Synthesis and characterization of sulfonated poly(vinylidene fluoride-co-hexafluoropropylene)/sAl2O3 composites as a novel-alternative electrolyte membranes of Nafion

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ABSTRACT

Fuel cell membrane of Nafion is commonly used as the electrolyte material of fuel cell which has good mechanical properties, but the hydrophobicity reduce its proton conductivity. Thus, the other polymer is used for the electrolyte membrane. A polymer modification of sulfonated poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) by attaching sulfonate group and oxide compounds such as sAl2O3 would enhance the proton conductivity. The research is aimed to modify PVDF-co-HFP via the addition of sAl2O3 or pristine Al2O3 and studying the effect of sulfonated Al2O3 on the conductivity. The research includes Al2O3 particles synthesis, the sulfonation of Al2O3, the membrane preparation, the sulfonation of membrane, and the characterisation of membrane using FTIR, SEM-EDX, and Four-point Probe Electrical Device Analysis. SEM-EDX analysis explained that the 6% addition of Al2O3 showed denser cross-sectioned membrane rather than the 9% addition of Al2O3. The highest conductivity achieved can be revealed at the 6% sAl2O3 addition on PVDF-co-HFP membrane as 2.27 × 10⁻³ S cm⁻¹ which is higher than a previous study.

1. Introduction

Energy-source device such as fuel cell can be engineered as an alternative to alleviate greenhouse effect from carbon emission in the entire world [1]. Polymer electrolytes have been extensively researched due to the possibility of their commercial use in a variety of electrochemical devices such as electrochemical cells, rechargeable batteries, and sensors [2]. Proton exchange membrane fuel cell (PEMFC) is one of the energy sources which applies the electrochemical principle to generate high-efficient electricity (40–60%), operate at low temperature (50–100 °C), be clean, and eco-friendly [3].

PEMFC necessitates an electrolyte membrane, as in the part of it, to exchange proton (H+) in the terms of electrons production over the circuit. Nafion, as the conventional membrane, is the copolymer perfluorosulfonate which has considerable proton conductivity, and good mechanical and thermal stability [4]. However, the conductivity of Nafion can diminish in low humidity at high temperature (80 °C). Dehydration of the membrane can cause shrinking-up, lowering the conductivity, thus reducing interface contact between the electrodes and the membrane, beside creating crossover of gaseous reactants to allow them escape to the bulk of membrane [5]. Thus, Nafion membrane is non-favourable and an alternative to this issue must be manifested to substitute Nafion. Another membrane requires good thermal and mechanical properties to lessen the dehydration issue.

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer with excellent mechanical and thermal properties [6]. The semi-crystalline properties, however, can inhibit proton diffusion. PVDF can be modified by combining with another polymer with low crystallinity such as HFP (hexafluoropropylene). PVDF-co-HFP has lower crystallinity than PVDF owing to an amorphicity of HFP, this amorphous character will allow collected water to flow freely within the structure [7]. On the other hand, the hydrophobicity of PVDF-co-HFP, due to high surface tension between water and membrane surface [8], will also clog proton diffusion through membrane and resulting in decreasing of proton conductivity [8].

