Synthesis and characterisation of PVDF-co-HFP/stTiO2 composites polymer electrolyte membranes

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Abstract
The Polyvinylidene fluoride (PVDF) can be combined with hexafluoroproplene (HFP) as to manifest a co-polymer called PVDF-co-HFP polymer. The PVDF-co-HFP polymer can be used as a proton exchange membrane due to its excellent mechanical strength, chemical resistance and thermal stability. It is, however, necessarily to modify the PVDF-co-HFP polymer, as an alternative to Nafton polymer membrane, by adding sulphonate groups via sulfonation and inorganic oxides such as TiO2 via oxide mixture. The research aimed to make a fuel cell membrane using PVDF-co-HFP polymer and study the effect of sulfonated TiO2 (sTiO2) on the membrane to increase proton conductivity. PVDF-co-HFP membrane was prepared by which adding sTiO2 particles before it was sulfonated using 97% H2SO4. The sulfonation degree value was determined using the titration method while the proton conductivity was determined using the four-line probe. The membranes were characterised using SEM-EDX to see surface morphology and membrane composition, FTIR to confirm the presence of the -SO3H group. The results of SEM show that TiO2 particles are scattered on the surface of the membrane. EDX and FTIR results showed that sulfonation was successful in the presence of S elements by 0.77% and wavelengths 1143.2 and 1208.8 cm\(^{-1}\) by confirming the presence of the S=O group. The PVDF-co-HFP membrane with the addition of 3% sTiO2 particles with a sulphonation time of 6 h at 80 °C gave the best result with a proton conductivity value of 4.3 \(\times\) \(10^{-3}\) S cm\(^{-1}\) and a saturation grade of 19.37%. Thus, the PVDF-co-HFP/sTiO2 membrane can be used as a proton exchange membrane in the fuel cell.

1. Introduction

BP Statistical Review of Energy [1] noted that total world energy consumptions in 2018 had reached 13,864.9 Mtoe at which 2.9% of growth rate increased from its last year. As for 33.63% or 4662.1 Mtoe and 23.87% or 3309.4 from the usage were allocated to oil and natural gases respectively, and only 4.05% or 561.3 Mtoe referred to renewable energy sources. On the other hand, the total world production of oil and natural gases consecutively were 4474.3 and 3325.8 Mtoe at which there was merely a few amount of them that can be preserved. Hence, sustainable-alternative energy source such as fuel cell should be set to balance this disparity in the availability of conventional fuels.

The fuel cell is a electrochemical device that can convert energy stored in gaseous chemicals directly to electricity with water vapour as the emission [2]. Proton exchange membrane (PEMFC) is one of the fuel cell types promising in the transport measure application. The PEMFC technology is capable to establish a electrochemical reaction between hydrogen and oxygen gas to originate the electricity [3].
Generally, fuel cell components comprise of anode, cathode, and electrolyte membrane at which it becomes a separator amid the electrodes. The oxidation will materialise at the anode site to release electrons to the circuit. The electrons from external circuit will arrive at the cathode side to undergo reduction reaction and capture hydrogen ion conducted along the membrane. The electrolyte membrane then become a substantial component owing to determinant in the whole reaction through conduction of hydrogen ion as the precursor for the other half reaction.

Nafion as one the the membranes is nowadays widely applied in PEMFC. Nafion possesses high conductivity and quite stable both chemically and physically at lower temperature, yet it costs economically, then plummets in stability and conductivity at high temperature and humidity [4]. Thus, its effectiveness is considerably low and it requires to improve.

The former studies were conducted in two disparate ways to alternate the nafion; firstly was by manifest a new polymer which links covalently to an acidic functional group species, secondly was by designing heterogeneous polymer combined with inorganic composites. Form these ways, both are focused on existing new polymer which links covalently to an acidic functional group species, secondly was by designing in stability and conductivity at high temperature and humidity. Owing to determinant in the whole reaction through conduction of hydrogen ion as the precursor for the other half reaction.

The hydrophocity of PVDF-co-HFP can be eliminated by an addition of sulfonate group through a sulfonation. Ernawati [7] noted that PVDF membrane sulfonation for 4 h did not meet optimum requirements due to low sulfonation degree (SD) as 19.54%. Meanwhile, the hydrophilicity in PVDF membrane can be enhanced by attaching -SO3H group via sulfonation [8]. This functional group will attract water to absorb smoothly beside increasing the proton conductivity (σ) [9].

