

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/360441444>

An overview of proton exchange membranes for fuel cells: Materials and manufacturing

Article in International Journal of Hydrogen Energy · May 2022

DOI: 10.1016/j.ijhydene.2022.04.099

CITATIONS

45

READS

604

6 authors, including:



Shahbaz Ahmad

American University Washington D.C.

16 PUBLICATIONS 88 CITATIONS

[SEE PROFILE](#)



Tahir Nawaz

American University of Sharjah

12 PUBLICATIONS 64 CITATIONS

[SEE PROFILE](#)



Asghar Ali

American University of Sharjah

34 PUBLICATIONS 187 CITATIONS

[SEE PROFILE](#)



Mehmet Fatih Orhan

American University of Sharjah

65 PUBLICATIONS 2,973 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Development of Efficient Photon Upconverters for Silicon Solar Cells [View project](#)



Fuel cell [View project](#)



ELSEVIER

Available online at www.sciencedirect.com**ScienceDirect**journal homepage: www.elsevier.com/locate/he**Review Article****An overview of proton exchange membranes for fuel cells: Materials and manufacturing**

Shahbaz Ahmad ^{a,b}, Tahir Nawaz ^{a,b}, Asghar Ali ^{a,b},
Mehmet Fatih Orhan ^{c,*}, Ayesha Samreen ^d, Arunachala M. Kannan ^e

^a Materials Science and Engineering Program, College of Arts and Sciences, American University of Sharjah, United Arab Emirates

^b Department of Physics, American University of Sharjah, United Arab Emirates

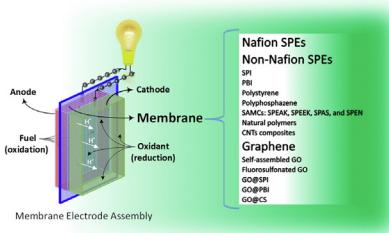
^c Department of Mechanical Engineering, American University of Sharjah, United Arab Emirates

^d Department of Physics, University of Peshawar, Peshawar, Pakistan

^e The Polytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, AZ 85212, USA

HIGHLIGHTS**GRAPHICAL ABSTRACT**

- The PFSA membranes (Nafion®) have been widely used as commercial membranes in PEMFC and DMFC.
- Nafion membranes possess issues like high cost, high-temperature degradation, oxygen leakage, and methanol permeability.
- Non-Nafion electrolytes e.g. SPI, PBI, polystyrene, polyphosphazene, SAMCs, & chitosan-based membranes have been reviewed.
- CNTs and GO-based composites have been proved as promising materials to replace Nafion membranes.

**ARTICLE INFO****Article history:**

Received 21 February 2022

Received in revised form

4 April 2022

ABSTRACT

Due to their efficient and cleaner operation nature, proton exchange membrane fuel cells are considered energy conversion devices for various applications including transportation. However, the high manufacturing cost of the fuel cell system components remains the main barrier to their general acceptance and commercialization. The main

* Corresponding author.

E-mail address: morhan@aus.edu (M.F. Orhan).

<https://doi.org/10.1016/j.ijhydene.2022.04.099>

0360-3199/© 2022 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Accepted 11 April 2022
Available online 6 May 2022

Keywords:

Solid polymer electrolytes
Nafion membranes
Proton conductivity
Proton exchange membranes fuel cell

strategy for lowering the cost of fuel cells which is critical for their general acceptance as alternative energy sources in a variety of applications is to lower the cost of the electrolyte and catalyst. An electrolyte is one of the most important components in the fuel cell and a major contributor to the cost (>\$500/m² for commercial Nafion® series). Nafion is widely used as an electrolyte in PEMs, but it has some limitations in addition to high costs such as low proton conductivity, high-temperature performance degradation, and high fuel crossover. Therefore, the development and manufacturing of low-cost and high-performance electrolyte membranes with higher conductivity (~0.1 S·cm⁻¹) at a wider temperature range is a top priority in the scientific community. Recent years have seen extensive research on the preparation, modification, and properties of PEMs such as non-Nafion membranes (SPI, PBI, polystyrene, polyphosphazene, SPAEK, SPEEK, SPAS, SPEN), and their composites by incorporating functionalized CNTs, GO as fillers to overcome their drawbacks. This paper provides a comprehensive review of membrane materials and manufacturing with a focus on PEMs. In particular, the review brings out the basic mechanism involved in proton conduction, important requirements, historical background, contending technologies, types, advantages and disadvantages, current developments, future goals, and directions design aspects related to thermodynamic and electrochemical principles, system assessment parameters, and the prospects and outlook.

© 2022 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Contents

Introduction	19087
Properties of an efficient proton conducting membranes	19088
Perfluorosulfonic acid membranes	19088
Proton conduction mechanism in nafion	19090
Limitations of nafion membrane	19091
Nafion based composite membranes	19092
Non-Nafion solid polymer electrolyte membranes	19093
Sulfonated polyimide-based membranes	19093
Polybenzimidazole based membranes	19094
Polystyrene-based membranes	19095
Polyphosphazene-based membranes	19097
Sulfonated aromatic main-chain polymers: SPAEK, SPEEK, SPAS and SPEN	19098
Membranes derived from natural polymers	19102
Carbon nanotubes based composites	19103
Graphene	19104
Graphene oxide (GO) based membranes	19105
Self-assembled GO PEMs	19105
Graphene oxide nanocomposites	19107
Challenges in PEMs	19112
Conclusion and future prospect	19113
Declaration of competing interest	19114
Abbreviations	19114
References	19114

Introduction

The world is undergoing a smooth transition from fossil fuel-based energy generation which is quickly depleting and poses a serious threat to the environment to more green and abundantly available renewable energy [1]. The hydrocarbon

to hydrogen economy adopting fuel cells was developed during this transition to be a sustainable way to meet the energy demand of the stationary, transportation, domestic, and commercial sectors [2,3]. Owing to these prospects, low-temperature fuel cells like the proton exchange membrane fuel cells (PEMFC) are the most prospective energy conversion technologies. PEMFCs are acidic electrolyte-based energy

converters that convert chemical energy to electrical through an oxidation-reduction (redox) reaction. PEMFC consists of two electrodes (anode and cathode) separated by a selective polymeric membrane for proton (H^+) conduction [4]. At the anode side of PEMFC, H_2 is fed as fuel that oxidizes to release H^+ ions along with a pair of electrons. The H^+ ions pass through the proton-conducting electrolyte membrane to the cathode while the electrons travel through the external circuit. Air is supplied at the cathode side, where O_2 (from the air) reacts with protons in the presence of a catalyst, producing H_2O ($E^\circ = 1.23$ V) [5]. As a green energy alternative, PEMFC technology promises zero carbon emissions if H_2 is the fuel, thus, saving the environment from harmful impacts of carbon build-up. A steady source of reliable power supply, easy refueling, all solid structure, fast start-up, and reasonable durability provides PEMFC a better standing in the world of power production resources [6] (see Tables 1–10).

Although huge advancements have been made in membrane science in the past couple of years, there are extensive challenges and significant difficulties related to membranes in the fuel cell [7]. The most critical challenges that are faced in current fuel cell membranes are high-temperature degradation, fuel crossover, water condensation, and balancing, production cost and safety issues, etc. Hence, the optimization of fuel cell membranes requires broad research regarding materials selection and their alterations, utilization of various techniques and conditions, and intensive structural and morphological study of membranes.

A membrane electrode assembly (MEA) is a central element in optimizing PEMFC because other components of fuel cell such as gas diffusion layer (GDL), electrode catalyst material, bipolar plates, current collector, and microchannels for water and gas must be designed according to the properties of the MEA [8]. Typically, a membrane is the heart of MEA because it provides a medium for the electrode reaction and facilitates the transfer of proton species, and creates a conductive path to an external circuit for the electron that has been created in the hydrogen oxidation process [9]. Therefore, membrane performance significantly affects the overall efficiency of PEMFC. During the last two decades, a lot of research in polymeric conducting membranes has been put together to optimize the performance of fuel cells. Particularly, in the PEMFC, Nafion is actively used as an efficient proton-conducting membrane. Scientists and engineers are focusing on the modification of Nafion using different composites while exploring other polymers to maximize the efficiency of proton-conducting membranes in PEMFC.

Properties of an efficient proton conducting membranes

An efficient PEM membrane must exhibit the following properties:

1. Excellent proton conductivity
2. High stability in an electrochemical environment
3. Excellent water retention properties
4. Resistant to fuel crossover/Poor permeability to reactant species
5. Must be compatible with different fuels
6. Mechanically stable with good strength

7. Low-cost materials
8. Facile synthesis
9. Thermally stable
10. Superior durability
11. Efficient performance
12. Biodegradable

At present, the few commercially available membranes for PEMFC are Nafion (Du Pont), perfluorinated ionomer (PFI), and Dow membranes (Dow chemical). Many issues are related to these membranes, which keeps the membrane research inactive phase. For instance, Dow membranes are very efficient as compared to the other two but they are very costly and they are not resistant to fuel crossover, which degrades the performance of fuel cells [10]. On the other hand, the Nafion membrane's performance drops significantly at temperatures higher than 80 °C. Furthermore, PFI membranes degrade in high-temperature PEM fuel cells (~150 °C) evolving toxic and emitting corrosive gases, which contaminates the fuel cell and the surrounding environment and compromises the FC performance [11]. Keeping these drawbacks in mind all these membranes are limited to research purposes and cannot be commercialized. Thus, there is a genuine need to search for an economical and more thermally stable polymer to acquire a decent membrane for PEMFC. New composite-based polymer membranes would be the best solution to achieve the target. However, getting desired properties out of membranes is not possible without tuning their chemistry with different functional groups. Some concise reviews are done in the past that discuss the role of alternative membranes in PEMFC on sulfonated hydrocarbons [12], PBI [13], PFSA [14], polyimide [15], solid acids [16], nanofiber [17], carbon nanomaterials [18,19] and other advanced materials [20] based membranes and their composites. The present work extensively discusses the recent development in the field of PEMs and their incorporation into fuel cell applications.

Perfluorosulfonic acid membranes

Perfluorosulfonic acids (PFSA) are electrically neutral ionomers with a fraction of ionized cations which were developed by Willard T. Grubb in 1959 [21]. The sole purpose of developing the PFSA membrane was to provide a proton-conducting gas barrier for PEMFCs. Initially, Grubb used strong acids to provide contact between the membrane and catalytic materials but later it was found that PEMFC can operate better without acid contact layers. The discovery of the PFSA membrane at that time changed the business of PEM-based fuel cells as it uses no additional electrolytes other than the membrane itself and acts as a controller of the MEA by controlling the reaction kinetics [22]. This discovery attracted scientists and researchers around the world to focus on improving both the physical and chemical properties of polymeric membranes for the PEMFCs.

In 1960, DuPont introduced its first commercially produced perfluorinated ion-exchange membrane with the Nafion® name. As shown in Fig. 1(a), state-of-the-art Nafion membrane is a fluorinated polymer consisting of a backbone chain of hydrophobic polytetrafluoroethylene (PTFE) also called

Table 1 – Summary of sulfonated polyimide (SPI)-based membranes.

Membrane	Conductivity (S.cm ⁻¹)	IEC (mmol. g ⁻¹)	Water uptake (%)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	RH (%)	Reference
SPI/PBI/SCYb	0.131	—	—	590	180	8	[95]
SPI-Rice husk ash	0.205	0.2519	55.24	13	30	100	[96]
SPI-BC	0.110	2.14	26.2	63.4	60	100	[102]
SPI/GO functionalized by [MIm]+H2PO4- (5 wt%) [NSDA/ODA (10/90)]	0.124	—	47.3	—	120	80	[103]
NSPI/3% SIGO	0.111	2.28	—	74.9	RT, 70	—	[105]

The dash sign (–) in the table means that the following authors did not report these results in the following papers.

Table 2 – Summary of anhydrous polybenzimidazole based membranes.

Membrane	Conductivity (S.cm ⁻¹)	Water uptake (%)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	Reference
Sulfonated crosslinked-OPBI	0.082	40	—	>100	[110]
TiO ₂ -PBI-based composite	>0.075	17.5	1000	175	[111]
c-sTiO ₂ -PBI-OO	0.098	392	356	160	[112]
TiOSO ₄ -PBI	0.0477	—	621	150	[113]
GO-PBI	0.0476	—	—	150	[114]
PBI/SNP-PBI-10	0.050	385	650	160	[115]
Cross-linked [HMIm][TFSI] using divinylbenzene (2.5 mol. %)	0.371	—	30	200	[117]
PBI (80% porosity)/polymerized [HMIm][TFSI]	0.309	—	—	200	[117]

Table 3 – Summary of polystyrene-based membranes.

Membrane	Conductivity (S.cm ⁻¹)	IEC (mmol. g ⁻¹)	Water uptake (%)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	RH (%)	Reference
S-PS/S-PSPA/MWCNT-based nanocomposite	2.55	3.6	30.9	—	80	94	[118]
S-PSEBS/CuO@g-C ₃ N ₄	0.0229	3.1	—	—	—	—	[119]
Quaternary-ammonium-group-functionalized bromoalkylated polystyrene	—	1.74	—	407	60	100	[122]
Alkyne-azide-functionalized PVBC	0.156	2.23	143	157	60	100	[123]
Quaternized- and azide-functionalized poly(styrene-block-vinylbenzylchloride) (B2- 8 EG)	0.109	1.35	91	—	60	100	[124]
Quaternized- azidated poly (2,6-dimethyl-1,4- phenylene oxide) crosslinked poly (4- vinylbenzyl chloride)	0.148	1.95	19.8	11	60	100	[125]
Chloromethylated SEBS ionomer	0.18	1.91	—	285	70	100	[126]
SPS-LS-SiO ₂ -4	0.432	3.21	28.84	—	60	100	[121]

Table 4 – Summary of polyphosphazene-based membranes.

Membrane	Conductivity (S.cm ⁻¹)	IEC (mmol. g ⁻¹)	Water uptake (%)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	RH (%)	Reference
sulfonated POP	0.082	1.4	—	—	65	100	[136]
PFMPP1-r-PFSPP9	0.14	2.1	41	—	80	100	[137]
F-PSBOS ₂₆	0.284	1.49	69.5	—	80	100	[138]
p-BMPP single bond	0.189	1.23	48	175	60	100	[139]
PSx-PSBSy- 4-BP (M4)	—	—	—	—	—	—	—
CF3-PSx-PSBOSy-SCNT	0.55	1.77	72.4	—	100	100	[140]

Table 5 – Summary of sulfonated aromatic main-chain polymers.

Membrane	Conductivity (S.cm ⁻¹)	IEC (mmol. g ⁻¹)	Water uptake (%)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	RH (%)	Reference
MNCS@SNF-PAEK-1.5	0.188	—	77.6	91	80	100	[166]
BSPAEEKS/S-Fu-0.75	0.322	1.81	52	74.38	60	100	[167]
SPEEK-Na/PBI (20%)	0.1985	—	52.5	—	170	100	[191]
SPEEK-PEG/10% SiO ₂	0.185	1.66	63	379	60	100	[193]
SPAES-LA-X6Y14	0.158	2.05	56	232	60	100	[243]
PPL/SQH-SPEN	0.0043	2.3	73	—	25	100	[277]
SN SPEN	0.123	1.99	65	109	80	100	[278]
SPEN-TPA 50 wt%	0.107	1.66	99	—	80	100	[279]

Table 6 – Summary of Carbon nanotubes-based composites.

Membrane	Conductivity (S.cm ⁻¹)	IEC (mmol. g ⁻¹)	Water uptake (%)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	RH (%)	Reference
SPEN/SCNTs-3 wt%	0.275	1.914	80	—	80	100	[342]
Nafion/PWA-PBI-CNT	0.1951	0.91	25	386	90	40	[343]
PBpNT-1%	0.115	—	—	780	140	>30	[344]
PBICNTPA	0.075	—	—	173.5	180	>30	[345]
0.3 wt% CNF/6FPBI	0.20	—	—	410	160	>30	[346]
MWNT-poly(NaSS))/ PBI	0.051	—	—	166	170	>30	[348]
MWNT-imidazole/PBI	0.043	—	—	164	170	>30	[348]
S-sCNT-5	0.125	2.19	44	—	90	100	[352]
SPEEK/ZCN-2.5	0.05	1.48	40	—	120	40	[353]

Table 7 – Summary of self-assembled GO PEMs.

Membrane	Conductivity (S.cm ⁻¹)	IEC (mmol. g ⁻¹)	Water uptake (%)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	RH (%)	Reference
free-standing GO membrane	-0.082	—	—	8	90	100	[410]
SGO membrane	0.04	1.1	—	113	40	25	[414]
OGO	0.24	—	—	—	35	40–100	[415]
F-TGO, SF-TGO	—	1.2, 1.5	—	81, 74	40	75	[416]
Thin film GO	—	—	—	410	25	25	[417]
SBDS-HGO membrane	0.0918	1.84	—	41	80	<30	[418]
SGO-1, SGO-20	0.120, 2.099	1.20, 1.97	24.15, 54.04	—	80	53.5	[419]

Teflon connected by the side chain of hydrophilic sulfonic acid ($-\text{SO}_3\text{H}$) has been widely used as the commercial proton-conducting polymer in PEMFC applications [23]. The hydrophobic PTFE provides excellent mechanical, thermal, and chemical properties while the hydrophilic sulfonic acid makes Nafion a good proton-conducting membrane due to its water retention property [24].

Commercially, the most widely used Nafion membranes grades are Nafion 112, 115, 117, 1110 which have a thickness of 2,5,7 and 10mil (1mil = 25.4 μm). Thinner membranes are employed in hydrogen fuel cells, whereas thicker ones are used in direct methanol fuel cells (DMFCs) to reduce methanol crossover [26]. Nafion has advanced fluorocarbon chemistry and has a similar structure to Teflon. Due to this similarity, Nafion is highly stable in strong chemicals and has an extremely low degradation rate in the surrounding medium. It can operate in high temperature ranges up to 190 °C. The presence of the $-\text{SO}_3\text{H}$ group makes it a strong proton

donor and acts as a good water-absorbent and transport material [27].

Proton conduction mechanism in nafion

Nafion, when fully hydrated, possesses very high proton conductivity up to 0.1 S·cm⁻¹ [28]. This is attributed to the molecular structure shown in Fig. 1(b), the hydrophilic $-\text{SO}_3\text{H}$ group of Nafion attached to the hydrophobic backbone chain of PTFE may be subjected to hydration as $-\text{SO}_3\text{H}$ will attract water molecules and accumulate around this group. The availability of water significantly affects proton conductivity by controlling the formation of proton conduction channels in Nafion. The accumulation of water around hydrophilic regions divides Nafion into hydrophobic regions and water-filled hydrophilic domains [29]. In the presence of very small water content, the bulk hydrophilic domain has lower water content and the proton transfer in

Table 8 – Summary of flurosulfonated GO-based nanocomposites.

Membrane	Conductivity (S.cm ⁻¹)	IEC (mmol. g ⁻¹)	Water uptake (%)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	RH (%)	Reference
Nafion-GO composite	0.013	—	—	415	30	>30	[422]
Nafion/PW-mGO	0.008, 0.2	0.84	37	841, 818	80	20, 100	[423]
NM/GO-0.05	0.082	—	53	886	80	100	[424]
GO-g-SPEEK/Nafion33	0.10, 0.17, 0.231	1.45	117,136	182, 213, 112	25, 60, 90	50	[426]
0.1% GO/Nafion	0.030, 0.067, 0.0781	—	122.51	—	20, 60, 80	>30	[427]
RGO-Nafion nanohybrid membrane	0.22	—	—	—	30	100	[428]
C-SPEEK/HPW/GO	0.119	1.45	40.99	877	80	100	[429]
SPTA-GO@SPAES	0.412	2.45	150	1580	80	100	[430]
SGO/SPAEK-1.5	0.124	1.23	19	—	90	100	[431]
SPEN-NGO 1 wt%	0.104, 0.167, 0.183	—	—	—	20, 60, 80	100	[432]
SGO-SPEN-2 wt%	0.183	1.825	48	—	80	100	[433]

Table 9 – Summary of Sulfonated Polyimide (SPI) and GO-based nanocomposites (SPI-GO).

Membrane	Conductivity (S.cm ⁻¹)	IEC (mmol. g ⁻¹)	Water uptake (%)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	RH (%)	Reference
SPI/GO-0.5%	0.667	2.58	81.84	—	90	60	[440]
SPBI/SIGO-15%	0.581	2.45	61.81	502	120	10	[441]
SPI/FGO 5%wt	0.0772, 0.1243	—	47.3	—	160, 120	80	[442]
SPI/SPSGO-8	0.0962	2.05	55.82	76, 98	70, 130	100	[443]
SPI/SIGO-15	0.1138	2.24	95.16	79	70	100	[444]

Nafion occurs through the $-\text{SO}_3\text{H}$ group which is attached to the PTFE surface and is called the surface mechanism. As the percolation threshold of proton conductivity is passed water clusters start to form at the borders of the chain ($-\text{SO}_3\text{H}$ groups) in the random networks embedded in a continuous sponge-like fluorocarbon phase [30]. This yields high activation energy for proton transfer which impedes a “hop-turn” (i.e., Grotthuss-type) proton conductivity and results in a primarily proton-diffusion-based conductivity called vehicular mechanism [31]. Generally, the proton conductivity through the vehicular mechanism is small and as the water content increases, these channels become wider, and more free molecules become available. In the presence of water, the proton (H^+) leaves $-\text{SO}_3\text{H}$ and attaches to water to form a hydronium ion (H_3O^+), which diffuses through the channels (Fig. 1(b)). However, the presence of hydronium ion (H_3O^+) forms strong electrostatic interaction with $-\text{SO}_3\text{H}$ groups which still impedes Grotthuss-type proton conduction, and thus the proton mobility due to surface mechanism, predominates in the Nafion membrane at low RH [29].

Further increase in water content increases the size of water clusters and proton-conducting channels become broader. This increase in water results in the dominance of

the Grotthuss-type mechanism in which proton diffuses through a network of hydrogen bonds in water molecules [32]. A fully saturated Nafion membrane resembles a two-phase system consisting of a hydrophobic backbone chain and hydrophilic water/acids segments. In this situation, the conductivity of Nafion almost reaches the conductivity value of bulk electrolyte solution, which is controlled by the Grotthuss mechanism. A new type of Nafion-type perfluorinated ionomer with the short side chain of a copolymer Tetrafluoroethylene (TFE) and Sulfonyl Fluoride Vinyl Ether (SFVE) called Aquiphon® (Solvay. co) is currently commercialized which has superior cation conductivity as well as an outstanding chemical and thermal stability [33].

Limitations of nafion membrane

Even though Nafion is currently dominating the commercial FC market, it has some considerable issues in its design that hinder its ability to perform at extreme levels. As discussed above, Nafion conductivity solely relies upon the presence of adequate water channels in hydrophilic domains, therefore Nafion is not suitable for operating at temperatures below 0 °C and/or above 100 °C [34,35]. Additionally, for redox reactions

Table 10 – Summary of Polybenzimidazole and GO-based nanocomposites (PBI-GO).

Membrane	Conductivity (S.cm ⁻¹)	IEC (mmol. g ⁻¹)	Fuel Cell Performance (mW.cm ⁻²)	Temperature (C)	RH (%)	Reference
PBI with 0.5 wt% ImGO	0.077	—	—	150	—	[447]
Py-PBI/PGO	0.0764	—	360	120	<30	[448]
PBI/RGO/PA membranes	0.028	—	—	170	<30	[449]
PBI-RGO/PPBI/PBI-RGO	0.114	—	—	170	<30	[450]
PBI-sGO-2wt%	0.0293	1.52	102	150	<30	[451]

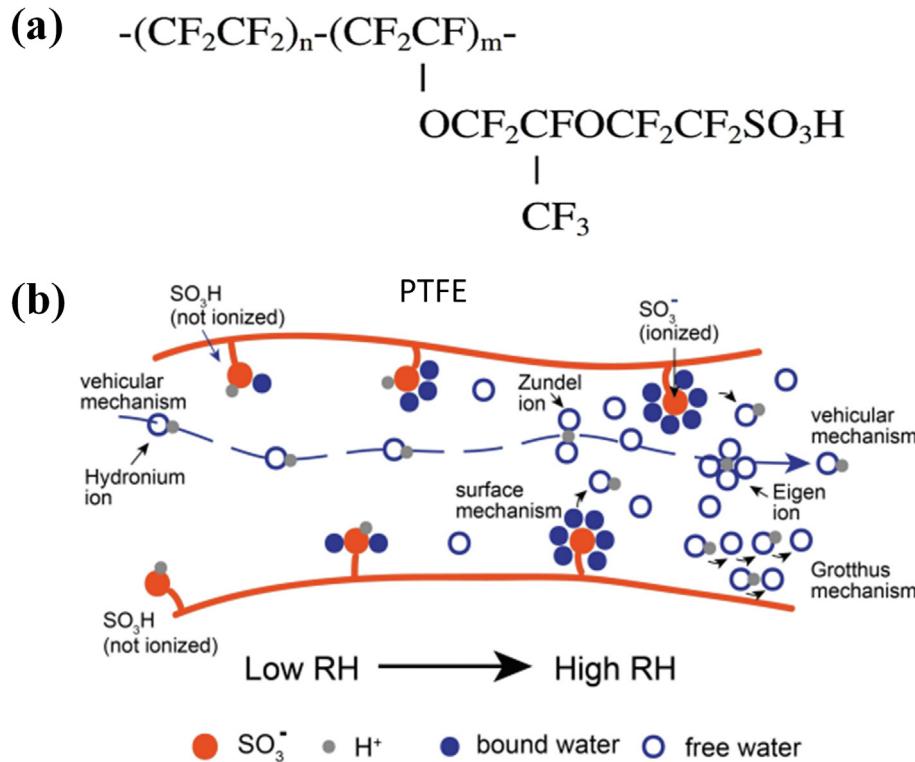


Fig. 1 – (a) Chemical Structure of commercial Nafion® (DuPont.co) [22], (b) Proton conduction mechanism in Nafion polymer chain. The H^+ from the $-\text{SO}_3\text{H}$ group detaches and combines with H_2O to form H_3O^+ which conducts through the channel [25].

in a fuel cell, there is always the formation of some intermediate products at the electrodes which affects its performance e.g., Nafion is stable against the formation of hydrogen peroxide (H_2O_2) up to 30% in solution. However, the decomposition of H_2O_2 to $\cdot\text{OH}$ or $\cdot\text{OOH}$ radicals attack the H-containing terminal groups and catalyze the decomposition of Nafion at low RH conditions and temperatures exceeding 80 °C [36]. This is generally regarded as the principal and most aggressive degradation mechanism. Furthermore, the presence of alien charged impurities (other than H^+) may also drastically decrease Nafion conductivity by decreasing the water content [37], therefore the contaminating ions should be minimized during the membrane manufacturing process. Nafion suffers poor chemical and thermal stability at elevated temperatures. As part of MEA, Nafion is susceptible to multiple thermal and hydration/dehydration cycles and suffers from severe degradation [38,39]. Additionally, the mechanical stresses generated on the surface of the membrane due to compression and external vibrations are the key reasons behind the mechanical damage to PEMFC compact layers and they are responsible for crack initiation, propagation, and layer delamination which can cause short circuit current [39,40]. However, the mechanical strength of Nafion can be improved by incorporating an inert matrix which can be a polymer or inorganic material [41–43]. The problem with inert materials is that they can decrease the H^+ conductivity and water uptake of the membrane as compared to bulk Nafion due to discontinuity and matrix-restricted macro-molecular transport [44]. Though the conductivity of reinforced Nafion

membranes can be increased by the addition of certain additives such as Phosphotungstic acid [45,46]. In addition to that, the presence of inorganic materials with tuned functional groups is more efficient and can enhance various properties in a membrane such as conductivity, water uptake, and ion exchange capacity, while maintaining the mechanical stability of the composite membrane. Apart from that, the shape of inorganic fillers [47–49], and surface treatment [50–54] can also play a significant role in enhancing the mechanical properties of Nafion. As the H^+ conductivity of the Nafion membrane relies on the presence of water-filled channels at the same time it provides a conductive pathway for methanol as it is miscible in water [50]. This issue can be solved by two methods: (I) introduction of fine inorganic particles to the polymer matrix, (II) Addition of other polymers inside Nafion voids with properties resisting methanol permeability [55]. The high methanol permeability is an issue in DMFCs where thick Nafion membranes are used. Nafion membranes are very expensive due to its complex manufacturing process. For this reason, the development of smart and engineered materials is pivotal as an alternative for the fuel cells and other electrochemical technology systems.

Nafion based composite membranes

Keeping in mind the sensitivity of Nafion towards water retention properties and poor mechanical, thermal, and chemical stabilities at elevated temperatures [56,57], significant research efforts have been made by the scientific

community to circumvent these issues in PEMFC. One of the solutions that have been reported so far is the modification of Nafion through the chemical grafting of ionic groups [58]. However, the grafting technique improved the proton conductivity but did not address the mechanical stability due to lumping. Recent studies showed that composite membrane by introducing inorganic particles in the Nafion matrix helps solve many of the reported issues and are very promising [59]. Several studies show the investigation of the effect of the composite membrane on PEM fuel cell performance. For instance, Yin et al. [60] prepared a multilayered sulfonated CNTs/Nafion composite membrane with a varying layer thickness ($0.5\text{ }\mu\text{m}$ – $40\text{ }\mu\text{m}$) through layer by layer assembly method. The diameter of Su-CNTs was on average 15 nm and the length of $1\text{ }\mu\text{m}$. The composite membrane with an ultra-thin layer ($<1\text{ }\mu\text{m}$) was having Su-CNTs aligned in a parallel direction along with proton-conducting pathways (parallel to membrane interface), while the multilayered stacking improved the dispersion of Su-CNTs with a uniformly distributed proton-conducting network. This morphology created a Su-CNTs/Nafion membrane with better heat resistance and the presence of multilayers having hydrophilic interfaces reaches a proton conductivity value of $0.33\text{ S}\cdot\text{cm}^{-1}$ at $150\text{ }^\circ\text{C}$. Son et al. [61] prepared SiO_2 /Nafion composite membrane by mixing MSUF- SiO_2 in Nafion ionomer and ethanol followed by solvent casting. The SiO_2 /Nafion composite membrane exhibited good proton conductivity and fuel cell power density of $0.1\text{ S}\cdot\text{cm}^{-1}$ and $363\text{ mW}\cdot\text{cm}^{-2}$ at $100\text{ }^\circ\text{C}$ as compared to $0.085\text{ S}\cdot\text{cm}^{-1}$ and $327\text{ mW}\cdot\text{cm}^{-2}$ of pristine Nafion 212, respectively. This was due to the presence of hygroscopic SiO_2 , which exhibits good water retention properties. Wei et al. [56] modified commercial Nafion membrane with copper phthalocyanine tetrasulfonic acid tetrasodium salt (CuTSPc). Successful incorporation of both Nafion and CuTSPc was obtained when characterized with FTIR, SEM, and XRD. The Nafion- CuTSPc showed an outstanding proton conductivity of $0.131\text{ S}\cdot\text{cm}^{-1}$ at $80\text{ }^\circ\text{C}$. Furthermore, the fuel cell performance of Nafion- CuTSPc composite was $43.3\text{ mW}\cdot\text{cm}^{-2}$, which is similar to pure cast Nafion membrane. A porous composite material composed of PEEK/SPEEK reinforced with Nafion was prepared using the phase inversion process [62]. Excellent proton conductivity ($\sim 0.56\text{ S}\cdot\text{cm}^{-1}$) was achieved with PEEK/SPEEK composite with a very high-power density of $91.7\text{ mW}\cdot\text{cm}^{-2}$ in a single cell test. Makinouchi et al. [63] used sulfonated polyamide (SPI) nanofibers in the matrix of Nafion to improve proton conductivity at relatively low humidity. Adjemian et al. [64] studied various metal oxide-based composite membranes by suspending (TiO_2 , SiO_2 , ZrO_2 , and Al_2O_3) in Nafion solution. The results showed that TiO_2 -Nafion composites performed better when compared to others and possessed higher performance at elevated temperatures and low RH. Other studies also showed the positive effect of membrane modification on the performance of PEM fuel cells [65]. Similarly, incorporation of different inorganic materials in Nafion such as Metal-organic framework [66–70], zeolites [71–74], metal oxides [75–80], and various polymers such as Chitosan [81], polybenzimidazole (PBI) [82], and polyvinylidene fluoride (PVDF) [83,84] were also made to improve the performance, stability, and hydration of Nafion membrane.

Non-Nafion solid polymer electrolyte membranes

With the introduction of Nafion in 1946, a subsequent decline in the non-Nafion SPEs was evidenced [85]. Although Nafion is the current market leader, however, it has its disadvantages as discussed in section 2.2. Today's solid polymer electrolyte (SPE) research revolves around the idea to develop low-cost, stable, high-temperature operable, and low methanol permeable SPEs. Fluorination is the major cost-incurring step in developing Nafion and other similar perfluoroalkyl sulfonic acid ionomers, and therefore non-perfluorinated membranes that don't involve fluorination chemistry are typically researched. Several alternative materials are being researched with the intent to surpass in performance and replace Nafion [86].

Polyaromatic membrane materials with sulfonated aromatic units are high-temperature stable polymers and are being widely studied as SPE candidates. The hydrophilic sulfonic acid group ($-\text{SO}_3\text{H}$) is responsible for the proton conductivity in such types of membranes and therefore its content control is important to realize optimal ionic conductivity. Such polymer architectures are designed to meet an ionic content of 1.8 mmol g^{-1} , required to match the typical $0.1\text{ S}\cdot\text{cm}^{-1}$ conductivity of Nafion. For a given ionic content, block copolymers are generally more conductive relative to random copolymers [73,74]. To improve the stability and mechanical properties of such membranes, some groups have focused on blending polymers of different functionalities [87–89]. For better stability and electrochemical response, semi-interpenetrating network membranes have also been suggested [90–92]. Radiation grafting, which involves introducing reactive sites into a base polymer through radiation exposure, followed by interaction with the constituent monomer to grow polymer chains onto the base polymer, is another process that has shown some promise in developing robust membranes [86]. An account of the molecular engineering practices applied to some of the recent hydrocarbon membranes to potentially replace the perfluorinated sulfonic acid membranes was given by Byun et al. [93]. In the following passages, we discuss some of the most recent non-Nafion SPEs and different strategies and the processing methodologies for synthesizing these polymers as well as their most striking performance indicators.

Sulfonated polyimide-based membranes

Sulfonated polyimide (SPI) is another promising polymer material for PEMFCs. SPI-based membranes offer good thermal and mechanical stability. However, since they hydrolyze in the hydrated state, therefore, many studies have been dedicated to improving their hydrolytic stability. The interaction between carbonyl carbon atoms and water results in hydrolysis in SPI-based membranes. Since water is essential for protonic conductivity, therefore, hydrolysis, which imparts detrimental effects on the membrane performance, needs to be properly addressed. A strategy to address this concern is to devise methodologies that would increase the electron density of the carbon species involved. However, there is still plenty of room for improvement and research is

underway to enhance its durability with its other traits at least comparable to that of Nafion [93].

There are hundreds of research articles that have been published in the past few years on SPI-based membranes to address durability and other related concerns. Here we outline a few of the most recent research trends associated with SPI-based membranes development. One such work dedicated to a discussion on polyimides and polyimide-based composites was presented by Ayesha Kausar [94] on polyimides-based membranes for fuel cells. This study discussed polyimide and its composite-based membranes. Modified polyimides such as sulfonated polyimides and the effect of nanofillers such as silica, CNTs, graphene, titania, etc., on the proton conductivity and water stability, were demonstrated. Recently, Hooshyari et al. [95] reported a high-temperature nanocomposite membrane for proton exchange purposes by blending SPI, PBI, and $\text{SrCe}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (SCYb) perovskites. Membranes were developed with solution casting. Perovskite was reported as one of the fastest proton conductors, and the maximum power density recorded was $590 \text{ mW}\cdot\text{cm}^{-2}$. For DMFCs, some authors have reported SPI composite with bio-fillers for improving the performance. In this regard, You et al. [96] reported rice husk ash-filled SPI and demonstrated that incorporating the bio-filler improved the performance compared to that of pristine SPI. They reported proton conductivity, ion exchange capacity, and water uptake equivalent to $0.2058 \text{ S}\cdot\text{cm}^{-1}$, $0.2829 \text{ mmol g}^{-1}$, and 55.24%, respectively. The maximum power density for a passive single cell test was observed to be $13.0 \text{ mW}\cdot\text{cm}^{-2}$. Other researchers tried composites of Nafion with SPI to somewhat complement one another's limitations [97–99]. The ion exchange capacity of such composite membranes is believed to enhance with the SPI component relative to pristine Nafion. Ali et al. [100] prepared different Nafion/SPI composites that depicted an improvement in the ion exchange capacity with an increase in the SPI component addition. A maximum ion exchange capacity (IEC) of 0.88 mmol g^{-1} was demonstrated for an 80 wt % SPI blend with Nafion. In an attempt to correlate the polymer structures with proton conductivity, Ito et al. [101] prepared a series of electrospun nanofibers of varying structures from different SPIs. The membranes were prepared with solution casting. Nanofiber framework composite membrane was prepared by proper application of block graft and random SPIs. The nanofibers depicted higher proton conductivities than the corresponding membranes. The best IEC equivalent to 2.01 was recorded for the sulfonated-random-polyamide nanofibers. The composite membrane depicted an overall superior conductivity, stability, and gas permeability. In an effort to improve the weak hydrolytic stability of SPI, a cross-linked SPI with a highly branched main chain (SPI-B) was synthesized via a direct polymerization reaction by Hu et al. [102]. The IEC was similar, whereas the proton conductivity was superior to that of a normal cross-linked SPI membrane. As shown in Fig. 2, the fuel cell power density with the branched SPI membrane was $63.4 \text{ mW}\cdot\text{cm}^{-2}$, which is higher than the $43.0 \text{ mW}\cdot\text{cm}^{-2}$ of a common cross-linked linear SPI membrane. In another study, it was shown that SPI and the phosphoric acid-doped-1-methylimidazole functionalized graphene oxide (SPI/GO functionalized by $[\text{MIm}]^+ \text{H}_2\text{PO}_4^-$ (5 wt%)) composite membranes had a proton conductivity of $0.1243 \text{ S}\cdot\text{cm}^{-1}$ at 80% RH and 120°C [103].

