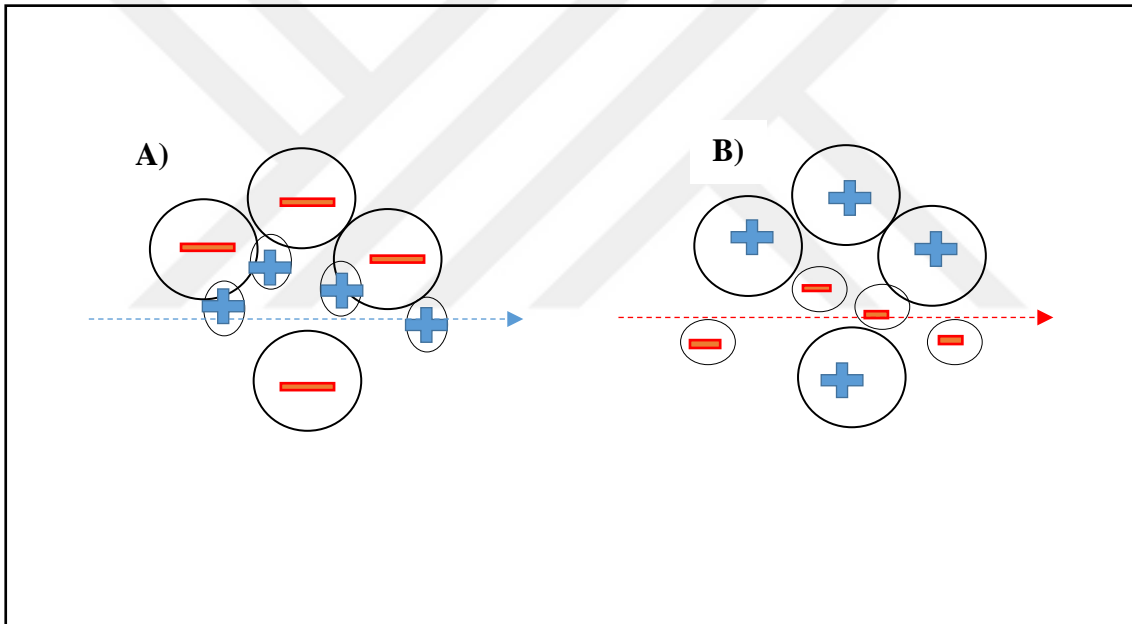


Figure 2.8. a ) Proton exchange membrane b) Anion exchange membrane

Ion exchange membrane is a type of membranes that are used to transport or carry out one ion from a reduced or oxidized chemical compound. This ion can be either anion or cation. Ion exchange process can be defined as a reversible chemical reaction in which an ion (Anion or cation ) from a chemical component is exchanged for an ion has the same charge attached to an immobile solid particle. Ion exchange resins are a stationary phase used as ion exchanger, there is cation resin and anion resin, cation exchangers are prepared by immerse the resin in an acid when anion exchangers are prepared by immerse the resin in an alkane. Other materials are used to enhance other important properties such

as mechanical strength and thermal stability. Ion exchange happens when the resin attracts the opposite charge ion of the operating material. Ion exchangers are functionalized porous or gel polymer such as zeolites and montmorillonite (Strathmann, 2004).

For mobile counter ions, the resin component of a cation exchange membrane would have negatively charged groups (e.g.  $\text{PO}_4^-$  or  $\text{SO}_3^-$ ) attached chemically to the polymer chain and the opposite for the anion exchangers. To maximize the protonic conductivity of the material sulfonate or doped in an acid. Also we should mention that most of the ion exchangers are carboxylates .

### 2.5.1. Mechanism Of Proton Exchanging Through The Ion Exchange Membrane

Protons flow molecularly through the membrane through two media. These are migration by proton hopping or Grotthuss mechanisms and diffusion. (Peighambardoust et.al, 2010).

The protons produced from oxidation reaction attaches to water particles producing Hydronium. Once the hydronium atoms get close to sulfuric acid groups they hop to the

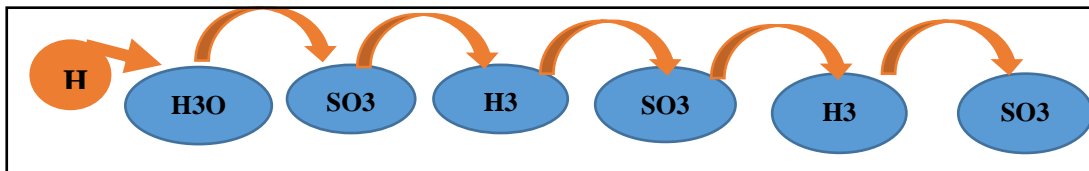


Figure 2.10. Proton hopping mechanism

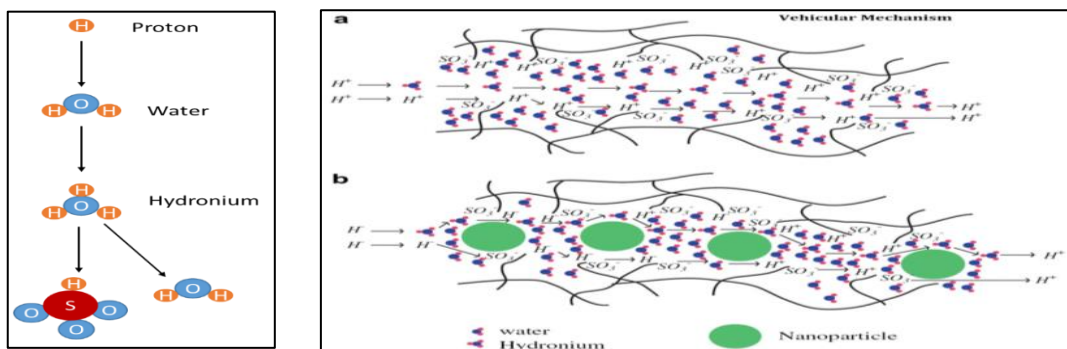


Figure 2.9 Scheme for proton movement by mean of diffusion: a) Pristine membrane b) Nano particles membrane diffusion. With a permission (Peighambardoust et.al, 2010).

sulfuric acid group in the membrane. This proton hopping happens all through the membrane till it passes to the other side (figures 2.9, 2.10).

### 2.5.2. Proton Exchange Membranes Used In Fuel Cells Applications

Membrane are used in proton exchange mebrane can be classified as followes (Toshikatsu, 2004): Perfluorinated and partially perfluorinated, Non-fluorinated hydrocarbons, including aliphatic or aromatic structures, and Acid-based complexes.

Table 2.1. Polymers are used in PEM fuel cells application

<b>Perfluorinated</b>	<b>P.Perfluorinated</b>	<b>Non-Perfluorinated</b>	<b>Acid-Based Blend</b>
• PFSA	• PTFE-g-TFS	• NPI	•SPEEK-PBI-P4VP
• PFCA	• PVDF-g-PSSA	• BAM3G	• SPEEK-PEI
• PFSI		• sPEEK	•SPEEK-PSU(NH2)
• Gore-select		• sPPBP	• SPSU-PBI/P4VP
		• MBS/PBI	• SPSU-PEI
			•SPSU-PSU(NH2)2
			•PVA-H3PO4

Per-fluorinated compounds (PFCs) contain big group of compounds. Their structure is a per-fluorinated hydro-phobic straight carbon chain attached with single or many hydrophilic head groups. PFC retains both water and oil. This makes it an ideal surface treatment chemical. PFCs are used in a variety of industrial applications such as antifouling agents (such as Teflon), textiles, paints, waxes, polishes, electronics, adhesives and food packaging (Ceric et al., 2017).

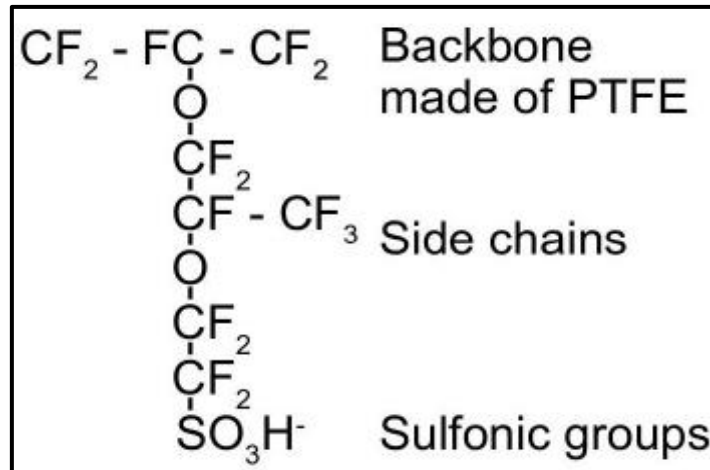


Figure 2.11. Perfluorinated materials general structure

They are considered the most popular membranes in PEM application since all other alternatives have not succeeded to achieve an acceptable level of conductivity. The most common type is Nafion which made by Dow Chemical Company. However, it has several disadvantages (Enrico Drioli et.al, 2017):

- They cannot operate with temperatures higher than 100°C.
- A lot of problem related to swelling.
- High cost material.
- Extremely harmful to the environment.
- Chemical degradation.

To overcome or mitigate the problems that are related to the hydration in Nafion membranes, nanocomposite materials were introduced to modify the membrane (Oh et.al, 2014). This improves their chemical and physical properties without affecting proton conductivity. Besides fluorinated membranes, several other materials are also used for membranes. That aims to reduce the high costs compared to the days when fluorine-based materials were the only used materials.

Some of the most common per-fluorinated material used in partially per-fluorinated membranes are:

- Sulphonated  $\alpha,\beta,\beta$ -trifluorostyrene and *m*-trifluoromethyl- $\alpha,\beta,\beta$ -trifluorostyrene Sulphonated polymer of  $\alpha,\beta,\beta$ -trifluorostyrene.

- Copolymer of  $\alpha,\beta,\beta$ -trifluorostyrene, *m*-trifluoromethyl- $\alpha,\beta,\beta$ -trifluorostyrene and *p*-sulfonyl fluoride- $\alpha,\beta,\beta$ -trifluorostyrene.
- Sulphonated copolymer of  $\alpha,\beta,\beta$ -trifluorostyrene and *p*-fluoro- $\alpha,\beta,\beta$ -trifluorostyrene  
Copolymer of  $\alpha,\beta,\beta$ -trifluorostyrene, *p*-fluoro- $\alpha,\beta,\beta$ -trifluorostyrene and *p*-sulfonyl fluoride- $\alpha,\beta,\beta$ -trifluorostyrene.

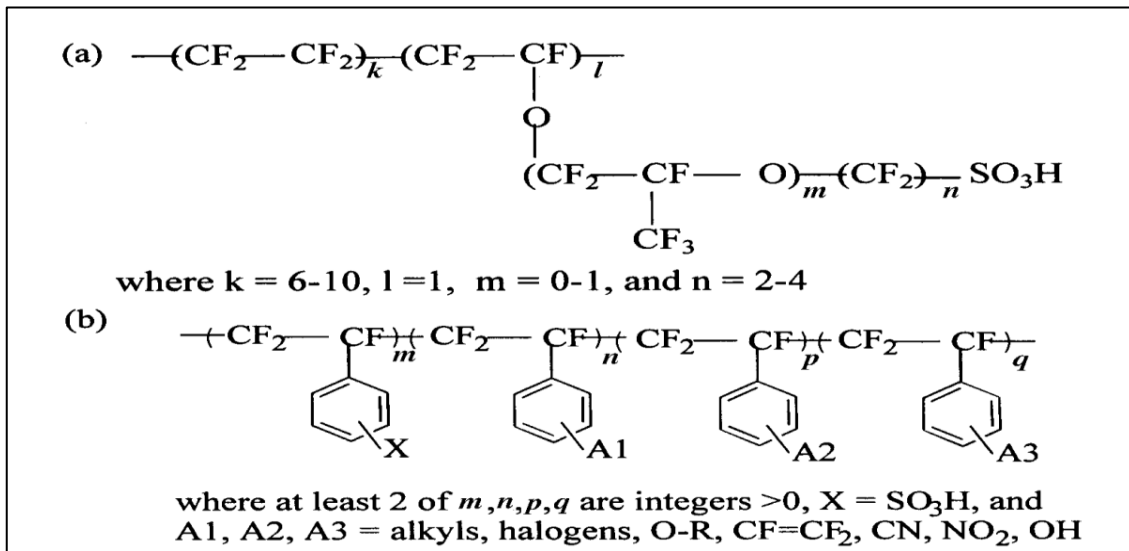


Figure 2.12. Chemical structure of: (a) Perfluorinated sulfonic acid-based membranes like Nafion (b)Sulfonated trifluorostyrene copolymer membranes (Partially perfluorinated).

Some partially per-fluorinated membranes succeed to achieve high protonic conductivity. Yet, they are still expensive since per-fluorinated material are used. The most popular partially fluorinated membrane is sulfonated copolymer incorporating  $\alpha, \beta,\beta$ -trifluorostyrene monomer.

Studies have been conducted to replace the pre-fluorinated materials with a low cost and available materials. Nonfluorinated membranes consist of polymeric materials that are functional. The following are some of the materials used as non-fluorinated membranes (De Dardel et.al, 2008):

- Poly-styrene materials.
- Poly-arylene-ether-sulfone (PAES).
- Poly-arylene-ether-ketone (PEEK).
- Acid-doped poly-benzi-mida-zole (PBI).

- Poly-vinyl-chloride (PVC)

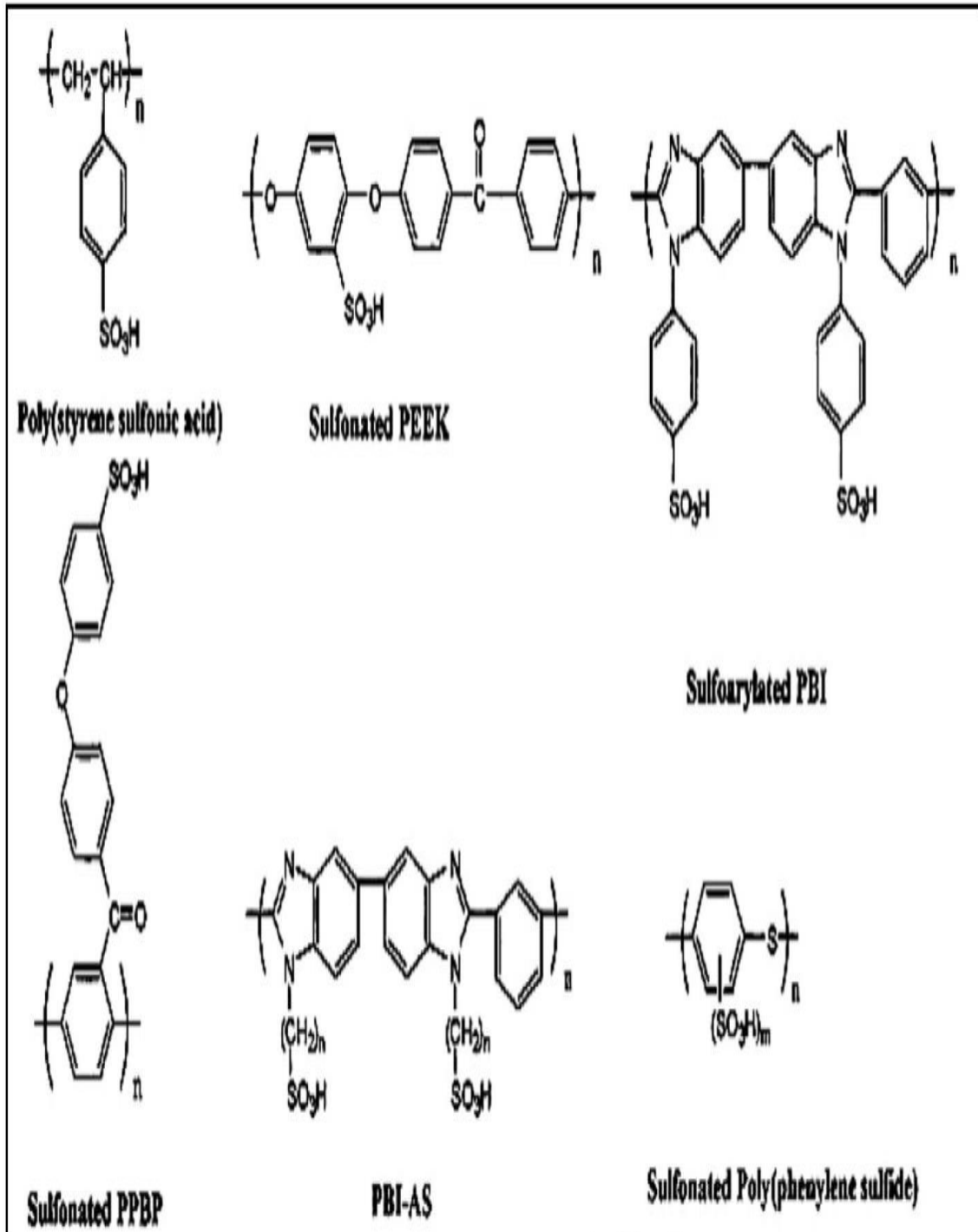


Figure 2.13. Some of the materials used as non-fluorinated membranes (De Dardel et.al, 2008)

All of the aforementioned membranes operate at low temperature except PBI. The listed membranes have lesser protonic conductivity than per-fluorinated and partially perfluorinated membranes as most of them failed to achieve high protonic conductivity.