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Metal oxide compounds such as silicate, titanate, and zirconate addition to the membrane can enhance its performance as it shown in water-treatment plant [9]. The hydrophilicity of these oxides can help membrane sustain the solvation of water molecule in the membrane under the operating process as it increase mechanical strength of the membrane [10]. PVDF-co-HFP composite membranes with ZrO2, TiO2, and SiO2 signified the highest proton conductivity of 9.3 × 10^{-5} S cm^{-1} [11]; maximum of 1 × 10^{-3} S cm^{-1} [12-13]; and 1.16 × 10^{-3} S cm^{-1}, respectively [14]. An addition of acidic species like sulfonate compounds can also improve the hydrophilicity and conductivity. Sulfonated poly-siloxane ethylene butylene polystyrene (SPSEBS) membranes with TiO2 can also improve the hydrophilicity and conductivity. Sulfonated poly-siloxane ethylene butylene polystyrene (SPSEBS) membranes with TiO2 and stTiO2 oxide had reached the conductivity of 1.08 × 10^{-3} S cm^{-1} and 3.57 × 10^{-3} S cm^{-1} which much higher that its pure SPSEBS, 1.52 × 10^{-3} S cm^{-1} [15]. A sulfonated TiO2 in PVDF-co-HFP membrane showed high conductivity of 3.6 × 10^{-3} S cm^{-1} [16]. The other study suggested that an addition of non-sulfonated Al2O3 into PVDF-co-HFP membrane can produce the highest conductivity of 0.98 × 10^{-3} S cm^{-1} [11]. Based on those studies, we were trying to directly add a sulfonate group into Al2O3 and compare it with the PVDF-co-HFP with non-sulfonated Al2O3. In this study, we experimented an addition of metal oxide compound (Al2O3 with the concentration of 3, 6, and 9% (w/v)) on PVDF-co-HFP membranes in order to study the effect of sulfonation of Al2O3 on the PVDF-co-HFP membrane comparing to the PVDF-co-HFP with pure Al2O3. Al2O3 is expected to enhance the hydrophilicity of the membrane by water absorption and increase its proton conductivity [17].

2. Experimental method

2.1. The preparation of Al2O3 particle

Al2O3 powder was obtained from Sigma. The powder was reduced into small particles using planetary ball mill using ZrO2 balls in a Polytetrafluoroethylene (PTFE) container. The mass ratio of balls and Al2O3 during the milling process is 10:1 for 32 h with 300 rpms. The reduced-size Al2O3 was then analysed using FDA/particle size analyser.

2.2. The sulfonating of Al2O3

An amount of 20 mL methanol as the solvent was added to 1.0000 g of Al2O3, subsequently 0.5M sulfuric acid was added as the source of –SO3H functional groups. The mixture was stirred for 12 h until the white-opaque solution formed. It was then heated at 100 °C for 24 h to form white precipitate.

2.3. The synthesis of PVDF-co-HFP/Al2O3 and PVDF-co-HFP/sAl2O3 membranes

An amount of 1.8 g PVDF-co-HFP was diluted in 10.0 mL DMAc to constitute a solution of PVDF-co-HFP 18% (w/v), DMAc can help shrink up the membrane porosity. Al2O3/sAl2O3, thereupon, was put into PVDF-co-HFP solution with variation of 3, 6, and 9% concentration and stirred for 24 h until the Al2O3/sAl2O3 dispersed in the PVDF-co-HFP membrane. To reduce the suspension, increase the dispersion and homogeneity, the mixture was sonicated using 40 kHz frequency for 4 h. Thereafter, the polymer mixture was cast onto glass mold to form a layer-sheet membrane. All these membrane were analysed using FTIR and SEM-EDX with the magnification of 1000×.

2.4. The sulfonating of PVDF-co-HFP/Al2O3 and PVDF-co-HFP/sAl2O3 membranes

PVDF-co-HFP, PVDF-co-HFP/Al2O3, and PVDF-co-HFP/sAl2O3 membranes were soaked, respectively, in H2SO4 (97%) solvent at 60 °C for 6 h. The membranes were then washed out using aquabidest to a neutral pH and dried at 60 °C for at least an hour, please be aware of membranes humidity.

