멤브레인(Membrane Journal)
Vol. 30 No. 4 August, 2020, 213-227

총 설

Print ISSN: 1226-0088
Online ISSN: 2288-7253
DOI: https://doi.org/10.14579/MEMBRANE_JOURNAL.2020.30.4.213

미생물 연료 전지 적용을 위한 양성자 교환막에 대한 검토

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(2020년 7월 5일 접수, 2020년 7월 16일 수정, 2020년 7월 17일 채택)

Review on Proton Exchange Membranes for Microbial Fuel Cell Application

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(Received July 5, 2020, Revised July 16, 2020, Accepted July 17, 2020)

요 약: 재생 불가능한 에너지 자원이 수년에 걸쳐 고갈됨에 따라, 재생 에너지 생산을 위한 보다 효과적인 방법에 대한 연구가 증가되었다. 연료전지 개발의 한 분야인 미생물 연료전지(MFC)는 이중 성능의 잠재력 덕분에 발전하였다. MFC는 박테리아와 같은 전극 감소 생물에서 전력을 모아서 전기 에너지를 생산한다. MFC는 폐수를 연료로 사용하여 에너지를 생산하고 폐수를 정화한다. 양성자 교환막(PEM)은 양극과 음극 챔버의 분리막으로, 양성자만 효과적으로 통과할 수 있게 하는 중요한 역할을 한다. Nafion은 MFC에 상업적으로 사용되는 PEM이지만 비용, 생산 시간, 양성자 전도성 차원에서 보완할 점들이 많다. 본 리뷰 논문에는 Nafion을 대체할 수 있는 새로 개발된 PEM 몇 가지를 논의하였다. 또한, PEM, 혼합 PEM 및 복합 PEM에 기반한 MFC를 요약하고자 한다.

Abstract: As unrenewable energy resources have depleted over the years, the demand for renewable energy has increased promoting research for more effective methods to produce renewable energy. The field of fuel cell development, specifically microbial fuel cells (MFCs), has developed because of the dual performance potential of the technology. MFCs convert power by facilitating electrode-reducing organisms such as bacteria (microbes) as a catalyst to produce electrical energy. MFCs use domestic and industrial wastewater as fuel to initiate the process, purifying the wastewater as a result. Proton exchange membranes (PEM) play a crucial role in MFCs as a separator between the anodes and cathodes chambers allowing only protons to effectively pass through. Nafion is the commercially used PEM for MFCs, but there are many setbacks: such as cost, production time, and less effective proton conductivity properties. In this review there will be largely two parts. Firstly, several newly developed PEM are discussed as possible replacements of Nafion. Secondly, MFC based on PEM, blended PEM and composite PEM are summarized.

Keywords: *microbial fuel cell, graphene oxide, proton exchange membrane, membrane*

1. Introduction

An alternative system to produce renewable energy is in large demand due to depleted levels of unrenewable natural energy and increased usage of energy worldwide. Polymer electrolyte membrane fuel cells (PEMFCs) is a key field within fuel cells which use a proton exchange membrane to transport ions (H^+ and OH^-). The key PEMFCs that will be focused on in this review

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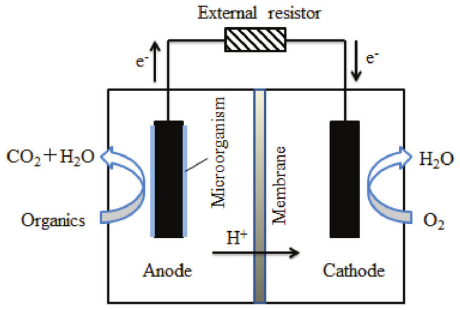

Fig. 1. Schematic diagram of microbial fuel cell.

paper are microbial fuel cells (MFCs) which use industrial/domestic wastewater to harvest energy and convert into electricity[1-14]. It can convert energy stored within the microbes (microorganisms) of the wastewater to electrical energy. Not only does MFCs generate electricity, but also purifies the domestic/industrial wastewater that produce fresh water for further use. Advanced research of optimizing MFC performance will result into many benefits such as energy generation, environmental safety, and freshwater production. Schematic representation of MFC is presented in Fig. 1. The most crucial factor of the MFC that effects the overall performance is the proton exchange membrane placed in the middle of the two chambers (anode and cathode). It allows the H^+ to effectively pass through from the anode chamber to the cathode chamber. Additionally, it avoids short circuiting between the electrons and protons and maintain anaerobic conditions in the anode chamber.

The most used proton exchange membrane (PEM) is the Nafion-117. Although Nafion is used the most, there are several setbacks to it including high cost of manufacture, unsatisfactory proton conductivity levels, and a long and complex manufacturing process. To improve MFC performance, extensive research is conducted to produce a superior alternative to the Nafion-117 with improved proton conductivity and anti-fouling properties. Performance of the different membranes in MFC is presented in Table 1. To characterize the synthesized membranes, the main imaging methods used were scanning electron microscopy (SEM), water uptake, proton conductivity, and transmission electron microscopy (TEM). Many of the membranes synthesized goes through multiple steps that need to be rechecked to make sure that the reactions occurred effectively on the membranes. All the membranes introduced further are also tested by performance in either a two-chambered or single-chambered MFC over a designated time period. The data is compared to the performance of Nafion-117 and if it performed better, it was thought to be a potential replacement for it. In this review microbial fuel cell primarily based on composite and blended proton exchange membrane are discussed.

