Role of protic ionic liquid concentration in proton conducting polymer electrolytes for improved electrical and thermal properties

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Abstract

Protonic liquid electrolytes (PILs) in the acidic medium are known to show higher ionic conductivity than neat PIL or PIL in alkaline media. Hence, polymer electrolyte membranes (PEM) containing both PIL and acids are considered ideal for non-humidified intermediate temperature PEM fuel cells. Herein, we report non-aqueous proton conducting PEM made up of diethylmethylammonium trifluoromethanesulfonate; [dema][TfO] and neat phosphoric acid (H₃PO₄) with poly (vinylidene fluoride-co-hexafluoropropylene); PVDF-HFP as the host matrix. The presence of PIL significantly modified the structure and microstructure of the electrolyte films with the emergence of micropores in the PIL containing membranes. SEM images suggest leaching of PIL and phosphoric acid above 80 wt% of PIL in the electrolyte membranes. Thermogravimetric studies show that the dehydration in the PEM films due to phosphoric acid condensation at 100 °C–200 °C region is arrested by the presence of PIL. The maximum ionic conductivity at room temperature is ~6.3 × 10⁻⁴ S cm⁻¹ at 40 wt% of [dema][TfO] addition, which is two orders higher than that of the primary electrolyte (PE) containing only phosphoric acid in PVDF-HFP. This high conductivity in PEM films can be correlated to the increase in polar β and γ phases as well as a drop in the total crystallinity fraction in the film. The study using dielectric spectroscopy reveals a strong coupling of ionic conductivity with the structural or segmental relaxation of the PVDF-HFP due to the presence of [dema][TfO] in the PEMs.

1. Introduction

As the demand for more clean and sustainable energy alternatives is increasing, the polymer electrolyte fuel cells (PEMFCs) have attained prominence in the grand scheme of things related to transportation and portable applications. In general, the PEMFCs are known to be low temperature fuel cells in comparison to solid oxide fuel cells (SOFCs). But recently, PEMFCs have evolved rapidly and broadly categorized into (i) low temperature (LT) PEMFC and (ii) high temperature (HT) PEMFC [1, 2]. The HT-PEMFCs work in the temperature range of 120 °C–200 °C to avoid Pt catalyst poisoning. Operational temperature being above 100 °C, anhydrous polymer electrolytes containing mineral acids are found suitable in these HT-PEMFCs (PBI + H₃PO₄) [3–5]. Whereas the LT-PEMFCs mostly work in a temperature range <80 °C. This requires pure hydrogen to be used as fuel. In such LT-PEMFCs the most preferred electrolyte membranes are made up of Nafion [6, 7], PVA [8, 9], PVDF-HFP [10, 11] containing either water or diluted mineral acids such as H₃PO₄, H₂SO₄ etc. As a drawback, these electrolyte membranes need to be hydrated constantly for optimal performance of LT-PEMFCs. To circumvent this water management issue in the electrolyte membrane, non-aqueous proton conducting electrolytes are considered most suitable as in the case of HT-PEMFCs. Hence, non-aqueous proton conducting electrolytes have a universal appeal for new generation PEMFC applications. This is evident from the emergence of a host of new materials (MOFs, COFs, protic ionic liquids etc) in the literature showing high proton conductivity over a
wide temperature range from sub-zero to moderately high temperature (125 °C) [12–15]. However, non-aqueous polymer membrane electrolytes developed by incorporating these materials doesn’t offer good protonic conductivity.