An addition of inorganic oxides to PEMFC membrane can improve the conductivity, intensify water resistance, and reduce high operating temperature. Inorganic oxides such as SiO2, TiO2, ZrO2 can have significant effect in the improvement of membrane characteristics. And from those oxides, TiO2 was selected in this study owing to its ability to maintain the hydration level of membrane and to improve the mechanical strength of the membrane [10]. TiO2 can be synthesised to nano-sized particles that will increase the proton conductivity (σ).

TiO2 has been prevalently applied as nanocomposite—a constituent in the composite system which scaled as nano-sized component. TiO2 can enhance the membrane ability to conduct proton at high operating temperature, 90 °C [2]. An introduction of inorganic oxide into PVDF polymer membrane can improve its proton conductivity (σ), thermos-mechanical stability, while sustaining its humidity [11]. A composite membrane of PVDF-TiO2 2% which may be implemented as PEMFC membrane can obtain a conductivity value of 3.17 × 10−3 S.cm−1 comparable to Nafion as for 6.08 × 10−3 S.cm−1 [7].

In this study, the synthesis of PVDF-co-HFP membrane was performed using casting method. Also, the influence of TiO2 addition to membrane with various concentration (3, 5, 10%) and the effect of membrane sulfonation to the improvement of proton conductivity (σ) were all carried out in this experiment.

2. Material and methods

2.1. Materials

Materials used in this study were demineralised water, oxalic acid (H2C2O4, Merck), tetraethyl orthotitanate (TEOT) Merck, concentrated sulfuric acid (H2SO4, 97%, PT. Smart Lab Indonesia), dimethyl acetamide (C3H6NO, 99%, Merck), ethanol (C2H5OH, Merck), methanol (CH3OH, Merck), sodium hydroxide (NaOH, Merck), sodium chloride (NaCl, Merck), phenolphthalein 1%, polyvinylidene fluoride co-polymer hexafluoropropylene (PVDF-co-HFP), tetraethyl orthotitanate (C8H20O8Ti, 95%, Merck).

2.2. Instruments

The equipment and tools necessarily used in this study comprises of planetary ball milling, centrifuge TJ-6 Centrifuge with TJ-R Refrigeration Unit, four point probe LCR meter impedance, Fourier transformation infrared (FTIR) spectrometer PerkinElmer Spectrum 100, analytical balance Mettler Toledo, AB164-S, oven Carbolite S30 2RR, magnetic stirrer and heater Hedolph, D91126 MR-Het Standard, Scanning electron microscope-energy dispersive x-ray (SEM-EDX) Hitachi SU 3500, furnace Thermolyne, FB1310M, ultrasonic bath 5510 Branson.
2.3. TiO₂ nanoparticle synthesis
Based on the research conducted by Paul et al (2015) [12], synthesis of TiO₂ particles can be carried out by means of 5.0 ml TEOT dissolved with 15.0 ml ethanol in a beaker 50.0 ml. Constantly stirring on a magnetic stirrer for 10 min which will form a white sol. Then 1.0 ml of deionized water was added to initiate the hydrolysis reaction. Stirring was continued for 3 h to form a TiO₂ white gel. The gel was then centrifuged for 4 × 5 min at a speed of 5000 rpm, washed with deionized water and ethanol alternately. After being separated from the solvent, the gel is then dried at 80 °C in the oven for 2 h to form a powder. After that the gel was crushed using ball milling to expand the surface and calcined at 600 °C for 4 h to form nano-TiO₂ crystals.

2.4. TiO₂ nanoparticle sulfonation process
Kumar et al (2016) [13] performed a sulfonation on TiO₂ inorganic oxide using sulfuric acid solution. TiO₂ weighed as much as 1.0 g and then added 20.0 ml of methanol and 15.0 ml of 0.5 M sulfuric acid and stirred for 12 h using a magnetic stirrer that would form a white solution. After that it is heated at 100 °C for 24 h which produces a white solid.

2.5. PVDF-co-HFP/TiO₂ membrane preparation
The PVDF-co-HFP/TiO₂ membrane synthesis process in this study was based on research conducted by Devrim et al (2012) [2]. At first, 1.8 g of PVDF-co-HFP were dissolved in 10.0 ml of DMAC solvent to form a 10% (w/v) PVDF-co-HFP solution. After that, TiO₂ nanoparticle crystals were put into a PVDF-co-HFP solution with variations of 3, 5, and 10% (w/v). The solution was stirred on a magnetic stirrer for 24 h to suspend TiO₂ and PVDF-co-HFP solution. After that the suspension is put into an ultrasonic bath at room temperature for 4 h to homogenize PVDF-co-HFP with TiO₂. Next, a polymer mixture is formed on a glass plate and flattened using a stirring rod. Then vacuum the membrane until the solvent vapoured. The procedure was then repeatedly applied for the preparation of PVDF-co-HFP/sTiO₂ membrane.

