Effect of Organic and Non Organic Acids on the Blend PES/PS/PVDF Polymer Membranes Efficiency for Microbial Fuel Cell

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Abstract

In this work proton exchange membranes were prepared by a modified microwave casting solution technique, using the polymers blend (polyethersulfone (PES), polystyrene (PS), polyvinylidenefluride (PVDF)). Modified casting method was used to overcome the poor compatibility between hydrophilic, (PES, PS) and hydrophobic PVDF, by cooling the substrate during the film casting process to (4.5-5.5°C). Membranes were chemically modified by three reaction types to study the differences between their effects on the required properties for microbial fuel cell application. These methods use blend organic sulfonic acid precasting process and sulfonation by sulfuric acid post-casting process (APS), blending organic sulfonic acid precasting process (AS) and sulfonation by sulfuric acid post-casting process (AP). The presence of organic sulfonic acid and the sulfonation were confirmed via FTIR spectra for the membranes. The membranes were characterized by proton conductivity, ion exchange capacity (IEC), [-SO$_3$H] value, and water uptake. MFC is characterized by electrochemical polarization tests and power densities obtained from it were used to evaluate the efficiency of the membrane in the cell.

Keyword: Proton exchange membrane; sulfonation; microbial fuel cell.

تأثير الحوامض العضوية واللاعضوية على كفاءة اغشية المزيج البوليمري (PES, PS, PVDF) لخلايا الوقود الميكروبية

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الخلاصة

في هذا العمل ,تم تحضير اغشية التبادل البروتوني باستخدام المايكرويف لمزيج البوليمرات (بولي ايثرسلفون PES, بولي ستيرين PS ,بولي فينيليدين فلورايد PVDF) كطريقة معدلة لتقنية صب المحلول المعروفة.وللتغلب على ضعف التوافق بين البوليمرات المحبة للماء (PES, PS) والبوليمر الكاره للماء , PVDFتم استخدام طريقة صب معدلة بتبريد قاعدة الصب الزجاجية خلال عملية صب المحلول الى − 4.5) (5.5°C. تم تعديل الاغشية كيميائيا" بواسطة ثلاثة طرق من تفاعلات السلفنة لدراسة اختلاف تأثيراتها على خصائص متطلبات التطبيق في خلايا الوقود الميكروبية. هذه الطرق هي السلفنة قبل وبعد عملية الصب (APS) والسلفنة قبل عملية الصب (AS) والسلفنة بعد عملية الصب (AP). تم تأكيد نجاح عملية السلفنة

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بالطرق الثلاث المستخدمة من خلال نتائج فحوصات FTIR. تم توصيف اغشية المزيج البوليمري بواسطة
التوصيل البروتوني ,قدرة التبادل البروتوني (IEC) ,قيم [SO3H–] ,امتصاص الماء.استخدام اختبار
الاستقطاب الكهروكيميائي وكثافة الطاقة لتقييم كفاءة الاغشية المحضرة في خلية الوقود الميكروبية.

1. Introduction

The quest for sustainable and effective fuel technology has been sparked by a rise in the scarcity of fossil fuels and environmental pollution associated with current fossil fuel processing technologies. Fuel cells seem to be a promising technology to solve the above problems and meet the existing requirements for the production of renewable fuel [1]. In the natural environment, alternative energy sources, commonly referred to as renewable, are available in nearly infinite amounts or regenerated by natural processes at a faster rate than they are consumed [2]. The interest in safer, more environmentally sustainable, and more efficient energy sources contributes to the increased interest in fuel cells, because and heat [3]. Fuel cells are electrochemical devices that directly transform intrinsic chemical energy into electrical energy. In 1839, William Grove first showed the fuel cell [4].

A microbial fuel cell (MFC) is a biological reactor that through synergistic responses of microorganisms proselytes concoction energy present in natural or inorganic compound substrates to electrical energy [5]. The growth and metabolic activities of microorganisms (such as exoelectrogenic bacteria) are used in microbial fuel cells (MFC) to directly transform chemical energy from organic waste into electricity [6]. The MFCs usually contain an anode and cathode compartments separated by a proton exchange membrane (PEM). Protons and electrons are generated by organic compound oxidation (via electrochemically active bacteria (EAB) catabolism in the anode compartment. Protons are transferred through the PEM to the cathode compartment, while the electrons pass through to the external circuit. . Subsequent H_2O formation at the cathode occurs through the reduction of oxygen with the transferred protons and electrons [7]. Three types of PEMs (Nafion112, SPEEK, and Nafion 117) used in MFC have been studied by Mostafa Ghasemi et al. [8]., and the amount of bioenergy generated with wastewater feed-in 5000m/l of chemical oxygen demand (COD) has been recorded. It was found that among the other MFCs, the MFC operating with Nafion 117 as a separator produced the highest power. For high-temperature proton exchange membrane (HT-PEM) applications, Liu et al.[9] reported a series of composite cross-linked membranes based on fluorine-containing polybenzimidazole (6FPBI) and across-linkable polymeric ionic liquid (cPIL) have been prepared. In particular, the obtained composite cross-linked membranes displayed an excellent ability for phosphoric acid doping and proton conductivity. Gaurav et al. [10] studied low-cost PEMs with higher conductivity which was performed using relatively low-priced polyvinylchloride content with varying amounts of silica (SiO_2), citric acid, and phosphotungstic acid (PWA) by the solution casting process. Different membrane properties, such as surface morphologies, ability for water absorption, ion exchange capacity (IEC), tensile strength, leaching test, and potential application in MFCs, were investigated. Bakonyi et al. [11] reviewed the background and recent advances in ionic liquid-containing separators, particularly supported ionic liquid membranes (SILMs) for MFC application were studied.