2. Microbial Fuel Cell

Hernandez-Florez *et al.* reported synthesis of agar membranes by mixing different weights of agar from red algae as a polymer and distilled water as a solvent[15]. Once mixed, it was poured in Petri dishes and dehydrated into dry membranes. Agar-KCl membranes were synthesized in a similar fashion but mixed with corresponding amounts of KCl salt and agar polymer into distilled water. Three sets of membranes were synthesized which are: different percentages of only agar polymer (2, 4, 6, 8%), different percentages of agar polymer (2, 4, 6, 8%) and same percentage of KCl salt (10%), same percentage of agar (2%) with different percentages of KCl salt (2, 4, 6, 8, 10%). The surface morphology of the synthesized membranes was analyzed using scanning electron microscopy. Mechanical properties such as tensile strength and maximum strain were tested as well as resistance and proton conductivity. SEM images revealed a superficial morphology of the composite membranes without porosity and the KCl salts as “dots” on the surface. The more KCl salt incorporated into the membranes, the weaker and more brittle it was while an increase of agar concentration with same concentration of KCl salt showed an increase in strength. Proton conductivity of membranes containing only agar polymer did not increase much as the concentration increased. But the conductivity of agar-KCl membranes increased drasti-

Table 1. Summary of Membranes used in MFC

Polymer	Filler	Power density (MFC) (mW/m^2)	Water uptake (%)	Proton conductivity (S/cm)	COD removal (%)	IEC (meq/g)	Reference
Agar	KCl	2,374 mW/m^3	-	0.00243	-	-	[15]
BPSH	-	126	33.3	0.144	-	1.82	[17]
PBI	Phosphoric acid	74.2 mW/cm^2	23.5	0.024	-	-	[19]
S-coPIs	Trifluoromethyl and benzyl ether side groups	576.1	35	0.244	-	2.79	[20]
PVDF-g-PSSA	SGO@SiO_2	185	34.2	0.078 ± 0.004	75	1.6 ± 0.1	[21]
PVDF-g-PSSA	SGO	180.27	32.56	0.083	-	1.24	[22]
PVDF-HFP; Nafion	TiO_2	552.12 ± 26	27.7	0.0347	88.97	0.43	[23]
SPEEK	Zeolite	176	15.83	0.00148	-	1.47	[24]
CNT-textile	-	1,098	-	1,250	-	-	[25]
Nafion	PVA	91 ± 1	21.2 ± 0.1	0.59 ± 0.02	-	0.46	[26]
SPEEK	AgGO-GO	1,049	75.27	0.037	83.36	-	[27]
SPEEK	cSMM	172.12	37.01 ± 0.17	0.06341	95	-	[28]
SPEEK	PAI	69	19 ± 0.03	0.00169	-	1.73 ± 0.01	[29]
QPEEK	PDA	918	22 ± 4	0.012	-	-	[30]
PVDF	SSS	106.7	25	0.046	85	-	[31]
S-OPBI	-	110	29	0.0783	-	1.0	[32]
PVC	Zeolite 4A	250 ± 5	37.8	0.13	89	1.92	[33]
SSEBS	S-SiO_2	1,209 ± 17	210 ± 8	0.0321	-	3.015	[34]

KCl: potassium chloride; BPSH: disulfonated poly (arylene ether sulfone); PBI: polybenzimidazole; S-coPI: sulfonated co-poly (ether imide); PVDF-g-PSSA: poly (-vinylidene fluoride) grafted poly (styrene sulfonic acid); SGO@SiO_2: sulfonated graphene oxide @ silicon dioxide; SGO: sulfonated graphene oxide; PVDF-HFP: poly (vinylidenefluoride-co-hexafluoropropylene); TiO_2: titanium dioxide; SPEEK: sulfonated polyether ether ketone; CNT: carbon nanotube; PVA: polyvinyl alcohol nanofiber; AgGO-GO: silver graphene oxide and graphene oxide; cSMM: charged surface modifying macromolecule; PAI: poly (amide imide); QPEEK: quarternized poly (ether ether ketone); PDA: polydopamine; PVDF: poly (vinylidene fluoride); SSS: sodium styrene sulfonate; S-OPBI: sulfonated polybenzimidazole; PVC: polyvinylchloride; SSEBS: Sulfonated polystyrene ethylene butylene polystyrene; S-SiO_2: sulfonated SiO_2: SGO@SiO_2.

cally as agar component increased and KCl component stayed the same at 10%. MFC incorporated with the synthesized membranes were tested in single-chambers with Nafion-117 as the control. The dry membranes were coated with a catalyst before use and the electrochemical characteristics were analyzed. SR-I was used as the biocatalyst over a short time interval. A trend showed which was that the increase of agar concentration resulted in better SC-MFC performance. When analyzed for a longer period of time of around 15 days, the same trend was found. Overall, the synthesized membranes seem to be a promising potential replacement of Nafion-117 which is not only expensive and time-consuming to produce. Pictorial presentation of MFC and time voltage plot is represented in Figs. 2 and 3[16].

2.1. Proton exchange membrane

Poly (arylene ether sulfone) membranes were synthesized by reacting 4,4'-Dichlorodiphenlysolfone (DCDPS), 4,4'-biphenyl (BP), 3,3'-Disulfonated-4,4'-dichlorodiphenylsulfone (SDCDPS), and potassium into a viscous solution[17]. The precipitate of the solution was then dried and dissolved in DMAc and finally cast onto a glass plate. Different samples were synthesized according to the different degrees of sulfonation (20, 30, 40, 60). The synthesized membranes were tested for ion exchange capacity using titration and proton con-

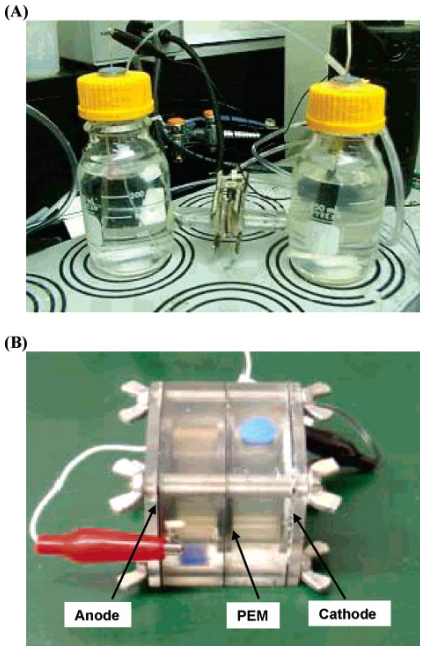

Fig. 2. (A) Two-bottle (B-MFC) and (B) and two-cube (C-MFC) MFCs used for experiments (Reproduced with permission from Kim *et al.*, 16, Copyright 2007, American Chemical Society).