In this work, we have developed non-aqueous proton conducting polymer electrolytes based on PVDF-HFP matrix and neat H₃PO₄ which is further incorporated with protic liquid (PIL) [dema][TfO]. Neat phosphoric acid is considered to be a pure protonic conductor (mostly grothuss transport) due to its very high proton transfer number of tₚ, ≈98% and hence, provides super-protonic conductivity ($\sigma_{dc}$ ≈ 0.15 S cm⁻¹). This makes it an ideal proton source in preparation of the electrolytic component for PEMFCs as well as for electrochemical double layer capacitors (EDLCs) [16, 17]. The polymer matrix; PVDF-HFP is a very stable and robust polymer having crystalline melting temperature; $T_m$ ≈ 150 °C. It is one of the most preferred membrane matrices for aqueous type membrane electrolytes as well. Conventionally these aqueous electrolyte membranes were made up of microporous PVDF-HFP films developed by phase-inversion method and dipped in electrolyte solution to soak it [18–20]. This synthesis route is cumbersome and the membranes are prone to leaching. To avoid this, we followed simple method of adding neat H₃PO₄ directly into the solution of PVDF-HFP. But as excess of neat phosphoric acid is corrosive, we maintained moderate concentration (40 wt%) of acid in all the series of polymer electrolyte membranes (PEMs) and added [dema][TfO] in varying concentrations. The PIL; [dema][TfO] itself exhibits high proton conductivity due to the presence of hydrogen-bond networks and remains stable over a wide range of temperature [21]. It was also reported that electrolytes containing both phosphoric acid and PIL supported better interfacial electrochemical activities (oxygen reduction reaction; ORR and hydrogen evolution reaction; HER) in comparison to the electrolytes based only on phosphoric acid [22, 23]. Hence, the incorporation of protic liquid ([dema][TfO]) can serve the twin purpose of improving proton conductivity and interfacial properties. Herein, we report the effect of [dema][TfO] concentration on structural, microstructural, thermal properties and electrical conductivity of the non-aqueous electrolyte membranes.

2. Materials and methodology

Both PVDF-HFP and H₃PO₄ (neat; 99.99%) procured from Sigma-Aldrich. The protic ionic-liquid; [dema][TfO] was supplied by IoLiTec. The polymer electrolyte with only PVDF-HFP and H₃PO₄ is the primary electrolyte (PE) system. Then a series of polymer electrolytes were prepared by addition of varying concentrations of [dema][TfO] into the PE system. Sufficient amount of PVDF-HFP with acetone was taken in a flask with screw cap. It was kept for magnetic stirring until the polymer is completely dissolved. Further 40 wt% of the neat H₃PO₄ was added to the solution using a micropipette. Varying concentration of [dema][TfO] (0, 20, 40, 60, and 80 wt%) was added in the PE solution and continued the stirring to obtain a homogeneous solution. Free standing polymer electrolyte membranes (PEMs) were obtained by solution casting technique and then by drying them in a vacuum oven.

The structural, microstructural, spectroscopic, thermal analyses and complex impedance analysis of the prepared samples were done. The XRD analyses of the prepared films were carried out using Bruker D8 series advance XRD in the range of 10° to 60°. The surface morphology of the samples was obtained using a scanning electron microscope (JEOL JSM 7610F). FTIR spectra of the prepared samples were collected in the range of 400 to 4000 cm⁻¹ using Jasco 4700 instrument. Thermogravimetric analysis (TGA) was carried out using a TGA 209 Netzsch instrument. It was carried out under nitrogen (25 ml min⁻¹) in the temperature range of 20 °C–800 °C at 10 °C min⁻¹ scanning rate. Differential scanning calorimetry (DSC) studies were conducted using DSC Q100 TA instrument, coupled with a Refrigerated Cooling System (RCS). The experiments were conducted under inert nitrogen atmosphere with a flow of 50 ml min⁻¹. The samples were heated up to 180 °C to erase the thermal history, and cooled down to –90 °C as fast as possible. Then, the samples were heated a second time up to 180 °C at a heating rate of 10 °C min⁻¹. Complex impedance spectra of the samples were recorded at room temperature in the frequency range of 1 Hz–10 MHz using Novocontrol Alpha-A analyzer.