The MFC performance depends on its ohmic resistance. There are three sources of ohmic voltage loss: (i) resistance of the electrolyte against ion migration, (ii) resistance to electron transport through the cell components (electrodes and electrical connections), and (iii) contact resistances. The migration of ions inside the membrane plays a major role in the resistance of internal cells. Several techniques were used by online fuel cell testing methods to analyze the membrane resistance.

The current interrupt method time-domain DC technique, developed 50years ago, is used for proton exchange membrane fuel cells, to quickly interrupt the fuel cell current and calculate

the terminal voltage quickly before and during the interruption [12]. This would need high precision devices to monitor the interrupting effect on the cell voltage since this effect concludes the ohmic, activation resistance, and double-layer capacitance. A recently developed method to measure membrane resistance ex-situ is using a four-probe conductive cell. In this work, a method similar, with minor adaptation, to that performed by the Florida solar energy center [13] and a method recently reported by Ziv and Dekel [14] were used.

The present work aims to study the effects of three sulfonation conditions: sulfonation done pre-and post-casting process (APS), sulfonation done precasting (AS) and sulfonation done postcasting (AP), on the characterization of the polymer blend membranes by including structural changes, ionic conductivity, IEC, and water uptake. Whereas, the effect of sulfonation condition on MFC efficiency was studied via electrochemical polarization and power density curves.

2. Experimental Procedure
2.1. Materials and Method
Materials used for the synthesis of the (PES-PS-PVDF) blend proton exchange membranes are as specified: polyethersulfone (PES) was purchased from Xiamen keyuan plastic company; polystyrene (PS) foam beads were purchased from Hangzhou Fuyang Wealth Imp&ExpCo., Ltd, China; Polyvinylidene fluoride (PVDF) from Allplastics Engineering Pty Ltd; organic sulfonic acid was supplied by the General Company for Vegetable Oils Baghdad (Iraq); sulfuric acid $H_2SO_4$was purchased from CDH -Central Drug House (P) Ltd., New Delhi(India), N, N-Dimethylformamide (DMF) was purchased from Sinopharm Chemical reagent co., Ltd; Sodium hydroxide pellets NaOH were purchased from Romil LTD the source convent drive water beatch Cambridge GB-CB25 9QT, United Kingdom; and Sodium chloride which was purchased from ALPHA CHEMIKA, India.

2.2. Membranes preparation
(PES, PS, and PVDF) polymers were dried in a microwave oven for (20 min) before dissolving them in DMF [15].

2.2.1. Blend solution and membranes preparation
(PES-PS-PVDF) solutions were prepared by heating with stirring. These were prepared according to the volumes shown in Table1. The blend solution was prepared by adding (2 ml) of PS solution drop by drop into (8 ml) of PES with heating and stirring 500 this was associated with a color change from light yellow to foggy white. The blend was left under heating and stirring to obtain a homogeneous solution. Then (2ml) of the PVDF solution was added to the previous blend solution with stirring and heating until a homogeneous solution was obtained. All membranes were prepared by casting on a cool glass plate (at 4.5 -5.5^{o}C) using a casting knife, the membranes were left for (15 min) under cool conditions then at room temperature before being dried at (45°C) for 4 hours. The obtained films were soaked in deionized water for 24h in order to extract the solvents by water. The obtained membrane was of (0.05mm) thickness, as shown in Figure 1.

Figure 1-Shape of the prepared blend membrane

2.2.2. Blending with organic sulfonic acid and sulfonation processes
The sulfonation post-casting process was used to sulfonate the membrane which is listed in Table 1.

The prepared membranes were sulfonated after casting by immersing them in 60% dilute sulfuric acid with heating for 3 hours and then washed several times using deionized water. These samples were labeled as (AP).

(AS) labeled samples were prepared by adding (0.5ml) of organic sulfonic acid to the homogenous blend polymers drop by drop with increasing the temperature under continuous stirring. A microwave oven with a low pulse was used to complete the process.

The (ASP) labeled samples were prepared by the same preparation method of the AS samples and were post sulfonated after the casting process by immersing it in 60% sulfuric acid with heating for 3 hours The membranes were washed several times using deionized water

Table 1-Membranes composition and sulfonation acid

Samples	PES solution composition	PS solution composition	PVDF solution composition	organic sulfonic acid, (ml)	Sulfonation Postcasting process by solution 60%H_2SO_4, (ml)
AS	(2g) of PES in(8ml)PES solution	(0.8g) of PS in (2ml) PS solution	(0.3g)of PVDF in (2ml) PVDF solution	0.5	___
AP	(2g) of PES in(8ml) PES solution	(0.8g)of PS in (2ml) PS solution	(0.3g) of PVDF in (2ml)PVDF solution	___	50
APS	(2g) of PES in(8ml) PES solution	(0.8g) of PS in (2ml) PS solution	(0.3g) of PVDF in (2ml) PVDF solution	0.5	50