Though they show lesser conductivity, reduced thermal and chemical properties, some authors think that manufacturers should be ready to concede some of the properties in favor of reducing the cost. As it was mentioned earlier, the researches now are focusing on producing a new low cost high protonic membrane. The best membrane to develop are acid- based hydrocarbons membranes. The membranes can be blended, cross linked, or filled with a high quality material to obtain a better properties than the original membrane.

Table 2.1. Commonly used Material for PEMFC Membrane

	<b>Strengths</b>	<b>Weaknesses</b>	<b>Conductivity (mS/cm)</b>
<b>SPEEK</b> (HUANG et.al 2001)	It has attractive mechanical stability, thermal durability and toughness, and an electrical conductivity depending on the DS property.	A large amount of sulfone groups attached to the polymer chain reduces the stability of the material in which the polymer is used.	77 -180
<b>PBI</b> (Nayak et.al, 2020)	It exhibits efficient proton conductivity even in the absence of water at temperatures above 100°C, ensuring excellent mechanical and thermochemical stability and low gas permeability.	Weak chemical resistance, low mechanical strength, acid leaching	5- 45 (Sulfonated) 0.001 (Pristine)
<b>PAES</b> (G. Lee et.al, 2006)	attractive proton conductivity, great carbon monoxide tolerance, and low fuel cross-over.	has weak chemical reactivity, mechanical properties, and thermal stability	79 - 109

## 2.6. Recent Studies On Membrane Materials For Fuel Cells

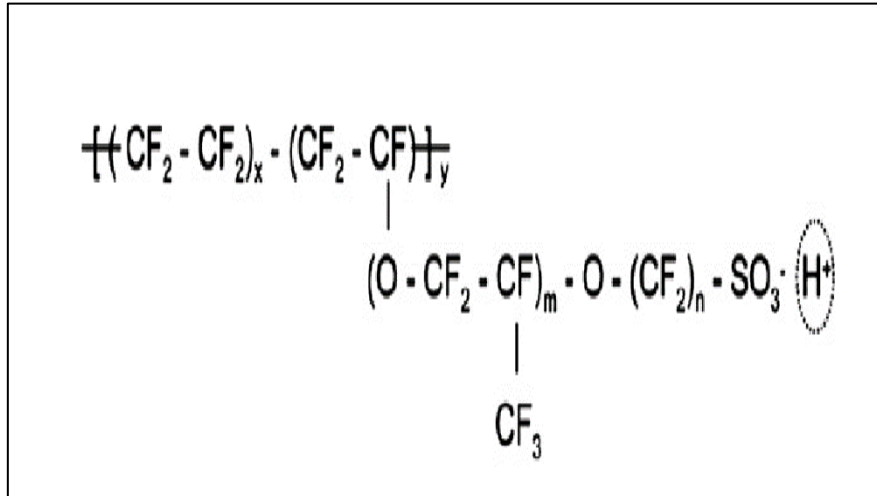


Figure 2.14. Structure of Nafion and its close polymers (Baroutaji et.al, 2016)

As mentioned earlier in this chapter, PEM fuel cells use a solid polymer proton-permeable electronic insulator membrane. The most common commercially available PEM material is DuPont's fluoropolymer (PFSA) Nafion. Nafion is a sulfonated polymer composed of a perfluorinated backbone and sulfonated side chains. The function of the perfluoroether side micro-phase of the sulfonic acid groups is hydrophilic, which means high proton conductivity. On the other hand, the polymeric-phase of the perfluorinated side chain is hydrophobic and it has a high mechanical strength [Baroutaji et.al, 2016: 1-9]. chains is to ensure chemical stability, and the sulfonated side chains have the function of pooling and promoting hydration (Figure 2.4.). This material has a unique feature in which the

Despite of all of these attractive features, Nafion has been facing many challenges such as (Baroutaji et.al, 2016)

- High cost material with around 700\$ per square meter.
- Can't be used in high operating temperatures.
- The protonic conductivity is so dependent on the water contents.
- Environmentally unfriendly and complicated manufacturing process.
- during humidity and thermal cycling some mechanical failures such as swelling and shrinking may occur.

- In long term peroxide formation affects the membrane causing chemical degradation.

The new researches are aiming to come with a new material that is cheaper and less water dependent. The below table lists of the latest researchers' suggestions for overcoming the aforementioned challenges of Nafion (Table ):

Table 2.2. Commonly used electrolyte membranes.

<b>Filler</b>	<b>Main Function</b>	<b>Ref</b>
<b>Nanoparticles</b>	Increment in the amount of adsorbed water or retaining-water in the membrane and provides additional contact area to improve the ion-exchange capacity and mitigate swelling.	( Lade et.al, 2017)
<b>GO</b>	Improves self humidification (i.e. water retention), reduced methanol and fuels cross-over. It also improves mechanical, thermal and chemical stabilities. Moreover, it enhances the proton conductivity, and make the preparation of membrane-electrode assembly processing easier.	(Pandey et.al, 2017)
<b>BN</b>	Extraordinary physical/chemical stability and high protonic conductivity. physicochemical, electrochemical, thermal, mechanical, and barrier properties.	(Yadav et.al, 2019)
<b>p-MWCNT</b>	Improve the membrane selectivity and transport number. Moreover it mitigates the electrical resistance resulting in less Ohmic losses.	(Hosseini et.al, 2013)
<b>Ionic liquids</b>	Facilitate the proton conductivity inside a PEMFC and improve the other properties.	(Padilha et.al, 2010)

Table 2.3. Most commonly used fillers for electrolytes membranes.

<b>Nanocomposite membranes</b>	Modifying Nafion membrane with micron nanoparticles such as TiSiO <sub>4</sub> , ZrO <sub>2</sub> , TiO <sub>2</sub> , and Silica	Higher water retention capacity, higher operating temperature. and Enhance the chemical and physical properties of the membrane ( e.g. elastic modulus, tensile strength and hydrophilicity) (R.N. Muthu et.al, 2015)
<b>Perfluorinated composite membrane</b>	reinforcing the perfluorinated membrane by PTFE foils.	extremely thin, and relatively high proton conductivity and excellent mechanical stability (G. Lee et.al, 2006)
<b>Hydrocarbon polymers</b>	Hydrocarbon polymers as alternatives	It has the same challenges of Nafion membranes, but, it has the following advantage: low cost, high water retention, relatively wider temperature range and it can be recycled .
<b>Fullerene-based membrane</b>	Fullerenes are a type of carbon allotropes that contain 60 carbon atoms organized in hexagons and pentagons.	High temperature (>150°C), moreover, electrode kinetic rate also increases, which results in less usage of the expensive catalyst (Klupp et.al, 2016).
<b>Graphene oxide based membrane</b>	Graphene oxide based membrane as alternative membranes	high thermal and electrical conductivity, great mechanical strength, optical transparency, inherent flexibility, huge surface area, and unique two-dimensional structure.

## 2.7. SPEEK-Based Membranes For Fuel Cells

Polyether ether ketone (PEEK) is a widely used low-cost thermoplastic material. Commercialization began in his early 1980s. Sulfonated poly-ether-ketone is a competitive alternative ion-exchange membrane material to PEM due to its low methanol permeability and relatively high electrical conductivity. However, some properties of SPEEK, such as proton exchange capacity, methanol resistance, mechanical properties,

and thermal stability, are directly related to the degree of sulfonation (DS) of SPEEK. Much research and improvement has been done on SPEEK membranes. The results of these studies indicate that the SPEEK/PES-C membrane has a methanol permeability of  $10 \text{ cm}^2/\text{s}$  to  $7 \text{ cm}^2/\text{s}$ . The proton conductivity of the SPPEK/SPEEK membrane reaches a maximum of  $0.212 \text{ S cm}^{-1}$  at a temperature of  $80 \text{ }^\circ\text{C}$ . Cross-linked Her SPEEK membranes have improved thermal and dimensional stability. Lack of solvent leads to accumulation of SPEEK scattering radicals. The proton conductivity of the SPEEK/BMIMPF/PA membrane also remains constant at  $2.0 \times 10^{-2} \text{ S cm}^{-1}$  after 600 hours of testing at  $160 \text{ }^\circ\text{C}$ . We found that the introduction of compatible carbon nanotubes into SPEEK improved the proton conductivity of the composite membrane and decreased the methanol permeability. PANI improves hydrothermal action. Previous studies have shown that the ion exchange capacity (IEC), water uptake and conductivity of SPEEK membranes are closely related to fuel cell structure, stability, mechanism and methanol permeability. Improvements to SPEEK foils will improve their applications in aerospace, military and other industries. Some recommendations and suggestions for future research are made (Shachidhara et.al, 2010)

**SPEEK/PBI Membranes for Fuel Cells:** To overcome the mechanical and thermal stability limitation in SPEEK membranes PBI was introduced to SPEEK membrane. The blend was prepared The membrane was prepared by sulfonating PEEK and dissolve it together with PBI in DMA solvent Akay RG, et al. The characterization of the membrane is shown in figure .Blends SPEEK/PBI-10 and SPEEK/PBI-15 seem to be the optimum blend. However, SPEEK/PBI-10 shows higher conductivity and excellent thermal, mechanical, and chemical stability.

The only limitation of the blind is the low protonic conductivity due to the poor conductivity of PBI. Yet, this limitation can be overcome by sulfonating PBI and or by filling the membrane with a high protonic conductive material or both.

a. Sulfonation treatment of PBI membrane is carried out through the following steps (Wang et.al, 2019):

➤ Firstly, immersing the solid prepared PBI membrane in a sulfuric acid aqueous solution at constant concentration at  $50^\circ\text{C}$  for two hours.

- Cleaning and pre-drying the membrane with a filter paper to remove the remaining acid solution.
- Further, the membrane is thermally treated in a furnace presat at 450 °C for certain time in air environment (no vacuum is needed).
- Lastly, the treated membrane is sinked in boiling water for almost s3 h to remove the remaining unreacted H<sub>2</sub>SO<sub>4</sub> acid followed with drying at 100 1C in a vacuum oven.

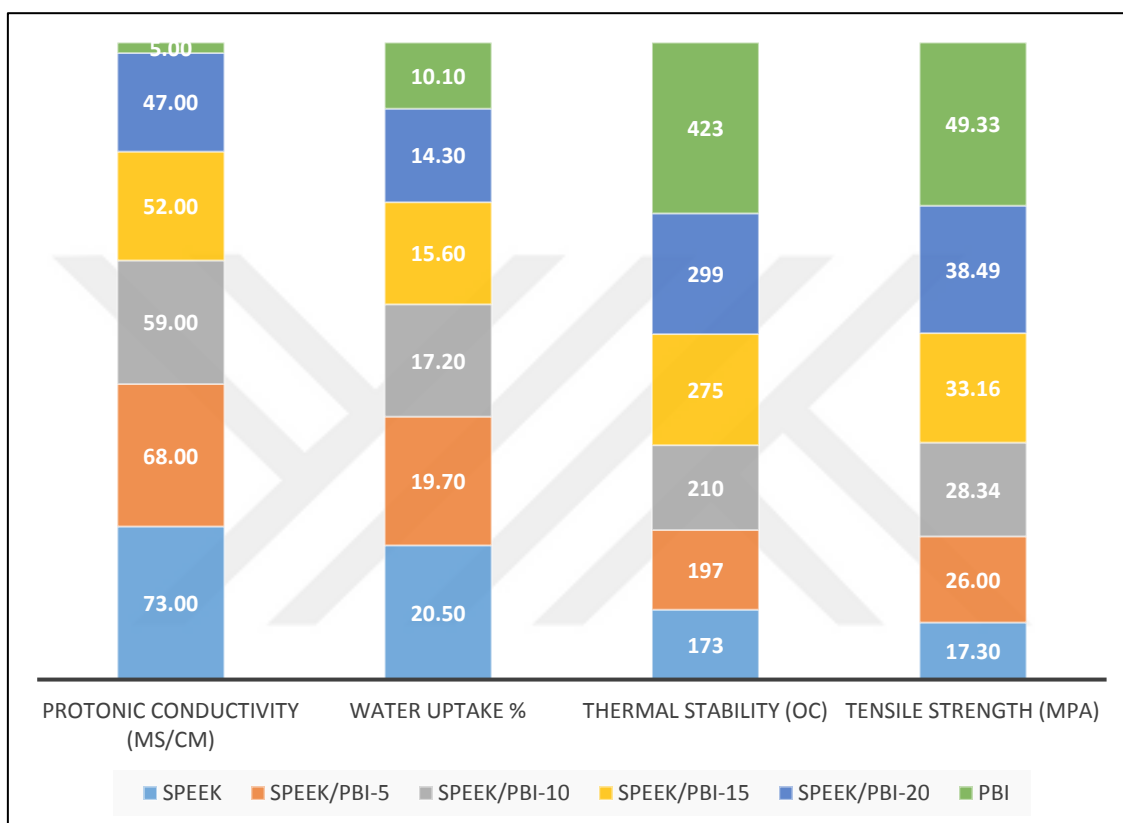


Figure 2.15. SPEEK/PBI Blend membrane characterization (Akay, R. G et.al, 2018).

- filling the membrane with a high protonic conductive material without affecting the physicochemical properties adversely:

Among all the possible fillers, BN nitride shows an extraordinary physicochemical, electrochemical, thermal, mechanical, and barrier properties, extraordinary physical/chemical stability and high protonic conductivity. properties. Therefore, BN can be introduced to SPEEK/PBI blend to enhance the protonic conductivity remarkably. In addition, it improve the other physicochemical properties.

That makes BN the absolute solution for SPEEK/PBI membrane limitation. Moreover, the expected high protonic conductivity, thermal and mechanical stability, and low cost make SPEEK-PBI/BN blend one of the best non-perfluorinated membrane to be used in various application.

## 2.8. Boron Nitride

Boron nitride (BN) has a structural formation based on boron and nitrogen atoms in the direction of the lattice. These structures are amorphous, hexagonal, cubic, and radical in shape.