2.6. Membrane sulfonating process
The sulfonation membrane method were initiated through soaking PVDF-co-HFP, PVDF-co-HFP/TiO₂, and PVDF-co-HFP/sTiO₂ membrane samples respectively soaked into H₂SO₄ (97%) at 80 °C for 6 h. Then each sample was removed and rinsed with distilled water to neutral pH and dried at 60 °C.

2.7. Membrane characterisation
2.7.1. FTIR
Membrane samples before and after being sulfonated were each cut to a size of 2 × 2 cm. Then the membrane samples were analyzed by FTIR and the spectrum results were analysed.

2.8. SEM-EDX
Membrane samples were observed surface visible at magnifications of 2000×, 5000× and 10000× using SEM. In addition to knowing the composition of membrane samples were analyzed using EDX tools.

2.8.1. Determination of membrane proton conductivity (σ)
All membrane samples were cut into 2 × 1.5 cm in size and measured in thickness. Then the membrane sample is inserted into the four-point probe with a distance between the probes of 0.2 cm and then the amount of current used and the membrane voltage obtained.

3. Results and discussions
3.1. TiO₂ Particles
TiO₂ particles were successfully synthesised by sol-gel method and 5-to-12-nm-TiO₂-white crystals were obtained. The method can support the formation of homogenous nano-sized particles. The method which comprises two main stages (hydrolysis and condensation process) is also quite simplified and defining controllable reaction parameters such as pH, temperature, and hydrolytic rate. Thus, it would corroborate the nanoparticle development.

TEOT, a titanium alkoxide, is the main precursor partaking in the reaction which suggested to not only produce feasible titanium dioxide, but also yield innocuous by-product. Ethanol was selected as the intermediate reagent between TEOT and the aqueous solvent due to similarity in the reaction site, ethoxide (OC₂H₅), to TEOT. Alkoxide can be functioning as inhibitor of transition rate in between hydrolytic and condensation phases, thus, promoting an initiation of nanoparticle through an inception of minute cluster colloids [14, 15].
The TEOT was first diluted with ethanol at which this will regulate the hydrolysis rate when the aqueous solvent is added into. The good regulation in this rate would advocate the production of tiny, arranged, unique-character particles. The addition of aqueous solvent drove to the hydrolysis of TEOS to commence sol. The solvent is added into. The good regulation in this rate would advocate the production of tiny, arranged, unique-Ti molecules themselves to create gel. Successively, at the condensation phase, as the water molecules released from Alcoholic condensation:

\[ n\text{Ti(OH)}_3(aq) \rightarrow n\text{Ti} - O - \text{Ti} + n\text{H}_2\text{O}(l) \]

Hydrolysis:

\[ \text{Ti(OC}_2\text{H}_3)_4(l) + 4\text{H}_2\text{O}(l) \rightarrow \text{Ti(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH}(aq) \]

3.2. PVDF-co-HFP/TiO\(_2\) and PVDF-co-HFP/sTiO\(_2\) Membranes

The thin-layered membrane was attained at which the homogeneous mixture of HFP/TiO\(_2\) and PVDF-co-HFP/sTiO\(_2\) composed the membrane. The preparation step of PVDF-co-HFP membrane were using 3 disparate variations of TiO\(_2\) and sulfoned TiO\(_2\) (sTiO\(_2\)) (3, 5, and 10%). These variation of TiO\(_2\) would suggest different responses of their conductivity of proton. Meanwhile, DMAC, an aprotic, as the solvent would dilute PVDF-co-HFP effortlessly at room temperature.

A combination of the polymer and the nanocomposites was executed by stirring it using magnetic stirrer for 24 h before being sonicated for 4 h using 42 Hz frequency. The sonication process would help the nanocomposite particle to impregnate the polymer matrix. Besides, the method could deplet agglomeration by breaking down the large particles to their tinier molecules homogeneously [2].

