Conductive behavior in relation to domain morphology and phase diagram of Naftion/poly(vinylidene-co-trifluoroethylene) blends

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Electron and proton conductive properties of Naftion/poly(vinylidene fluoride)-co-trifluoroethylene (PVDF-TrFE) blends were investigated in relation to domain morphology guided by phase diagram using differential scanning calorimetry, polarized optical microscopy, and AC impedance analyzers. A theoretical phase diagram was established by self-consistently solving the combined free energy density of Flory-Huggins theory for liquid-liquid demixing and the phase field theory for crystal solidification. Naftion/PVDF-TrFE blends revealed an hourglass type phase diagram, consisted of single phase crystal (Cr1), liquid + liquid (L1 + L2) and crystal + liquid (Cr1 + L2) coexistence regions. Guided by the phase diagram, the co-continuous or dispersed droplet domains were produced via phase separation induced either by solvent evaporation or thermal quenching. Fourier transformed infrared spectroscopy and water uptake measurements revealed swelling reduction in the Naftion/PVDF-TrFE blends. Accompanying the ferroelectric to paraelectric transition, the PVDF-TrFE copolymer exhibited a change of capacitor to insulator behavior with increasing temperature. Neat Naftion is poor electron conductor, but it becomes an ion conductor when hydrated. Electron/ion and proton conductivities of the 60/40 Naftion/PVDF-TrFE blend were discussed in relation to the comingled percolated morphology of the membrane.

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1. Introduction

Perfluorinated ionomer membrane, commercially known as Naftion, was developed originally for chloro-alkaline cell applications [1–3]. By virtue of its excellent perm-selectivity toward proton transport Naftion has found broader utility and becomes the benchmark for proton exchange membranes (PEMs) with minimal electrons crossing over from anode to cathode, i.e., one of the desirable properties for an electrolyte membrane in the proton fuel cell operations.

The molecular structure of Naftion is made up of poly(tetrafluoroethylene) backbone and perfluorovinyl ether side chain terminated by sulfonic acid groups which governs its ion transport properties [1–6]. One of the major shortcomings of Naftion is the dimensional instability caused by excessive swelling in aprotic solvents such as water or methanol due to the hydrophilic nature of the terminating sulfonate groups of Naftion [5–7]. Gore Associates, Inc. developed Teflon grid supported Naftion membranes, in which the mesh of hydrophobic Teflon gives mechanical support to the films with better dimensional stability, preventing the excessive swelling of Naftion [8].

Simple solution blending is an alternative approach to introduce the hydrophobic fluorocarbon polymer into Naftion to improve swelling suppression. Kyu et al. [9,10] were the first to blend Naftion with fluorocarbon polymer such as poly(vinylidene fluoride) (PVDF) by co-dissolving in dimethylacetamide (DMAc). The effect of solvent casting conditions on phase morphology and miscibility of Naftion/PVDF blends was demonstrated, exhibiting the lower critical solution temperature (LCST) phase behavior above 186 °C. Later, Landis and Moore [11] found that larger counterions of Naftion such as tetrabutylammonium (TBA+) lowered the crystallization rate of PVDF molecules, thereby enhancing the miscibility of Naftion/PVDF blends [11]. However, it is desirable for the blends to possess the unmitting phase separated morphologies with the hydrophobic fluorocarbon matrix rendering swelling suppression and the hydrophilic ion interconnected domains for ion/proton transports.

The main objective of the present work is to provide a better dimensional stability of Naftion though blending with fluorocarbon polymers while maintaining proton (H+) and ion conductions (e.g., hydronium ions such as H3O+, H2O2) upon hydration. Copolymer of poly(vinylidene fluoride)-trifluoroethylene (PVDF-TrFE) was chosen because pure PVDF would be too miscible with Naftion at low fuel cell
operating temperatures due to the LCST behavior with a minimum at 186 °C [9]. It was reported that PVDF-TrFE copolymer readily developed the β-crystal [12–15] with exceptionally high capacitance in the order of nano-Farads at the 30% trifluoroethylene (TrFE) molar ratio [16,17]. This copolymer is known for its ferroelectric property that transforms to paraelectric crystal with increasing temperature through a so-called Curie transition at 73 °C [18].