A novel sulfonated polyimide (NSPI) [NSDA/ODA (10/90)] with a pendant sulfonic acid group was prepared from the imidization of sulfonated polyamic acid. The sulfonated polyamic acid was in turn fabricated from a sulfonated diamine (NSDA), 4,4'-oxydianiline (ODA), and 4,4'-oxydiphtthalic anhydrides (OPDA). The ionic conductivity of NSPIs was lower than that of Nafion 117 and was attributed to enhanced crosslinking in the NSPI. However, for DMFC application, the NSPI exhibited superior open-circuit voltage, current density, and power density to Nafion 117, at 70°C . Likewise, the NSPI depicted even improved power density equivalent to $46 \text{ mW}\cdot\text{cm}^{-2}$ at 140°C and was found quite stable at that temperature [104].

Graphene-based polymer membranes are another class of membranes, and a separate section has been dedicated to their discussion. However, here we would like to mention a few notable graphene-based SPI composite membranes. Generally, composites of functionalized graphene or GO and SPI are employed as composite membranes. In one study, the composite of SPI and functionalized graphene oxide was developed by adding a known amount of SPI into a suspension of sulfonated imidized GO (SIGO) (NSPI/3% SIGO). SIGO was in turn fabricated from the reaction of sulfonated diamine (NSDA), triethylamine (TEA), 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA), benzoic acid, and aminopropyl silane graphene oxide (APSGO). Whereas SPI was fabricated from the combination of NSDA, 4,4'-oxydianiline (ODA), TEA, NTDA, and benzoic acid. An IEC equivalent to 2.28 mmol g^{-1} , a proton conductivity of $0.112 \text{ S}\cdot\text{cm}^{-1}$ at room temperature, and a power density of $74.9 \text{ mW}\cdot\text{cm}^{-2}$ were reported [105].

Polybenzimidazole based membranes

High-temperature proton exchange membrane fuel cell (HT-PEMFC), is becoming of significant attraction for its high proton conductivity at elevated temperatures, low carbon monoxide contamination, no issues with water management and flooding, and simple design [106]. In this regard, PBI-based membranes are widely used in HT-PEMFCs [107]. PBI possesses outstanding proton conductivity and thermochemical and oxidative properties at high temperatures and low RH [108]. PBI is a cheap alternative to Nafion and is sufficiently stable under varying chemical and thermal conditions. These types of polymers are synthesized by the chemical casting method with phosphoric acid (PA) used as a dopant [108]. PA increases the conductivity of PBI-based composite polymers but the high amount of doping affects the mechanical and thermochemical properties of PBI due to its plasticizing nature [109].

Strong acids such as sulfuric acid and phosphoric acid tend to easily modify the heterocyclic benzimidazole ring in PBI, and hence induce protonic conductivity [110]. PBIs are usually very brittle, and this rigidity often imparts a reduction in proton conductivity. The flexibility may be optimized by dicarboxyphenyl ether, which results in poly (oxyphenylene benzimidazoles) (OPBI) development, and in turn, renders greater flexibility to the PBI because of the oxygen in the PBI main chain. Hwang et al. [110] addressed this flexibility issue by developing sulfonated OPBI by employing the above method, and further treating it with sulfuric acid and/or phosphoric acid to enhance the proton conductivity and introduce crosslinking. The sulfonated crosslinked-OPBI depicted a proton

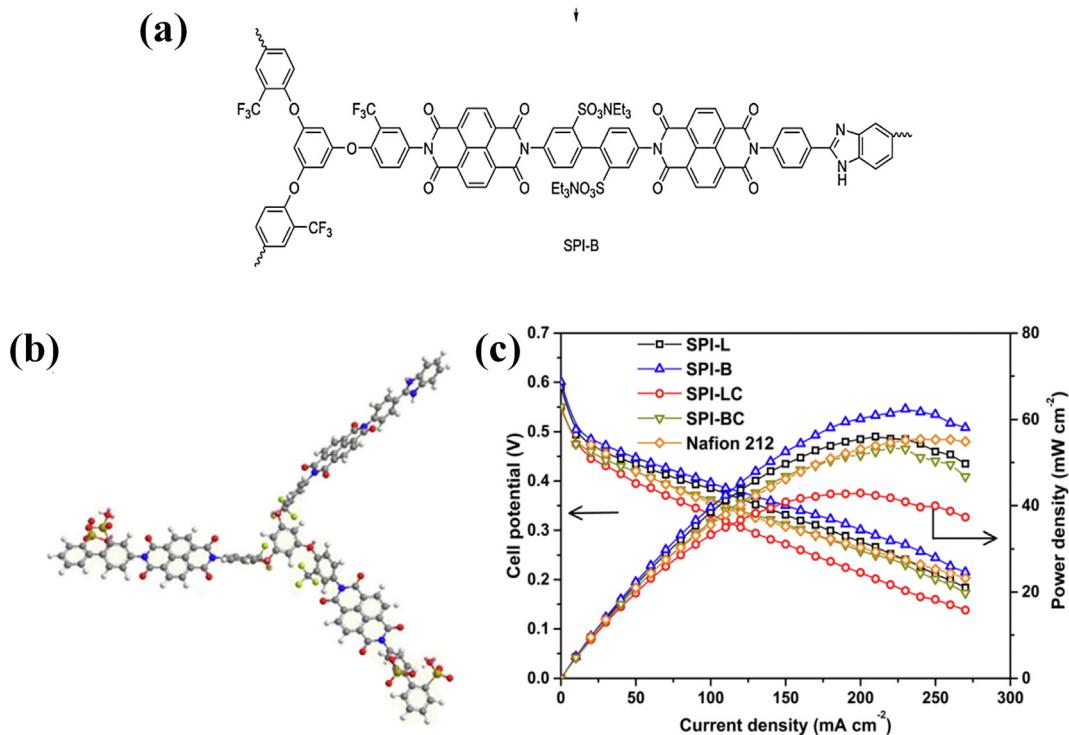


Fig. 2 – Branched Sulfonated Polyimide (SPI-B) membrane: (a-b) Chemical structure and (c) PEMFC performance (adapted from [102]).

conductivity of $0.082 \text{ S} \cdot \text{cm}^{-1}$ similar to that of commercial Nafion in this particular study ($0.09 \text{ S} \cdot \text{cm}^{-1}$), with good water uptake and dimensional stability.

The inclusion of inorganic fillers into PBI composites is also found to enhance the performance of the PBIs relative to pristine PBIs. The performance of TiO₂ incorporated PBI-composite membrane was compared with pristine PBI-based membranes and it was found that composite membrane with a power density of $1000 \text{ mW} \cdot \text{cm}^{-2}$ surpassed the performance of the pristine membranes. Moreover, it was more stable compared to pristine PBI-based membranes. The enhanced stability was traced back to the enhanced phosphoric acid retention capacity [111]. In a separate study, sulfophenylated TiO₂(s-TiO₂) was employed as a filler as well as a crosslinker to enhance the properties of PBI-based high-temperature membranes. It was noted that thermal curing turns ionic crosslinking into covalent crosslinking (Fig. 3). Moreover, both the conductivity and the fuel cell power density improved in the case of the c-sTiO₂-PBIOO based membranes [112]. In another study composite membranes of titanium oxysulfate (TiOSO₄) and poly[2,2'-(m-phenylene)-5,5'-benzimidazole] (polybenzimidazole: PBI) were prepared and it was shown that the composite membrane, due to its good acid retention, was more stable than the pristine standard PBI [113].

High temperature fuel cell stacks were reported with Poly[2,2-(m-phenylene)-5,5'-bibenzimidazole and graphene oxide (GO) composite PEM. The stack was tested with pure H₂ and a reformate gas mixture of H₂/CO/CO₂ at 160 °C. GO addition was observed to improve the PEMFC output power density relative to that of pristine PBI. The power density was also higher in the case of the reformate gas. The improved performance was associated with the improved proton conductivity due to acid retention in PBI/GO membrane. GO helps

interconnect the proton transfer channels in the polymer matrix and facilitates proton transfer [114].

N-(*p*-carboxyphenyl) maleimide (pPCM) functionalized silica nanoparticles (SNP-pPCM) modified PBI was used to enhance the interfacial properties of the SNP/PBI nanocomposites. The thermomechanical properties were found to improve with the SNP-PBI filling of PBI membranes. The ionic conductivity at 160 °C as well as the power density improved relative to the pristine PBI [115].

Since fuel cells perform better at higher temperatures and with protonic ions available in ILs, the protic ILs are known to increase the operating temperature by employing low vapor pressure ionic liquids [116]. Among the high-temperature PEMs, protic IL-based PBI is an important contender. One such high conductivity-high temperature membrane is the UV cured 1-H-3-vinylimidazolium bis(trifluoromethanesulfonyl) imide [HMIm][TFSI] protic IL cross-linked divinylbenzene (2.5 mol %). Another important protic IL/PBI-based membrane is that of UV-cured [HMIm][TFSI] ionic liquid infiltrated porous PBI (80% porosity) [117]. These were reported to depict a proton conductivity of 0.371 and $0.309 \text{ S} \cdot \text{cm}^{-1}$, respectively at 200 °C in the absence of H₂O and H₃PO₄.

Polystyrene-based membranes

Polystyrene-based membranes, based on applications are broadly classified as proton exchange/conducting membranes for the PEMFCs and anion (hydroxyl) exchange/conducting membranes for anion exchange membrane fuel cells (AEMFCs).

For proton exchanging membranes, proton conductivity is achieved by introducing sulfonic groups in the polymer, whereas the polymer backbone determines the thermal and

mechanical durability as well as ionic conductivity. Sulfonic groups could be introduced either by post sulfonation that comprises polymer treatment with a sulfonating agent or by employing sulfonated monomers to synthesize the polymer [118].

Gubler et al. [86] reviewed radiation grafted membranes with a special focus on their stability and mechanical properties. Among the different radiation grafted membranes, the review also discussed polystyrene grafts and the associated polymers as ion-exchange membranes. Kausar et al. [118] prepared nanocomposite membranes of sulfonated polystyrene (S-PS), sulfonated poly(sulfone-pyridine-amide) (S-PSPA), and functionalized multiwalled carbon nanotubes (MWCNTs) as a filler for reinforcement. Sulfonation of polystyrene was achieved by treating polystyrene with concentrated sulfuric acid. Whereas S-PSPA was developed by the phosphorylation polyamidation of sulfonated 1-(4-thiocarbamoylaminophenylsulfonylphenyl) thiourea with a 2,6-pyridine dicarboxylic acid. S-PS and S-PSPA solutions were mixed and blended with functionalized MWCNTs, followed by casting and drying. A maximum conductivity of $2.55 \text{ S} \cdot \text{cm}^{-1}$ at 80°C and 94% RH was recorded for this type of membrane.

Recently, Mahimai et al. [119] reported a series of sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (S-PSEBS) based composite membranes with CuO loaded in graphitic carbon nitride ($\text{CuO}@\text{g-C}_3\text{N}_4$) embedded with the 2,4,6-triphenylpyrylium tetrafluoroborate ionic liquid. The ion-exchange capacity of the membrane without $\text{CuO}@\text{g-C}_3\text{N}_4$ was found to be 1.8 mmol g^{-1} , whereas the 8.0 wt% $\text{CuO}@\text{g-C}_3\text{N}_4$ membrane demonstrated a maximum ion-exchange

capacity of 3.1 mmol g^{-1} . The maximum conductivity for this type of membrane was $0.0229 \text{ S} \cdot \text{cm}^{-1}$.

Sulfonated polystyrene is an important contender for PEMFCs and is widely being studied. Jalal et al. [120] reported a facile method of sulfonated polystyrene preparation. They reported the successful sulfonation of electrospun polystyrene by immersing it in dilute sulfuric acid for PEMFC applications. A maximum ion exchange capacity of 3.6 mmol g^{-1} was reported. Gong et al. [121] studied the influence of inorganic nanosilica in sulfonated polystyrene lignosulfonate-based membranes by mixing various weight percentages (SPS-LS-SiO₂% w/w). The SPS-LS-SiO₂ membranes with the nano-silica composition of 2%–5% (w/w) exhibited proton conductivity and IEC of $0.432 \text{ S} \cdot \text{cm}^{-1}$ and 3.21 mmol g^{-1} which is significantly greater than $0.374 \text{ S} \cdot \text{cm}^{-1}$ and 0.94 mmol g^{-1} of Nafion 117 with a 35% decrease in methanol crossover.

Besides proton conducting membranes, hydroxide ion-conducting membranes are widely studied for anion exchange membrane fuel cells (AEMFCs). Polystyrene-based anion exchange membranes are currently being heavily investigated for such applications. Chae et al. [122] fabricated a polystyrene-based electrode ionomer via radical polymerization, followed by grafting polystyrene with Bromo-alkyl chains through Friedel–Crafts acylation, reduction, and subsequent quaternization. As shown in Fig. 4, the quaternary-ammonium-group-bearing ionomers exhibited a maximum ion exchange capacity of 1.74 mmol g^{-1} with a fuel cell performance of $407 \text{ mW} \cdot \text{cm}^{-2}$ was evidenced for optimized ionomer-based AEMFCs.

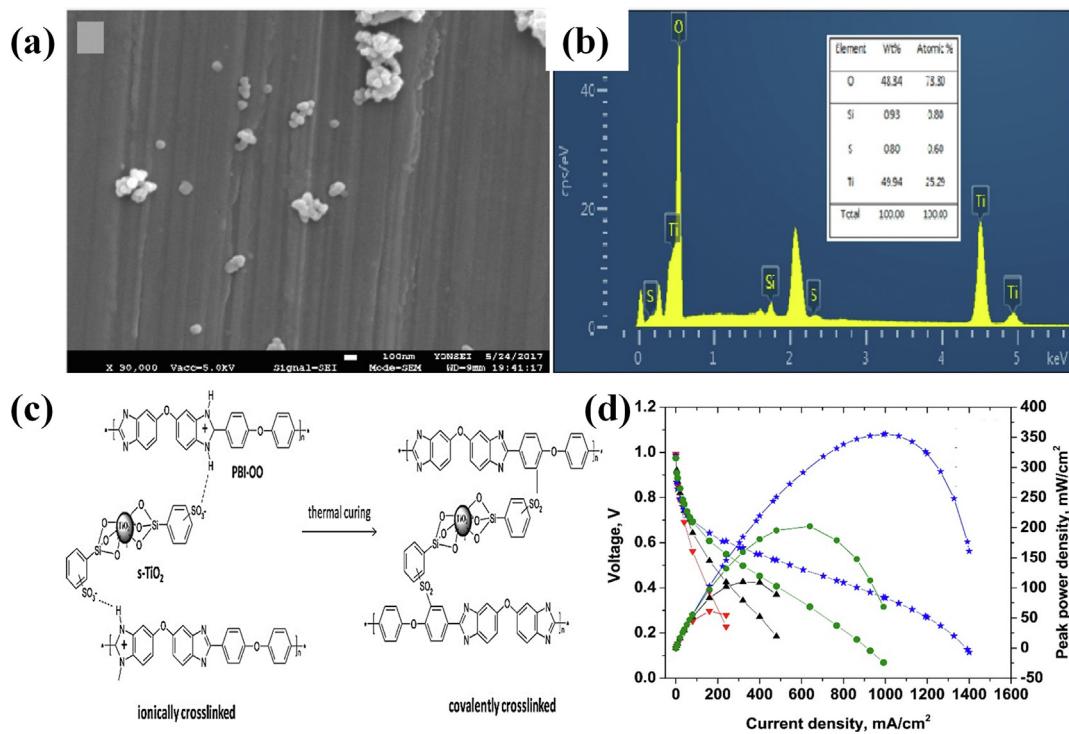


Fig. 3 – Covalently crosslinked nanocomposite of sulfophenylated TiO_2 and PBI (c-s TiO_2 -PBIOO): (a) SEM, (b) EDS (c) Structure and (d) PEMFC performance (adapted from [112]).

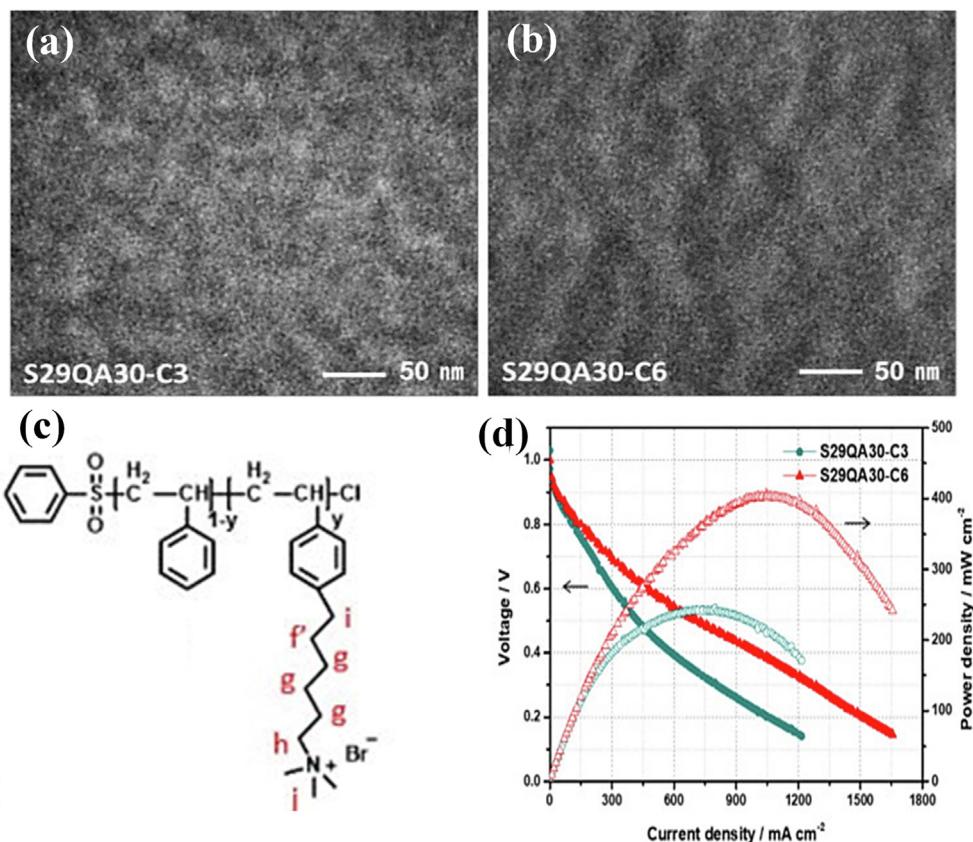


Fig. 4 – Polystyrene based ionomer membrane: (a-b)TEM, (c) structure, and (d) AMFC performance (adapted from [122]).

Tuli et al. [123] employed the *in situ* click crosslinking to fabricate poly(vinyl benzyl chloride) (PVBC) based membranes functionalized with alkyne and azide side groups for alkaline fuel cells. The trimethylammonium cationic groups rich membrane with 20% crosslinking, when immersed in KOH exhibited a maximum hydroxide ion conductivity of $156 \text{ mS} \cdot \text{cm}^{-1}$. The recorded peak power density was $157 \text{ mW} \cdot \text{cm}^{-2}$. In a separate study, Tuli et al. [124] synthesized azide and trimethylammonium functionalized polystyrene-based block and random copolymers via nitrogen-mediated living radical polymerization and correlated the morphology with anion ion conductivity. The block copolymers had ordered spherical nanostructure and depicted superior conductivity to the random copolymers in high molar KOH solutions. Moreover, a higher hydration number was conceived as beneficial for enhanced conductivity of block copolymers in free hydroxyl environments. Similarly, Xue et al. [125] proposed a quaternized-azidated poly(2,6-dimethyl-1,4-phenylene oxide) crosslinked poly(4-vinylbenzyl chloride) for alkaline fuel cells. The azidated poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-N₃) crosslinked poly(4-vinylbenzyl chloride) (PVBC) was obtained by UV exposure of the mixed casted solution of these precursors. The benzyl chloride was subsequently converted into quaternized benzyl trimethylammonium chloride groups by treating it with trimethylamine solution. The crosslinking improved the mechanical and chemical properties of the membranes. The maximum conductivity recorded for this type of membrane is $14.8 \text{ mS} \cdot \text{cm}^{-1}$ at 20°C , whereas the ion exchange capacity equals $1.95 \text{ mmol} \cdot \text{g}^{-1}$. A power density of $11 \text{ mW} \cdot \text{cm}^{-2}$ was achieved at 60°C under full humidification.

Likewise, Gupta et al. [126] prepared a chloromethylated polystyrene-based soluble ionomer for anion ion exchange in alkaline fuel cells. Polystyrene-b-poly(ethylene/butylene)-b-polystyrene (60 wt % styrene) was dissolved in chloroform, followed by trioxane, chlorotrimethylsilane, and tin chloride addition in a controlled environment. The mixture was subsequently washed with methanol/water mixture to remove the reagents. An IEC of 1.91 mmol g^{-1} and the hydroxyl conductivity equivalent to $0.18 \text{ S} \cdot \text{cm}^{-1}$ were reported at 100% relative humidity and 70°C operating temperature. Similar work has also been done by mixing polystyrene with PEEK [127–129], PVDF [130–133], PTFE [134,135], and other acids to improve the performance of polystyrene-based membranes.

Polyphosphazene-based membranes

Due to its superior thermal and chemical stability, as well as ease of side chains attachment to the $-\text{P}=\text{N}-$ backbone, polyphosphazene-based cation exchange membranes are important for H_2/O_2 PEMFCs and DMFCs [136]. Due to the $-\text{P}=\text{N}-$ bond, polyphosphazene-based membranes have high torsional mobility. Since the P and N species are in their highest oxidation states, they are resistant to further oxidation. Moreover, it is preferred for PEMFCs because of the stable backbone in the free-radical cleavage reaction. Likewise,

structural modifications are possible relative to the pendant groups. Because of the limited number of studies dedicated to polyphosphazene-based membranes, the true potential of this class of PEMs is yet to be explored [93].

It was in 1999 when its potential application for fuel cells was explored. Sulfonated and crosslinked polyphosphazene (sulfonated-POP) membranes with IEC of 1.4 mmol g^{-1} were developed from poly[bis(3-methylphenoxy) phosphazene]. The membranes were found to be thermochemically stable at operating temperatures up to 173°C [136].

Polyphosphazene-based copolymers containing alkyl sulfonated side chains ($\text{PFMPP}_1\text{-r-PFSPP}_9$) were reported to exhibit a proton conductivity of 0.14 S cm^{-1} as well as significant methanol resistance in the range from 1.35 to $7.18 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ [137]. Crosslinked polyphosphazene-based graft co-polystyrenes with alkyl sulfonate branch chained membranes (F-PSBOS_{26}) are also being studied for methanol diffusion mitigation. The proton conductivity is almost 1.5 times that of Nafion 117 at 80°C [138].

To study the effects of the degree of sulfonation on the cross-linked polyphosphazene grafted butylphenoxy PEMs, a study was conducted by Ouadah et al. [139]. It was revealed that the proton conductivity increased as a function of the grafting degree of the sulfonic acid. Moreover, the proton conductivity was found to increase with the operating temperature. The membranes which were thermally stable up to

250°C , were also found to be more conductive than Nafion 117. The swelling ratio and water uptake were found acceptable.

Composite membranes are also important contenders. The composite membranes of sulfonated polyphosphazene-graft-copolystyrenes and sulfonated carbon nanotubes ($\text{CF}_3\text{-PS}_x\text{-PSBOS}_y\text{-SCNT}$) exhibited excellent proton conductivity (i.e. 2.6 times that of Nafion 117) and methanol resistance [140]. Recently researchers have used Zirconium [141–143], Titanium [144–147], Cerium [148,149], and many others [150] to enhance the performance of PBI-based composites.

Sulfonated aromatic main-chain polymers: SPAEK, SPEEK, SPAS and SPEN

Low cost, better mechanical strength, and good chemical and thermal stability are among the features that made sulfonated aromatic main-chain polymers the materials of interest for membranes [151,152]. The most studied compounds for the PEMs in sulfonated aromatic main-chain polymers are sulfonated poly (arylene ether ketones) (SPAEKs) and sulfonated poly(ether ether ketone)s (SPEEKs) [153–155]. Due to the commercial availability of PEEK polymers (progenitor) and possessing properties of other compounds, the SPEEK based membranes are most widely used than SPAEK [156]. Fig. 5 shows the basic structures of aromatic sulfonated poly

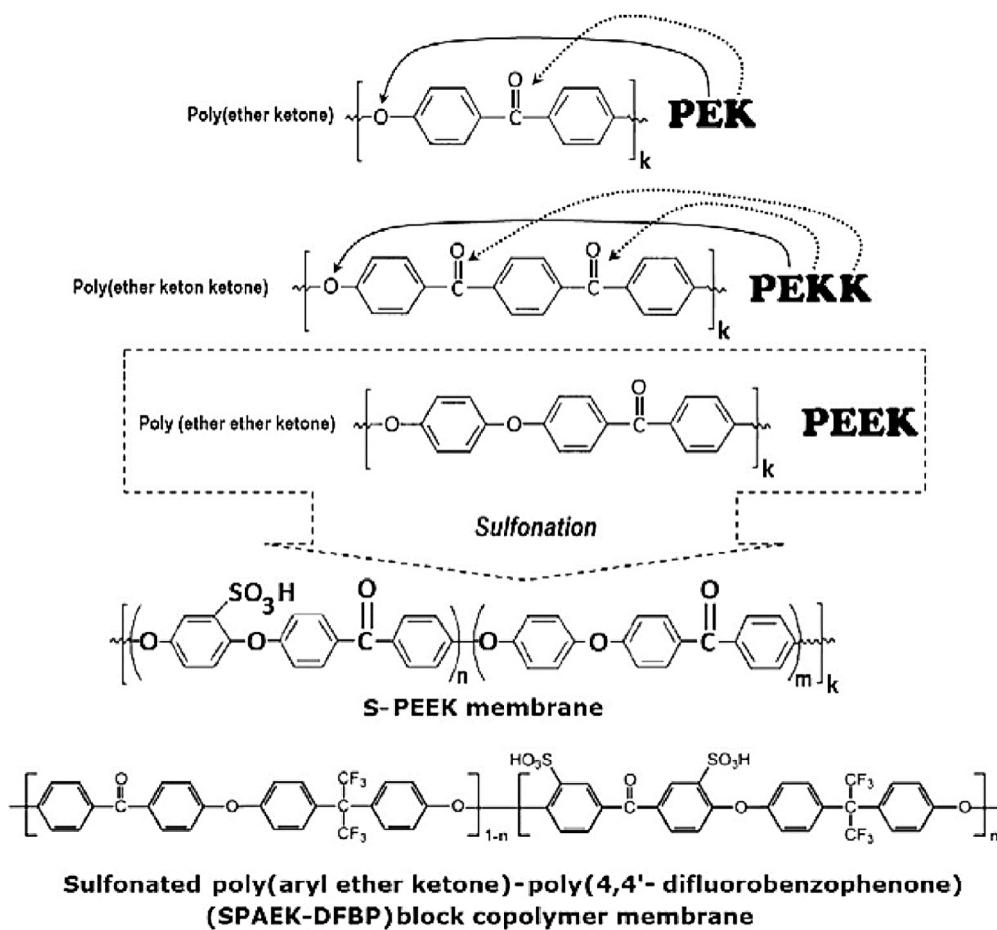


Fig. 5 – The basic structures of PEK evolved into PEKK, PEEK, and SPEEK [157].

(ether ketone) and its copolymer membranes i.e. PEKK, PEEK and SPEEK [157].

SPAEK-based membranes suffer low operational stability and degrade faster than Nafion despite the reported 3000 operational hours [158]. This is due to the attack of OH^- radicals on the non-sulfonated phenyl ether aromatic rings (Fig. 6) which causes scissions in the main SPAEK chain and results in material degradation [159,160].

The above Fig. 6 shows that optimization of the sulfonic group location (SPAEK is more stable when SO_3 groups are linked to the pendant chain rather than the main chain) and fluorination of the main-chain phenyl groups have both been attempted to increase the stability of SPAEK [161]. The level of

dissociation of sulfonic groups is very little compared to Nafion. This is because rigid aromatic structure along with low acidity of SPAEK results in thinner hydrophilic channels compared to the Nafion which creates wider gaps among sulfonic acid functional groups thus delaying proton transport [162–164]. In general, the strength, conductivity, and water absorption of the membrane are controlled by the hydrophilic and hydrophobic domains of the polymer materials [165]. However, crosslinking can enhance conductivity along with chemical and mechanical properties. Duan et al. [166] prepared an amino-sulfonic acid-based bi-functionalized metal-organic framework (MOF) MNCS@SNF-PAEK consisting of ionic cross-linking structure in SPAEK. As shown in Fig. 7, the

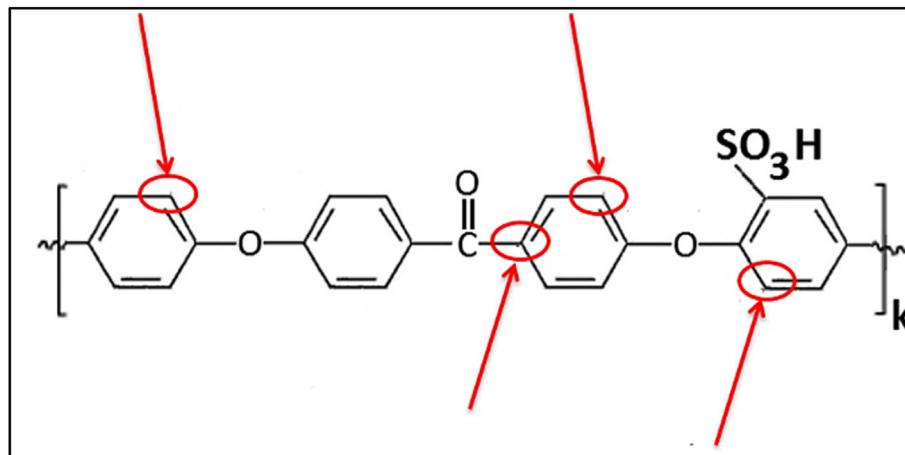


Fig. 6 – Weak points for OH^- radical attack [160].

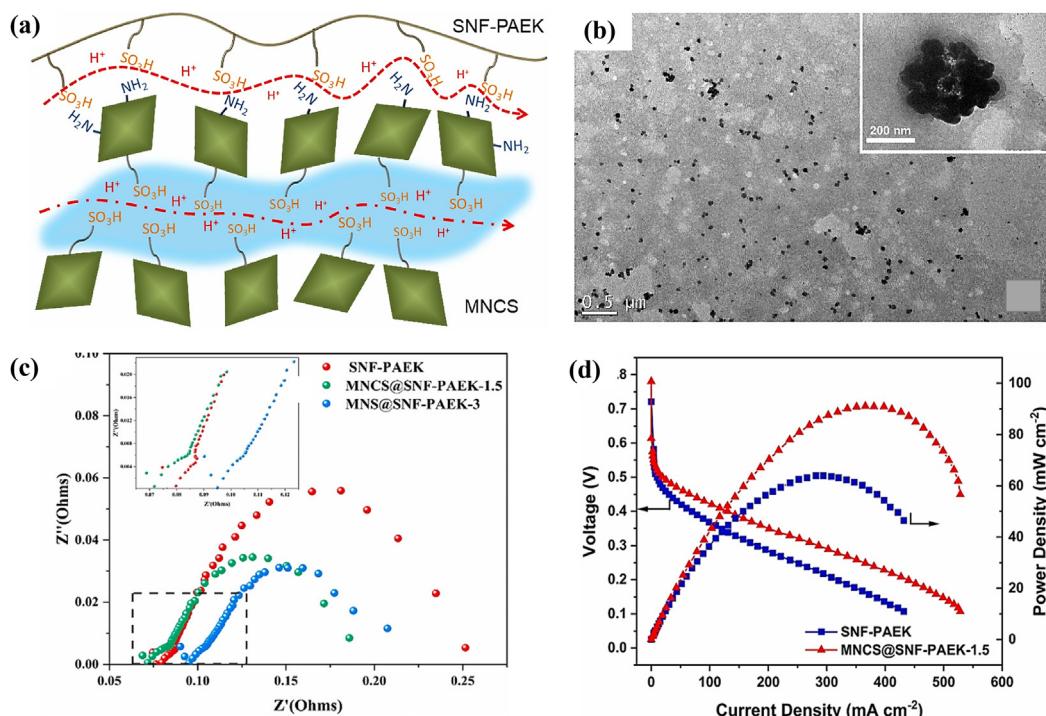


Fig. 7 – Amino-sulfonic acid-based bi-functionalized MOF (MNCS), containing flexible SPAEK: (a) Structure, (b) TEM, (c) EIS analysis, and (d) DMFC performance (adapted from [166]).

membrane MNCS@SNF-PAEK-1.5 with 1.5 wt% MNCS exhibited excellent proton conductivity of $0.188 \text{ S}\cdot\text{cm}^{-1}$ along with a fuel cell power density of $91 \text{ mW}\cdot\text{cm}^{-2}$. This is due to the high content of amino groups on its surface, which could form more acid-base ionic pairs with the sulfonic acid groups of SNF-PAEK. Neelakandan et al. [167] synthesized SPAEK composite membrane with surface-functionalized fullerene (BSPAEEKS/S-Fu) through the solution casting method with 0.25–1.0 %wt. of s-Fu. BSPAEEKS/S-Fu with 0.75 wt % displayed maximum proton conductivity of $0.322 \text{ S}\cdot\text{cm}^{-1}$ with fuel cell performance of $74.38 \text{ mW}\cdot\text{cm}^{-2}$ which is higher than both pristine BSPAEEKS and Nafion-212 membrane. This is due to the addition of s-Fu into the BSPAEEKS matrix providing the additional proton conduction sites and hydrogen bond formation between the filler and polymer results in better proton conduction pathways. The recently reported data regarding the cross-linked SPAEKs suggests that they might be suitable for high temperatures fuel cell applications [168–174].

In addition to that, several researchers have incorporated different inorganic materials such as sulfonated/silylated polyphenylsulfone [175], PVDF [176] phosphonated polysulfone [177], poly acids [178], Zirconia [179], SiO_2 [180], TiO_2 [181], and Nafion, etc. with SPAEK materials to obtain improved desired properties for electrochemical applications.

Sulfonation increases the conductivity of SPEEK based membranes e.g. SPEEK membranes with a sulfonation level of 80%, possess conductivity over $0.102 \text{ S}\cdot\text{cm}^{-1}$ [182]. However, high sulfonation of SPEEK membranes affects the chemical stability because of OH^- attack [183,184]. Chen et al. [185], reported that the SPEEK membrane can be deformed and may turn into gel-like material if immersed in hot water for a long time. This is due to the addition of the hydrophilic sulfonic acid group contributing to the poor mechanical stability of the membrane [186]. SPEEK membrane-based FCs perform best at a certain threshold sulfonation level, which is dependent on the specific polymer backbone structure and membrane morphology. For example, optimal fuel cell performances were reported for a SPEEK based membrane with a sulfonation ratio of 43 [187] and 80% [162], respectively. Optimized properties have been obtained from the development of modified membranes [188]. Lower hydrophilicity and methanol diffusion along with better mechanical, thermal, hydrolytic, and oxidative stability have been obtained through cross-linking SPEEK based membranes. However, crosslinking also makes the SPEEK structure more rigid which impedes proton conduction of the membrane [189].

With the advancement of the techniques, various cross-linkers have been developed which in turn enhanced the properties of cross-linked SPAEKs [190]. Song et al. [191] prepared SPEEK/PBI composite membrane for HT-PEMFC through the ionic crosslinking method by dipping SPEEK-Na/PBI in dilute acid. Maximum proton conductivity of $0.1985 \text{ S}\cdot\text{cm}^{-1}$ was obtained for SPEEK/PBI (20% wt.) at 170°C at 100% RH. Che et al. [192] polymerized ionic liquid (IL) monomer of (acryloyloxy)propylimidazolium chloride having unsaturated C=C double bond with SPEEK resulting in crosslinked SPEEK/PIL. Along with chemical stability, the SPEEK/PIL was further doped with phosphoric acid (SPEEK/PIL/PA) to increase the proton conductivity up to $0.04 \text{ S}\cdot\text{cm}^{-1}$. Highest conductivity of $0.185 \text{ S}\cdot\text{cm}^{-1}$ was obtained for SPEEK-based composite

membrane with sulfonated poly(ether ether ketone)-poly(ethylene glycol) cross-linked interpenetrating polymer network/ SiO_2 (SPEEK-PEG/ SiO_2) by sol-gel method [193]. As shown in Fig. 8 the membrane with 10% Wt. SiO_2 showed excellent properties $379 \text{ mW}\cdot\text{cm}^{-2}$ at 60°C . Hasani et al. [194] prepared sulfonated polyether ether ketone (SPEEK) and intercalated it with different proportions of organically-modified montmorillonite (MMT). The SPEEK membrane with 1% MMT showed excellent performance owing to high proton conductivity, power density, and open-circuit voltage (OCV) as compared to the original SPEEK and Nafion 117.