2.5. The determination of sulfonation degree (SD)

The Sulfonation degree was determined by using a titration method. All membranes were soaked in a 0.50 M NaCl solution for 24 h. The 24-hours-soaked solution were then titrated using 0.01 M NaOH. The SD can be calculated using Eq. (1):

\[ \text{SD} = \frac{\text{Mw PVDF-co-HFP} \times \text{CNaOH} \times \text{VNaOH} \times 100}{W_{\text{dry}} - (\frac{\text{Mw sulfonic group}}{1000} \times \text{CNaOH} \times \text{VNaOH})} \]

Where:

- SD = sulfonation degree (%)
- Mw of PVDF-co-HFP = 214 g/mol
- VNaOH = volume of NaOH (mL)
- Mw of sulfonate group = 81 g/mol
- CNaOH = concentration of NaOH (M)
- W_{\text{dry}} = Dried weight of membrane (g)

2.6. Proton conductivity measurement

All 4-cm²-cut membranes with measured thickness were put onto the four line probe plate with the probe width of 0.2 cm. The electrical current was applied in the magnitude of 1–5 × 10^{-5} A to obtain the output voltage. The electrical conductivity of membranes were calculated by using Eq. (2).

\[ \sigma = \frac{(i \times d) \times \text{V}}{\text{lxT}} \]

Where:

- \( \sigma \) = proton conductivity (S.cm^{-1})
- T = membrane thickness (cm)
- i= current (A)
- d = probe width (cm)
- V= output voltage (V)
- l = membrane length (cm)

3. Results and discussion

3.1. Analysis of Al2O3 particle size

The PSA analysis of commercial Al2O3 signified an average particles size of 112,5 µm as shown in Figure 1. A milling using planetary ball mill is required to reduce the size to enlarge the particle surface area, thus the water-particle contact can be considerably amplified to maintain the membranes being hydrated during the operating process [18] (see
The particle size of Al$_2$O$_3$ can decrease up to 100 times smaller as the milling process was deployed. The ball-milled Al$_2$O$_3$ was re-analysed using PSA and showed an average particle size of 1.26 $\mu$m with the mode of 1.92 $\mu$m, and the smallest size of 0.48 $\mu$m. Agglomeration of the particles during milling process can induce the size inhomogeneity of Al$_2$O$_3$ [18]. Diameter size of ball-milled particles will conform equally to $<80\%$ of the particles volume [19]. We may perceive a disparate distribution in between commercial Al$_2$O$_3$ and the ball-milled one. The commercial Al$_2$O$_3$ showed a single peak in range of 2.21–300 $\mu$m which indicates a uniform distribution of the particles, while the ball-milled one depicted a double peak in the range of 0.21–2.92$\mu$m which suggested that the ball-milled process can reduce the particle size, yet proposed a polarization in particle distribution at which the size was split into 2 different size distribution of 0.21–1.05$\mu$m and 1.05–2.92$\mu$m.

### 3.2. FTIR analysis of Al$_2$O$_3$ and sulfonated Al$_2$O$_3$

FTIR spectrum of Al$_2$O$_3$ and sAl$_2$O$_3$ can be seen in Figure 3. The spectrum pointed peaks of 1393, 1027, and 974 cm$^{-1}$ which indicate the sulfonate group bond. The band of 1393 cm$^{-1}$ which has medium-shoulder intensity and 1027 cm$^{-1}$ with strong-sharp intensity at which they signified the peaks of both asymmetry and symmetry strain of the S=O bond, and at 974 cm$^{-1}$ with strong-sharp intensity is the peak of the SO bond strain. The band of 1635 cm$^{-1}$ which has moderate-sharp intensity and 3376 cm$^{-1}$ with strong-width intensity respectively is the bending vibration distribution and strain of the –OH group found on the surface of Al$_2$O$_3$. Al–O bond strain of Al$_2$O$_3$ has been also seen at 511 cm$^{-1}$ with weak-shoulder intensity. These bands indicated that the sulfonation attachment on Al$_2$O$_3$ has successfully occurred.

