Highly methanol resistant and selective ternary blend membrane composed of sulfonated PVdF-*co*-HFP, sulfonated polyaniline and nafion

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ABSTRACT: Partially sulfonated poly(vinylidene fluoride-co-hexafluoro propylene)/partially sulfonated polyaniline (SPVdF-co-HFP/SPAni) binary blend membranes have shown promising results in terms of low methanol permeability and high membrane selectivity compared to Nafion-117 membrane. However, the proton conductivity and IEC of this binary blend membrane was much lower than Nafion-117. It was found that incorporation of minimal quantity of Nafion within SPVdF-co-HFP/SPAni blend membrane at a constituent weight % ratio of SPVdF-co-HFP:SPAni:Nafion = 50:40:10 induced significant improvements in ion-exchange capacity (IEC), proton conductivity and tensile strength over that of the binary blend membrane. In addition, the SPVdF-co-HFP/SPAni/Nafion ternary blend membrane exhibited much lower methanol permeability, higher membrane and relative selectivities and comparable IEC to Nafion-117. In effect, presence of minimal quantity of Nafion induced significant positive attributes to the ternary blend membrane; and assisted in reaching a balance between material cost and properties. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43294.

INTRODUCTION

Poly(vinylidene fluoride-*co*-hexafluoro propylene) (PVdF-*co*-HFP) is a well-known membrane forming material, possessing extremely low methanol affinity and permeability.[1–6] On the other hand, commercial Nafion® membranes suffer from high methanol affinity and permeability, especially at high methanol concentrations.[7–9] However, Nafion® membranes possess much superior proton conductivity and ion-exchange capacity (IEC) compared to PVdF-*co*-HFP membrane.[7,10–12] As a result, although PVdF-*co*-HFP possesses low methanol permeability, its low proton conductivity results in it exhibiting low membrane selectivity ratio (i.e., the ratio between proton conductivity and methanol permeability). Commercial Nafion® membranes too, by virtue of possessing high methanol permeability, exhibit low membrane selectivity ratio. In this respect, it should be noted that a polymer electrolyte membrane (PEM) in direct methanol fuel cell (DMFC) should possess high membrane selectivity ratio.[13] Another important consideration for PEMs is their cost, and commercial Nafion® membranes are very expensive. Therefore, alternative membrane materials which possess higher membrane selectivity ratio and are comparatively cheaper than Nafion® are required to be investigated.

A variety of such alternative membrane materials have been reported over the years by investigators, including the authors of this work.[14–30] For example, Zhang *et al.* reported low methanol permeable Nafion composite membranes with multiple layers of chitosan and silicotungstic acid.[14] They obtained a 47% reduction in methanol permeability, accompanied by a simultaneous 22% reduction in proton conductivity, compared to pristine Nafion membrane. As a result the composite membrane produced ∼18% improvement in membrane selectivity. Similarly, Cozzi *et al.* reported a methanol resistant titanium oxide/Nafion composite membrane which exhibited high IEC and proton conductivity.[17] Paneri *et al.* fabricated a PEM consisting of laminated graphene oxide nanoplatelets, which exhibited reduced methanol permeability at high methanol concentration.[18] Zhao *et al.* achieved high membrane selectivity of the order of ∼10^4 upon utilization of sulfonated poly(arylene ether ketone) membrane decorated with alternative layers of polyaniline (PAni) and phosphotungstic acid.[22] Li and Zhang developed Nafion membrane modified with 3,4-ethylenedioxy-thiophene which exhibited a reduction in methanol permeability from 30 to 72%, and a simultaneous reduction in proton conductivity from 4 to 58%, compared to Nafion-117 membrane.[31] However, majority of the reported works so far either

deals with modification of costly Nafion membrane (present as the major membrane component), or alternative membrane materials which require complex and expensive synthetic and fabrication routes. As a result, although the PEM properties of the modified or alternative membranes get enhanced, however, the cost of the membrane remains high. Other works targeted at reducing the membrane cost often suffer from low PEM performance. Therefore, the performance to cost ratio remains much low compared to that required for fruitful commercialization of DMFC.

In our laboratory, the prime focus has been to develop various low cost and high performing membrane materials for application in DMFCs. Partially sulfonated polymers PVdF-co-HFP (SPVdF-co-HFP) and polyaniline (SPAni) have been two such prospective and cheaper materials.[25–28] For instance, SPVdF-co-HFP/SPAni (60/40 w/w) blend membrane produced higher water uptake (WU), water swelling ratio (SR) and membrane selectivity ratio, and lower methanol uptake (MU) and methanol permeability, compared to Nafion-117 membrane.[26,27] On the other hand, Nafion/SPAni (70/30 w/w) blend membrane exhibited higher WU, SR, IEC and membrane selectivity ratio, and lower MU and methanol permeability, compared to Nafion-117 membrane.[28]

It should be noted that for effective fabrication of a good alternative PEM material, striking an optimized balance between membrane cost and membrane properties is critically important. Therefore, based on the above observations, it was intuited that incorporation of a minimal quantity of Nafion within SPVdF-co-HFP/SPAni blend membrane can bring about a balance between cost and properties of the membrane. In this work, we demonstrate: (a) fabrication of SPVdF-co-HFP/SPAni/Nafion ternary blend membrane, consisting of minimal quantity of expensive Nafion; and (b) the resulting improvements obtained over the SPVdF-co-HFP/SPAni (60:40) and the Nafion/SPAni (70:30) binary blend membranes, as well as, the pristine Nafion-117 and the pristine SPVdF-co-HFP membranes.

EXPERIMENTAL

Materials

Aniline (Ani), ammonium persulfate (APS) and PVdF-co-HFP (Mw: 455,000) were purchased from Sigma Aldrich. Reagent grade HCl was purchased from Loba Chemie. CSA, methanol, acetone, 1,2-dichloroethane and NMP (N-methyl-2-pyrrolidone) were obtained from Merck Millipore India. Nafion-117 membrane was bought from M/S Anabond Synergy Fuel Cell India. All the chemicals were used as received. De-ionized (DI) water was used for all the experiments.

Instruments Used

Proton conductivities were determined using a Gamry Potentiostat-600 instrument. Methanol permeability analyses were conducted by using an Optizen UV-vis spectrophotometer. Scanning electron micrographs (SEMs) were recorded using a Zeiss Scanning Electron Microscope. Tensile strengths of the membrane were determined using a Universal Tensile Testing Machine (Nexygen plus, Lloyd Instruments), following ASTM D 882-02 procedure. For this purpose, a 5 T tensiometer was

used. The analyses were conducted using a crosshead speed of 5 mm min^{-1} and a temperature of 25°C.

