Preparation, characterization and properties of PVDF-g-PAMPS/PMMA-co-PAMPS/silica nanoparticle as a new proton exchange nanocomposite membrane

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HIGHLIGHTS

- PVDF containing vinyl pendent groups was synthesized by a novel strategy.
- The PVDF-g-PAMPS copolymer was synthesized by grafting through RAFT polymerization.
- Nanoparticles as protonic conductor can provide a special pathway for proton transport.
- The high proton conductivity (20 mS/cm at room temperature) was observed for the new PEM.
- The power density as high as 34.3 mW/cm² at peak current density of 140 mA/cm² was observed for the new PEM.

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ABSTRACT

In this study, preparation and characterization of PVDF/PMMA-co-PAMPS/silica nanocomposite membranes as a new proton exchange membrane were investigated. Polyvinylidene fluoride (PVDF) containing pendant sulfonic acid groups was synthesized by grafting through RAFT polymerization of 2-acrylamido-2-methyl-propanesulfonic acid (AMPS) from vinyl pendent groups of already modified PVDF as a macro-monomer. The synthesized PVDF graft copolymer (PVDF-g-PAMPS) was blended with miscible copolymer containing sulfonated segments (PMMA-co-PAMPS) and sulfonic acid functionalized silica nanoparticles in order to achieve high performance nanocomposite proton exchange membrane. It was found that the addition of PMMA-co-PAMPS copolymer resulted in a significant increase in porosity and slight reduction in crystallinity of the nanocomposite membranes, which favored the water uptake and proton transport at ambient temperature. Both the water uptake and the ion-exchange capacity (IEC) of the nanocomposite membranes were increased by increasing silica nanoparticles loading. The maximum proton conductivity was 20 mS/cm at 25 °C for the nanocomposite membrane containing 10% silica nanoparticles. Also, this nanocomposite membrane showed a power density as high as 34.3 mW/cm² at peak current density of 140 mA/cm². The thermal and mechanical properties of these nanocomposite membranes were also studied.

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1. Introduction

Polymer electrolyte membrane fuel cells are one of the promising energy sources because of their high power conversion and environmentally friendly system. Among all kinds of fuel cell technologies, proton exchange membrane fuel cells (PEMFCs) are one of the best candidates for portable applications due to their lower operating temperature, higher power density and lightweight. The technology of PEMFCs could provide clean and efficient energy for stationary, transportation and portable electronics. Recently, polymer electrolyte membrane (PEM) has attracted a considerable attention as a key component in the PEMFCs. The main necessity of a suitable proton exchange membranes are: high proton conductivity and low electron conductivity, high mechanical, thermal and electrochemical stability under operating conditions, low fuel and oxygen permeability and low production cost. Perfluorinated polymer membranes, e.g., Nafion, on account of their excellent chemical and thermal stability and high proton conductivity in the hydrated state have been widely used as the proton exchange membrane in PEMFCs.
membrane in PEMFCs [1]. However, the main limitation of Nafion is its high cost. For this reason, most studies in the field of PEMFCs have been extensively focused on the introducing of new polymeric membranes.

Different strategies have been followed to introduce new polymeric membranes using non-fluorinated polymers as alternative materials [2], blend modification [3] and nanofillers [4]. Non-fluorinated polymers such as poly(arylene ether ketone) [5], poly-sulfone (PSU) [6] or polybenzimidazole (PBI) [7] and their sulfonated counterparts have been extensively studied as alternative materials because of their rigid aromatic backbones which favor high thermal stability, good mechanical strength, and reasonable chemical durability. However, the polyaromatic backbone rigidity and the acidic groups anchored on their main chain prevent the continuous ion transport channels from forming distinct phase-separated structures. To improve the PEM performance, various modification approaches are applied by bulk modification of polymers by vinyl monomers with a strongly anionic sulfonate group. The sulfonic acid groups on side chains grafted onto the polymer main chains have been introduced with ionic monomers by various surface grafting techniques such as high energy irradiation [8] and "living"/controlled radical polymerization (CRP) [9,10]. In another approach, nanofiller materials have been used to modify polymeric membranes in order to make them ideal candidates for PEM. The incorporation of various types of nanofiller to prepare candidate nanocomposite membrane for PEM fuel cells has been shown to be able to enhance membrane properties and improved proton conductivities at low relatively humidity [4]. In addition, the sulfonic acid functionalized nanofillers can be induced the continuous ion transport channels in polymer matrix [4]. Another approach to enhance the membrane performance is polymer blending [3]. The blending of polymers may benefit from the advantages of different material properties and overcome the deficiencies of individual components.

PVDF and its copolymers as the partially fluorinated polymer electrolyte membranes are of great interest due to their improved properties such as high polarity (high dielectric constant), electron withdrawing fluoride atoms in the backbone, excellent thermal and mechanical properties, stability in acidic environment and low costs with comparable electrochemical properties to perfluorinated membranes [11]. According to the fact that there is a great similarity in backbone of the PVDF and perfluorinated polymer membranes, such as Nafion, Aciplex, Flemion and Dow membranes, it seems that PVDF membranes have a promising future for PEMFCs as replacements for the expensive fluorinated membranes. It is expected that the sulfonation of PVDF and its blending with miscible comonomer containing sulfonated segments can produce a strongly acidic blend membrane and enhance the proton conductivity properties of PVDF-based membrane.