The results indicated that the nanocomposite approach (cross-linking along with inorganic additive) enhanced the membrane properties to a great extent and the membrane can be used as an alternative in fuel cell application. There is much literature that reports the incorporation of other inorganic materials such as TiO_2 [195–197], SiO_2 [198–203], CeO_2 [204], metal oxides MO_x 's [205], CNT's [206,207], Zirconia [208–211], and other polymers such as PVDF [203,212–214], PBI [215–218], PTFE [219–222] and ionic liquid-based polymers [223–230] in SPEEK matrix to enhance properties along with conductivity in proton exchange membrane fuel cell.

Sulfonated poly(aryl sulfones) (SPAS) membrane based on sulfonated aromatic mainchain polymers was first synthesized by Zschocke et al. [231] in 1985 and was utilized for the first time in 1988 by Arnold Jr et al. in redox batteries [232]. SPAS like polysulfones, polysulfone ethers, and polyphenyl sulfones are polymers similar in nature to the SPAEKs polymers. These materials are non-crystalline thus unlike SPAEKs, the chemical alteration governs their mechanical properties. Also, it is expected to possess certain properties like thermal and chemical stability after the sulfonation of the material as the precursor polymer material is thermally and chemically stable [233,234].

Materials having these characteristics are thought to be feasible for PEMFC applications [235]. For example, the SPAS-based materials (SPAEK-based materials) showed poor stability against superoxides than Nafion [236]. Moreover, the SPAS molecular structure possesses similar characteristics to SPAEK in terms of the material degradation process and critical OH^- attacking points [237]. The conductivity, water absorption, and stability of the SPAS materials are considerably affected by the sulfonation process and specific point of attachment of the sulfonic acid group to the polymer structure [238]. Furthermore, techniques like including thioether to the SPAS main-chain and preparing them with greater electro-negative groups [239,240] partial fluorination of the phenyl group [241], and sulfonation of side chains can improve the material stability [242].

Lee et al. [243] synthesized the SPAES membrane with aliphatic chains (SPAES-LAs) via controlling oligomer lengths. The membrane possessed conductivity and fuel cell performance of $0.158 \text{ mS}\cdot\text{cm}^{-1}$ and $232 \text{ mW}\cdot\text{cm}^{-2}$, which is less than the commercial Nafion membrane. Yet, due to the effects posed by limited proton mobility owing to small channels and low dielectric permeability of water within the hydrophobic channels, the SPAS membranes can only achieve the conductivity equivalent to Nafion if the polymer chain has a significant amount of sulfonation [244]. The high level of sulfonation of the SPAS polymer chain can alter the physical

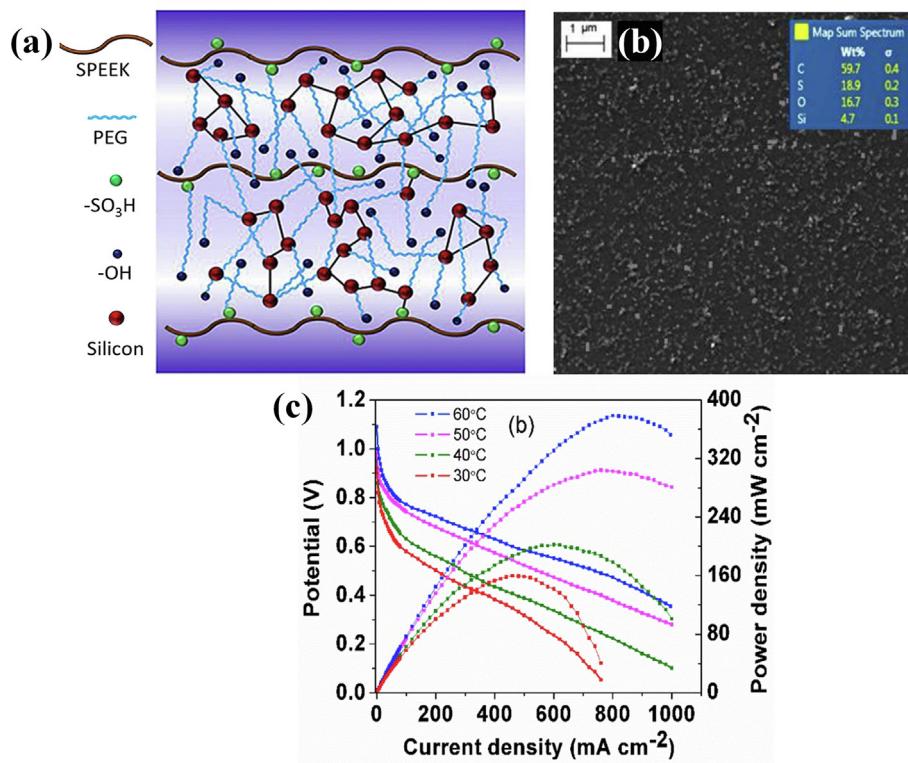


Fig. 8 – Sulfonated poly(ether ether ketone)-poly(ethylene glycol) cross-linked interpenetrating polymer network/SiO₂ (SPEEK-PEG/SiO₂): (a) Conduction mechanism in chemical structure, (b) SEM, and (c) DMFC performance (adapted from [190]).

properties of the material and decrease its permeability to the methanol [245]. So far different techniques like SPAS/inorganic composites [245–254], blending with other polymers [255–257], attaching various functional groups to the main and side chain [258–263], crosslinking between the polymer chains [189,260,264–270], etc. have been utilized to optimize the conductivity and physical and chemical properties SPAS-based membranes.

Among the sulfonated aryl ether group, the Sulfonated poly(arylene ether nitrile)s (SPEN) have been identified as an excellent matrix for proton conduction in advanced composite membranes in DMFCs [271,272]. SPEN possesses remarkable chemical resistance, excellent mechanical properties, high thermal stability, and good malleability [273]. The presence of the side nitrile polar group in SPEN has a great potential for functionalization with other cross-linking polymers through intermolecular interactions to provide enhanced properties in PEM such as water uptake, and reduced swelling ratio, without compromising the conductivity of the membrane [274]. In addition, the nitrile group promotes the adhesion of the polymer to many substrates with other chemical groups through functionalization to facilitate the adhesion of catalyst to PEM [275,276]. In this regard, Pu et al. [277], synthesized a series of SPEN-based membranes through the nucleophilic aromatic substitution polymerization of hydroquinone sulfonic acid potassium salt (HQ), 2,6-difluorobenzonitrile (DFBN) with various bisphenol monomers using K₂CO₃ as a catalyst. The synthesized polymers exhibited good thermal stability, water uptake,

proton conductive, and an outstanding IEC. In particular SPEN with bisphenol monomer, “phenolphthalin (PPL/SQH) exhibited outstanding IEC of 2.3 mmol. g⁻¹ with proton conductivity and water uptake value of 0.0043 S·cm⁻¹ and 73% respectively. The membrane was recorded with the wet tensile strength of 23 Mpa and methanol permeability of 10⁻⁷ cm² s⁻¹. Results indicate that these SPEN copolymers are prospective candidates for application in DMFCs. Shin et al. [278], Sulfonated poly(arylene sulfide sulfone nitrile)s (SN) to investigate the effects of naphthalene units in the polymer backbone on membrane properties. Molecular dynamic simulations and small-angle X-ray scattering patterns (SAXS) show that naphthalene in the main chain reduced interdomain distance and exhibited excellent chemical and mechanical properties, better than those of their sulfonated phenylene (SP) counterpart. The SN membranes exhibited proton conductivity, IEC, and water uptake of 0.123 S·cm⁻¹, 1.99 mmol. g⁻¹ and 65% respectively. Furthermore, a single cell DMFC performance of SN membranes showed a power density of 109 mW·cm⁻² compared to 97 mW·cm⁻² of SP membranes with the lowest methanol permeability (62×10^{-8} cm² s⁻¹) at 80 °C using 2 M methanol and air as a fuel and oxidant. These results were higher than commercial DMFC Nafion-212 which has a DMFC power density of 83 mW·cm⁻². These results demonstrate favorable effects of the naphthalene unit in SN polymer membranes. This result demonstrates the beneficial effects of the naphthalene in SN membranes on the chemical and mechanical properties of the PEMs during fuel cell operation. In another study, a series

of SPEN composite membranes with embedded tungstophosphoric acid (TPA) were prepared with various weight percentages (10 wt%, 30 wt%, and 50 wt% of 2 g SPEN) [279]. The SPEN-TPA 50 wt% composite membrane showed good proton conductivity of $0.107 \text{ S} \cdot \text{cm}^{-1}$ at 80°C with an excellent IEC value of $1.66 \text{ mmol. g}^{-1}$ compared to $0.89 \text{ mmol. g}^{-1}$ of Nafion-117. Furthermore, the water uptake and swelling ratio were recorded to be 99% and 47% at the same temperature. The high performance at elevated temperatures was regarded to the presence of the hydrogen bonding networks and the electrostatic interactions. Researchers around the world have prepared various composites of SPEN to enhance DMFC performance including GO and CNTs [274,280–283], phenolphthalein [281], and carboxylic groups [282,284], sulfonated covalent triazine framework (SCTF) [285], and silica [286], etc.

Membranes derived from natural polymers

Polymeric membranes derived from natural materials are nontoxic and inexpensive natural candidates for PEMFCs that have the potential to replace synthetic polymer electrolyte membranes e.g., Nafion. There are very limited studies that investigated natural polymer-based membranes in PEMFCs such as cellulose [287–289], pectin [290,291], chitin [292–294], and alginic acid [295–298]. On the other hand, there has been extensive research going on the use of chitosan-based membranes in PEMFCs.

Chitosan (CS) is the second most abundant polysaccharide-based biopolymer that is obtained by alkaline deacetylation of chitin. It exists in the exoskeleton of crustacean animals such as crabs, shrimps, prawns, etc. [299]. CS is a biodegradable, non-toxic, material and possesses pH dependent cationic charge density in solution so that it can form complexes with other anionic polymers [300]. CS is a promising membrane material for PEM due to its biocompatibility, low methanol (fuel) crossover, and ecofriendly but it suffers from low proton conductivity as compared to Nafion i.e. ($10^{-4} \text{ S} \cdot \text{cm}^{-1}$) which is insufficient for FC operation [301,302]. This is due to its highly crystalline nature and lack of proton mobility [301]. The lack of proton mobility in CS is

due to partial protonation of weak alkaline groups in its main chain [301,302]. The conductivity in CS occurs through the transport of OH^- across the small amorphous region shown in Fig. 9.

The proton conductivity of the CS membrane can be increased by introducing proton donors into its matrix which might be achieved by adding inorganic fillers. In this regard, Divya et al. [303] incorporated 2D MoS₂ sheets with various wt. % in CS for proton exchange membranes. The composite membrane with 0.75% MoS₂ possesses good proton conductivity of $0.00361 \text{ S} \cdot \text{cm}^{-1}$ along with the highest water uptake and IEC compared to commercial Nafion 212. In addition, the incorporation of MoS₂ increased the hydrophilic nature of the composite membrane along with thermal and chemical stability due to hydrogen bonding between CS and MoS₂. In a separate study, CNTs were coated with silica through the sol-gel technique and later mixed with CS to obtain CS/SCNTs based composite membrane [304]. The silica-coated CNTs eliminated short circuit current between SCNTs and CS and provided uniform dispersion through the CS matrix which in turn enhanced the thermal stability and mechanical properties of CS/SCNTs. Moreover, CS/SCNTs-5 with 5 wt% of SCNTs exhibited $0.025 \text{ S} \cdot \text{cm}^{-1}$ with decreased water uptake compared to uncoated silica. This is because the coating has covered the functional groups of CNTs. Wang et al. [305] functionalized CNTs with polydopamine through the facile coating method and later incorporated them into the CS matrix followed by ion cross-linking with sulfuric acid (CS/PDA@CNTs) for PEMs. Maximum proton conductivity of $0.028 \text{ S} \cdot \text{cm}^{-1}$ was obtained at 80°C with 2 wt% loading of PDA@CNTs. The hydrogen bonding formed between the $-\text{OH}$ group of the PDA@CNTs and the $-\text{NH}_2$ group of the CS matrix improved thermal, chemical, and oxidative stability while NH_3^+ in both PDA and CS chains that were ion cross-linked by sulfate ions (SO_4^{2-}) provided an additional and low barrier pathway for proton transfer through the electrostatic interaction, which makes such composites attractive candidates in PEM applications. Several researchers have incorporated different acids and acidic salts [306–314], inorganic fillers [315–321], polymers [322–328], and other natural biopolymers [329–331] in CS to improve the properties of CS-based membranes for PEMFC.

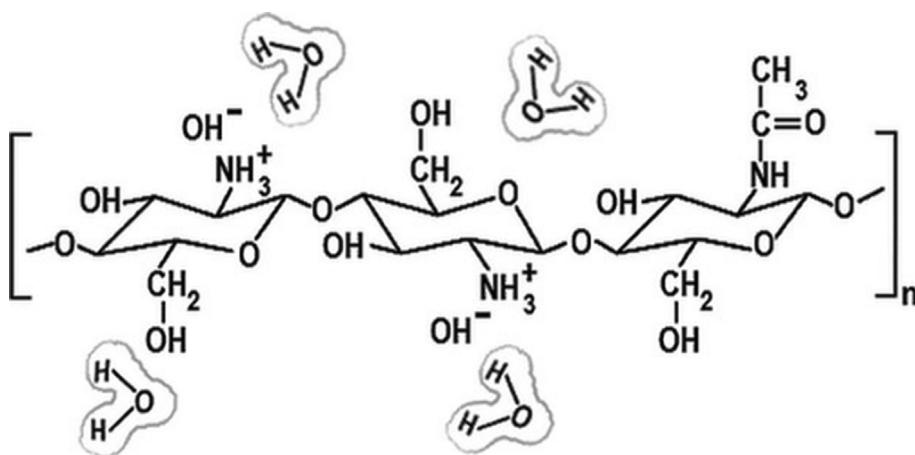


Fig. 9 – Partially hydrated/alkylated CS [302].

Carbon nanotubes based composites

Carbon and its allotropes have attracted significant attention to be used in fuel cell systems due to their high abundance, chemical, and thermal stability, large surface area, high electron mobility, and being environmentally friendly. Such properties make it attractive for applications in the fuel cell membrane and electrode materials. The commercial-scale electrode used for PEM fuel cell is Platinum dispersed on high surface area carbon (comm Pt/C) [332]. Carbon nanotubes (CNTs) have been a hot topic in energy materials for storage and conversion for many years due to their large surface area. For example, the theoretical surface area of single-walled carbon nanotube (SWCNTs) has been estimated to be $1315 \text{ m}^2 \text{ g}^{-1}$ [333]. CNTs are 2D single sheets of graphene material rolled up in the form of tubes. The electronic structure of CNTs consists of both sp^2 hybridized σ and delocalized π bonds. The σ bonds are not actively involved in the bonding process while π bonds are the active ones and overlap one another, which tends to minimize the surface energy and, as a result, accounts for the exceptional stability of CNTs [334].

CNTs have wide applications due to their superior mechanical, chemical, and electronic properties. The applications include fiber-reinforced polymer composite for automotive [335], aerospace [336], construction [337], textile [338] and energy [339]. In particular, CNTs find wide applications as energy storage materials for hydrogen storage [340] and anode material Li-Ion batteries [341]. CNTs offer a huge advantage when it comes to enhancing the conductivity of an

electrolyte. Feng et al. [342], synthesized multi-layer composite membranes containing SCNTs with various wt.% embedded in the SPEN matrix through a facile step-by-step solution casting technique. As shown in Fig. 10, the SPEN/SCNTs/SPEN composite membrane with 3 wt% SCNTs achieved an excellent proton conductivity of 0.094 and $0.275 \text{ S}\cdot\text{cm}^{-1}$ at 20 °C and 80 °C which is higher than commercial Nafion-117. Furthermore, the multilayered structure made the membrane more compact leading to lower-dimensional swelling and methanol permeability. A PBI-decorated CNTs were doped with phosphotungstic acid (PWA-PBI-CNT) as a superacid and were incorporated into the Nafion matrix to fabricate composite membranes [343]. The synthesized composite membrane possessed good water retention properties and provided higher proton conduction ($0.1951 \pm 0.0078 \text{ S}\cdot\text{cm}^{-1}$) at 90 °C. This is due to the acid-base interaction between imidazole groups of PBI and sulfonate groups of Nafion which facilitate proton conductivity at elevated temperatures. Moreover, a single cell PEMFC test resulted in an outstanding power density of $386 \text{ mW}\cdot\text{cm}^{-2}$ compared to the commercial Nafion-117 membrane ($73 \text{ mW}\cdot\text{cm}^{-2}$) at 40% RH. Kannan et al. [344], developed a highly stable PBI-based composite PEM by incorporating phosphonated MWCNTs (P-MWCNTs) in phosphoric acid doped PBI. Superior proton conductivity ($0.115 \text{ S}\cdot\text{cm}^{-1}$) along with maximum fuel cell power density ($780 \text{ mW}\cdot\text{cm}^{-2}$) was observed for 1 wt% of P-MWCNT doping (PBpNT-1%). The authors attributed the high performance to the formation of a network of proton conduction paths in the composite membrane by the incorporation of functionalized MWCNTs which improved key parameters contributing to

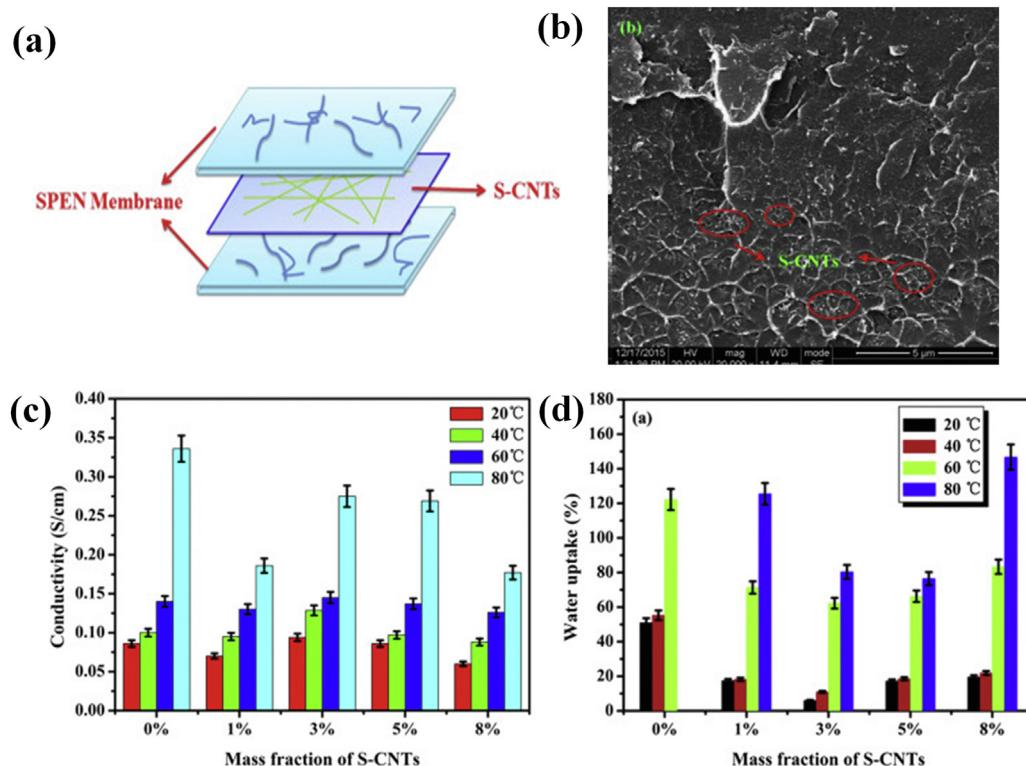


Fig. 10 – Multi-layers CNTs/SPEN PEM membrane: (a) Schematic, (b) SEM, (c) Conductivity and (d) Water uptake analysis.

enhanced fuel cell performance. In another study, a PA doped composite membrane consisting of PBI and non-functionalized MWCNTs (PBICNTPA) was prepared for PEMFC [345]. PBICNTPA an excellent thermal and chemical stability and possessed proton conductivity and a single-cell PEMFC power density of $0.075 \text{ S}\cdot\text{cm}^{-1}$ and $173.5 \text{ mW}\cdot\text{cm}^{-2}$ at 180°C . Similarly, other literature studies also demonstrate incorporating PBI and CNTs to improve the performance of high-temperature PEMs [346–349].

Proton conductivity in SPEEK membranes can be increased by more sulfonation but usually, it reduces its resistance toward chemical oxidation and mechanical strength [350]. The incorporation of CNTs in the SPEEK matrix can be an alternative route to increase the overall performance of SPEEK membranes [351]. Gahlot et al. [352], increased the proton conductivity and water retention of the SPEEK membrane by incorporating electrically aligned functionalized carbon nanotube f-CNT with sulfonated polyether ether ketone (SPEEK) through the solution casting method. The alignment of CNTs was done by applying a constant electric field of 500 V cm^{-2} to avoid misorientation during the membrane drying process. In particular, the nanohybrid membrane with 0.5 wt% concentrations of functionalized CNTs possessed the highest proton conductivity and IEC of $0.125 \text{ S}\cdot\text{cm}^{-1}$ and 2.19 mmol g^{-1} . In addition, the membrane has the lowest methanol permeability of $1.68 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and 44% water uptake. Sun et al. [353], prepared a series of composite PEMs by hybridizing 2D zeolitic imidazolate framework (ZIF-8) with CNTs (ZCN) through hybrid crosslinking and incorporating into the SPEEK matrix. Taking advantage of the morphological and compositional properties of MOF [116], and CNTs, the SPEEK/ZCN-2.5 (2.5 wt% of ZCN) showed an appreciable improvement in proton conductivity ($0.05 \text{ S}\cdot\text{cm}^{-1}$ at 120°C) which was better than recast SPEEK and SPEEK/ZIF membrane by 11 and 2 folds. In addition, the IEC and water uptake were recorded to be 1.48 mmol g^{-1} and 40% with a low methanol permeability and swelling ratio of $2.45 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and 8.6% respectively. The authors concluded that proton conductivity and methanol permeability of the MOF/polymer composite membranes can be effectively tailored through engineering MOFs structures rather than altering the chemical component.

Similarly, CNTs have been incorporated as reinforcements in many polymer matrices such as PBI [354,355], SPEEK [129,356–361], SPAS [362–364], phosphotungstic acid [365–368], and chitosan [305,369–372] to enhance the overall performance of PEMs over a wide range of temperatures.

With time, the research direction was shifted from cylindrical shape CNTs towards the use of 2D carbon material called graphene [373,374]. Since that time graphene has been used in various applications such as electrochemical energy devices [375], polymer composites [376,377], sensing and detection [378,379], electronics [380,381], Photonics [382,383] nanoelectromechanical systems [384], drug delivery [385], and other biomedical applications [386].

Graphene

Graphene is a 2D carbon allotrope, atomic scale, honeycomb lattice in which one atom forms each vertex. It is the basic

structural element of other allotropes such as graphite, charcoal, carbon nanotubes, and fullerenes. It can be considered an infinitely large aromatic molecule. Graphene is a single layer of carbon packed in a hexagonal lattice, with a carbon distance of 0.142 nm [387]. It is two-dimensional crystalline material and representative of a whole class of 2D materials, including a single layer of Boron Nitride (BN), and molybdenum disulfide (MoS₂). The 2D carbon allotrope graphene is about 100 times stronger than the strongest steel with a hypothetical thickness of 3.35 A° , which is equal to the thickness of the graphene sheet. The carbon-carbon bond length in graphene is about 0.142 nm . Graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm [388]. The single-atom-thick layer graphene is synthesized from graphite sheets through different techniques and shows excellent thermal, mechanical, and electrical properties. The nanostructure of graphene played important role in the field of material science, condensed matter physics, and renewable energy [389–394,465].

The idiosyncratic physical, chemical and thermal properties of graphene attracted the researcher's attention [395], wherein various electrochemical applications it is used as an electrode material [396–398]. Graphene as compared to other materials is highly acknowledged for its electrode surface area in energy storage and conversion systems. The reported theoretical surface area of graphene due to its plan hexagonal structure is $2600 \text{ m}^2 \text{ g}^{-1}$ which is quite greater than $10 \text{ m}^2 \text{ g}^{-1}$ and $1315 \text{ m}^2 \text{ g}^{-1}$ of graphite and single-walled carbon nanotube (SWCNTs), respectively [399]. In addition to this, graphene possesses an electrical conductivity of 64 mS m^{-1} , which is about 60 times higher than SWCNTs. The reason for this conduction is the spacious conjugated sp² hybridization of the carbon network [400]. Graphene shows high thermal stability at various ranges of temperature in different photochemical and electrochemical energy systems, where the operating temperature has a significant effect on the performance of membrane and electrode materials [393]. It is interesting to note that the charge density of graphene is powered through the gate electrode. Furthermore, the charge carriers of graphene can be effectively tuned among holes and electrons, where at both chemical and electrical devices the mobility exists at high and low concentration points [396]. Additionally, the high young modulus (1500 GPa) [401], charge mobility ($200,000 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$) [402], optical transparency (~98%), thermal conductivity (64 ms m^{-1} and $5000 \text{ Wm}^{-1} \text{ K}^{-1}$) make graphene very promising material in fuel cells and other electrochemical applications [403].

Since 2004, graphene has attracted the attention of engineers, and scientists for its incredible properties to be used in different applications. In particular, GO with different functional groups such as (-O-, -OH, -COOH) in a 2D basal plane is functionalized to be used in organic solvents which are used as fillers in PEMs. The presence of these interfacial functional groups (carboxylic acid and hydrophilic sites) facilitates the hopping of electrons [404]. Functionalized graphene oxide (FGO) is used in the form of fillers, in particular, to extend the use of graphene in PEMFC as pure graphene is mostly insoluble in organic solvents due to strong hydrogen bonding [405]. Moreover, the proton conductivity and water retention of GO-based membranes can be enhanced at high temperatures and

low RH by the functionalization of GO [406]. GO can increase the mechanical properties of membranes by developing nanohybrid composite membranes.

Owing to these excellent properties, graphene is considered the future of carbon materials and has resolved major problems and challenges associated with fuel cell membranes which are discussed in the following sections.

Graphene oxide (GO) based membranes

After considering the entirety of the special electrochemical properties of graphene, it tends to be deducted that graphene has the fastest electron mobility, most noteworthy its high conductivity, large surface area, and fantastic electronic abilities, contrasted with different choices like CNTs, graphite, and customary metals. Furthermore, the compelling pi-pi bond, staggering absorptive capacity, and ideal electronic carrying abilities make graphene the most feasible research material in energy-related applications. Numerous researchers still accept that graphene isn't at its best as of now. Also, it has many secret features that are yet to be uncovered soon.

Polymer electrolyte membrane fuel cell typically works with Nafion membranes because of their great ionic conductivity, high mechanical strength, and magnificent chemical strength, though very costly. Graphene oxide (GO) has an oxygen functional group with a large surface area, which is very promising for the transport of protons and possesses hydrophilic nature. At first, graphene was not considered for membrane modifications because of its large thermal conductivity, which leads to a low value of cell voltage [407,408]. While other properties like large surface area, good mechanical strength, and efficient gas permeability show some good results. The graphene oxide examined in cutting-edge research is profoundly oxidized with carbon to oxygen proportion of 2:1 in any case, GO is a likely filler and an electronic insulator [409].

Self-assembled GO PEMs

Self-assembled graphene oxide-based proton exchange membranes are free-standing GO membranes that are not supported through any Nafion or other polymer matrix structure. They are solid proton conducting materials

alternative to Nafion, which are fabricated from pure carbon materials. Kumar et al. [410] fabricated GO paper with approximately 100 μm thickness (Fig. 11) from graphite oxide using the directed assembly method. High ionic conductivity ($\sim 0.041\text{--}0.082 \text{ S}\cdot\text{cm}^{-1}$) was observed in free-standing GO membrane at a temperature range (25–90 °C) which was due to the presence of acidic functional group and filtration of an oxygen molecule through a porous structure ($\sim 0.2 \mu\text{m}$) of GO membrane that enhances the proton conductivity. However, the membranes were suffering from enormous methanol fuel cross-over ($1.82 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and poor mechanical properties which resulted in a poor power density of $8 \text{ mW}\cdot\text{cm}^{-2}$ at 60 °C. This is due to the presence of non-stoichiometric composition and distribution of the oxygen functional groups at the basal plane of GO which affects the mechanical properties of the graphene [411]. However, the utilization of the oxygen functional groups enables exceptional dispersion of GO in water and other solvents thus allowing for the easy synthesis of polymer nanocomposites and scale-up process for high-volume GO manufacturing [412]. Moreover, the presence of a covalent oxygen functional group in GO is responsible for the inclusion of structural defects which impact the properties of GO like electrical conductivity and mechanical strength but in turn, enhance the proton conduction in GO-based membranes [413].

One year later, the problem of high methanol cross-over and mechanical stability was addressed by using sulfonic acid functionalized graphite oxide (SGO) [414]. The presence of multiple acidic functional groups enhanced the proton conductivity of the SGO membrane and good mechanical stability was achieved in a low RH environment. Furthermore, the PEMFC performance was significantly improved to $113 \text{ mW}\cdot\text{cm}^{-2}$ (Fig. 12) at very low RH, but the high methanol crossover was still an issue that affected the durability of SGO based membranes.

Gao et al. [415] synthesized Ozonized freestanding GO (OGO) for the PEMFCs through the ozonated process. The morphological modification of GO resulted in enhanced proton conductivity as compared to simple GO which is due to the better proton hopping from the high concentration of oxygen functional groups in the basal plane and edges of OGO. Robin

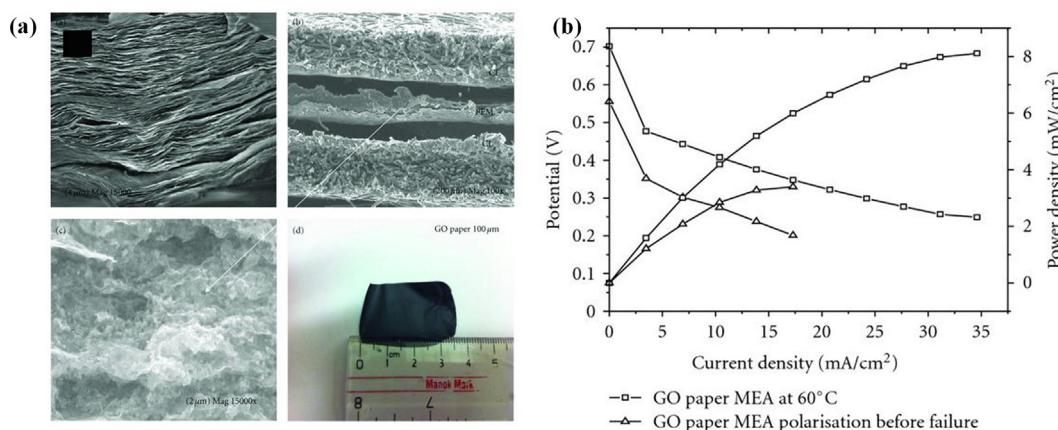


Fig. 11 – Freestanding GO paper: (a) Cross-sectional SEM, (b) DMFC performance (adapted from [410]).

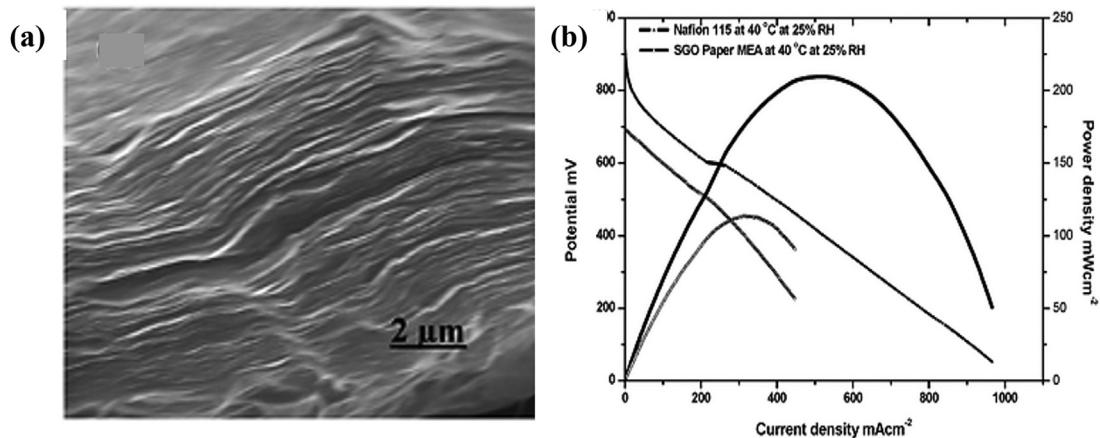


Fig. 12 – Freestanding SGO paper-based membrane: (a) SEM micrograph, and DMFC performance (adapted from [416]).

et al. [416] modified GO through the fluorination and sulfonation process to evaluate the combined effect of fluorine (F) and sulfonic acid (SO_3^-) groups on PEM. The fuel cell test of fluorinated GO (F-TGO) initially showed high performance at elevated temperatures and removed the structural degradation of the membrane at low RH values but there was a rapid loss observed in F-TGO which was further alleviated with sulfonation (SF-TGO). The attachments of (F) and (SO_3^-) groups were confirmed through XPS, Raman, contact angle measurement, and FTIR tests.

Thimmappa et al. [417] showed that through-plane proton conductivity and impermeability of thin-film GO membrane make it a very suitable and inexpensive alternative for commercial Nafion membrane. At room temperature, the cationic conductivity of thin-film GO is several times lower than state-of-the-art Nafion. However, the performance of thin-film GO membranes can be enhanced by reducing the interlayers between graphene nanosheets. As shown in Fig. 13, the fuel cell performance of the thin-film GO membrane yielded a power density of $\sim 411 \text{ mW} \cdot \text{cm}^{-2}$ as compared to $308 \text{ mW} \cdot \text{cm}^{-2}$ of

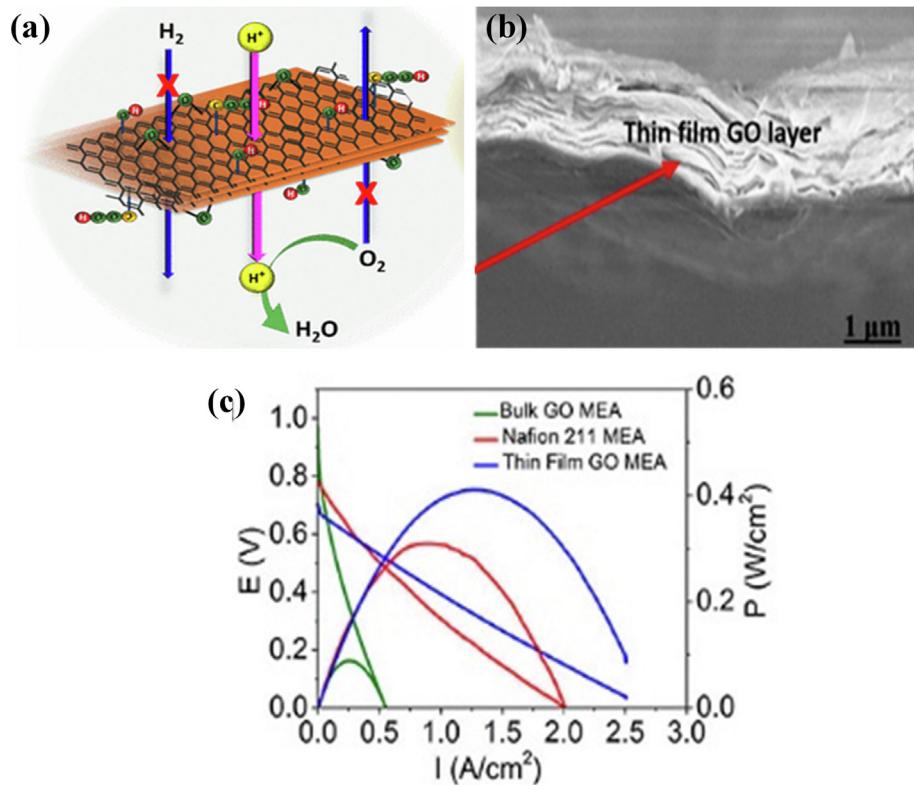


Fig. 13 – Thin layered Graphene Oxide membrane (a) Schematics of through-plane conduction, (b) Cross-sectional SEM, and (c) PEMFC performance (adapted from [417]).