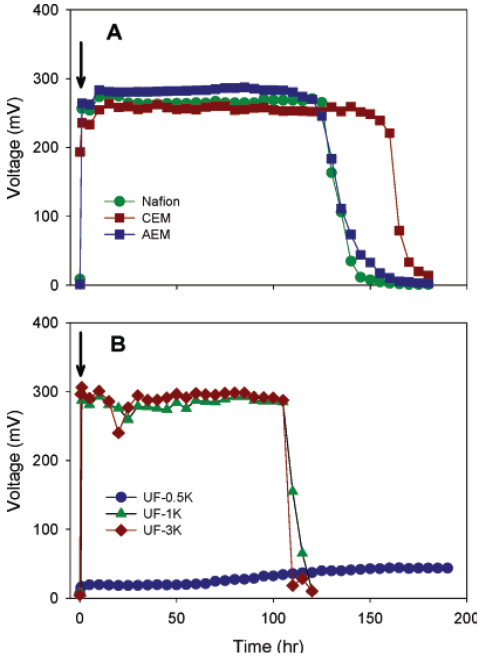

Fig. 3. Time-voltage curves of B-MFCs using (A) proton, cation, and anion exchange membranes and (B) UF membranes. Arrow indicates acetate injection (1 mM at final) (Reproduced with permission from Kim *et al.*, 16, Copyright 2007, American Chemical Society).

ductivity using the four-point probe technique in water. Water uptake was measured by comparing dry and wet membranes and the surface morphology of microbial growth was tested using scanning electron microscopy. Compared to the other research articles, Nafion-212 was used as the reference of commercial products rather than Nafion-117 which is more widely used. IEC of the synthesized membranes increased as the degree of sulfonation increased and was all higher than Nafion-212 (0.93 meq/g). The highest was 2.21 meg/q for BPSH 60. Proton conductivity also increased as the degree of sulfonation increased but BPSH 20 (0.039 S/cm) and BPSH 30 (0.066 S/cm) had lower conductivity than Nafion-212 (0.118 S/cm). The highest was 0.186 S/cm for BPSH 60. Water uptake of BPSH 60 was significantly higher (160%) than the rest of the samples and even Nafion-212 at 11.6% proving that the highest sulfonation was better for membrane characterization. Bacteria clustering on the membrane may cause biofouling leading to decreased performance of the MFC. Surprisingly, the least bacterial cluster occurred in BPSH 60 leading to the analysis that hydrophilicity has an impact in biofouling.

The performance of MFC incorporated with the synthesized membranes were analyzed in both two-chamber and single-chamber MFCs. Two-chamber MFC performance was analyzed in a continuous feeding system and voltage rapidly increased and peaked for all the samples but a rapid decrease followed right after showing that proton conductivity is highly susceptible to the cations related to microbial metabolism. For the single-chamber MFCs, performance was highly dependent on the PEM and BPSH 40 generated the highest voltage of 20 mV which was higher than Nafion-212 of 15 mV. This revealed that the membranes result in different activities in two- and single-chamber MFCs. Because these membranes performed better in the single-chamber MFCs, they seem to be a better alternative, specifically BPSH 40, for single-chamber MFCs than two-chamber MFCs. Fig. 4 represents the pictorial diagram of MFC membrane with Nafion membrane [18]. SEM image of bacteria grown on the MFC mem-

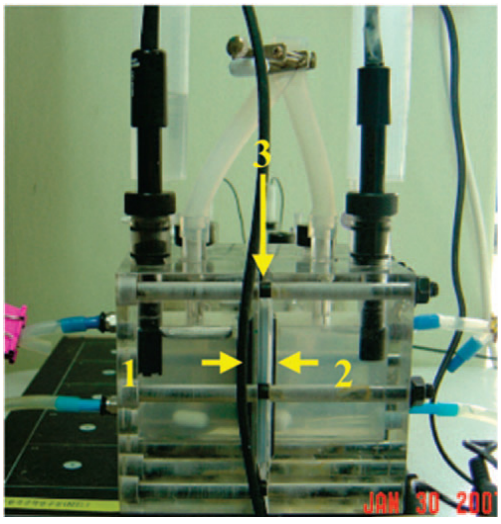

Fig. 4. Two-chamber MFC used in this experiment: (1) anode, (2) cathode, and (3) Nafion. The arrows indicate where the components are (Reproduced with permission from Chae *et al.*, 18, Copyright 2008, American Chemical Society).

brane is shown in Fig. 5[18]. Picture of bacterial growth on the membrane after use of 50 days and SEM image is presented in Fig. 6[18].

To synthesize acid-doped polybenzimidazole (PBI) membranes, PBI, N, N-dimethyl acetamide (DMAc), and lithium chloride (LiCl) were reacted, filtered, and concentrated into a viscous solution[19]. The solution was then cast on glass plates and dried. Finally, the membranes were doped using phosphoric acid yielding about 500 mol% of doping. Because the synthesized membrane is incorporated in air-breathing MFCs, oxygen permeability was analyzed as well as the proton conductivity using a four-point probe measurement. The lower the oxygen permeability, the better the performance of the MFCs. Pristine PBI membranes had a higher oxygen permeability than the commercial Nafion-117 membranes which negatively affects the performance of MFCs but PBI membranes doped with 500 mol% phosphoric acid showed a sharp decrease in oxygen permeability. Also, water uptake was lower than Nafion-117 for pristine PBI membranes but once it was acid-doped, it increased significantly. This was due to strong interactions of phosphoric acid and water

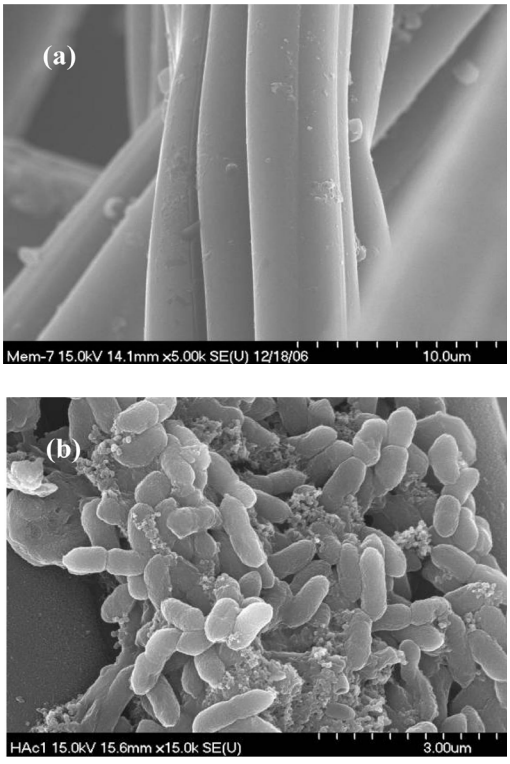

Fig. 5. SEM images: (a) new carbon felt and (b) bacteria growing on the anode carbon felt surface in the MFC fed with acetate (0.5 mM) as an electron source for over 50 days (Reproduced with permission from Chae *et al.*, 18, Copyright 2008, American Chemical Society).

molecules. This trend was also visible for maximum power density of the synthesized membranes. Pristine PBI membranes on its own had a significantly lower maximum power density. Acid-doped PBI membranes reached a maximum power density of 471 mV which was higher than that of Nafion membranes of 396 mV. Overall, acid-doped polybenzimidazole membranes seem to be a suitable alternative to the commercial Nafion membranes.