### 3.3. FTIR analysis of PVDF-co-HFP and sulfonated PVDF-co-HFP membranes

FTIR analysis results of PVDF-co-HFP/Al$_2$O$_3$ membrane and sPVDF-co-HFP/Al$_2$O$_3$ membrane are shown in Figure 4. The band of 1395 cm$^{-1}$ which has strong-sharp intensity and 1256 cm$^{-1}$ with strong shoulder-intensity are asymmetric and symmetry strains of the S=O bond. While the band of 890 cm$^{-1}$ with low-shoulder intensity is the peak of the S–O bond strain. In addition, there are asymmetrical stretch peaks and C–F bond symmetries at 1216 cm$^{-1}$ with shoulder-strong intensity and 946 cm$^{-1}$ wide-strong bands, respectively. The band of 2906 cm$^{-1}$ with shoulder-strong intensity is the peak of the C–H bond stretching, while the...
band at 1454 cm\(^{-1}\) weak-shoulder is the bending vibration of the CH\(_2\) bond. A peak of 3422 cm\(^{-1}\) with shoulder-strong intensity constitutes a strain of the –OH group of water contained in the membrane. The peak at 635 cm\(^{-1}\) with medium-wide intensity is the Al–O bond stretching. This spectrum shows that the sulfonate group has been affixed to the PVDF-co-HFP/Al\(_2\)O\(_3\) membrane.

### 3.4. Scanning electron microscope-energy dispersive X-Ray (SEM-EDX)

Figure 5 depicts the surface of PVDF-co-HFP membranes with the various addition of Al\(_2\)O\(_3\) and sAl\(_2\)O\(_3\) at which the subtle conformity of the surface was displayed. A single PVDF-co-HFP membrane has more porous rather than when Al\(_2\)O\(_3\) was added into PVDF-co-HFP membrane [20]. The discrepancies occurred when the less amount of porous membranes emerge at which the Al\(_2\)O\(_3\) and sAl\(_2\)O\(_3\) were added to the membrane in sPVDF-co-HFP/9%sAl\(_2\)O\(_3\) and sPVDF-co-HFP/9%Al\(_2\)O\(_3\) samples, respectively as shown in Figures 5a and 5c. The agglomeration of Al\(_2\)O\(_3\) during the sonication process accounts for the formation of porous which led to inequality of particle dispersion over the surface membrane.

Figures 5c and 5e displayed the cross-section of sPVDF-co-HFP/6%Al\(_2\)O\(_3\) and sPVDF-co-HFP/6% sAl\(_2\)O\(_3\) membranes, respectively. Figure 5c of sPVDF-co-HFP/6%Al\(_2\)O\(_3\) showed a denser structure than sPVDF-co-HFP/9%Al\(_2\)O\(_3\). At high concentration of Al\(_2\)O\(_3\), the agglomerates take more control to the porosity of the membranes resulted in changes in membrane morphologies. Moreover, the sulfonated Al\(_2\)O\(_3\) tend to densify the membrane comparing to non-sulfonated Al\(_2\)O\(_3\).

A 4-cm\(^2\)-cut sPVDF-co-HFP/6%Al\(_2\)O\(_3\) membrane was analysed using EDX to examine the elemental compositions in the membrane. We considered using this analysis to confirm if the sulfonated Al\(_2\)O\(_3\) has been successfully incorporated throughout the membrane. Figure 6 presents EDX qualitative analysis of sPVDF-co-HFP/6% Al\(_2\)O\(_3\) membrane which indicated the contents of fluor, carbon, aluminium, oxygen, and sulfur. The carbon and fluor are the most abundant elements in the membrane as 49.83% and 41.23% that constitute the main elements of PVDF-co-HFP. The oxygen made up 5.22%, while aluminium and sulfur account for 1.95% and 1.77% of the membrane, respectively which signified the composition of the membrane constituents from Al\(_2\)O\(_3\) and –SO\(_3\)H groups. The EDX spectrum confirmed that the Al\(_2\)O\(_3\) and sulfonated group have been successfully incorporated into the membrane.

### 3.5. Sulfonation degree (SD)

Figure 7 reveals the result of sulfonation degree determination, it can be seen that the sPVDF-co-HFP membrane has the lowest sulfonation degree compared to the sPVDF-co-HFP membrane with the addition of Al\(_2\)O\(_3\) or sAl\(_2\)O\(_3\), then it can be concluded that increasing oxide compounds will increase the degree of sulfonation. Hydrophilic oxide compounds such as Al\(_2\)O\(_3\) can help in the sulfonation process, because the hydrophilic sulfonate group will more easily diffuse and bind to the membrane [21].