In proton fuel cell applications, a conventional wisdom is to have a composite material with the highest proton transport, but the lowest electron conductivity. Hence, blending of PVDF-TrFE with Nafion has been sought because PVDF-TrFE may be a good capacitor but poor electron conductor, whereas Nafion is an excellent ion and/or proton conductor. Upon phase separation, PVDF-TrFE and Nafion may provide different pathways for electron and proton transports. Moreover, PVDF-TrFE will act as physical networks to provide better dimensional stability to Nafion membranes subjected to hydration.

We shall first establish experimental and theoretical phase diagram of Nafion/PVDF-TrFE mixture to obtain the desired final morphology such as comingled or bicontinuous domains. The solution blended mixture may be phase separated during solvent casting or upon thermal treatment, which in turn develops various domain morphologies of Nafion and PVDF-TrFE, including sea–and–island or biphasic comingled structures [19]. Electron and proton conductivities will be determined for the 60/40 Nafion/PVDF-TrFE blend and discussed in relation to the bicontinuous phase separated domains. Because of the profound moisture sensitivity of Nafion, the transport of hydronium ions is anticipated to affect both electron and proton conductivities, especially those of the neat Nafion and its blends with PVDF-TrFE. The alternating current (AC) impedance and proton conductivity measurements will be conducted and analyzed by comparing the ‘dried’ versus the ‘hydrated’ samples.

2. Sample preparation and experimental methods

Nafion 115 membranes with an equivalent weight of 1100 in acid form were purchased from the Fuel Cell Store, Inc. To ensure complete conversion to the acid form, the as-received Nafion 115 membranes were first pretreated by boiling in 3% hydrogen peroxide solution for 2 h and subsequently rinsed in boiling deionized water [17]. The membranes were then boiled in 0.5 M sulfuric acid and rinsed again in boiling deionized water (at least 1 h for each step) to remove excess sulfuric acid, and then dried in a vacuum oven and kept in a desiccator prior to solution blending. PVDF-TrFE (33 mol% of TrFE) having the molecular weight, $M_w$ of 69,000 and polydispersity, $M_w/M_n$ of 1.4 was used in the present study. Prior to blending, the Nafion membrane was cut into tiny pieces and dried at 100 °C in vacuum oven for 48 h in order to eliminate residual moisture. Nafion membrane and PVDF-TrFE pellets were dissolved separately by rigorous stirring in dimethylacetamide (DMAc) at 120 °C and at room temperature, respectively. These solutions were then mixed at various blend ratios while maintaining polymer concentration at 5 wt%. The homogeneous solution was cast on pre-cleaned microscope slides and dried in a vacuum oven at 100 °C for 3 days. For optical microscopic analysis, thin film with average thickness of about 20 μm was prepared. Thicker films (approximately 90–100 μm nominal thicknesses) were used for differential scanning calorimetry (DSC), water uptake, and AC impedance measurements.

Phase transition temperature of the Nafion/PVDF-TrFE mixtures was determined using differential scanning calorimetry (DSC, Perkin Elmer). Approximately 10 mg of the sample was hermetically sealed in aluminum pans and heated at 10 °C/min from room temperature to 200 °C under nitrogen environment; only the DSC thermograms obtained from the second runs were used in the analysis to avoid sample’s prehistory or moisture absorption. The morphology of the pure and blend samples were examined by polarized optical microscopy (POM) (BX 60, Olympus) equipped with a digital camera (EOS 300D, Canon) and a hot stage (TMS 93, Linkam). Samples were heated up to 280 °C at a heating rate of 5 °C/min and quenched to 27 °C to monitor the morphology development following solid–liquid phase transition and liquid–liquid phase separation.