3.3. Membrane characterisation

3.3.1. Determination of Sulfonation Degree (SD)

The determination of sulfonating degrees was performed by submerging the samples into NaCl solution for 24 h. This soaking process would aid the H\(^+\) ion to detach from \(-\text{SO}_3\text{H}\) group by a substitution of Na\(^+\) from NaCl. An amount of H\(^+\) was then analysed using regular acid-base titration. The amount of these ions equals to \(-\text{SO}_3\text{H}\) attached to sulfonated membranes [14] (Shin et al., 2014). An accomplished sulfonation process can be acquired from resulted sulfonation degree (SD) which denotes a number of sulfonate groups attached to the network membrane of PVDF-co-HFP [7]. The results from this study are depicted in figure 1 which suggested a dissimilarity in SD between PVDF-co-HFP/TiO\(_2\) and PVDF-co-HFP/sTiO\(_2\) membranes.

Both PVDF-co-HFP/TiO\(_2\) and PVDF-co-HFP/sTiO\(_2\) membranes denoted the highest SD as 19% for the samples with 3% Titio and sTiO\(_2\) concentration within the 6-hour sulfonation time at 80 °C as shown in figure 1. According to Yee et al.[17] SD value is influenced by several factors, including sulfonating agents, reaction temperatures, polymer concentrations, and reaction times. SD value, subsequently will determine the effects on thermal stability, proton conductivity (\(\sigma\)), and molecular weight of the membranes [18].

In a study by Das et al.[9], a 6-hour soaking time resulted in 31% of SD. This proposed that if the sulfonation exceeds the optimum time temperature of the membrane, the SD will decrease. This is due to the formation of sulfon crosslinking (O=S=O) which will reduce the –OH group contained in the membrane. The –OH groups portray an important role in the proton exchange process that occurs in membranes. However, in the study of Kumar et al.[13], the value of the SD at a temperature of 80 °C for 6 h produced a high conductivity value due to the heating temperature of the membrane. During high heating, the function of TiO\(_2\) as an inorganic oxide will
thus both the -OH group and one of the -SO₃H groups bind to the other -SO₃H groups. The reaction will release
movement of the polymer chain so that it can help speed up ion exchange.

This sulfonate crosslinking occurs when it exceeds the optimum operating temperature of the membrane,
thus both the -OH group and one of the -SO₃H groups bind to the other -SO₃H groups. The reaction will release
sulfuric acid and the two groups forming sulfonate crosslinking. This crosslinking will reduce the flexibility of
the PVDF-co-HFP membrane so that the membrane will be firm and rigid. The sulfonation process is carried
out at a temperature of 80 °C because sulfonation reactions at room temperature are difficult to achieve. Heating
process is carried out in order to catalyse the membrane sulfonation reaction. Based on Kim et al [19], it can
attach sulfonate groups to the membrane so that the hydrophilic nature and conductivity of protons on the
membrane can be increased. According to Kumar et al (2016) [13] the sulfonation process in the PVDF-co-HFP
polymer chain occurs through the substitution reaction of one of the H atoms which is bounded to the C atom in
the membrane with the SO₃H group from the sulfonating agent.

In figure 1, the pure PVDF-co-HFP membrane has a degree of sulfonation of 14.13% while in the addition of
TiO₂ particles, SD increases except in the addition of TiO₂. According to Peighambardoust [4], TiO₂ particles
can enhance the hydrophilic nature of membrane surfaces so that hydrophilic groups such as sulfonates are
more easily bonded to membranes. However, the addition of TiO₂ samples by 10% decreased the SD value.

Peighambardoust et al [4] delineated that addition of TiO₂ particles with high concentrations exceeding their
optimum conditions can reduce SD because sulfonate groups cannot bind to the membrane maximally due to
the presence of TiO₂ particles attached to the pore and membrane surface. This proves that the degree of
sulfonation would be optimum at increasing the concentration of TiO₂ by 3% which could increase the number
of groups—SO₃H attached to the PVDF-co-HFP membrane.

3.3.2. Proton conductivity (σ) Measurement
Proton conductivity (σ) is the ability of a membrane to deliver protons. The greater the conductivity value, the
more the membrane ability to pass protons along the membrane structure. The proton conductivity (σ) value is
a significant parameter for assessing the contribution of a functional group of a polymer matrix, such as water
content and interactions between ionic groups to proton conduction.

The determination of conductivity values in this study was determined by the four point probe method, with
each probe describing the different characteristics of the four parts of the sample. In this method, each probe
obtained the value of the voltage and electric current in four parts of the sample which can then be calculated
conductivity values [20].

The determination of PVDF-co-HFP/TiO₂ and PVDF-co-HFP/sTiO₂ membrane conductivity values was
carried out with various variations of TiO₂ and sTiO₂ concentrations of 3, 5, and 10% with 4 h of sonication.
Proton conductivity (σ) values can be seen in figure 2.