In related studies, Kim et al. synthesized (PVDF-co-CTFE)-g-PHEA in which poly(hydroxy ethyl acrylate) (PHEA) side chains were grafted from a (PVDF-co-CTFE) backbone via ATRP using CTFE units as a macroinitiator [12]. Interpenetrating polymer network of copolymer poly(AMPS-co-BAA) with hydrophobic PVDF was synthesized by Zygodło-Monikowska and co-workers. [13]. Moreover, preparation of PVDF-based nanocomposite membranes was demonstrated by Shen and co-workers [14]. After synthesis of poly(2-acylamido-2-methyl propylene sulfonic acid), blend membranes prepared in the presence of nano-sized ceramic fillers [14]. Moreover, Choi et al. reported synthesis of sulfonated poly(styrene-b-methyl methacrylate) (PS-b-PDMA) and is blended with PVDF [15]. Interpenetrating polymer networks combining poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (AMPS) copolymerized with a fluorinated cross-linker and a second fluoropolymer-based network were synthesized according to an in situ synthesis by Delhorbe and co-workers [16].

This paper describes the development of a novel and facile technique to produce PVDF containing pendant sulfonic acid groups by grafting through RAFT polymerization. We take advantage of RAFT method in order to modify PVDF chains with AMPS as a hydrophilic and sulfonated monomer by grafting through method in which PAMPS chains initiated from the carbon–carbon double bond introduced to PVDF chains. The objective of the present study is to prepare a new PVDF/(PMMA-co-PAMPS) blend nanocomposite membranes filled with sulfonic acid functionalized silica nanoparticles for PEMFC applications. We have tried to investigate not only the effect of silica nanoparticles and (PMMA-co-PAMPS) copolymer content on thermal and mechanical properties, but also the discrepancies in characteristic of morphology and proton conductivity behavior of these polymeric nanocomposite membranes by addition of (PMMA-co-PAMPS) copolymer content for PEMFC applications.

2. Experimental

2.1. Materials

PVDF (average Mw = 145,000) was used as polymer matrix. Silica nanoparticles from Sigma with 5-15 nm in diameter were dried under reduced pressure at 70 °C for 24 h before use. Methyl methacrylate (MMA) (Aldrich, 99%), AMPS (Aldrich, 99%), 4-dimethylaminopyridine (DMAP) (Aldrich, ≥99%), N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDAC) (Sigma–Aldrich), chlorosulfuric acid (H2SO3Cl) (Sigma–Aldrich, 99%), acryloyl chloride (AC) (Aldrich, 97%), 4-cyano-4-((p-hydroxybenzothioylthio)pentanoic acid (CTA) (Aldrich, ≥97%), 4,4′-Azobis-(4-cyanovaleic acid) (ACVA) (Aldrich, ≥98%), triethylamine (TEA) (Sigma–Aldrich, ≥99%), 2,2′-azobisobutyronitrile (AIBN) (Aldrich, 98%) and N,N-dimethylformamide (DMF) (Merck, 99.9%) were used as received.

2.2. Synthesis of silica macro-initiator (SiO2-azo)

Silica (0.3 g) was suspended in deionized-distilled water (100 ml) through sonication. DMAP (0.03 g, 2.455 × 10−4 mol) and EDAC (1.91 g, 0.01 mol) were added and stirred for 10 min. Then, ACVA (0.5 g, 0.0017 mol) was added and the resulting suspension was stirred for 48 h at room temperature. After centrifuging, the obtained functionalized silica was washed several times with ethanol and distilled water. The modified silica nanoparticles were then freeze-dried for further use.

2.3. Surface-initiated radical polymerization of AMPS from silica macro-initiator

The radical graft polymerization was performed in a 100 ml lab reactor which was placed in an oil bath thermostated at the desired temperature. SiO2-azo (1 g) was suspended in deionized water (40 ml) and the reactor was degassed and back-filled with nitrogen gas three times, and left under N2. The bath experiment was run by adding deoxygenated AMPS monomer (7 g, 0.034 mol) dissolved in deionized water (10 ml). Then, the reaction temperature was increased to 70 °C and the mixture was stirred at this temperature for 24 h. After polymerization, this suspension was neutralized with 5% NaOH and precipitated with adding excess amount of acetone. The product was purified by an acetone/water mixture three times and dried under reduced pressure at 60 °C.

2.4. Functionalization of silica nanoparticles with chlorosulfonic acid

Sulfonic acid functionalized silica nanoparticles were prepared as previously reported method [17]. Briefly, this modification was
performed in a 50 ml lab reactor which was equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (0.2 ml, 0.003 mol) and a gas inlet tube for conducting HCl gas over an absorbing solution (water). It was charged with silica nanoparticles (0.5 g) and chlorosulfonic acid was added dropwise over a period of 30 min at room temperature and stirred for 30 min. The modified silica nanoparticles were then dried using the freeze-drying machine.

2.5. Hydroxylation of PVDF

Hydroxylated PVDF was prepared as previously procedure [18–21]. Briefly, the PVDF powder was suspended in the aqueous solution of potassium hydroxide (0.5 M) and potassium permanganate (1.0%). The reaction was kept at 60 °C for 15 min. The color of the PVDF powder changed from originally white to black. Then, the powder obtained was moved to the acidic solution of NaHSO3 (1.2%) until it resumed white. The modified PVDF powder was washed with distilled water and put into the deionized water at 25 °C.

2.6. Synthesis of PVDF macro-monomer

PVDF macro-monomer was prepared by the reaction between hydroxylated PVDF (5 g) and acryloyl chloride (13.4 ml, 0.165 mol) in dried NMP (40 ml) in the presence of TEA (2.7 ml, 0.03 mol) in a reactor degassed under nitrogen atmosphere. The bath experiment was run by slow addition of acryloyl chloride and the mixture was stirred at 0 °C for 24 h. The product was precipitated in n-hexane and dried under reduced pressure at 60 °C.