3. Results and discussions

3.1. Structural and micro-structural analysis

Figure 1 shows the XRD pattern of the polymeric electrolyte membranes. The matrix copolymer PVDF-HFP in the electrolyte membrane is inherently semi-crystalline. Its amorphous phase is owing to the HFP (hexafluoropropylene) part while VDF (vinylidene fluoride) part mostly contributes to the crystalline content. The crystalline phase of PVDF-HFP is known to exist with different chain conformations named as $\alpha$ (TGTG), $\beta$ (TTTT) and $\gamma$ (T₂G₃T₂G). Among them, $\alpha$ phase is non-polar in nature while the other two phases are polar and exhibit ferroelectric and piezoelectric properties [16, 24]. The structural investigations from XRD suggest that
the electrolytic films are semicrystalline where the background due to amorphous phase is modulated with relatively sharp Bragg peaks. The crystalline fraction may have contributions from α, β and γ phases of PVDF-HFP. The peak around ∼20° corresponds to (110) reflection of polar β and γ phase of PVDF-HFP. As shown in figure 1(b) the peak around 18.43° is due to (020) of α phase is suppressed in PEM films containing higher concentration of [dema][TfO]. Another Bragg peak at 2θ ∼ 20° is very sensitive to the type of crystalline phases of PVDF-HFP and appears quite broad due to overlapping of contributions from α, β and γ phases of PVDF-HFP. For the PE film (free from [dema][TfO]), this peak is observed at 19.8° and is assigned to α phase. It is shifted to 20.05° (γ phase) and 20.3° (β phase) for [dema][TfO] concentration 20–60 wt%, and 80 wt%, respectively. This suggests that non-polar α-phase is decreasing and polar (β and γ) phases are increasing with [dema][TfO] addition.

The scanning electron micrographs of the prepared polymer electrolytes are shown in figure 2. The figures 2(a) and (b) present the SEM images of the electrolyte membrane containing only polymer and H$_3$PO$_4$ (PE film). It shows the lamellar structure of the membrane film without the presence of any pores. Even the magnified image of the PE film as shown in (b) does not show any pores on its surface.

With addition of 20 wt% of [dema][TfO] into the system, granular structure is observed with the emergence of micro-pores on the surface (figure 2(c)). Further addition of 40 wt% of PIL, the pore size is increased. Addition of 80 wt% of PIL also shows presence of bigger pores along with some white elongated structures. These structures may be attributed to the presence of PIL/H$_3$PO$_4$ coming out of the electrolyte membranes due to leaching. The pore size and surface microstructures of the films demonstrate strong dependence on [dema][TfO] concentration [21].

3.2. Infrared spectroscopy analysis

To investigate the interaction between PVDF-HFP, H$_3$PO$_4$ and [dema][TfO] at the molecular level, FTIR spectroscopy is employed. The infrared spectra of the prepared electrolyte membranes in the range of 500–1500 cm$^{-1}$ and 2500–3500 cm$^{-1}$ are shown in figures 3(a) and (b). The FTIR spectra are quite sensitive to different polymorphs of the host polymer due to their different chain conformation. In the range of 500 cm$^{-1}$ to 1500 cm$^{-1}$, the characteristic peaks corresponding to α (TGTG), β (TTTT) and γ (T$_3$GT$_3$G) are very much useful for phase identification and their quantification. However, as some of the absorption peaks are commonly observed for all the three phases or at least two of them, focus must be to find undisputed exclusive peaks for individual phases [24–26]. As such in the PE membrane, the α-phase is the dominant one with little traces of β and γ phases. The exclusive peaks for the α-phase at 614 cm$^{-1}$, 760 cm$^{-1}$, 795 cm$^{-1}$, 972 cm$^{-1}$, 1149 cm$^{-1}$, 1209 cm$^{-1}$ and 1384 cm$^{-1}$ are present in the PE membrane. But in the PIL based membranes, most of these α phase peaks disappear except the one at ∼760 cm$^{-1}$. However, the intensity of 760 cm$^{-1}$ peak decreases consistently with increasing PIL concentration. This suggests that in the PIL containing electrolyte membrane non-polar α-phase is suppressed. The exclusive β phase peak 840 cm$^{-1}$ seems superimposed with the γ phase at 833 cm$^{-1}$. Also, another exclusive β phase peak at 1275 cm$^{-1}$ is observed as a shoulder of 1179 cm$^{-1}$ strong
Figure 2. Scanning electron micrographs of PE and PEM films.