Polymerization of Aniline

PAni was oxidatively synthesized from 0.1M Ani monomer (dissolved in acidified aqueous solution), using 0.1M APS as the oxidant. The polymer obtained was filtered and vacuum dried.[32]

Partial Sulfonation of PAni and PVdF-co-HFP

Details regarding partial sulfonation procedures of PAni and PVdF-co-HFP have been reported previously.[25,26] In brief, vacuum-dried granular PVdF-co-HFP was sulfonated by using CSA under a continuous stirring condition at 60°C for 7 h. Black pellets obtained were then collected and washed with 1,2-dichloroethane, 100% methanol and water, and finally vacuum-dried at 60°C.[25] On the other hand, vacuum-dried PAni granules were sulfonated by CSA at 80°C for 5 h with constant stirring. This solution was then added drop-wise to 200 mL methanol at 0 to 5°C, followed by addition of 100 mL acetone. The resulting green powder precipitate was filtered, washed and vacuum-dried.[26] SPAni, having a degree of sulfonation (DS) of ~29%, and SPVdF-co-HFP, having a DS of ~31%, have been utilized in this work.

Preparation of Ternary Blend Membrane

The SPVdF-co-HFP/SPAni/Nafion ternary blend membrane was fabricated using a constituent weight % ratio of SPVdF-co-HFP:SPAni:Nafion = 50:40:10. Details regarding blending and membrane casting procedures have been described previously.[26,28] In brief, the abovementioned ratio of the polymers was dissolved in NMP (under stirring) at 60°C. The resulting blend solution was then casted on a flat glass plate, and kept at 80°C for drying.

Pre-Treatment of the Membrane

The ternary blend membrane was pre-treated by first immersing into a 5M H$_2$O$_2$ solution. This was followed by treating the membrane with a mixture of water and H$_2$SO$_4$ (7:3) for 2 h under a continuous stirring condition. Finally, the membrane was neutralized by washing with DI water and kept in an oven under a constant temperature of 80°C.[33]

Water Uptake, Water Swelling Ratio, Methanol Uptake, ion-Exchange Capacity, Methanol Permeability, Proton Conductivity, and Membrane Selectivity Ratio

WU and SR analyses were carried out at 20, 40, 60, and 80°C temperatures; while MU and methanol permeability analyses were performed at 2M, 4M, 6M, and 8M concentrations of methanol in aqueous solutions, at a temperature of 20°C. IEC and proton conductivity were measured at room temperature (i.e., 20°C). All these analyses we carried out following the same procedure and mathematical expressions as described previously.[24–28]

In brief, WU and MU analyses of the membranes were performed on 2 × 2 cm^2 cut pieces. The weights of the vacuum-dried pieces (W_{dry}) were first measured and noted. The pieces were then dipped in DI water/aqueous methanol solutions for 24 h. The weights of the wet pieces (W_{wet}) were then measured after wiping off the unabsorbed liquid. The %liquid uptake

(i.e., %WU and %MU) values of the membranes were determined from the following eq. (1):

$$\%\text{Liquid uptake} = \left(W_{\text{wet}} - W_{\text{dry}}\right) \times 100/W_{\text{dry}} \qquad (1)$$

The %SR values were determined from the differences in the thicknesses obtained for 2×2 cm^2 membrane cut pieces before (T_{dry}) and after (T_{wet}) soaking in DI water. The %SR values were calculated from the following eq. (2):

$$\%\text{SR} = \left(T_{\text{wet}} - T_{\text{dry}}\right) \times 100/T_{\text{dry}} \qquad (2)$$

The IEC analysis of the membranes was performed on 2×2 cm^2 membrane cut pieces by adopting the conventional titration technique. At first, the vacuum-dried pieces were acidified by soaking in H$_2$SO$_4$ (1M) solution for 24 h. This was followed by washing with distilled water to remove the excess acid. Then the H$^+$ ions attached to the membrane pieces were replaced by Na$^+$ ions by treating the acidified membrane pieces with NaCl (1M) solution (50 mL) for 24 h at 40°C. The replaced H$^+$ ions, remaining in the solution, were quantified by titrating with 0.01N NaOH solution using phenolphthalein indicator. The IEC values in meq g^{-1} were calculated from the following eq. (3):

$$\text{IEC} = V_{\text{NaOH}} \times S_{\text{NaOH}}/W_{\text{dry}} \qquad (3)$$

where, V_{NaOH} and S_{NaOH} are the volume and strength, respectively, of the NaOH solution utilized.

The proton conductivities (σ) of the membranes, having thickness (T) and cross-sectional area (A), were analyzed from their respective impedance values from the following eq. (4):

$$\sigma = T/RA \qquad (4)$$

where the resistance value obtained from the low intersect of the high frequency semi-circle on a complex impedance plane with the real (Z) axis has been symbolized by R.

The methanol permeability analysis of the membranes were performed in a two-chambered glass diffusion cell, in which one chamber (chamber 'a') was filled with aqueous methanol solution (2M, 4M, 6M, or 8M) while the other chamber (chamber 'b') was filled with pure water. A mixture of sodium nitroprusside, potassium ferrocyanide and NaOH was used as the chromogenic reagent. The permeability values were determined from the changes in the absorbance value of the aliquots taken from chamber "b" by UV-vis spectroscopy. The following eq. (5) was used for this purpose:

$$-\ln\left(1 - 2C_b/C_a\right) = 2ADK\left(t - t_0\right)/lV_b \qquad (5)$$

where, the concentrations of aqueous methanol solutions in chambers "a" and "b" have been presented by C_a and C_b, respectively; the methanol diffusivity, partition coefficient and permeability of the membranes have been presented by D, K, and DK, respectively; the area of the membrane available for methanol permeation and the thickness of the membrane have been presented by A and l, respectively; the initial time and the time values when aliquots were withdrawn for analysis have been presented by t_0 and t, respectively, and the volume of the chamber "b" has been presented by V_b.

The membrane selectivity ratios of the membranes at different methanol concentrations were determined from their respective proton conductivity and methanol permeability (at different methanol concentrations) values by using the following eq. (6):

$$\text{Membrane selectivity}_{M,x} = \text{Proton conductivity}_M$$
$$/\text{Methanol permeability}_{M,x} \qquad (6)$$

where, M represents a given membrane material and x denotes a given methanol concentration.