Nafion 211, which shows remarkable advancement in free-standing GO-based membranes. High-performance sulfonic acid-functionalized holey GO was prepared by mixing HGO in sodium dodecylbenzene sulfonate (SDBS) [418]. The holey structure in SBDS-HGO provided a pathway for proton conduction while strong proton groups enhanced the conductivity of the SBDS-HGO membrane. The resulted membrane showed better performance ($92 \text{ mS}\cdot\text{cm}^{-1}$) as compared to Nafion 112. Basso et al. [419] reported a very simple method for the preparation of self-supported sulfonated graphene oxide (SGO-X) where X represents the molar ratio of HSO_3^- . The different molar ratios of HSO_3^- and GO were tested to identify the optimal functionalities. Proton conductivity and electrochemical impedance for SGO-1 and SGO-20 demonstrated higher water uptake and proton-conducting properties ($0.120 \pm 0.001 \text{ S}\cdot\text{cm}^{-1}$ and $2.099 \pm 0.0695 \text{ S}\cdot\text{cm}^{-1}$) at higher temperatures (80°C) and low RH (53%) as compared to $0.055 \pm 0.0002 \text{ S}\cdot\text{cm}^{-1}$ and $0.457 \pm 0.0013 \text{ S}\cdot\text{cm}^{-1}$ of free-standing GO and Nafion 212. These studies show the potential of self-supporting GO-based membrane materials to be further optimized for their commercial use in high-temperature PEM fuel cells.

Graphene oxide nanocomposites

Fluorosulfonated GO-based nanocomposites. Graphene oxide (GO) has a great similarity with Nafion polymer and demonstrated its possible benefits in membrane alteration for PEMFCs. As anyone might expect, Nafion polymer has pulled in numerous specialists because of its remarkable similarity with GO due to their solid interfacial fascination [420]. GO can improve both side chains and base chains of Nafion which brought about improved thermal and mechanical properties [421]. Many researchers have altered Nafion with GO over time and have improved both mechanical and chemical properties in PEMFC. For instance, Ansari et al. [422] functionalize Nafion with GO expansion into a polymer framework and found notable changes in ionic sites. Microscopic characterization showed that the graphene was efficiently intercalated with Nafion polymer. The Nafion-GO composite showed a PEMFC power density of $415 \text{ mW}\cdot\text{cm}^{-2}$ at 30°C which was much better than the pure Nafion. Besides, Nafion has been researched in PEMFCs at low relative humidity (RH) and elevated temperature. Kim et al. [423] modified Nafion with polyoxometalate coupled with GO. Graphene oxide was combined with phosphotungstic acid (PW) and was merged into Nafion polymer (Nafion/PW-mGO) with excellent proton conductivity as compared to Nafion membrane. Moreover, the power density of the graphene-added membrane was tremendous i.e., $841 \text{ mW}\cdot\text{cm}^{-2}$, compared to $210 \text{ mW}\cdot\text{cm}^{-2}$ of Nafion at 20% RH and 80°C . The reduction in ohmic resistance of Nafion/PW-mGO composite was regarded to the presence of hygroscopic solid acids, which attract and retains water molecule through H-bonding with protons thus enhancing the conductivity. Peng et al. [424] modified the Nafion chain structure by incorporating GO into the membrane. The nanohybrid membrane (NM/GO-X) was collected and done all the necessary characterization like SEM, TEM, FTIR, XPS, etc. Results showed that the proton transport across the membranes was enhanced 1.6 times in the presence of GO in the

Nafion membrane as compared to the pure Nafion. It is also worth noting that the PEM fuel cell performance was increased from 30 to 40% of total power density. Feng et al. [425] prepared GO/Nafion nanohybrid composite membrane by deposition of Nafion over rolled-up graphene oxide sheets (GOss) which were prepared by mixing GOss insolvent and then evaporating the dispersion on the aluminum foil. The resulting composite exhibited excellent proton conductivity in PEMFC at elevated temperature as compared to recast Nafion. Gao et al. [426] bonded hydrogenated SPEEK to GO and incorporated it into Nafion (GO-g-SPEEK/Nafion) by grafting technique in a 2:1 mass ratio. The composite SPEEK was much hydrophilic with more efficient proton conductivity ($0.219 \text{ S}\cdot\text{cm}^{-1}$) at elevated temperatures. The covalent bonding between GO and SPEEK prevented sulfonic polymer chains from segmental motion even at hydrated conditions. Besides, GO-g-SPEEK/Nafion performed excellently in PEMFC by delivering a power density of $182 \text{ mW}\cdot\text{cm}^{-2}$, $213 \text{ mW}\cdot\text{cm}^{-2}$ and $112 \text{ mW}\cdot\text{cm}^{-2}$ at 25°C , 60°C and 90°C , respectively. In the other study, GO-Nafion nanofiber membranes were prepared through the electrospinning technique to improve the stability (Chemical, thermal and mechanical), and proton conductivity also reducing the fuel cross-over [427]. Asefa and his coworkers synthesized RGO-Nafion nanohybrid membrane by the solution casting method [428]. At first GO-Nafion composite was made which was treated with 1 M NaCl for ion exchange (GO-Nafion- Na^+). In a later step, the GO-Nafion- Na^+ composite was heat sintered at 200°C which decomposes the oxygen functional group of GO resulting in RGO-Nafion- Na^+ . Finally, RGO-Nafion- Na^+ were treated with 1 M H_2SO_4 which replaces the Na^+ ion with H^+ by ion-exchange method thus yielding RGO-Nafion- H^+ . XPS and Raman analysis showed a strong interaction between all three and showed a proton conductivity of $0.22 \text{ S}\cdot\text{cm}^{-1}$, which is about 30 times greater than $0.0071 \text{ S}\cdot\text{cm}^{-1}$ recast Nafion. In addition, the reduction of GO to RGO increased the water uptake by the oxygen functional group.

Sun et al. [429] synthesized self-crosslinked sulfonated polyetheretherketone membrane (C-SPEEK) by the Friedel-Crafts alkylation method. Later he doped C-SPEEK with carbon material such as GO, RGO, and CNTs as well as Phosphotungstic acid (HPW). Together with carbon materials, HPW improved the conductivity of the C-SPEEK membrane through Grothuss and Vehicle mechanism (Fig. 14) and C-SPEEK/HPW/GO showed excellent proton conduction of $0.119 \text{ S}\cdot\text{cm}^{-1}$, which was 2.4 times higher than C-SPEEK. Furthermore, C-SPEEK/HPW/GO showed significantly improved fuel cell performance of $877 \text{ mW}\cdot\text{cm}^{-2}$ compared to $777 \text{ mW}\cdot\text{cm}^{-2}$ of C-SPEEK.

Han et al. [430] modified GO with sulfonated polytriazole (SPTA-GO) by using Cu catalyzed azide-alkyne 1,3-dipolar cycloaddition between ethynyl-terminated sulfonated polytriazole (E-SPTA) and azide functionalized GO ($\text{N}_3\text{-GO}$) and deposited it on a sulfonated polyarylene ether sulfone (SPAES) polymer electrolyte sheet for PEM fuel cell. Significant improvements in PEM fuel cell performance were noticed for SPTA-GO@SPAES with a power density of 1580 as compared to $1330 \text{ mW}\cdot\text{cm}^{-2}$ of the commercial Nafion 212 at 80°C and 100% RH. The enhanced performance of SPTA-GO@SPAES was

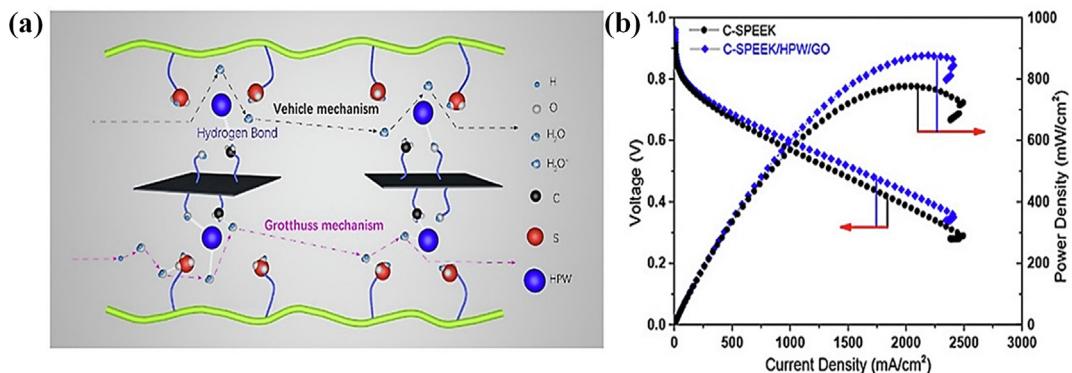


Fig. 14 – Self-crosslinked sulfonated polyether ether ketone membrane doped with GO and HPW (C-SPEEK/HPW/GO) (a) Conduction mechanism in chemical structure (b) PEMFC performance (adapted from [429]).

attributed to the presence of sulfonic acid and triazole groups on SPTA-GO (Fig. 15) that improved the conduction of SPEAS by inducing proton-conducting channels. A nanohybrid membrane of sulfonated poly(arylene ether ketone) (SPAEK) and SGO was prepared with different weight ratios (0.5–1.5%) through the solvent casting method [431]. The SGO/SPAEK composite membrane with 1.5% wt. showed outstanding thermal properties with initial weight loss at 200 °C in TGA analysis. Apart from that, SGO/SPAEK showed a conductivity value of 0.124 S·cm⁻¹ with a 19% water absorption. TM-AFM analysis showed that conductivity and water adsorption was enhanced due to the presence of channels between hydrophilic and hydrophobic regions, which provided a wider pathway for proton conduction.

A fair balance between proton conduction and methanol crossover for PEM membrane in direct methanol fuel cells (DMFCs) is of crucial importance. In this regard Sulfonated poly(arylene ether nitrile) membrane having amine-functionalized GO (SPEN-NGO) was prepared by a simple solution casting method [432]. Different loadings of NGO were applied in the composite membrane structure to check its effect on proton conductivity, methanol diffusion, and stability. SPEN-NGO composite membrane with 1 wt% NGO

exhibited better proton conductivity (0.104, 0.167, and 0.183 S·cm⁻¹ at 20, 60, and 80 °C) balanced with low methanol crossover (1.74×10^{-7} cm² s⁻¹ at 20 °C) as compared to pure SPEN and Nafion 117. As shown in Fig. 16, The SEM and AFM analysis show that this balanced trade-off between ionic conductivity and methanol crossover was due to long interfacial ionic nanochannels and zigzag transportation pathways. In another study, Feng and his co-workers [433], synthesized hydroxylated sulfonated poly(ether ether ketone) (SPEEK-OH) grafted GO and incorporated it in SPEN as filler to explore the effect of varying loading on performances of proton exchange membranes. The resulted composite contains a uniformly dispersed perpendicular structure of SGO in the matrix thus forming continuous and long-range proton transfer channels. Particularly, SGO-SPEN-2 wt% composite membranes showed an excellent proton conductivity of 0.183 S·cm⁻¹ with good IEC and water uptake of 1.825 mmol g⁻¹ and 48% at 80 °C respectively. The authors attributed these supplemented results to the formation of strong interfacial interaction between SPEN and functionalized SGO.

Sulfonated polyimide (SPI) and GO-based nanocomposites (SPI-GO). SPIs are highly stable polymers with excellent thermal,

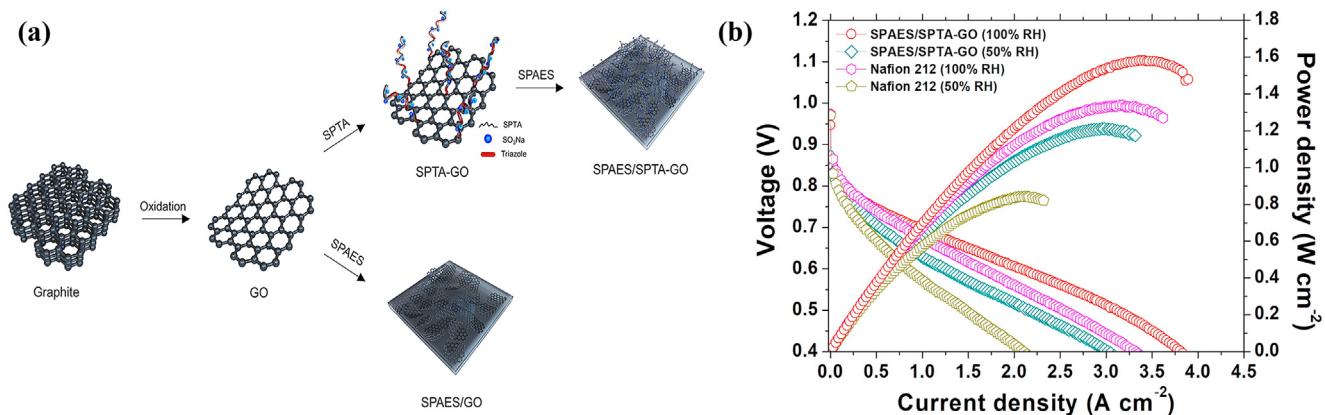


Fig. 15 – PEM fuel Cell performance of sulfonated polytriazole (E-SPTA) and azide functionalized GO deposited on sulfonated polyarylene ether sulfone (SPEAS) polymer electrolyte (SPTA-GO@SPEAS) (a) Synthesis schematic, (b) PEMFC performance (adapted from [430]).

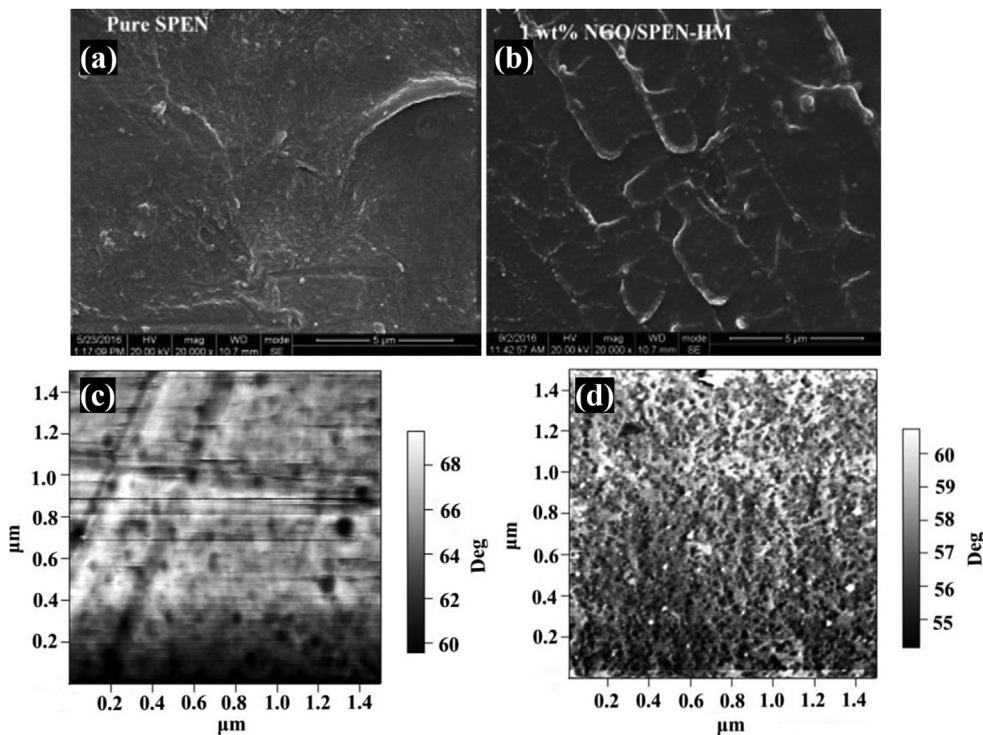


Fig. 16 – SEM images of (a) Pure SPEN (b) SPEN-NGO and 2D-AFM images (c) Pure SPEN, (d) SPEN-NGO (adapted from [432]).

mechanical and chemical properties. The high stability of SPI polymers arises from their stiff backbone of aromatic hydrocarbons [434]. Owing to their thermal properties, SPIs are used as matrix materials in GO-based nanocomposites for PEM fuel cells [435–438]. These types of composite polymers are typically prepared through the chemical casting method with various functionalized GO materials to tune chemical, mechanical, and ion-conducting properties with low methanol crossover [439]. For instance, Tseng et al. [440] for the first time prepared SPI/GO composite membrane with a different %wt. ratio. He showed that SPI/GO with a 5% wt. ratio possessed higher proton conductivity ($0.667 \text{ S} \cdot \text{cm}^{-1}$) and low methanol crossover ($\times 5$ times lower) than commercial Nafion117 at elevated temperatures.

Imran et al. [441] synthesized sulfonated polybenzimidazole (SPBI)/sulfonated imidized graphene oxide (SIGO) by incorporating SIGO in the SPBI matrix. The composite polymer was synthesized by polycondensation in phosphoric acid. The composite membrane SPBI/SIGO with 15% wt. GO shows excellent proton conductivity ($0.581 \text{ S} \cdot \text{cm}^{-1}$) at 120°C and low RH. A series of polymer composite membranes of sulfonated polyimide with phosphoric acid doped GO functionalized with 1-methylimidazole ionic liquid SPI/FGO was prepared by solution imidization method for high-temperature PEM fuel cell to study the different %wt. content of FGO filler on membrane properties [442]. At higher loading content such as 7–10% some agglomeration of FGO nanoparticles was observed however the FGO fillers with 1–5% showed improved mechanical (high young modulus) and thermal properties (low-temperature degradation) with increased water uptake. The presence of a phosphoric acid group with ionic liquid enhances the proton conductivity of

polymer composite membrane such that SPI/FGO 5%wt shows the highest value of $0.0772 \text{ S} \cdot \text{cm}^{-1}$ and $0.1243 \text{ S} \cdot \text{cm}^{-1}$ at 160°C and 120°C with ambient and 80% RH respectively. Pandey et al. [443] prepared SPI/sulfonated propylsilane graphene oxide (SPSGO) by grafting 3-mercaptopropyltrimethoxysilane (MPTMS) on GO followed by oxidation of thiol groups with hydrogen peroxide (Fig. 17). The incorporation of functionalized various wt.% of GO with SO_3H and $-\text{COOH}$ group significantly enhanced thermochemical stability with bounded water content to be used in low RH. The SPI/SPSGO-8 (8 wt% of SPSGO) composite membrane was fabricated to promote self-humidification due to the bounded water content of 6.58% which promotes proton conduction ($0.0962 \text{ S} \cdot \text{cm}^{-1}$) due to the presence of $-\text{SO}_3\text{H}$ and $-\text{COOH}$ functional groups. A single fuel cell test of the SPI/SPSGO composite membrane revealed a power density of $76 \text{ mW} \cdot \text{cm}^{-2}$ which was better than $62 \text{ mW} \cdot \text{cm}^{-2}$ of commercial Nafion 117 at 70°C . In addition, SPI/SPSGO showed a maximum power density of $98 \text{ mW} \cdot \text{cm}^{-2}$ at 130°C . However, SPI/SPSGO composite membrane prepared by the above method was having a leaching problem of nanofillers in the matrix due to which obtaining SPI/SPSGO with high wt.% was not possible. Therefore a new method was developed in the succeeding paper by Pandey et al. [444] in which sulfonated imidized graphene oxide tethered sulfonated polyimide (SPI/SIGO) of different weight percentages (1–15 %wt.) was prepared by polycondensation of dianhydride and sulfonated diamine. The resultant polymer composite exhibited excellent chemical mechanical and thermal properties with high bound water content, which helps in proton conduction in low RH through self-humidification. The incorporation of SIGO in SPI structure resulted in phase separation of hydrophilic-hydrophobic and proton conducting

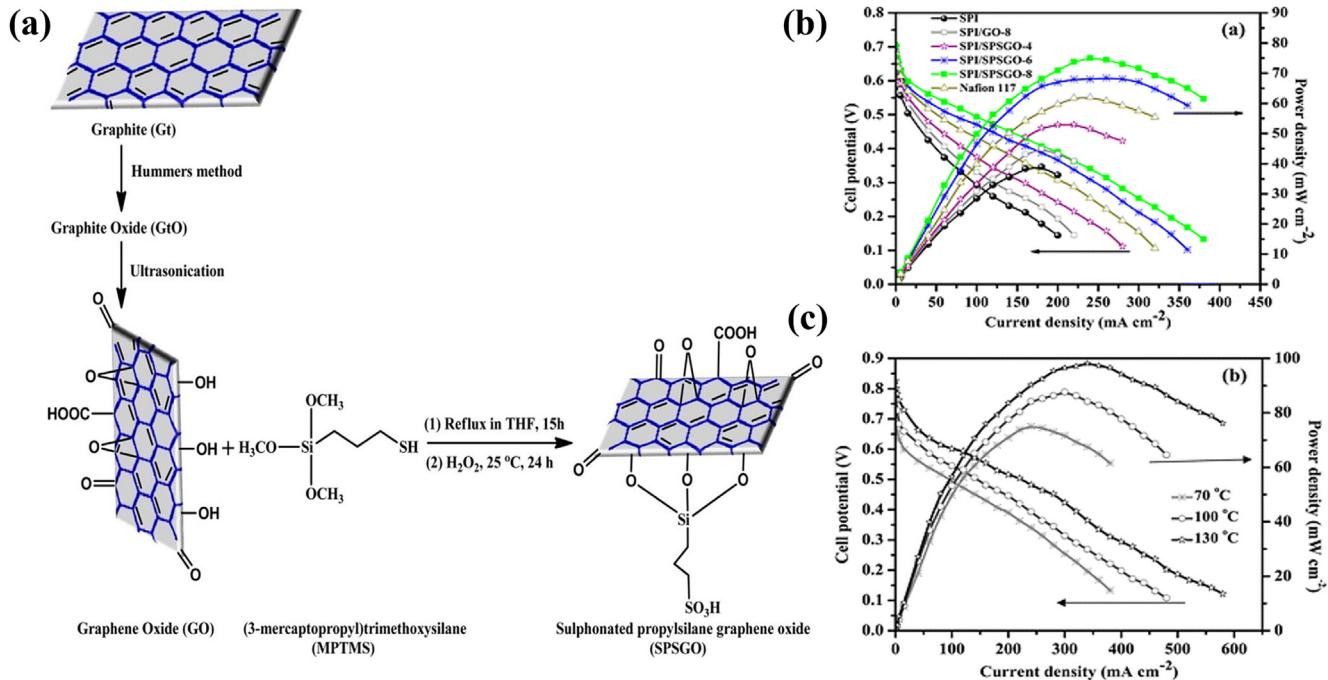


Fig. 17 – SPI/sulfonated propylsilane graphene oxide (SPI/SPSGO): (a) Synthesis and chemical structure, PEMFC performance (b) Comparison with Nafion and other wt.% at 100 °C (C) SPI/SIGO-15 at 70, 100 and 130 °C (adapted from [443]).

channels. SPI/SIGO-15 (15 %wt. of SIGO in SPI matrix) showed proton conductivity, bound water content, and ion exchange capacity of $0.1138\ S\cdot cm^{-1}$, 5.12% and $2.24\ mmol.\ g^{-1}$ respectively. A single fuel cell test at 70 °C for SPI/SIGO-15 composite PEM exhibited $79\ mW\cdot cm^{-2}$ power density as compared to $62.40\ mW\cdot cm^{-2}$ of Nafion 117.

Polybenzimidazole and GO-based nanocomposites (PBI-GO). Graphene oxide (GO) has been used as filler in the PBI matrix due to its excellent properties (chemical, mechanical and thermal), large surface area, 2D structure, and a large number of oxygen functional groups attached to the basal plane which can be easily modified for the required polymer property [445]. In this respect, Kim et al. [446] prepared PBI based composite membrane by incorporating imidazole functionalized graphene oxide (ImGO) in the PBI matrix through the solution casting method. Later the composite was treated with phosphoric acid (H_3PO_4) for 24h to induce superior proton conductivity. ImGO was prepared by synthesizing GO through the modified hummers method followed by functionalization of GO with the imidazole group. Due to the presence of the same functional group (imidazole), ImGO was much more compatible with PBI as compared to simple GO [404]. PBI with 0.5 wt% ImGO exhibits excellent physical and chemical properties with an enhanced tensile strength of 219.2 MPa (181 MPa without ImGO) and proton conductivity of $0.077\ S\cdot cm^{-1}$ at 150 °C which is much higher than PBI/GO based composite polymers [404,447].

Abouzari et al. [448] used pyridine functionalized polybenzimidazole (Py-PBI) as substrate material to attach highly dispersed phosphonated graphene oxide (PGO) through the solution casting method. The Py-PBI/PGO composite membrane doped with phosphoric acid exhibits significant proton

conduction of $0.0764\ S\cdot cm^{-1}$ at 140 °C under anhydrous conditions. A single cell fuel cell performance with commercial Pt/C (40% wt.) catalysts on Py-PBI/PGO composite membrane delivered a peak power density of $360\ mW\cdot cm^{-2}$ at 120 °C which shows 75% improvement as compared to Py-PBI/GO. A novel polybenzimidazole composite membranes modified graphene oxide functionalized through grafting reaction of ^{60}Co γ -ray irradiation were prepared for high-temperature PEM fuel cell [449]. The PA doped PBI/RGO/PA membranes exhibited improved proton conductivity ($0.028\ S\cdot cm^{-1}$) at completely anhydrous condition (170 °C) showing about a 72% increase as compared to PA/PBI membrane. To further increase the conductivity of PBI based polymers, Cai and co-workers prepared three layered PBI based composite membranes (Fig. 18) with radiation grafting graphene oxide reinforced polybenzimidazole/porous polybenzimidazole/radiation grafting graphene oxide reinforced polybenzimidazole (PBI-RGO/PPBI/PBI-RGO) [450]. The tri-layered PBI membrane (TLM) was treated with phosphoric acid before testing in HT-PEMFC. PBI-RGO/PPBI/PBI-RGO possess excellent mechanical and oxidative properties with tensile strength up to 38 MPa which is 5 times higher than PA doped PBI membrane (~7 MPa) and has much improved proton conductivity of $0.114\ S\cdot cm^{-1}$ in completely anhydrous conditions. Thus, the sandwich structure makes it a promising membrane in HT-PEMFC applications.

Nadzirah et al. [451] used different wt.% of sulfonated graphene oxide (0.5–6%) as an inorganic filler in polybenzimidazole matrix for HT-PEMFC membrane. The composite PBI-SGO-x membrane was prepared through the solution casting method followed by evaporation. The SGO filler was synthesized from precursor (3-mercaptopropyl) trimethoxysilane (MPTMS). PBI-SGO-2wt% exhibited the highest

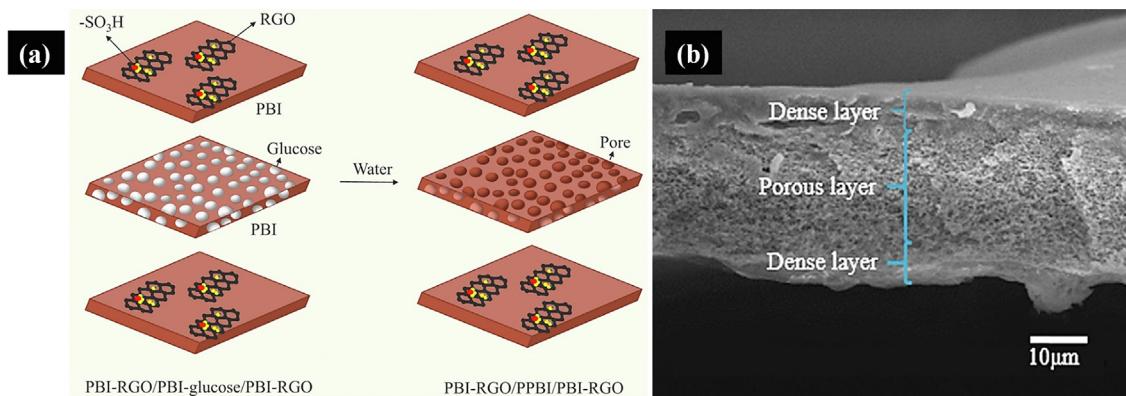


Fig. 18 – PBI-RGO/PPBI/PBI-RGO membrane (a) Synthesis schematic, (b) Cross-sectional SEM (adapted from [450]).

proton conductivity ($\sim 0.0293 \text{ S} \cdot \text{cm}^{-1}$) than pure PBI and other PBI-SGO-x at 150 °C with a maximum level of acid doping (11.63 mol of PA/PBI repeat unit) and high tensile strength of 48.86 MPa respectively. As shown in Fig. 19, the single cell HT-PEMFC test of PBI-SGO-2wt% at 150 °C exhibited a power density of $100 \text{ mW} \cdot \text{cm}^{-2}$ which is 40% greater than pure PBI. Thus PBI-SGO-2wt% has great potential to be used in HT-PEMFC applications.

Chitosan and GO based nanocomposites (CS-GO). The oxygen-containing functional groups (e.g. $-\text{OH}$, $-\text{COOH}$, and $\text{C}-\text{O}-\text{C}$) on the basal planes enable GO for further modification by chemical reaction to introduce various other functional groups [452]. Recently sulfonated graphene oxide (SGO) has been developed to overcome the lack of proton conduction in

polymeric membranes which provides a continuous pathway for facile proton transport [453]. Moreover, the negatively charged acidic groups make GO negative thus the positively charged CS owing to its excellent membrane properties, low cost, and feasibility to be modified easily with functional groups makes CS and GO to be used as matrix and nanofiller.

Shridast et al. [454] sulfonated GO along with CS (CS/SCS/SGO) to be incorporated in CS membrane for PEM. SGO was prepared by the nucleophilic reaction between the epoxy group of GO with an amine group of taurine while SCS was prepared by adding CS into a solution mixture of chlorosulfonic acid and sulfuric acid. Finally, the CS/SCS/SGO composite membrane was prepared through the solution casting technique. The composite membrane with 10 wt% SCS

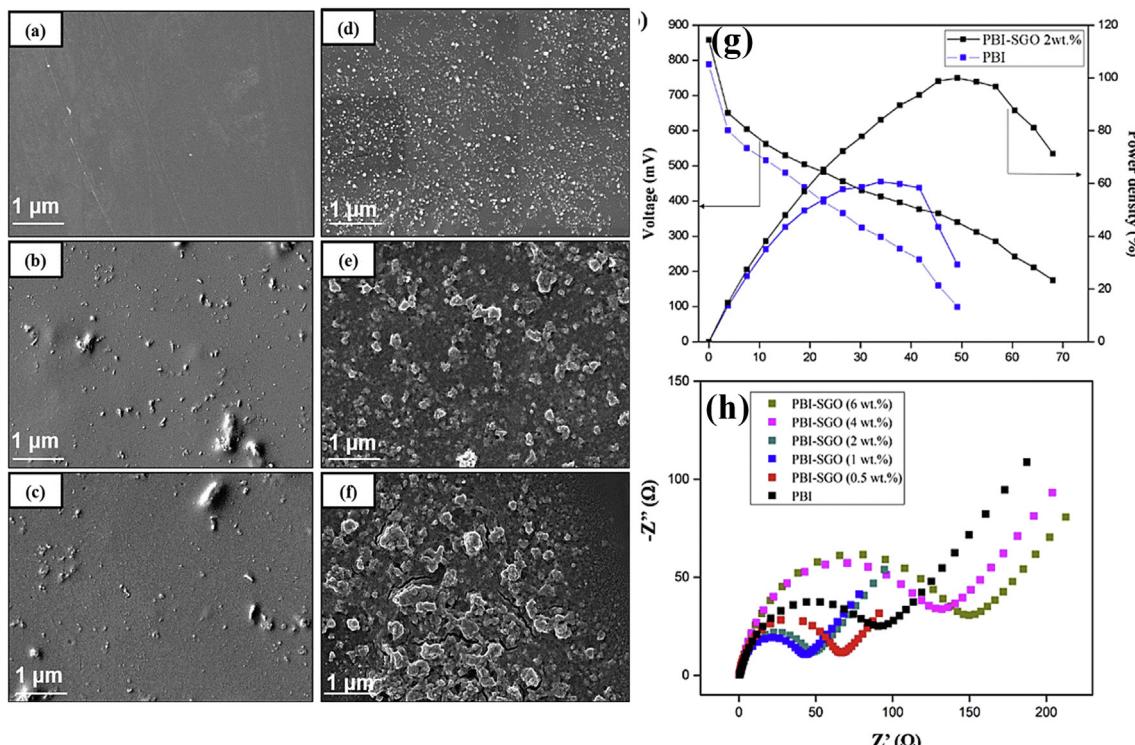


Fig. 19 – PBI-SGO- SEM images (a-f) 0.5–6 wt%, (g) PEMFC performance and (h)EIS analysis (adapted from [451]).

and 5 wt% of SGO possessed 4.5 folds to increase in conductivity along with a 23% decrease in methanol crossover.

A CS composite membrane with silica nanoparticles on SGO ($\text{CS}/\text{SGO}/\text{SiO}_2$) was prepared through the solution casting technique by adding 0.5% - 2 wt% of SGO/ SiO_2 with 2 wt% of CS in an aqueous acetic acid solution [455]. As shown in Fig. 20, the uniform distribution of SGO/ SiO_2 in the CS matrix and strong bond interaction between functionalized GO and SiO_2 nanofillers enhanced the thermal stability of the $\text{CS}/\text{SGO}/\text{SiO}_2$ nanocomposite. The hydrophilic sites of sulfonated moieties in functionalized GO and hygroscopic characteristics of SiO_2 provide better water adsorption capabilities. The strong interaction between the alkyl group of CS and an acidic group of SGO/ SiO_2 enhanced the proton conduction via the Grotthuss mechanism. In addition, the pilling up of SiO_2 (Fig. 20(b)) in SGO created resistive paths for methanol permeability. A single cell fuel cell test of $\text{CS}/\text{SGO}/\text{SiO}_2$ provided a power density of 87.18 mW cm^{-2} for a considerable amount of time conferring to be a promising low-cost and ecofriendly PEM membrane. Cui et al. [456] incorporated anatase titania attached with GO (TGO) and sodium lignosulfonate (SLS) into the CS membrane by the chemical casting method. TGO was prepared through a simple hydrothermal technique. The $\text{CS}/\text{TGO}/\text{SLS}$ nanocomposite with 2 wt% and 3 wt% of TGO and SLS (CS/

TGO2/SLS3) showed enhanced proton conductivity ($0.0483 \text{ S}\cdot\text{cm}^{-1}$) as compared to neat CS whereas selectivity was increased by 17 folds. These enhancements may be regarded as the introduction of TGO and SLS that extended proton-conducting channels along with creating active sites. A study of the influence of sulfonated GO (SGO) on sulfonated chitosan polyethylene oxide (S-CS/PEO) was performed by Kalaiselvimary et al. [457]. The S-CS/PEO/SGO membrane was prepared through the casting method with different percent ratios of SGO in which 6% wt. SGO possessed superior ionic conductivity of $0.01 \text{ S}\cdot\text{cm}^{-1}$ at elevated temperatures.

Challenges in PEMs

Many improvements have been done throughout the past years to overcome major issues incurring Nafion and its novel alternative membranes for commercialization but still, they are facing some challenges which needs to be addressed.

1. PEMs suffer from low membrane durability. It is generally believed that the formation of peroxy and hydroperoxy radicals during redox reactions attacks the loosely attached groups of polymer electrolyte chains.

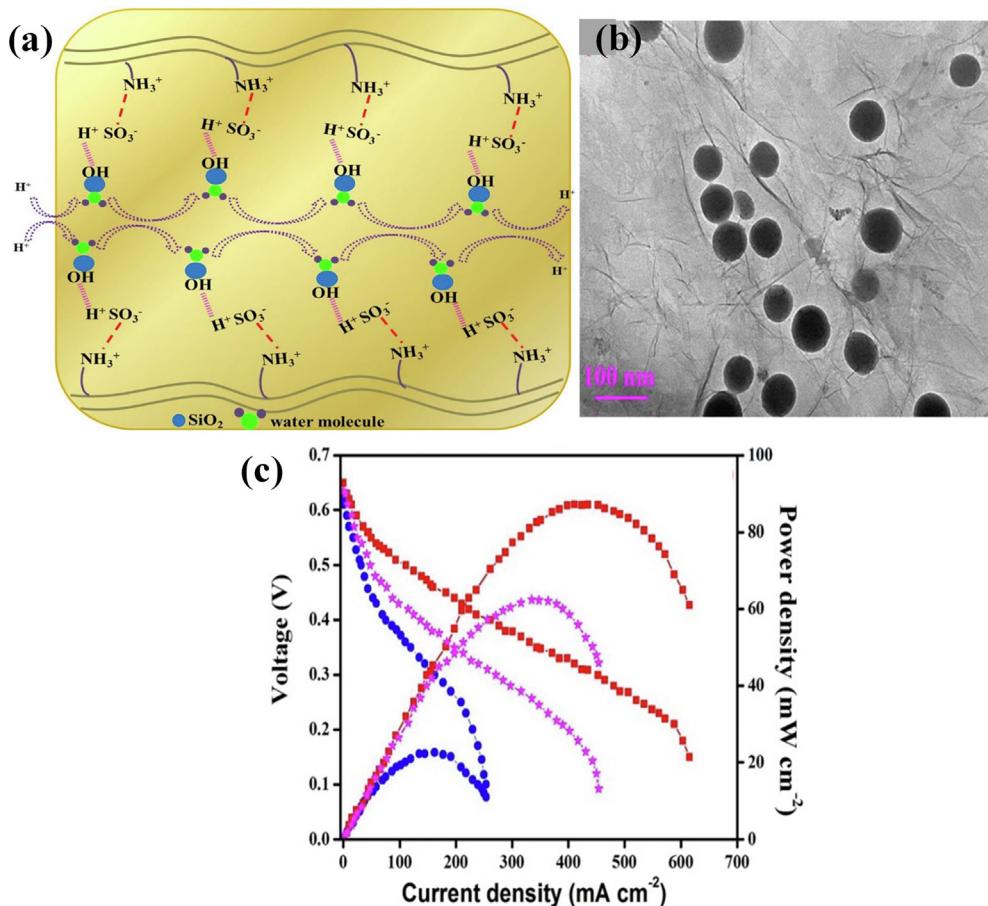


Fig. 20 – $\text{CS}/\text{SGO}/\text{SiO}_2$ membrane (a) Conduction mechanism in chemical structure, (b) TEM, and (c) DMFC performance: Red squares ($\text{CS}/\text{SGO}/\text{SiO}_2$), Pink stars (CS/SGO), Blue circles (CS) (adapted from [455]).