2.3. Application in MFC
MFC Construction
The laboratory microbial fuel cell was manufactured from two airtight perspex as anode and cathode compartments with holes of (3cm) diameter in the center of their interface. Synthesized membranes were inserted in between the anode and cathode compartments using a rubber gasket tightened by bolts. The anode (graphite sheet) and the cathode (Aluminum sheet) electrodes were positioned into the chamber through the cover of the airtight containers as shown in Figure 2. Before conducting tests, the cathode chamber must be well aerated. Therefore, an air pump was used to add oxygen to it. This would increase the efficiency of the fuel cell. The electrodes were connected to a data logger (USB Data Logger, Hantek365A), and a multimeter (Digital Multimeter, DDM230B, ORWSON) to record data into the principal component analysis (pc). The anode chamber was completely anaerobic.
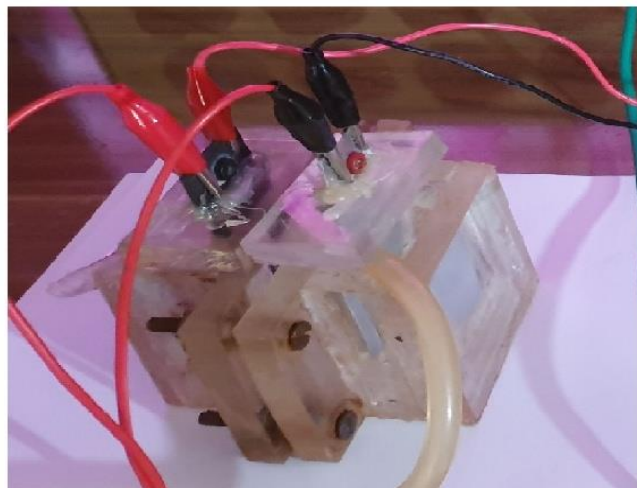
Figure 2-Laboratory Microbial fuel cell

Anolyte was wastewater of PH (3-5.5), Chemical Oxygen Demand (COD) 700-2500 ppm, Biochemical Oxygen Demand (BOD) 400-1200 ppm, glucose (5 g\l) which was obtained from the wastewater treatment lab, ministry of science and technology. Catholyte was one liter of distilled water containing (35 g) of solid NaCl. MFC usually operates at (37oC). The electrochemical polarization curve was obtained from using different loads (10-40000 Ω). There should be a 2minutes lapse after applying each load. The electrochemical polarization measurements were held after 24 hours. The power density was determined by the following equation:

$$P = \frac{(V.I)}{A} \tag{1}$$

Where V and *I* are the recorded voltage and current, respectively, A = the area of the electrodes [10]**.**

2.4. Membrane characterization
2.4.1. Proton Conductivity
The membranes were soaked in deionized water for 24 hours in order to let it fully hydrated before mounting it directly in the conductive test cell. Figure 3 illustrates schematically the membrane electrical contacts of the cell. The outer contacts were for DC current application while the inner ones were for connecting the membrane to the digital oscilloscope to monitor the voltage drop A constant DC current was used whose value was obtained from the MFC I-V characterization curve. The test was done under an inert atmosphere. After the voltage becomes stable, on the digital oscilloscope, the current was interrupted quickly. The in-plane ion conductivity was calculated using the following equation:

$$\sigma = \frac{L}{R.W.T} \tag{2}$$

Where L= the length between the inner connected wires, W = the membrane width, and T = the membrane thickness, R= the membrane resistance calculated by the ratio of the voltage difference (V1 during current applied and V2 after interrupted, to the current applied at the moment of interruption.) [13.[
Figure 3. illustrates schematically the membrane electrical contacts in the cell.
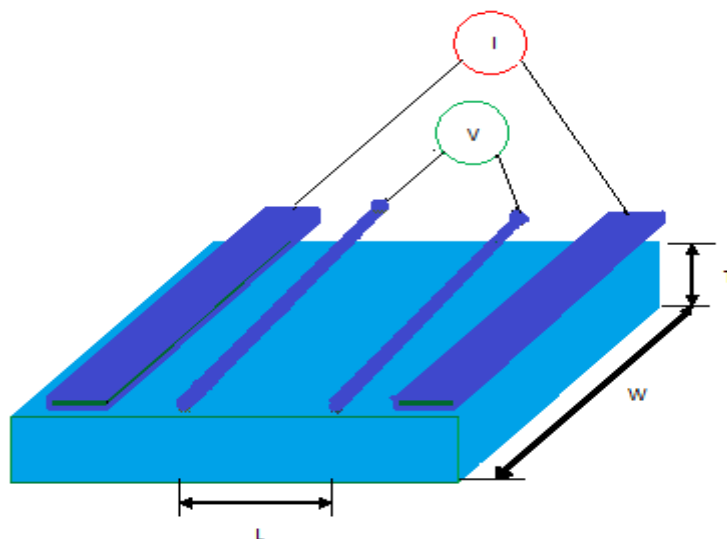
Figure 3- Schematic diagram of the membrane electrical contacts of the cell [13]