The relative selectivity ratios of a membrane at different methanol concentrations were determined from the membrane selectivity value of that membrane at a particular methanol concentration and the membrane selectivity value of Nafion-117 at the same methanol concentration by using the following eq. (7):

$$\text{Relative selectivity}_{M,x} = \text{Membrane selectivity of a membrane}_{M,x}$$
$$/\text{Membrane selectivity of Nafion-117}_x \qquad (7)$$

where, M represents a given membrane material and x denotes a given methanol concentration.

RESULTS AND DISCUSSION

Analysis of Water Uptakes and Water Swelling Ratios of the Membranes

PVdF-*co*-HFP is a hydrophobic copolymer.[2,4,34] However, it can be rendered hydrophilic by incorporation of –SO$_3$H groups within its chemical structure.[25] On the other hand, PAni is a hydrophilic polymer;[35–38] and incorporation of –SO$_3$H groups within its chemical structure renders it even more hydrophilic.[26–28] As a result, the ternary blend membrane, consisting of SPVdF-*co*-HFP and SPAni as the major constituents, exhibited a high %WU value of 22 at 20°C [Figure 1(a)]. Furthermore, the %WU capacity of the ternary blend membrane got continuously enhanced with increasing temperature to values of 22.9 at 40°C [Figure 1(b)], 23.8 at 60°C [Figure 1(c)], and 25 at 80°C [Figure 1(d)]. While comparing with the other membranes reported in this work, this ternary blend membrane exhibited higher %WU capacity than the pristine Nafion-117 and the pristine SPVdF-*co*-HFP membranes at all studied temperatures (Figure 1). This enhancement can be attributed to the presence of SPAni within the blend membrane, as can be evident from the corresponding higher %WU values exhibited by the SPVdF-*co*-HFP/SPAni (60:40) and the Nafion/SPAni (70:30) blend membranes over that of the pristine SPVdF-*co*-HFP and the pristine Nafion membranes, respectively (Figure 1).[26,28] In addition, the ternary blend membrane exhibited equal %WU capacity to that of the SPVdF-*co*-HFP/SPAni (60:40) blend membrane at 20°C [Figure 1(a)]. However, the %WU values of the ternary blend membrane got superior to that the SPVdF-*co*-HFP/SPAni (60:40) blend membrane at higher temperatures of 40°C [Figure 1(b)], 60°C [Figure 1(c)], and 80°C [Figure 1(d)]. This particular result can be attributed to the presence of 10 wt % Nafion within the ternary blend membrane. However, the %WU capacity exhibited by the ternary blend membrane was found to be lower than that of the Nafion/SPAni (70:30) blend membrane at all studied temperatures (Figure 1); owing to the minor presence of Nafion within the ternary blend membrane (i.e., 10 wt %), as compared to the Nafion/SPAni (70:30) blend membrane (i.e., 70 wt %).
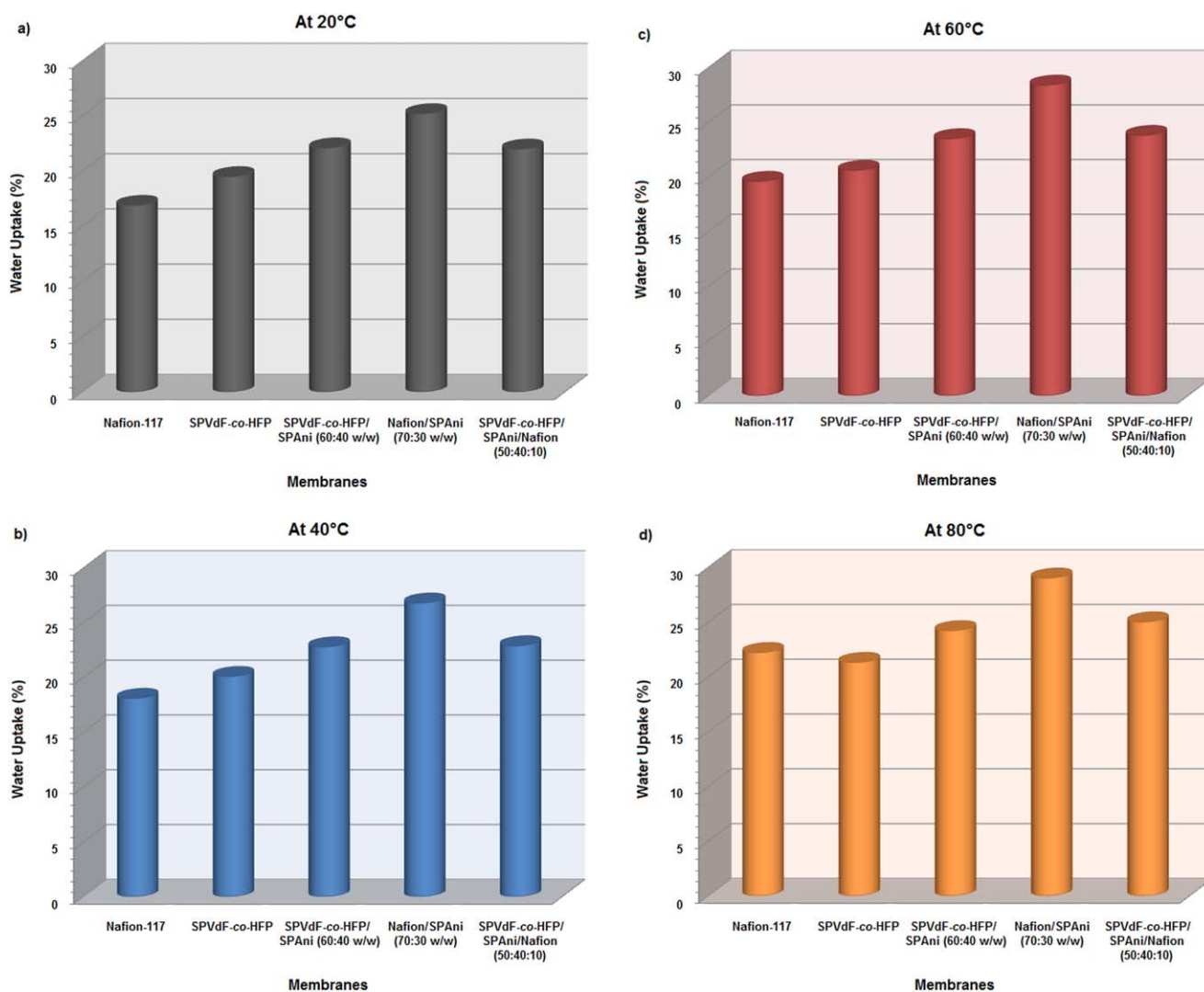
Figure 1. %WUs of the membranes at (a) 20°C, (b) 40°C, (c) 60°C, and (d) 80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A membrane, upon absorption of water, swells; a measure of which gets reflected in its increased thickness. Therefore, in effect, the extent of swelling of a membrane is proportional to the amount of water absorbed by the membrane material. In this work too, the %SR values were found to be proportional to that of the %WU values of the membranes. As a result, the various trends observed while analyzing the %WU values of the membranes at different temperatures were also observed while analyzing their %SR values at those temperatures (Figure 2).