Figure 2 shows the conductivity values of the PVDF-co-HFP/TiO₂ membrane proton and PVDF-co-HFP/
sTiO₂. At the proton conductivity (σ) value of 0% the addition of TiO₂ is equal to 2.02 × 10⁻⁴ S.cm⁻¹. Thus,
the concentration of 0% to 3% relatively increased from 2.02 × 10⁻⁴ S.cm⁻¹ to 4.77 × 10⁻⁴ S.cm⁻¹ on the
addition of TiO₂ and 2.02 × 10⁻⁴ S.cm⁻¹ to 7.99 × 10⁻⁴ S.cm⁻¹ in addition to sTiO₂. This phenomenon
suggested that the addition of TiO₂ particles would play an important role in increasing the proton conductivity
(σ). The addition of TiO₂ particles into the polymer can help the membrane to expedite the proton transfer
process by enhancing hydrophilicity of the membrane, hence the proton conductivity (σ) will increase [7].
Polarity of Ti-O bonds will attract the hydrogen from water molecule to carry out the solvation of H⁺ ion by
increasing its solubility in the membrane. Thus, by an introduction of TiO₂ into PVDF-co-HFP membrane, the
conductivity will increase.

![Figure 1. SD values of PVDF-co-HFP/TiO₂ and sulfonated PVDF-co-HFP/sTiO₂ at 80 °C for 6 h.](image-url)
It can be seen from the graph data in figure 3 that the proton conductivity ($\sigma$) values in the samples with TiO$_2$ concentrations of 3, 5, and 10% decreased from $4.77 \times 10^{-4}$ S.cm$^{-1}$; $4.26 \times 10^{-4}$ S.cm$^{-1}$; $7.83 \times 10^{-4}$ S.cm$^{-1}$ at the addition of TiO$_2$ and $7.99 \times 10^{-4}$ S.cm$^{-1}$; $7.10 \times 10^{-4}$ S.cm$^{-1}$; $9.74 \times 10^{-4}$ S.cm$^{-1}$ in addition to sTiO$_2$. This decrease in conductivity can be caused by excessive addition of TiO$_2$ which will cause probability of the dissociated H$^+$ to attract onto its particle surface. The more available particle surfaces are, the dissociated H$^+$ ion decreases due to a surge in negative forces lowered the accessible proton to pass, thus the proton conductivity ($\sigma$) was turning smaller.

It can be seen from the graph data in figure 3 that the proton conductivity ($\sigma$) values in the samples with TiO$_2$ concentrations of 3, 5, and 10% with sulfonation time for 6 h at 80 °C. The proton conductivity ($\sigma$) value at the concentration of 0% TiO$_2$ with sulfonation time is $2.21 \times 10^{-3}$ S.cm$^{-1}$. Proton conductivity ($\sigma$) values on PVDF-co-HFP/TiO$_2$ membranes after sulfonation at concentrations of 3, 5 and 10% are $1.72 \times 10^{-3}$ S.cm$^{-1}$, $1.32 \times 10^{-3}$ S.cm$^{-1}$, and $1.98 \times 10^{-4}$ S.cm$^{-1}$. Whereas on PVDF-co-HFP/sTiO$_2$ membranes after sulfonation at concentrations of 3, 5 and 10%, they are $4.39 \times 10^{-4}$ S.cm$^{-1}$, $1.92 \times 10^{-3}$ S.cm$^{-1}$, and $7.67 \times 10^{-4}$ S.cm$^{-1}$, respectively.

From the results shown in figures 2 and 3 an increase in the proton conductivity ($\sigma$) value is inversely proportional to the increasing concentration of TiO$_2$. In addition, the proton conductivity ($\sigma$) of the 3% PVDF-co-HFP/sTiO$_2$ membrane shows the highest conductivity value as $4.39 \times 10^{-4}$ S.cm$^{-1}$.

The addition of hygroscopic inorganic oxides into membrane composites will increase water resistance and reduce the cross-over effect that occurs at high operating temperatures [21]. Hydrogen bonds that occur between nanocomposites and water molecules will cause nanocomposite membranes to pertain water better than membranes without nanocomposites [22]. Particles from nanocomposites will function as stabilizers in proton transfer so that protons in the hydronium ion can be connected to the –SO$_3$H group [23]. A Water functions as a proton binder of the hydronium ion so that protons can easily move from one proton source to another proton source quickly. So the proton conductivity ($\sigma$) will be the same as the movement of water molecules in the membrane.