2.4.2. Ion Exchange Capacity (IEC)
Ion exchange capacity (IEC) [meq.g^{-1}] is a measure of the ionic content in a dry membrane. The theoretical IEC value can be determined through ^{1}H-NMR or be calculated experimentally[16]. To exchange all protons with ions of sodium, in the sample, the dried samples were weighed and immersed in (1 M) NaCl solution for 24 h. The HCl content was measured by back titration with (0.01N) sodium hydroxide. Phenonephthalene solution (0.1%) in ethanol/water was used to determine the neutralized point[17,18]. IEC was calculated using the given equation:

$$IEC = \frac{(consumed\ of\ NaOH)(Molarity\ of\ NaOH)}{Dried\ membrane\ weight} \qquad (3)$$

2.4.3. The analytical acid concentration [-SO₃H] (M)
[-SO$_3$H] concentration has a significant effect on proton conductivity and depends on the content of acid and water. In the wet membrane, it can be determined by:

$$[-SO_3H] = \frac{M_{dry} \times IEC}{V_{wet}} \times 100 \qquad (4)$$

Where M$_{dry}$= the weight of the dried membrane, V$_{wet}$= the volume of the membrane[19].

2.4.4. Water uptake
Sulfonated dry membranes were weighted and submerged for a day in deionized water. The surface area of completely hydrated samples, dried with filter paper and weighed water absorption was measured by the following equation:

$$W_u(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (5)$$

Where W$_{wet}$ and W$_{dry}$= the weight of fully hydrated and dried samples, respectively[1, 10]

3. Results and discussion
The backbone of the synthesized membranes, polyethersulfone polymer (PES), was chosen as the principal chain due to its high adaptive flexibility to the PEM application [20]. As well as its good chemical resistance, it has excellent thermal and dimensional stability [21]. It has been widely modified and used in membrane separation applications in fuel cells because of its low cost compared to the costly fluorinated polymers [22]. It is a partly crystalline polymer which is known for its exceptional solvent resistance, thermo-oxidative degradation, and hydrolytic stability, has high chemical resistance for many acids and alkalis [23, 1]. All these features make PVDF an attractive membrane material; its crystalline phase provides thermal

stability, while its amorphous phase provides the flexibility of the desired membrane [21]. High contrast in polarity between hydrophilic and hydrophobic helps the creation of efficient proton tracks. Even in a random copolymer, and an amphiphilic block copolymer system[20].

3.1.FTIR spectroscopy

Direct sulfonation is an electrophilic reaction. The sulfonation occurs at electron-rich sites of the polymer backbone [24]. The FTIR spectra were used to confirm the presence of (-SO$_3$H) group on the polymer chains. Figure 4. shows the spectra of the pure polymer blend membrane and the three polymer blend membranes (APS, AP, AS). The peaks at 1585 cm^{-1} and 1489 cm^{-1} are attributed to the vibration of the aromatic ring skeleton [25, 19, 26]. The small peak at ~3059cm^{-1}is attributed to the C-H stretching peak of the benzene ring[26].Stretching band, at 2848 cm^{-1}, represents CH$_2$groups[27]. At 1149cm^{-1} the distinctive absorption band for the aromatic sulfone group emerges, and the peak for aryl oxide appears at 1240 cm^{-1}[25, 26]. It is possible, in fact, to identify signals at 1323 and 1149 cm^{-1} due to S=O stretching (asymmetric and symmetric, respectively) together with a band at 1103 and 1074cm^{-1} (C–S) [27,28]. The adsorption peak at ~1029 cm^{-1} is characteristic of the aromatic (SO$_3$H) symmetric stretching vibration[25,19,29,27], and the peak at ~1170 cm^{-1} is due to two contributions of -SO$_3$ groups and ring modes of 1:2-substituted benzene[27, 25]. The broad band at 3437 cm^{-1} indicates the stretching vibrations of -OH groups [27, 8]. Transformed infrared spectra indicated an increase in the peak located in the OH stretching region, which is associated with acid formation [30]. The FTIR spectra revealed the successful sulfonation of the (APS, AP) samples, and presents an organic sulfonic acid for (APS, AS) samples.
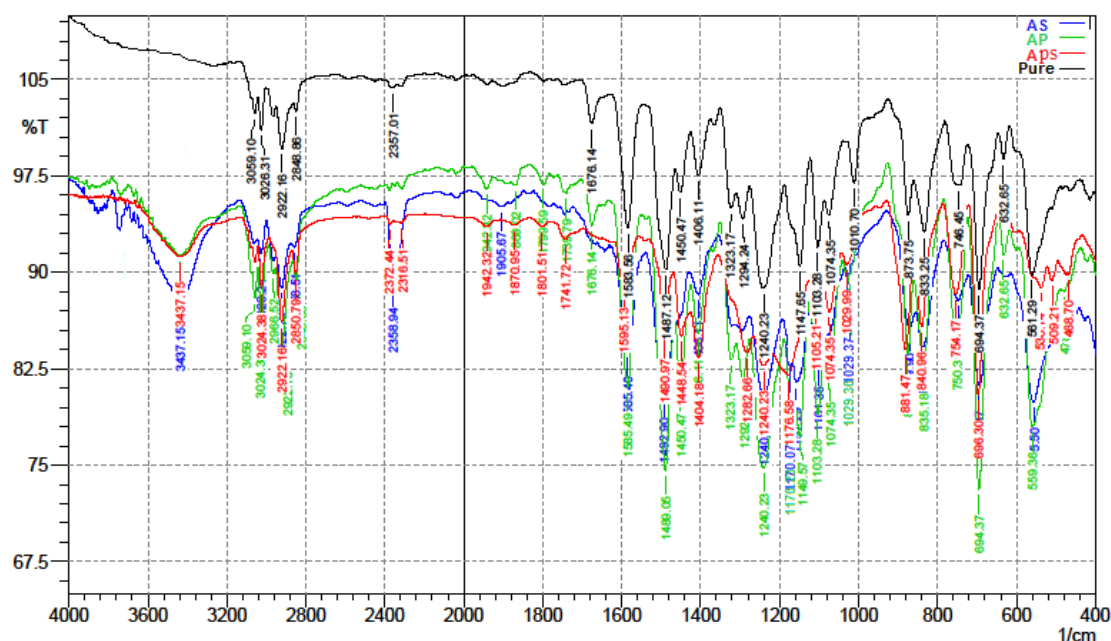