- However, the simulation models developed for their degradation mechanism are still controversial [458].
2. In HT-PEMFCs the impact of high temperature and low RH in addition to large Ohmic losses and CO poisoning can lead to irreversible dryness by extracting all the bonded water molecules out of the electrolyte membrane thus affected by high thermal degradation [459].
 3. The nonuniform pressure applied to MEA in a low RH environment can crack the membrane thus creating short circuit currents. Therefore, the requirement of mechanical and dimensional stability is very important.
 4. Water maintenance issue in LT-PEMFCs is directly related to membrane performance. Excessive hydration can prevent reactant diffusion to the catalyst sites by flooding the electrodes.
 5. The material compatibility issue between the membrane and conductive ionomer electrolyte used for the adhesion of the catalyst layer [460]. It has been found [461,462], that MEA consisting of Nafion ionomer and Nafion based membranes have low interfacial resistance and degradation rates compared to non-Nafion membranes.
 6. Gas and methanol crossover issue in PEMFCs and DMFCs through the membrane without generating useful work.
 7. Freestanding GO membranes possess low proton conductivity and cannot be used as standalone membrane materials.
 8. Loading optimization in wt.% of inorganic fillers in PEM is a challenging task because excessive loadings can block the proton-conducting paths [463].
 9. It is necessary to establish the architectural compatibility between carbon-based fillers (CNTs, GO etc) and polymer matrices with interconnected routes to ensure efficient proton conduction and low fuel crossover [463,464].
 10. Defect-free carbon fillers have excellent mechanical and chemical properties but lower proton conductivity. To overcome this issue it is highly required to introduce defects, heteroatoms, and functional groups into basal planes of GO which makes it susceptible to the acidic environment.
 11. There is an extra cost added to the fuel cell stack by modifying membranes and ionomer electrolytes.

Conclusion and future prospect

This review summarizes the up-to-date membrane technology, with a focus on the history, materials, and manufacturing processes of the proton exchange membranes. The characterizing advantages and disadvantages of membrane types have been briefly described leading to a review of the most recent developments and demonstration initiatives along with market status and prospects. In addition, current progress and future targets for membrane technology have been identified to accelerate the market penetration of fuel cells. Furthermore, the review also covered the design levels, thermodynamic and electrochemical fundamentals, and

component evaluation factors to offer the reader an insight into the design and manufacturing details of membrane technology along with the global paths to the future to make fuel cells an economically viable.

Rapid growth in the H₂ economy is a strong force in pushing the scientific community to commercialize fuel cells for various applications. The cost of fuel cell systems is targeted to be lowered by as large as 50% in the near future for automotive applications, through efficient electrocatalysts and membrane technology. PEMFC is now a well-established technology at the lab scale but its commercialization is hindered by the high maintenance cost of electrode catalysts, membranes, and auxiliary power units. However, this problem can be minimized by selecting an economical catalyst composite with active material and high surface area conductive substrate (e.g Fe-N-C) and membrane along with a compatible ionomer.

The perfluorosulfonic acid membranes (Nafion®) with proton conductivity up to 0.1 S·cm⁻¹ are considered today the best electrolyte membranes for fuel cells. However, Nafion membranes are expensive (>\$500/m²) and pose some serious issues, which make it necessary to find alternative membrane types with comparably high proton conductivity. As of now, all the alternative membranes are ranked below Nafion membranes over an entire set of important properties. It could be worth sacrificing conductivity to develop alternative membranes that outperform Nafion in terms of thermal stability, and operability in a wider operating range (e.g., RH<30%) with less overall swelling, lower fuel crossover, and, most importantly, lower cost, etc. Given the vast potential of polymer materials, numerous approaches have been attempted on the polymer front for developing alternative proton conducting membranes. Among them, hydrocarbon membranes based on SPI, PBI, polystyrene, polyphosphazene, sulfonated aromatic main chain polymers (SPEAK, SPEEK, SPEAS and SPEN), nonsynthetic polymers, and CNTs based composites have been extensively studied in achieving desired mechanical and chemical characteristics.

The versatile features like the chemical functionality of GO provide a great platform for exploring the structural and functional relationship in polymer composite membranes. Various types of GO sheets have been developed to be used as freestanding membranes and to replace Nafion in PEM fuel cells, but most of them suffered from thermal stabilities along with high methanol crossover. To overcome these problems, various approaches have been adopted to produce functionalized GO-based nanohybrid PEMs by incorporating them into various polymer matrices such as flurosulfonated GO-based nanocomposites (e.g. Nafion-GO) with excellent chemical, thermal and mechanical properties. Many promising properties of GO-polymer-based PEMs reported in this study make them an encouraging candidate for PEM fuel cell applications. However, there are still certain mysteries with GO as filler that need to be solved such as C/O ratio, degree of sulfonation, percentage of water content, and amount of GO as filler in different polymer matrices. Research and development of graphene-based composite materials are increasing extensively and GO-polymers composites have found diversified commercial applications in multiple industries and energy-related applications. The use of GO-based materials as filler

in polymer nanocomposites can increase the durability and efficiency of PEM fuel cells by selecting the most suitable choice of polymer matrix and covalently functionalized GO. The following insights will provide some significant routes for the development of potential Nafion alternatives/composites for fuel cells.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

Proton Exchange Membrane Fuel Cell PEMFC
 Anion Exchange Membrane Fuel Cell AEMFC
 Direct Methanol Fuel Cell DMFC
 Membrane Electrode Assembly MEA
 Gas Diffusion Layer GDL
 Oxygen Reduction Reaction ORR
 Functionalized graphene oxide FGO
 Sulfonated Carbon Nanotubes SCNTs
 Fullerene FF
 Relative Humidity RH
 High Temperature HT
 Low Temperature LT
 Solid Polymer Electrolyte SPE
 Ion Exchange Capacity IEC
 Open Circuit Voltage OCV
 Perfluorinated Ionomer PFI
 Perfluorosulfonic Acid PFSA
 Polytetrafluoroethylene PTFE
 Metal Oxides MOx
 Sulfonyl Fluoride Vinyl Ether SFVE
 Sulfonated Su
 Single-walled Carbon Nanotubes SWCNT
 Mesoporous Silica MSUF
 Phthalocyanine Tetrasulfonic Acid Tetrasodium CuTSPc
 Sulfonated Poly Ether Ether Ketone SPEEK
 Polybenzimidazole PBI
 Sulfonated Polyimide SPI
 Sulfonated Diamine NSDA
 Triethylamine TEA
 Tetracarboxylic Dianhydride NTDA
 Potassium Hydroxide KOH
 Polyvinyl Benzyl Chloride PVBC
 Sulfonated Poly Arylene Ether Ketones SPAEK
 Metal Organic Framework MOF
 Montmorillonite MMT
 Sulfonated poly Aryl Sulfones SPAS
 Chitosan CS
 Platinum Carbon Pt/C
 Boron Nitride BN
 Molybdenum Disulfide MoS₂
 Thermogravimetric Analysis TGA
 Sodium Dodecylbenzene Sulfonate SDBS
 Phosphotungstic Acid HPW
 Sulfonated Polytriazole SPTA

Sulfonated Propylsilane SPS
 Sulfonated poly arylene ether nitrile SPEN
 X-ray Photoelectron Spectroscopy XPS
 Scanning Electron Microscopy SEM
 Transmission Electron Microscopy TEM
 Atomic Force Microscopy AFM
 Fourier Transformed Infrared Spectroscopy FTIR

REFERENCES

- [1] Nazir H, Louis C, Jose S, Prakash J, Muthuswamy N, Buan MEM, et al. Is the H₂ economy realizable in the foreseeable future? Part I: H₂ production methods. *Int J Hydrogen Energy* 2020;45:13777–88. <https://doi.org/10.1016/J.IJHYDENE.2020.03.092>.
- [2] Ahmad S, Nawaz T, Ullah A, Ahmed M, Khan MO, Saher S, et al. Thermal optimization of manganese dioxide nanorods with enhanced ORR activity for alkaline membrane fuel cell. *Electrochim Sci Adv* 2020;1:e2000032. <https://doi.org/10.1002/elsa.202000032>.
- [3] Abdin Z, Zafranloo A, Rafiee A, Mérida W, Lipiński W, Khalilpour KR. Hydrogen as an energy vector. *Renew Sustain Energy Rev* 2020;120:109620. <https://doi.org/10.1016/J.RSER.2019.109620>.
- [4] Alaswad A, Palumbo A, Dassisti M, Olabi AG. Fuel cell technologies, applications, and state of the art. A reference guide. *Ref. Modul. Mater. Sci. Mater. Eng.* Elsevier; 2016. <https://doi.org/10.1016/b978-0-12-803581-8.04009-1>.
- [5] Gahlot S, Kulshrestha V. Graphene based polymer electrolyte membranes for electro-chemical energy applications. *Int J Hydrogen Energy* 2020;45:17029–56. <https://doi.org/10.1016/j.ijhydene.2019.06.047>.
- [6] Sazali N, Wan Salleh WN, Jamaludin AS, Mhd Razali MN. New perspectives on fuel cell technology: a brief review. *Membranes* 2020;10:99. <https://doi.org/10.3390/membranes10050099>.
- [7] Wang J, Wang H, Fan Y. Techno-economic challenges of fuel cell commercialization. *Engineering* 2018;4:352–60. <https://doi.org/10.1016/J.ENG.2018.05.007>.
- [8] Song K, Wang Y, Ding Y, Xu H, Mueller-Welt P, Stuermlinger T, et al. Assembly techniques for proton exchange membrane fuel cell stack: a literature review. *Renew Sustain Energy Rev* 2022;153:111777. <https://doi.org/10.1016/J.RSER.2021.111777>.
- [9] Petrik L, Ndungu P, Nechaev A, Iwuoha E. Challenges in the assembly of membrane electrode assemblies for regenerative fuel cells using Pt/C, iridium black, and IrO₂ catalysts. *New Futur Dev Catal Batter Hydrog Storage Fuel Cells* 2013;191–216. <https://doi.org/10.1016/B978-0-444-53880-2.00012-0>.
- [10] Walkowiak-Kulikowska J, Wolska J, Koroniak H. Polymers application in proton exchange membranes for fuel cells (PEMFCs). *Phys Sci Rev* 2017;2. <https://doi.org/10.1515/PSR-2017-0018>.
- [11] Othman MHD, Ismail AF, Mustafa A. Recent development of polymer electrolyte membranes for direct methanol fuel cell application-A review CORE view metadata, citation and similar papers at core.ac.UK provided by universiti teknologi Malaysia institutional repository. *Malaysian Polym J* 2010;5:1–36.
- [12] Park CH, Lee CH, Guiver MD, Lee YM. Sulfonated hydrocarbon membranes for medium-temperature and low-humidity proton exchange membrane fuel cells (PEMFCs). *Prog Polym Sci* 2011;36:1443–98. <https://doi.org/10.1016/J.PROGPOLYMSCI.2011.06.001>.

- [13] Escorihuela J, Olvera-Mancilla J, Alexandrova L, del Castillo LF, Compañ V. Recent progress in the development of composite membranes based on polybenzimidazole for high temperature proton exchange membrane (PEM) fuel cell applications. *Polymers* 2020;12. <https://doi.org/10.3390/POLYM12091861>.
- [14] Dupuis AC. Proton exchange membranes for fuel cells operated at medium temperatures: materials and experimental techniques. *Prog Mater Sci* 2011;56:289–327. <https://doi.org/10.1016/J.PMATSCI.2010.11.001>.
- [15] Kausar A. Progression from polyimide to polyimide composite in proton-exchange membrane fuel cell: a review. *Polym Plast Technol Eng* 2017;56:1375–90. <https://doi.org/10.1080/03602559.2016.1275688>.
- [16] Goni-Urtiaga A, Presvytes D, Scott K. Solid acids as electrolyte materials for proton exchange membrane (PEM) electrolysis: Review. *Int J Hydrogen Energy* 2012;37:3358–72. <https://doi.org/10.1016/J.IJHYDENE.2011.09.152>.
- [17] Wang H, Zhang J, Ning X, Tian M, Long Y, Ramakrishna S. Recent advances in designing and tailoring nanofiber composite electrolyte membranes for high-performance proton exchange membrane fuel cells. *Int J Hydrogen Energy* 2021;46:25225–51. <https://doi.org/10.1016/J.IJHYDENE.2021.05.048>.
- [18] Vinothkannan M, Kim AR, Yoo DJ. Potential carbon nanomaterials as additives for state-of-the-art Nafion electrolyte in proton-exchange membrane fuel cells: a concise review. *RSC Adv* 2021;11:18351–70. <https://doi.org/10.1039/D1RA00685A>.
- [19] Farooqui UR, Ahmad AL, Hamid NA. Graphene oxide: a promising membrane material for fuel cells. *Renew Sustain Energy Rev* 2018;82:714–33. <https://doi.org/10.1016/J.RSER.2017.09.081>.
- [20] Kravtsberg A, Ein-Eli Y. Review of advanced materials for proton exchange membrane fuel cells. *Energy Fuel* 2014;28:7303–30. <https://doi.org/10.1021/EF501977K>.
- [21] Kravtsberg A, Ein-Eli Y. Review of advanced materials for proton exchange membrane fuel cells. *Energy Fuel* 2014;28:7303–30. <https://doi.org/10.1021/EF501977K>.
- [22] Resnick PR. Matériaux et nouvelles technologies A short history of Nafion n.d.
- [23] Sasikumar G, Ihm JW, Ryu H. Optimum Nafion content in PEM fuel cell electrodes. In: *Electrochim. Acta*. 50. Pergamon; 2004. p. 601–5. <https://doi.org/10.1016/j.electacta.2004.01.126>.
- [24] Sun H, Sun Z, Wu Y. Proton transfer mechanism in perfluorinated sulfonic acid polytetrafluoroethylene. *Int J Hydrogen Energy* 2012;37:12821–6. <https://doi.org/10.1016/j.ijhydene.2012.05.096>.
- [25] Klose C. Novel polymer electrolyte membrane compositions for electrolysis and fuel cell systems. University of Freiburg; 2020.
- [26] Kumar P, Bharti RP, Kumar V, Kundu PP. Polymer electrolyte membranes for microbial fuel cells: Part A. Nafion-based membranes. *Prog Recent Trends Microb Fuel Cells* 2018;47–72. <https://doi.org/10.1016/B978-0-444-64017-8.00004-X>.
- [27] Goswami S, Klaus S, Benziger J. Wetting and absorption of water drops on nafion films. *Langmuir* 2008;24:8627–33. <https://doi.org/10.1021/LA800799A>.
- [28] Zeis R. Materials and characterization techniques for high-temperature polymer electrolyte membrane fuel cells. *Beilstein J Nanotechnol* 2015;6:68–83. <https://doi.org/10.3762/BJNANO.6.8>.
- [29] Ling X, Bonn M, Domke KF, Parekh SH. Correlated interfacial water transport and proton conductivity in perfluorosulfonic acid membranes. *Proc Natl Acad Sci Unit States Am* 2019;116:8715–20. <https://doi.org/10.1073/PNAS.1817470116>.
- [30] Hammer R, Schönhoff M, Hansen MR. Comprehensive picture of water dynamics in nafion membranes at different levels of hydration. *J Phys Chem B* 2019;123:8313–24. <https://doi.org/10.1021/ACS.JPCB.9B05093>.
- [31] Agmon N. The Grothuss mechanism. *Chem Phys Lett* 1995;244:456–62. [https://doi.org/10.1016/0009-2614\(95\)00905-J](https://doi.org/10.1016/0009-2614(95)00905-J).
- [32] Grancha T, Ferrando-Soria J, Cano J, Amorós P, Seoane B, Gascon J, et al. Insights into the dynamics of Grothuss mechanism in a proton-conducting chiral bioMOF. *Chem Mater* 2016;28:4608–15. <https://doi.org/10.1021/ACS.CHEMMATER.6B01286>.
- [33] Li T, Shen J, Chen G, Guo S, Xie G. Performance Comparison of proton exchange membrane fuel cells with nafion and aquivion perfluorosulfonic acids with different equivalent weights as the electrode binders. *ACS Omega* 2020;5:17628–36. <https://doi.org/10.1021/ACOSOMEGA.OC02110>.
- [34] Uosaki K, Okazaki K, Kita H. Conductivity of Nation membranes at low temperatures. *J Electroanal Chem Interfacial Electrochem* 1990;287:163–9. [https://doi.org/10.1016/0022-0728\(90\)87166-H](https://doi.org/10.1016/0022-0728(90)87166-H).
- [35] Ozen DN, Timurkutluk B, Altinisik K. Effects of operation temperature and reactant gas humidity levels on performance of PEM fuel cells. *Renew Sustain Energy Rev* 2016;59:1298–306. <https://doi.org/10.1016/J.RSER.2016.01.040>.
- [36] Curtin DE, Lousenberg RD, Henry TJ, Tangeman PC, Tisack ME. Advanced materials for improved PEMFC performance and life. *J Power Sources* 2004;131:41–8. <https://doi.org/10.1016/J.JPOWSOUR.2004.01.023>.
- [37] Borup R, Meyers J, Pivovar B, Kim YS, Mukundan R, Garland N, et al. Scientific aspects of polymer electrolyte fuel cell durability and degradation. *Chem Rev* 2007;107:3904–51. <https://doi.org/10.1021/CR050182L>.
- [38] McDonald RC, Mittelstaedt CK, Thompson EL. Effects of deep temperature cycling on Nafion® 112 membranes and membrane electrode assemblies. *Fuel Cell* 2004;4:208–13. <https://doi.org/10.1002/FUCE.200400015>.
- [39] Dafalla AM, Jiang F. Stresses and their impacts on proton exchange membrane fuel cells: a review. *Int J Hydrogen Energy* 2018;43:2327–48. <https://doi.org/10.1016/J.IJHYDENE.2017.12.033>.
- [40] Pham TA, Nam LV, Choi E, Lee M-S, Jun T-S, Jang S, et al. Mechanically stable thinned membrane for a high-performance polymer electrolyte membrane fuel cell via a plasma-etching and annealing process. *Energy Fuel* 2021;35:11525–32. <https://doi.org/10.1021/ACS.ENERGYFUELS.1C01225>.
- [41] Karimi MB, Mohammadi F, Hooshayri K. Recent approaches to improve Nafion performance for fuel cell applications: a review. *Int J Hydrogen Energy* 2019;44:28919–38. <https://doi.org/10.1016/J.IJHYDENE.2019.09.096>.
- [42] Sizov VE, Zefirov VV, Abramchuk SS, Korlyukov AA, Kondratenko MS, Vasil'ev VG, et al. Composite Nafion-based membranes with nanosized tungsten oxides prepared in supercritical carbon dioxide. *J Membr Sci* 2020;609:118244. <https://doi.org/10.1016/J.JMEMSCI.2020.118244>.
- [43] Boaretti C, Pasquini L, Sood R, Giancola S, Donnadio A, Roso M, et al. Mechanically stable nanofibrous sPEEK/Aquivion® composite membranes for fuel cell applications. *J Membr Sci* 2018;545:66–74. <https://doi.org/10.1016/J.JMEMSCI.2017.09.055>.
- [44] Rodgers MP, Berring J, Holdcroft S, Shi Z. The effect of spatial confinement of Nafion® in porous membranes on macroscopic properties of the membrane. *J Membr Sci*

- 2008;321:100–13. <https://doi.org/10.1016/J.MEMSCI.2008.01.007>.
- [45] Lu JL, Fang QH, Li SL, Jiang SP. A novel phosphotungstic acid impregnated meso-Nafion multilayer membrane for proton exchange membrane fuel cells. *J Memb Sci* 2013;427:101–7. <https://doi.org/10.1016/J.MEMSCI.2012.09.041>.
- [46] Ramani V, Kunz HR, Fenton JM. Effect of particle size reduction on the conductivity of Nafion®/phosphotungstic acid composite membranes. *J Memb Sci* 2005;266:110–4. <https://doi.org/10.1016/J.MEMSCI.2005.05.019>.
- [47] Li J, Xu G, Luo X, Xiong J, Liu Z, Cai W. Effect of nano-size of functionalized silica on overall performance of swelling-filling modified Nafion membrane for direct methanol fuel cell application. *Appl Energy* 2018;213:408–14. <https://doi.org/10.1016/J.APENERGY.2018.01.052>.
- [48] Matos BR, Santiago EI, Rey JFQ, Ferlauto AS, Traversa E, Linardi M, et al. Nafion-based composite electrolytes for proton exchange membrane fuel cells operating above 120 °C with titania nanoparticles and nanotubes as fillers. *J Power Sources* 2011;196:1061–8. <https://doi.org/10.1016/J.JPOWSOUR.2010.08.025>.
- [49] Truffier-Boutry D, De Geyer A, Guetaz L, Diat O, Gebel G. Structural study of zirconium Phosphate–Nafion hybrid membranes for high-temperature proton exchange membrane fuel cell applications. *Macromolecules* 2007;40:8259–64. <https://doi.org/10.1021/MA0706576>.
- [50] Jansto A, Davis EM. Role of surface chemistry on nanoparticle dispersion and vanadium ion crossover in nafion nanocomposite membranes. *ACS Appl Mater Interfaces* 2018;10:36385–97. <https://doi.org/10.1021/ACSAIMI.8B11297>.
- [51] Omosebi A, Besser RS. Electron beam patterned Nafion membranes for DMFC applications. *J Power Sources* 2013;228:151–8. <https://doi.org/10.1016/J.JPOWSOUR.2012.11.076>.
- [52] Van Nguyen T, Vu Nguyen M, Nordheden KJ, He W. Effect of bulk and surface treatments on the surface ionic activity of nafion membranes. *J Electrochem Soc* 2007;154:A1073. <https://doi.org/10.1149/1.2781247/PDF>.
- [53] Van Nguyen T, Vu Nguyen M, Nordheden KJ, He W. Effect of bulk and surface treatments on the surface ionic activity of nafion membranes. *J Electrochem Soc* 2007;154:A1073. <https://doi.org/10.1149/1.2781247/META>.
- [54] Nguyen T Van, Nguyen MV, Nordheden KJ, He W. Effect of bulk and surface treatments on the surface ionic activity of nafion membranes. *J Electrochem Soc* 2007;154:A1073. <https://doi.org/10.1149/1.2781247>.
- [55] Zhou J, Cao J, Zhang Y, Liu J, Chen J, Li M, et al. Overcoming undesired fuel crossover: goals of methanol-resistant modification of polymer electrolyte membranes. *Renew Sustain Energy Rev* 2021;138:110660. <https://doi.org/10.1016/J.RSER.2020.110660>.
- [56] Wei Y, Qian T, Liu J, Guo X, Gong Q, Liu Z, et al. Novel composite Nafion membranes modified with copper phthalocyanine tetrasulfonic acid tetrasodium salt for fuel cell application. *J Mater* 2019;5:252–7. <https://doi.org/10.1016/j.jmat.2019.01.006>.
- [57] Hou J, Yu H, Wang L, Xing D, Hou Z, Ming P, et al. Conductivity of aromatic-based proton exchange membranes at subzero temperatures. *J Power Sources* 2008;180:232–7. <https://doi.org/10.1016/j.jpowsour.2008.01.052>.
- [58] Eldin MSM, Elzatahy AA, El-Khatib KM, Hassan EA, El-Sabbah MM, Abu-Saied MA. Novel grafted nafion membranes for proton-exchange membrane fuel cell applications. *J Appl Polym Sci* 2011;119:120–33. <https://doi.org/10.1002/app.32613>.
- [59] Ercelik M, Ozden A, Devrim Y, Colpan CO. Investigation of Nafion based composite membranes on the performance of DMFCs. *Int J Hydrogen Energy* 2017;42:2658–68. <https://doi.org/10.1016/J.IJHYDENE.2016.06.215>.
- [60] Yin C, Xiong B, Liu Q, Li J, Qian L, Zhou Y, et al. Lateral-aligned sulfonated carbon-nanotubes/Nafion composite membranes with high proton conductivity and improved mechanical properties. *J Memb Sci* 2019;591:117356. <https://doi.org/10.1016/J.MEMSCI.2019.117356>.
- [61] Son B, Oh K, Park S, Lee T-G, Lee DH, Kwon O. Study of morphological characteristics on hydrophilicity-enhanced SiO₂/Nafion composite membranes by using multimode atomic force microscopy. *Int J Energy Res* 2019;43:4157–69. <https://doi.org/10.1002/ER.4528>.
- [62] Zhang C, Yue X, Luan J, Lu N, Mu Y, Zhang S, et al. Reinforced poly(ether ether ketone)/nafion composite membrane with highly improved proton conductivity for high concentration direct methanol fuel cells. *ACS Appl Energy Mater* 2020;3:7180–90. <https://doi.org/10.1021/acsael.0c01212>.
- [63] Makinouchi T, Tanaka M, Kawakami H. Improvement in characteristics of a Nafion membrane by proton conductive nanofibers for fuel cell applications. *J Memb Sci* 2017;530:65–72. <https://doi.org/10.1016/j.memsci.2017.02.018>.
- [64] Adjemian KT, Dominey R, Krishnan L, Ota H, Majsztrik P, Zhang T, et al. Function and characterization of metal oxide-nafion composite membranes for elevated-temperature H₂/O₂ PEM fuel cells. *Chem Mater* 2006;18:2238–48. <https://doi.org/10.1021/cm051781b>.
- [65] Zhu LY, Li YC, Liu J, He J, Wang LY, Lei J Du. Recent developments in high-performance Nafion membranes for hydrogen fuel cells applications. *Petrol Sci* 2021. <https://doi.org/10.1016/J.PETSCI.2021.11.004>.
- [66] Kabir MDL, Kim HJ, Choi S-J. Highly proton conductive Zn(II)-Based metal-organic framework/nafion ® composite membrane for fuel cell application. *Sci Adv Mater* 2018;10:1630–5. <https://doi.org/10.1166/SAM.2018.3355>.
- [67] Donnadio A, Narducci R, Casciola M, Marmottini F, D'Amato R, Jazestani M, et al. Mixed membrane matrices based on nafion/Uio-66/SO₃H-Uio-66 nano-MOFs: revealing the effect of crystal size, sulfonation, and filler loading on the mechanical and conductivity properties. *ACS Appl Mater Interfaces* 2017;9:42239–46. <https://doi.org/10.1021/ACSAIMI.7B14847>.
- [68] Zhang J, Bai H-J, Ren Q, Luo H-B, Ren X-M, Tian Z-F, et al. Extra water- and acid-stable MOF-801 with high proton conductivity and its composite membrane for proton-exchange membrane. *ACS Appl Mater Interfaces* 2018;10:28656–63. <https://doi.org/10.1021/ACSAIMI.8B09070>.
- [69] Wang L, Deng N, Liang Y, Ju J, Cheng B, Kang W. Metal-organic framework anchored sulfonated poly(ether sulfone) nanofibers as highly conductive channels for hybrid proton exchange membranes. *J Power Sources* 2020;450:227592. <https://doi.org/10.1016/J.JPOWSOUR.2019.227592>.
- [70] Guo X, Fan Y, Xu J, Wang L, Zheng J. Amino-MIL-53(Al)-Nanosheets@Nafion composite membranes with improved proton/methanol selectivity for passive direct methanol fuel cells. *Ind Eng Chem Res* 2020;59:14825–33. <https://doi.org/10.1021/ACS.IECR.0C02741>.
- [71] Krathumkhet N, Vongjtiphol K, Chuesutham T, Changkhamchom S, Phasuksum K, Sirivat A, et al. Preparation of sulfonated zeolite ZSM-5/sulfonated polysulfone composite membranes as PEM for direct methanol fuel cell application. *Solid State Ionics* 2018;319:278–84. <https://doi.org/10.1016/J.SSI.2018.02.019>.

- [72] Prapainainar P, Du Z, Theampetch A, Prapainainar C, Kongkachuchay P, Holmes SM. Properties and DMFC performance of nafion/mordenite composite membrane fabricated by solution-casting method with different solvent ratio. *Energy* 2020;190:116451. <https://doi.org/10.1016/J.ENERGY.2019.116451>.
- [73] Cui Y, Liu Y, Wu J, Zhang F, Baker AP, Lavorgna M, et al. Porous silicon-aluminium oxide particles functionalized with acid moieties: an innovative filler for enhanced Nafion-based membranes of direct methanol fuel cell. *J Power Sources* 2018;403:118–26. <https://doi.org/10.1016/J.JPOWSOUR.2018.09.090>.
- [74] Prapainainar P, Du Z, Kongkachuchay P, Holmes SM, Prapainainar C. Mordenite/Nafion and analcime/Nafion composite membranes prepared by spray method for improved direct methanol fuel cell performance. *Appl Surf Sci* 2017;421:24–41. <https://doi.org/10.1016/J.APSUSC.2017.02.004>.
- [75] Jang S, Kang YS, Choi J, Yeon JH, Seol C, Nam LV, et al. Prism patterned TiO₂ layers/Nafion® composite membrane for elevated temperature/low relative humidity fuel cell operation. *J Ind Eng Chem* 2020;90:327–32. <https://doi.org/10.1016/J.JIEC.2020.07.031>.
- [76] Seo DC, Jeon I, Jeong ES, Jho JY. Mechanical properties and chemical durability of nafion/sulfonated graphene oxide/cerium oxide composite membranes for fuel-cell applications. *Polym* 2020;12:1375. <https://doi.org/10.3390/POLYM12061375>. 2020;12:1375.
- [77] Mazzapoda L, Navarra MA, Trequattrini F, Paolone A, Elamin K, Martinelli A, et al. Composite nafion membranes with CaTiO₃–δ additive for possible applications in electrochemical devices. *Membr* 2019;9:143. <https://doi.org/10.3390/MEMBRANES9110143>. 2019;9:143.
- [78] Oh K, Kwon O, Son B, Lee DH, Shanmugam S. Nafion-sulfonated silica composite membrane for proton exchange membrane fuel cells under operating low humidity condition. *J Memb Sci* 2019;583:103–9. <https://doi.org/10.1016/J.MEMSCI.2019.04.031>.
- [79] Chen F, Mecheri B, D'Epifanio A, Traversa E, Licoccia S. Development of nafion/tin oxide composite MEA for DMFC applications. *Fuel Cell* 2010;10:790–7. <https://doi.org/10.1002/FUCE.200900179>.
- [80] Nam LV, Choi E, Jang S, Kim SM. Patterned mesoporous TiO₂ microplates embedded in Nafion® membrane for high temperature/low relative humidity polymer electrolyte membrane fuel cell operation. *Renew Energy* 2021;180:203–12. <https://doi.org/10.1016/J.RENENE.2021.08.062>.
- [81] Kabir MDL, Kim HJ, Choi SJ. Comparison of several acidified chitosan/Nafion® composite membranes for fuel cell applications. *J Nanosci Nanotechnol* 2017;17:8128–31. <https://doi.org/10.1166/JNN.2017.15082>.
- [82] Jung M, Lee W, Nambi Krishnan N, Kim S, Gupta G, Komsisyska L, et al. Porous-Nafion/PBI composite membranes and Nafion/PBI blend membranes for vanadium redox flow batteries. *Appl Surf Sci* 2018;450:301–11. <https://doi.org/10.1016/J.APSUSC.2018.04.198>.
- [83] Yang X, Zhu H, Jiang F, Zhou X. Notably enhanced proton conductivity by thermally-induced phase-separation transition of Nafion/Poly(vinylidene fluoride) blend membranes. *J Power Sources* 2020;473:228586. <https://doi.org/10.1016/J.JPOWSOUR.2020.228586>.
- [84] Fan L, Shi J, Xi Y. PVDF-modified nafion membrane for improved performance of MFC. *Membr* 2020;10:185. <https://doi.org/10.3390/MEMBRANES10080185>. 2020;10:185.
- [85] Grot W. Commercial membrane types. *Fluorinated Ionomers* 2011:185–99. <https://doi.org/10.1016/B978-1-4377-4457-6.10007-X>.
- [86] Gubler L. Polymer design strategies for radiation-grafted fuel cell membranes. *Adv Energy Mater* 2014;4:1300827. <https://doi.org/10.1002/AENM.201300827>.
- [87] Walkowiak-Kulikowska J, Wolska J, Koroniak H. Polymers application in proton exchange membranes for fuel cells (PEMFCs). *Phys Sci Rev* 2017;2. <https://doi.org/10.1515/psr-2017-0018>.
- [88] Lavorgna M, Mensitieri G, Scherillo G, Shaw MT, Swier S, Weiss RA. Polymer blend for fuel cells based on SPEKK: effect of cocontinuous morphology on water sorption and proton conductivity. *J Polym Sci, Part B: Polym Phys* 2007;45:395–404. <https://doi.org/10.1002/POLB.21058>.
- [89] Yoon S, Ahmed F, Zhang W, Ryu T, Jin L, Kim D, et al. Flexible blend polymer electrolyte membranes with excellent conductivity for fuel cells. *Int J Hydrogen Energy* 2020;45:27611–21. <https://doi.org/10.1016/J.IJHYDENE.2020.07.076>.
- [90] Wang S, He Z, Wang X, Wang C, Li X, Zhao Y. Ultrathin semi-interpenetrating network membranes based on perfluorinated sulfonic acid resin and polydivinylbenzene with declined hydrogen crossover for proton exchange membrane fuel cell. *J Electrochem Soc* 2021;168. <https://doi.org/10.1149/1945-7111/AC1B04.084508>.
- [91] Xue J, Liu L, Liao J, Shen Y, Li N. Semi-interpenetrating polymer networks by azide–alkyne cycloaddition as novel anion exchange membranes. *J Mater Chem A* 2018;6:11317–26. <https://doi.org/10.1039/C8TA02177E>.
- [92] Zeng L, He Q, Liao Y, Kuang S, Wang J, Ding W, et al. Anion exchange membrane based on interpenetrating polymer network with ultrahigh ion conductivity and excellent stability for alkaline fuel cell. *Research* 2020;2020:1–11. <https://doi.org/10.34133/2020/4794706>.
- [93] Byun GH, Kim JA, Kim NY, Cho YS, Park CR. Molecular engineering of hydrocarbon membrane to substitute perfluorinated sulfonic acid membrane for proton exchange membrane fuel cell operation. *Mater Today Energy* 2020;17:100483. <https://doi.org/10.1016/j.mtener.2020.100483>.
- [94] Kausar A. Progression from polyimide to polyimide composite in proton-exchange membrane fuel cell: a review. *Polym Plast Technol Eng* 2017;56:1375–90. <https://doi.org/10.1080/03602559.2016.1275688>.
- [95] Hooshyari K, Rezania H, Vatanpour V, Salarizadeh P, Askari MB, Beydaghi H, et al. High temperature membranes based on PBI/sulfonated polyimide and doped-perovskite nanoparticles for PEM fuel cells. *J Memb Sci* 2020;612:118436.
- [96] You PY, Kamarudin SK, Masdar MS. Improved performance of sulfonated polyimide composite membranes with rice husk ash as a bio-filler for application in direct methanol fuel cells. *Int J Hydrogen Energy* 2019;44:1857–66.
- [97] Makinouchi T, Tanaka M, Kawakami H. Improvement in characteristics of a Nafion membrane by proton conductive nanofibers for fuel cell applications. *J Memb Sci* 2017;530:65–72. <https://doi.org/10.1016/J.JMEMSCI.2017.02.018>.
- [98] Ma J, Ni HJ, Su DY, Huang MY, Wang XX. The research status of Nafion ternary composite membrane. *Int J Hydrogen Energy* 2012;37:13185–90. <https://doi.org/10.1016/J.IJHYDENE.2012.03.132>.
- [99] Ali N, Ali F, Khan S, Sheikh ZA, Said A, Nawaz Z, et al. Novel sulfonated polyimide-nafion nanocomposite membranes: fabrication, morphology and physicochemical investigations for fuel cell applications. *J Mol Struct* 2021;1231:129940. <https://doi.org/10.1016/J.MOLSTRUCT.2021.129940>.
- [100] Ali N, Ali F, Khan S, Sheikh ZA, Said A, Nawaz Z, et al. Novel sulfonated polyimide-nafion nanocomposite membranes:

- fabrication, morphology and physicochemical investigations for fuel cell applications. *J Mol Struct* 2021;1231:129940.
- [101] Ito G, Tanaka M, Kawakami H. Sulfonated polyimide nanofiber framework: evaluation of intrinsic proton conductivity and application to composite membranes for fuel cells. *Solid State Ionics* 2018;317:244–55. <https://doi.org/10.1016/J.SSI.2018.01.029>.
- [102] Hu M, Zhang B, Chen J, Xu M, Liu D, Wang L. Cross-linked polymer electrolyte membrane based on a highly branched sulfonated polyimide with improved electrochemical properties for fuel cell applications. *Int J Energy Res* 2019;43:8753–64. <https://doi.org/10.1002/ER.4879>.
- [103] Kowsari E, Zare A, Ansari V. Phosphoric acid-doped ionic liquid-functionalized graphene oxide/sulfonated polyimide composites as proton exchange membrane. *Int J Hydrogen Energy* 2015;40:13964–78. <https://doi.org/10.1016/J.IJHYDENE.2015.08.064>.
- [104] Liaqat K, Rehman W, Saeed S, Waseem M, Fazil S, Shakeel M, et al. Synthesis and characterization of novel sulfonated polyimide with varying chemical structure for fuel cell applications. *Solid State Ionics* 2018;319:141–7. <https://doi.org/10.1016/j.ssi.2018.02.018>.
- [105] Rehman W, Liaqat K, Fazil S, Saeed S, Waseem M, Shakeel M, et al. Chemically tethered functionalized graphene oxide based novel sulfonated polyimide composite for polymer electrolyte membrane. *J Polym Res* 2019;26:82. <https://doi.org/10.1007/s10965-019-1744-2>.
- [106] Rosli RE, Sulong AB, Daud WRW, Zulkifley MA, Husaini T, Rosli MI, et al. A review of high-temperature proton exchange membrane fuel cell (HT-PEMFC) system. *Int J Hydrogen Energy* 2017;42:9293–314. <https://doi.org/10.1016/j.ijhydene.2016.06.211>.
- [107] Li Q, Jensen JO, Savinell RF, Bjerrum NJ. High temperature proton exchange membranes based on polybenzimidazoles for fuel cells. *Prog Polym Sci* 2009;34:449–77. <https://doi.org/10.1016/j.progpolymsci.2008.12.003>.
- [108] Escorihuela J, Olvera-Mancilla J, Alexandrova L, Felipe Del Castillo L, Compañ V. polymers recent progress in the development of composite membranes based on polybenzimidazole for high temperature proton exchange membrane (PEM) fuel cell applications n.d. doi:10.3390/polym12091861.
- [109] Escorihuela J, Ó Sahuquillo, García-Bernabé A, Giménez E, Compañ V. Phosphoric acid doped polybenzimidazole (PBI)/Zeolitic imidazolate framework composite membranes with significantly enhanced proton conductivity under low humidity conditions. *Nanomaterials* 2018;8:775. <https://doi.org/10.3390/nano8100775>.
- [110] Hwang K, Kim J-H, Kim S-Y, Byun H. Preparation of polybenzimidazole-based membranes and their potential applications in the fuel cell system. *Energies* 2014;7:1721–32. <https://doi.org/10.3390/EN7031721>. 2014;7:1721–1732.
- [111] Lobato J, Cañizares P, Rodrigo MA, Úbeda D, Pinar FJ. Enhancement of the fuel cell performance of a high temperature proton exchange membrane fuel cell running with titanium composite polybenzimidazole-based membranes. *J Power Sources* 2011;196:8265–71. <https://doi.org/10.1016/J.JPOWSOUR.2011.06.011>.
- [112] Krishnan NN, Lee S, Ghorpade RV, Konovalova A, Jang JH, Kim H-J, et al. Polybenzimidazole (PBI-OO) based composite membranes using sulfophenylated TiO₂ as both filler and crosslinker, and their use in the HT-PEM fuel cell. *J Memb Sci* 2018;560:11–20. <https://doi.org/10.1016/j.memsci.2018.05.006>.
- [113] Lobato J, Cañizares P, Rodrigo MA, Úbeda D, Pinar FJ. Promising TiOSO₄ composite polybenzimidazole-based membranes for high temperature PEMFCs. *ChemSusChem* 2011;4:1489–97. <https://doi.org/10.1002/cssc.201100032>.
- [114] Budak Y, Devrim Y. Micro-cogeneration application of a high-temperature PEM fuel cell stack operated with polybenzimidazole based membranes. *Int J Hydrogen Energy* 2020;45:35198–207. <https://doi.org/10.1016/J.IJHYDENE.2019.11.173>.
- [115] Suryani Chang YN, Lai JY, Liu YL. Polybenzimidazole (PBI)-functionalized silica nanoparticles modified PBI nanocomposite membranes for proton exchange membranes fuel cells. *J Memb Sci* 2012;403–404:1–7. <https://doi.org/10.1016/J.MEMSCI.2012.01.043>.
- [116] Ren HM, Wang HW, Jiang YF, Tao ZX, Mu CY, Li G. Proton conductive lanthanide-based metal–organic frameworks: synthesis strategies, structural features, and recent progress. *Top Curr Chem* 2022;380:1–58. <https://doi.org/10.1007/S41061-022-00367-9/FIGURES/23>.
- [117] Lemus J, Eguizábal A, Pina MP. Endurance strategies for the preparation of high temperature polymer electrolyte membranes by UV polymerization of 1-H-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide for fuel cell applications. *Int J Hydrogen Energy* 2016;41:3981–93. <https://doi.org/10.1016/j.ijhydene.2015.11.006>.
- [118] Kausar A, Khurram M, Siddiq M. Sulfonated poly(sulfone-pyridine-amide)/sulfonated polystyrene/multiwalled carbon nanotube-based fuel cell membranes. *Polym Eng Sci* 2015;55:1776–86. <https://doi.org/10.1002/PEN.24016>.
- [119] Mahimai BM, Sivasubramanian G, Kulasekaran P, Deivanayagam P. Sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene based membranes containing CuO@g-C3N4 embedded with 2,4,6-triphenylpyrylium tetrafluoroborate for fuel cell applications. *Soft Matter* 2021;17:8387–93. <https://doi.org/10.1039/D1SM01015H>.
- [120] Jalal NM, Jabur AR, Hamza MS, Allami S. Preparation, microstructure and morphology of electrospun sulfonated polystyrene films for proton exchange membrane hydrogen fuel cell. *Energy Proc* 2019;157:1494–505. <https://doi.org/10.1016/J.EGYPRO.2018.11.314>.
- [121] Gonggo ST, Bundjali B, Hariyawati K, Arcana IM. The influence of nano-silica on properties of sulfonated polystyrene-lignosulfonate membranes as proton exchange membranes for direct methanol fuel cell application. *Adv Polym Technol* 2018;37:1859–67. <https://doi.org/10.1002/ADV.21844>.
- [122] Chae JE, Lee SY, Yoo SJ, Kim JY, Jang JH, Park H-Y, et al. Polystyrene-based hydroxide-ion-conducting ionomer: binder characteristics and performance in anion-exchange membrane fuel cells. *Polym* 2021;13:690. <https://doi.org/10.3390/POLYM13050690>. 2021;13:690.
- [123] Tuli SK, Roy AL, Elgammal RA, Zawodzinski TA, Fujiwara T. Polystyrene-based anion exchange membranes via click chemistry: improved properties and AEM performance. *Polym Int* 2018;67:1302–12. <https://doi.org/10.1002/PI.5657>.
- [124] Tuli SK, Roy AL, Elgammal RA, Tian M, Zawodzinski TA, Fujiwara T. Effect of morphology on anion conductive properties in self-assembled polystyrene-based copolymer membranes. *J Memb Sci* 2018;565:213–25. <https://doi.org/10.1016/J.MEMSCI.2018.08.028>.
- [125] Xue J, Liu L, Liao J, Shen Y, Li N. UV-crosslinking of polystyrene anion exchange membranes by azidated macromolecular crosslinker for alkaline fuel cells. *J Memb Sci* 2017;535:322–30. <https://doi.org/10.1016/J.MEMSCI.2017.04.049>.
- [126] Gupta G, Scott K, Mamlouk M. Soluble polystyrene-b-poly(ethylene/butylene)-b-polystyrene based ionomer for anion

- exchange membrane fuel cells operating at 70 °C. *Fuel Cell* 2018;18:137–47. <https://doi.org/10.1002/FUCE.201700176>.
- [127] Samaei SH-A, Bakeri G, Lashkenari MS. Performance of the sulfonated poly(ether ether ketone) proton exchange membrane modified with sulfonated polystyrene and phosphotungstic acid for microbial fuel cell applications. *J Appl Polym Sci* 2021;138:50430. <https://doi.org/10.1002/JAPP.50430>.
- [128] Nilurout N, Shukla A, Dhavale VM, Unni SM, Bhat SD. Sulfonated poly(ether ether ketone) reinforced with polystyrene sulfonic acid functionalized micelle templated mesoporous MCM-41 for direct methanol fuel cells. *Int J Hydrogen Energy* 2021;46:20640–9. <https://doi.org/10.1016/J.IJHYDENE.2021.03.156>.
- [129] Shukla A, Dhanasekaran P, Sasikala S, Nagaraju N, Bhat SD, Pillai VK. Covalent grafting of polystyrene sulfonic acid on graphene oxide nanoplatelets to form a composite membrane electrolyte with sulfonated poly(ether ether ketone) for direct methanol fuel cells. *J Membr Sci* 2020;595:117484. <https://doi.org/10.1016/J.MEMSCI.2019.117484>.
- [130] Moharir PV, Tembhurkar AR. Comparative performance evaluation of novel polystyrene membrane with ultrex as Proton Exchange Membranes in Microbial Fuel Cell for bioelectricity production from food waste. *Bioresour Technol* 2018;266:291–6. <https://doi.org/10.1016/J.BIOTECH.2018.06.085>.
- [131] Ponomarev AN, Abdushitov EF, Kritskaya DA, Bokun VC, Sanginov EA, Dobrovols'kii YA. Synthesis of polymer nanocomposite ion-exchange membranes from sulfonated polystyrene and study of their properties. *Russ J Electrochim* 2017;53:589–607. <https://doi.org/10.1134/S1023193517060143>. 536 2017.
- [132] Sadeghi S, İşıkel Şanlı L, Güler E, Alkan Gürsel S. Enhancing proton conductivity via sub-micron structures in proton conducting membranes originating from sulfonated PVDF powder by radiation-induced grafting. *Solid State Ionics* 2018;314:66–73. <https://doi.org/10.1016/J.SSI.2017.11.017>.
- [133] Abdel-Hady EE, Abdel-Hamed MO, Awad S, Hmamm MFM. Characterization and evaluation of commercial poly(vinylidene fluoride)-g-sulfonated polystyrene as proton exchange membrane. *Polym Adv Technol* 2018;29:130–42. <https://doi.org/10.1002/PAT.4095>.
- [134] Ponomarev AN, Kritskaya DA, Abdushitov EF, Bokun VC, Sanginov EA, Novikova KS, et al. Thermal polymerization of styrene sorbed from the gas phase into polymer films as a method for synthesizing precursors of ion-exchange membranes. *Russ J Electrochim* 2019;55:738–44. <https://doi.org/10.1134/S1023193519080123>. 558 2019.
- [135] Golubenko DV, Gerasimova EV, Yaroslavtsev AB. Proton conductivity and performance in fuel cells of grafted membranes based on polymethylpentene with radiation-grafted crosslinked sulfonated polystyrene. *Int J Hydrogen Energy* 2021;46:16999–7006. <https://doi.org/10.1016/J.IJHYDENE.2021.01.102>.
- [136] Guo Q, Pintauro P N, Tang H, O'Connor S. Sulfonated and crosslinked polyphosphazene-based proton-exchange membranes. *J Membr Sci* 1999;154:175–81. [https://doi.org/10.1016/S0376-7388\(98\)00282-8](https://doi.org/10.1016/S0376-7388(98)00282-8).
- [137] Fu F, Xu H, Dong Y, He M, Luo T, Zhang Y, et al. Polyphosphazene-based copolymers containing pendant alkylsulfonic acid groups as proton exchange membranes. *Solid State Ionics* 2015;278:58–64. <https://doi.org/10.1016/J.SSI.2015.05.018>.
- [138] Fu F, Xu H, Dong Y, He M, Zhang Z, Luo T, et al. Design of polyphosphazene-based graft copolystyrenes with alkylsulfonate branch chains for proton exchange membranes. *J Membr Sci* 2015;489:119–28. <https://doi.org/10.1016/J.MEMSCI.2015.04.016>.
- [139] Ouadah A, Luo T, Gao S, Zhu C. Controlling the degree of sulfonation and its impact on hybrid cross-linked network based polyphosphazene grafted butylphenoxy as proton exchange membrane. *Int J Hydrogen Energy* 2018;43:15466–80. <https://doi.org/10.1016/J.IJHYDENE.2018.06.105>.
- [140] Luo T, Zhang Y, Xu H, Zhang Z, Fu F, Gao S, et al. Highly conductive proton exchange membranes from sulfonated polyphosphazene-graft-copolystyrenes doped with sulfonated single-walled carbon nanotubes. *J Membr Sci* 2016;514:527–36. <https://doi.org/10.1016/J.MEMSCI.2016.04.071>.
- [141] Lv Y, Li Z, Song M, Sun P, Yin X, Wang S. Preparation and properties of ZrPA doped CMPSU cross-linked PBI based high temperature and low humidity proton exchange membranes. *React Funct Polym* 2019;137:57–70. <https://doi.org/10.1016/J.REACTFUNCTPOLYM.2019.01.014>.
- [142] da Trindade LG, Zanchet L, Dreon R, Souza JC, Assis M, Longo E, et al. Microwave-assisted solvothermal preparation of Zr-BDC for modification of proton exchange membranes made of SPEEK/PBI blends. *J Mater Sci* 2020;55:14938–52. <https://doi.org/10.1007/S10853-020-05068-6>. 5530 2020.
- [143] Yin B, Liang R, Liang X, Fu D, Wang L, Sun G. Construction of stable wide-temperature-range proton exchange membranes by incorporating a carbonized metal–organic frame into polybenzimidazoles and polyacrylamide hydrogels. *Small* 2021;17:2103214. <https://doi.org/10.1002/SMLL.202103214>.
- [144] Krishnan NN, Lee S, Ghorpade RV, Konovalova A, Jang JH, Kim HJ, et al. Polybenzimidazole (PBI-OO) based composite membranes using sulfophenylated TiO₂ as both filler and crosslinker, and their use in the HT-PEM fuel cell. *J Membr Sci* 2018;560:11–20. <https://doi.org/10.1016/J.MEMSCI.2018.05.006>.
- [145] Özdemir Y, Üreğen N, Devrim Y. Polybenzimidazole based nanocomposite membranes with enhanced proton conductivity for high temperature PEM fuel cells. *Int J Hydrogen Energy* 2017;42:2648–57. <https://doi.org/10.1016/J.IJHYDENE.2016.04.132>.
- [146] Barati S, Mehdipourghazi M, Abdollahi M, Hooshayri K, Khoshandam B. Preparation, characterization and proton transport of new porous nanocomposite membranes based on polybenzimidazole, lignin and TiO₂ nanoparticles for high temperature PEM fuel cells. *Int J Energy Res* 2021;45:20057–72. <https://doi.org/10.1002/ER.7083>.
- [147] Lee S, Seo K, Ghorpade RV, Nam KH, Han H. High temperature anhydrous proton exchange membranes based on chemically-functionalized titanium/polybenzimidazole composites for fuel cells. *Mater Lett* 2020;263:127167. <https://doi.org/10.1016/J.MATLET.2019.127167>.
- [148] Sun P, Li Z, Dong F, Wang S, Yin X, Wang Y. High temperature proton exchange membranes based on cerium sulfophenyl phosphate doped polybenzimidazole by end-group protection and hot-pressing method. *Int J Hydrogen Energy* 2017;42:486–95. <https://doi.org/10.1016/J.IJHYDENE.2016.09.174>.
- [149] Guo H, Li Z, Sun P, Pei H, Zhang L, Cui W, et al. Enhancing proton conductivity and durability of crosslinked PBI-based high-temperature PEM: effectively doping a novel cerium triphosphonic-isocyanurate. *J Electrochim Soc* 2021;168. <https://doi.org/10.1149/1945-7111/ABE290.024510>.
- [150] Escorihuela J, Olvera-Mancilla J, Alexandrova L, Castillo LF del, Compañ V. Recent progress in the development of

- composite membranes based on polybenzimidazole for high temperature proton exchange membrane (PEM) fuel cell applications. *Polym* 2020;12:1861. <https://doi.org/10.3390/POLYM12091861>. 2020;12:1861.
- [151] Wang F, Li J, Chen T, Xu J. Synthesis of poly(ether ether ketone) with high content of sodium sulfonate groups and its membrane characteristics. *Polymer* 1999;40:795–9. [https://doi.org/10.1016/S0032-3861\(98\)00292-4](https://doi.org/10.1016/S0032-3861(98)00292-4).
- [152] Colomban P. Proton conductors and their applications: a tentative historical overview of the early researches. *Solid State Ionics* 2019;334:125–44. <https://doi.org/10.1016/J.SSI.2019.01.032>.
- [153] Jin X, Bishop MT, Ellis TS, Karasz FE. A sulphonated poly(aryl ether ketone). *Br Polym J* 1985;17:4–10. <https://doi.org/10.1002/PI.4980170102>.
- [154] Park CH, Lee CH, Sohn J-Y, Park HB, Guiver MD, Lee YM. Phase separation and water channel formation in sulfonated block copolyimide. *J Phys Chem B* 2010;114:12036–45. <https://doi.org/10.1021/JP105708M>.
- [155] Jouanneau Julien, Mercier Régis, Gonon Laurent, Gebel G. Synthesis of sulfonated polybenzimidazoles from functionalized monomers: preparation of ionic conducting membranes. *Macromolecules* 2007;40:983–90. <https://doi.org/10.1021/MA0614139>.
- [156] Zhang Z, Ren J, Ju M, Chen X, Xu J, Wang Z, et al. Construction of new alternative transmission sites by incorporating structure-defect metal-organic framework into sulfonated poly(arylene ether sulfone)s. *Int J Hydrogen Energy* 2021;46:27193–206. <https://doi.org/10.1016/J.IJHYDENE.2021.05.167>.
- [157] Kraytsberg A, Ein-Eli Y. Review of advanced materials for proton exchange membrane fuel cells. *Energy Fuel* 2014;28:7303–30. <https://doi.org/10.1021/EF501977K>.
- [158] Iulianelli A, Basile A. Sulfonated PEEK-based polymers in PEMFC and DMFC applications: a review. *Int J Hydrogen Energy* 2012;37:15241–55. <https://doi.org/10.1016/J.IJHYDENE.2012.07.063>.
- [159] Mahato N, Jang H, Dhyani A, Cho S. Recent progress in conducting polymers for hydrogen storage and fuel cell applications. *Polym* 2020;12:2480. <https://doi.org/10.3390/POLYM1212480>. 2020;12:2480.
- [160] Hou H, Di Vona ML, Knauth P. Durability of sulfonated aromatic polymers for proton-exchange-membrane fuel cells. *ChemSusChem* 2011;4:1526–36. <https://doi.org/10.1002/CSSC.201000415>.
- [161] Adamski M, Peressin N, Holdcroft S. On the evolution of sulfonated polyphenylenes as proton exchange membranes for fuel cells. *Mater Adv* 2021;2:4966–5005. <https://doi.org/10.1039/D1MA00511A>.
- [162] Shi M, Liu L, Tong Y, Huang L, Li W, Xing W. Advanced porous polyphenylsulfone membrane with ultrahigh chemical stability and selectivity for vanadium flow batteries. *J Appl Polym Sci* 2019;136:47752. <https://doi.org/10.1002/APP.47752>.
- [163] Palamara D, Bruzzaniti P, Calabrese L, Proverbio E. Effect of degree of sulfonation on the performance of adsorbent SAPO-34/S-PEEK composite coatings for adsorption heat pumps. *Prog Org Coating* 2021;154:106193. <https://doi.org/10.1016/J.PORGCOAT.2021.106193>.
- [164] Molina J, Pablo JJ de, Hernández-Ortiz JP. Structure and proton conduction in sulfonated poly(ether ether ketone) semi-permeable membranes: a multi-scale computational approach. *Phys Chem Chem Phys* 2019;21:9362–75. <https://doi.org/10.1039/C9CP00598F>.
- [165] Kim M, Ko H, Nam SY, Kim K. Study on control of polymeric architecture of sulfonated hydrocarbon-based polymers for high-performance polymer electrolyte membranes in fuel cell applications. *Polym* 2021;13:3520. <https://doi.org/10.3390/POLYM13203520>. 2021;13:3520.
- [166] Duan Y, Ru C, Li J, Sun Y nan, Pu X, Liu B, et al. Enhancing proton conductivity and methanol resistance of SPAEK membrane by incorporating MOF with flexible alkyl sulfonic acid for DMFC. *J Memb Sci* 2022;641:119906. <https://doi.org/10.1016/J.MEMSCI.2021.119906>.
- [167] Neelakandan S, Liu D, Wang L, Hu M, Wang L. Highly branched poly(arylene ether)/surface functionalized fullerene-based composite membrane electrolyte for DMFC applications. *Int J Energy Res* 2019;43:3756–67. <https://doi.org/10.1002/ER.4536>.
- [168] Liu Z, Wang P, Hu W, Liu B. Preparation and properties of hybrid silane-crosslinked sulfonated poly(aryl ether ketone)s as proton exchange membranes. *Chem Res Chin Univ* 2019;35:937–44. <https://doi.org/10.1007/S40242-019-9066-9>. 355 2019.
- [169] Bae I, Oh KH, Yun M, Kang MK, Song HH, Kim H. Nanostructured composite membrane with cross-linked sulfonated poly(arylene ether ketone)/silica for high-performance polymer electrolyte membrane fuel cells under low relative humidity. *J Memb Sci* 2018;549:567–74. <https://doi.org/10.1016/J.MEMSCI.2017.12.060>.
- [170] Munavalli BB, Kariduraganavar MY. Enhancement of fuel cell performance of sulfonated poly(arylene ether ketone) membrane using different crosslinkers. *J Memb Sci* 2018;566:383–95. <https://doi.org/10.1016/J.MEMSCI.2018.09.023>.
- [171] Ni C, Wang H, Zhao Q, Liu B, Sun Z, Zhang M, et al. Crosslinking effect in nanocrystalline cellulose reinforced sulfonated poly(aryl ether ketone) proton exchange membranes. *Solid State Ionics* 2018;323:5–15. <https://doi.org/10.1016/J.SSI.2018.05.004>.
- [172] Lee S-W, Abdi ZG, Chen J-C, Chen K-H. Optimal method for preparing sulfonated polyaryletherketones with high ion exchange capacity by acid-catalyzed crosslinking for proton exchange membrane fuel cells. *J Polym Sci* 2021;59:706–20. <https://doi.org/10.1002/POL.20200872>.
- [173] Purwanto MNA. Preparation and properties of chitosan/montmorillonite supported phosphotungstic acid composite membrane for direct methanol fuel cell application. *Korean J Mater Res* 2021;31:375–81. <https://doi.org/10.3740/MRSK.2021.31.7.375>.
- [174] Kim K, Heo P, Han J, Kim J, Lee JC. End-group cross-linked sulfonated poly(arylene ether sulfone) via thiol-ene click reaction for high-performance proton exchange membrane. *J Power Sources* 2018;401:20–8. <https://doi.org/10.1016/J.JPOWSOUR.2018.08.053>.
- [175] Kim JD, Ohira A, Nakao H. Chemically crosslinked sulfonated polyphenylsulfone (CSPPSU) membranes for PEM fuel cells. *Membranes* 2020;10. <https://doi.org/10.3390/MEMBRANES10020031>.
- [176] Xu D, Xu J, Wang X, Wang Z. Excellent performance of resistance methanol of a novel sulfonated poly (aryl ether ketone sulfone)/poly (vinylalcohol) composite membrane for direct methanol fuel cell applications. *Int J Hydrogen Energy* 2016;41:20536–48. <https://doi.org/10.1016/J.IJHYDENE.2016.08.113>.
- [177] Rr S, R W, K M, Ww Y, P J. Recent progress in the development of aromatic polymer-based proton exchange membranes for fuel cell applications. *Polym* 2020;12:1061. <https://doi.org/10.3390/POLYM12051061>. 2020;12:1061.
- [178] Walkowiak-Kulikowska J, Wolska J, Koroniak H. Polymers application in proton exchange membranes for fuel cells (PEMFCs). *Pol Eng* 2017;293–348. <https://doi.org/10.1515/9783110469745-010/HTML>. 10.
- [179] Hu H, Ding F, Ding H, Liu J, Xiao M, Meng Y, et al. Sulfonated poly(fluorenyl ether ketone)/Sulfonated α -zirconium

- phosphate Nanocomposite membranes for proton exchange membrane fuel cells. *Adv Compos Hybrid Mater* 2020;3:498–507. <https://doi.org/10.1007/S42114-020-00182-0>. 34 2020.
- [180] Liu Y, Huo P, Ren J, Wang G. Organic–inorganic hybrid proton-conducting electrolyte membranes based on sulfonated poly(arylene ether sulfone) and $\text{SiO}_2\text{--SO}_3\text{H}$ network for fuel cells. *High Perform Polym* 2016;29:1037–48. <https://doi.org/10.1177/095408316667790>.
- [181] Kim AR, Vinothkannan M, Lee KH, Chu JY, Park BH, Han MK, et al. Enhanced performance and durability of composite membranes containing anatase titanium oxide for fuel cells operating under low relative humidity. *Int J Energy Res* 2022;46:4835–51. <https://doi.org/10.1002/ER.7477>.
- [182] Kreuer KD. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. *J Memb Sci* 2001;185:29–39. [https://doi.org/10.1016/S0376-7388\(00\)00632-3](https://doi.org/10.1016/S0376-7388(00)00632-3).
- [183] Jiang S, Sun H, Wang H, Ladewig BP, Yao Z. A comprehensive review on the synthesis and applications of ion exchange membranes. *Chemosphere* 2021;282:130817. <https://doi.org/10.1016/J.CHEMOSPHERE.2021.130817>.
- [184] Chen Y, Meng Y, Wang S, Tian S, Chen Y, Hay AS. Sulfonated poly(fluorenyl ether ketone) membrane prepared via direct polymerization for PEM fuel cell application. *J Memb Sci* 2006;280:433–41. <https://doi.org/10.1016/J.MEMSCI.2006.01.052>.
- [185] Chen J, Maekawa Y, Asano M, Yoshida M. Double crosslinked polyetheretherketone-based polymer electrolyte membranes prepared by radiation and thermal crosslinking techniques. *Polymer* 2007;48:6002–9. <https://doi.org/10.1016/J.POLYMER.2007.08.005>.
- [186] Huang H, Cao Z, Gadelrab KR, Mailoa JP, Alexander-Katz A. Controlled water uptake in fuel cell membranes with dual chemistry confinement. *Chem Mater* 2021;33:6662–70. <https://doi.org/10.1021/ACS.CHEMMATER.1C00431>.
- [187] Vetter S, Ruffmann B, Buder I, Nunes SP. Proton conductive membranes of sulfonated poly(ether ketone ketone). *J Memb Sci* 2005;260:181–6. <https://doi.org/10.1016/J.MEMSCI.2005.02.036>.
- [188] Zhang H, Shen PK. Recent development of polymer electrolyte membranes for fuel cells. *Chem Rev* 2012;112:2780–832. <https://doi.org/10.1021/CR200035S>.
- [189] Khomeini P, Ketelaars W, Lap T, Liu G. Sulfonated aromatic polymer as a future proton exchange membrane: a review of sulfonation and crosslinking methods. *Renew Sustain Energy Rev* 2021;137:110471. <https://doi.org/10.1016/J.RSER.2020.110471>.
- [190] Pugalenthi MR, Cao G, Manimuthu RP. Cross-linked SPEEK–PEG–APTEOS-modified CaTiO_3 perovskites for efficient acid–base cation-exchange membrane fuel cell. *Energy Fuel* 2020;34:10087–99. <https://doi.org/10.1021/ACS.ENERGYFUELS.0C01933>.
- [191] Song M, Lu X, Li Z, Liu G, Yin X, Wang Y. Compatible ionic crosslinking composite membranes based on SPEEK and PBI for high temperature proton exchange membranes. *Int J Hydrogen Energy* 2016;41:12069–81. <https://doi.org/10.1016/J.IJHYDENE.2016.05.227>.
- [192] Che Q, Yue J. Polymerized imidazolium ionic liquids crosslinking sulfonated poly(ether ether ketone) (SPEEK) for high-temperature proton exchange membrane. *RSC Adv* 2016;6:111729–38. <https://doi.org/10.1039/C6RA21616A>.
- [193] Kumari M, Sodaye HS, Bindal RC. Cross-linked sulfonated poly(ether ether ketone)-poly ethylene glycol/silica organic–inorganic nanocomposite membrane for fuel cell application. *J Power Sources* 2018;398:137–48. <https://doi.org/10.1016/J.JPOWSOUR.2018.07.053>.
- [194] Hasani-Sadrabadi MM, Dashtimoghadam E, Sarikhani K, Majedi FS, Khanbabaei G. Electrochemical investigation of sulfonated poly(ether ether ketone)/clay nanocomposite membranes for moderate temperature fuel cell applications. *J Power Sources* 2010;195:2450–6. <https://doi.org/10.1016/j.jpowsour.2009.11.090>.
- [195] Vidhyeswari D, Surendhar A, Bhuvaneshwari S. Evaluation of power generation and treatment efficiency of dairy wastewater in microbial fuel cell using TiO_2 – SPEEK as proton exchange membrane. *Water Sci Technol* 2021. <https://doi.org/10.2166/WST.2021.467>.
- [196] Tsen W-C. Hydrophilic TiO_2 decorated carbon nanotubes/sulfonated poly(ether ether ketone) composite proton exchange membranes for fuel cells. *Polym Eng Sci* 2020;60:1832–41. <https://doi.org/10.1002/PEN.25420>.
- [197] Roy T, Wanchoo SK, Pal K. Novel sulfonated poly (ether ether ketone)/rGONR@ TiO_2 nanohybrid membrane for proton exchange membrane fuel cells. *Solid State Ionics* 2020;349:115296. <https://doi.org/10.1016/J.JSSI.2020.115296>.
- [198] Bisht S, Balaguru S, Ramachandran SK, Gangasalam A, Kweon J. Proton exchange composite membranes comprising SiO_2 , sulfonated SiO_2 , and metal–organic frameworks loaded in SPEEK polymer for fuel cell applications. *J Appl Polym Sci* 2021;138:50530. <https://doi.org/10.1002/APP.50530>.
- [199] Sivsankaran A, Sangeetha D. Influence of sulfonated SiO_2 in sulfonated polyether ether ketone nanocomposite membrane in microbial fuel cell. *Fuel* 2015;159:689–96. <https://doi.org/10.1016/J.FUEL.2015.07.002>.
- [200] Cui L, Geng Q, Gong C, Liu H, Zheng G, Wang G, et al. Novel sulfonated poly (ether ether ketone)/silica coated carbon nanotubes high-performance composite membranes for direct methanol fuel cell. *Polym Adv Technol* 2015;26:457–64. <https://doi.org/10.1002/PAT.3473>.
- [201] Wang H, Li X, Zhuang X, Cheng B, Wang W, Kang W, et al. Modification of Nafion membrane with biofunctional SiO_2 nanofiber for proton exchange membrane fuel cells. *J Power Sources* 2017;340:201–9. <https://doi.org/10.1016/J.JPOWSOUR.2016.11.072>.
- [202] Ali MM, Rizvi SJA, Azam A. Fabrication of proton exchange membranes and effect of sulfonated SiO_2 (S-SiO_2) in sulfonated polyether ether ketone (SPEEK) for fuel cells applications. *IOP Conf Ser Mater Sci Eng* 2019;577. <https://doi.org/10.1088/1757-899X/577/1/012039>. 012039.
- [203] Martina P, Gayathri R, Raja Pugalenthi M, Cao G, Liu C, Ramesh Prabhu M. Nanosulfonated silica incorporated SPEEK/SPVdF-HFP polymer blend membrane for PEM fuel cell application n.d. doi:10.1007/s11581-020-03478-9/ [Published].
- [204] Parnian MJ, Rowshanzamir S, Prasad AK, Advani SG. Effect of ceria loading on performance and durability of sulfonated poly (ether ether ketone) nanocomposite membranes for proton exchange membrane fuel cell applications. *J Memb Sci* 2018;565:342–57. <https://doi.org/10.1016/J.MEMSCI.2018.08.029>.
- [205] Elakkiya S, Arthanareeswaran G, Venkatesh K, Kweon J. Enhancement of fuel cell properties in polyethersulfone and sulfonated poly (ether ether ketone) membranes using metal oxide nanoparticles for proton exchange membrane fuel cell. *Int J Hydrogen Energy* 2018;43:21750–9. <https://doi.org/10.1016/J.IJHYDENE.2018.04.094>.
- [206] Gahlot S, Kulshrestha V. Dramatic improvement in water retention and proton conductivity in electrically aligned functionalized CNT/SPEEK nanohybrid PEM. *ACS Appl Mater Interfaces* 2014;7:264–72. <https://doi.org/10.1021/AM506033C>.