Analysis of Methanol Uptakes of the Membranes
Nafion, as a material, is known to possess high affinity towards methanol.[7,39] This, in turn, gets reflected in the highest %MU values exhibited by Nafion-117 membrane at all methanol concentrations (Figure 3). The pristine SPVdF-co-HFP, by virtue of having lower affinity towards methanol, exhibited lower %MU compared to the pristine Nafion-117 membrane at all methanol concentrations (Figure 3).[25] On a similar note, the Nafion/SPAni (70:30) blend membrane exhibited higher %MU than the SPVdF-co-HFP/SPAni (60:40) blend membrane at all methanol

concentrations (Figure 3).[26,28] However, the role of SPAni in reducing the MUs of the blend membranes can be easily realized upon comparing the %MU values of the pristine Nafion-117 with the Nafion/SPAni (70:30) blend membrane and of the pristine SPVdF-co-HFP with the SPVdF-co-HFP/SPAni (60:30) blend membrane (Figure 3).[26,28] From the above discussion, the %MU exhibited by the present ternary blend membrane can be easily justified. The ternary blend membrane produced lower %MU than the pristine Nafion-117, the pristine SPVdF-co-HFP and the Nafion/SPAni (70:30) blend membrane at all methanol concentrations (Figure 3). However, its %MU is slightly higher than that exhibited by the SPVdF-co-HFP/SPAni (60:40) blend membrane at all methanol concentrations, owing to the presence of methanophilic Nafion as a membrane co-constituent (Figure 3).

Analysis of the IECs of the Membranes
The presence of $-SO_3H$ groups in Nafion-117 is responsible for imparting in it an IEC of 0.8 meq g^{-1} (Figure 4). The pristine SPVdF-co-HFP, by virtue of possessing a %DS of ~31, exhibited
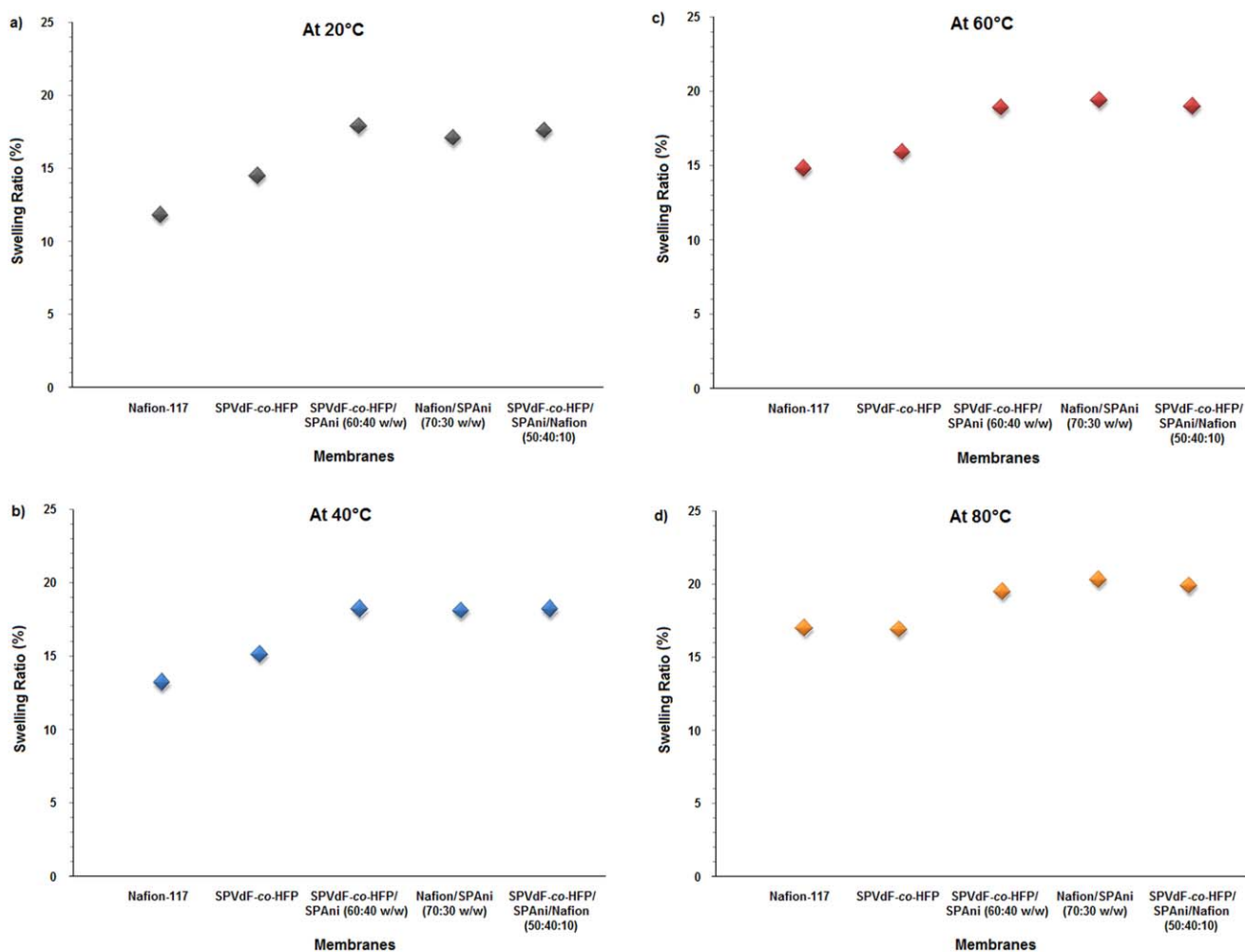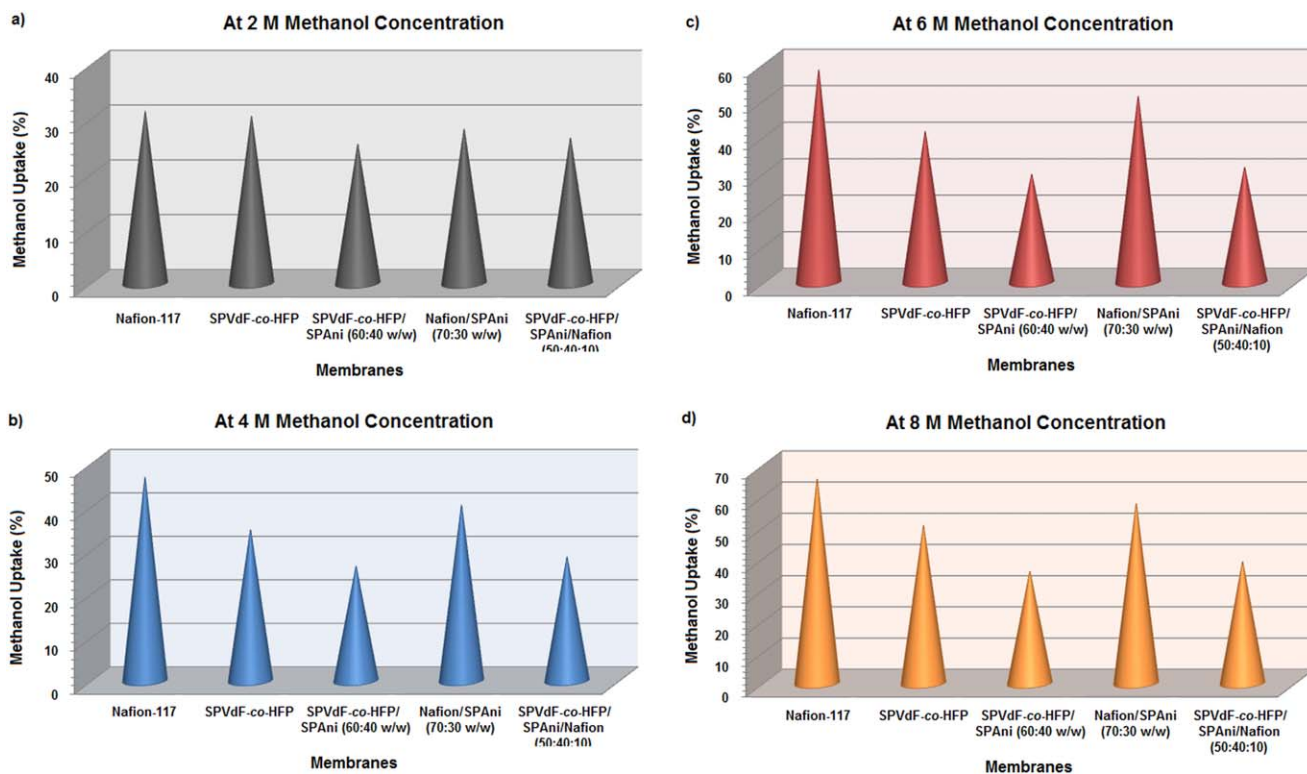
Figure 2. %SRs of the membranes at (a) 20°C, (b) 40°C, (c) 60°C, and (d) 80°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