Diamine monomer TADBE is used to synthesize sulfonated co-poly (ether imide) s reacted with six-membered dianhydride and 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA)[20]. Different degrees of sulfonation was applied and labeled correspondingly (DBN-60, 70, 80, 90). Transmission electron microscope (TEM) was used to analyze the surface morphology. IEC values were found using titration method and wa-

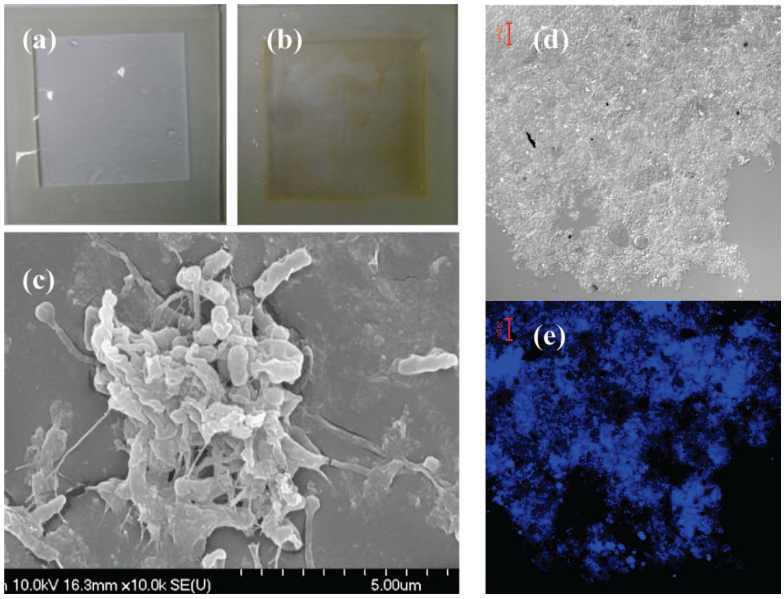

Fig. 6. (a) Photograph of new Nafion. (b) Photograph of Nafion used for over 50 days in an acetate fed MFC. (c) SEM image of bacteria growing on the anodic side of the used Nafion in part b. (d) Differential interference contrast (DIC) image. (e) DAPI (4',6-diamidino-2-phenylindole dihydrochloride) image for the biofilm taken out of the used Nafion in part b (Reproduced with permission from Chae *et al.*, 18, Copyright 2008, American Chemical Society).

ter uptake was calculated by comparing wet and dry polymer films. Proton conductivity of the synthesized polymer membranes were tested in different humidity levels. TEM images of the copolymer membranes shows dark spots corresponding to the hydrophilic parts and the bright parts to the hydrophobic parts. Ionic clusters were small which is a positive feature and the hydrophobic parts depicts the bulky group which decreases the cohesive forces between the polymer chains leading to the small clusters[20]. Both water uptake and IEC values increased as the degree of sulfonation increased showing that sulfonation enhances the PEM performance in MFCs. Moreover, proton conductivity increased significantly as degrees of sulfonation increased.

MFCs incorporating the synthesized copolymer membranes were tested using synthetic wastewater and 3,000 mg/L chemical oxygen demand (COD) as the feed. It was operated under fed batch mode with three days retention time in moderate temperatures[20]. The highest power density was recorded for the highest sulfonated membrane (DBN-90) which was higher than the commercial Nafion-117. Conclusively, DBN-90 is the most ideal alternative to be used in PEM to the commercial Nafion-117 membranes.

2.2. Composite proton exchange membrane

A mixture of Graphene Oxide (GO) and a solution of CH3OH and sulfuric acid was centrifuged and dried to obtained SGO particles. SGO@SiO_2 nanoparticles were obtained through ultrasonication and centrifugation of SGO particles mixed in a solution of ethanol and water[21]. Different ratios of SGO@SiO_2 particles and PVDF-g-PSSA were mixed at moderate temperatures and cast into glass molds. The resulting PEM had a thickness of around 80 μm. PEM immersed in sulfuric acid to change to H^+ from Na^+. BET was used to obtain specific surface area of the synthesized hybrid particle with the result of 99.053 and 101.196 m^2/g for GO and SGO@SiO_2 particles respectively. No significant difference was found. Particles were observed using TEM at 120 kV which showed that the thin-membrane structure of SGO and agglomerated state of SiO_2 was favorable to produce the sandwich structure of SGO@SiO_2 nanoparticles. Proton conductivity of the

membrane was experimented using four-point probe AC impedance spectroscopy (EIS) while water uptake was obtained by observing the membrane in DI water for 48 hours. Proton conductivity data proved that synthesized membranes performed at the same rate or superior to the control, Nafion-117. Water uptake was significantly higher for the synthesized membrane (an average of 10% difference) resulting from the adequate water absorption capacity of SGO and SiO_2. Overall, the results proved that doping of SGO@SiO_2 significantly enhanced performance when compared to the commercial product Nafion-117. The performance of MFCs incorporated with the synthesized SGO@SiO_2/PVDF-g-PSSA was tested by obtaining power density and internal resistance. Maximum power density of MFC with Nafion-117 was 132 mW/m^2 while MFC with synthesized membrane was 185 showing a significant increase. Internal resistance was 210 Ω for Nafion-117 while it was 152 Ω for the synthesized membrane. These data show that performance of MFC using SGO@SiO_2/PVDF-g-PSSA membrane shows superior performance over Nafion-117 proving that doping SGO@SiO_2 not only brings down the cost of MFCs but performs equally if not better than the commercial membrane Nafion-117.