- [207] Kim AR, Vinothkannan M, Song MH, Lee JY, Lee HK, Yoo DJ. Amine functionalized carbon nanotube (ACNT) filled in sulfonated poly(ether ether ketone) membrane: effects of ACNT in improving polymer electrolyte fuel cell performance under reduced relative humidity. *Compos B Eng* 2020;188:107890. <https://doi.org/10.1016/J.COMPOSITESB.2020.107890>.
- [208] Mossayebi Z, Saririchi T, Rowshanzamir S, Parnian MJ. Investigation and optimization of physicochemical properties of sulfated zirconia/sulfonated poly (ether ether ketone) nanocomposite membranes for medium temperature proton exchange membrane fuel cells. *Int J Hydrogen Energy* 2016;41:12293–306. <https://doi.org/10.1016/J.IJHYDENE.2016.05.017>.
- [209] Batalha JAFL, Dahmouche K, Sampaio RB, Gomes A de S. Structure and properties of new sPEEK/zirconia/protic ionic liquid membranes for fuel cell application. *Macromol Mater Eng* 2017;302:1600301. <https://doi.org/10.1002/MAME.201600301>.
- [210] Silva VS, Ruffmann B, Silva H, Gallego YA, Mendes A, Madeira LM, et al. Proton electrolyte membrane properties and direct methanol fuel cell performance: I. Characterization of hybrid sulfonated poly(ether ether ketone)/zirconium oxide membranes. *J Power Sources* 2005;140:34–40. <https://doi.org/10.1016/J.JPOWSOUR.2004.08.004>.
- [211] Mossayebi Z, Parnian MJ, Rowshanzamir S. Effect of the sulfated zirconia nanostructure characteristics on physicochemical and electrochemical properties of SPEEK nanocomposite membranes for PEM fuel cell applications. *Macromol Mater Eng* 2018;303:1700570. <https://doi.org/10.1002/MAME.201700570>.
- [212] Daud SNSS, Norddin MNAM, Jaafar J, Sudirman R. High degree sulfonated poly(ether ether ketone) blend with polyvinylidene fluoride as a potential proton-conducting membrane fuel cell. *High Perform Polym* 2019;32:103–15. <https://doi.org/10.1177/0954008319853337>.
- [213] Selvakumar K, Ramesh Prabhu M. Investigation on meta-polybenzimidazole blend with sulfonated PVdF-HFP proton conducting polymer electrolytes for HT-PEM fuel cell application. *J Mater Sci Mater Electron* 2018;29:15163–73. <https://doi.org/10.1007/S10854-018-9658-Z>.
- [214] Inan TY, Doan H, Unveren EE, Eker E. Sulfonated PEEK and fluorinated polymer based blends for fuel cell applications: investigation of the effect of type and molecular weight of the fluorinated polymers on the membrane's properties. *Int J Hydrogen Energy* 2010;35:12038–53. <https://doi.org/10.1016/J.IJHYDENE.2010.07.084>.
- [215] Ngamsantivongsa P, Lin HL, Yu TL. Properties and fuel cell applications of polybenzimidazole and ethyl phosphoric acid grafted polybenzimidazole blend membranes. *J Membr Sci* 2015;491:10–21. <https://doi.org/10.1016/J.MEMSCI.2015.04.045>.
- [216] Zhang H, Li X, Zhao C, Fu T, Shi Y, Na H. Composite membranes based on highly sulfonated PEEK and PBI: morphology characteristics and performance. *J Membr Sci* 2008;308:66–74. <https://doi.org/10.1016/J.MEMSCI.2007.09.045>.
- [217] Lai S, Park J, Cho S, Tsai M, Lim H, Chen K. Mechanical property enhancement of ultra-thin PBI membrane by electron beam irradiation for PEM fuel cell. *Int J Hydrogen Energy* 2016;41:9556–62. <https://doi.org/10.1016/J.IJHYDENE.2016.04.111>.
- [218] Akay RG, Ata KC, Kadioğlu T, Çelik C. Evaluation of SPEEK/PBI blend membranes for possible direct borohydride fuel cell (DBFC) application. *Int J Hydrogen Energy* 2018;43:18702–11. <https://doi.org/10.1016/J.IJHYDENE.2018.07.129>.
- [219] Xing DM, Yi BL, Liu FQ, Fu YZ, Zhang HM. Characterization of sulfonated poly(ether ether ketone)/polytetrafluoroethylene composite membranes for fuel cell applications. *Fuel Cell* 2005;5:406–11. <https://doi.org/10.1002/FUCE.200500089>.
- [220] Zhang Y, Zhang H, Zhu X, Gang L, Bi C, Liang Y. Fabrication and characterization of a PTFE-reinforced integral composite membrane for self-humidifying PEMFC. *J Power Sources* 2007;165:786–92. <https://doi.org/10.1016/J.JPOWSOUR.2006.12.060>.
- [221] Zhang Y, Zhang H-M, Zhu X-B, Liang Y-M. A low-cost PTFE-reinforced integral multilayered self-humidifying membrane for PEM fuel cells. *Electrochim Solid State Lett* 2006;9:A332. <https://doi.org/10.1149/1.2201249>.
- [222] Park GC, Kim D. Porous PTFE reinforced SPEEK proton exchange membranes for enhanced mechanical, dimensional, and electrochemical stability. *Polymer* 2021;218:123506. <https://doi.org/10.1016/J.POLYMER.2021.123506>.
- [223] Wu W, Li Y, Chen P, Liu J, Wang J, Zhang H. Constructing ionic liquid-filled proton transfer channels within nanocomposite membrane by using functionalized graphene oxide. *ACS Appl Mater Interfaces* 2015;8:588–99. <https://doi.org/10.1021/ACSAM.5B09642>.
- [224] Arias JJR, Carlos Dutra J, Gomes A de S. Hybrid membranes of sulfonated poly ether ether ketone, ionic liquid and organically modified montmorillonite for proton exchange membranes with enhanced ionic conductivity and ionic liquid lixiviation protection. *J Membr Sci* 2017;537:353–61. <https://doi.org/10.1016/J.MEMSCI.2017.05.044>.
- [225] Trindade LG da, Becker MR, Celso F, Petzhold CL, Martini EMA, Souza RF de. Modification of sulfonated poly(ether ether ketone) membranes by impregnation with the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate for proton exchange membrane fuel cell applications. *Polym Eng Sci* 2016;56:1037–44. <https://doi.org/10.1002/PEN.24334>.
- [226] Da Trindade LG, Pereira EC. SPEEK/Zeolite/Ionic-Liquid anhydrous polymer membranes for fuel-cell applications. 2017. <https://doi.org/10.1002/ejic.201601559>.
- [227] da Trindade LG, Borba KMN, Zanchet L, Lima DW, Trench AB, Rey F, et al. SPEEK-based proton exchange membranes modified with MOF-encapsulated ionic liquid. *Mater Chem Phys* 2019;236:121792. <https://doi.org/10.1016/J.MATCHEMPHYS.2019.121792>.
- [228] Elumalai V, Ganesh T, Selvakumar C, Sangeetha D. Phosphonate ionic liquid immobilised SBA-15/SPEEK composite membranes for high temperature proton exchange membrane fuel cells. *Mater Sci Energy Technol* 2018;1:196–204. <https://doi.org/10.1016/J.MSET.2018.08.003>.
- [229] Malik RS, Verma P, Choudhary V. A study of new anhydrous, conducting membranes based on composites of aprotic ionic liquid and cross-linked SPEEK for fuel cell application. *Electrochim Acta* 2015;152:352–9. <https://doi.org/10.1016/J.ELECTACTA.2014.11.167>.
- [230] Rangasamy VS, Thayumanasundaram S, Greef N de, Seo JW, Locquet J-P. Organic–inorganic hybrid membranes based on sulfonated poly(ether ether ketone) and tetrabutylphosphonium bromide ionic liquid for PEM fuel cell applications. *Eur J Inorg Chem* 2015;2015:1282–9. <https://doi.org/10.1002/EJIC.201402558>.
- [231] Zschocke P, Quellmalz D. Novel ion exchange membranes based on an aromatic polyethersulfone. *J Membr Sci* 1985;22:325–32. [https://doi.org/10.1016/S0376-7388\(00\)81290-9](https://doi.org/10.1016/S0376-7388(00)81290-9).

- [232] Arnold C, Assink RA. Development of sulfonated polysulfone membranes for redox flow batteries. *J Memb Sci* 1988;38:71–83. [https://doi.org/10.1016/S0376-7388\(00\)83276-7](https://doi.org/10.1016/S0376-7388(00)83276-7).
- [233] Zhang Y, Li J, Ma L, Cai W, Cheng H. Recent developments on alternative proton exchange membranes: strategies for systematic performance improvement. *Energy Technol* 2015;3:675–91. <https://doi.org/10.1002/ENTE.201500028>.
- [234] Yoo DJ, Hyun SH, Kim AR, Kumar GG, Nahm KS. Novel sulfonated poly(arylene biphenylsulfone ether) copolymers containing bisphenylsulfonyl biphenyl moiety: structural, thermal, electrochemical and morphological characteristics. *Polym Int* 2011;60:85–92. <https://doi.org/10.1002/PI.2914>.
- [235] Schuster M, Araujo Cc de, Atanasov V, Andersen HT, Kreuer K-D, Maier J. Highly sulfonated poly(phenylene sulfone): preparation and stability issues. *Macromolecules* 2009;42:3129–37. <https://doi.org/10.1021/MA900333N>.
- [236] He S, Yu J, Li C, Fang J, Xu J, Guan R. Sulfonated poly(bis-A)-sulfones as proton exchange membranes for direct methanol fuel cell application. *Polym Eng Sci* 2011;51:264–71. <https://doi.org/10.1002/PEN.21822>.
- [237] Sun X, Li Y, Qi F, Jing F, Sun H, Sun G. Degradation studies of single cell and short stack for high temperature proton exchange membrane fuel cells based on PBI/H3PO4 membrane. *ChemistrySelect* 2019;4:12313–9. <https://doi.org/10.1002/SLCT.201903849>.
- [238] Xu M, Xue H, Wang Q, Jia L. Sulfonated poly(arylene ether)s based proton exchange membranes for fuel cells. *Int J Hydrogen Energy* 2021;46:31727–53. <https://doi.org/10.1016/J.IJHYDENE.2021.07.038>.
- [239] Vondrasek B, Wen C, Cheng S, Riffle JS, Lesko JJ. Hydration, ion distribution, and ionic network formation in sulfonated poly(arylene ether sulfones). *Macromolecules* 2020;53:302–15. <https://doi.org/10.1021/ACS.MACROMOL.0C01855>.
- [240] Sorte EG, Paren BA, Rodriguez CG, Fujimoto C, Poirier C, Abbott LJ, et al. Impact of hydration and sulfonation on the morphology and ionic conductivity of sulfonated poly(phenylene) proton exchange membranes. *Macromolecules* 2019;52:857–76. <https://doi.org/10.1021/ACS.MACROMOL.8B02013>.
- [241] Katzfuß A, Krajinovic K, Chromik A, Kerres J. Partially fluorinated sulfonated poly(arylene sulfone)s blended with polybenzimidazole. *J Polym Sci Part A Polym Chem* 2011;49:1919–27. <https://doi.org/10.1002/POLA.24624>.
- [242] Hou H, Di Vona ML, Knauth P. Durability of sulfonated aromatic polymers for proton-exchange-membrane fuel cells. *ChemSusChem* 2011;4:1526–36. <https://doi.org/10.1002/CSSC.201000415>.
- [243] Lee KH, Chu JY, Mohanraj V, Kim AR, Song MH, Yoo DJ. Enhanced ion conductivity of sulfonated poly(arylene ether sulfone) block copolymers linked by aliphatic chains constructing wide-range ion cluster for proton conducting electrolytes. *Int J Hydrogen Energy* 2020;45:29297–307. <https://doi.org/10.1016/J.IJHYDENE.2020.07.197>.
- [244] Pirali-Hamedani M, Mehdipour-Ataei S. Effect of sulfonation degree on molecular weight, thermal stability, and proton conductivity of poly(arylene ether sulfone)s membrane. *Des Monomers Polym* 2016;20:54–65. <https://doi.org/10.1080/15685551.2016.1231035>.
- [245] Suter TAM, Smith K, Hack J, Rasha L, Rana Z, Angel GMA, et al. Engineering catalyst layers for next-generation polymer electrolyte fuel cells: a review of design, materials, and methods. *Adv Energy Mater* 2021;11:2101025. <https://doi.org/10.1002/AENM.202101025>.
- [246] Wang Y, Xu J, Zang H, Wang Z. Synthesis and properties of sulfonated poly(arylene ether ketone sulfone) containing amino groups/functional titania inorganic particles hybrid membranes for fuel cells. *Int J Hydrogen Energy* 2019;44:6136–47. <https://doi.org/10.1016/J.IJHYDENE.2019.01.035>.
- [247] Wu Y, Liu X, Yang F, Lee Zhou L, Yin B, Wang P, et al. Achieving high power density and excellent durability for high temperature proton exchange membrane fuel cells based on crosslinked branched polybenzimidazole and metal-organic frameworks. *J Memb Sci* 2021;630:119288. <https://doi.org/10.1016/J.MEMSCI.2021.119288>.
- [248] Xu J, Zhang Z, Yang K, He W, Yang X, Du X, et al. Construction of new transport channels by blending POM-based inorganic-organic complex into sulfonated poly(ether ketone sulfone) for proton exchange membrane fuel cells. *J Memb Sci* 2020;596:117711. <https://doi.org/10.1016/J.MEMSCI.2019.117711>.
- [249] Anahidzade N, Abdolmaleki A, Dinari M, Firouz Tadavani K, Zhiani M. Metal-organic framework anchored sulfonated poly(ether sulfone) as a high temperature proton exchange membrane for fuel cells. *J Memb Sci* 2018;565:281–92. <https://doi.org/10.1016/J.MEMSCI.2018.08.037>.
- [250] Zhang Z, Ren J, Xu J, Wang Z, He W, Wang S, et al. Adjust the arrangement of imidazole on the metal-organic framework to obtain hybrid proton exchange membrane with long-term stable high proton conductivity. *J Memb Sci* 2020;607:118194. <https://doi.org/10.1016/J.MEMSCI.2020.118194>.
- [251] Haragirimana A, Li N, Ingabire PB, Hu Z, Chen S. Multi-component organic/inorganic blend proton exchange membranes based on sulfonated poly(arylene ether sulfone)s for fuel cells. *Polymer* 2020;210:123015. <https://doi.org/10.1016/J.POLYMER.2020.123015>.
- [252] Kim Dae Sik, Gilles P. Robertson and, guiver* MD. Comb-shaped poly(arylene ether sulfone)s as proton exchange membranes. *Macromolecules* 2008;41:2126–34. <https://doi.org/10.1021/MA7027215>.
- [253] Liu L, Pu Y, Lu Y, Li N, Hu Z, Chen S. Superacid sulfated SnO₂ doped with CeO₂: a novel inorganic filler to simultaneously enhance conductivity and stabilities of proton exchange membrane. *J Memb Sci* 2021;621:118972. <https://doi.org/10.1016/J.MEMSCI.2020.118972>.
- [254] Kesava M, Dinakaran K. SnO₂ nanoparticles dispersed carboxylated Poly(arylene ether sulfones) nanocomposites for proton exchange membrane fuel cell (PEMFC) applications. *Int J Hydrogen Energy* 2021;46:1121–32. <https://doi.org/10.1016/J.IJHYDENE.2020.09.178>.
- [255] Haragirimana A, Ingabire PB, Liu Y, Li N, Hu Z, Chen S. An effective strategy to enhance the performance of the proton exchange membranes based on sulfonated poly(ether ether ketone)s. *Int J Hydrogen Energy* 2020;45:10017–29. <https://doi.org/10.1016/J.IJHYDENE.2020.01.180>.
- [256] Haragirimana A, Ingabire PB, Zhu Y, Lu Y, Li N, Hu Z, et al. Four-polymer blend proton exchange membranes derived from sulfonated poly(aryl ether sulfone)s with various sulfonation degrees for application in fuel cells. *J Memb Sci* 2019;583:209–19. <https://doi.org/10.1016/J.MEMSCI.2019.04.014>.
- [257] Haragirimana A, Li N, Hu Z, Chen S. A facile, effective thermal crosslinking to balance stability and proton conduction for proton exchange membranes based on blend sulfonated poly(ether ether ketone)/sulfonated poly(arylene ether sulfone). *Int J Hydrogen Energy* 2021;46:15866–77. <https://doi.org/10.1016/J.IJHYDENE.2021.02.022>.

- [258] Liu W, Wang Z, Du X, Xu J, Liu C, Li H, et al. Poly(arylene ether ketone) with an ultrahigh-selectivity hydrophilic phase proton transport channel by grafting sulfonated benzotriazole groups onto pendant chains. *ACS Sustainable Chem Eng* 2020;8:6505–16. <https://doi.org/10.1021/ACSSUSCHEMENG.0C01137>.
- [259] Long Z, Miyake J, Miyatake K. Partially fluorinated polyphenylene ionomers as proton exchange membranes for fuel cells: effect of pendant multi-sulfophenylene groups. *ACS Appl Energy Mater* 2019;2:7527–34. <https://doi.org/10.1021/ACSAEM.9B01513>.
- [260] Xu J, Zhang Z, Yang K, Zhang H, Wang Z. Synthesis and properties of novel cross-linked composite sulfonated poly (aryl ether ketone sulfone) containing multiple sulfonic side chains for high-performance proton exchange membranes. *Renew Energy* 2019;138:1104–13. <https://doi.org/10.1016/J.RENENE.2019.02.042>.
- [261] Ban T, Guo M, Wang Y, Wang Y, Zhang Y, Zhang J, et al. Densely functionalized proton exchange membrane from sulfonated poly(aryl ether ketone) containing multiple flexible side chains for fuel cell. *Solid State Ionics* 2021;372:115777. <https://doi.org/10.1016/J.SSI.2021.115777>.
- [262] Liu Q, Li X, Zhang S, Wang Z, Chen Y, Zhou S, et al. Novel sulfonated N-heterocyclic poly(aryl ether ketone ketone)s with pendant phenyl groups for proton exchange membrane performing enhanced oxidative stability and excellent fuel cell properties. *J Membr Sci* 2022;641:119926. <https://doi.org/10.1016/J.MEMSCI.2021.119926>.
- [263] Han X, Pang J, Liu D, Zhang H, Jiang Z. Novel branched sulfonated poly(arylene ether)s based on carbazole derivative for proton exchange membrane. *Int J Hydrogen Energy* 2020;45:4644–52. <https://doi.org/10.1016/J.IJHYDENE.2019.12.120>.
- [264] Yu H, Xia Y, Zeng K, Wang Y. Facile fabrication of sulfonated poly(aryl ether sulfone)/polybenzoxazine crosslinked membrane for vanadium flow battery application. *Polym Bull* 2020 788 2020;78:4509–25. <https://doi.org/10.1007/S00289-020-03330-0>.
- [265] Wang J, Dai Y, Xu S, Jiang H, He R. Simultaneously enhancing proton conductivity and mechanical stability of the membrane electrolytes by crosslinking of poly(aromatic ether sulfone) with octa-amino polyhedral oligomeric silsesquioxane. *J Power Sources* 2021;506:230217. <https://doi.org/10.1016/J.JPOWSOUR.2021.230217>.
- [266] Ahn MK, Lee B, Jang J, Min CM, Lee S Bin, Pak C, et al. Facile preparation of blend proton exchange membranes with highly sulfonated poly(arylene ether) and poly(arylene ether sulfone) bearing dense triazoles. *J Membr Sci* 2018;560:58–66. <https://doi.org/10.1016/J.MEMSCI.2018.05.011>.
- [267] Zhu H, Jia M, Li Q, Zhang C, Zheng P. Research the effect of crosslinking degree on the overall performance of novel proton exchange membranes. *Solid State Ionics* 2020;351:115325. <https://doi.org/10.1016/J.SSI.2020.115325>.
- [268] Yuan C, Wang Y. Synthesis and characterization of a crosslinked membrane based on sulfonated poly(aryl ether sulfone) and sulfonated polyvinyl alcohol applied in direct methanol fuel cells. *J Polym Res* 2020;27:1–13. <https://doi.org/10.1007/S10965-020-02305-Z>. 2711 2020.
- [269] He F, Wang S, Yuan D, Weng Q, Chen P, Chen X, et al. Crosslinked poly(arylene ether sulfone) block copolymers containing quinoxaline crosslinkage and pendant butanesulfonic acid groups as proton exchange membranes. *Int J Hydrogen Energy* 2020;45:25262–75. <https://doi.org/10.1016/J.IJHYDENE.2020.06.149>.
- [270] Zhang X, Lu Y, Yan X, Hu Z, Chen S. Sulfonated oligomer-crosslinked fluorinated poly(aryl ether sulfone)-based proton exchange membranes for fuel cells. *Fuel Cell* 2018;18:397–407. <https://doi.org/10.1002/FUCE.201700166>.
- [271] Gao Y, Robertson GP, Kim DS, Guiver MD, Mikhailenko SD, Li X, et al. Comparison of PEM properties of copoly(aryl ether ether nitrile)s containing sulfonic acid bonded to naphthalene in structurally different ways. *Macromolecules* 2007;40:1512–20. https://doi.org/10.1021/MA0623542SUPPL_FILE/MA0623542SI20061219_041512 [PDF].
- [272] Gao Y, Robertson GP, Guiver MD, Mikhailenko SD, Li X, Kalagiunis S. Low-swelling proton-conducting copoly(aryl ether nitrile)s containing naphthalene structure with sulfonic acid groups meta to the ether linkage. *Polymer* 2006;47:808–16. <https://doi.org/10.1016/J.POLYMER.2005.12.015>.
- [273] Yang X, Zhan Y, Yang J, Zhong J, Zhao R, Liu X. Synergetic effect of cyanogen functionalized carbon nanotube and graphene on the mechanical and thermal properties of poly (arylene ether nitrile). *J Polym Res* 2012;19:1–6. <https://doi.org/10.1007/S10965-011-9806-0/TABLES/1>.
- [274] Shin DW, Lee SY, Kang NR, Lee KH, Guiver MD, Lee YM. Durable sulfonated poly(arylene sulfide sulfone nitrile)s containing naphthalene units for direct methanol fuel cells (DMFCs). *Macromolecules* 2013;46:3452–60. https://doi.org/10.1021/MA400154T/SUPPL_FILE/MA400154T_SI_001.PDF.
- [275] Sumner MJ, Harrison WL, Weyers RM, Kim YS, McGrath JE, Riffle JS, et al. Novel proton conducting sulfonated poly(arylene ether) copolymers containing aromatic nitriles. *J Membr Sci* 2004;239:199–211. <https://doi.org/10.1016/J.MEMSCI.2004.03.031>.
- [276] Okonkwo PC, Igwe OO, Barhoumi EM, Uzoma PC, Emori W, Benamor A, et al. Platinum degradation mechanisms in proton exchange membrane fuel cell (PEMFC) system: a review. *Int J Hydrogen Energy* 2021;46:15850–65. <https://doi.org/10.1016/J.IJHYDENE.2021.02.078>.
- [277] Pu Z, Chen L, Long Y, Tong L, Huang X, Liu X. Influence of composition on the proton conductivity and mechanical properties of sulfonated poly(aryl ether nitrile) copolymers for proton exchange membranes. *J Polym Res* 2013;20:1–9. <https://doi.org/10.1007/S10965-013-0281-7/TABLES/4>.
- [278] Shin DW, Lee SY, Kang NR, Lee KH, Guiver MD, Lee YM. Durable sulfonated poly(arylene sulfide sulfone nitrile)s containing naphthalene units for direct methanol fuel cells (DMFCs). *Macromolecules* 2013;46:3452–60. https://doi.org/10.1021/MA400154T/SUPPL_FILE/MA400154T_SI_001.PDF.
- [279] Lin G, Bai Z, Han M, Jia K, Huang Y, Liu X. Tungstophosphoric acid-doped sulfonated poly(arylene ether nitrile)s composite membranes with improved proton conductivity and excellent long-term stability. *Solid State Ionics* 2020;357:115487. <https://doi.org/10.1016/J.SSI.2020.115487>.
- [280] Cheng T, Zhang X, Ma Y, Huang Y, Liu X. Constructing continuous proton-conducting highways within sulfonated poly(arylene ether nitrile) composite membrane by incorporating amino-sulfo-bifunctionalized GO. *Polym* 2018;10:1005. <https://doi.org/10.3390/POLYM10091005>. 2018;10:1005.
- [281] Wang Q, Zhang S, Dai F, Yan X, Qian G, Chen C, et al. Enhanced antifouling property of poly(aryl ether nitrile) ultrafiltration membranes via copolymerization with phenolphthalein. *J Environ Chem Eng* 2021;9:106132. <https://doi.org/10.1016/J.JECE.2021.106132>.
- [282] Liu C, Liu S, Lin J, Wang L, Huang Y, Liu X. Component adjustment of poly(arylene ether nitrile) with sulfonic and carboxylic groups for dielectric films. *Polym* 2019;11:1135. <https://doi.org/10.3390/POLYM11071135>. 2019;11:1135.
- [283] Huang Y, Cheng T, Zhang X, Zhang W, Liu X. Novel composite proton exchange membrane with long-range

- proton transfer channels constructed by synergistic effect between acid and base functionalized graphene oxide. *Polymer* 2018;149:305–15. <https://doi.org/10.1016/J.POLYMER.2018.07.009>.
- [284] Cheng T, Feng M, Zhang X, Huang Y, Liu X. Influence of the carboxylic acid groups on the structure and properties of sulfonated poly(arylene ether nitrile) copolymer. *Ionics* 2018;24:2611–9. <https://doi.org/10.1007/S11581-017-2419-9>. TABLES/3.
- [285] Cui W, Zhou S, Bai J, Qian H, Zheng J, Li S, et al. SCTF nanosheets@sulfonated poly (p-phenylene-co-aryl ether ketone) composite proton exchange membranes for passive direct methanol fuel cells. *Int J Hydrogen Energy* 2021;46:34344–55. <https://doi.org/10.1016/J.IJHYDENE.2021.07.218>.
- [286] Wang Q, Dai F, Zhang S, Wang M, Chen C, Yu Y. Design of a novel poly(aryl ether nitrile)-based composite ultrafiltration membrane with improved permeability and antifouling performance using zwitterionic modified nano-silica. *RSC Adv* 2021;11:15231–44. <https://doi.org/10.1039/D1RA00376C>.
- [287] Jiang GP, Zhang J, Qiao JL, Jiang YM, Zarrin H, Chen Z, et al. Bacterial nanocellulose/Nafion composite membranes for low temperature polymer electrolyte fuel cells. *J Power Sources* 2015;273:697–706. <https://doi.org/10.1016/J.JPOWSOUR.2014.09.145>.
- [288] Bayer T, Cunning BV, Selyanchyn R, Nishihara M, Fujikawa S, Sasaki K, et al. High temperature proton conduction in nanocellulose membranes: paper fuel cells. *Chem Mater* 2016;28:4805–14. <https://doi.org/10.1021/ACS.CHEMMATER.6B01990>.
- [289] Wang Likun, Zuo Xianghao, Raut Aniket, Isseroff Rebecca, Yuan Xue, Zhou Yuchen, et al. Operation of proton exchange membrane (PEM) fuel cells using natural cellulose fiber membranes. *Sustain Energy Fuels* 2019;3:2725–32. <https://doi.org/10.1039/C9SE00381A>.
- [290] Mohanapriya S, Rambabu G, Bhat SD, Raj V. Pectin based nanocomposite membranes as green electrolytes for direct methanol fuel cells. *Arab J Chem* 2020;13:2024–40. <https://doi.org/10.1016/J.ARABJC.2018.03.001>.
- [291] Muthukrishnan M, Shanthi C, Selvasekarpandian S, Manjuladevi R, Perumal P, Christopher Selvin P. Synthesis and characterization of pectin-based biopolymer electrolyte for electrochemical applications. *Ionics* 2018;25:203–14. <https://doi.org/10.1007/S11581-018-2568-5>. 251 2018.
- [292] Nasirinezhad M, Ghaffarian SR, Tohidian M. Nanocomposite membranes based on imidazole-functionalized chitin nanowhiskers for direct methanol fuel cell applications. *J Macromol Sci Part B* 2021;60:663–85. <https://doi.org/10.1080/00222348.2021.1892977>.
- [293] Zhang C, Zhuang X, Li X, Wang W, Cheng B, Kang W, et al. Chitin nanowhisker-supported sulfonated poly(ether sulfone) proton exchange for fuel cell applications. *Carbohydr Polym* 2016;140:195–201. <https://doi.org/10.1016/J.CARBPOL.2015.12.029>.
- [294] Wong CY, Wong WY, Loh KS, Mohamad AB. Study of the plasticising effect on polymer and its development in fuel cell application. *Renew Sustain Energy Rev* 2017;79:794–805. <https://doi.org/10.1016/J.RSER.2017.05.154>.
- [295] Honma I, Yamada M. Bio-inspired membranes for advanced polymer electrolyte fuel cells. *Anhydrous Proton-Conducting Membrane via Molecular Self-Assembly* 2006. <https://doi.org/10.1246/bcsj.80.2110>.
- [296] Munavalli B, Torvi A, Kariduraganavar M. A facile route for the preparation of proton exchange membranes using sulfonated side chain graphite oxides and crosslinked sodium alginate for fuel cell. *Polymer* 2018;142:293–309. <https://doi.org/10.1016/J.POLYMER.2018.03.044>.
- [297] Yamada M, Honma I. Alginic acid-imidazole composite material as anhydrous proton conducting membrane. *Polymer* 2004;45:8349–54. <https://doi.org/10.1016/J.POLYMER.2004.10.017> (Guildf).
- [298] Połomska M, Pogorzelec-Glaser K, Pawlaczyk C. FT-NIR Raman and proton conductivity studies of new polymer composite: alginic acid-heterocyclic molecules. *Phase Trans* 2010;83:844–53. <https://doi.org/10.1080/01411594.2010.509154>.
- [299] Dave PN, Gor A. Natural polysaccharide-based hydrogels and nanomaterials: recent trends and their applications. *Handb Nanomater Ind Appl* 2018;36–66. <https://doi.org/10.1016/B978-0-12-813351-4.00003-1>. Elsevier.
- [300] Zhao D, Yu S, Sun B, Gao S, Guo S, Zhao K. Biomedical applications of chitosan and its derivative nanoparticles. *Polymers* 2018;10:462. <https://doi.org/10.3390/polym10040462>.
- [301] Ma J, Sahai Y. Chitosan biopolymer for fuel cell applications. *Carbohydr Polym* 2013;92:955–75. <https://doi.org/10.1016/j.carbpol.2012.10.015>.
- [302] Wan Y, Creber KAM, Peppley B, Bui VT. Ionic conductivity of chitosan membranes. *Polymer* 2003;44:1057–65. [https://doi.org/10.1016/S0032-3861\(02\)00881-9](https://doi.org/10.1016/S0032-3861(02)00881-9).
- [303] Divya K, Rana D, Alwarappan S, Abirami Saraswathi MSS, Nagendran A. Investigating the usefulness of chitosan based proton exchange membranes tailored with exfoliated molybdenum disulfide nanosheets for clean energy applications. *Carbohydr Polym* 2019;208:504–12. <https://doi.org/10.1016/J.CARBPOL.2018.12.092>.
- [304] Liu H, Gong C, Wang J, Liu X, Liu H, Cheng F, et al. Chitosan/silica coated carbon nanotubes composite proton exchange membranes for fuel cell applications. *Carbohydr Polym* 2016;136:1379–85. <https://doi.org/10.1016/J.CARBPOL.2015.09.085>.
- [305] Wang J, Gong C, Wen S, Liu H, Qin C, Xiong C, et al. A facile approach of fabricating proton exchange membranes by incorporating polydopamine-functionalized carbon nanotubes into chitosan. *Int J Hydrogen Energy* 2019;44:6909–18. <https://doi.org/10.1016/J.IJHYDENE.2019.01.194>.
- [306] Yin S, Gao S, Shen C, Li W, Li H. Synthesis and characterisation of chitosan–nitrogen polyphosphonic acid poly(organosiloxane) high temperature proton exchange membranes for fuel cells. *Mater Technol Adv Perform Mater* 2016;31:197–202. <https://doi.org/10.1179/175355715Y.0000000041>.
- [307] Cui Z, Liu C, Lu T, Xing W. Polyelectrolyte complexes of chitosan and phosphotungstic acid as proton-conducting membranes for direct methanol fuel cells. *J Power Sources* 2007;167:94–9. <https://doi.org/10.1016/J.JPOWSOUR.2006.12.112>.
- [308] Kourasi M, Wills RGA, Shah AA, Walsh FC. Heteropolyacids for fuel cell applications. *Electrochim Acta* 2014;127:454–66. <https://doi.org/10.1016/J.ELECTACTA.2014.02.006>.
- [309] Fadzallah IA, Majid SR, Careem MA, Arof AK. A study on ionic interactions in chitosan–oxalic acid polymer electrolyte membranes. *J Memb Sci* 2014;463:65–72. <https://doi.org/10.1016/J.MEMSCI.2014.03.044>.
- [310] Göktepe F, Çelik SÜ, Bozkurt A. Preparation and the proton conductivity of chitosan/poly(vinyl phosphonic acid) complex polymer electrolytes. *J Non-Cryst Solids* 2008;354:3637–42. <https://doi.org/10.1016/J.JNONCRYSL.2008.03.023>.
- [311] Smitha B, Sridhar S, Khan* AA. Polyelectrolyte complexes of chitosan and poly(acrylic acid) as proton exchange membranes for fuel cells. *Macromolecules* 2004;37:2233–9. <https://doi.org/10.1021/MA0355913>.

- [312] Wang S, Shi L, Zhang S, Wang H, Cheng B, Zhuang X, et al. Proton-conducting amino acid-modified chitosan nanofibers for nanocomposite proton exchange membranes. *Eur Polym J* 2019;119:327–34. <https://doi.org/10.1016/J.EURPOLYMJ.2019.07.041>.
- [313] Ahmed S, Cai Y, Ali M, Khannal S, Xu S. Preparation and properties of alkyl benzene sulfonic acid coated boehmite/chitosan nanocomposite membranes with enhanced proton conductivity for proton exchange membrane fuel cells. *Mater Express* 2019;9:42–50. <https://doi.org/10.1166/MEX.2019.1468>.
- [314] Ahmed S, Cai Y, Ali M, Khanal S, Xu S. Preparation and performance of nanoparticle-reinforced chitosan proton-exchange membranes for fuel-cell applications. *J Appl Polym Sci* 2019;136:46904. <https://doi.org/10.1002/APP.46904>.
- [315] Ahmed S, Arshad T, Zada A, Afzal A, Khan M, Hussain A, et al. Preparation and characterization of a novel sulfonated titanium oxide incorporated chitosan nanocomposite membranes for fuel cell application. *Membr* 2021;11:450. <https://doi.org/10.3390/MEMBRANES11060450>. 2021;11:450.
- [316] Hassan F, Woo HJ, Aziz NA, Kufian MZ, Majid SR. Synthesis of Al₂TiO₅ and its effect on the properties of chitosan–NH₄SCN polymer electrolytes. *Ionics* 2012 193 2012;19:483–9. <https://doi.org/10.1007/S11581-012-0763-3>.
- [317] Aziz NA, Majid SR, Yahya R, Arof AK. Conductivity, structure, and thermal properties of chitosan-based polymer electrolytes with nanofillers. *Polym Adv Technol* 2011;22:1345–8. <https://doi.org/10.1002/PAT.1619>.
- [318] Vijayakumar V, Khastgir D. Hybrid composite membranes of chitosan/sulfonated polyaniline/silica as polymer electrolyte membrane for fuel cells. *Carbohydr Polym* 2018;179:152–63. <https://doi.org/10.1016/J.CARBPOL.2017.09.083>.
- [319] Gómez EER, Hernández JHM, Astaiza JED. Development of a chitosan/PVA/TiO₂ nanocomposite for application as a solid polymeric electrolyte in fuel cells. *Polym* 2020;12:1691. <https://doi.org/10.3390/POLYM12081691>. 2020;12:1691.
- [320] Rosli NAH, Loh KS, Wong WY, Lee TK, Ahmad A. Hybrid composite membrane of phosphorylated chitosan/poly (vinyl alcohol)/silica as a proton exchange membrane. *Membr* 2021;11:675. <https://doi.org/10.3390/MEMBRANES11090675>. Page 675 2021;11.
- [321] Wang W, Shan B, Zhu L, Xie C, Liu C, Cui F. Anatase titania coated CNTs and sodium lignin sulfonate doped chitosan proton exchange membrane for DMFC application. *Carbohydr Polym* 2018;187:35–42. <https://doi.org/10.1016/J.CARBPOL.2018.01.078>.
- [322] Tadavani KF, Abdolmaleki A, Molavian MR, Borandeh S, Sorvand E, Zhiani M. Synergistic behavior of phosphonated and sulfonated groups on proton conductivity and their performance for high-temperature proton exchange membrane fuel cells (PEMFCs). *Energy Fuel* 2017;31:11460–70. <https://doi.org/10.1021/ACS.ENERGYFUELS.7B01065>.
- [323] Abu-Saied MA, Soliman EA, Desouki EAA. Development of proton exchange membranes based on chitosan blended with poly (2-acrylamido-2-methylpropane sulfonic acid) for fuel cells applications. *Mater Today Commun* 2020;25:101536. <https://doi.org/10.1016/J.MTCOMM.2020.101536>.
- [324] Anu Karthi AKS, Cindrella L. Self-humidifying novel chitosan-geopolymer hybrid membrane for fuel cell applications. *Carbohydr Polym* 2019;223:115073. <https://doi.org/10.1016/J.CARBPOL.2019.115073>.
- [325] Wu Q, Wang H, Lu S, Xu X, Liang D, Xiang Y. Novel methanol-blocking proton exchange membrane achieved via self-anchoring phosphotungstic acid into chitosan membrane with submicro-pores. *J Memb Sci* 2016;500:203–10. <https://doi.org/10.1016/J.JMEMSCI.2015.11.019>.
- [326] Hu F, Li T, Zhong F, Wen S, Zheng G, Gong C, et al. Preparation and properties of chitosan/acidified attapulgite composite proton exchange membranes for fuel cell applications. *J Appl Polym Sci* 2020;137:49079. <https://doi.org/10.1002/APP.49079>.
- [327] Faudzi NFAM, Nur H. Fabrication of polybenzimidazole membrane based on phosphotungstic acid doped for fuel cell application. *EProceedings Chem* 2020;5:21–5.
- [328] Liu R, Dai Y, Li J, Chen X, Pan C, Yang J, et al. 1-(3-Aminopropyl)imidazole functionalized poly(vinyl chloride) for high temperature proton exchange membrane fuel cell applications. *J Memb Sci* 2021;620:118873. <https://doi.org/10.1016/J.JMEMSCI.2020.118873>.
- [329] Peter S, Lyczko N, Gopakumar D, Maria HJ, Nzihou A, Thomas S. Chitin and chitosan based composites for energy and environmental applications: a review. *Waste Biomass Valor* 2020;12:4777–804. <https://doi.org/10.1007/S12649-020-01244-6>. 129 2020.
- [330] Nasirinezhad M, Ghaffarian SR, Tohidian M. Eco-friendly polyelectrolyte nanocomposite membranes based on chitosan and sulfonated chitin nanowhiskers for fuel cell applications. *Iran Polym J* 2021;30:355–67. <https://doi.org/10.1007/S13726-020-00895-5>. 304 2021.
- [331] Muhmed SA, Nor NAM, Jaafar J, Ismail AF, Othman MHD, Rahman MA, et al. Emerging chitosan and cellulose green materials for ion exchange membrane fuel cell: a review. *Energy, Ecol Environ* 2019;5:85–107. <https://doi.org/10.1007/S40974-019-00127-4>. 52 2019.
- [332] Chandran P, Ghosh A, Ramaprabhu S. High-performance Platinum-free oxygen reduction reaction and hydrogen oxidation reaction catalyst in polymer electrolyte membrane fuel cell. *Sci Rep* 2018;8:1–11. <https://doi.org/10.1038/s41598-018-22001-9>.
- [333] Peigney A, Laurent C, Flahaut E, Bacsa RR, Rousset A. Specific surface area of carbon nanotubes and bundles of carbon nanotubes. *Carbon N Y* 2001;39:507–14. [https://doi.org/10.1016/S0008-6223\(00\)00155-X](https://doi.org/10.1016/S0008-6223(00)00155-X).
- [334] Mukherjee S, Bates A, Lee SC, Lee DH, Park S. A review of the application of CNTs in PEM fuel cells. *Int J Green Energy Technol* 2015;12:787–809. <https://doi.org/10.1080/15435075.2013.867270>.
- [335] Zhang C, Sun L, Huang B, Yang X, Chu Y, Zhan B. Electrical and mechanical properties of CNT/CB dual filler conductive adhesives (DFCAs) for automotive multi-material joints. *Compos Struct* 2019;225:111183. <https://doi.org/10.1016/J.COMPSTRUCT.2019.111183>.
- [336] Iqbal A, Saeed A, Ul-Hamid A. A review featuring the fundamentals and advancements of polymer/CNT nanocomposite application in aerospace industry. *Polym Bull* 2021;78:539–57. <https://doi.org/10.1007/S00289-019-03096-0/FIGURES/2>.
- [337] Kim GM, Nam IW, Yang B, Yoon HN, Lee HK, Park S. Carbon nanotube (CNT) incorporated cementitious composites for functional construction materials: the state of the art. *Compos Struct* 2019;227:111244. <https://doi.org/10.1016/J.COMPSTRUCT.2019.111244>.
- [338] Shahidi S, Moazzzenchi B. Carbon nanotube and its applications in textile industry – a review. *J Text Inst* 2018;109:1653–66. <https://doi.org/10.1080/00405000.2018.1437114>.
- [339] Wu X, Mu F, Zhao H. Recent progress in the synthesis of graphene/CNT composites and the energy-related applications. *J Mater Sci Technol* 2020;55:16–34. <https://doi.org/10.1016/J.JMST.2019.05.063>.
- [340] ullah Rather S. Preparation, characterization and hydrogen storage studies of carbon nanotubes and their composites: a