Prior to water uptake measurement, samples were dried and subsequently soaked in deionized water at room temperature for 24 h. Water uptake was determined by monitoring weight change before and after hydration, i.e., $(M_{\text{wet}}-M_{\text{dry}})/M_{\text{dry}}$, where $M_{\text{wet}}$ is mass of the membrane in the wet state and $M_{\text{dry}}$ is mass of the membrane in the dry state. The hydration effect on Nafion/PVDF-TrFE blends was further investigated by Fourier transformed infrared spectroscopy (FTIR). FTIR spectra (Nicolet 380, Thermo Scientific) in attenuated reflected (ATR) mode were acquired at room temperature with an average of 32 scans and a spectral resolution of 4 cm⁻¹.

The complex quantities of impedance ($Z'(\omega) = Z'(\omega) - i Z''(\omega)$) of neat Nafion and PVDF-TrFE as well as their blends were determined using the AC impedance analyzer (Gain-Phase Analyzer, Schlum-berger) over the frequency range $\omega$ of 1 Hz–100 kHz, where $\omega$ is the angular frequency, given as $\omega = 2\pi f$. The temperature was varied from ambient temperature to 150 °C using a heating stage controlled by a temperature regulator (CN8500 Omega). Film samples were sandwiched between two parallel condenser plates coated with indium tin oxide (ITO), having a contact area of 1 cm² and a film thickness of 90–110 μm.

The capacitive value or polarization capacitance of the membrane, $C_p$, may be calculated from the peak of the Cole–Cole plot, denoted as the maximum frequency, $f_{\text{max}}$.

$$C_p = \frac{1}{2\pi f_{\text{max}}R_p}$$

with $R_p = 2R_{\text{max}}$ where $R_{\text{max}}$ is the resistance value that corresponds to the maximum frequency [20].

On the other hand, conductivity ($\sigma$) is calculated using the equation below:

$$\sigma = \frac{d}{R_p A}$$

where $d$ is bulk thickness of the membrane, and $A$ is the contact area of the condenser cell. The cell resistance ($R_p$) is obtained from the intersection of the Cole–Cole plot and the storage impedance $Z'(\omega)$axis [20].

Proton conductivity of neat Nafion and impregnated membranes was measured using the AC impedance fuel cell device (Scribner, Model 850e Multi Range) equipped with an adjustable reactant humidifier unit. Membranes were coated with platinum supported carbon solution catalyst using a spray gun (Badger Gun, Model No. 150). The membranes with total catalyst weights of 2 mg and 1 mg on the cathode and anode side, respectively, were compressed with 13.8 MPa at 60 °C for 20 s. Prior to spraying the catalyst, membranes were pretreated in sulfuric acid (H₂SO₄) again as to regenerate and fully convert the ionic clusters into the acid form. Hydrogen gas and compressed air were used as reactants with a flow rate of 0.2 L/min. The membranes with contact cell dimension of 5 cm² were tested at a frequency range of 0.1 Hz–10 kHz. Measurements were performed at two different relative humidity (RH) levels, i.e., 10%RH and 74%RH, from 30 °C to 110 °C. Complex impedance data obtained were analyzed using the ZView program and the proton conductivity was calculated in accordance with Eq. (2).
3. Theoretical scheme for establishment of phase diagram

A theoretical phase diagram containing crystalline and amorphous polymer may be constructed by combining the free energy density of Flory–Huggins (FH) [21], phase field (PF) [22], and their coupling interaction [22,23]. The FH theory may be employed to describe liquid–liquid demixing.

\[ f_{FH} = \frac{\varphi_1 \ln \varphi_1}{r_1} + \frac{\varphi_2 \ln \varphi_2}{r_2} + \chi_{ad} \varphi_1 \varphi_2 \]  

(3)

where \( \varphi_1 \) and \( \varphi_2 \) are the volume fraction of respective constituent, and \( r_1 \) and \( r_2 \) represent the numbers of statistical segments. The FH interaction parameter, \( \chi_{FH} \) or \( \chi_{ad} \), representing amorphous–amorphous interaction and may be expressed empirically as a function of temperature [22],

\[ \chi_{ad} = \left( A + \frac{B}{T} + C \ln T \right) \]  

(4)

where \( A, B \) and \( C \) are constants, in which only two are independent variables, which may be used as adjustable in the case of an hourglass phase diagram; otherwise they can be estimated from the critical temperature.