Membrane with the addition of sAl\(_2\)O\(_3\) has a higher degree of sulfonation compared to Al\(_2\)O\(_3\) without disulfonation beforehand, this can be due to the sulfonate group on sAl\(_2\)O\(_3\) contributing H\(^+\) so that the value of the sulfonation degree is higher than Al\(_2\)O\(_3\). However, the membrane with the addition of 6% sAl\(_2\)O\(_3\) has a lower value compared to the degree of sulfonation on the 6% Al\(_2\)O\(_3\) membrane, this can occur because the 6% sAl\(_2\)O\(_3\) membrane has been saturated or cannot react again during sulfonation for 6 h so that no sulfonate groups are present to bound to the membrane.

Based on Figure 7, at a concentration of 9% both oxide compounds have a low degree of sulfonation when compared to a concentration of 6%. The addition of oxide compounds with concentrations exceeding their optimum conditions can affect the freedom of movement of diffused sulfonate groups in the membrane due to the presence of aggregated Al\(_2\)O\(_3\) and sAl\(_2\)O\(_3\) particles on the surface [22].

The SD which indicated less than 15%, can be influenced by several factors, including sulfonating agents, reaction temperatures, polymer concentrations, and reaction times [23]. Besides the concentration of oxide compounds can affect the value of the degree of sulfonation as discussed earlier.

![Figure 5](image-url)

Figure 5. (a) surface of sPVDF-co-HFP/6%Al\(_2\)O\(_3\), (b) cross-section of sPVDF-co-HFP/6%Al\(_2\)O\(_3\), (c) surface of sPVDF-co-HFP/9%Al\(_2\)O\(_3\), and (d) cross-section of sPVDF-co-HFP/9%Al\(_2\)O\(_3\).
3.6 Proton conductivity

The proton conductivity value was determined by means of a four line probe, by flowing a predetermined current and then measuring the voltage from the membrane. It can be seen in Figure 8 that PVDF-co-HFP membrane added with sAl_2O_3 (orange) and Al_2O_3 (purple) has a decreasing conductivity value with increasing concentration. This can be due to the higher content of oxide compounds in the membrane will form two phases, first the oxide compound is in the membrane and second is located on a surface rich in oxide compounds so that the diffusion of protons on the membrane will slow down [24], this is also explained from the conductivity value of the membrane 9% with Al_2O_3 which is considerably small of 0.221 \times 10^{-3} \text{ S cm}^{-1}.

The proton value of PVDF-co-HFP membrane added by sAl_2O_3 is higher than that added by Al_2O_3, because the membrane with sAl_2O_3 has sulfonate groups in Al_2O_3 so that it can increase proton conductivity in the membrane even though the results have not exceeded the pure PVDF-co-HFP membrane (1.06 \times 10^{-3} \text{ S cm}^{-1}) [25]. The conductivity value of the proton membrane without sulfonation has a lower value than the sulfonated membrane because the sulfonate group plays an important role in the proton transfer process.

Figure 8 shows that the sPVDF-co-HFP membrane with the addition of Al_2O_3 (green) and sAl_2O_3 (blue) at various concentrations has an increasing conductivity value as the concentration of oxide compounds increases. However, the 3% Al_2O_3 membrane has a smaller conductivity value than the pure sPVDF-co-HFP membrane and its conductivity is adjacent to the 3% sAl_2O_3 membrane that is 1.110 \times 10^{-3} \text{ S cm}^{-1} for PVDF-co-HFP/3% sAl_2O_3 and 1.16 \times 10^{-3} \text{ S cm}^{-1} for sPVDF-co-HFP/3% Al_2O_3 membranes. This can occur because the value of the degree of sulfonation produced is almost the same, the value of sulfonation of the sPVDF-co-HFP/3% Al_2O_3 membrane is 6.30% while the pure sPVDF-co-HFP membrane is 6.24%. Thus, the number of sulfonate groups in the two membranes is almost comparable, and the decrease in conductivity can be caused by the presence of Al_2O_3 particles on the surface. Al_2O_3 can slow down the proton diffusion process in the membrane so that the conductivity value of pure membrane protons is higher.