Figure 3. (a) FTIR spectra of polymer electrolytes in the range 500–1500 cm$^{-1}$ and (b) 2500–3500 cm$^{-1}$. 
Similarly, the signature peak for the $\gamma$ phase is observed in all the PEM films at $\sim 1234 \text{ cm}^{-1}$. Hence, considering the polar phase of the PVDF-HFP having both $\beta$ and $\gamma$-phases, we estimated polar phase fraction using the absorbance values at 833 cm$^{-1}$ peak. The relative fraction of polar phases ($F_P$) is quantified using the following formula based on Beer–Lambert’s law given as:

$$F_P = \frac{I_{840}}{K_{840} \cdot I_{763} + K_{763} \cdot I_{840}} \times 100\%$$

where $I_{840}$ and $I_{763}$ ($\alpha$ phase) are the absorbencies at 840 cm$^{-1}$ and 763 cm$^{-1}$, respectively. The absorption coefficients $K_{840}$ and $K_{763}$ are taken to be $7.7 \times 10^4$ and $6.1 \times 10^4$ cm$^2$ mol$^{-1}$ [25, 27]. The individual phase fraction of $\beta$ and $\gamma$-phases from the total polar phase is calculated using:

$$F(\beta) = F_P \times \frac{I_{1275}}{I_{1275} + I_{1234}} \times 100\% \quad \text{and} \quad F(\gamma) = F_P \times \frac{I_{1234}}{I_{1275} + I_{1234}} \times 100\%,$$

where $I_{1275}$ and $I_{1234}$ are the absorbencies at 1275 cm$^{-1}$ ($\beta$ phase) and 1234 cm$^{-1}$ ($\gamma$-phase), respectively [28]. The fraction of $\alpha$ phase is given as $1 - F_P$. The variation of all these phase fractions as a function of [dema][TIO] concentration is presented in Table 1.

It is observed that, the crystalline content of the PE film consisting of 80% of $\alpha$ phase and 17% of $\gamma$-phase with very little contribution from the $\beta$ phase. In the PEM film with 20 wt% of PIL, the $\alpha$ phase fraction drops to 24% and the polar phase increases to 76% in which 20% is $\beta$ phase. Similarly, for the PEM films with [dema][TIO] concentration 40–80 wt%, polar phase remains the major phase though $\alpha$ phase fraction increased a little. However, from the polar phase fraction, $\beta$ phase fraction remains always $\sim 20\%$ and independent of [dema][TIO] concentration. The significant increase in polar phases in the PIL containing electrolyte membranes is due to the interaction of cations and anions of PIL ([dema][TIO]) with the dipoles in the vinylidene fluoride (VDF) monomer units and induces the trans conformation in the C–C chain [27]. At higher wt% of PIL (60 and 80 wt%), there is a chance of liquid phase ([dema][TIO] and $\text{H}_3\text{PO}_4$) segregation and they may be coming out to the pores. Hence, a small decrease in polar phase is seen at these higher concentrations as a result of withdrawal of some of PIL/$\text{H}_3\text{PO}_4$. 

![Figure 4. (a) FTIR spectra of the PE and PEM films in the range 900–1100 cm$^{-1}$ and (b) 1120–1300 cm$^{-1}$. In (a) the spectrum in navy blue color represents pristine PVDF-HFP film.](image)

| Concentration of PIL ([dema][TIO]) in wt% | Percentage of $\alpha$ phase; $F(\alpha)$ | Percentage of $\beta$ phase; $F(\beta)$ | Percentage of $\gamma$ phase; $F(\gamma)$ | Percentage of polar phase; $F_P$ |
|-----------------------------------------|-----------------------------------------|-----------------------------------------|-----------------------------------------|----------------------------------|
| 0 (PE film)                             | 81                                      | 2                                       | 17                                      | 19                               |
| 20                                      | 24                                      | 19                                      | 57                                      | 76                               |
| 40                                      | 26                                      | 22                                      | 31                                      | 73                               |
| 60                                      | 31                                      | 22                                      | 47                                      | 69                               |
| 80                                      | 37                                      | 21                                      | 42                                      | 63                               |