an IEC of 0.41 meq g^{-1}. However, the SPAni used in our study possesses two ion-exchange sites, that is, incorporated –SO$_3$H groups (%DS of ~29) and lone pair of electrons on N-atoms present in each repeating unit. As a consequence, presence of SPAni as a co-constituent in the Nafion/SPAni (70:30) blend membrane resulted in enhancement of the IEC value from 0.8 meq g^{-1} to 1.18 meqg^{-1} (Figure 4).[28] Similarly, presence of SPAni increased the IEC value from 0.41 meq g^{-1} (pristine SPVdF-co-HFP membrane) to 0.71 meq g^{-1} (SPVdF-co-HFP/SPAni (60:40) blend membrane) (Figure 4).[26] In addition, the inherent higher ion-exchange capacity of Nafion resulted in increasing the IEC value of the ternary blend membrane (i.e., 0.76 meq g^{-1}) over that of the SPVdF-co-HFP/SPAni (60:40) blend membrane (Figure 4).

Analysis of Methanol Permeabilities, Proton Conductivities, and Membrane Selectivity Ratios of the Membranes
The methanol permeability values obtained for the different membranes under consideration followed the same trend as observed for the determined %MU values (Table I). The ternary blend membrane exhibited lower methanol permeability at all four methanol concentrations (particularly at higher methanol