In Figure 8, the sPVDF-co-HFP/3%-Al_2O_3 membrane has a small conductivity value when compared to the sPVDF-co-HFP/6%-sAl_2O_3 membrane. This result can be influenced because the sulfonation degree of 6% sAl_2O_3 has the highest sulfonation degree compared to other concentrations, so it can be concluded that the sPVDF-co-HFP/6%-sAl_2O_3 membrane is the optimum sAl_2O_3 concentration that can be added to the PVDF-co-HFP membrane. The HFP supported by the high degree of sulfonation and proton conductivity was 10.76% and 2.27 \times 10^{-3} \text{ S cm}^{-1}, respectively.

When comparing the value of the degree of sulfonation with the conductivity value of the proton membrane PVDF-co-HFP/9%-Al_2O_3 has a value that is not comparable. The 9% Al_2O_3 membrane has a low degree of sulfonation compared to 6% Al_2O_3, while for the proton conductivity value 9% Al_2O_3 has a value higher than 6% Al_2O_3. The conductivity value...
is influenced not only by sulfonate groups in the membrane but also by hydrated membranes. The addition of composites can assist membranes in holding water, because hydrogen bonding occurs between composites and water molecules, in addition to that the composite functions to stabilize proton displacement so that it protects the proton exchange process in the hydronium ion with the –SO3H group. The addition of Al2O3 can accelerate the process of transfer of protons because water functions as a proton binder, can be held or guarded by Al2O3 so that it facilitates the process of proton transfer [26, 27].

The diffusion of protons in the membrane is very dependent on water and the number of sulfonate groups, but can also be influenced by the crystallinity and membrane pores. Decreased crystallinity in the membrane will increase conductivity, the addition of oxide compounds in the membrane can reduce crystallinity [28]. Crystalline membranes can inhibit the proton diffusion process and reduce water contact on the membrane. Porous membranes can cause gas reactant crossovers and proton diffusion in the membrane to slow down [29]. However, porous membranes can increase water contact on the membrane because water particles can be retained in the pore so that water absorption and moisture membrane increases.

The highest proton conductivity value produced is 2.27 × 10−3 S cm−1 almost close to the conductivity value of Nafion NAFNR-212 which is 6.08 × 10−3 S cm−1 [30] and PVDF-co-HFP/sTiO2 which showed the conductivity of 4.30 × 10−3 S cm−1 [31]. Although the conductivity cannot match Nafion NAFNR-212, the addition of sAl2O3 or Al2O3 concentration can increase the conductivity value of sPVDF-co-HFP membrane.

4. Conclusion

Al2O3 particles can improve proton conductivity. The 6% sulfonated Al2O3 can achieve the most optimum conductivity value of 2.270 × 10−3 S cm−1. The optimum sulfonation degree that can be obtained is 10.94%. The particles size can be reduced more to nanoparticle size to increase the effect on proton conductivity of for PVDF-co-HFP/sAl2O3 composites membranes.