2.7. Grafting through RAFT polymerization of AMPS from PVDF macro-monomer

The post polymerization of PVAF macro monomer was performed in a 100 ml laboratory which was placed in an oil bath thermostated at desired temperature. PVDF macro monomer (1 g) was suspended in an aqueous 1:7 acetic acid/sodium acetate buffer solution (40 ml, pH 5.5) under N2. A desired amount of Si-SO3H was suspended in an aqueous 1:7 acetic acid/sodium acetate buffer solution (40 ml, pH 5.5) under N2. Afterwards, deoxygenated AMPS monomer (4 g, 0.02 mol, dissolved in 10 ml buffer solution), CTA-RAFT (0.171 g, 6.15 × 10−4 mol, dissolved in 1.0 ml dioxane), ACVA (20 mg, 7.13 × 10−2 mmol) were added to the reactor. The reaction temperature was increased to 70 °C; the mixture was stirred at this temperature for 24 h. The obtained PVDF amphiphilic graft copolymer was washed several times with distilled water and dried under reduced pressure at 60 °C.

2.8. Synthesis of (PMMA-co-PAMPS) copolymer

Free radical polymerization was performed in a 100 ml lab reactor. At first, AMPS monomer (1 g, 4.8 mmol, dissolved in 3 ml DMF) and MMA monomer (0.5 ml, 4.8 mmol) were added into the reactor. The reactor was degassed and backfilled with nitrogen for 15 min. Subsequently, AIBN initiator (5.3 mg, 3.21 × 10−2 mmol) was added to start copolymerization. Finally, the (PMMA-co-PAMPS) was precipitated in n-hexane and dried under reduced pressure at 60 °C.

2.9. Preparation of nanocomposite membrane

PVDF-g-PAMPS2 and PMMA-co-PAMPS were added to a 50 ml flask containing DMF. The mixture was stirred on a heating plate at 40 °C for 24 h. A desired amount of Si-SO3H was suspended in DMF and was sonicated for 15 min. Then, the mixture of PVDF-g-PAMPS2 and PMMA-co-PAMPS solution with the mass ratio of 50:50 was added to the silica nanoparticle solution, and the mixture was stirred at 40 °C for 24 h. When the homogenization of the mixture was completed, all nanocomposite membranes were obtained by casting the polymeric solution onto a glass plate and drying at 70 °C for 48 h. The silica loading in the resulting casting mixture was calculated as the mass percent of silica with respect to PVDF-g-PAMPS/PMMA-co-PAMPS. For the preparation of nanocomposite membranes filled with silica nanoparticle, the casting mixtures had Si-SO3H loadings of 5%, 8%, and 10%. The thickness of all membranes was around 70 μm. Fig. 1 display prepared PVDF-based nanocomposite membranes. Designation of the samples and the detailed composition of all membranes are summarized in Table 1.

2.10. Characterization

Fourier-transform infrared spectroscopy (FTIR) was carried out on a Brucker FTIR instrument by averaging 32 scans with a wave number resolution of 4 cm−1. Proton nuclear magnetic resonance spectroscopy (1H NMR) spectra were recorded on a Bruker 400-

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>PVDF-g-PAMPS (g)</th>
<th>PMMA-co-PAMPS (g)</th>
<th>Si-SO3H (g)</th>
<th>DMF (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI</td>
<td>0.225</td>
<td>0.225</td>
<td>–</td>
<td>4.7</td>
</tr>
<tr>
<td>MI1</td>
<td>0.225</td>
<td>0.225</td>
<td>0.022</td>
<td>4.7</td>
</tr>
<tr>
<td>MI11</td>
<td>0.225</td>
<td>0.225</td>
<td>0.036</td>
<td>4.7</td>
</tr>
<tr>
<td>MI111</td>
<td>0.225</td>
<td>0.225</td>
<td>0.045</td>
<td>4.7</td>
</tr>
</tbody>
</table>
The amount of water taken up by the membranes was determined by water uptake measurement. Each membrane was weighed after keeping in distilled water for 24 h at room temperature. The wet membrane was dried to constant weight at 70°C for 48 h. The water uptake of membrane was calculated according to the following Eq. (1).

\[
\text{Water uptake (\%)} = \left( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100
\]  

where \( W_{\text{wet}} \) is the weight of wet membrane and \( W_{\text{dry}} \) is the weight of dried membrane.

### 2.12. Ion exchange capacity (IEC)

The IEC of membranes was measured by titration. The membranes were kept in 2.0 M NaCl solution for 2 days and then the solution was titrated with 0.05 M NaOH solution. The IEC was calculated according to the following Eq. (2).

\[
\text{IEC (meq g}^{-1}\text{)} = \frac{M_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}} (2)
\]

where \( M_{\text{NaOH}} \), \( V_{\text{NaOH}} \) are the mole concentration and volume of the NaOH consumed in the titration and \( W_{\text{dry}} \) is the weight of the dry membranes.

### 2.13. Proton conductivity

Autolab PGSTAT302N Potentiostat-Galvanostat Impedance Analyzer (Ecochemie) was used to obtain ionic conductivity of the membranes under an oscillation potential of 5 mV from 0.1 to 10^3 Hz. The conductivity was calculated as:

\[
\sigma = \frac{L}{RA} (3)
\]

where \( \sigma \), \( A \) and \( L \) are conductivity (S cm^-1), electrode area (cm^2) and membrane thickness (cm), and \( R \) is the bulk resistance of membranes (Ω).