Modified Hummer's method was used to synthesize graphene oxide (GO) from natural graphite. Graphite powder, sodium nitrate, and sulfuric acid was stirred at 0°C and potassium permanganate was added to produce the solution form of GO[22]. DI water and HCl is incorporated to produce the final GO solution which is freeze-dried at -40°C. GO nanosheets and DI water is sonicated and mixed with sulfanilic acid at 70°C then dried in an oven to produce sulfonated graphene oxide (SGO). PVDF-g-PSSA copolymer at its H^+ form is used to produce SGO/PVDF-g-PSSA membrane by solution casting method. Copolymer is dissolved in NMP with different amounts of SGO. The resulting solutions are cast in glass plates to produce membranes that are around 80μm thick. The different percentages of SGO loadings are 0.1, 0.5 1.0, 1.5, and 2.0 wt%. Water uptake of all the SGO samples were higher and particularly highest for the SGO/PPSSA1.0 membrane (32.56%) which was significantly higher than that of Nafion-117. SEM imaging of the SGO/PPSSA1.0 membrane showed a uniform surface without any visible flaws (such as cracks) which could be seen as result of strong interactions between the membrane and copolymer. While other sample of SGO/PPSSA showed a lower proton conductivity than Nafion-117, SGO/PPSSA1.0 showed higher conductivity showing that this sample could be an ideal replacement of Nafion-117. MFCs using the composite membranes synthesized were operated with a mixture of 20% anaerobic sludge and 80% PBS. The performance was compared to MFC using PPSSA and Nafion-117. Since data of SGO/PPSSA1.0 showed the highest performance efficiency, the data of other wt% samples were not considered for the comparison with the control (Nafion-117). The maximum power density was observed for the MFC using SGO/PPSSA1.0 composite membrane at 180.27 mW/m^2 while Nafion-117 had a maximum of 132.02 mW/m^2. To further observe the effect of biofouling of the membranes, the MFCs were observed for three months after initial operation. The lowest reduction of performance was measured for SGO/PPSSA1.0 while the greatest reduction was observed for Nafion-117. Overall, SGO/PPSSA1.0 seems to be a promising alternative to the commercial composite membranes such as Nafion-117 and PPSSA.

VDF-HFP polymer is sulfonated with chlorosulfonic acid at 60°C, washed, and dried to produce sulfonated polymer pellets[23]. The pellets dissolved in NMP, Nafion resins, and nano-TiO_2 are mixed in certain ratios (5 different ratios) at moderate temperature. The polymer solutions are poured into Petri-dishes and dried to produce nanocomposite membranes. Furthermore, SEM imaging was obtained to analyze the morphology and proton conductivity was tested to analyze the efficiency of the nanocomposite membranes. Water uptake of the nanocomposite membranes increased with increasing amounts of TiO_2 content proving that TiO_2 plays a significant role in performance enhancement. Of the nanocomposite membrane samples, T-7 showed

the highest water uptake of 27.7% which was significantly higher than Nafion-117 of 17.4%. The same trend was observed for the proton conductivity where T-7 membrane had the highest at 34.7 mS/cm compared to Nafion-117 at 30.2 mS/cm which is a smaller difference compared to water uptake but still worth highlighting. SEM imaging of the samples showed that the nanoparticles made a more porous surface and distribution was uniform. MFCs incorporating the nanocomposite membranes were operated for 48 days using air as catholyte and microbial enriched wastewater as anolyte. Highest power density and COD removal was observed of the T-7 sample membrane incorporated MFC at 552.12 mW/m^2 and 88.97% respectively. It had higher levels even compared to Nafion-117 incorporated MFC further proving its potential to replace commercial membranes. Furthermore, SEM images of Nafion-117 and T-7 membranes after bio-fouling shows that an anti-biofouling effect occurred due to TiO_2 incorporated in the membrane resulting in enhanced hydrophilicity. Not only does T-7 show great potential as an alternative to Narion-117, it predicts a future significance of nanocomposites being utilized in different systems of bio-electrochemistry.

Sulfonated poly (ether ether ketone) (SPEEK) was obtained by sulfonating PEEK polymer with sulfuric acid as the sulfonating agent[24]. The obtained SPEEK is washed to neutral pH, dried, then dissolved in NMP to be cast in petri dishes. Different weight percentages of zeolite (2.5, 5, 7.5, 10%) is added to SPEEK ionomers dissolved in the NMP solvent and cast into petri dishes. To view the surface morphology of the synthesized membranes, SEM was used, and proton conductivity was measured using electrochemical impedance spectrometer. Water uptake was calculated by comparing wet and dry composite membranes and ion exchange capacity was determined using a volumetric method. Water uptake of the membranes increased as zeolite component increased until 7.5% due to the 3D structure of pores absorbing water well. The same trend occurred for IEC and proton conductivity further proving that 7.5 wt.% of zeolite is the ideal proportion. SEM images of the composite membranes show a uniform dispersity as well as specks of zeolite particles increasing as zeolite content increases. The performance of single chamber MFCs incorporating the synthesized composite membranes were tested using *E. coli* as bacteria in the anodic chamber. Columbic efficiency increased until 7.5% (74%) and decreased to 73% finally. All the composite membranes showed a better performance than the commercial Nafion-117 and pristine SPEEK membranes. The SPEEK/zeolite composite membranes resulted in superior characteristics such as IEC, proton conductivity, and power density. Overall, the synthesized composite membranes proved to be a promising and cheaper alternative to the costly commercial membranes such as Nafion-117.

Various carbon-based porous anodes such as carbon cloth, carbon paper, and carbon foam have been incorporated in MFCs, but the quick microbial growth clogs the pores decreasing the efficiency of MFCs at a fast pace[25]. For satisfactory MFC application, a large specific surface area should be acquired. To meet the requirements, a 3D anode configuration design with a porous structure for improved electron transfer has been introduced. The proposed carbon nanotube (CNT) is suitable for substrate transport and colonization of microorganisms which results in a high anolyte-biofilm-anode interfacial area[25]. Since it is a highly conductive structure, a strong interaction with microbial biofilms is possible. The synthesized CNT was tested in MFCs using domestic wastewater and glucose. Although not active right after operation of the MFC, the voltage increased significantly after 12 days. SEM images proved that the CNT-textile anode was biocompatible and able to support colonization. Compared to the MFCs incorporated with the commercial carbon cloth, CNT-textile anode had greater porosity allowing for more substrate transport and colonization to occur. Moreover, charge-transfer resistance improved 10-fold from 300 Ω to 30 Ω also meaning that is has a significantly higher electron-transfer efficiency which proves to be a promising alternative to the commercial carbon-based porous anodes available.