Declarations

Author contribution statement

Iman Rahayu: Conceived and designed the experiments. Akmalia Riasalatul Umma: Performed the experiments; Wrote the paper.
Juliandri: Conceived and designed the experiments; Analyzed and interpreted the data.
Yoga Trianzar Malik: Analyzed and interpreted the data; Wrote the paper.
Muhammad Nasir: Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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References

[1] K. Gerardin, S. Raoul, C. Boitet, A. Lapicque. Direct coupling of PEM fuel cell to supercapacitors for higher durability and better energy management, J. Fuel Cell 18 (3) (2018) 315–325.
[2] M.A. Gebrayesus, Y. Purushotham, J.S. Kumar, Preparation and characterization of lithium polymer conducting polymer electrolytes based on a blend of poly(vinylidene fluoride-co-hexafluoropropylene) and poly(methyl methacrylate), Heliyon 2 (7) (2016), e00134.
[3] C. Qin, J. Wang, D. Yang, B. Li, C. Zhang, Proton exchange membrane fuel cell reversal: a review, Catalysts 6 (12) (2016) 1–21.
[4] Q. Zhao, P. Majztrik, J. Benziger, Diffusion and interfacial transport of water in Nafion, J. Phys. Chem. 115 (2011) 2717–2727.
[5] J.R. O’Dea, N.J. Economou, S.K. Buratto, Surface morphology of Nafion at hydrated and dehydrated conditions, Macromolecules 46 (6) (2013) 2267–2274.
[6] Y.H. Teow, A.A. Latif, J.K. Lim, P. Ngang, L.Y. Sunan, B.S. Ooi, Hydroxyl functionalized PVDF–TiO2 ultrafiltration membrane and its anti fouling properties, J. Appl. Polym. Sci. 132 (21) (2014).
[7] P. Martins, A.C. Lopes, S. Lancereros-Mendez, Electroactive phases of poly(vinylidene fluoride): determination, processing and applications, Prog. Polym. Sci. 4 (2014) 683–706.
[8] N.C. Zhou, C. Xu, W.R. Burghardt, R.J. Compoto, K.J. Winey, Phase behavior of polystyrene and polystyrene-styrene sulfonate blends, J. Macromolecules 39 (6) (2006) 2373–2379.
[9] R.K. Nagarele, W. Shin, P.K.S. Singh, Progress in ionic organic-inorganic composite membranes for fuel cell applications, J. Pol. Chem 1 (2009).
[10] Y. Devrim, S. Erkan, N. Bac, I. Ergolu, Preparation and characterization of sulfonated polystyrene/titanium dioxide composite membranes for proton exchange membrane fuel cells, Int. J. Hydrog. Energy 34 (2009) 3467–3475.
[11] M. Johnsi, S.A. Sultanhanirjar, Synthesis of PVDF-PQF-ZrO2 based composite polymer electrolyte for battery applications, Adv. Mater. Res. 598 (June 2014) 275–279.
[12] K.M. Kim, J.C. Kim, K.S. Ryu, Characteristics of PVDF-PQF/TiO2 composite electrolytes prepared by a phase inversion technique using dimethyl acetamide solvent and water non-solvent, Macromol. Mater. Eng. 291 (12) (2006) 1495–1502. A998/A904.
[13] K.M. Kim, N.G. Park, K.S. Ryu, S.H. Chang, Characteristics of PVDF-PQF-TiO2 composite membrane electrolytes prepared by phase inversion and conventional casting methods, Electrochim. Acta 51 (26) (2006) 5636–5644.
[14] V. Aravindan, P. Vockraman, Characterization of SiO2 and Al2O3 incorporated PVDF-PQF based composite polymer electrolytes with Li3PF6/CF3(CF2)3SO3 as J. Polym. Sci. 108 (2) (2008) 1314–1322.
[15] S. Ayasru, S. Dharmalingam, A study of influence on nanocomposite membrane of sulfonated TiO2 and sulfonated polystyrene-ethylene-butylene-polystyrene for microbial fuel cell application, J. Energy 88 (August 2015) 205–208.
[16] K.S. Kumar, S. Rajendran, M.R. Prabhu, A Study of influence on sulfonated TiO2-poly(vinylidene fluoride-co-hexafluoropropylene) nano composite membranes for PEM Fuel cell application, Appl. Surf. Sci. 418 (October 2017) 64–71.
[17] F. Liu, M.R. Mogareh Adeb, K. Li, Preparation and characterization of poly(vinylidene fluoride/PVDF) based ultrafiltration membranes using nano γ-Al2O3, J. Membr. Sci. 366 (1–2) (2011) 97–103.
[18] L. Li, S. Pu, Y. Liu, L. Zhao, J. Ma, J. Li, Particle electretization and levitation in a continuous particle feed and dispersion system with vibration and external electric fields, J. Adv. Powder Technol 29 (9) (2018).
[19] M.K. Schlesinger, M.J. King, K.C. Sole, W.G. Davenport, Extractive Metallurgy of Copper (2011) 13–30.
[20] I. Kim, B.S. Kim, S. Nam, H.J. Lee, H.K. Chung, S.M. Cho, T.H.T. Luu, S. Hyun, C. Kang, Cross-linked poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) gel polymer electrolyte for flexible Li-ion battery integrated with organic light emitting diode (OLED), Materials 11(4) (543) (2018) 1.
[21] S.J. Pehghammadoust, S. Rowshanazamir, M. Anjadi, Review of the proton exchange membranes for fuel cell applications, Int. J. Hydrogen Energy 35 (17) (2010) 9349–9384.
[22] P. Zapata, J.H. Lee, J.C. Meredith, Composite proton exchange membranes from zirconium-based solid acids and PVDF/acylic polyelectrolyte blends, J. Appl. Polym. Sci. 124 (31) (2012) E241–E250.
[23] L. Umnikrishnan, S.K. Nayak, S. Mohanty, G. Sarkhel, Polyethersulfone membranes: the effect of sulfonation on the properties, Polym. Plast. Technol. Eng. 49 (14) (2010) 1419–1427.
[24] N. Miyake, J.S. Wainright, R.F. Savinell, Evaluation of a sol-gel derived Nafion/silica hybrid membrane for polymer electrolyte membrane fuel cell applications: II. Methanol uptake and methanol permeability, J. Electrochem. Soc. 148 (8) (2001) A905–A909.
[25] W. Liu, X.K. Zhang, F. Wu, Y. Xiang, A study on PVDF-HFP gel polymer electrolyte for lithium-ion batteries, IOP Conf. Ser. Mat. Sci. Eng. 213 (1) (2017).
[26] Y. Devrim, S. Erkan, N. Bac, I. Ergolu, Preparation and characterization of Nafion/inorganic nanocomposite membrane electrode assembly prepared by