Figure 4-FTIR spectra of the prepared blend membranes

3.2. Membrane characterizations

Table 2 shows the measurement values of IEC and active ionic group content [-SO$_3$H], for the synthesized membranes. It is clear that the AS membrane has higher values of active ionic group content and IEC than the AP membrane. . While the APS membrane revealed the highest content of the active ionic group and IEC. For the AP sulfonated membrane using the process of dipping the membrane with dilute acid 60% H$_2$SO$_4$ led to the reduction of sulfonation on the surface of the membrane, which led to the possibility of cross-linking side effect [31]. Also, the presence of a hydrophobic polymer PVDF in the structure of the membrane played an important role in decreasing the hydrogen bond on the surface of the

membrane [32]. Thus reducing the acid performance in the sulfonation process can decrease the content of the active ionic group, as well as, reducing the efficiency of the membrane.

For the AS membrane, the use of organic sulfonic acid during the reaction with the use of microwave helped in the successful introduction of (R-SO$_3$H) to blend it directly into the internal structure of the membrane as proved by the FTIR results. Thus, better content of the active ionic group was obtained from the AP membrane.

For the APS sulfonated membrane, using blending organic sulfonic acid inside the membrane and dilute H$_2$SO$_4$on the surface, the sulfonyl group concentration for the membrane was increased. It showed increase content of the active ionic group, IEC, proton conductivity, and water uptake.

Water uptake values for the three membranes (see Table2.) changed directly with changing IEC values. The APS sulfonated membrane showed the highest water uptake values 160.41%, as shown in Figure 5. This was explained by Linet al. [29], who found that the positive end of the dipole water molecule is drawn by the sulfonate group's negative charge (SO$_3^-$). Therefore, increasing the membrane negative surface charge density can improve its hydrophilicity. The negative surface charge density could be achieved by increasing the content of the negative charged sulfonated group, (-SO$_3^-$) as part of the moiety of the polymer. IEC measurement of APS membrane can be considered as a qualitative measure for the water uptake of the membrane [1]

The APS sulfonated membrane was shown to have the highest proton conductivity (3.77) S/cm compared with the AS and AP membranes (0.032, 0.01218) S/cm, respectively. These results are compatible with the IEC and the active ionic group, (-SO$_3$H) content in the sulfonated membrane listed in Table 2.

According to (the Grotthus mechanism) which claimed that the proton exchange membrane conductivity depends on the active ionic group content in the backbone of the polymer such as *(SO$_3^-$, COO$^-$, PO$_3^{-2}$, PO$_3$H$^-$, C$_6$H$_4$O$^-$)* and the role presence of water to transport proton (H) between that active ionic groups. From our results, it is clear that increasing the active ionic group (-SO$_3$H)content in the membrane structure strongly provides an active site for the protons to jump easily from one active ion to another with the aid of water molecules between them, forming hydronium ions and increasing the membrane proton conductive ability.

Jalal et al. [18] confirmed that water sorption can be considered as a key parameter in PEM measurement since it is related to both proton conductivity and mechanical stability. So if the membrane cannot take up enough water, there will be a leakage in the interconnecting channels between ionic groups for the protons to use in crossing the membrane.

Proton conductivity improvements depend upon the fraction of water uptake and the active ionic group concentrations [33]. Tsang et al. ascribed the higher water uptake and conductivities of the proton exchange membrane and the increased flexibility of the gap between groups of sulfonic acid in connection to the increased local concentration of [-SO$_3$H] [34, 35].