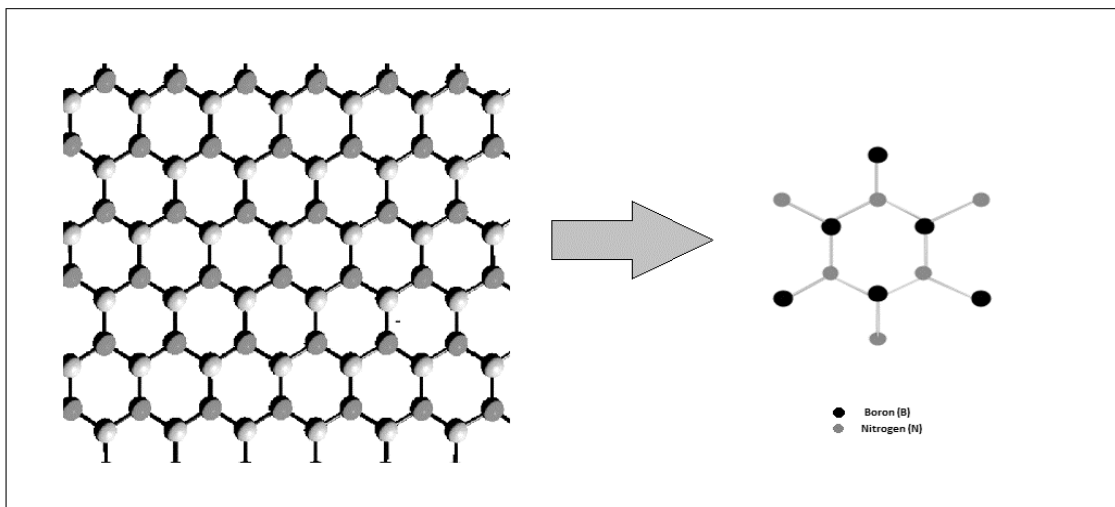


Figure 2.16. Boron Nitride

The nano-mesh network of boron nitride and aerogel is also used in many applications especially in the biomedical field (Smith M.W. et.al, 2009). Initially, boron nitride was developed early in 18th century, but it had not been applied up to the 1940s. Nowadays, it is mainly formed by reacting ammonia (or sometimes urea) with boron trioxide or boric acid in an atmosphere of nitrogen. Boron nitride is a unique filler since it is similar to the most diverse element carbon, in electronic structures, they share the same number of electrons as neighboring atoms. Like the synthetic graphite diamond, cubic boron nitride is made from the primary hexagonal version at very high pressure and temperature. The produced material is stones that are almost as solid as diamonds and some other abilities strike with their hands on their carbon brothers (Naresh Muthu et.al, 2015).

Hexagonal boron nitride is an excellent proton conductor (Figure 2.2) at room temperature with a monolayer h-BN; at higher temperatures, h-BN is outperformed by

(Golberg et.al, 2010) Further research has shown that the rates of h-BN increase in the exponential plot of the Arrhenius type with increasing temperature compared to graphene rapidly increase . These results can be a step forward in improving fuel cell performance and, perhaps, even a substitute for perfluorinated membranes, e.g. Nafion, which has several disadvantages. An isostructural of covalently-bound alternating boron and nitrogen, h-BN makes its way to sophisticated applications . Boron nitride (BN), Often known as "white graphene", a large band gap in h- BN makes it an electrically insulating material with excellent mechanical and thermal properties making it a viable filler material for polymer composites . A reasonable proton conductor should be an ideal polymer electrolyte membrane with electrical insulator properties . H-BN is only in its early stages as a composite membrane filler used in fuel cells. There have been very few efforts to evaluate the use of h-BN in polymers composite (Golberg et.al, 2010). H-BN provides the polymer with thermal and mechanical strength when incorporated in the matrix. while its high surface area also makes it a good absorbent for organic pollutants, dyes. Hu et al. found that h-BN is an excellent proton conductor, referring to the highest proton conductivity at room temperature and higher with a monolayer h-BN (Smith et.al, 2009).

## **2.9. Main Properties And Characterization Of Ion Exchange Membrane**

According to the function of the ion exchange and the function of the ion exchange membrane (is mention in part 2.4.), The important properties of the ion exchange in fuel cell are (Ogungbemi et.al, 2019):

- Ion exchange capacity.
- Fuel permeability.
- Ionic conductivity.
- Electric osmotic coefficient.
- Mechanical strength.
- Water uptake.
- Chemical stability.
- Thermal stability.
- Homogeneity.

Electro-catalyst Layer, the electro-catalyst layer initiate and increase the rate of the oxidation and reduction reactions. Platinum is used as catalyst basically because it is the most active Nobel metal. However, when the fuel is not clean and mixed with some contaminations like carbon monoxide the platinum-based catalyst gets poisoned leads to high activation polarization by the time. Thus, to overcome this problem platinum-alloys such as Platinum- ruthenium is suggested (Gasa et.al, 2007), many Pt-alloy catalyst were investigated but Pt-Ru found to be the best due to it is chemical stability and durability in the electrochemical reaction.

As it was mentioned in part 2.6 and 2.7 that the material used in the ion exchange membrane affect the amount of the catalyst used, however, the platinum content in the catalyst can be reduced either by alloying it with low cost metal or by the application of core shell catalyst (covering a low cost metal by a platinum shell). Some platinum alternatives catalysts such as Cobalt (Co) and Ruthenium (Ru) were investigated and they showed a good stability in the acidic environment of the Proton exchange fuel cell.

The contact between the catalysts, the reactants, and the electrolytes should be maximized, that is to insure the electronic conductivity and the protonic conductivity, that results in an efficient utilization of the. However, that is can be achieved by embed the catalyst on a porous conductive material, this layer is called catalyst support layer (CSL). In PEMFC platinum nano-particles high surface area carbon black (Pt/C) is the most widely used catalyst, however, different carbon-based nanostructure such as fiber carbon, single and multiple wall carbon nanotubes (SWNTs, MWNTs), and graphene have been recently investigated for the CSL (Long et.al, 2000).

### **3. MATERIAL AND METHODS**

#### **3.1. Materials**

Polybenzimidazole (PBI) was purchased from Danish Power Systems (Denmark). Polyphosphoric acid (PPA) (around 110% phosphate equivalent). N-N-dimethylacetamide (DMAc), phosphoric acid ( $H_3PO_4$ , 80%), poly-tetrafluoroethylene (60% w/w distributed in water), 2-propanol and de-ionized water have purchased from Sigma Aldrich (USA). Boron Nitride powder with high purity and fine Size hexagonal system was purchased from Nanografi Nano Technology company in Türkiye.

#### **3.2. Membrane Preparation**

In this study, SPEEK based composite membranes was prepared with functionalized Boron Nitride as an inorganic filler. The composite membranes were obtained by the solvent casting method.

##### **3.2.1. Sulfonation Of PEEK**

10 grams of PEEK was firstly dissolved in a 100ml aqueous sulfuric acid (97%) and then left under stirring for 170 h to have high sulfonating at ambient temperature. Subsequently after the sulfonating process is done, the mixture was slowly being poured into an ice cold de-ionized water under low stirring to stop the sulfonating reaction. During the stirring, the water was being changed constantly to remove the excess remaining acid. The obtained SPEEK was then dried up in vacuum oven, crushed into small particles and kept for further characterizations and membrane preparation.

##### **3.2.2. Functionalization Of BN**

Meanwhile, boron nitride was functionalized and then sulfonated. Firstly, 2 gm of boron nitride particles was dissolved in 40ml mixture of  $H_2SO_4$  and  $H_2PO_4$  (8:1) under stirring at room temperature for 24hrs. Subsequently, 15gm of  $KMNO_4$  was added to homogenize the reaction and to complete the sulfonating process. The mixture left under stirring at  $80^\circ C$  for more 12hrs. The color of the mixture stayed green for a more than an hour which was a sign that the reaction is completed. That followed by adding 15ml of peroxide hydrogen  $H_2O_2$  and 250ml of deaionized water. A centrifugal separator (BIOSAn) was

used to separate the sulfonated boron nitride particles from the acidic solution. Then the final produced sulfonated boron nitride was dried and kept for characterizing and blending purposes (Rajput et.al, 2021).

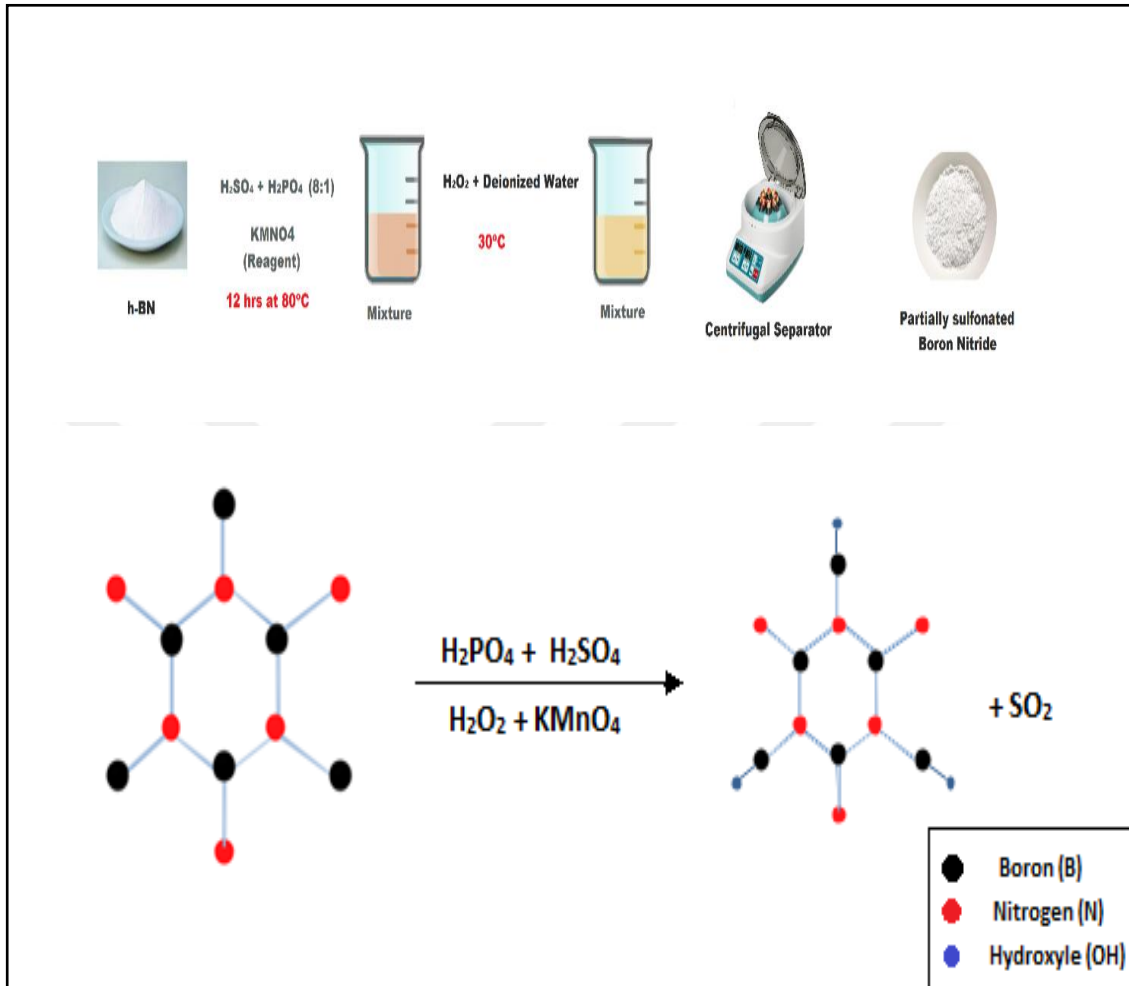


Figure 3.1. Preparing BN (functionalization and sulfonation)

### 3.2.3. Preparation Of The Composite Membrane SPEEK/PBI

The blend was prepared as follows

- Dissolve w g weight of PBI in 20x ml DMAc under strong stirring for at least 10hrs.
- Dissolve  $\frac{2}{0.2}$ w g weight of SPEEK in DMAc in a separated baker
- Mix the two solutions under stirring for 5 mins and then put it in ultrasonic for a while to ensure the homogeneity.

- Cast the membrane in a patera dish and put it in a vacuum oven for 24 hrs at 80°C.

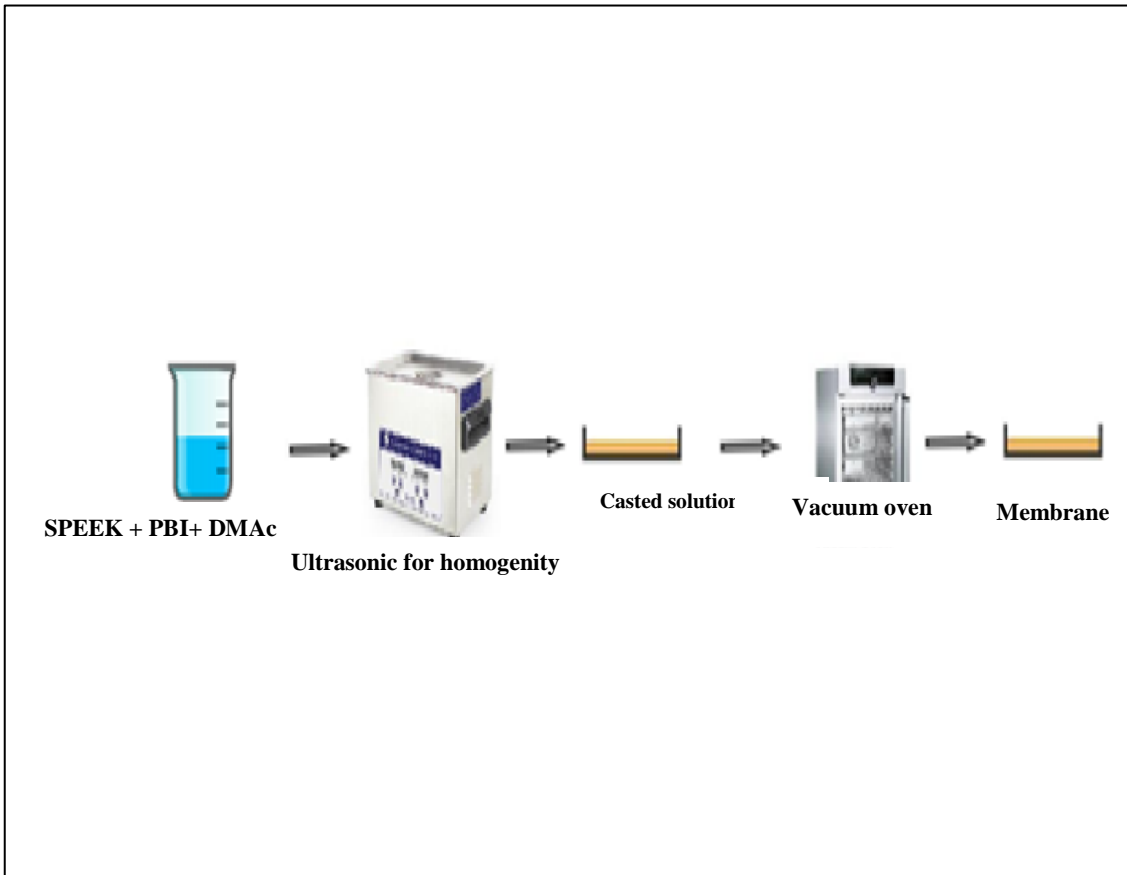


Figure 3.2. Preparing SPEEK/BPI membrane

### 3.2.4. Preparation Of The Composite Membrane SPEEK-BN/PBI Composite Membrane

Steps:

- Dissolve w g weight of PBI in 20x ml DMAc under strong stirring for at least 10hrs.
- Dissolve  $\frac{2}{0.2}w$  g weight of SPEEK in DMAc.
- Mix the two solutions under stirring for 5 mins and then put it in ultrasonic for a while to ensure the homogeneity.
- Cast the membrane in a patera dish and put it in a vacuum oven for 24 hrs at 85°C.