The free energy density of crystal solidification is given by phase field model which pertains to the crystal order parameter (\( \psi \)) of asymmetric Landau–type double well potential for phase transition [22], i.e.,

\[ f_{PF} = W \left[ c_1 \varphi_1^2 + \frac{\zeta}{3} \varphi_3^3 - \frac{1}{4} \psi^4 \right] \]  

(5)

\( W \) is related to the energy barrier for crystal nucleation to overcome. \( \zeta \) and \( c_1 \) are the locations of the nucleation hump and the crystal solidification potential with respect to \( \psi \)-axis, respectively. The crystal order parameter (\( \psi \)) may be defined as the ratio of the lamellar crystal thickness (\( l \)) to that of a perfect crystal at equilibrium (\( P \)), viz., \( \psi = \frac{l}{P} \).

In addition, the coupling free energy between the crystal phase order parameter and concentration fields may be described, viz.,

\[ f_{coupling} = \chi_{aa} \varphi (1 - \varphi) \psi^2 \]  

(6)

where the crystalline–amorphous interaction parameter is proportional to the heat of fusion of that crystalline component, i.e., \( \chi_{aa} = \frac{\alpha_c \Delta H_{fi}}{RT} \), and the proportional constant, \( \alpha_c \), can be determined from the slope of \( (1 - T_m/T_m^{fi}) \) versus \( (1 - \varphi) \) [23].

The total free energy may be obtained by combining Eqs. (3), (5), and (6) that gives:

\[ f(\psi, \varphi) = \frac{\varphi}{r_1} \ln(\varphi) + \frac{1 - \varphi}{r_2} \ln(1 - \varphi) + \left( \chi_{ad} + \chi_{aa} \psi^2 \right) \varphi (1 - \varphi) \]  

(7)

The equilibrium coexistence points were determined by balancing the chemical potential at each phase: \( \mu_{\phi} = \mu_{\psi} \) in conjunction with the double tangent method [22], while the spinodal points can be obtained from the inflection points of the free energy curve by setting \( \partial^2 f / \partial \psi^2 = 0 \).

4. Results and discussions

4.1. Phase transition and binary phase diagram

Fig. 1 shows the DSC thermograms of Nafion/PVDF-TrFE blends obtained at a heating rate of 10 °C/min. The pure PVDF-TrFE showed two endothermic peaks. The first peak at 73 °C corresponds to the Curie transition, \( T_{Curie} \). This transition has been assigned to the order–disorder phase transition from ferroelectric to paraelectric [13,14]. The second peak observed at 163 °C corresponds to the crystal melting transition, \( T_m \), which shows slight movement to a lower temperature with the addition of Nafion, implying partial miscibility of the mixtures.

The overall phase behavior of the blends may be understood by establishing a theoretical phase diagram by self-consistently solving Eq. (7). Fig. 2 depicts the phase diagram of Nafion/PVDF-TrFE blends. The theoretical binodal (solid lines) curves accord well with the experimental data obtained from DSC (as denoted by ‘○’) and POM (as denoted by ‘□’ for isotropic phase and ‘●’ for liquid–liquid phase separated region) measurements. The model parameters used for calculation were \( r_1 = 70, r_2 = 90, A = -0.4, C = 6.1 \times 10^{-2}, \chi_{aa} = 3.0 \times 10^{-2}, \) and \( \chi_{ad} = 7.4 \times 10^{-1} \) at \( T_m \) along with \( \Delta H_{fi} = 1.8 \text{kJ/mol} \), respectively. Consistent with the previous DSC results, the melting transition of PVDF-TrFE was found to be slightly depressed with increasing Nafion content, thus giving very small \( \chi_{ad} \) value. Above melting temperature (\( T_m \)), the crystalline PVDF-TrFE melts to isotropic (I) phase at extreme concentrations, but it exhibits liquid + liquid (L1 + L2) coexistence phase at intermediate compositions, as shown in the insets of Fig. 2(I), (ii) and (iii). It is reasonable to infer that the observed phase diagram is an hourglass type, in which the LCST and UCST curves are seemingly merged at the intermediate compositions. Upon lowering temperature below \( T_m \), three distinct regions are discerned, viz., crystal + liquid (Cr1 + L2) coexistence between the single phase crystal (Cr1) and the isotropic liquid (I). The insets in Fig. 2 labeled with (iv), (v) and (vi) illustrate the morphologies of PVDF-TrFE crystals that correspond to their coexistence regions.