Porous PVA mats were obtained through standard electrospinning using water-based solution of polyvinyl alcohol (PVA)[26]. Water was removed through heating and catalyzed in 4-formyl-1,3-benzenedisulfonic acid disodium salt and chlorhydric acid. Nanofiber mats dipped in 5 wt.% Nafion solution in isopropanol and water is then annealed using a hot plate press to 125°C and the resulting composite membranes' thickness was measured (an average of ten samples was calculated). The thickness of Nafion-PVA-15 was around 15 μm while Nafion-PVA-23 was around 23 μm. SPEEK-based membranes were produced using two different bases (water and DMAc). After dissolving SPEEK and the corresponding bases separately, they are mixed until complete homogenization and cast on Teflon dishes which are left overnight. The membranes are crosslinked at different temperatures. The last type of sample, SPEEK-PVA-PVB composite membranes were synthesized by first obtaining SPEEK-30PVB nanofibers using SPEEK solution in DMAc using electrospinning and repetition of heating and drying. Finally, SPEEK-35PVA composite membranes were reinforced using the SPEEK-30PVB nanofibers in climate chambers of moderate temperature and humidity. Water uptake was calculated by comparing the weight of dry and wet membrane samples and ion-exchange capacity (IEC) was obtained by submerging in NaCl solution and titration with NaOH. Membrane conductivity was measured using impedance analysis. Water uptake was highest for the DMAc-based SPEEK-35PVA composite membrane with 490% and the lowest for Nafion-PVA-15 with 21.2% mostly because the thickness of Nafion-PVA-15 was much thinner than DMAc-based SPEEK-35PVA. Conductivity of SPEEK-30PVB-35PVA was the highest at 1.03×10^{2} S/cm and the other composite membranes were significantly higher than the commercial Nafion-117 membrane at 3.1×10^{-2} S/cm.

The performance of MFCs incorporated with the synthesized composite membranes were tested in single chamber microbial fuel cells. Electrochemically enriched sodic saline inocula was used as the biocatalyst. The conductivity of the composite membranes did not correspond to the results of the MFC performance. Nafion-PVA-15 resulted in the highest power density at 1,053 mW/m^3 which was significantly higher than all the other composite membranes synthesized for this research. Furthermore, the current density was the highest at 3,099 mA/m^3 followed by Nafion-117 at 3,009 mA/m^3. Overall, any composite membrane which incorporated PVA nanofibers seem to result in the better performance offering a cheaper alternative to Nafion-117.

A homogeneous mixture of graphene oxide solution and silver nitrate solution prepared separately was mixed with a reducing agent solution (sodium borohydride solution) at a controlled temperature of 15°C[27]. The resulting mixture was washed and centrifuged multiple times and dried to obtain silver graphene oxides. A dry phase inversion method using N-Methyl-2-Prrolidone as a solvent was used to fabricate the composite membranes GO-SPEEK and AgGO-GO-SPEEK. The respective membrane solutions were ultrasonic to obtain homogeneous mixtures and cast on glass plates. The cast membrane is dried at two different temperatures (45 and 60°C) for 48 h each. The dried membrane is peeled off and put in H_2SO_4 solution for activated sulfonic groups and finally washed off with DI water. Characterization of the synthesized membranes were performed to obtain the water uptake level and proton conductivity and ultimately compared with Nafion-117 membranes. Water uptake was found by comparing masses of hydrated and dried membrane while the Electrochemical Impedance Spectroscopy (EIS) was used to determine the proton conductivity ultimately obtaining the membrane's resistance. Water uptake was significantly higher for the synthesized membranes (around 76%) compared to Nafion-117 (23.76%). This proves that the structure of the said membranes was more ideal for water uptake than Nafion-117. Proton conductivity also showed to be superior to the Nafion-117. The synthesized membranes averaged at about 3.75 while Nafion-117 was at 2.40 proving that incorporation of graphene oxide significantly improved performance of the membrane. Performance was tested in a dual-chamber MFC chamber with the

anolyte solution made up of synthetic wastewater (90%) and mixed bacteria culture (10%). The catholyte solution was 50.0 mM phosphate buffer solution and the data obtained were internal resistance, maximum power density, and COD (Chemical oxygen demand) removal rate. Results showed that MFC incorporated with GO-SPEEK membrane has the lowest internal resistance of 48.59 Ω with the highest maximum power density of 1,134 mM/m^2. AgGO-GO-SPEEK membrane followed meaning that Nafion-117 was the least effective out of the three samples. COD removal rate was not significantly different for the three samples with an average of 83%. The three different MFCs were observed for 100 days and the results showed that durability of the synthesized membranes (AgGO-GO-SPEEK in particular) were better than the MFC system equipped with Nafion-117. Overall, this proves that both GO-SPEEK and AgGO-GO-SPEEK membranes showed adequate potential as replacements of Nafion-117 in MFC systems.