Our results confirmed that the sulfonation process for the PES/PS/PVDF blend membrane improved its properties.
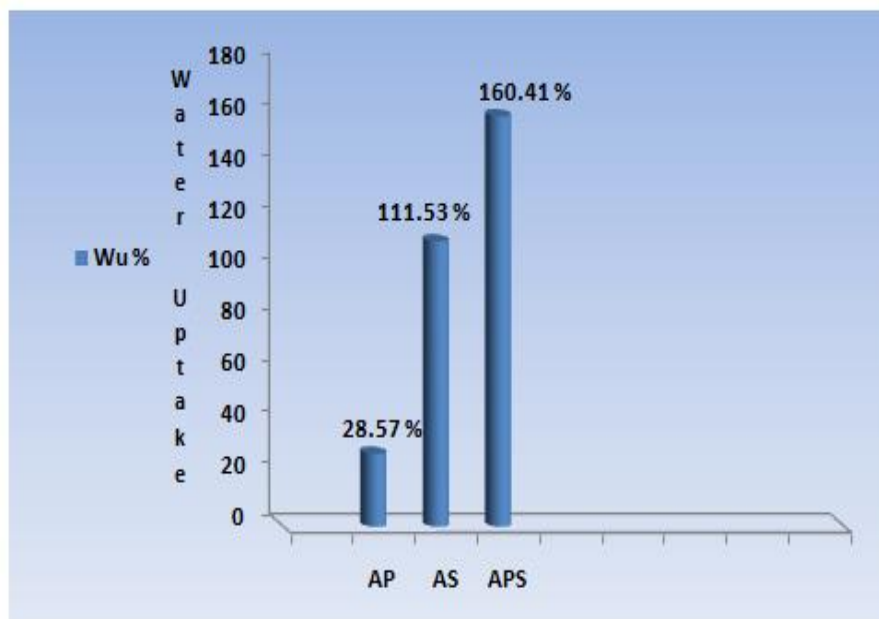
Figure 5-Water uptake of selected membranes

3.3. Fuel cell characterization

After MFC construction by inserting the sulfonated blended member in the cell, the cell was left for 24 hours to become stable and let the membranes fully hydrated. From open circuit voltage curves, the APS membrane showed the highest value compared with the other membranes. The electrochemical polarization curves of the MFC with the prepared membranes are shown in Figure 6. The activation polarization regions show the same behavior since the reaction parameters for the tested cell is constant. The slope of the polarization curve in the ohmic losses region indicates the cell ohmic resistance; the difference of slope in this region could be related to the membrane conductivity since all the other cell components were kept constant. The curve of the cell with the APS sulfonated blend membrane showed the lowest slope. These results are in good compatibility with the proton conductivity measurement results. The APS membrane, as it was mentioned before, has the highest proton conductivity SO_3H) content, IEC, and water uptake. The AP membrane suffered from a cross-linking effect in addition to the sulfonation reaction, which decreased the active ions in the polymer chain and reduced its conductivity hence the reduction of the cell output. From this work, the cell power density figures out the efficiency of the used membrane. The power densities for the APS, AS, and AP membranes were (4.5826, 2.0155, and 1.42234 mW/cm^2), respectively.

Table 2-Data measurements for prepared membranes

Samples	IEC (meq./g)	[SO$_3$H] (M)	Water uptake, (%)	Proton conductivity (S/cm)	Power density (mW/cm^2)	Current density (mA/cm^2)
AP	0.0341	0.124	28.57	0.0128	1.42234	0.013
AS	0.0496	0.202	111.53	0.032	2.0155	0.027
APS	0.229	0.7366	160.41	3.77	4.5826	0.0388
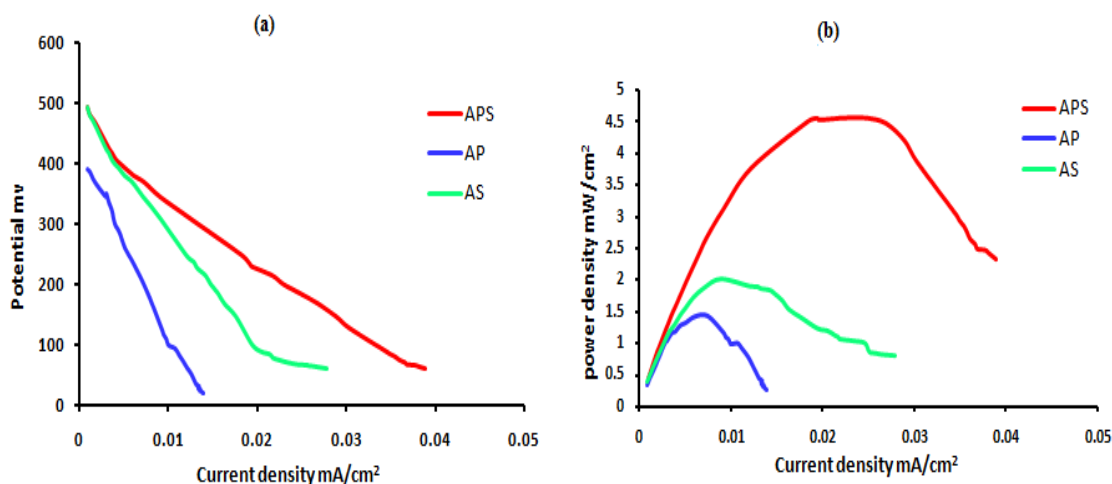
Figure 6-Curves of potential (a)and power density (b) of the prepared membrane used in MFC

4. Conclusions

Blend polymers of (PES, PS, PVDF) were prepared as proton exchange membranes modified with the sulfonic group using three methods. blending organic sulfonic acid precasting and sulfonation post-casting (APS), blending organic sulfonic acid precasting process (AS), and sulfonation post-casting process (AP). FTIR spectra confirmed the success of the (APS) membrane. This membrane showed the highest proton conductivity, (-SO$_3$H) content, water uptake, and power density. These membranes were used in the two-chamber microbial fuel cell. All the membranes had stable open circuit potential, workability, durability, good proton conductivity, and successful operation in the same MFC fuel cell under constant conditions.