### 2.14. MEA and fuel cell test

The nanocomposite membrane containing 10% sulfonic acid functionalized silica nanoparticles was used to fabricate membrane electrode assembly (MEAs). Pt/C with Pt loading of 0.5 mg/cm^2 was used for both anode and cathode. To prepare the catalyst ink, the mixture of Pt/C and PVDF binder solution was sonicated for 1 h and then was painted onto carbon cloth (E-TEK, HT 2500-W) and dried at 100°C in a conventional oven. The prepared membrane was sandwiched between two gas diffusion electrodes and hot-pressed under a pressure of about 50 kg/cm^2 at 130°C for 5 min. The performances of single cells were tested at 25°C by a FCT 1505 fuel cell testing system (CHINO Inc., Japan). The area of testing fixture was 5 cm × 5 cm and H₂ and O₂ were input with flow rates of 200 and 100 ml/min.

### 3. Results and discussion

#### 3.1. Modification and characterization of silica nanoparticles

The successful synthesis of azo-group-bound silica (SiO₂-azo) and surface initiated radical polymerization of AMPS from silica nanoparticle surface were confirmed by FTIR and TGA analysis. The FTIR spectra of Si-SO₃H and Si-g-PAMPS are shown in Fig. 2. A strong band at about 1100 cm⁻¹ assigned to the stretching vibration of Si–O–Si in the silica [21], was observed in all samples spectra. The stretching vibration of Si–O is appeared at around 800 cm⁻¹. For SiO₂-azo, the characteristic weak vibration bands of the carbonyl and methylene groups appeared at around 1657 and 2925 cm⁻¹, respectively (Fig. 2b). All data indicate that ACVA has been successfully attached onto the surface of silica nanoparticles. The characteristic bands of the polymers can be observed in FTIR spectrum of the polymer-grafted silica nanoparticles (Fig. 2d). For silica/PAMPS hybrid nanoparticles (Si-g-PAMPS in Fig. 2d), the NH band at around 3440 cm⁻¹ has overlapped with the band of OH group located at the surface of silica nanoparticles. The carbonyl group band has appeared at around 1657 cm⁻¹. The bands at around 1113 and 1193 cm⁻¹ can be assigned to the symmetric vibration of the sulfonic group [21]. The aliphatic C–H bands have appeared at about 2850–2950 cm⁻¹ [21]. The intensities of
the bands, that appeared at about 1100, 629 and 3440 cm⁻¹ in the FTIR spectrum of Si-g-PAMPS (Fig. 2d), are significantly lower than those in the FTIR spectrum of Si-SO₃H (Fig. 2c) and SiO₂ (Fig. 2a). These could be attributed to the higher amount of the SO₃H grafted onto the surface of Si-SO₃H (see also TGA results). Consequently, the FTIR spectra showed that the PAMPS polymers and the sulfonic acid group have been successfully grafted to the surface of the silica nanoparticles.

The different weight loss of the modified silica nanoparticles in comparison with the silica nanoparticles confirmed that the surface modification was successful. Fig. 3 shows TGA thermograms of weight loss as a function of temperature for pristine and modified silica nanoparticles. The amount of weight loss of pristine silica nanoparticles is about 2 wt% at 130 °C which is attributed to the evaporation of residual water in the sample. Weight loss of all silica nanoparticles is more than that for the pristine silica nanoparticles. It is clear from this Fig. 3 that the weight loss of the Si-SO₃H nanoparticles is much larger than the Si-g-PAMPS. This observation is attributed to its higher surface modification efficiency. These results are in good agreement with FTIR results, indicating that both PAMPS polymer and sulfonic acid group have been successfully grafted onto the surface of the silica nanoparticles. The weight loss at about 200 °C was observed for SiO₂-azo nanoparticles (Fig. 3), which was attributed to the ACVA attached onto the surface of the silica nanoparticles. The weight loss for Si-SO₃H nanoparticles is more than that for the pristine silica nanoparticles and SiO₂-azo nanoparticles. The weight loss was observed at around 320 °C which could be related to the degradation of PAMPS grafted onto the surface of silica nanoparticles. The difference between the weight loss for the pristine silica nanoparticle and modified silica nanoparticles is attributed to the amount of surface modification. From the TGA curves in conjunction with the graft polymerization recipe, the grafting percentage (Eq. (4)) was calculated to be 17% for PAMPS

\[
G(\%) = \left( \frac{m_{200} - m_{600}}{m_{600}} \right) \times 100
\]

where \(m_{200}\) and \(m_{600}\) indicate the residual weights of the sample used in the TGA at 200 °C and 600 °C, respectively. The results obtained from TGA and FTIR analysis indicate that the sulfonic acid group is grafted onto the surface of silica nanoparticle.

TEM micrographs of sulfonic acid functionalized silica (Si-SO₃H) and Si-g-PAMPS nanoparticles are shown in Fig. 4. The branched network morphology observed for sulfonic acid functionalized silica nanoparticles (Fig. 4a) results from agglomeration of silica nanoparticles, which may indicate that exist van der Waals interparticle interactions exist between the silica nanoparticles and their smaller particle size. As shown in Fig. 4a, most of the Si-SO₃H has diameters less than 5 nm. Whereas, Si-g-PAMPS nanoparticles are hybrid nanoparticles with particle size below 20 nm with a (semi)spherical morphology. Because the amount of PAMPS grafted onto the silica’s surface is relatively low (17%), it seems that the observed hybrid silica nanoparticle size is slightly large. It is suggested that several silica nanoparticles may form a core with PAMPS shell existing around the silica nanoparticles, presumably due to the aggregations of silica nanoparticles caused by the van der Waals interparticle or interparticle termination. In fact, relatively good dispersion and (semi)spherical morphology of the nanoparticles modified with the hydrophilic sulfonated polymeric chains in comparison with the sulfonic acid functionalized silica nanoparticles confirmed that the polymer chains grafted onto the surface of silica nanoparticles can prevent macroscopic aggregation and thereby precipitation of the particles in the polymerization reaction. Therefore, homogeneous nanoparticles with a relatively narrow distribution are observed for the surface modified Si-g-PAMPS hybrid nanoparticles, as shown in Fig. 4b. The modified silica nanoparticles were further characterized by EDX analysis. The EDX analysis show that sulfur content of Si-g-PAMPS and Si-SO₃H is 0.23 at. wt% and 0.49 at. wt%, respectively. In Si-g-PAMPS sample (Fig. 4b), the appearance of carbon peak also confirm the presence of organic PAMPS. The IEC values of 0.36 meq g⁻¹ and 0.98 meq g⁻¹ were obtained for Si-g-PAMPS and Si-SO₃H, respectively. Because of high-efficiency surface
functionalization of the Si-SO$_3$H nanoparticle, the Si-SO$_3$H nanoparticles were employed for the preparation of nanocomposite membrane.