2.3. Blended proton exchange membrane

Sulfonated poly (ether ether ketone) referred as SPEEK is produced by sulfonating PEEK. Dried PEEK dissolved in concentrated sulfuric acid (room temperature) produces the polymer solution[28]. Temperature is increased to around 70°C until needed degree of sulfonation (60, 70, and 76%) is achieved. Temperature is dropped significantly to stop the sulfonation and washed/dried to obtain SPEEK at different sulfonation degrees. 10% solution of pure SPEEK is produced by dissolving SPEEK in NMP and cSMM is mixed with SPEEK to prepare cSMM in solid state. The membranes were then cast on glass plates and dried. Finally, the membranes were ionized using sulfuric acid solution. SEM images captured 2 months after initial operation of the MFC showed different microorganisms attached to the electrode. This proves that not only was the MFC in a stable condition, there were enough microorganisms attached to produced protons and electrons from the membrane synthesized. Characterization of the membrane was performed to obtain proton conductivity levels using AC impedance technique and water uptake (method mentioned above). Water uptake was significantly higher for all three synthesized membranes (29~37%) compared to Nafion-117 (9.31%) and SPEEK76/cSMM particularly had the highest percentage. This proves that the morphology of the SPEEK membranes were better suitable for water uptake. Proton conductivity for SPEEK60 (25.71 mS/cm) and SPEEK68 (35.68 mS/cm) were significantly lower than Nafion-117 (61.03 mS/cm). On the other hand, SPEEK76 (63.41%) was superior to Nafion-117 showing that the higher level sulfonation improved performance drastically. The performance of MFCs incorporated with the four samples were observed for 2 months from initial experimentation. The highest power density of 172.1 mW/m was measured from the MFC with SPEEK76/cSMM membrane followed by Nafion-117. This might be due to the high sulfonic acid group content which is associated with high water uptake levels. COD removal showed no significant differences between the four samples ranging from 85 to 94%. The overall data showed that SPEEK76/cSMM performed the most efficiently out of the four samples and it is suitable as a replacement of the Nafion-117 membranes for its lower cost and higher performance levels.

Sulfonated poly (ether ether ketone) (SPEEK) was prepared by dissolving PEEK into sulfuric acid and precipitating in cold deionized water[29]. The resulting fiber is tested to be 65% sulfonated. Solvent casting method is used to synthesize the polymer electrolyte membrane by dissolving corresponding amounts of PAI and SPEEK in DMF. The solution is then dried on a petri dish until the solvent it completely evaporated. The different PAI/SPEEK compositions are labeled as YA1 (0/100), YA2 (5./95), YA3 (10/90), and YA4 (20/80). Water uptake was calculated by comparing the weight of dry and wet membranes and proton conductivity of polymer electrolytes were analyzed. SEM images of the membranes were obtained to analyze the surface morphology. Water uptake results showed that the percentage decreases as PAI component increases from 37% to 13%. This is due to the reduction of block-

age of porous structure[29]. Proton conductivity showed the same decreasing trend as PAI component increased. As PEEK is sulfonated, it is turned into a cation exchange membrane which is hydrophilic compared to the hydrophobic nature of PEEK membranes. SEM images show a smooth surface for YA1 while an even distribution of PAI particles can be seen for the other membranes. The performance of MFCs incorporated with YA2 used as the electrolyte was observed for about 30 days containing both pure and mixed culture. Both MFCs increased in voltage production each time the PBS was fed and stabilized for longer days. This showed that biodegradation occurred in a slow rate while power output was effective. But due to biofouling, the energy decreased significantly meaning that passage of protons through the membrane was restricted. Overall, this study shows that the increased SPEEK component of synthesized membranes resulted in enhanced performance of MFCs. Although highest water uptake and proton conductivity was measured for YA1, YA2 was chosen as the ideal PAI/SPEEK proportion because it decreased the least in proton conductivity over time.

A solvent casting method was used to synthesize quaternized poly (ether ether ketone) (QPEEK) membranes. The membranes were further modified using different concentrations of PDA (0.5, 1.0, 1.5, 2 kg/m^3) and were named accordingly[30]. Different concentrations of dopamine hydrochloride are dissolved in Tris-HCl buffer which polymerizes from the PDA. Surface morphology of the synthesized membranes were viewed using SEM as well as the surface roughness using a noncontact profile meter. Hydrophilicity was tested using water drops and water uptake was measured by comparing wet and dry membranes. Because antiadhesion is an important feature of antibiofouling potential, it was tested using a mixed culture bacteria. SEM images of the different membranes reveal an undulated morphology showing that the membranes were successfully modified although grains of PDA can be seen as the concentration increases. As the concentration of PDA increases, the water contact angle increased meaning that hydrophilicity improved too. The reference membrane in this research is AMI-7001. Antiadhesion tests were performed on four membranes which revealed that hydrophilicity was the highest for QPEEK-1.0 and lowest for the commercial membrane (AMI-7001). Because high antiadhesion means less microorganism buildup on the membranes, it is beneficial for MFC performance. MFC performance incorporated with QPEEK, QPEEK-0.5, QPEEK-1.0, and AMI-7001 membranes were tested in single-chambered MFCs. 10% v/v of sewage culture was used to inoculate the MFCs and sodium acetate was used as microbial oxidation meal source. Power density of the modified membranes showed significantly higher power density curves compared to the AMI-7001 membrane proving that the increase of hydrophilicity led to enhanced performance of MFCs with slower buildup of microorganisms on the surface. In summary, PDA modification of membranes led to improved antibiofouling properties ultimately improving MFC performance.

O_3/O_2 mixture was continuously bubbled through a polyvinylidene fluoride (PVDF)/NMP mixture at room temperature for ozone pretreatment[31]. After degassing the treated PVDF with nitrogen, nitrogen-bubbled SSS/DMSO and benzoyl peroxide (BPO) is reacted together resulting in a PVDF-g-PSSS copolymer. The copolymer was cast as a liquid film on a glass plate at a thickness of around 100 μm. Finally, the membranes were protonated to H^+ form with 1 M HCl solution. Water uptake was analyzed by comparing the soaked membranes with dry membranes at room temperature. Proton conductivity was measured using the AC impedance technique and the results is as following. Compared to pristine PVDF membranes, additional peaks corresponding to C-C aromatic rings and SO_3^- groups were seen for PVDF-g-PSSA membranes. The water uptake increased as SSS monomer concentration increased due to the increase of sulfonate groups. Proton conductivity showed the same trend of increasing as SSS component increased. The highest proton conductivity was seen for 1 : 5 mass ratio of PVDF/SSS at 0.046 S/cm. MFC incorporating the synthesized composite membranes were

observed and analyzed. Compared to the other research articles, MFC with PVDF-g-PSSA membranes performed less effectively than Nafion-117 membrane incorporated MFCs. The PVDF-g-PSSA membrane power density was 106.7 mW/m^2 while Nafion-117 was 132.0 mW/m^2. The same trend applied to internal resistance. Although performance was inferior to Nafion-117, the data still showed significant possibility to be used in MFCs and lower production cost and easier production process also makes this composite membrane an adequate candidate to be used in MFCs.