Table 1. Estimation of $\alpha$, $\beta$, $\gamma$ and total polar phase fraction in PE and PEM films.
The presence of PIL in the electrolyte membranes is manifested in terms of appearance of 575 cm$^{-1}$ and 639 cm$^{-1}$ peaks owing to asymmetric deformation of CF$_3$ and symmetric deformation of SO$_3$ present in the [dema][TIO], respectively [29]. Also, a peak corresponding to S=O stretching mode vibration starts appearing at 1026 cm$^{-1}$ (figure 4(a)) with the introduction of PIL into the membrane and this peak getting sharper with increase in PIL addition [30]. Another characteristic band of the PIL is due to N-H stretching observed at 2800 cm$^{-1}$ and 3070 cm$^{-1}$. As seen in figure 3(b), these two peaks appear in the FTIR spectra of all the PIL containing membranes and are absent in the PE membrane. Their intensity steadily increases with PIL concentration. The 2800 cm$^{-1}$ peak is due to the stretching of N-H group present in [dema]$^+$ ion when it is free while that of at 3067 cm$^{-1}$ is due to its interaction with [TIO]$^-$ ions. The presence of these two peaks suggests a dynamical state of hydrogen bond network in the membranes containing higher concentration of PIL just as in the case of neat PIL [31, 32]. This may have a direct influence over proton conductivity in these electrolytes. In figure 4(a), the peak ∼997 cm$^{-1}$ in PE and PEM films may be attributed due to the symmetric stretching of PO$_4^{3-}$ in phosphoric acid [33]. This peak is absent in the pristine PVDF-HFP film as shown in figure 4(a). In figures 4(a) and (b), the peaks observed at 1064 cm$^{-1}$ and 1178 cm$^{-1}$ in the PE film are due to the CF$_3$ out of plane deformation and C-F stretching respectively [25, 30 and 34]. It is observed in the PEM films that these peaks show sensitivity towards PIL concentration in terms of peak shift and intensity variation.

3.3. Thermal analysis

In order to analyze the thermal stability of the prepared polymer electrolytes, thermogravimetric analyses were carried out for all the samples and presented in figure 5. In the PE film, the initial weight loss up to 100 °C is due to evaporation of residual water present in the membrane which may be accumulated during sample preparation stage. However, beyond 100 °C also, there is a steady decrease in weight up to 330 °C. This weight loss is due to the dehydration of H$_3$PO$_4$ that occurs at ∼150 °C giving rise to diphosphoric acid (H$_4$P$_2$O$_7$) and water. This dehydration process may lead to the formation of metaphosphoric acid (HPO$_3$) at relatively higher temperature (∼300 °C). The weight loss in the form of decomposition of H$_3$PO$_4$ into poly (phosphoric acids) at higher temperature will lead to decrease in charge carrier (protons) in the membrane [35]. Hence, this limits the use of these membranes for moderately high temperature applications. However, as seen in figure 5(a) for all the PEM films, the region from 100 °C to 200 °C is contrastingly flat suggesting no weight loss. This implies that the decomposition of H$_3$PO$_4$ is arrested in that region due to interaction between [dema][TIO] and H$_3$PO$_4$. Hence, the presence of PIL may offer the performance stability and reliability even at higher temperature. Also in the PE film, two step weight loss regions are observed from 330 °C–400 °C and 400 °C–490 °C corresponding to the boiling of phosphoric acid and degradation of PVDF-HFP, respectively. In the PEM film containing 20 wt% and 40 wt% of [dema][TIO], the thermograms suggest that these two weight loss regions shifted to lower temperature side. On further increase in [dema][TIO] concentration (60 and 80 wt%), the two weight loss regions merged to one over a temperature range of 280 °C–420 °C. This also can be confirmed from DTGA (figure 5(b)) plots for 60 and 80 wt% of [dema][TIO] containing membranes showing single large peak centered around 362 °C while that for others having two peaks around 365 °C and 470 °C. This suggests that the degradation of the electrolyte membranes containing PIL initiated at lower temperature.