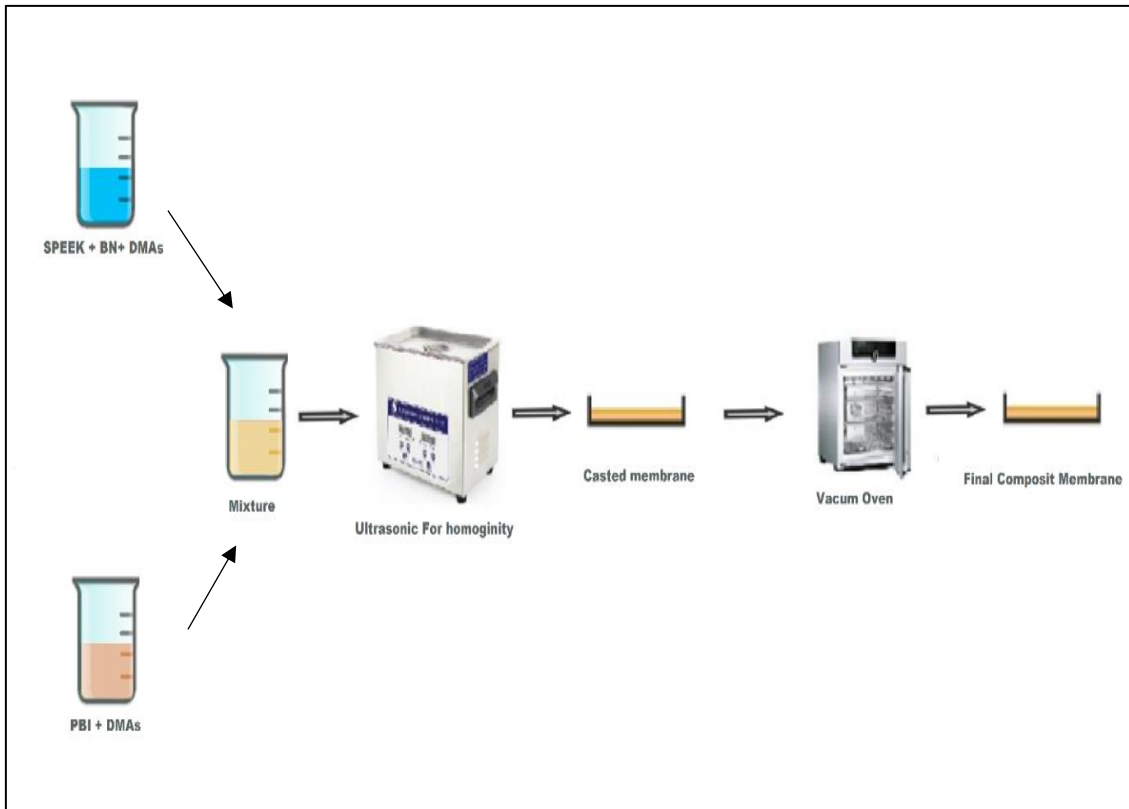


Figure 3.3. Preparing SPEEK-BN/PBI composite membrane: A- Casual Blend membrane B- Thin film PBI on SPEEK-BN membrane.

Table 3.1. Currently Membrane Used In Proton Exchange Fuel Cell (Dupuis et.al, 2011)

	<b>SPEEK (g)</b>	<b>PBI (g)</b>	<b>DMC (ml)</b>	<b>BN (g)</b>
<b>SPEEK/PBI</b>	2	0.2	40	0.00
<b>SPEEK-PBI/BN- 10</b>	2	0.2	40	0.24
<b>SPEEK-PBI/BN- 15</b>	2	0.2	40	0.38
<b>SPEEK-PBI/BN- 20</b>	2	0.2	40	0.50

### 3.3. Membrane And Material Characterizations

#### 3.3.1. FTIR Identifying The Samples

Both SPEEK and BN were tested using FTIR and were compared to their non-sulfonated material to insure that the reaction and the sulfonating process had successfully achieved. Peaks indicate the sulfate and the alcohol are expected to show in the FTIR spectra.

#### 3.3.2. Degree Of Sulfonation (DS)

The most common used methods for determining the degree of sulfonation are back titration and FTIR method. Back titration was performed to determine the degree of the sulfonation as follows:

0.1gm, 0.08gm, 0.088gm, 0.08gm, 0.09gm of SPEEK, SPEEK/PBI, SPEEK/PBI/BN-10, SPEEK/BN-15, SPEEK/BN-20 respectively were weighted and separately put in 20ml of 0.05M NaOH aqueous solution and then kept for a three days for neutralization reaction as it shown in the following equation the following equation:

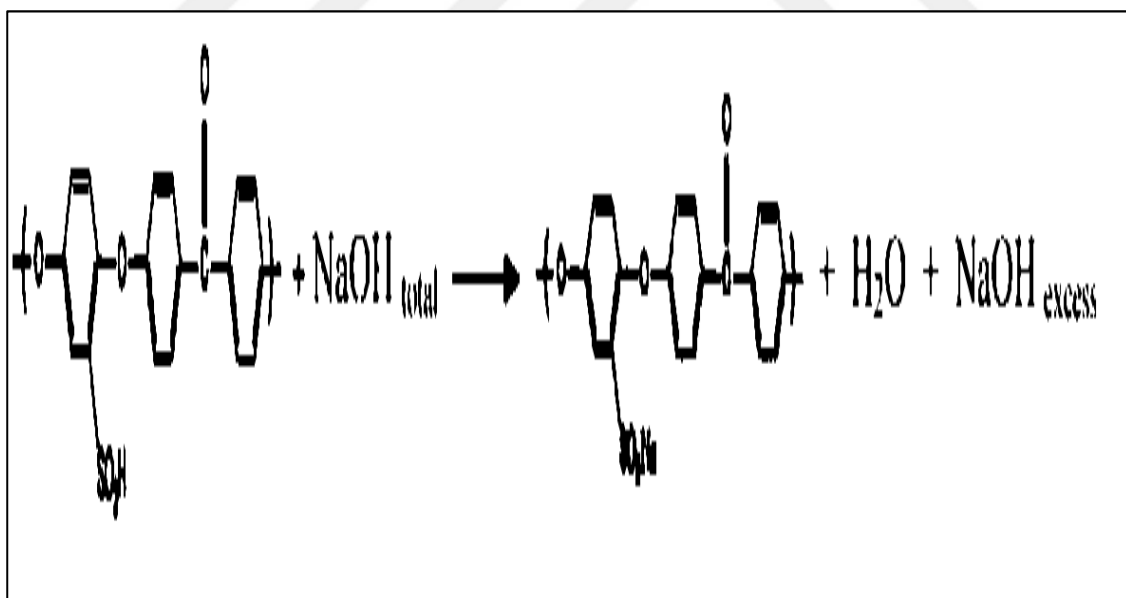


Figure 3.4. Back titration reaction for SPEEK using NaOH aqueous solution.

The solution was then titrated with 0.003M H<sub>2</sub>SO<sub>4</sub> aqueous solution. The titration process was carried out using a burette and Phenolphthalein as indicator. Phenolphthalein

appear in a pink color before the titration (Basic medium) and changed into colorless when the titration had been done (Acidic medium).



The times of sulfonated repeated units in the molecules of the membrane (x), had been calculated from the equation below (eq. 3.3) [Huang et.al, 2001: 82(11), 2651–2660]:

$$s = V_{NaOH}M_{NaOH} - 2V_{H_2SO_4}M_{H_2SO_4} \quad (3.2)$$

Where  $V_j$  and  $M_j$  are the volume and the molarity of the component “j” respectively.

And the number of nonsulfonated units in the membrane molecules,  $n_s$ , was then calculated from eq. (3.4).

$s$  is the sample weight,  $M_s$  and  $M_{non}$  are the sulfonated repeated molecular weight and the non-sulfonated and non-sulfonated repeated units, respectively. The degree of sulfonation, was then calculated as follow (Huang et.al, 2001):

$$DS = \frac{s}{n_s + s} \quad (3.3)$$

### 3.3.3. Ion Exchange Capacity Of The Membrane

The ion exchange capacity can be determined using the obtained parameters from the titration in section 3.2.2. as follows:

$$IEC = \frac{1000s}{W} \quad (3.4)$$

### 3.3.4. Water Uptake

The water holding capacity of the membranes was calculated using the mass changes in the dry and wet conditions. The prepared membranes were cut in 3 cm x 2 cm dimensions and dried in a vacuum oven at 60 °C and weighed. Dry membranes are immersed in water

and kept for one day and their wet weights are weighed. The water uptake of membrane was calculated by Equation (3.7):

$$\text{Water uptake} = \frac{W_{wet} - W_{Dry}}{W_{Dry}} \times 100\% \quad (3.5)$$

### 3.3.5. Mechanical Tests

To examine the mechanical performance of the membrane a tensile tests were performed. The experiments were carried out with ASTM 638. An Instron 3367 universal test machine was used (Figure 3.4). The test speed was taken as 10 mm/min. For the test, the samples were cut in square using special apparatus to prepare it for tensile test machine. Load force (F) was applied on the sample uniformly. Later, an extensometer used to measure the change in the length of the specimen ( $\Delta l$ ) all along with the original length as reference ( $l_0$ ).

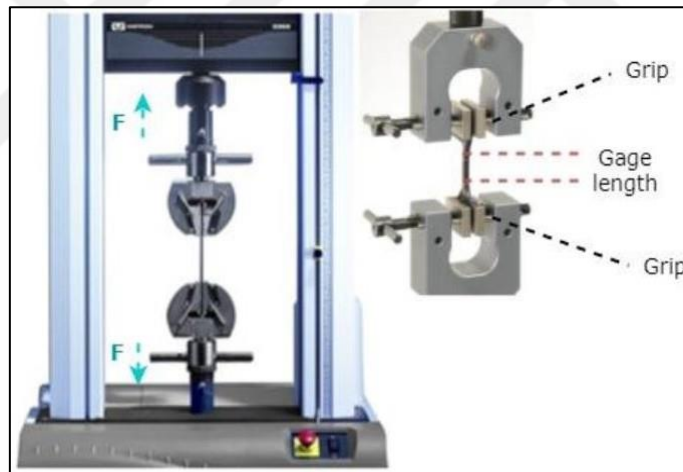


Figure 3.5. Instron 3367 tensile machine and a representative apparatus 29.

### 3.3.6. Proton Conductivity Measurement

The conductivity of the membranes in the thickness direction was measured at room temperature using the electrochemical impedance spectroscopy (EIS) method. To carry out this test, Gamry potentiostat/galvanostat purchased within the scope of the project, and a 4 probe electrode conductivity cell that was built specially by Erdes Kimya ve teknoloji company were used. Membranes were conditioned by soaking in 1M cidic solution for one day before ionic conductivity measurement. 2cm x 2cm dimensions piece

of the membrane was cut to perform the test on were used. Subsequently, it was placed in a cell with 4 platinum wire electrodes. The electrodes are positioned as two opposites to each other in contact with both surfaces of the membrane. The measurements were carried out in the 1-105 Hz frequency range and in a potentiostatic mode in a humid environment. The ion conductivities of the membranes were calculated with the help of Equation (3.8) (Akay, R. G et.al, 2018).

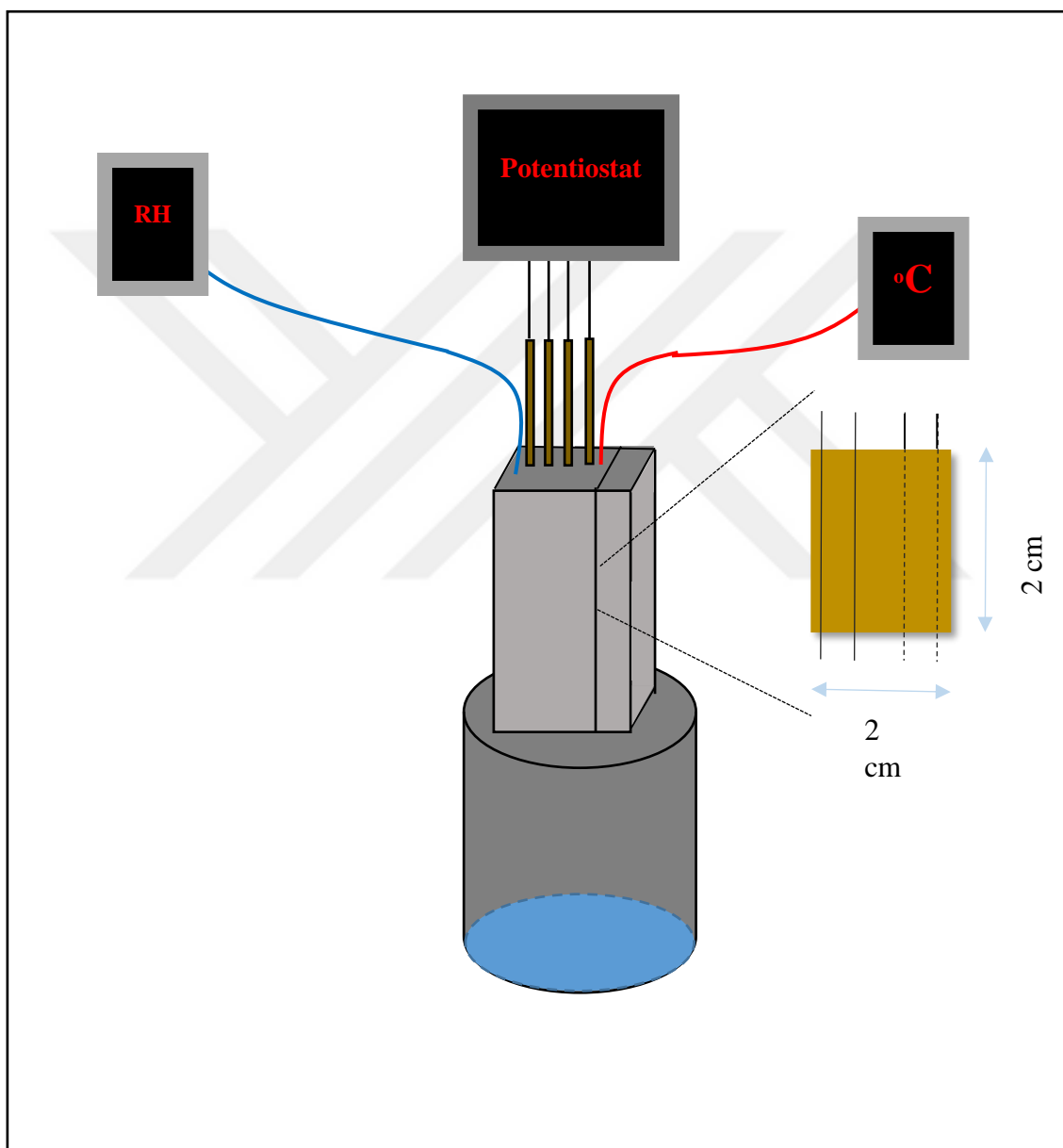


Figure 3.6. A 4 probe electrode conductivity cell for measuring the protonic conductivity ( device setup interior part)

$$\sigma = \frac{L}{Z \times A} \quad (3.6)$$

Where:

$\sigma$  is the ionic conductivity in S/cm.

$Z$  is the impedance in ohm.

$A$  is the surface area in  $\text{cm}^2$ .