The present hourglass phase diagram of Nafion/PVDF-TrFE is drastically different from the LCST type phase diagram of the Nafion/PVDF blends [9,10]. Given the LCST phase behavior, the Nafion/PVDF blends can revert back to the isotropic state at the low operation temperatures of fuel cells (e.g., below 200 °C), which can compromise the fuel cell performance. In this regards, the Nafion/PVDF-TrFE blends are expected to be in two phase regions at all fuel cell operation temperatures.

4.2. Water uptake and hydration effect on the Nafion/PVDF-TrFE blends

As shown in Fig. 3(a), the hydration of Nafion/PVDF-TrFE blends was significantly reduced with increasing amount of PVDF-TrFE.
Hydrated Naﬁon exhibited dimensional increment of 27% in length and 20% in width. Note that the average thickness of the Naﬁon/PVDF-TrFE blend membrane (90–110 μm) was adjusted to be close to the thickness of pure Naﬁon membrane (~ 110 μm) in order to validate the comparison of the warping of each sample. As can be seen in the inset right picture, the excessive swelling of Naﬁon exhibited membrane warping. The water uptake at the intermediate compositions, i.e., the 60/40 Naﬁon/PVDF-TrFE blend was reduced to 15–20 wt % and the membrane warping is visibly reduced (see the inset middle picture) showing only slight dimensional increment for 10% in length and 7% in width. The reduced water uptake indicates better dimensional stability to the blend membranes. In this intermediate region, the turbidity of the membranes also increases due to macroscopic phase separation. As expected, there is little or no change in length and width occurring at the 10/90 PVDF-TrFE blend because this blend is primarily made up of hydrophobic PVDF-TrFE-rich phase.

The composition-dependent hydration effect has been further examined by FTIR based on the characteristic bands of O–H stretching band at around 3700–3000 cm⁻¹ attributable to water sorption [20]. As evident in Fig. 3(b), the intensity of O–H stretching decreases upon increasing PVDF-TrFE concentration. At the intermediate Naﬁon/PVDF-TrFE compositions, water sorption is reduced to about 80% relative to that of the neat Naﬁon, suggesting the intermediate blends becoming progressively hydrophobic. When PVDF-TrFE concentration is increased above 90 wt %, the mixture contained less than 5% of water. The water content as measured by FTIR and weight increment shows a similar sigmoidal trend, except that the physical weighing methodology is qualitative and rather crude.

As is well known, phase separation of polymer blend can take place via nucleation and growth (NG) or spinodal decomposition (SD) mechanisms [21]. As envisaged from the optical micrographs (see insets of Fig. 3(b)), the intermediate composition, i.e., 60/40 Naﬁon/PVDF-TrFE shows bicontinuous morphology (i.e., interconnected spinodal structure) while in the extreme compositions, viz., 10/90 and 90/10, exhibit the sea-and-island type morphology, which probably occurs through nucleation and growth although it is by no means a proof. The sea-and-island type morphology is not particularly interesting in the evaluation of the electron/ion or proton conductivity performance due to the isolated and discontinuous droplet structures of Naﬁon in PVDF-TrFE matrix or vice versa. The preferred morphology is the interconnected spinodal structure that gives the percolated pathways for electron and/or proton transport. For qualitative illustration, the sea-and-island (i.e., nucleation and growth) morphology was simulated for the compositions rich in either constituent, which may be contrasted to the bicontinuous percolated morphology (spinodal decomposition, SD) occurring at an intermediate composition. For simplicity, the crystallization of PVDF-TrFE was not taken into consideration in the simulation because the liquid + liquid SD structures would dominate in the hourglass phase diagram, especially above the Tm. Even cooling to ambient temperature, the crystal structure may develop within the existing spinodal structure.