3.2. Synthesis and characterization of (PVDF-g-PAMPS) and PMMA-co-PAMPS

Chemical structure of PVDF, hydroxylated PVDF and PVDF-g-PAMPS were characterized by FTIR analysis. Scheme 1 shows the possible chemical reactions caused by treatment of the PVDF polymer with alkaline solution [18–20]. This alkaline treatment of the PVDF polymer shows great tolerance for a wide variety of functional groups including carbonyl, carbon–carbon double bond, epoxy and hydroxyl. For hydroxylated PVDF sample (PVDF-OH in Fig. 5), the alkaline treatment of PVDF leads to the appearance of new peak at 1604 cm$^{-1}$ which can be attributed to the carbon–carbon double bond unsymmetrical stretching vibrations [18–20]. Furthermore, weak signal of the hydroxyl groups was appeared at around 3445 cm$^{-1}$ [18–20].

Despite the widespread use of alkaline treatment for hydrophilic modification of the PVDF membrane, exploration of the ability of this treatment for grafting hydrophilic and ionic chains onto PVDF chain has not been reported. These carbon–carbon double bonds and the hydroxyl groups were used as active sites for modification of the PVDF chain by direct graft copolymerization via RAFT method. Conversion of the hydroxyl moiety to a vinyl pendant group is a novel strategy to attain the side chain containing pendant sulfonic acid groups onto a PVDF backbone. One of the most common ways to achieve this is by esterifying hydroxylated PVDF with acryloyl chloride. Activation of carbon–carbon double bonds of PVDF backbone under radical polymerization condition is another important goal. As shown in Scheme 2, both vinyl pendant groups and carbon–carbon double bonds in PVDF backbone were considered and used as active sites for grafting through RAFT.

![Scheme 1. Treatment of the PVDF powder with alkaline solution [18].](image-url)
polymerization of AMPS monomer and to improve the grafting density. PVDF-g-PAMPS with two different degree of polymerization (DP) were designed.

FTIR and TGA analysis were used to study the changes in degree of polymerization obtained by different monomer concentrations and polymerization time. The appearance of new peaks at 3440 and 1665 cm\(^{-1}\) are associated to N–H and C=O vibrations of PAMPS, respectively. The vibration peaks at 2941 and 2943 cm\(^{-1}\) result from the asymmetric stretching vibration of CH\(_2\). Furthermore, a series of characteristic peaks of CF\(_2\) groups are also found at 1404, 1072 and 878 cm\(^{-1}\). The stretching vibration of C–F is also observed at 1172 cm\(^{-1}\). As shown in Fig. 5, intensity of characteristic peak at 3440 cm\(^{-1}\), which is originated from the N–H vibrations, increased by increasing concentration of AMPS and polymerization time. According to the results (Figs. 5 and 6), there is a good agreement between the FTIR and TGA results. Weight loss of PVDF-g-PAMPS2 increases by increasing the molar ratio of AMPS and polymerization time. Higher value of thermal degradation in PVDF-g-PAMPS2 in respect to another modified PVDF is attributed to higher grafting of PAMPS and its higher modification efficiency. Difference between the weight loss of the PVDF and modified PVDF is attributed to the amount of PAMPS grafting.

FTIR analysis was used to confirm the chemical structure of the PMMA-co-PAMPS copolymer (Fig. 5e). The broad vibration band at 3420 cm\(^{-1}\) is due to the presence of N–H groups. The sharp peaks at 1725 and 1150 cm\(^{-1}\) are attributed to the carbonyl groups and C–O groups, respectively. The peaks at 1200 and 1050 cm\(^{-1}\) are attributed to the vibration of −SO\(_3\) group. In addition, \(^1\)H NMR analysis was also used to investigate the chemical composition of graft copolymer (PVDF-g-PAMPS) and (PMMA-co-PAMPS) copolymer. \(^1\)H NMR spectra of PMMA-co-PAMPS copolymer is presented in Fig. 7. For both samples, the peaks of solvent (DMSO) appeared at 2.6 and 3.5 ppm. The peaks between 0.8 and 1.5 ppm are assigned to the methine, methylene, and methyl hydrogens, respectively. \(^1\)H NMR spectrum of the PVDF-g-PAMPS2 is also shown in Fig. 7. Characteristic signals for the protons of the methylene groups of PVDF are observed around 2.3 and 2.9 ppm. Molar ratio of the PAMPS grafted on the PVDF backbone was estimated by integrating the methyl peaks (I\(_a\), 1.3 ppm, 6H) corresponding to the methyl groups of AMPS and the methylene group of PVDF backbone (I\(_b\), 2.9 ppm, 2H), according to the Eq. (5).

\[
\text{AMPS\%} = \frac{I_a}{I_a + I_b} \times 100
\]  

The grafting ratio of PAMPS in the PVDF graft copolymer was determined to be 11.2\% on a molar basis. Molar ratio of each monomer in PMMA-co-PAMPS copolymer was also estimated from \(^1\)H
NMR spectra (Fig. 7). The results show that molar ratio of PAMPS and PMMA in copolymer is 60% and 40%, respectively. The results are approximately in agreement with the molar ratio of AMPS and MMA which is used for copolymerization.