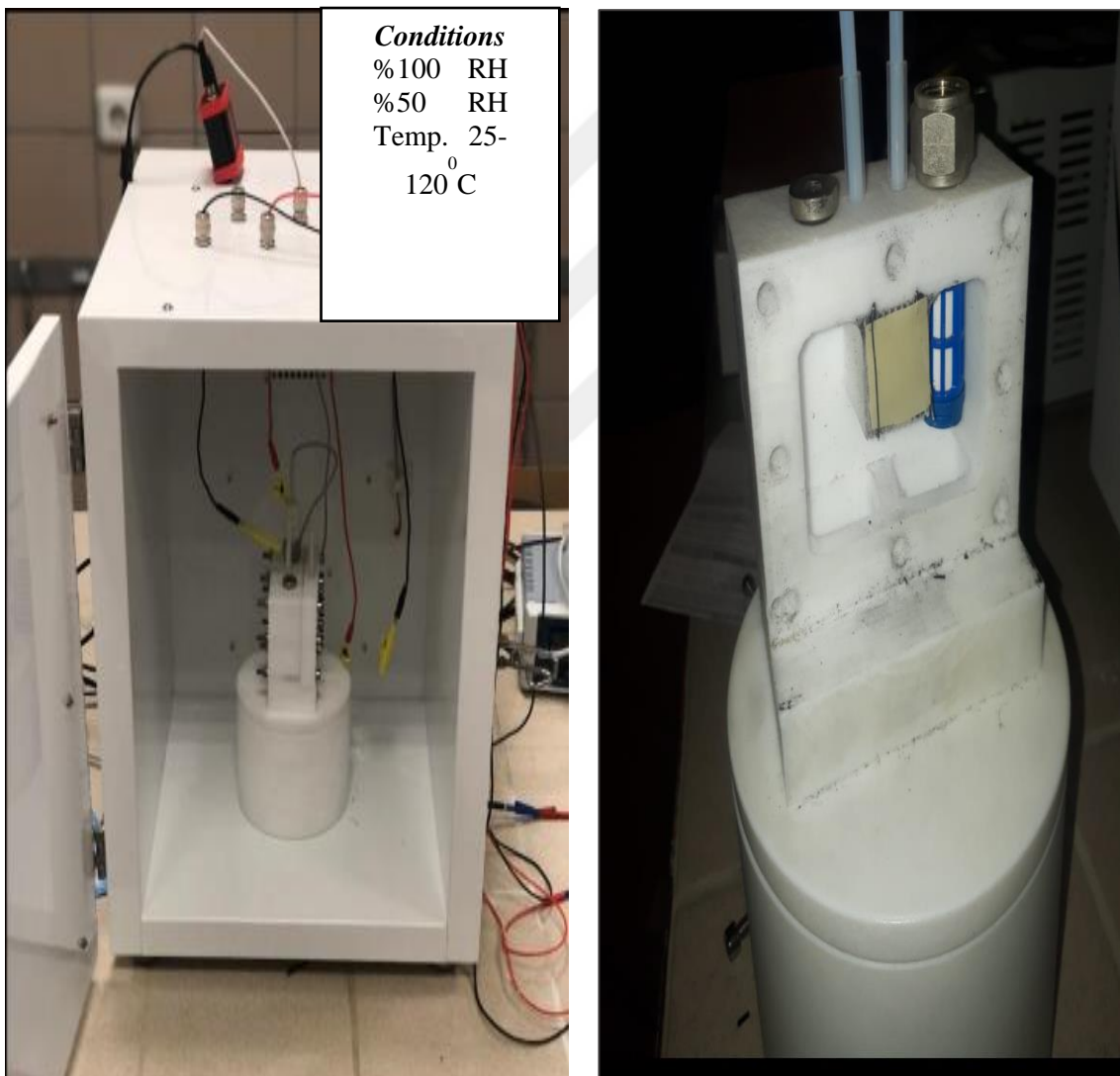


Figure 3.7. EIS conductivity cell that was built specially by Erdes Kimya ve eknoloji company

### 3.2.8 Thermal Characterization (Thermogravimometer Analysis TGA)

TGA test is a thermoanalytical technique performed to test the temperature range and the thermal stability of the membrane. In the first runs, samples were heated to 300 °C from room temperature, cooled down, then in second run heated to 600 °C. Heating rate was 20 °C/min.

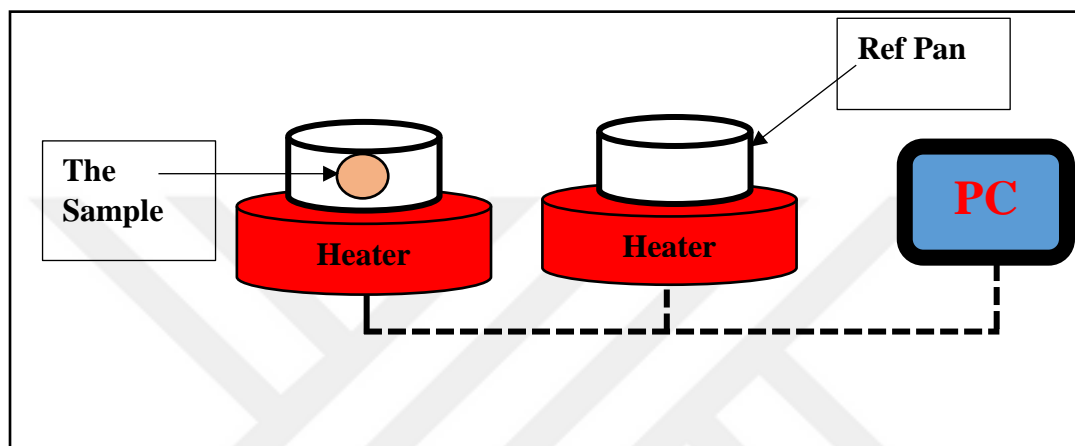


Figure 3.8. Setup used for measuring the thermal stability for the membrane

### 3.2.9 Chemical stability (Fenton Reagent Test)

Chemical stability of the membrane was tested at 25 °C temperature using Fenton reagent which is 4 part per million Fe salt and 3 percentage Hydrogen peroxide. At first, 0.2 grams sample of each membrane were weighted and put in an aqueous solution of iron (+2) sulfate hepta-hydrate (5 ppm, 55 mL. Then, 7 mL of 3% hydrogen peroxide was added into the solution. The remaining weights were checked each one hour.

### 3.2.10 X-ray Diffraction Analysis For The Optimum Membrane

For the optimal membranes, XRD analysis was performed to characterize the membrane and verify the effects of sulfonation and hydroxylation on the membrane. However, the XRD results were used to verify the uniformity across the film.

### **3.2.11 Homogeneity Test ( Scanning Electron Microscopy)**

The morphology and homogeneity through the membrane and on the surface of the membrane had been tested with Scanning Electron Microscopy (SEM) and microscope (range zooming of 15- 30 mili meter). The microscopy shows wiehther if the distribution of the SPEEK, PBI, and BN in the membrane is in uniform or not.



## 4. RESULTS AND DISCUSSION

### 4.1 Verifying The Sulfonating Process Using FTIR Test

The FT-IR spectrum is divided into four areas:

- (a) the single-bond site ( in the range of 2501-4000  $\text{cm}^{-1}$ ).
- (b) The triple bond site ( from 2001  $\text{cm}^{-1}$  to 2500  $\text{cm}^{-1}$ ).
- (c) The double bond site (From 1501  $\text{cm}^{-1}$  to 2000  $\text{cm}^{-1}$ ).
- (d) The fingerprint region (from 601-1500  $\text{cm}^{-1}$ ).

To confirm the sulfonating process, a new wide peak must appear in the single bond region (the alcohol part that of the sulfonic acid) (Nandiyanto et.al, 2019). On the other hand, the presence of sulfonic acid group in SPEEK chain can be confirmed by the strong characteristic peaks in the range 1251 – 1000  $\text{cm}^{-1}$  (Rajput et.al, 2021).

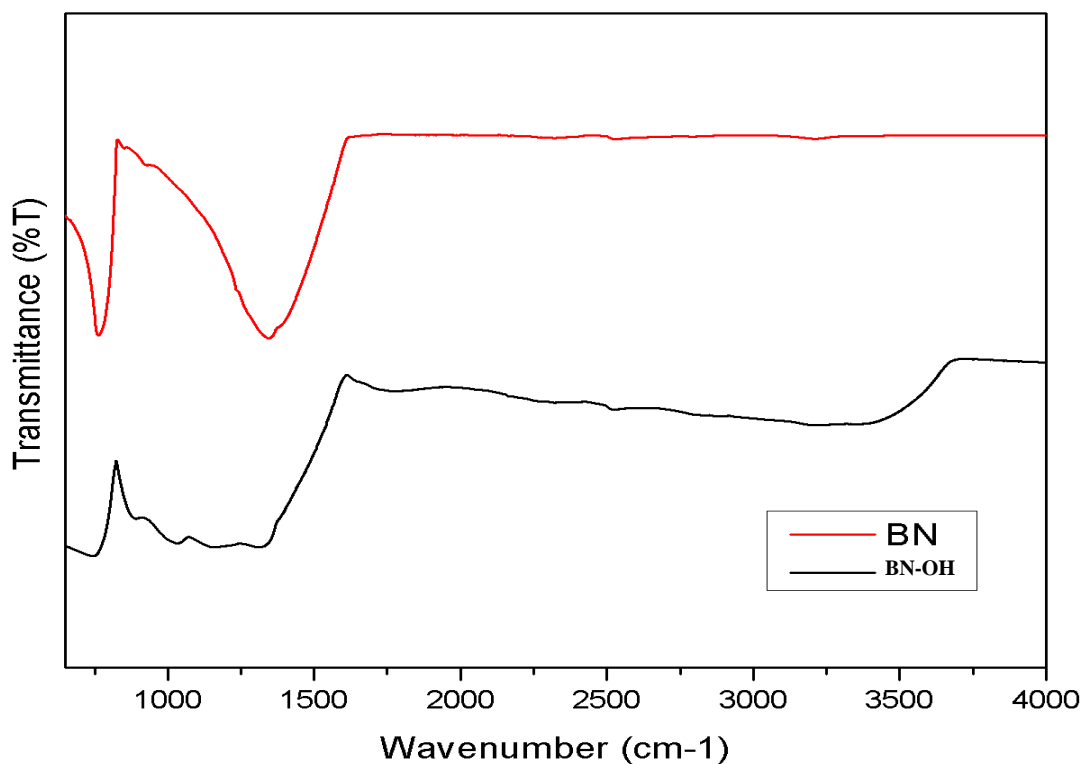


Figure 4.1. FTIR spectra for BN and BN-OH.

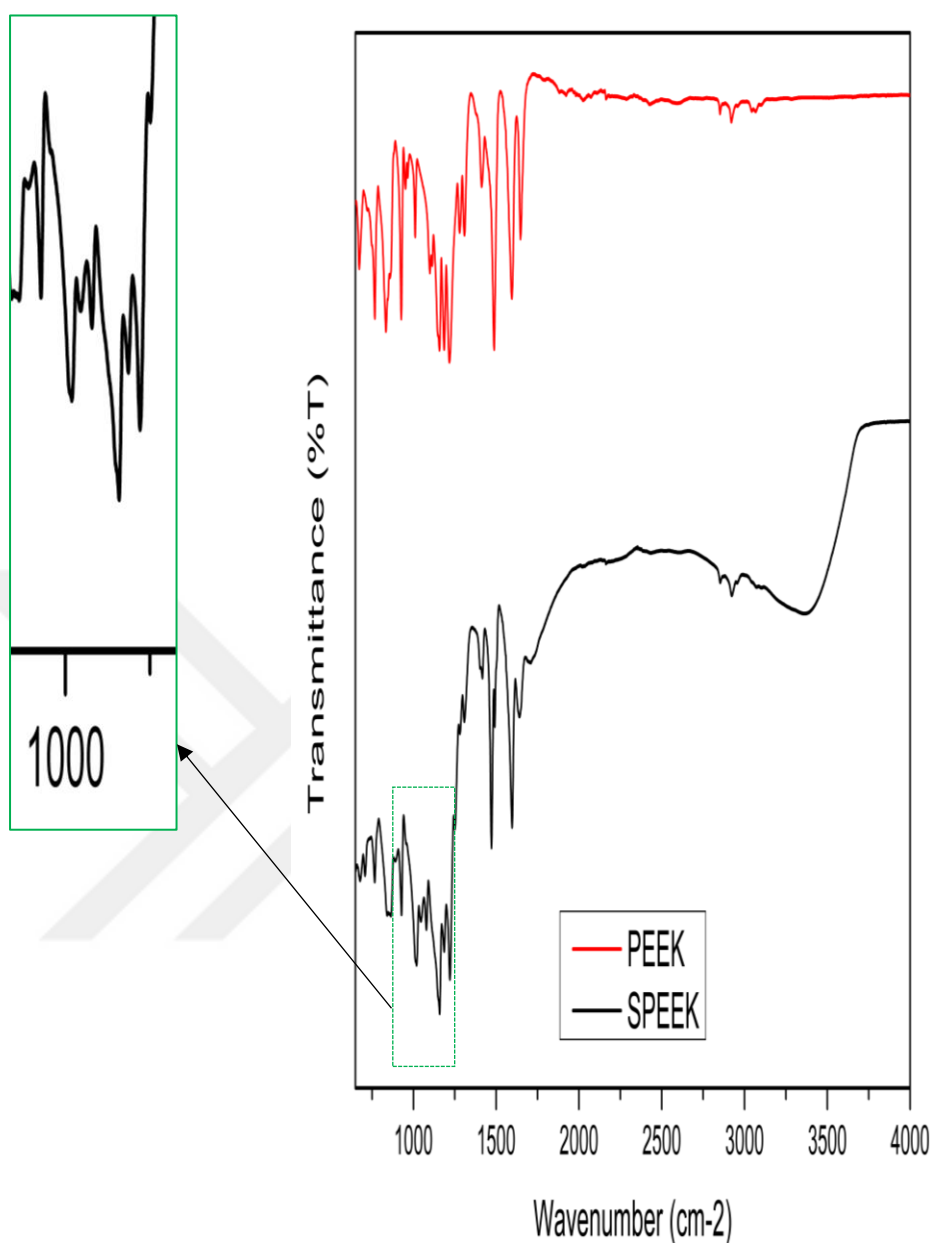


Figure 4.2. FTIR spectra for PEEK and sPEEK.

On figure 4.2 it can be noticed that new peaks show in the wavenumber range 1300 – 1000  $\text{cm}^{-1}$  which indicates the presence of the sulfonate. The same thing shows on figure 4.3. in the spectra of SPEEK, two symmetric and asymmetric peak were detected. Moreover, the wide peak in 3300 – 3000 in both figure 4.2. and Figure 4.3 indicates to the presence of the acid (i.e. O-H bond).

However, in Figure 4.3. it can be noticed that a wide peak shows in the wavenumber range 3460 – 1570  $\text{cm}^{-1}$  which indicates the presence of the hydroxyl group intensively. According to the above results the presence of sulfuric acid in PEEK and hydroxyl group in BN was confirmed.

Table 4.1. Calculations for degree of sulfonation and IEC for SPEEK membrane

	$V_{NaOH}$	$M_{NaOH}$	$V_{H_2SO_4}$	$M_{H_2SO_4}$	W	s
<b>SPEEK</b>	20	0.01	1.00	0.003	0.100	0.194

Table 4.2. Degree of sulfonation and IEC for SPEEK membrane

	DS	IEC
<b>SPEEK</b>	70.0%	1.94

Degree of sulfonation and IEC for the produced PEEK, the degrees of sulfonating were found using back titration. Results in table 4.3 shows the degree of sulfonating and the parameters related to the sulfonated chains.

## 4.2. SPEEK-BN/PBI Composite Membrane

### 4.2.1. Preparation of SPEEK/BN Preparation

The prepared membrane has shown good homogeneities especially SPEEK/BN and SPEEK/PBI. The ratio of SPEEK to PBI was always 1:0.2 while the the solution kept 10% diluted. Too much amount of solvent affects the homogeneity of the membrane adversely. Moreover, it was found that the thinner the membrane the more homogeneous is. Due to the low solubility of PBI, SPEEK@BN/PBI membrane was prepared by two methods: mixing all the material in one beaker (Casual blend) and by dissolving SPEEK/BN and PBI separately and then mix them at 80°C.