5. References

[1] V. Sagadevan and K. Rambabu, "Development and characterization of polyvinylidene fluoride–Imidazolium functionalized polysulfone blend anion exchange membrane, " *J. Eng. Sci. Tech*, Vol.10, No.9, pp. 1162 – 1179, 2015.

[2] R. A. Felseghi, E. Carcadea, M. S. Raboaca,C. N. Trufin, C. Filote "Hydrogen Fuel Cell Technology for the Sustainable Future of Stationary Applications," *Ener.*, Vol. 12, No. 23, p. 4593, 2019.

[3] R.S.L. Yee, K.Zhang, B.P. Ladewig, "The Effects of Sulfonated Poly(ether ether ketone) Ion Exchange Preparation Conditions on Membrane Properties," *Mem*b., Vol. 3, No.3, pp. 182-195, 2013.

[4] K. Scott, E. H. Yu, M. M. Ghangrekar, B. Erable and N. M. Duţeanu, "United States Biological and microbial fuel cells," *C. R.. En.*, Vol. 4, pp. 277-300, 2012.

[5] S.Shaikh, and N. P. Patil "Microbial Fuel Cell: Design and Operation," J. Mic. Bioe, ISSN: 2320-3528, pp. 1-8, 2016.

[6] Siddharth Gadkari Jean-Marie Fontmorin EileenYuJhuma Sadhukhan, G. Siddharth, M. F. Jean, Y. Eileen and S. Jhuma, "Influence of temperature and other system parameters on microbial fuel cell performance: Numerical and experimental investigation*," Chem. Eng. J.*, vol 388, pp.1-9, 2020.

[7] Taeyoung Kim, Sukwon Kang, Je Hoon Sung, Youn Koo Kang, Young Hwa Kim, Jae Kyung Jang, K. Taeyoung, K. Sukwon, H. S. Je, K. K. Youn, H. K. Young, and K. J. Jae, "Characterization of Polyester Cloth as an Alternative Separator to Nafion Membrane in Microbial Fuel Cells for Bioelectricity Generation Using Swine Wastewater," J.Mic.Bio., vol. 26, no. 12, pp. 2171–2178, 2016. J Microbiol Biotechnol. 2016 Dec 28; 26(12):2171-2178. doi: 10.4014/jmb.1608.08040. PMID: 27666990.

[8]   Mostafa Ghasemi, Elnaz Halakoo, Mehdi Sedighi, Javed Alamd, MajidSadeqzadehe, G. Mostafa, H. Elnaz, S. Mehdi, A. Javed and S. Majid, "Performance comparison of three common proton exchange membranes for sustainable bioenergy production in microbial fuel cell," *Proc. CIRP*, vol. 26, pp.162 – 166, 2015.

[9]   F. Liu, S. Wang, H. Chen, J. Li, X. Tian, X. Wang,T. Mao, J. Xu, and Z. Wang, "Cross-Linkable Polymeric Ionic Liquid Improve Phosphoric Acid Retention and Long-Term Conductivity Stability in Polybenzimidazole Based PEMs," *ACS. Sustainable Chem., Eng.,* Vol. 6, No.12, pp.16352–16362, 2018.

[10] *K. Gaurav, R. Singh, B. K. Tiwari and R. Srivastava*, "Novel proton exchange membranes based on PVC for microbial fuel cells (MFCs)," *J. P. Eng.*, Vol. 39, No.4, pp.360–367, 2019.

[11] P. Bakonyi, L. Koók, T. Rózsenberszki, G. Tóth, K. Bélafi-Bakó and N. Nemestóthy,, "Development and Application of Supported Ionic Liquid Membranes in   Microbial Fuel Cell Technology: A Concise Overview," *Memb., V*ol. 10, *N*o. 16, pp. 1-13, 2020.

[12] K. R. Cooper and M. Smith, "Electrical test methods for on-line fuel cell ohmic resistance measurement," *J. Pow. Sou,* Vol. 160, No.2, pp. 1088-1095, 2006.

[13] Work performed by the Florida solar energy center, " Procedures   For Performing In-Plane Membrane Conductivity Testing ”*Work Performed Under DOE Contract*, DE-FC36-06GO16028, pp. 1-19, 2008.

[14] N . Ziv, D.R.Dekel, "A practical method for measuring the true hydroxide conductivity of anion exchange membranes*," Electrochemistry Communication ,* Vol. 88, pp.109–113, 2018.

[15] I. Ahmed, K. Faridah, A. Idris, R.M. YunusZ.Hassan, R. Prasad" Preparation of PES ultrafiltration Membrane using Novel Modified Microwave Casting Solution Technique," *J. A. Sci*, Vol. 10, No. 21, pp. 2733-2736, 2010.

[16] T. J. Peckham, J. Schmeisser, M. Rodgers, and S. Holdcroft, "Main-Chain, Statistically Sulfonated Proton Exchange Membranes: The Relationships of Acid Concentration and Proton Mobility to Water Content and Their Effect Upon Proton Conductivity," *J. M. Chem.,* Vol. 17, No. 30, pp. 3255–3268, 2007.

[17] K. K. Hyung, H. K. Dong, Ch. Jisu, and Ch. K. Sung, "Compositional Effect on the Properties of Sulfonated and Nonsulfonated Polymer Blend Membranes for Direct Methanol Fuel Cell," *Macro. Res*., vol. 1, pp. 928-942, 2011.