To further understand the impact of PIL incorporation on overall thermodynamic properties of electrolyte membranes, the DSC thermograms were analyzed and presented in figure 6. The thermograms during the heating cycle from −85 °C up to 175 °C are shown in figure 6(a). For the PE film, the endothermic peak

![Figure 5. TGA and DTGA thermograms of the prepared polymer electrolytes.](image-url)
corresponding to crystalline melting temperature ($T_m$) is observed at $\sim 142$ °C. This $T_m$ shifts to lower temperatures with increasing PIL concentrations in the PEM films. This suggests that the polymer matrix becomes more flexible with improved segmental motion (chain mobility) as the concentration of PIL increases in the membrane. Crystallization melting process in different polymorphs of PVDF-HFP is also sensitive to the chain conformation. Among the three major phases of PVDF-HFP, $\beta$ is thermally the most stable one while the $\beta$ is the least. The order of their crystalline melting temperature is $T_m(\beta) < T_m(\alpha) < T_m(\gamma)$ [36]. The decrease of $T_m$ in the PEM with increase in PIL concentration and also appearance of shoulder in the higher temperature side of the endothermic peaks (40 and 60 wt%) suggest increase of polar phases ($\beta$ and $\gamma$). The area under the endothermic peak gives enthalpy of crystalline melting ($\Delta H_m$) which can be used to calculate the crystallinity fraction in electrolyte membranes. The calculated $\Delta H_m$ is steadily decreasing as PIL concentration increases in the membrane as recorded in table 2. This indicates that the crystallinity fraction ($\chi_c$) is decreasing in the electrolyte membrane with respect to the total weight of the sample. However, to see how the presence of PIL affects the crystallization process, the calculation of $\chi_c$ must be done with respect to the weight fraction of polymer in the membrane. We calculated $\chi_c$ using the formula as: 

$$\chi_c = \frac{\Delta H_m}{(1 - \Phi) \Delta H_m^{\text{corr}}} \times 100$$

where, $\Delta H_m$ is the melting enthalpy as calculated from the area under the endothermic peak, $\Delta H_m^{\text{corr}}$ is the melting enthalpy of 100% crystalline PVDF-HFP (105 J g$^{-1}$) [37, 38] and $\Phi$ is the weight fraction of fillers (H$_3$PO$_4$ + PIL). The weight corrected crystallinity fraction for PE film is 27% and didn’t show much change at 20 wt% of the PIL. However, with further increase in PIL concentration, $\chi_c$ decreases and attains a minimum of 17% for 40 wt% PIL loaded electrolyte. This suggests that the presence of PIL not only improves the polymer chain flexibility, rather also affects the polymer crystallization process. The increased polar phase and amorphous fraction in the electrolyte membrane may have direct effect on the electrical charge transport process. The glass transition temperature ($T_g$) which marks the transition from a glassy rigid framework structure of polymer matrix to beginning of chain/segmental motion is observed around $-41$ °C in the PE membrane. The change in $T_g$ on addition of PIL is presented on the table 2.

Figure 6(b) shows the DSC plots in the cooling cycle for the electrolyte membranes. The crystallization temperature ($T_m$) is observed to be decreasing gradually with increase in PIL concentration. For PE film, $T_m$ is observed around 98 °C and drops down to 85 °C for the electrolyte membrane containing 80 wt% PIL. This result is consistent with the change in $T_m$ as already recorded from figure 6(a) and both suggests increasing chain flexibility on addition of PIL.
3.4. Electrical analysis

Figure 7(a) shows the Nyquist ($Z^\prime$ versus $Z^\prime\prime$) plots of the prepared electrolyte membranes at room temperature. It is observed for the PE (inset) and PEM films that the typical Nyquist plot consists of a semicircle at higher frequency side followed by a slanted line at lower frequency. The bulk resistance ($R_b$) of each sample was obtained from the intercept of the semicircle on the real axis. It is observed that the $R_b$ value for PE is $\sim 3294 \ \Omega$ and drops drastically on PIL incorporation to $\sim 54 \ \Omega$ for 20 wt\% PIL addition. The minimum resistance of $\sim 30 \ \Omega$ is observed for 40 wt\% of PIL incorporated electrolyte. The dc ionic conductivity ($\sigma$) of the prepared samples were calculated as

$$\sigma = \frac{1}{R_b} \times \frac{d}{A}$$

where $d$ is the thickness of the samples and $A$ is the area of the electrode used to measure the dc ionic conductivity of the samples. Figure 7(b) shows the room temperature dc ionic conductivity variation with respect to increase in [dem][TfO] concentration in the electrolytes. The ionic conductivity increases by two orders in all polymer electrolytes in comparison to the PE films and show a little dependence on PIL concentration after getting saturated at 40 wt\%. The maximum ionic conductivity $\sim 6.3 \times 10^{-4} \ \text{S cm}^{-1}$ is observed around 40 wt\% of PIL. However, there is a small drop in the conductivity value at higher content of PIL. This may be attributed to the leaching of PIL/H$_3$PO$_4$ from the electrolytes at higher loading of [dem][TfO].