Solutions of oxy-polybenzimidazole (OPBI) and sulfonated oxy-polybenzimidazole (S-OPBI) were used to form membranes on petri dishes through evaporation using a vacuum oven[32]. S-OPBI goes through an extra step of protonation using sulfuric acid followed by evaporation once again. Proton conductivity was measured using AC impedance spectroscopy and the result proved that S-OPBI membrane (0.0783) had a proton conductivity slightly higher than Nafion-117 (0.0765) while OPBI was less conductive than Nafion-117. Water uptake was higher for both OPBI and S-OPBI at around 27% while Nafion-117 was 12.5%. Because water uptake is a crucial property for proton conductivity, this result proves that the synthesized S-OPBI membrane was a possible alternate to Nafion-116 produced at a significantly lower cost. The performance of MFCs using OPBI and S-OPBI as proton exchange membranes (PEM) was tested and observed for approximately 14 hours after initial operation. Power density of S-OPBI membrane was the highest followed by Nafion-117 and OPBI membrane proving that sulfonation helped the efficiency of PEM to increase drastically. Over time, the voltage of the S-OPBI membrane dropped the least of the three samples. The overall data showed that sulfonation plays a key role in enhancing the membrane potential and is a suitable replacement of the commercial Nafion-117 membrane. Further research and analysis of sulfonated-OPBI as an alternative to Nafion-117 will further prove its potential.

A proton conducting composite membrane made of polyvinyl chloride (PVC) and inorganic hydrophilic zeolite 4A is synthesized and tested for incorporation in microbial fuel cells[33]. Different amounts of zeolite-4A (5, 10, 15, and 20 wt%) are mixed with NMP and stirred until a homogeneous mixture is obtained. PVC was added to the different mixtures and stirred for another 6~8 hours. The prepared solutions are cast on petri dish and evaporated until fully dry. The samples are named Z1, Z2, Z3, Z4 according to the amounts of zeolite incorporated (5, 10, 15, 20 wt% respectively). SEM images of the samples indicate that there is an increase of crystal-like structures as the zeolite content increased. Membranes showed a suitable surface until 15 wt% but 20 wt% zeolite content started to show agglomeration. Proton conductivity of the samples were measured and Z3 membrane had the highest at 0.13 S/cm while Nafion-117 was significantly lower at 0.067 S/cm. The same trend appeared for water uptake and tensile strength further proving the potential of 4A zeolite composite membrane as an alternative of Nafion-117.

Performance of MFC incorporated with the synthesized composite membrane (Z3) was tested using bacterial cultures obtained from kitchen wastewater and buttermilk which is sufficient in generating electrons for MFC operation. The Z3 membrane was the most efficient with maximum power density at around 250 mW/m^2 while Nafion-117 was significantly lower at 125 mW/m^2. The COD reduction rate was also the highest for Z3 membranes further proving its potential as Nafion-117 replacement. The performance was observed for around 18 days and the performance of the Z3 membrane incorporated MFC was the most improved superior to Nafion-117. Overall, Z3 membrane proved to be a better alternative cost and performance wise.

Polystyrene ethylene butylene polystyrene (SEBS) is mixed with required amounts of chloroform, tributyl phosphate (TBP), and CSA in a nitrogen atmosphere until a uniformly mixed solution is obtained[34]. The obtained solution is cast on glass plates and evaporated until a dry sulfonated polymer is obtained. The composite membranes are synthesized by adding varying

amounts of sulfonated SiO_2 to the SSEBS/THF solution. The mixtures are cast on glass plates and evaporated. All membranes are pretreated (boiled) in DI water. Compared to non-sulfonated membranes, sulfonated products showed additional peaks corresponding to Si-O-SO_3H bonds proving that sulfonation occurred. SEM images of the composite membranes showed that they were uniformly dispersed in the polymer matrix. Sulfonation further distributed the component membranes evenly proving that sulfonation is a procedure that enhances composite membrane morphology. Of the six samples synthesized, SSEBS-S-SiO_2 7.5% membrane showed the highest water uptake and ion exchange capacity at around 210% and 3.015 meq/g respectively. As S-SiO_2 component increased, the proton conductivity increased but it decreased from 7.5% component. MFC performance incorporating the synthesized membranes were observed for about 3 weeks. Of the synthesized samples, SSEBS-S-SiO_2 exhibited the highest performance data of proton conductivity at 3.21×10^{-2} S/cm and IEC of 3.01 meq/g which are both significantly higher than the Nafion-117 membrane. The sulfonated membranes reduced the internal resistance which means a faster reaction between the electrode and electrolyte ultimately leading to satisfactory performance. Not only is the performance superior to the Nafion-117 membranes, the cost of production is estimated to be significantly lower which is another merit of membranes incorporated sulfonated inorganic components to nanocomposite membranes.

3. Conclusions

Developing an alternative to Nafion-117 PEM to enhance the performance of microbial fuel cells have become an important crucial field of research and it is still a relatively new topic compared to other renewable energy sources. Although many new procedures and upgraded materials have been introduced throughout this paper, none of them have been actually approved for commercial use meaning that much more research needs to be done to lessen the risk and cost while increasing the performance of MFCs. This review paper aimed to introduce the different research that has been going on around the world to synthesize more effective PEMs while highlighting the fact that there is still a large gap to cover to synthesize an ideally performing PEM. Several different approaches were introduced throughout the paper and PEMs that incorporated sulfonated functional groups such as SPEEK, QPEEK, GO-SPEEK, and SSEBS show higher proton conductivity levels than Nafion-117. Not only was the proton conductivity levels higher, but also the overall performance of MFCs incorporated with those PEMS were relatively consistent and better performing over the time it was tested. PEMs which incorporated nanomaterial proved to perform well, but the toxic nature of the material hinders it from commercial use unless researchers find a more effective way to control the toxicity. All the membranes introduced had a more evenly dispersed surface morphology than Nafion-117 which means that it is beneficial regarding biofouling and can be used for a longer time than Nafion-117.

Further research should be conducted on improving the sulfonated and other functionalized material surfaces because it seems to result in the most satisfactory performance results. Materials such as carbon nanotubes, ozone-induced grafts, and graphene oxide nanomaterials used to fabricate PEMs are also promising routes to take since the application of these materials improves the performance of MFCs overall significantly. With further research, an optimum replacement of Nafion-117 might be synthesized with lower cost, better performance, and improved properties.

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