3.3. Thermal properties study of the nanocomposite membranes

Highly sulfonic acid functionalized components such as PVDF-g-PAMPS2 and Si-SO3H were used in order to prepare high performance nanocomposite proton exchange membrane for possible use in a PEMFC. It is expected that each of these components as a proton exchanger can help to improve the proton conductivity of proton exchange membranes in fuel cells. In the following discussion, we will focus on some of the most important properties of prepared proton exchange nanocomposite membranes. TGA was employed to study the effect of silica loading on thermal stability of the PVDF-g-PAMPS/PMMA-co-PAMPS blend membranes (Fig. 8). TGA results indicate that the PVDF blend membranes have very good thermal stability. According to the TGA results, decomposition temperature of nanocomposite membranes differs from the PVDF blend membrane and a considerable increase in the thermal stability of all nanocomposite membranes in comparison with the neat blend membrane is observed. Such an improvement in the degradation temperature by addition of silica nanoparticles is attributed to the interactions between polymer matrix and silica surface groups. Further, the silica nanoparticles might strongly hinder the volatility of the pyrolysis products and limit the continuous decomposition of PVDF nanocomposite membrane which is mainly on account of good dispersion of silica nanoparticles, thereby enhancing thermal decomposition temperature. In the present case, TGA analysis does not offer to estimate the content of silica nanoparticles in PVDF-based nanocomposites, because the degradation of PVDF leads to the formation of HF, which degrades the silica nanoparticles [22]. Under such conditions, the observed final char value of the nanocomposites is unreliable.

To evaluate the glass transition temperature (\(T_g\)) of the neat PVDF and its blend, DSC analysis has been carried out. As shown in Fig. 9, \(T_g\) of the PVDF blend membrane increases with addition of PMMA-co-PAMPS copolymer. The midpoint of the inflection in
the heat flow curves shifts to 27.3 °C by the addition of 50 wt% PMMA-co-PAMPS copolymer into the PVDF matrix. The crystallinity of the neat PVDF and its blend were also investigated by DSC. The degree of crystallinity (χ_c) of the blend membrane was calculated by:

\[ \chi_c = \frac{\Delta H_f}{\Delta H_f^0} \phi \]

where \( \Delta H_f \) is the melting enthalpies of pure PVDF and its value is 104.5 J/g [23], \( \Delta H_f^0 \) is the melting enthalpy of the blend sample and \( \phi \) is the weight fraction of PVDF in the blend. The degree of crystallinity calculated from DSC thermograms were 42% and 40.7% for neat PVDF and its blend, respectively. The occurrence of a lower crystallinity degree in the PVDF blend membrane can be due to the addition of PMMA-co-PAMPS copolymer. In fact, this copolymer disrupts the alignments of the PVDF molecular chains during the membranes formation. The increase of the amorphous regions in the PVDF matrix is beneficial for the purpose of achieving higher proton conductivity.

3.4. Morphology

The morphology of the membrane has a fundamental role in the transport of ions across membrane and its conductivity behavior. It has been reported that the increase in pore size and porosity increase the electrolyte or water uptake of the membrane matrix, thereby facilitating transport of ions [24,25]. As shown in SEM image (Fig. 10A1–A3), addition of hydrophilic copolymer resulted in an obvious morphology variation from a very dense structure to a honey comb-like structure. Overall, the addition of hydrophilic PMMA-co-PAMPS not only enhances the amorphous regions in the PVDF matrix, but also improves the membrane porosity and pore structure. Moreover, the SEM micrographs of the PVDF-based nanocomposites show a tendency toward larger average pore size and a broader pore size distribution by the increase of silica nanoparticles loading. This result can be attributed to hydrophilicity of the silica nanoparticles. The porosity of membrane is a key factor to increase the amount of water uptake; however, it is important to point out that an increase in membrane porosity might result in poor mechanical properties of the membrane. This finding suggests that the degree of porosity with the associated water uptake should be optimized to obtain the desired mechanical properties and proton conductivity.

Additionally, SEM imaging of the nanocomposite samples at a higher magnification showed homogeneous dispersion of silica nanoparticles and no silica nanoparticle agglomeration. This observation is more confirmed by the EDX analysis. Presence of sulfur and silicon elements in nanocomposite membrane containing 10% silica nanoparticles was detected and confirmed by EDX and EDX mapping. As shown in EDX mapping image of each element (Fig. 11B), a uniform distribution and high element concentration of Si and S can be clearly observed in the membrane cross-section. The uniform distribution of sulfur element indicates that the current approach is a good route for attaining ideal PEM for PEMFC application. Good dispersion of sulfonic acid groups and silica nanoparticles as proton hopping sites is an important parameter to make the interconnected and continuous ion transport channels in polymer matrix, which ensure an efficient transport of protons in the membranes.