3.3.3. FTIR Analysis of TiO$_2$ and sulfonate TiO$_2$

The sulfonate group contained in TiO$_2$ can be confirmed using FTIR characterisation. Where the functional group analysis is done qualitatively to confirm the entry of the sulfon group (–SO$_3$H) on TiO$_2$ which is done by...
interpreting the peaks in the absorption of the infrared spectrum. The infrared spectra of TiO$_2$ and TiO$_2$–SO$_3$H are respectively shown in figures 4 and 5.

Characterisation using FTIR is a qualitative identification of a functional group in a sample. The identification is done by interpreting data from the spectrum produced. In the infrared spectrum there are peaks with certain wave numbers that indicate certain functional groups. The peaks in the infrared spectrum arise because the molecules absorb energy from infrared radiation. The energy absorbed causes an increase in amplitude so that the bonds in the functional group can vibrate, then it will give a signal in the form of a peak in the infrared spectrum. The amount of energy absorbed varies depending on the bond corresponding to the change in dipole moment ($\mu \neq 0$) at the time the energy is absorbed.

In figure 4 shows the spectrogram that has not been sulfonated. The spectrogram has a sharp peak at the wave number 470 cm$^{-1}$ which is a typical range of bonds for the Ti–O strain and the existence of a wavelength at a length of 3310.8 cm$^{-1}$ which indicates the vibrational bonding of the $-\text{OH}$ group. Whereas at a wavelength of 1628.3 cm$^{-1}$ it is a bond with water to form Ti–OH [24].

According to Ba-Abbad et al [25] the typical uptake of TiO$_2$ is in the range 450–800 cm$^{-1}$. Whereas in figure 6 shows that the sulfonated spectrogram has a different peak compared to before sulfonation (figure 5), that is the typical absorption of the $-\text{OH}$ group in the SO$_3$H group at 3366.7 cm$^{-1}$ with moderate intensity and wide band shape and 1634 cm$^{-1}$ with moderate intensity and pointed band shape. Then the absorption of 1055.4 cm$^{-1}$ with moderate intensity indicates the asymmetrical strain of the S–O group. Whereas 1143.2 and 1208.8 cm$^{-1}$ were associated with the separation of S–O groups into symmetric and asymmetric strain. So that the SO$_3$H type as bidentate complex is coordinated with TiO$_2$ [26]. To see the difference of the FTIR results before and after sulfonation can be seen on the spectogram on figure 6. Table 1 provides the detailed FTIR spectrum assignments of sulfonated/non-sulfonated-TiO$_2$ functional group.

| Wavenumber/cm$^{-1}$ | Functional group assignment |
|----------------------|-----------------------------|
| TiO$_2$              | TiO$_2$–SO$_3$H References | Functional group assignment |
| 470                  | 751.8                       | 450–800 Stretch Ti–O |
| 1055.4               | 1040                        | Asymmetric Stretch S=O |
| 1143.2               | 1139                        | Symmetric Stretch S=O |
| 1208.8               | 1237                        | Asymmetric Stretch SO$_3$ |
| 1628.3               | 1630.4                      | Vibration $-\text{OH}$ |
| 3310.8               | 3366.7                      | $-\text{OH}$ group from (SO$_3$H) |

Table 1. Functional groups assignment of TiO$_2$, before and after sulfonation process.
3.3.4 FTIR Analysis of PVDF-co-HFP/TiO2 and PVDF-co-HFP/sTiO2

Sulfonate groups found in PVDF-co-HFP/TiO2 and PVDF-co-HFP/sTiO2 were confirmed using FTIR characterisation. Sulfonation is carried out using concentrated sulfuric acid as a sulfonating agent that is commonly used in several studies. Concentrated sulfuric acid can be used as a sulfonation agent because the sulfonate group (-SO3H) in sulfuric acid is easy to attach to the polymer structure. The SO3H group will exchange the hydrogen groups contained in the PVDF-co-HFP structure. PVDF-co-HFP/TiO2 and PVDF-co-HFP/sTiO2 are carried out by soaking the membrane in a solution of concentrated sulfuric acid at a temperature of 80 °C. In the research conducted by Kim et al [19] temperatures above 25 °C will accelerate the attachment of sulfone groups to the membrane structure, but when the temperature reaches more than 80 °C membrane PVDF-co-HFP will be degraded in hot sulfuric acid solution. The results of the FTIR obtained in the form of a spectrum can be seen in figures 7 and 8.