concentrations), compared to that observed for the pristine Nafion-117, the pristine SPVdF-co-HFP and the Nafion/SPAni (70:30) blend membranes. Moreover, the higher methanol affinity of Nafion resulted in the Nafion/SPAni (70:30) blend membrane exhibiting higher methanol permeability than the SPVdF-co-HFP/SPAni (60:40) blend membrane.[26,28,39] The methanol-channel blocking effect caused by incorporation of SPAni as a membrane co-constituent can be observed while comparing the methanol permeability values of the pristine Nafion-117 membrane with the Nafion/SPAni (70:30) blend membrane and of the pristine SPVdF-co-HFP membrane with the SPVdF-co-HFP/SPAni (60:40) blend membrane (Table I).[26,28] Similar channel/pore-blocking phenomena have been reported earlier via formation of blend and composite membranes.[24,27,40–42] However, the ternary blend membrane was found to possess slightly higher methanol permeability (at all methanol concentrations) compared to the SPVdF-co-HFP/SPAni (60:40) blend membrane, owing to the presence of methanophilic Nafion as a membrane co-constituent. Furthermore from the SEM images it can be observed that pristine SPVdF-co-HFP membrane possessed a porous morphology [Figure 5(a)], which got significantly reduced in the SPVdF-co-HFP/SPAni (60:40) blend membrane
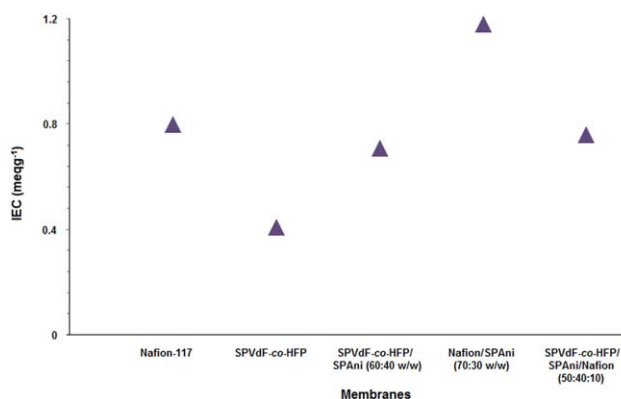
Figure 3. %MUs of the membranes at (a) 2*M*, (b) 4*M*, (c) 6*M*, and (d) 8*M* aqueous methanol concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[Figure 5(b)]. However, incorporation of 10 wt % Nafion within this blend membrane resulted in reappearance of pores [Figure 5(c)]. It can thus be explained that the ternary blend membrane, possessing a more porous morphology compared to the SPVdF-*co*-HFP/SPAni (60:40) blend membrane, exhibited higher methanol permeability compared to the latter. Similarly, since the pores regenerated within the ternary blend membrane were much smaller in size and density than the pristine SPVdF-*co*-HFP membrane; therefore, it exhibited much lower methanol permeability compared to the pristine membrane.

Nafion possess a high proton conducting ability; although it suffers from high methanol permeability. Therefore, it is a challenge for the researchers to fabricate membranes which can hinder permeation of methanol through it, while maintaining a proton conductivity value comparable to that exhibited by Nafion. SPAni is a good proton conducting material, by virtue of possessing (a) incorporated –SO$_3$H groups, (b) presence of lone pair of electrons on the *N*-atoms, and (c) presence of extended conjugated bonds.[43,44] Therefore, its incorporation resulted in increasing the proton conductivity value of SPVdF-*co*-HFP/SPAni (60:40) blend membrane (i.e., 6.78×10^{-3} S cm^{-1}) over that of the pristine SPVdF-*co*-HFP membrane (3.75×10^{-3} Scm^{-1}) [Figure 6(a)].[26] In addition, the ternary blend membrane, by virtue of possessing highly proton conducting Nafion as a co-constituent, resulted in an enhanced proton conductivity of 8.81×10^{-3} Scm^{-1}; which although is lower than that of the pristine Nafion (i.e., 3.02×10^{-2} Scm^{-1}), is higher than that exhibited by the Nafion/SPAni (70:30) blend membrane (i.e., 7.21×10^{-3} Scm^{-1}) [Figure

6(a)]. The impedance plot obtained for the ternary blend membrane has been presented in Figure 6(b).

Presence of PAni and SPAni as co-constituents of blend membrane have been reported to produce high membrane selectivity ratios.[23,45] It was pleasing to observe that the reported ternary blend membrane exhibited higher membrane selectivity ratio, at all methanol concentrations, compared to the pristine Nafion-117, the pristine SPVdF-*co*-HFP and the Nafion/SPAni (70:30) blend membranes (Table II). Moreover, the membrane selectivity ratio exhibited by the ternary blend membrane was higher than the SPVdF-*co*-HFP/SPAni (60:40) blend membrane at higher methanol concentrations of 4*M*, 6*M*, and 8*M* (Table II).

Figure 4. IECs of the membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
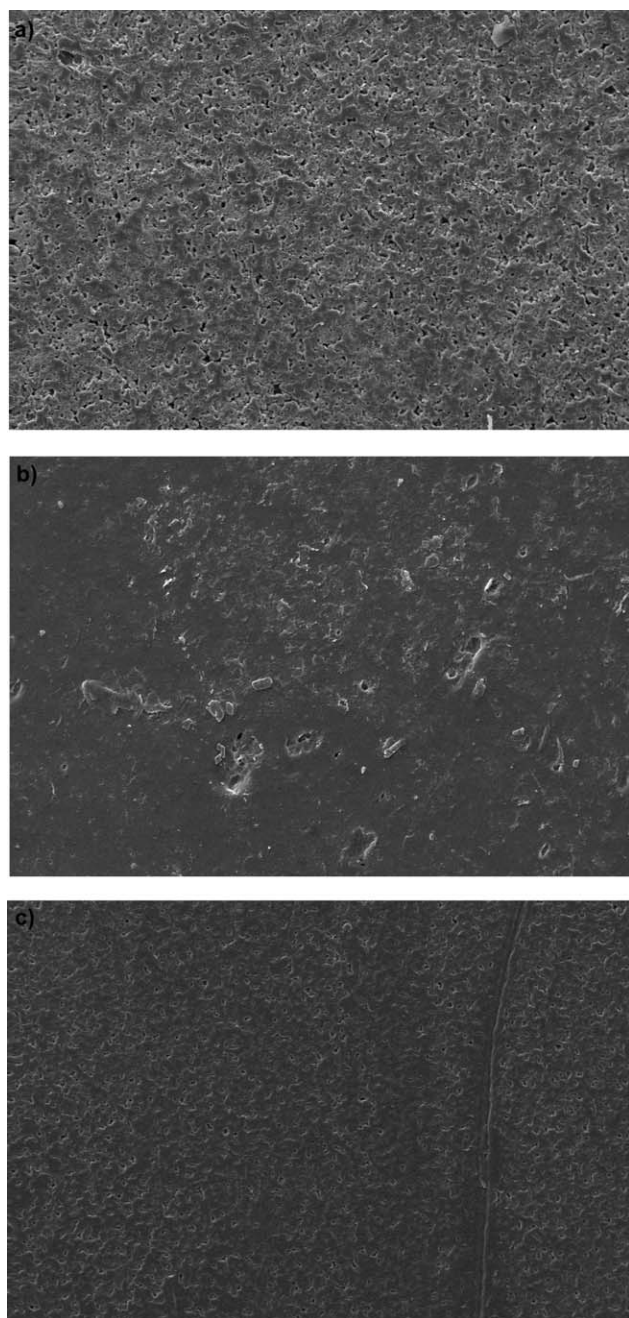
Figure 5. SEM images of (a) pristine SPVdF-*co*-HFP, (b) SPVdF-*co*-HFP/SPAni (60 : 40), and (c) ternary blend membranes. (Scale: 10 μm; Magnification: 2000×).
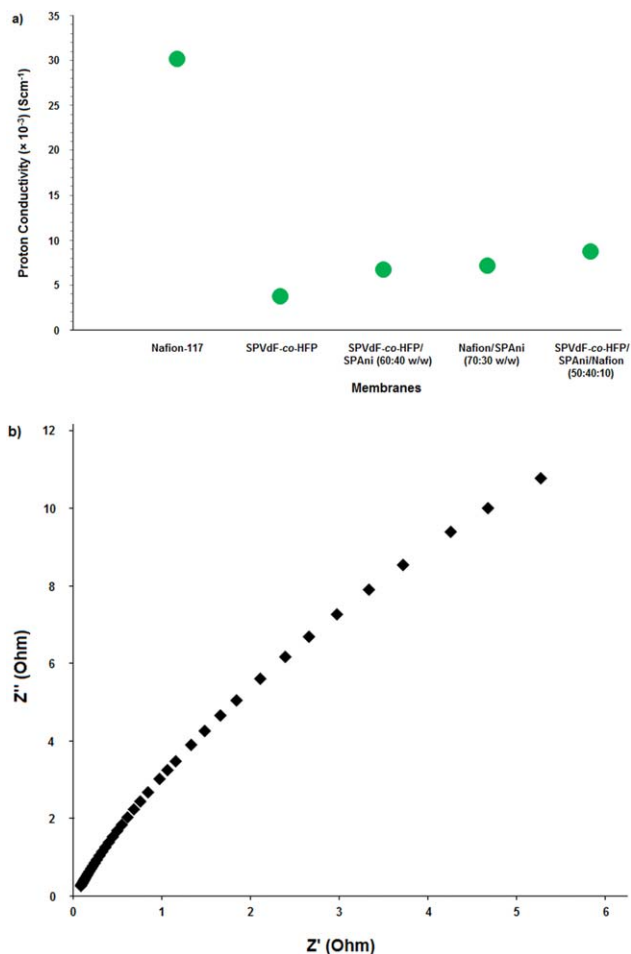
Figure 6. (a) Proton conductivities of the membranes and (b) impedance plot obtained for the ternary blend membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