- review. *Int J Hydrogen Energy* 2020;45:4653–72. <https://doi.org/10.1016/J.IJHYDENE.2019.12.055>.
- [341] De Las Casas C, Li W. A review of application of carbon nanotubes for lithium ion battery anode material. *J Power Sources* 2012;208:74–85. <https://doi.org/10.1016/J.JPOWSOUR.2012.02.013>.
- [342] Feng M, You Y, Zheng P, Liu J, Jia K, Huang Y, et al. Low-swelling proton-conducting multi-layer composite membranes containing polyarylene ether nitrile and sulfonated carbon nanotubes for fuel cells. *Int J Hydrogen Energy* 2016;41:5113–22. <https://doi.org/10.1016/J.IJHYDENE.2016.01.085>.
- [343] Hasani-Sadrabadi MM, Dashtimoghadam E, Majedi FS, Moaddel H, Bertsch A, Renaud P. Superacid-doped polybenzimidazole-decorated carbon nanotubes: a novel high-performance proton exchange nanocomposite membrane. *Nanoscale* 2013;5:11710–7. <https://doi.org/10.1039/C3NR02886K>.
- [344] Kannan R, Kagalwala HN, Chaudhari HD, Kharul UK, Kurungot S, Pillai VK. Improved performance of phosphonated carbon nanotube –polybenzimidazole composite membranes in proton exchange membrane fuel cells. *J Mater Chem* 2011;21:7223–31. <https://doi.org/10.1039/C0JM04265J>.
- [345] Guerrero Moreno N, Gervasio D, Godínez García A, Pérez Robles JF. Polybenzimidazole-multiwall carbon nanotubes composite membranes for polymer electrolyte membrane fuel cells. *J Power Sources* 2015;300:229–37. <https://doi.org/10.1016/J.JPOWSOUR.2015.09.070>.
- [346] Jheng LC, Rosidah AA, Hsu SLC, Ho KS, Pan CJ, Cheng CW. Nanocomposite membranes of polybenzimidazole and amine-functionalized carbon nanofibers for high temperature proton exchange membrane fuel cells. *RSC Adv* 2021;11:9964–76. <https://doi.org/10.1039/DORA09972D>.
- [347] Li HY, Liu YL. Polyelectrolyte composite membranes of polybenzimidazole and crosslinked polybenzimidazole-polybenzoxazine electrospun nanofibers for proton exchange membrane fuel cells. *J Mater Chem* 2012;1:1171–8. <https://doi.org/10.1039/C2TA00270A>.
- [348] Jheng LC, Huang CY, Hsu SLC. Sulfonated MWNT and imidazole functionalized MWNT/polybenzimidazole composite membranes for high-temperature proton exchange membrane fuel cells. *Int J Hydrogen Energy* 2013;38:1524–34. <https://doi.org/10.1016/J.IJHYDENE.2012.10.111>.
- [349] Suryani, Chang CM, Liu YL, Lee YM. Polybenzimidazole membranes modified with polyelectrolyte-functionalized multiwalled carbon nanotubes for proton exchange membrane fuel cells. *J Mater Chem* 2011;21:7480–6. <https://doi.org/10.1039/C1JM10439J>.
- [350] Robertson GP, Mikhailenko SD, Wang K, Xing P, Guiver MD, Kaliaguine S. Casting solvent interactions with sulfonated poly(ether ether ketone) during proton exchange membrane fabrication. *J Membr Sci* 2003;219:113–21. [https://doi.org/10.1016/S0376-7388\(03\)00193-5](https://doi.org/10.1016/S0376-7388(03)00193-5).
- [351] Xu Q, Kong Q, Liu Z, Wang X, Liu R, Zhang J, et al. Cellulose polysulfonamide composite membrane as a high performance lithium-ion battery separator. *ACS Sustainable Chem Eng* 2014;2:194–9. https://doi.org/10.1021/SC400370H/ASSET/IMAGES/SC400370H.SOCIAL.JPG_V03.
- [352] Gahlot S, Kulshrestha V. Dramatic improvement in water retention and proton conductivity in electrically aligned functionalized CNT/SPEEK nanohybrid PEM. *ACS Appl Mater Interfaces* 2015;7:264–72. https://doi.org/10.1021/AM506033C/SUPPL_FILE/AM506033C_SI_001 [PDF].
- [353] Sun H, Tang B, Wu P. Two-dimensional zeolitic imidazolate framework/carbon nanotube hybrid networks modified proton exchange membranes for improving transport properties. *ACS Appl Mater Interfaces* 2017;9:35075–85. https://doi.org/10.1021/ACSAI.7B13013/SUPPL_FILE/AM7B13013_SI_001 [PDF].
- [354] Kannan R, Aher PP, Palanisvam T, Kurungot S, Kharul UK, Pillai VK. Artificially designed membranes using phosphonated multiwall carbon nanotube-polybenzimidazole composites for polymer electrolyte fuel cells. *J Phys Chem Lett* 2010;1:2109–13. https://doi.org/10.1021/JZ1007005/SUPPL_FILE/JZ1007005_SI_001 [PDF].
- [355] Escorihuela J, Olvera-Mancilla J, Alexandrova L, del Castillo LF, Compañ V. Recent progress in the development of composite membranes based on polybenzimidazole for high temperature proton exchange membrane (PEM) fuel cell applications. *Polym* 2020;12:1861. <https://doi.org/10.3390/POLYM12091861>. 2020;12:1861.
- [356] Dong C, Hao Z, Wang Q, Zhu B, Cong C, Meng X, et al. Facile synthesis of metal oxide nanofibers and construction of continuous proton-conducting pathways in SPEEK composite membranes. *Int J Hydrogen Energy* 2017;42:25388–400. <https://doi.org/10.1016/J.IJHYDENE.2017.08.136>.
- [357] Tsen WC. Hydrophilic TiO₂ decorated carbon nanotubes/sulfonated poly(ether ether ketone) composite proton exchange membranes for fuel cells. *Polym Eng Sci* 2020;60:1832–41. <https://doi.org/10.1002/PEN.25420>.
- [358] Rambabu G, Bhat SD. Simultaneous tuning of methanol crossover and ionic conductivity of sPEEK membrane electrolyte by incorporation of PSSA functionalized MWCNTs: a comparative study in DMFCs. *Chem Eng J* 2014;243:517–25. <https://doi.org/10.1016/J.CEJ.2014.01.030>.
- [359] Vidhyeswari D, Surendhar A, Bhuvaneshwari S. Enhanced performance of novel carbon nanotubes - sulfonated poly ether ether ketone (speek) composite proton exchange membrane in mfc application. *Chemosphere* 2022;293:133560. <https://doi.org/10.1016/J.CHEMOSPHERE.2022.133560>.
- [360] Gui L, Geng Q, Gong C, Liu H, Zheng G, Wang G, et al. Novel sulfonated poly (ether ether ketone)/silica coated carbon nanotubes high-performance composite membranes for direct methanol fuel cell. *Polym Adv Technol* 2015;26:457–64. <https://doi.org/10.1002/PAT.3473>.
- [361] Gahlot S, Sharma PP, Jha PK, Kulshrestha V. CNT/SPEEK nano-composite membranes: toward improved properties. *Macromol Symp* 2017;376:1700048. <https://doi.org/10.1002/MASY.201700048>.
- [362] Rambabu G, Bhat SD, Figueiredo FML. Carbon nanocomposite membrane electrolytes for direct methanol fuel cells—a concise review. *Nanomaterials* 2019;9:1292. <https://doi.org/10.3390/NANO0901292>. 2019;9:1292.
- [363] Joo SH, Pak C, Kim EA, Lee YH, Chang H, Seung D, et al. Functionalized carbon nanotube-poly(arylene sulfone) composite membranes for direct methanol fuel cells with enhanced performance. *J Power Sources* 2008;180:63–70. <https://doi.org/10.1016/J.JPOWSOUR.2008.02.014>.
- [364] Yun S, Heo Y, Im H, Kim J. Sulfonated multiwalled carbon nanotube/sulfonated poly(ether sulfone) composite membrane with low methanol permeability for direct methanol fuel cells. *J Appl Polym Sci* 2012;126:E513–21. <https://doi.org/10.1002/APP.36741>.
- [365] He S, Dai W, Yang W, Liu S, Bian X, Zhang C, et al. Nanocomposite proton exchange membranes based on phosphotungstic acid immobilized by polydopamine-coated halloysite nanotubes. *Polym Test* 2019;73:242–9. <https://doi.org/10.1016/J.POLYMERTESTING.2018.11.038>.

- [366] Sun F, Qin LL, Zhou J, Wang YK, Rong JQ, Chen YJ, et al. Friedel-Crafts self-crosslinking of sulfonated poly(etheretherketone) composite proton exchange membrane doped with phosphotungstic acid and carbon-based nanomaterials for fuel cell applications. *J Membr Sci* 2020;611:118381. <https://doi.org/10.1016/J.MEMSCI.2020.118381>.
- [367] Li Y, Wang H, Wu Q, Xu X, Lu S, Xiang Y. A poly(vinyl alcohol)-based composite membrane with immobilized phosphotungstic acid molecules for direct methanol fuel cells. *Electro Acta* 2017;224:369–77. <https://doi.org/10.1016/J.ELECTACTA.2016.12.076>.
- [368] Hasani-Sadrabadi MM, Dashtimoghadam E, Majedi FS, VanDersarl JJ, Bertsch A, Renaud P, et al. Ionic nanopeapods: next-generation proton conducting membranes based on phosphotungstic acid filled carbon nanotube. *Nano Energy* 2016;23:114–21. <https://doi.org/10.1016/J.NANOEN.2016.01.024>.
- [369] Tsen WC. Composite proton exchange membranes based on chitosan and phosphotungstic acid immobilized one-dimensional attapulgite for direct methanol fuel cells. *Nanomaterials* 2020;10:1641. <https://doi.org/10.3390/NANO10091641>. 2020;10:1641.
- [370] Liu H, Wang J, Wen S, Gong C, Cheng F, Wang G, et al. Composite membranes of chitosan and titania-coated carbon nanotubes as promising materials for new proton-exchange membranes. *J Appl Polym Sci* 2016;133. <https://doi.org/10.1002/APP.43365>.
- [371] Wang W, Shan B, Zhu L, Xie C, Liu C, Cui F. Anatase titania coated CNTs and sodium lignin sulfonate doped chitosan proton exchange membrane for DMFC application. *Carbohydr Polym* 2018;187:35–42. <https://doi.org/10.1016/J.CARBPOL.2018.01.078>.
- [372] Liu H, Gong C, Wang J, Liu X, Liu H, Cheng F, et al. Chitosan/silica coated carbon nanotubes composite proton exchange membranes for fuel cell applications. *Carbohydr Polym* 2016;136:1379–85. <https://doi.org/10.1016/J.CARBPOL.2015.09.085>.
- [373] Dikin DA, Stankovich S, Zimney EJ, Piner RD, Dommett GHB, Evmenenko G, et al. Preparation and characterization of graphene oxide paper. *Nature* 2007;448:457–60. <https://doi.org/10.1038/nature06016>.
- [374] Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, et al. Electric field in atomically thin carbon films. *Science* 2004;306:666–9. <https://doi.org/10.1126/science.1102896>. 80.-.
- [375] Lv W, Li Z, Deng Y, Yang QH, Kang F. Graphene-based materials for electrochemical energy storage devices: opportunities and challenges. *Energy Storage Mater* 2016;2:107–38. <https://doi.org/10.1016/j.ensm.2015.10.002>.
- [376] Mohan VB, Lau K tak, Hui D, Bhattacharyya D. Graphene-based materials and their composites: a review on production, applications and product limitations. *Compos B Eng* 2018;142:200–20. <https://doi.org/10.1016/j.compositesb.2018.01.013>.
- [377] Bafeckpour E, Tang L-C, Zhao L, Guan L-Z. 7 graphene/polymer composite materials: processing, properties and applications. *Adv Compos Mater Prop Appl*, De Gruyter Open 2017:349–419. <https://doi.org/10.1515/9783110574432-007>.
- [378] Roy S, Soin N, Bajpai R, Misra DS, McLaughlin JA, Roy SS. Graphene oxide for electrochemical sensing applications. *J Mater Chem* 2011;21:14725–31. <https://doi.org/10.1039/c1jm12028j>.
- [379] Donarelli M, Ottaviano L. 2D materials for gas sensing applications: a review on graphene oxide, MoS₂, WS₂ and phosphorene. *Sensors* 2018;18:3638. <https://doi.org/10.3390/s18113638>.
- [380] Aissa B, Memon NK, Ali A, Khraisheh MK. Recent progress in the growth and applications of graphene as a smart material: a review. *Front Mater* 2015;2:1. <https://doi.org/10.3389/fmats.2015.00058>.
- [381] Yang J, Hu P, Yu G. Perspective of graphene-based electronic devices: graphene synthesis and diverse applications. *Apl Mater* 2019;7. <https://doi.org/10.1063/1.5054823>. 020901.
- [382] Bonaccorso F, Sun Z, Hasan T, Ferrari AC. Graphene photonics and optoelectronics. *Nat Photonics* 2010;4:611–22. <https://doi.org/10.1038/nphoton.2010.186>.
- [383] Charlier JC, Eklund PC, Zhu J, Ferrari AC. Electron and phonon properties of graphene: their relationship with carbon nanotubes. *Top Appl Phys* 2008;111:673–709. https://doi.org/10.1007/978-3-540-72865-8_21.
- [384] Zalalutdinov MK, Robinson JT, Junkermeier CE, Culbertson JC, Reinecke TL, Stine R, et al. Engineering graphene mechanical systems. *Nano Lett* 2012;12:4212–8. <https://doi.org/10.1021/nl3018059>.
- [385] McCallion C, Burthem J, Rees-Unwin K, Golovanov A, Pluen A. Graphene in therapeutics delivery: problems, solutions and future opportunities. *Eur J Pharm Biopharm* 2016;104:235–50. <https://doi.org/10.1016/j.ejpb.2016.04.015>.
- [386] Yang Y, Asiri AM, Tang Z, Du D, Lin Y. Graphene based materials for biomedical applications. *Mater Today* 2013;16:365–73. <https://doi.org/10.1016/j.mattod.2013.09.004>.
- [387] Dinadayalane TC, Leszczynski J. Fundamental structural, electronic, and chemical properties of carbon nanostructures: graphene, fullerenes, carbon nanotubes, and their derivatives. *Handb. Comput. Chem.. Springer Netherlands*; 2012. p. 793–868. https://doi.org/10.1007/978-94-007-0711-5_22.
- [388] Karlický F, Zbořil R, Otyepka M. Band gaps and structural properties of graphene halides and their derivates: a hybrid functional study with localized orbital basis sets. *J Chem Phys* 2012;137. <https://doi.org/10.1063/1.4736998>. 034709.
- [389] Castro Neto AH, Guinea F, Peres NMR, Novoselov KS, Geim AK. The electronic properties of graphene. *Rev Mod Phys* 2009;81:109–62. <https://doi.org/10.1103/RevModPhys.81.109>.
- [390] Nair RR, Blake P, Grigorenko AN, Novoselov KS, Booth TJ, Stauber T, et al. Fine structure constant defines visual transparency of graphene. *Science* 2008;320:1308. <https://doi.org/10.1126/science.1156965>. 80.-.
- [391] Zhu Y, Murali S, Cai W, Li X, Suk JW, Potts JR, et al. Graphene and graphene oxide: synthesis, properties, and applications. *Adv Mater* 2010;22:3906–24. <https://doi.org/10.1002/adma.201001068>.
- [392] Compton OC, Nguyen ST. Graphene oxide, highly reduced graphene oxide, and graphene: versatile building blocks for carbon-based materials. *Small* 2010;6:711–23. <https://doi.org/10.1002/smll.200901934>.
- [393] Geim AK, Novoselov KS. The rise of graphene. *Nanosci. Technol. A collect. Rev. From nat. Journals. World Scientific Publishing Co.*; 2009. p. 11–9. https://doi.org/10.1142/9789814287005_0002.
- [394] Geim AK. Graphene: status and prospects. *Science* 2009;324:1530–4. <https://doi.org/10.1126/science.1158877>. 80.-.
- [395] Su H, Hu YH. Recent advances in graphene-based materials for fuel cell applications. *Energy Sci Eng* 2020;833. <https://doi.org/10.1002/ese3.833>. ese3.
- [396] Brownson DAC, Banks CE. Graphene electrochemistry: an overview of potential applications. *Analyst* 2010;135:2768–78. <https://doi.org/10.1039/c0an00590h>.
- [397] Pumera M. Electrochemistry of graphene: new horizons for sensing and energy storage. *Chem Rec* 2009;9:211–23. <https://doi.org/10.1002/tcr.200900008>.

- [398] Chen D, Tang L, Li J. Graphene-based materials in electrochemistry. *Chem Soc Rev* 2010;39:3157–80. <https://doi.org/10.1039/b923596e>.
- [399] Liu G, Alwarappan S, Chen Z, Kong X, Li CZ. Membraneless enzymatic biofuel cells based on graphene nanosheets. *Biosens Bioelectron* 2010;25:1829–33. <https://doi.org/10.1016/j.bios.2009.12.012>.
- [400] Wang X, Zhi L, Müllen K. Transparent, conductive graphene electrodes for dye-sensitized solar cells. *Nano Lett* 2008;8:323–7. <https://doi.org/10.1021/nl072838r>.
- [401] Lee JU, Yoon D, Cheong H. Estimation of young's modulus of graphene by Raman spectroscopy. *Nano Lett* 2012;12:4444–8. <https://doi.org/10.1021/nl301073q>.
- [402] Morozov SV, Novoselov KS, Katsnelson MI, Schedin F, Elias DC, Jaszcak JA, et al. Giant intrinsic carrier mobilities in graphene and its bilayer. *Phys Rev Lett* 2008;100. <https://doi.org/10.1103/PhysRevLett.100.016602>. 016602.
- [403] Balandin AA. Thermal properties of graphene and nanostructured carbon materials. *Nat Mater* 2011;10:569–81. <https://doi.org/10.1038/nmat3064>.
- [404] Xue C, Zou J, Sun Z, Wang F, Han K, Zhu H. Graphite oxide/functionalized graphene oxide and polybenzimidazole composite membranes for high temperature proton exchange membrane fuel cells. *Int J Hydrogen Energy* 2014;39:7931–9. <https://doi.org/10.1016/j.ijhydene.2014.03.061>.
- [405] Xu C, Liu X, Cheng J, Scott K. A polybenzimidazole/ionic-liquid-graphite-oxide composite membrane for high temperature polymer electrolyte membrane fuel cells. *J Power Sources* 2015;274:922–7. <https://doi.org/10.1016/j.jpowsour.2014.10.134>.
- [406] Enotiadis A, Angjeli K, Baldino N, Nicotera I, Gournis D. Graphene-based nafion nanocomposite membranes: enhanced proton transport and water retention by novel organo-functionalized graphene oxide nanosheets. *Small* 2012;8:3338–49. <https://doi.org/10.1002/smll.201200609>.
- [407] Ye YS, Tseng CY, Shen WC, Wang JS, Chen KJ, Cheng MY, et al. A new graphene-modified protic ionic liquid-based composite membrane for solid polymer electrolytes. *J Mater Chem* 2011;21:10448–53. <https://doi.org/10.1039/c1jm11152c>.
- [408] Sun Y, Shi G. Graphene/polymer composites for energy applications. *J Polym Sci, Part B: Polym Phys* 2013;51:231–53. <https://doi.org/10.1002/polb.23226>.
- [409] Dreyer DR, Park S, Bielawski CW, Ruoff RS. The chemistry of graphene oxide. *Chem Soc Rev* 2010;39:228–40. <https://doi.org/10.1039/b917103g>.
- [410] Kumar R, Mamlouk M, Scott K. A graphite oxide paper polymer electrolyte for direct methanol fuel cells. *Int J Electrochem* 2011;2011:1–7. <https://doi.org/10.4061/2011/434186>.
- [411] Dreyer DR, Park S, Bielawski CW, Ruoff RS. The chemistry of graphene oxide. *Chem Soc Rev* 2009;39:228–40. <https://doi.org/10.1039/B917103g>.
- [412] Papageorgiou DG, Kinloch IA, Young RJ. Mechanical properties of graphene and graphene-based nanocomposites. *Prog Mater Sci* 2017;90:75–127. <https://doi.org/10.1016/J.PMATSCL.2017.07.004>.
- [413] Gao Y, Liu LQ, Zu SZ, Peng K, Zhou D, Han BH, et al. The effect of interlayer adhesion on the mechanical behaviors of macroscopic graphene oxide papers. *ACS Nano* 2011;5:2134–41. [https://doi.org/10.1021/NN103331X_SUPPLFILE/NN103331X_SI_001](https://doi.org/10.1021/NN103331X_SUPPL_FILE/NN103331X_SI_001) [PDF].
- [414] Kumar R, Scott K. Freestanding sulfonated graphene oxide paper: a new polymer electrolyte for polymer electrolyte fuel cells. *Chem Commun* 2012;48:5584–6. <https://doi.org/10.1039/c2cc31771k>.
- [415] Gao W, Wu G, Janicke MT, Cullen DA, Mukundan R, Baldwin JK, et al. Ozonated graphene oxide film as a proton-exchange membrane. *Angew Chem Int Ed* 2014;53:3588–93. <https://doi.org/10.1002/anie.201310908>.
- [416] Sandström R, Annamalai A, Boulanger N, Ekspong J, Talyzin A, Mühlbacher I, et al. Evaluation of fluorine and sulfonic acid co-functionalized graphene oxide membranes under hydrogen proton exchange membrane fuel cell conditions. *Sustain Energy Fuels* 2019;3:1790–8. <https://doi.org/10.1039/c9se00126c>.
- [417] Thimmappa R, Gautam M, Devendrachari MC, Kottaichamy AR, Bhat ZM, Umar A, et al. Proton-conducting graphene membrane electrode assembly for high performance hydrogen fuel cells. *ACS Sustainable Chem Eng* 2019;7:14189–94. <https://doi.org/10.1021/acssuschemeng.9b02917>.
- [418] Jiang Z, Shi Y, Jiang ZJ, Tian X, Luo L, Chen W. High performance of a free-standing sulfonic acid functionalized holey graphene oxide paper as a proton conducting polymer electrolyte for air-breathing direct methanol fuel cells. *J Mater Chem A* 2014;2:6494–503. <https://doi.org/10.1039/c4ta00208c>.
- [419] Basso Peressut A, Latorrata S, Gallo Stampino P, Dotelli G. Development of self-assembling sulfonated graphene oxide membranes as a potential proton conductor. *Mater Chem Phys* 2021;257:123768. <https://doi.org/10.1016/j.matchemphys.2020.123768>.
- [420] Seo DC, Jeon I, Jeong ES, Jho JY. Mechanical properties and chemical durability of nafion/sulfonated graphene oxide/ cerium oxide composite membranes for fuel-cell applications. *Polymers* 2020;12. <https://doi.org/10.3390/POLYM12061375>.
- [421] Mishra AK, Kim NH, Jung D, Lee JH. Enhanced mechanical properties and proton conductivity of Nafion-SPEEK-GO composite membranes for fuel cell applications. *J Memb Sci* 2014;458:128–35. <https://doi.org/10.1016/j.memsci.2014.01.073>.
- [422] Ansari S, Kelarakis A, Estevez L, Giannelis EP. Oriented arrays of graphene in a polymer matrix by in situ reduction of graphite oxide nanosheets. *Small* 2010;6:205–9. <https://doi.org/10.1002/smll.200900765>.
- [423] Kim Y, Ketpang K, Jaritphun S, Park JS, Shanmugam S. A polyoxometalate coupled graphene oxide-Nafion composite membrane for fuel cells operating at low relative humidity. *J Mater Chem A* 2015;3:8148–55. <https://doi.org/10.1039/c5ta00182j>.
- [424] Peng KJ, Lai JY, Liu YL. Nanohybrids of graphene oxide chemically-bonded with Nafion: preparation and application for proton exchange membrane fuel cells. *J Memb Sci* 2016;514:86–94. <https://doi.org/10.1016/j.memsci.2016.04.062>.
- [425] Feng K, Tang B, Wu P. Evaporating" graphene oxide sheets (GOSs) for rolled up GOSs and its applications in proton exchange membrane fuel cell. *ACS Appl Mater Interfaces* 2013;5:1481–8. <https://doi.org/10.1021/am302995c>.
- [426] Gao S, Xu H, Fang Z, Ouadah A, Chen H, Chen X, et al. Highly sulfonated poly(ether ether ketone) grafted on graphene oxide as nanohybrid proton exchange membrane applied in fuel cells. *Electro Acta* 2018;283:428–37. <https://doi.org/10.1016/j.electacta.2018.06.180>.
- [427] Zhang S, Li D, Kang J, Ma G, Liu Y. Electrospinning preparation of a graphene oxide nanohybrid proton-exchange membrane for fuel cells. *J Appl Polym Sci* 2018;135:46443. <https://doi.org/10.1002/app.46443>.
- [428] Aragaw BA, Su WN, Rick J, Hwang BJ. Highly efficient synthesis of reduced graphene oxide-Nafion nanocomposites with strong coupling for enhanced proton and electron conduction. *RSC Adv* 2013;3:23212–21. <https://doi.org/10.1039/c3ra44207a>.
- [429] Sun F, Qin LL, Zhou J, Wang YK, Rong JQ, Chen YJ, et al. Friedel Crafts self-crosslinking of sulfonated poly(etheretherketone)

- composite proton exchange membrane doped with phosphotungstic acid and carbon-based nanomaterials for fuel cell applications. *J Membr Sci* 2020;611:118381. <https://doi.org/10.1016/j.memsci.2020.118381>.
- [430] Han J, Lee H, Kim J, Kim S, Kim H, Kim E, et al. Sulfonated poly(arylene ether sulfone) composite membrane having sulfonated polytriazole grafted graphene oxide for high-performance proton exchange membrane fuel cells. *J Membr Sci* 2020;612:118428. <https://doi.org/10.1016/j.memsci.2020.118428>.
- [431] Jang HR, Vinothkannan M, Kim AR, Yoo DJ. Constructing proton-conducting channels within sulfonated(poly arylene ether ketone) using sulfonated graphene oxide: a nano-hybrid membrane for proton exchange membrane fuel cells. *Bull Kor Chem Soc* 2018;39:715–21. <https://doi.org/10.1002/bkcs.11459>.
- [432] Feng M, Huang Y, Wei M, Liu X. Sulfonated poly(arylene ether nitrile)-based hybrid membranes containing amine-functionalized GO for constructing long-range ionic nanochannels. *Int J Hydrogen Energy* 2018;43:11214–22. <https://doi.org/10.1016/j.ijhydene.2018.04.227>.
- [433] Feng M, Huang Y, Cheng Y, Liu J, Liu X. Rational design of sulfonated poly(ether ether ketone) grafted graphene oxide-based composites for proton exchange membranes with enhanced performance. *Polymer* 2018;144:7–17. <https://doi.org/10.1016/J.POLYMER.2018.04.037>.
- [434] Zhang X, Chen S, Liu J, Hu Z, Chen S, Wang L. Preparation and properties of sulfonated poly(phenylene arylene)/sulfonated polyimide (SPA/SPI) blend membranes for polymer electrolyte membrane fuel cell applications. *J Membr Sci* 2011;371:276–85. <https://doi.org/10.1016/j.memsci.2011.01.054>.
- [435] Ivanov V, Yegorov A, Wozniak A, Zhdanovich O, Bogdanovskaya M, Averina E. Perspective non-fluorinated and partially fluorinated polymers for low-temperature PEM FC. In: Prot. Exch. Membr. Fuel cell. InTech; 2018. <https://doi.org/10.5772/intechopen.71250>.
- [436] Geng L, He Y, Liu D, Dai X, Lü C. Facile in situ template synthesis of sulfonated polyimide/mesoporous silica hybrid proton exchange membrane for direct methanol fuel cells. *Microporous Mesoporous Mater* 2012;148:8–14. <https://doi.org/10.1016/j.micromeso.2011.07.010>.
- [437] Ahmadian-Alam L, Teymoori M, Mahdavi H. Polymer grafted GO/sulfonated copolyimide proton exchange nanocomposite membrane: as a polymer electrolyte membranes fuel cell. *J Polym Res* 2020;27:1–13. <https://doi.org/10.1007/s10965-020-02049-w>.
- [438] Kardos JL. In: The role of the interface in polymer composites — some myths, and modifications. *Mol. Charact. Compos. Interfaces*. Boston, MA: Springer US; 1985. p. 1–11. https://doi.org/10.1007/978-1-4899-2251-9_1.
- [439] Adanur S, Zheng H. Synthesis and characterization of sulfonated polyimide based membranes for proton exchange membrane fuel cells. *J Fuel Cell Sci Technol* 2013;10. <https://doi.org/10.1115/1.4024564>.
- [440] Tseng C-Y, Ye Y-S, Cheng M-Y, Kao K-Y, Shen W-C, Rick J, et al. Sulfonated polyimide proton exchange membranes with graphene oxide show improved proton conductivity, methanol crossover impedance, and mechanical properties. *Adv Energy Mater* 2011;1:1220–4. <https://doi.org/10.1002/aenm.201100366>.
- [441] Imran MA, He G, Wu X, Yan X, Li T, Khan A. Fabrication and characterization of sulfonated polybenzimidazole/sulfonated imidized graphene oxide hybrid membranes for high temperature proton exchange membrane fuel cells. *J Appl Polym Sci* 2019;136:47892. <https://doi.org/10.1002/app.47892>.
- [442] Kowsari E, Zare A, Ansari V. Phosphoric acid-doped ionic liquid-functionalized graphene oxide/sulfonated polyimide composites as proton exchange membrane. *Int J Hydrogen Energy* 2015;40:13964–78. <https://doi.org/10.1016/j.ijhydene.2015.08.064>.
- [443] Pandey RP, Thakur AK, Shahi VK. Sulfonated polyimide/acid-functionalized graphene oxide composite polymer electrolyte membranes with improved proton conductivity and water-retention properties. *ACS Appl Mater Interfaces* 2014;6:16993–7002. <https://doi.org/10.1021/am504597a>.
- [444] Pandey RP, Shahi VK. Sulphonated imidized graphene oxide (SIGO) based polymer electrolyte membrane for improved water retention, stability and proton conductivity. *J Power Sources* 2015;299:104–13. <https://doi.org/10.1016/j.jpowsour.2015.08.093>.
- [445] Farooqui UR, Ahmad AL, Hamid NA. Graphene oxide: a promising membrane material for fuel cells. *Renew Sustain Energy Rev* 2018;82:714–33. <https://doi.org/10.1016/j.rser.2017.09.081>.
- [446] Kim J, Kim K, Ko T, Han J, Lee JC. Polybenzimidazole composite membranes containing imidazole functionalized graphene oxide showing high proton conductivity and improved physicochemical properties. *Int J Hydrogen Energy* 2021;46:12254–62. <https://doi.org/10.1016/j.ijhydene.2020.02.193>.
- [447] Wang Y, Shi Z, Fang J, Xu H, Yin J. Graphene oxide/polybenzimidazole composites fabricated by a solvent-exchange method. *Carbon N Y* 2011;49:1199–207. <https://doi.org/10.1016/j.carbon.2010.11.036>.
- [448] Abouzari-Lotf E, Zakeri M, Nasef MM, Miyake M, Mozarmnia P, Bazilah NA, et al. Highly durable polybenzimidazole composite membranes with phosphonated graphene oxide for high temperature polymer electrolyte membrane fuel cells. *J Power Sources* 2019;412:238–45. <https://doi.org/10.1016/j.jpowsour.2018.11.057>.
- [449] Cai Y, Yue Z, Xu S. A novel polybenzimidazole composite modified by sulfonated graphene oxide for high temperature proton exchange membrane fuel cells in anhydrous atmosphere. *J Appl Polym Sci* 2017;134. <https://doi.org/10.1002/app.44986>.
- [450] Cai Y, Yue Z, Teng X, Xu S. Radiation grafting graphene oxide reinforced polybenzimidazole membrane with a sandwich structure for high temperature proton exchange membrane fuel cells in anhydrous atmosphere. *Eur Polym J* 2018;103:207–13. <https://doi.org/10.1016/j.eurpolymj.2018.02.020>.
- [451] Yusoff YN, Loh KS, Wong WY, Daud WRW, Lee TK. Sulfonated graphene oxide as an inorganic filler in promoting the properties of a polybenzimidazole membrane as a high temperature proton exchange membrane. *Int J Hydrogen Energy* 2020;45:27510–26. <https://doi.org/10.1016/j.ijhydene.2020.07.026>.
- [452] Olabi AG, Abdelkareem MA, Wilberforce T, Sayed ET. Application of graphene in energy storage device – a review. *Renew Sustain Energy Rev* 2021;135:110026. <https://doi.org/10.1016/j.rser.2020.110026>.
- [453] Zhao L, Li Y, Zhang H, Wu W, Liu J, Wang J. Constructing proton-conductive highways within an ionomer membrane by embedding sulfonated polymer brush modified graphene oxide. *J Power Sources* 2015;286:445–57. <https://doi.org/10.1016/j.jpowsour.2015.04.005>.
- [454] Shirdast A, Sharif A, Abdollahi M. Effect of the incorporation of sulfonated chitosan/sulfonated graphene oxide on the proton conductivity of chitosan membranes. *J Power Sources* 2016;306:541–51. <https://doi.org/10.1016/j.jpowsour.2015.12.076>.
- [455] Ranjani M, Pannipara M, Al-Sehemi AG, Vignesh A, Kumar GG. Chitosan/sulfonated graphene oxide/silica

- nanocomposite membranes for direct methanol fuel cells. *Solid State Ionics* 2019;338:153–60. <https://doi.org/10.1016/j.ssi.2019.05.010>.
- [456] Cui F, Wang W, Shan B, Liu C, Xie C, Zhu L, et al. Enhanced performance of the chitosan proton exchange membrane via anatase titania anchored GO and sodium ligninsulfonate constructing proton transport channels. *Energy Fuel* 2020. <https://doi.org/10.1021/acs.energyfuels.0c00367>.
- [457] Kalaiselvimary J, Prabhu MR. Influence of sulfonated GO/sulfonated biopolymer as polymer electrolyte membrane for fuel cell application. *J Mater Sci Mater Electron* 2018;29:5525–35. <https://doi.org/10.1007/s10854-018-8521-6>.
- [458] Collier A, Wang H, Zi Yuan X, Zhang J, Wilkinson DP. Degradation of polymer electrolyte membranes. *Int J Hydrogen Energy* 2006;31:1838–54. <https://doi.org/10.1016/J.IJHYDENE.2006.05.006>.
- [459] Dhimish M, Vieira RG, Badran G. Investigating the stability and degradation of hydrogen PEM fuel cell. *Int J Hydrogen Energy* 2021;46:37017–28. <https://doi.org/10.1016/J.IJHYDENE.2021.08.183>.
- [460] Transport and structure in fuel cell proton exchange membranes - ProQuest. [n.d].
- [461] Jörissen L, Gogel V, Kerres J, Garche J. New membranes for direct methanol fuel cells. *J Power Sources* 2002;105:267–73. [https://doi.org/10.1016/S0378-7753\(01\)00952-1](https://doi.org/10.1016/S0378-7753(01)00952-1).
- [462] Hickner MA, Pivovar BS. The chemical and structural nature of proton exchange membrane fuel cell properties. *Fuel Cell* 2005;5:213–29. <https://doi.org/10.1002/FUCE.200400064>.
- [463] Ahmad AL, Farooqui UR, Hamid NA. Effect of graphene oxide (GO) on Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) polymer electrolyte membrane. *Polymer* 2018;142:330–6. <https://doi.org/10.1016/J.POLYMER.2018.03.052>.
- [464] Simari C, Lufrano E, Godbert N, Gournis D, Coppola L, Nicotera I. Titanium dioxide grafted on graphene oxide: hybrid nanofiller for effective and low-cost proton exchange membranes. *Nanomaterials* 2020;10:1–18. <https://doi.org/10.3390/NANO10081572>.
- [465] Ahmed M, Ahmad S, Nawaz T, et al. Performance evaluation of graphene oxide–MnO₂ nanocomposite for alkaline membrane fuel cell. *Electrochim Sci Adv* 2021:e2100085. <https://doi.org/10.1002/elsa.202100085>.