3.5. Ion-exchange capacity and water uptake

The ion exchange capacity and water content of membranes are very important factors that affect proton transport across membranes. It is known that IEC values directly relate to the content of the sulfonic acid groups present in the membrane. The PVDF-based blend membrane shows the IEC value of 0.33 meq g^{-1} and degree of sulfonation (DS) 3.8%. IEC and water uptake of the prepared nanocomposite membranes and Nafion 117 are summarized in Table 2. It is clearly realized that the IEC value of all nanocomposite membranes increases by increasing sulfonic acid functionalized silica nanoparticles loading. Furthermore, PVDF-based blend membrane exhibited a high water uptake because of its porous structure. As shown in SEM images (Fig. 10B–E), the honey comb-like structure and high porosity of these membranes can provide free volumes to absorb water molecules and thereby increasing the water uptake.

The absorbed water can be divided into two groups of bound water and free water [26–28]. The absorbed water by the membrane as a proton carrier and proton hopping sites play a key and complex role in the proton transport phenomena. In fact, the state of absorbed water and its amount are key determinants of the predominant mechanism of proton conduction across membrane. Referring to the literatures [1,4,29], the Grotthuss mechanism and vehicular diffusion as the predominant modes of proton conduction were proposed to describe the proton conduction. In the vehicle mechanism, the proton diffusion across membrane occurs in combination with solvent molecules as proton carriers. Hence, the presence of free volumes and interconnected pore structure is vital to absorb water and the proton transport across proton exchange membrane [26–29]. Rigidity of polymer backbone, absence of free volume and interconnected pore in the dense membranes confine the diffusion and transport of proton in the proton exchange membrane by the vehicle mechanism. Subsequently, it is necessary that membranes have a sufficient water uptake content to play a proton carrier role in vehicle mechanism. Since the water content of membrane decreases in the high temperature, transport of proton together with water molecules decreases. Under such condition, the Grotthuss mechanism is proposed which offer the proton transport through the protons jump from one acidic group to the next through hydrogen bonds. Consequently, proton conduction across proton exchange membrane is mainly continued by Grotthuss mechanism in low humidity and high temperature. Establishing equilibrium between different kinds of water molecules is the key factor that affects the performance of the proton exchange membrane in fuel cell applications. In the presence of
sulfonic acid functionalized silica nanoparticles and sulfonated polymer expect that water molecules mainly aggregate near the hydrophilic sulfonate groups and increase the content of bound water. These combinatory roles of sulfonated and hydrophilic additive make it easy to achieve a desirable proton exchange membrane with high ratio of bound water to the total water which is suitable for different temperature and humidity conditions.

From Table 2, it is also observed that nanocomposite membranes absorb more water than PVDF-based blend membrane. The water uptake increased up to 8% silica nanoparticles content, because the amount of sulfonic acid groups increased by increasing sulfonic acid functionalized silica nanoparticles loading. However, the nanocomposite membrane containing 10% silica nanoparticles showed a decrease in water uptake value. The contradictory effects
of silica nanoparticles on the water uptake behavior have also been reported in the literatures [26,30]. Two contradictory aspects for silica nanoparticles which effect on the water uptake behavior have been offered. All of the related works suggested that increasing water uptake is closely related to hygroscopic effect of silica nanoparticles by providing sites that can absorb water, those being both the silica nanoparticles and the sulfonic acid groups, which help to increase the content of bound water [26,30]. Another considerable aspect explains a cross-linking effect of silica nanoparticles and polymer [26,31]. Together, the crosslinking effect of silica nanoparticle results in reduction of polymer chain mobility (free volume) and the space where absorbed water can be located [26,31]. Therefore, with an increase in sulfonic acid functionalized silica nanoparticles loading, the cross-linking effect is more prominent than the hygroscopic effect. This led to the total decrease in water content, whereas the IEC value of nanocomposite membranes increases.

3.6. Mechanical properties

Wet PVDF-based nanocomposite membranes have been analyzed using stress–strain measurements. The mechanical properties of the PVDF blend membrane and its nanocomposite membranes are shown in Fig. 12 and summarized in Table 2. Tensile results demonstrate that the addition of sulfonic acid

![Fig. 11. (A) EDX spectrum and (B) X-ray mapping of the cross section of nanocomposite membrane containing 10% silica nanoparticles loading.](image)

**Table 2**

**Properties of the membranes.**

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>WU (%) a</th>
<th>IEC (meq g⁻¹) b</th>
<th>Elongation (%) c</th>
<th>Tensile strength (MPa) d</th>
<th>σ (mS cm⁻¹) (at 25 °C)</th>
<th>σ (mS cm⁻¹) (at 80 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 117</td>
<td>22</td>
<td>0.80</td>
<td>36</td>
<td>18</td>
<td>40</td>
<td>72</td>
</tr>
<tr>
<td>M1</td>
<td>153</td>
<td>0.33</td>
<td>19.6</td>
<td>7.20</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>MII</td>
<td>164</td>
<td>0.44</td>
<td>13.20</td>
<td>5.70</td>
<td>9</td>
<td>23</td>
</tr>
<tr>
<td>MIII</td>
<td>181</td>
<td>0.54</td>
<td>11.30</td>
<td>4.30</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>MIV</td>
<td>129</td>
<td>0.56</td>
<td>13.45</td>
<td>6.25</td>
<td>20</td>
<td>32</td>
</tr>
</tbody>
</table>

a Measured under dry conditions.
b Measured WU of the membranes at 25 °C.
c,d Measured IEC of the membranes by titration.
e Measured under wet conditions.
Fictionalized silica nanoparticles causes a reduction in elongation at break in comparison with the neat PVDF blend membrane. The incorporation of sulfonic acid functionalized silica nanoparticles into the polymeric membrane results in a slight decrease in the membrane flexibility and thus leads to decrease in elongation at break. Moreover, tensile results show that the tensile strength of PVDF-based nanocomposite membranes decreases by the addition of 5% and 8% sulfonic acid functionalized silica nanoparticles. However, the nanocomposite membrane containing 10% sulfonic acid functionalized silica nanoparticles showed a higher tensile strength. As expected, the reinforcing effect has been observed only with a good dispersion of silica nanoparticles within the matrix. Hence, the higher tensile strength value of this nanocomposite membrane in respect to the other nanocomposite membranes can be attributed to good dispersion of silica nanoparticles and the effective crosslinker role of silica nanoparticles between polymer chains which provides localized regions of enhanced strength [26,27].