These enhancements of the membrane selectivity ratio exhibited by the ternary blend membrane are a result of the corresponding enhancement of its proton conducting ability, while maintaining its low methanol permeability. In addition, while comparing the relative selectivity ratios (i.e., the ratio of the selective exhibited by a membrane to that exhibited by Nafion-117 membrane) of the different membranes at different molar concentrations of aqueous methanol, it was observed that all the fabricated SPVdF-*co*-HFP based membranes exhibited the highest relative selectivity at 4*M* methanol concentration and

Table I. Methanol Permeabilities of the Membranes at 20°C, Using 2*M*, 4*M*, 6*M*, and 8*M* Methanol Concentrations

Membranes	Methanol Permeability (cm^2 s^{-1})			
	2*M*	4*M*	6*M*	8*M*
Nafion-117	1.22×10^{-6}	4.56×10^{-5}	9.87×10^{-5}	3.21×10^{-4}
SPVdF-*co*-HFP	2.51×10^{-7}	5.62×10^{-6}	2.49×10^{-5}	6.10×10^{-5}
SPVdF-*co*-HFP/SPAni (60 : 40 w/w) blend	1.16×10^{-8}	5.12×10^{-8}	1.99×10^{-7}	6.45×10^{-7}
Nafion/SPAni (70 : 30 w/w) blend	9.12×10^{-8}	6.70×10^{-6}	5.25×10^{-5}	8.21×10^{-5}
SPVdF-*co*-HFP/SPAni/Nafion (50 : 40 : 10) blend	1.64×10^{-8}	5.91×10^{-8}	2.45×10^{-7}	7.89×10^{-7}

Table II. Membrane Selectivity Ratios of the Membranes at 20°C, Using 2M, 4M, 6M, and 8M Methanol Concentrations

Membranes	Membrane selectivity ratio (Ss cm^{-3})			
	2M	4M	6M	8M
Nafion-117	2.47×10^4	6.62×10^2	3.05×10^2	9.40×10^1
SPVdF-co-HFP	1.49×10^4	6.67×10^2	1.50×10^2	6.14×10^1
SPVdF-co-HFP/SPAni (60 : 40 w/w) blend	5.84×10^5	1.32×10^5	3.40×10^4	1.05×10^4
Nafion/SPAni (70 : 30 w/w) blend	7.90×10^4	1.07×10^3	1.37×10^2	8.78×10^1
SPVdF-co-HFP/SPAni/Nafion (50 : 40 : 10) blend	5.37×10^5	1.49×10^5	3.60×10^4	1.12×10^4

that the ternary blend membrane produced the highest relative selectivity among all the membranes at high methanol concentrations (i.e., 4M, 6M, and 8M) (Table III).

Analysis of Tensile Strengths of the Membranes

The ternary blend membrane exhibited considerable amount of tensile strength (i.e., 9.1 MPa), which is superior to that exhibited by the SPVdF-co-HFP (60:40) blend membrane (Figure 7). This enhancement can be attributed to the presence of Nafion within the blend membrane. It should be noted in this respect, that the tensile strength of pristine Nafion (i.e., 12.79 MPa) is much higher than that of the pristine SPVdF-co-HFP (i.e., 10.43 MPa), resulting in a higher tensile strength of the Nafion/SPAni (70:30) blend membrane (i.e., 10.17 MPa) compared to the SPVdF-co-HFP/SPAni (60:40) blend membrane (i.e., 8.58 MPa) (Figure 7).

**Analysis of Membrane Cost and Rationale behind Fabrication of the Ternary Blend Membrane**

PVdF and its copolymer (PVdF-co-HFP) are widely reported low cost membrane materials.[5,15,46–48] Similarly, PAni is also a low cost polymer.[49,50] Therefore, blend membrane composed of SPVdF-co-HFP and SPAni should be of much lower cost compared to that of the highly expensive commercial Nafion-117 membrane. Nevertheless, certain critical PEM properties, such as IEC and proton conductivity, exhibited by SPVdF-co-HFP/SPAni binary blend membrane are much inferior compared to those obtained for commercial Nafion-117 membrane. However, other PEM properties, such as WU, MU, methanol permeability,

and membrane selectivity, of the binary blend membrane exhibited improvements over that of commercial Nafion-117 membrane.