![Figure 5. FTIR spectrum of TiO2.](image1)

![Figure 6. FTIR spectrum of TiO2 before sulfonation (black line) and sulfonated TiO2 (blue line).](image2)
PVDF-co-HFP/TiO₂ membranes that was prior to be sulfonated only have functional groups from PVDF-co-HFP and TiO₂. Figure 7 shows the IR spectrogram before sulfonation. The spectrogram has a sharp peak at a wavelength of 483.6 cm⁻¹ which is a typical region for the Ti–O strain. A sharp peak with the number 832.8 cm⁻¹ is a typical area of the C–F strain of the polymer PVDF-co-HFP. Absorption at 1399 cm⁻¹ shows the strain on Ti–O–Ti in the sample indicates that the TiO₂ particles were successfully attached to the PVDF-co-HFP membrane but it was also suspected that the wavelength of 1399 cm⁻¹ was an F-C-F strain.

In this research, sulfonation was carried out on the PVDF-co-HFP/TiO₂ membrane using concentrated sulfuric acid which produced sulfonate groups on the membrane as evidenced by the results of the FTIR spectrum in figure 8.

Figure 7. FTIR spectrum of PVDF-co-HFP/TiO₂ membrane before sulfonation.

Figure 8. FTIR spectrum of PVDF-co-HFP/TiO₂ membrane after sulfonation.

Figure 8 shows the sulfonated PVDF-co-HFP/TiO₂ membrane has a different peak compared to before sulfonation (in figure 7), namely the typical absorption of the -OH group in the -O₃H group at 3417 cm⁻¹ with moderate intensity and the shape of the band that is wide. The incorporation of the spectrogram on the PVDF-co-TiO₂ membrane before and after sulfonation can be seen in figures 7 and 8. The combination of figures 7 and 8 can be seen in figure 9 and the data after and before sulfonation can be interpreted with the results listed in table 2.
3.3.5. SEM-EDX analysis

Morphological analysis using SEM-EDX was carried out with sulfonated PVDF-co-HFP/sTiO₂ membrane samples. SEM-EDX analysis was performed to observe the membrane surface morphology and composition. The composite membrane analyzed through SEM-EDX is a membrane with a high proton conductivity ($\sigma$) value that is sulfonated PVDF-co-HFP/sTiO₂ membrane. SEM results can be observed from figure 10.

In figure 10(a) with a magnification of 2000 × and figure 10(b) with 5000 × magnification, it appeared that there are a few pores formed on the membrane surface which suggested that the sonication time for 4 h was optimal time for the process of adding TiO₂ particles to the membrane. The existence of the pore can be caused by the process of evaporation of the solvent (DMAc) which causes the porous membrane forming too quickly or also due to the addition of particles to the membrane. TiO₂ particles were not only on the surface but into the membrane to form pores. These pores can reduce the effectiveness of the membrane in helping proton mobility, but the pore can function to increase water absorption so that the membrane will be more moist because water particles can be retained in the pore. If we look at figure 10(c) with a magnification of 10000×, it appears that there is a buildup of TiO₂ at a certain position. This could be due to the large number of TiO₂ compositions or to the less long stirring process and the less optimal ultra-sonication process. The distribution of TiO₂ particles appeared to be distributed fairly evenly on the surface of the PVDF-co-HFP membrane and only a small number of particles were found on the membrane surface. This is due to particles with polymer solutions that are less than optimal so that the distribution of particles is not evenly distributed throughout the membrane.

The EDX analysis result of PVDF-co-HFP/3% sTiO₂ surface membrane in figure 11 illustrated the presence of carbon (C), fluorine (F), oxygen (O), sulfur (S), and titanium (Ti) elements with weights and atoms listed in table 3. Carbon and fluorine elements have greater weight of 50.01% and 31.12% because they are the membrane constituents of PVDF-co-HFP polymer. Carbon and fluorine occupied at least 69.75 and 24.51%, respectively, the atomic compositions in PVDF-co-HFP polymer. Meanwhile, the titanium element came from TiO₂ with a total weight of 10.40%. The presence of sulfur and oxygen which could be derived from denoted the percentages of

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Table 2. Functional groups assignment of PVDF-co-HFP/TiO₂ membrane, before and after sulfonation process.