[18] N. M. Jalal, A. R. Jabur, M. S. Hamza and S. Allami, "Sulfonatedelectrospun polystyrene as cation exchange membranes for fuel cells," *.Ene.Rep*., Vol.6, Supplement.3 11, pp.287-298, 2019.

[19] M. M., Nielsen, *"*Proton-Conducting SulfonatedIonomers by Chemical Modification and Atom Transfer Radical Polymerization," Ph.D. Thesis, TechnicalUniversity of Denmark, 2013.

[20] K. Matsumoto, T.Higashihara, M. Ueda, T." Locally SulfonatedPoly(ether sulfone)s with Highly Sulfonated Units as Proton Exchange Membrane," *J. P. Sci. Part A*, Vol. 47, No.13 pp. 3444–3453, 2009.

[21] L. Wu, J. Sun and Q.Wang, "Poly(vinylidene fluoride)/polyethersulfone blend membranes: Effects of solvent sort polyethersulfone and polyvinylpyrrolidone concentration on their properties and morphology," *J. Mem.Sci*., Vol. 285, No. 1, pp. 290–298, 2006.

[22] C. Klaysom, B. P.Ladewig, G. Q. Max Lu and L. Wang, "Preparation and characterization of sulfonated polyethersulfone for cation-exchange membranes," *J. Mem. Sci*., Vol. 368, No.1-2,pp. 48–53, 2011.

[23] Y.S. Ye, Rick and B.J.Hwang, "Water Soluble Polymers as Proton Exchange Membranes for Fuel Cells," *Poly*., Vol. 4, No.2, pp. 913-963, 2012.

[24] G. Maier,   and J. Meier-Haak, "Sulfonated Aromatic Polymers for Fuel Cell Membranes," *Mem.Adv.Polym.Sci*., Vol.216, No.1 pp. 135, 2008.

[25] C. Klaysom,L. Germain, S. Burr, B. P. ladewig, L.Wang. J. D. da Costa, G. Q. Max Lu, "Preparation of new composite membranes for water desalination using Electrodialysis,"Proc. SPIE 7267, Smart Materials V, 72670C (30 December 2008); https://doi.org/10.1117/12.810443

[26] M. Masheane, A. Verliefde, S. Mhlanga, "PES/Quaternized-PES Blend Anion Exchange Membranes: Investigation of Polymer Compatibility and Properties of the Blend," *J.Mem.Sci.and Res*., Vol. 4, No.2, pp. 93-100, 2018.

[27] M. L. Di Vona, E.Sgreccia, M.Tamilvanan, M.Khadhraoui, C. Chassigneuxand P. Knauth, "High ionic exchange capacity polyphenylsulfone (SPPSU) and polyethersulfone(SPES) cross-linked by annealing treatment: Thermal stability, hydration level and mechanical properties," *J.Mem. Sci*., Vol. 354,No.1-2, pp.134–141, 2010.

[28] B.Smitha, S. Sridhar and A. A. Khan, "Synthesis and characterization of proton conducting polymer membranes for fuel cells,"*J.Mem.Sci.*, Vol. 225, No.1, pp. 63–76, 2003.

[29] W. L.Shui, J. L. G. Fernando, P. S. Sergio andM. F. N. Rosa, "New method of synthesis of sulfonatedpolyethersulfone (SPES) and effect of pH on synthetic gray water filtration performance by negatively charged SPES/PS UF membranes*," D.W.Treat*., Vol.57, No.52, pp.24807-24819, 2016.

[30] M. Kakimoto, S. J. Grunzinger and T. Hayakawa.,"Hyperbranchedpoly (ether sulfone)s: preparation and application to ion-exchange membranes*," Poly.J*., Vol. 42, pp. 697–705, 2010.

[31] Y.Hu, L.Yan, and B.Yue,"Sulfonation Mechanism of Polysulfone in Concentrated Sulfuric Acid for Proton Exchange Membrane Fuel cell Applications*," ACS Omega*, Vol. 5, No. 22, pp. 13219–13223, 2020.

[32] M.Eikerling, A. A.Kornyshevand U.Stimming, "Electrophysical Properties of Polymer Electrolyte Membranes: A Random Network Model*," J. Phys. Chem. B.,* Vol. 101, No.50, pp. 10807-10820, 1997.

[33] S. J.Peighambardoust, S.Rowshanzamirand M.Amjadi, "Review of the proton exchange membranes for fuel cell applications*," I. J. Hy.Eneg*., Vol. 35, No.17, pp. 9349- 9384, 2010.

[34] E. M. W. Tsang, Z. Zhang, Z. Shi, T.Sobolevaand S.Holdcroft, "Considerations of MacromolecularStructure in the Design of Proton Conducting Polymer Membranes: Graft Versus DiblockPolyelectrolytes," *J. Am. Chem. Soc*., Vol. 129, No. 49, pp. 15106–15107, 2007.

[35] E. M. W. Tsang, Z. Zhang, A. C. C. Yang, Z. Shi, T. J.Peckham, R.Narimani, B. J. Friskenand S.Holdcroft, "Nanostructure, Morphology, and Properties of Fluorous Copolymers Bearing Ionic Grafts," *Macro.*, Vol. 42, No. 24, pp. 9467–9480, 2009.