Table 4.3. Contents of the membrane

	Solution Concentration	SPEEK (g)	PBI 26% doped	DMC (ml)	BN-OH (g)
<b>SPEEK/PBI</b>	5%	1.20	0.2	22.80	0.00
<b>SPEEK-PBI/BN-10%</b>	5%	1.20	0.2	23.51	0.037
<b>SPEEK-PBI/BN-15%</b>	5%	1.20	0.2	24.00	0.063
<b>SPEEK-PBI/BN-20%</b>	5%	1.20	0.2	24.65	0.097

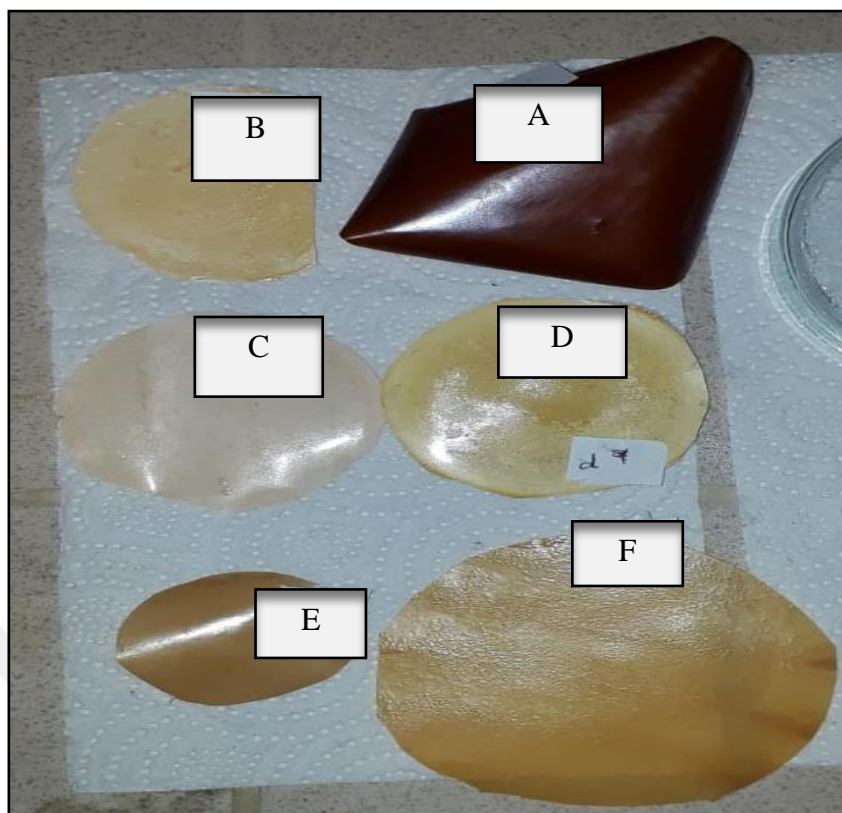


Figure 4.3. a) PBI, B) SPEEK@PBI/BN-20, C) SPEEK-PBI/BN-15, D) SPEEK-PBI/BN-10, E) SPEEK/PBI 12hrs stirring and ultrasonic , F) SPEEK/PBI 24hrs stirring.

## 4.2.2. Membrane And Material Characterizations

### 4.2.2.1. Ion Exchange Capacity

The degrees of sulfonation and IEC were found using back titration. Results in table 4-4 show that the degree of sulfonation after adding the filler to the SPEEK/PBI is higher than the prstede; that could be a result from the acid reatment of BN. However, a higher DS of SPEEK/PBI can be obtained by increasing the time and the temperature of sulfonation process for PEEK.

On the other hand IEC increased remarkably with the addition of BN, But it stays almost constant when the filler content increases. In conclusion, it was confirmed that modyfing the membrane with BN enhance the DS and IEC remarkably, whilst the percentage of the filler doesn't seem affected by the percentage of the filler in the membrane.

Table 4.4. Degree of sulfonation and IEC for SPEEK/PBI/BN membrane

	IEC (meq/g)	DS
<b>SPEEK/PBI</b>	1.88	66.99%
<b>SPEEK-PBI/BN-10%</b>	2.18	80.53%
<b>SPEEK-PBI/BN-15%</b>	2.18	80.84%
<b>SPEEK-PBI/BN-20%</b>	2.20	81.48%

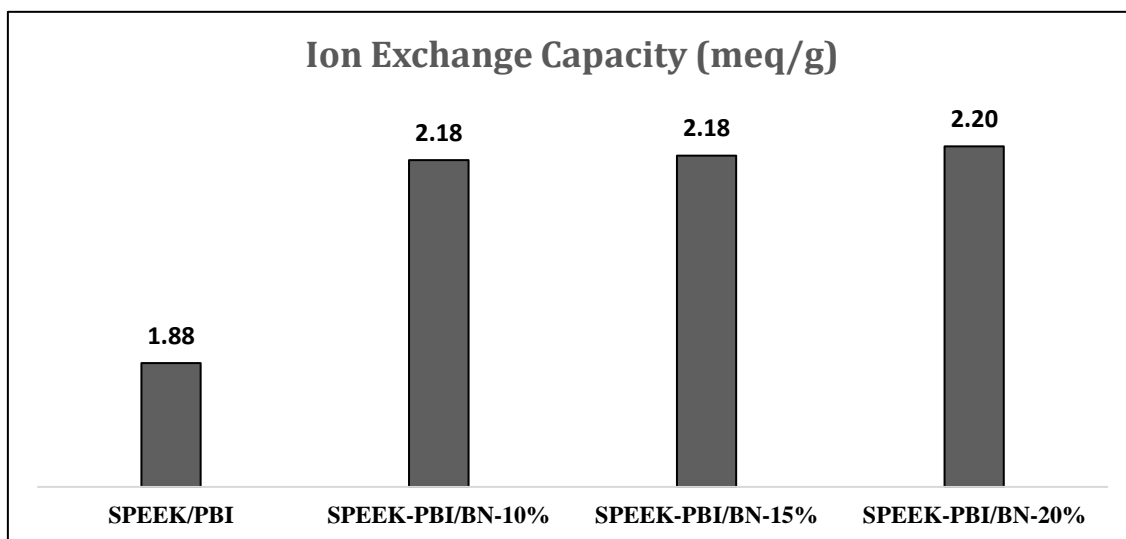


Figure 4.4. Ion Exchange Capacity of SPEEK/PBI/BN membrane

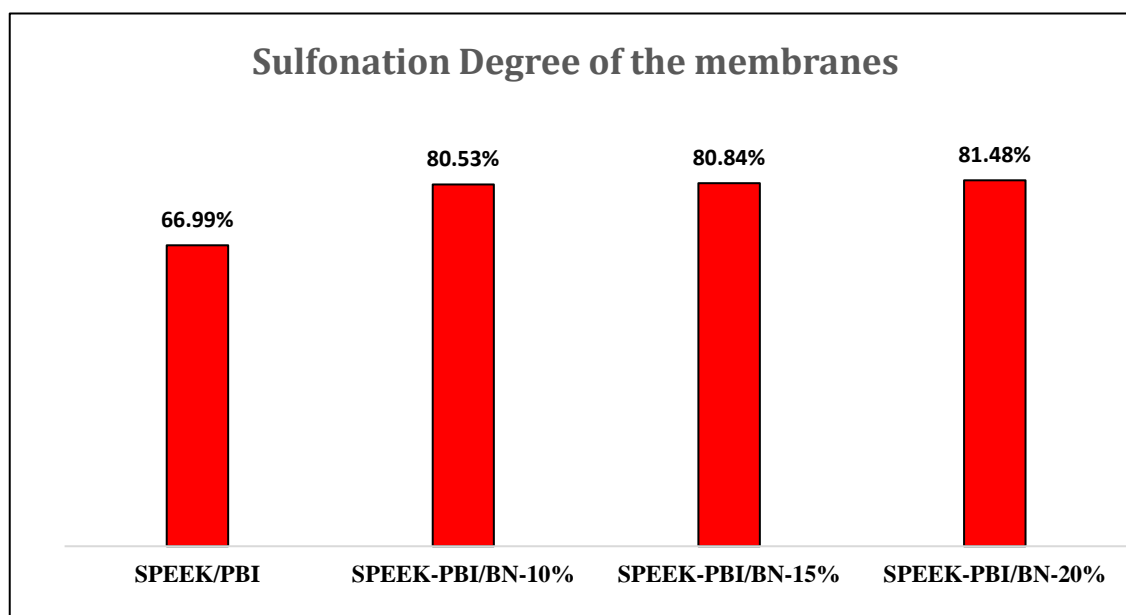


Figure 4.5. Degree of sulfonation for SPEEK/SBN membrane

#### 4.2.2.2. Water Uptake

Water uptake values are shown in Figure 4-11 and Table 4-10. The values of water uptake for SPEEK/PBI which is 4.37%. The water uptake of SPEEK/PBI/BN-10 were found around %6.13. Water uptake of the membrane seems to decrease with content of the filler BN, However, this decrement is very small and can be neglected. uptake decreased

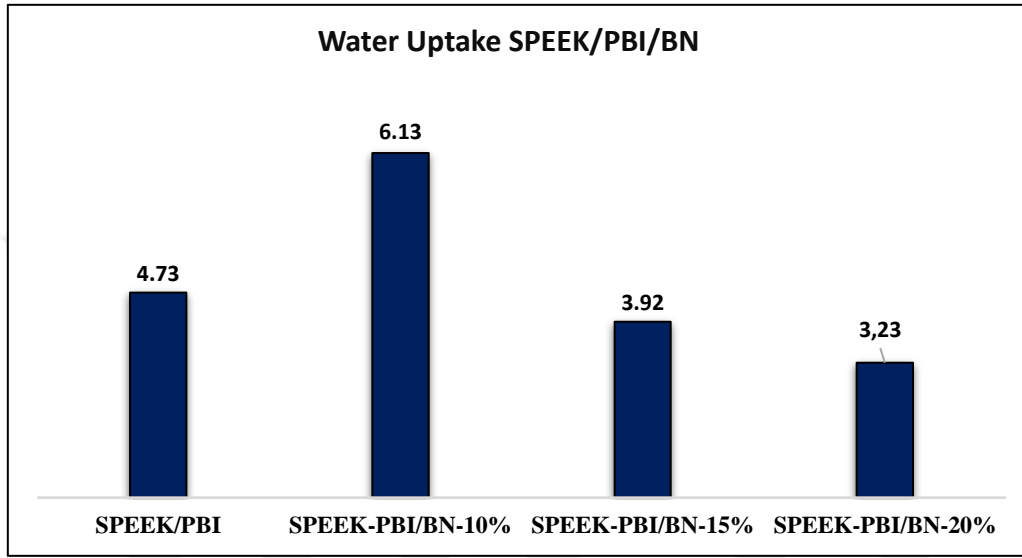


Figure 4.6. Water uptake of SPEEK/PBI/BN membrane

steadily as expected with increasing BN percent since it is dependent on the acid groups and it is known that BN interacts with these groups after the treatment.

Table 4.5. Water uptake of SPEEK/PBI/BN membrane

	Dry weight(g)	Wet weight (g)	Water-uptake
<b>SPEEK/PBI</b>	0.05	0.05	4.37%
<b>SPEEK-PBI/SBN-10%</b>	0.07	0.08	6.13%
<b>SPEEK-PBI/SBN-15%</b>	0.02	0.03	3.92%
<b>SPEEK-PBI/SBN-20%</b>	0.04	0.04	3.23%

### 4.2.2.3. Mechanical Tests

The membrane shows poor mechanical stability when the percentage of BN exceeds 10%. However, SPEEK/PBI/BN showed the maximum tensile strength of 8.61 MPa, while the pristine membrane (i.e. SPEEK/PBI) showed the maximum tensile strain. This poor mechanical stability when BN is high results from the nonhomogeneity of the membrane (since boron nitride does not dissolve in DMAs). Therefore, the mechanical stability can be enhanced by enhancing the homogeneity of the membrane.

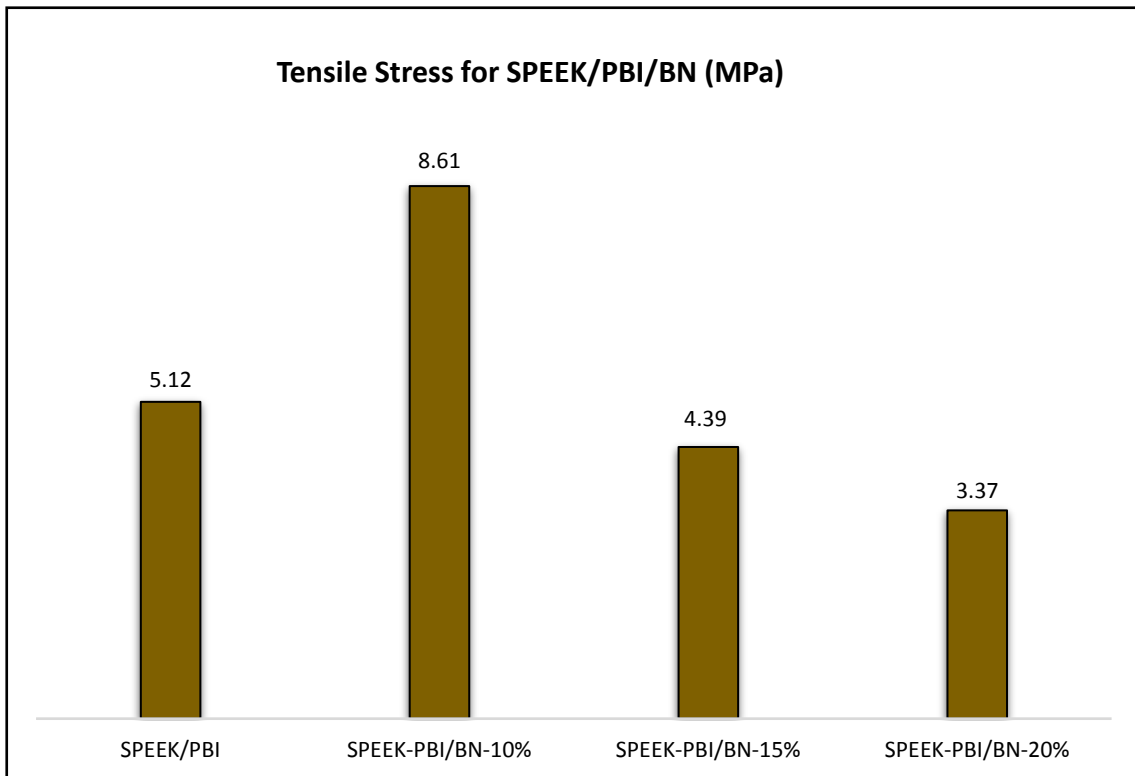


Figure 4.7. Mechanical stability for SPEEK/PBI/BN membrane at maximum loads

Table 4.6. Mechanical stability for SPEEK/PBI/BN membrane at maximum loads

	<i>Tensile Strength (MPa)</i>	<i>Tensile Strain %</i>
<b>SPEEK/PBI</b>	5.12	16
<b>SPEEK-PBI/SBN-10%</b>	8.61	3.06
<b>SPEEK-PBI/SBN-15%</b>	4.39	2.11
<b>SPEEK-PBI/SBN-20%</b>	3.37	9.83

#### 4.2.2.4. Proton conductivity measurement

Conductivity increased with increasing BN content up to %10 in the composite according to the Speek-PBI. The highest conductivity was obtained for SPEEK-PBI/10BN as 0.0245 S/cm. But further increasing in BN content up to %15 and %20 conductivity decreased. It may be possible self-agglomeration of BN particles at higher contents. The ionic conductivity increases with the increasing the temperature (see figure 4-8a).