The observed interconnected SD structure at the 60/40 Naﬁon/PVDF-TrFE composition possibly contains PVDF-TrFE crystals in
the PVDF-TrFE-rich regions. Of particular importance is that the bicontinuous pathways of Na$_{i}$ on upon hydration will allow protons and hydronium ions to conduct, whereas hydrophobic percolated PVDF-TrFE will restrict the excessive swelling, but allows electron conduction. Since PVDF-TrFE primarily forms the β-form crystals, the capacitor behavior is expected to prevail in this percolated PVDF-TrFE network channel. Hence, it is of paramount importance to determine both electrical and proton conductivities of the intermediate composition, i.e., 60/40 Na$_{i}$ on/PVDF-TrFE, especially the interplay between the Na$_{i}$ on-rich channels for proton transport and PVDF-TrFE-rich percolated network having high capacitance. Because of the profound moisture sensitivity of Na$_{i}$ on in the neat form and also its blend with PVDF-TrFE, the AC impedance values may be influenced by both electronic and ionic conduction.

Similarly, the proton and hydronium ion transports occur simultaneously in the proton conductivity measurement of the neat Na$_{i}$ on as well as the Na$_{i}$ on/PVDF-TrFE blends.

4.3. Electron conductivity and capacitance behavior of Na$_{i}$ on/PVDF-TrFE blends

Fig. 4(a) and (b) show the storage impedance and loss tangent as a function of frequency for pure PVDF-TrFE. Since neat PVDF-TrFE is a hydrophobic polymer, the AC impedance is mainly due to the electron transport. The storage impedance exhibits the sigmoidal reduction of AC impedance with frequency, whereas the loss tangent peaks move systematically toward a higher frequency as temperature is raised. However, the loss tangent peak intensity declines with increasing temperature. This peak temperature is attributable to mechanical α relaxation associated with intra- and/or inter-crystalline chain motions [6].

Next, the Cole–Cole plots of pure copolymer PVDF-TrFE at various temperatures are depicted in Fig. 5. At low temperature, the observed upward slope implies that pure PVDF-TrFE behaves like a capacitor. When the temperature exceeded the ferroelectric–paraelectric transition ($T_{\text{Curie}}$) at around 73 °C, the capacitor behavior changes to a semicircle shape above 100 °C in the Cole–Cole plot, implying conductor behavior.

Fig. 6 illustrates the variation of capacitance and electron conductivity with temperature. The capacitance and conductivity values were obtained from Eqs. (1) and (2); the low temperature data may be interpreted with reservation because the polarized resistance ($R_p$) was estimated simply from the highest value. Nevertheless, it should be emphasized that the capacitance of pure PVDF-TrFE increases with increasing temperature, but it declines above the Curie temperature (e.g., at 80 °C) undergoing phase transformation from the ferroelectric to paraelectric phases. In contrast to the decreasing trend of capacitance, the electron conductivity shows an increasing trend with temperature. However, the electron conductivity value is so small (in the order of $10^{-12}$ to $10^{-10}$) and thus it is practically an insulator to electron transport. This high capacitance or insulator behavior is one of the

![Fig. 4.](image-url) (a) Log–log plot of storage impedance, $Z'$ versus frequency and (b) semi log plot of loss tangent versus frequency of pure PVDF-TrFE from 43 °C to 150 °C over the frequency range of 1 Hz–100 kHz. Note that the complex AC impedance was defined as $Z'(\omega) = Z'(\omega) - i Z''(\omega)$ in conformity with the compliance form.

![Fig. 5.](image-url) Cole–Cole plot of pure PVDF-TrFE copolymer for various temperatures obtained from the AC impedance measurement illustrating the transition of capacitor to conductive behavior at the Curie transition temperature.
desired properties for the electrolyte membrane in the proton electrolyte fuel cells, i.e., the poor electron transport of the PVDF-TrFE phase coupled with the good proton conduction [23] through the Nafion-rich bicontinuous network domains.