Since Nafion is a very costly material, however, with good PEM properties; therefore, it was intuited that judicious incorporation of Nafion within the SPVdF-co-HFP/SPAni binary blend membrane should result in a PEM with properties which are significantly improved over that of the SPVdF-co-HFP/SPAni binary blend membrane and comparable or improved over that of commercial Nafion-117 membrane. In this respect, it should also be kept in mind that although incorporation of higher amount of Nafion within the blend membrane will result in much superior PEM properties, however the cost of the membrane will also simultaneously increase substantially. Therefore, in order to realize significant membrane properties while keeping the cost of the membrane as low as possible, the ternary blend membrane constituting 10 wt % of Nafion was fabricated. Higher amount (>10 wt %) of incorporated Nafion resulted in a membrane that suffered from (a) higher cost, (b) higher MU and methanol permeability, (c) lower WU and (d) lower membrane and relative selectivities. On the other hand, lower amount (<10 wt %) of incorporated Nafion resulted in a membrane that suffered from lower proton conductivity and IEC. Most importantly, in terms of membrane properties, the ternary blend membrane proposed in this work exhibited the best membrane and relative selectivity ratios; since (i) higher incorporation of Nafion resulted in much increased methanol permeability in comparison to the increase in proton conductivity,

Table III. Relative Selectivity Ratios of the Membranes at 20°C, Using 2M, 4M, 6M, and 8M Methanol Concentrations

Membranes	Relative selectivity ratio			
	2M	4M	6M	8M
Nafion-117	1	1	1	1
SPVdF-co-HFP	0.60	1.01	0.49	0.65
SPVdF-co-HFP/SPAni (60 : 40 w/w) blend	23.64	199.40	111.48	111.70
Nafion/SPAni (70 : 30 w/w) blend	3.20	1.62	0.45	0.93
SPVdF-co-HFP/SPAni/Nafion (50 : 40 : 10) blend	21.74	225.08	118.03	119.15
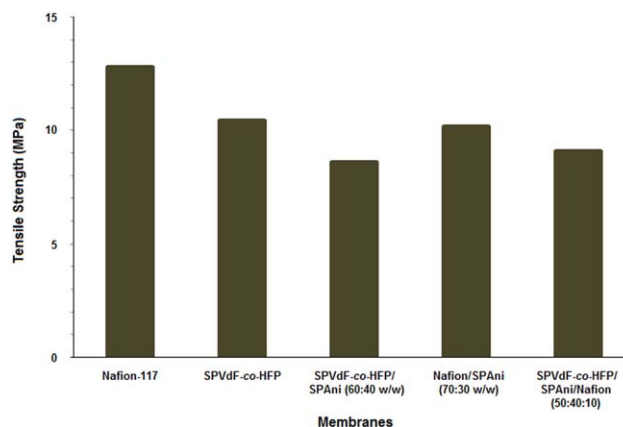
Figure 7. Tensile strengths of the membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Cost Comparison of the Fabricated Membranes with Respect to Commercial Nafion-117 Membrane

Membranes	Reference No.	Cost (US$m^{-2})
Nafion-117	51	~500–800
SPVdF-co-HFP	25	~0.1–0.3
SPVdF-co-HFP/SPAni (60 : 40) blend membrane	26	~0.7–0.9
Nafion/SPAni (70 : 30) blend membrane	28	~ 60–80
SPVdF/Nafion (70 : 30) blend membrane	29	~ 4–6
SPVdF/SPAni (80 : 20) blend membrane	30	~0.5–0.7
SPVdF-co-HFP/SPAni/Nafion (50 : 40 : 10) blend membrane	This work	~ 2–4

thus, resulting in decreased membrane and relative selectivity ratios, while (ii) lower incorporation of Nafion resulted in much decreased proton conductivity in comparison to the decrease in methanol permeability, thus, resulting in decreased membrane and relative selectivity ratios. The cost comparison of the fabricated membranes with respect to commercial Nafion-117 membrane has been presented in Table IV.

CONCLUSIONS

A ternary blend membrane, composed of 50 wt % SPVdF-co-HFP, 40 wt % SPAni, and 10 wt % Nafion, was fabricated. Based on the observations reported earlier with the pristine Nafion-117, the pristine SPVdF-co-HFP, the SPVdF-co-HFP/SPAni (60:40 w/w) blend and the Nafion/SPAni (70:30 w/w) blend membranes,[24–28] the present ternary blend membrane was fabricated with the objective of realizing a balance between properties and cost of the membrane material. It was observed that this ternary blend membrane exhibited superior WU capacity and water SR than the pristine Nafion-117, the pristine SPVdF-co-HFP and the SPVdF-co-HFP/SPAni (60:40) blend membranes; and lower MU capacity than the pristine Nafion-117, the pristine SPVdF-co-HFP and the Nafion/SPAni (70:30) blend membranes. In addition, the IEC of the ternary blend membrane was found to be superior to the pristine SPVdF-co-HFP and the SPVdF-co-HFP/SPAni (60:40) blend membranes; while it exhibited higher proton conducting ability compared to the pristine SPVdF-co-HFP, the SPVdF-co-HFP/SPAni (60:40) and the Nafion/SPAni (70:30) blend membranes. Moreover, the methanol permeability of the ternary blend membrane was found to be lower than the pristine Nafion-117, the pristine SPVdF-co-HFP and the Nafion/SPAni (70:30) blend membranes; while its membrane selectivity and relative selectivity ratios were superior to all the other reported membranes (especially at higher methanol concentrations). Therefore, in effect, incorporation of only a minimal quantity (i.e., 10 wt %) of costly Nafion within the blend of SPVdF-co-HFP/SPAni resulted in the fabrication of a membrane which exhibited multiple enhancements in several properties over that of the other studied membranes. The cost comparison analysis has also revealed that the cost of the fabricated ternary blend membrane is significantly low compared to the commercial Nafion-117 membrane. Moreover, this particular ternary blend composition (i.e., the ternary blend membrane with 10 wt % incorporated Nafion) exhibited the best membrane and relative selectivity ratios among all other compositions (i.e., incorporation of >10 wt % or <10 wt % of Nafion). Therefore, based on the summary of all the obtained properties and cost analysis, the ternary blend membrane composition of SPVdF-co-HFP:SPAni:Nafion = 50:40:10 was found to be the most optimized one.

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