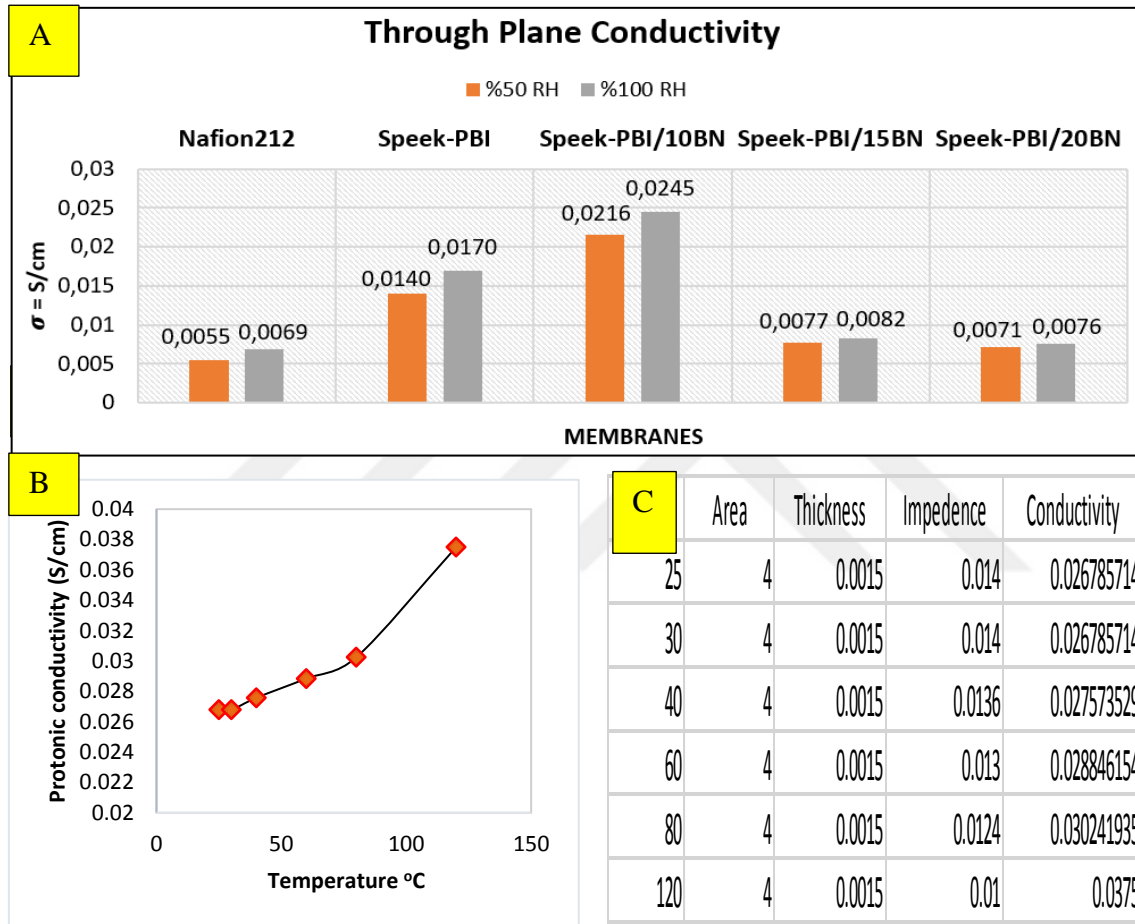


Figure 4.8. Ionic conductivities for SPEEK/PBI/BN membrane at A) standard temperature B) various temperatures C) Thickness of the membrane

#### 4.2.2.5. The Thermal Stability Of The Membrane

The membrane shows great improvement in the thermal stability with a TG up to 305-317 °C (Figure 4-9a). That allows HT-PEM fuel cells to work in very high temperatures resulting in a high efficiency and less catalyst content.

However, as PBI has higher thermal stability than BN, the thermal stability goes down with increasing the percentage of BN.

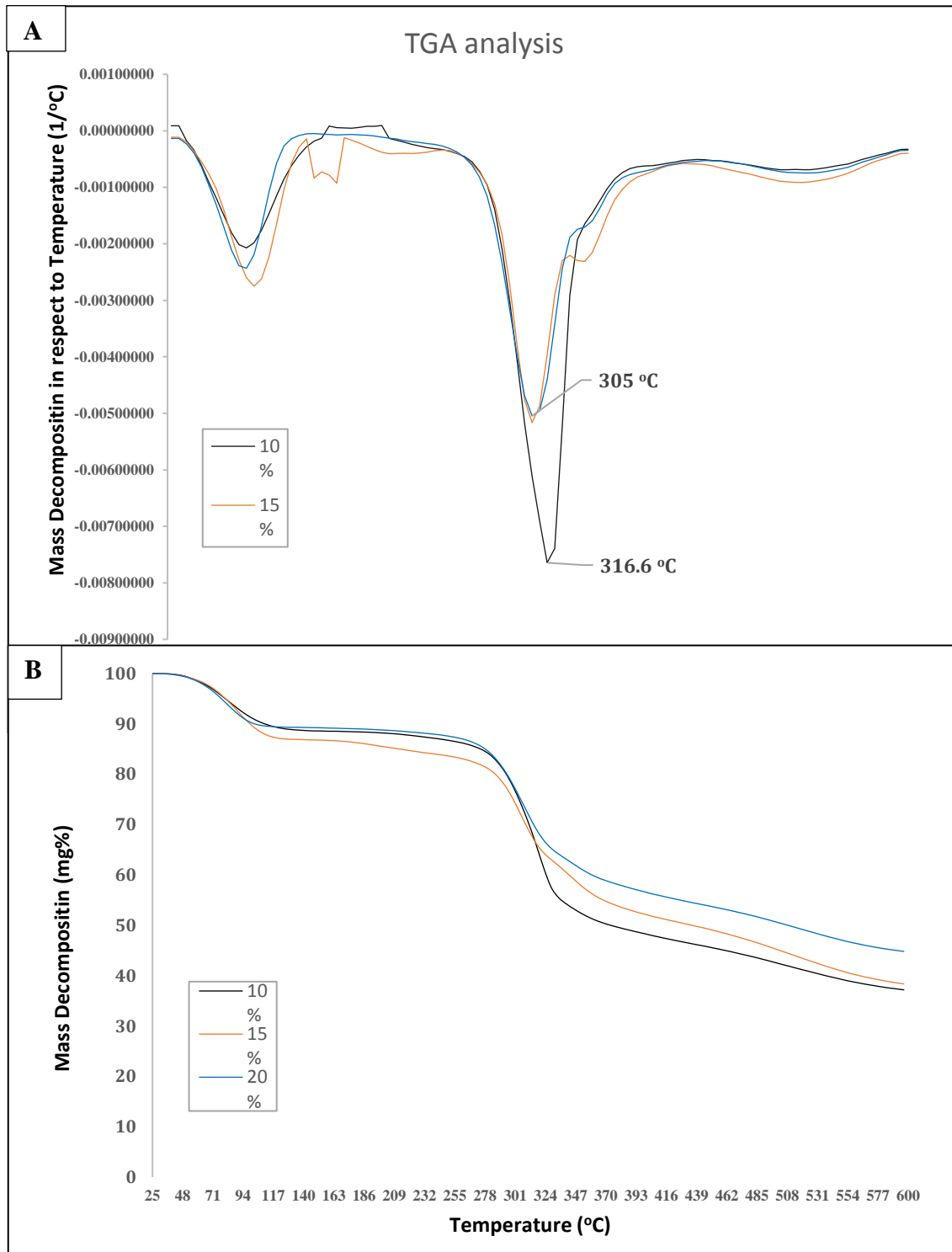


Figure 4.9. a) Thermal stability for SPEEK/PBI/BN membranes (derivative mass decomposition in respect to temperature). b) Thermal stability for SPEEK/PBI/BN membranes (Mass decomposition)

Table 4-7. Thermal stability for SPEEK/PBI/BN membranes

Membrane	TGA (°C)
SPEEK-PBI/SBN-10%	316.6
SPEEK-PBI/SBN-15%	305
SPEEK-PBI/SBN-20%	304.5

#### 4.2.2.6. Chemical Stability

The chemical stability of the membrane is enhanced by adding Boron nitride, however, it increases as the filler percentage increases See figure 4.10.

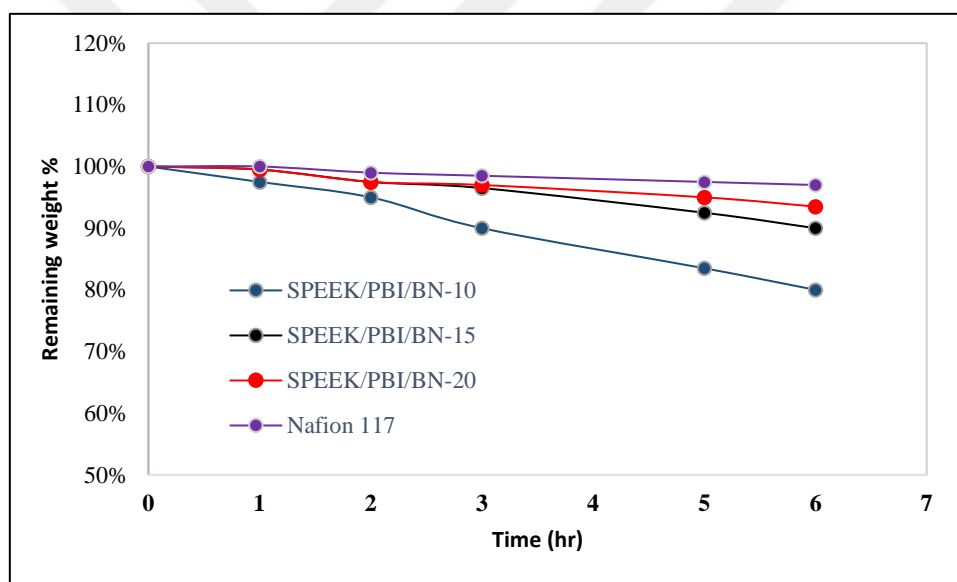


Figure 4.10:Chemical stability for the proposed membrane

#### 4.2.2.7. X-ray Diffraction Analysis For The Optimum Membrane

The X-ray diffraction pattern of the SPEEK/PBI/BN-10 film are shown in Figure 4.11. The membrane is completely amorphous. A wide diffraction peak around  $2\theta$  20° indicates a absence of crystallinity. The amorphous nature of the films indicates SPEEK with moderate and high DS. The introduction of SO<sub>3</sub> H and OH groups into PEEK changes the chain structure and packing, that leads to a loss of crystallinity. It is known that the

amorphous nature of the membrane facilitates the movement of polymer chains, leading to faster proton exchange. This makes the membrane more proton conductive.

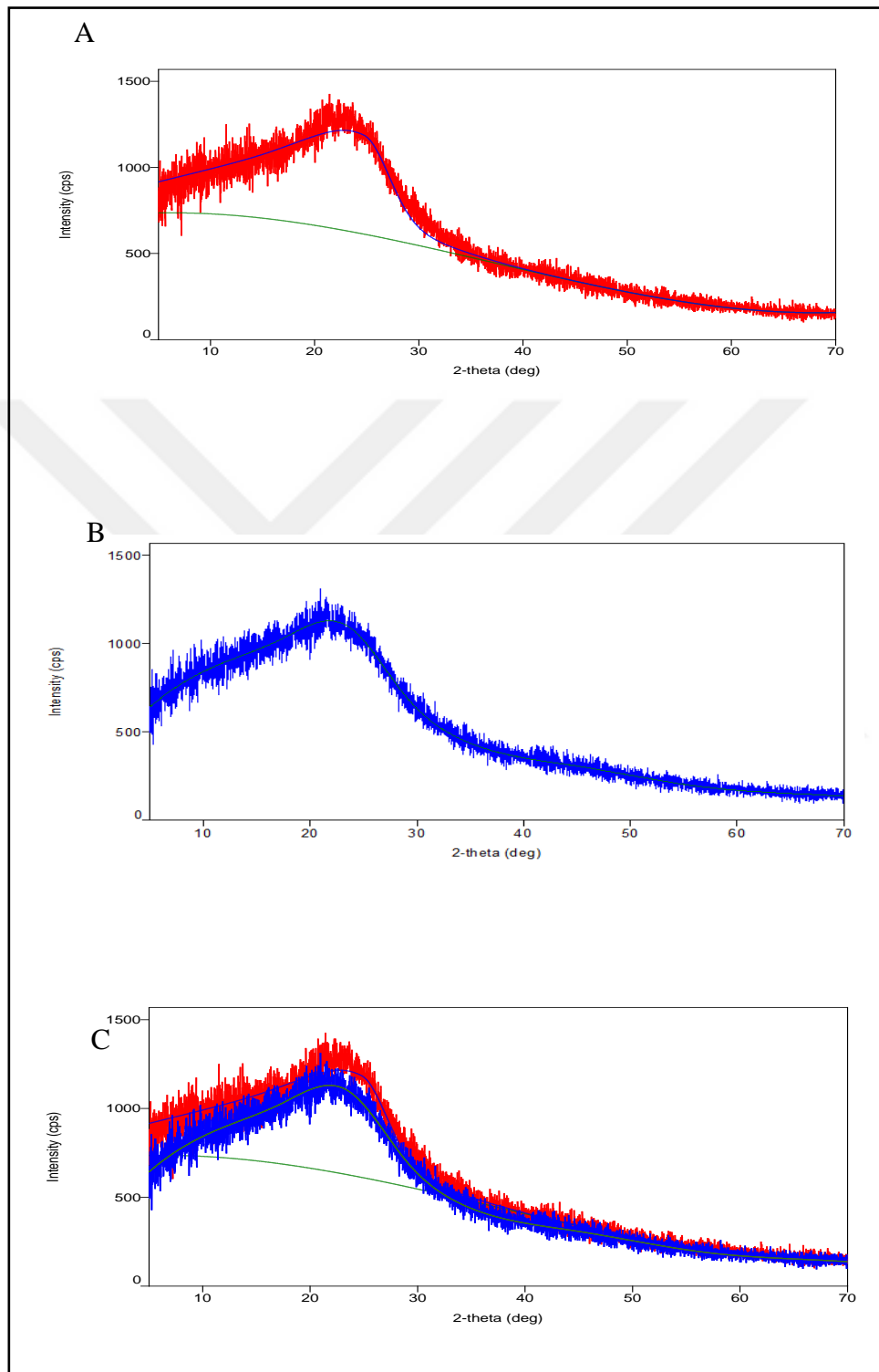


Figure 4.11. XRD analysis for the optimum membrane (i.e. SPEEK/PBI/BN -10). A) The front side B) The back side C) Comparison

#### 4.2.2.8. Scanning Electron Microscopy Analysis (SEM)

The morphology and the topography of the membrane were investigated with SEM. It is likely to have an agglomeration of the small particles from its high surface energy specially after they are well mixed in the polymeric material. This is likely to be a major problem for preparing the polymeric composite membranes resulting in unwanted thermal and mechanical properties (Kumar et.al, 2009).

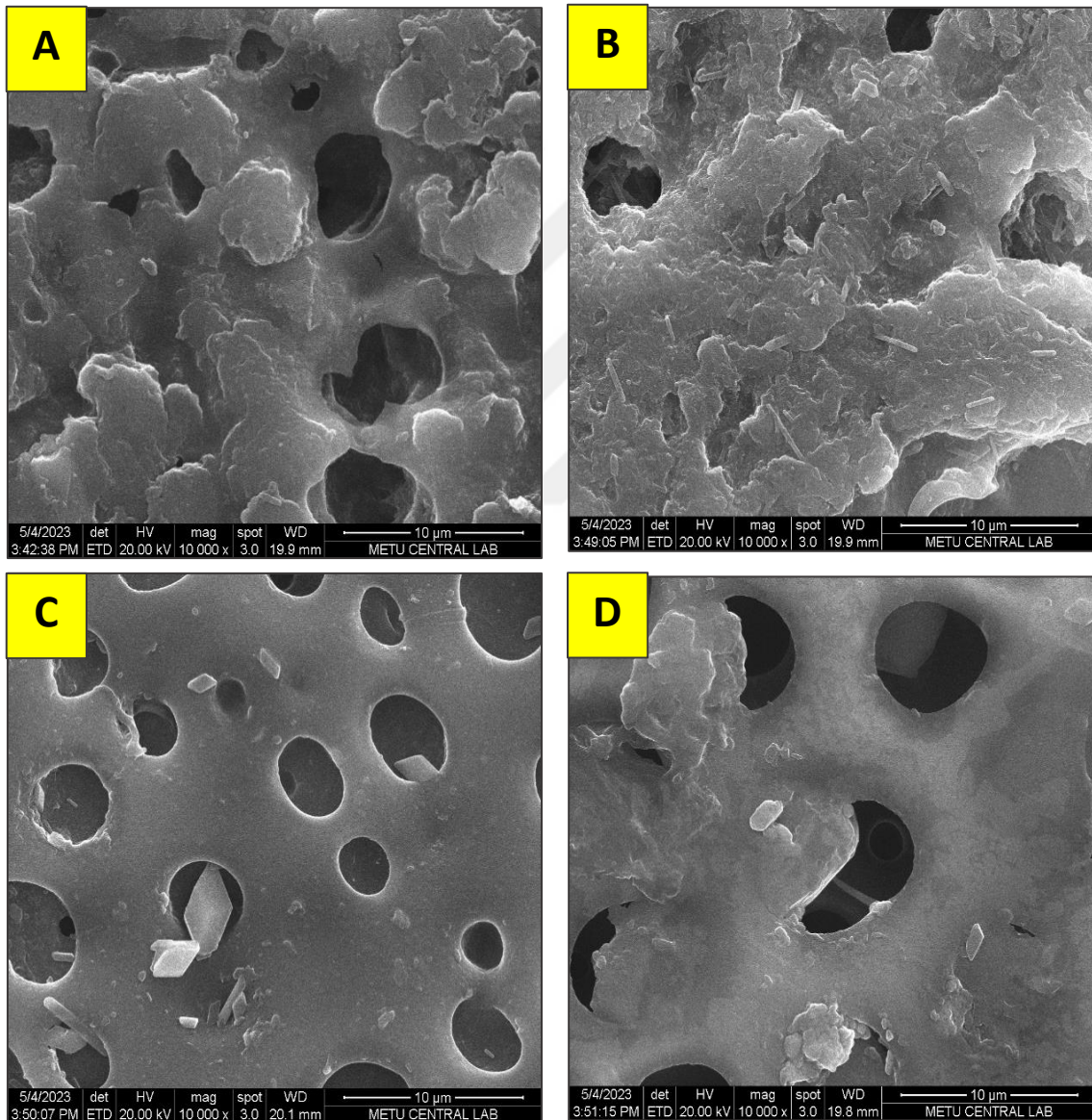


Figure 4.12 . SEM surface images for a) SPEEK/PBI , b)SPEEK/PBI/BN -10%, c) SPEEK/PBI/BN-15%, d) SPEEK/PBI/BN-20

In this study, as there is no advanced technology for casting the membrane and the temperature wasn't monitored carefully, the solvent evaporation had left some tiny pores formed on the surface and through the membrane. These pores are expected to affect the methanol permeability and the mechanical strength. However, all the membranes show high homogeneity, in which SPEEK/PBI had perfectly mixed and the distribution of BN in the membrane is almost uniform with no concentrated or totally empty blocks.