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ultrasonic coating technique, Int. J. Hydrogen Energy 37 (21) (2012) 16748–16758.

[27] D.W. Shin, K.R. Kang, K.H. Lee, D.H. Cho, J.H. Kim, W.H. Lee, H.M. Lee, Proton conducting, composite sulfonated polymer membrane for medium temperature and low relative humidity fuel cells, J. Power Sources 262 (15) (2014) 162–168.

[28] Y.J. Kim, C.H. Ahn, M.B. Lee, M.S. Choi, Characteristics of electrospun PVDF/SiO2 composite nanofiber membranes as polymer electrolyte, Mater. Chem. Phys. 127 (1–2) (2011) 137–142.

[29] J. Shen, J. Xi, W. Zhu, L. Chen, X. Qiu, A nanocomposite proton exchange membrane based on PVDF, poly(2-acrylamido-2-methyl propylene sulfonic acid), and nano-Al2O3 for direct methanol fuel cells, J. Power Sources 159 (2) (2006) 894–899.

[30] Y. Kim, S.H. Shin, I.S. Chang, S.H. Moon, Characterization of uncharged and sulfonated porous poly(vinylidene fluoride) membranes and their performance in microbial fuel cells, J. Membr. Sci. 463 (1) (2014) 205–214.

[31] I. Rahayu, M. Ariffin, Juliandri, Y.T. Malik, M. Nasir, Synthesis and characterisation of PVDF-co-HFP/sTiO2 composites polymer electrolyte membranes, Mater. Res. Express 6 (12) (2019).