Fig. 7 shows the plot of impedance loss tangent versus log frequency of ‘dried’ neat Nafion. Note that the term ‘dried’ implies that some amount of unavoidable ambient moisture might be absorbed during the sample mounting. Initially the loss tangent peak of ‘dried’ neat Nafion sample at 43 °C shows a movement to a higher frequency as temperature is raised to 63 °C. This shift may be attributed to the increased mobility of absorbed moisture in the Nafion membrane from the ambient humidity (~37%). The water level within Nafion membrane has been reported to be about 2.2 mol of water per sulfonic acid site [24]. Upon further increase of temperatures to 100 °C, the loss tangent peaks showed an opposite shift to lower frequencies, which may be attributed to the loss of water at such boiling temperature. This complex behavior of the loss tangent peak with temperature is due to the profound water sensitivity of the ionic domains of Nafion.

To eliminate any ambiguity on the consistency of water content within the membrane neat, Nafion samples were equilibrated in deionized water at room temperature for 24 h. According to our recent NMR study, the hydrated neat Nafion contained 23 mol of \( \text{H}_2\text{O/\,SO}_3^- \) [25]. The electron/ion conductivity value was determined from the Cole–Cole plot of the ‘hydrated’ neat Nafion. As shown in Fig. 8, the semi-circular Cole–Cole plot indicates that hydrated neat Nafion behaves like an ionic conductor, as the ion transport predominates over the electron transport. With further increase of temperature, the Nafion begins to lose water resulting in higher resistivity as manifested by the increase in the storage impedance (\( Z' \)) value for two orders of magnitude. Evidently, the conductivity of Nafion as obtained from the Cole–Cole plot...
reduces drastically when the temperature exceeds the boiling point of water, making the Nafion to become a poor ionic conductor due to loss of hydronium ions. In the dehydrated state, these electron conductivity values are extremely low, implying that Nafion has become essentially an insulator due to lack of ion transport.

The dependencies of storage impedance and loss tangent on frequency of the 60/40 Nafion/PVDF-TrFE blend are shown in Fig. 9(a) and (b), respectively. The storage impedance of 60/40 blends decreases with increasing frequency and temperature, while a systematic movement of loss tangent peak to higher frequencies is seen with increasing temperature. Fig. 10 illustrates the Cole–Cole plot of 60/40 Nafion/PVDF-TrFE blend, showing a linear slope signifying the capacitor behavior. It is anticipated that the percolated ionic channels may be disrupted, making the ionic conductivity values are extremely low, implying the proton conductivity with increasing temperature. As temperature exceeds 80 °C, the neat Nafion shows an increasing trend of proton conductivity due to loss of hydronium ions. This finding may be attributed to the dehydration of the membrane where the interconnected/percolated ionic channels may be disrupted, making the ionic domains to be increasingly isolated, and therefore lowering the overall proton conductivity. Consequently, the proton conductivity of neat Nafion samples declined abruptly ($\sigma = 0.043$ S/cm) as the temperature reaches 115 °C at 74% RH.

4.4. Proton conductivity of Nafion/PVDF-TrFE blends

Proton conductivity measurements of both neat Nafion and Nafion/PVDF-TrFE blends were carried out in the AC impedance fuel cell environment at 74% and 100% RH. Fig. 11(a) and (b) illustrate the Cole–Cole plots of neat Nafion and the 60/40 Nafion/PVDF-TrFE samples measured at 100% RH, respectively. The first intersection of the plot at the x-axis, denoted as $R_s$, indicates the resistance between the electrolyte membrane and the catalyst layer, known as the solution resistance [26]. The diameter of the semi-circular plot, denoted by $R_p$, is the resistance from the electrolyte membrane, termed as polarization resistance [26]. The $R_p$ value was used to evaluate the conductivity in accordance with Eq. (2). An equivalent circuit of the fuel cell may be represented by a resistor in series with a parallel circuit containing a capacitor and a resistor. It is seen that the diameter of the Cole–Cole plots for both samples contracted when temperature is raised up to 80 °C, suggesting less resistance within the cell. However, upon reaching the boiling temperature of water, both samples exhibit an increase in the polarization resistance due to the loss of hydronium ions, which ultimately reduces its overall proton transport efficiency.