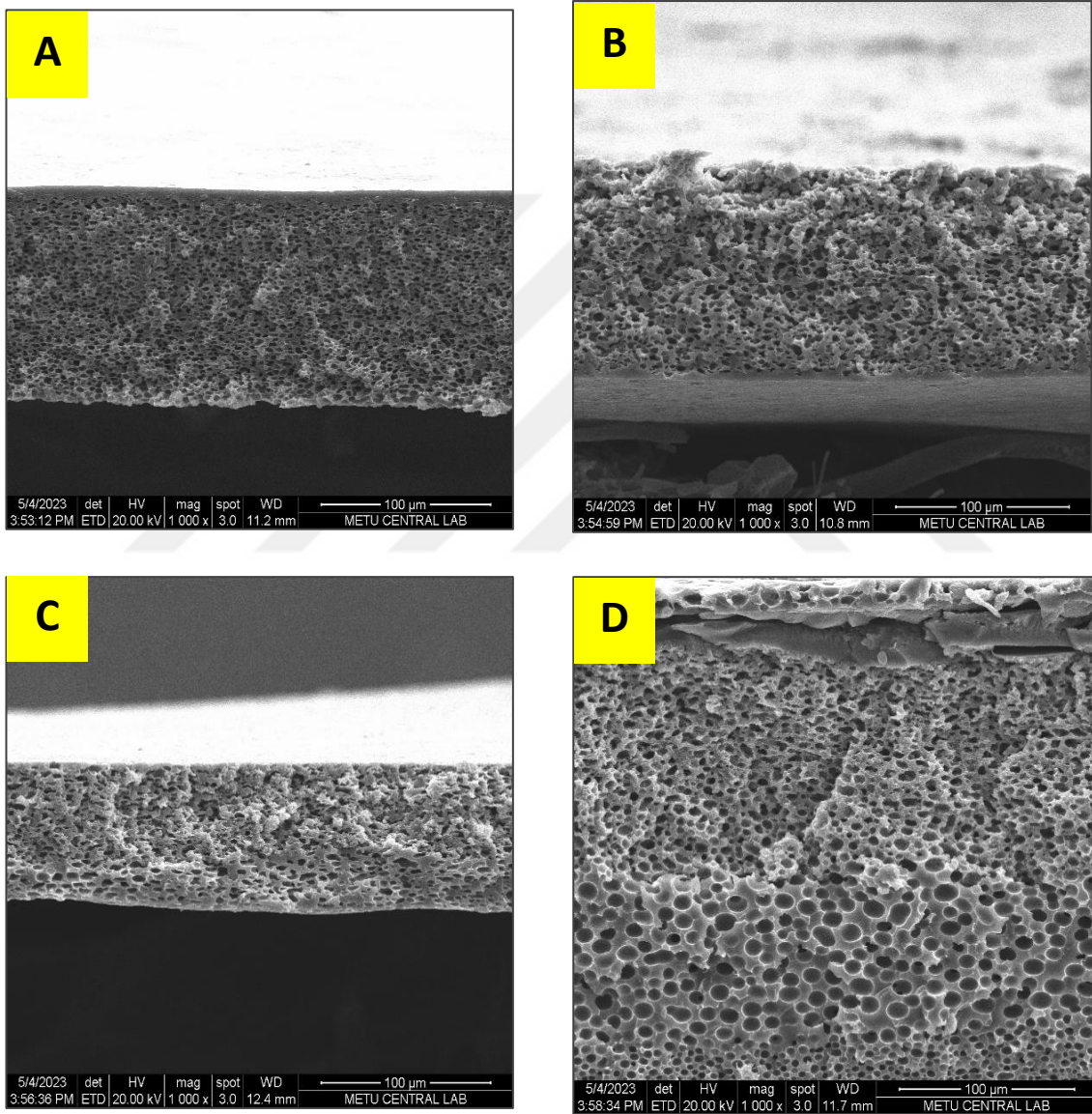


Figure 4.13. SEM cross sectional images for a) SPEEK/PBI , b)SPEEK/PBI/BN-10%, c) SPEEK/PBI/BN-15%, d) SPEEK/PBI/BN-20

The homogeneity (uniform distribution of SPEEK, PBI, and BN over the membranes' surface) was also checked on the both sides using Microscopy (15-30 nano).The membrane looks homogeneous except little PBI fine particles had not dissolved properly.

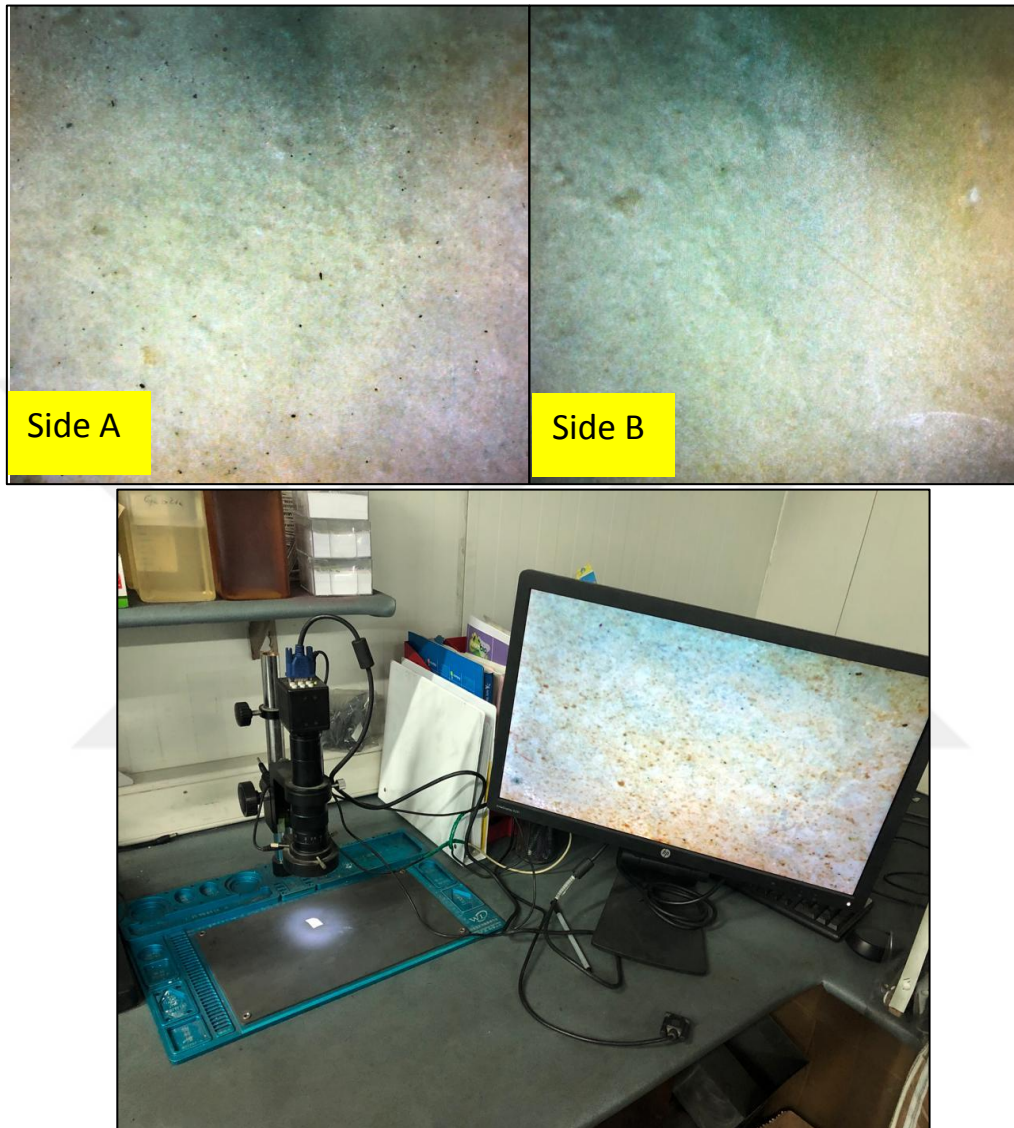


Figure 4.14. Microscopy image at 2.5 micrometer zooming for both sides.

#### 4.2.2.9. Comparison With Other Membranes

The addition of BN enhanced the physiochemical properties of the membrane remarkably, but it affects the membrane adversely when the percentage exceeds 10%. However, the optimum percentage of the filler was found as 10%. The membrane proved its durability when it is exposed to high mechanical pressure (i.e. 8.61MPa) . It also shows

high thermal stability ( i.e. ) due to the existence of PBI and BN. In this study, the BN was functionalized but was not sulfonated, the sulfonated boron nitride expected to have extremely high protonic conductivity.

Table 4.8. Ionic conductivity of SPEEK/PBI/BN compared to other developed membranes.

Membrane	Conductivity (S/cm)	T (°C)	Reference
PBI-BN	0.022	150	( Hussin et.al, 2021)
PBI-GO	0.017	180	(Üregen et.al, 2017)
PBI-PTFE	0.013	150	( Xu et.al, 2011)
PBI- Nanoparticles	0.018 - 0.0045	140-180	( Özdemir et.al, 2017)
SPEEK-SBN	0.021	30	( Rajput et.al, 2021)
SPEEK-GO	0.008	80	( Dai et.al, 2014)
SPEEK- PBI	0.0059	25	( Akay et.al, 2018)

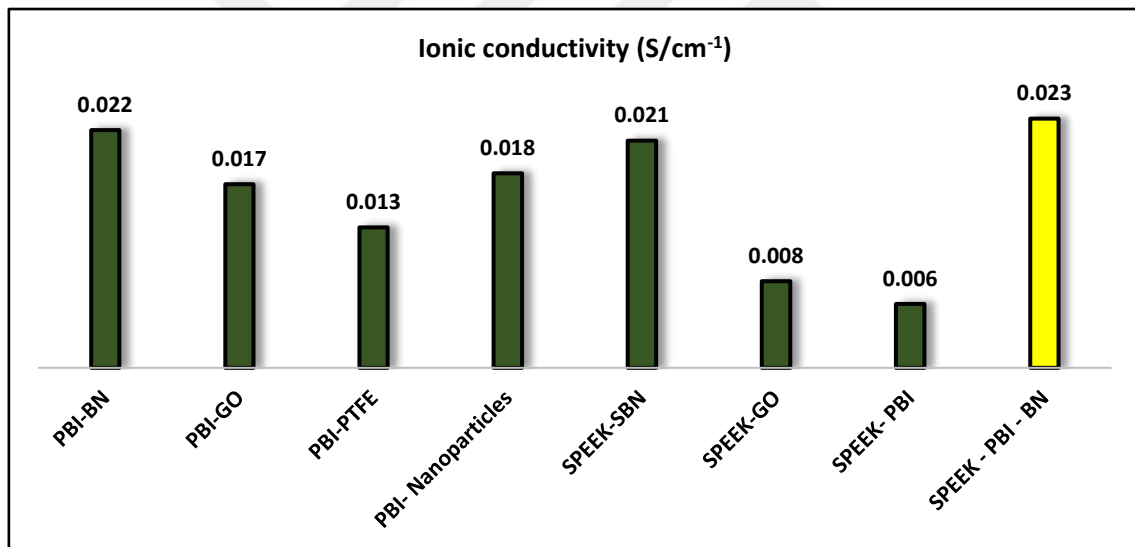


Figure 4.15 . Ionic conductivity of SPEEK/PBI/BN compared to other developed membranes.

## 5. CONCLUSION

The membranes showed good ionic exchange capacity in which the IEC value for the optimum membrane were found 2.18 meq/g. On the other hand, the membranes showed excellent thermal stability up to 305°C with small loss in mass. However, the membrane showed poor mechanical stability as the tensile stress do not exceed 8.61 MPa. The membrane showed excellent ionic conductivity at room temperature (up to 245 mS/m<sup>2</sup>) and at high temperatures up to 120°C. The membrane is amorphous and homogeneous.

It was found that BN does overcome the limitation of SPEEK/PBI blend, and it is a very promising membrane for Fuel cells and Hydrogen storage applications as it shows great physicochemical properties and high protonic conductivity compared to the other non-perfluorinated membranes.

The author suggests to apply the membrane on a fuel cell experiment and observe the performance. Moreover, trying different ways for BN functionalization is likely to be interesting study.

Table 5.1. Physicochemical properties for SPEEK/PBI/BN membranes

	<b>0%</b>	<b>10%</b>	<b>15%</b>	<b>20%</b>
<b>IEC</b>	1.88	2.18	2.18	2.20
<b>DS %</b>	66.99	80.53	80.84	81.48
<b>Water uptake</b>	4.37	6.13	3.92	3.23
<b>Tensile Strength (MPa)</b>	5.12	8.61	4.39	3.37
<b>Tensile Strain %</b>	16	3.06	2.11	9.83
<b>Ionic Conductivity (mS/cm)</b>	170	245	89	76
<b>Max temperature °C</b>	275	316.6	305	304.5

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## PUBLICATIONS AND WORKS

**Harameen, H. M., & Akay, R. G.** (2023). Investigation into the influence of boron nitride addition on the properties of SPEEK/PBI based electrolyte membrane. *International Journal of Hydrogen Energy*.  
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**Huzaiifa M.A. Harameen, AKAY, R.** (2022). Modifying SPEEK/PBI Blend Membrane with Boron Nitride for PEM Fuel Cells, *6th International Symposium on Materials for Energy Storage and Conversion*, Bol, island of Brač, Croatia, 05-08 July 2022.



## **BIOGRAPHY**

Mr. HUZAIFA MOHAMMED ADAM HARAMEEN graduated from Basheer Mohammed Saeed model secondary school (Sudan Republic). he started a bachelor in chemical engineering at University of Khartoum in 2013 in which he obtained his degree in 2018 with first class UK grading system. As soon as he graduated, he started working as a teaching and research assistance at the same university until July 2019 when he won Turkish government scholarship to pursue his graduate studies at Kocaeli University in chemical engineering department. During his graduate research, he had been working on developing an electrolyte membrane for fuel cells and electrolysis applications which is part of TUBITAK project no.215M255.