| Wavenumber (cm⁻¹) | Sulfonated PVDF-co-HFP/3% sTiO₂ Membrane | Reference | Functional groups assignment |
|-------------------|----------------------------------------|-----------|-----------------------------|
| 483.6             | 500.3                                  | 450–800   | Stretch Ti-O                |
| 599.8             | 599.8                                  | 570–710   | Symmetrical stretch O=S=O   |
| 839.4–882.9       | 832.8–882                             | 830–1000  | Regangan C–F               |
| 1193.5            | 1195                                  | 1030–1303 | Symmetrical stretch F–C–F  |
| 1399              | 1394                                  | 1402      | Symmetrical stretch F–C–F  |
| 1689.2            | 1634                                  | 1634      | Vibration –OH               |
| 3014.2            | 3040                                  | 2900–3100 | Stretch C–H                |
| 3371              | 3417                                  | 3417      | Stretch OH dari SO₃H        |

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3.3.5. SEM-EDX analysis

Morphological analysis using SEM-EDX was carried out with sulfonated PVDF-co-HFP/sTiO₂ membrane samples. SEM-EDX analysis was performed to observe the membrane surface morphology and composition. The composite membrane analyzed through SEM-EDX is a membrane with a high proton conductivity ($\sigma$) value that is sulfonated PVDF-co-HFP/sTiO₂ membrane. SEM results can be observed from figure 10.

In figure 10(a) with a magnification of 2000 × and figure 10(b) with 5000 × magnification, it appeared that there are a few pores formed on the membrane surface which suggested that the sonication time for 4 h was optimal time for the process of adding TiO₂ particles to the membrane. The existence of the pore can be caused by the process of evaporation of the solvent (DMAc) which causes the porous membrane forming too quickly or also due to the addition of particles to the membrane. TiO₂ particles were not only on the surface but into the membrane to form pores. These pores can reduce the effectiveness of the membrane in helping proton mobility, but the pore can function to increase water absorption so that the membrane will be more moist because water particles can be retained in the pore. If we look at figure 10(c) with a magnification of 10000×, it appears that there is a buildup of TiO₂ at a certain position. This could be due to the large number of TiO₂ compositions or to the less long stirring process and the less optimal ultra-sonication process. The distribution of TiO₂ particles appeared to be distributed fairly evenly on the surface of the PVDF-co-HFP membrane and only a small number of particles were found on the membrane surface. This is due to particles with polymer solutions that are less than optimal so that the distribution of particles is not evenly distributed throughout the membrane.

The EDX analysis result of PVDF-co-HFP/3% sTiO₂ surface membrane in figure 11 illustrated the presence of carbon (C), fluorine (F), oxygen (O), sulfur (S), and titanium (Ti) elements with weights and atoms listed in table 3. Carbon and fluorine elements have greater weight of 50.01% and 31.12% because they are the membrane constituents of PVDF-co-HFP polymer. Carbon and fluorine occupied at least 69.75 and 24.51%, respectively, the atomic compositions in PVDF-co-HFP polymer. Meanwhile, the titanium element came from TiO₂ with a total weight of 10.40%. The presence of sulfur and oxygen which could be derived from denoted the percentages of
0.77% and 7.07%, respectively. The EDX results suggested that the -SO₃H group is present in the membrane as it conforms with the FTIR spectrum (figure 9). To understand the binding position of -SO₃H group in the surface membrane, X-ray photoelectron spectroscopy/XPS might be necessarily accounted. Thus, form this analysis, we can say that the sulfonation process was successfully carried out. So that in figure 11 and table 3 it can be concluded that TiO₂ particles have entered the membrane with the the peaks of the elements contained in the membrane.
4. Conclusion

PVDF-co-HFP/TiO₂ and Sulfonated PVDF-co-HFP/sTiO₂ composite membranes were successfully fabricated. Based on FTIR spectrum, sulfonated TiO₂ constituent showed peaks in the range of 1200—1300 cm⁻¹. SEM analysis suggested that the distribution of TiO₂ in the surface membranes depicted disperedly with some porosity in them. The EDX denoted the composition of titanium as 10.40%, oxygen as 7.70%, and sulfur as 0.77%. The addition of various amount of TiO₂ proposed an increasing in the proton conductivity (σ) of PVDF-co-HFP/TiO₂ and sulfonated PVDF-co-HFP/sTiO₂ composite membranes, yet decreasing as reached the optimum concentration. The addition of sTiO₂ 3% for 4 h using sonication and 6 h using sulfonation at 80°C yield 4.3 x 10⁻³ S.cm⁻¹ in conductivity which was comparable to Nafion with 6.08 x 10⁻³ S.cm⁻¹ conductivity. The SD value noted as 19.37% for sulfonated PVDF-co-HFP/3% sTiO₂ membrane.

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