The variation of proton conductivity is plotted against temperature in Fig. 12. Neat Nafion shows an increasing trend of proton conductivity with increasing temperature. As temperature exceeds 80 °C, the neat Nafion shows a declining trend of proton conductivity due to loss of hydronium ions. This finding may be attributed to the dehydration of the membrane where the interconnected/percolated ionic channels may be disrupted, making the ionic domains to be increasingly isolated, and therefore lowering the overall proton conductivity. Consequently, the proton conductivity of neat Nafion samples declined abruptly ($\sigma = 0.043$ S/cm) as the temperature reaches 115 °C at 74% RH.

Table 1

<table>
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<tr>
<th>Temperature (°C)</th>
<th>Capacitance, $C_p$ (nF)</th>
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Fig. 9. (a) Log–log plot of storage impedance, $Z'$ versus frequency and (b) semi log plot of loss tangent versus frequency of 60/40 Nafion/PVDF-TrFE from 43 °C to 125 °C over the frequency range of 1 Hz–100 kHz. Note that the complex impedance was defined as $Z''(u) = Z'(u) - iZ''(u)$ to conform with the compliance form.

Fig. 10. Cole–Cole plot of 60/40 Nafion/PVDF-TrFE blend obtained from the AC impedance measurements showing the capacitor behavior of the blend.
The 60/40 Nafton/PVDF-TrFE blend was found to exhibit lower proton conductivity at all temperatures by almost one half to those of neat Nafton due to the hydrophobicity of PVDF-TrFE. At 80 °C, the 60/40 blend manages to achieve a reputable proton conductivity value of 0.048 S cm\(^{-1}\) at 100% RH. Although Eq. (2) is valid for homogeneous materials in which proton conductivity of the blend membrane depends on the bulk thickness and the macroscopic resistance of the particular membrane, and thus its simple application to a heterogeneous system like the present phase separated Nafton/PVDF-TrFE blend is questionable. It may be conjectured that proton conductivity of the blend membrane may depend on not only composition or volume fraction of Nafton, but also the orientation of its percolated pathways. Therefore, the use of the bulk thickness of the blend membranes will not reflect the actual conductivity of the heterogeneous structure. The individual percolated channel thickness needs to be compensated in the conductivity calculation. Nevertheless, the proton conductivity of the blend, based on its bulk thickness is plotted in Fig. 12. Given the actual fraction of the Nafton of 60 wt% in the blend, the proton conductivity (i.e., almost one half relative to that of neat Nafton) thus obtained appears reasonable. Interestingly, the proton conductivity of the blend shows a similar decreasing trend with temperature to that of neat Nafton due to loss of hydronium ions transports.

5. Conclusions

Phase diagram of Nafton and PVDF-TrFE copolymer blends were established experimentally and theoretically. At intermediate compositions, the crystal + liquid coexistence region transforms to liquid + liquid upon increasing temperature above the melting temperature of PVDF-TrFE, showing an hourglass type phase
diagram intercepted by the melting transition. The constructed phase diagram was employed to manipulate the bicontinuous or dispersed domains via phase separation following thermal quenching. The bicontinuous morphology at the 60/40 Nafton/PVDF-TrFE composition provided pathways for both electrical and proton transports. This supports the hypothesis that the percolated networks not only act as the physical crosslink and suppress swelling, but also exhibits moderate but respectable proton conductivities in fuelled by hydronium ion transports within the individual percolated channels. Formation of the randomly oriented bicontinuous microscopic pathways within the Nafton/PVDF-TrFE blend may have compromised the conductive properties of the membrane and thus the alignment of conductive channels is highly desirable to maximize the proton conductivity.

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References