3.7. Proton conductivity

From impedance data, the proton conductivity of all membranes and Nafion 117 is calculated by Eq. (3) and is represented in Table 2. In correlation with the water uptake and IEC results, the proton conductivity of the nanocomposite membranes at room

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**Table 3**

Properties of various PVDF-based nanocomposite membranes.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Nanoparticle (wt%)</th>
<th>Test condition $T$ (°C)</th>
<th>Proton conductivity $\sigma$ (mS cm$^{-1}$)</th>
<th>PEMFC or DMFC performance $P$ (mW cm$^{-2}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF/(PMMA-co-PAMPS)/SiO$_2$</td>
<td>10</td>
<td>25</td>
<td>25</td>
<td>34.3</td>
<td>This work</td>
</tr>
<tr>
<td>PVDF/(PS-b-PMMA)</td>
<td>–</td>
<td>25</td>
<td>4.2</td>
<td>NR</td>
<td>[15]</td>
</tr>
<tr>
<td>PVDF/PAMPS/Al$_2$O$_3$</td>
<td>16</td>
<td>25</td>
<td>13.9</td>
<td>NR</td>
<td>[14]</td>
</tr>
<tr>
<td>PVDF/PMMA-g-PHEA/IDA/H$_3$PO$_4$</td>
<td>–</td>
<td>120</td>
<td>15</td>
<td>NR</td>
<td>[12]</td>
</tr>
<tr>
<td>PSSA/PVDF</td>
<td>–</td>
<td>23</td>
<td>55</td>
<td>52</td>
<td>[32]</td>
</tr>
<tr>
<td>PA/PVDF-PVP80</td>
<td>–</td>
<td>100</td>
<td>37</td>
<td>360</td>
<td>[33]</td>
</tr>
</tbody>
</table>

* Not reported.
temperature increases by increasing sulfonic acid functionalized silica nanoparticle content. The enhancement of proton conductivity in nanocomposite polymer electrolyte membranes has been mainly attributed to the sulfonic acid number density (IEC). In the case of nanocomposite membranes, presence of sulfonic acid functionalized silica nanoparticles provides a higher ratio of accessible sulfonic groups. According to IEC value, it is expected that the higher silica loaded nanocomposite membranes show a higher proton conductivity among the other nanocomposite membranes. Nanocomposite membrane containing 10% sulfonic acid functionalized silica nanoparticles showed higher proton conductivity in comparison with the other nanocomposite membranes. It is suggested that the sulfonic acid functionalized silica nanoparticles as polar and ionic groups can increase the content of bound water in polymer matrix and improve the proton transport in the proton exchange membrane by the Grothuss mechanism in low humidity condition. The proton conductivity of these nanocomposite membranes in the different conditions under dry condition was also investigated (Table 2). It can be observed that these nanocomposite membranes display slightly higher proton conductivity with increasing temperature. These obtained results can be attributed to lack of adequate humidity and its important role in the transport of protons across membrane in high temperatures (as mentioned in Section 3.5). In conclusion, nanocomposite membrane containing 10% sulfonic acid functionalized silica nanoparticles (MIV) showed high proton conductivity and low bulk impedance. Thus, this nanocomposite membrane (MIV) was selected for the fuel cell performance study based on its higher proton conductivity.

3.8. Fuel cell performance test

The nanocomposite membrane containing 10% silica nanoparticles was used in order to evaluate its fuel cell performance in H2/O2 PEM fuel cells. The fuel cell performance of this nanocomposite membrane is shown in Fig. 13. As can be seen this nanocomposite membrane demonstrated a power density of 34.3 mW/cm2 at peak current density of 140 mA/cm2 and 25 °C with 50% RH. Further, the highest open circuit voltage (OCV) was 0.85 V. The comparative performance evaluation of the prepared nanocomposite membrane in respect to the other PVDF-based membranes is given in Table 3.

4. Conclusion

PVDF was modified by grafting through RAFT polymerization of 2-acrylamido-2-methyl-propanesulfonic acid (AMPS) from vinyl pendant groups of already modified PVDF as a macro-monomer. Novel PVDF/(PMMA-co-PAMPS) blend nanocomposite membranes filled with sulfonic acid functionalized silica nanoparticles were prepared by solvent-casting method. 1H NMR, FT-IR, and TGA results confirm the success of the “grafting through” method using RAFT and synthesis of PMMA-co-PAMPS copolymer. It was found that the introducing of PMMA-co-PAMPS copolymer leads to the significant increase in porosity which favored the water uptake and proton transport at ambient temperature. The IEC value and proton conductivity of all nanocomposite membranes increased by increasing sulfonic acid functionalized silica nanoparticle content. Also, the prepared nanocomposite membranes showed high water uptake and significant thermal stability in comparison with the pristine PVDF blend membrane. The nanocomposite membrane containing 10% sulfonic acid functionalized silica nanoparticle showed high proton conductivity (20 mS/cm at 25 °C) and desired properties compared with the other nanocomposite membranes. Moreover, this nanocomposite membrane demonstrated a power density of 34.3 mW/cm2 at peak current density of 140 mA/cm2.

References