Further to investigate the ion-transport dynamics and the role of [dem][TfO] concentration, the dielectric spectra at room temperature are plotted for the PEM films. The complex dielectric function can be written as $\varepsilon_r = \varepsilon_r^\prime (\omega) - i \varepsilon_r^\prime\prime (\omega)$, where $\varepsilon_r^\prime (\omega)$ and $\varepsilon_r^\prime\prime (\omega)$ are the real and imaginary part of the relative permittivity. The $\varepsilon_r^\prime$ and $\varepsilon_r^\prime\prime$ are also known as the dielectric storage and loss can be directly calculated from the complex impedance ($Z^\prime$) following the relation as $Z^\prime = Z^\prime + iZ^\prime\prime = \frac{1}{\omega C_0 \varepsilon_0}$, where $C_0$ is the geometrical capacitance. The $C_0$ is estimated using the relation $C_0 = \varepsilon_0 \frac{A}{d}$ where $A$ and $d$ are the area of the electrode and thickness of the sample; and $\varepsilon_0$ is the absolute permittivity. The spectra of $\varepsilon_r^\prime$ and $\varepsilon_r^\prime\prime$ for the PE and PEM films are presented in figure 8(a). For the PE sample, the low frequency rise in the dielectric storage ($\varepsilon_r^\prime$) is due to the electrode polarization which occurs as a result of space charge accumulation at the interfaces.

For PEM films, there is a more than one order increase in $\varepsilon_r^\prime$ in the low frequency region. This is due to the increase in charge carrier concentration contributed by the [dem][TfO]. At higher frequency, the charge carriers can’t follow the fast changing electric field and hence the polarization due to space charge accumulation drops. This leads to decrease in $\varepsilon_r^\prime$ values at higher frequency. The dielectric loss ($\varepsilon_r^\prime\prime$) pattern of PE films in figure 8(a) can be segregated into three different regions: (1) low frequency region due to electrode polarization, (2) dc conductivity contribution in the middle and (3) structural or segmental relaxation at high frequency end. This loss pattern can give useful information regarding conductivity (electrode polarization) relaxation and segmental relaxation of the polymer host. However, in many cases, the dc conductivity contribution mostly obscures the loss peaks corresponding to different dielectric relaxation phenomena. Even in the PEM films, the dc conductivity region is broadened encompassing the higher frequency region and so the segmental relaxation is either shifted to further higher frequency or concealed under the dc conductivity contribution.

Hence, to visualize the relaxation peaks in the dielectric loss spectra, either the dc conductivity contribution ($\frac{\sigma}{\varepsilon_0}$) must be subtracted or the $\varepsilon_r^\prime\prime$ can be calculated from $\varepsilon_r^\prime$ using the relation ($\varepsilon_r^\prime\prime_{\text{corrected}} = -\frac{\pi}{2 \ln 2} \frac{d_{\text{corrected}}}{d_{\text{real}}} \varepsilon_r^\prime$) [39, 40].

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**Figure 7.** (a) Complex impedance spectra of polymer composite electrolytes (b) room temperature dc conductivity variation with PIL concentration.
Another way to analyze these relaxation peaks is by plotting the imaginary part of other dielectric/electric functions such as complex modulus ($M^* = \frac{1}{\omega C^*}$), admittance ($Y^* = \frac{1}{\omega Z^*}$) and loss tangent ($\tan(\delta)$). But it should be carefully noticed that there is a relative shift in the relaxation peaks depending on the dielectric functions used. The relaxation time corresponding to a particular relaxation phenomena follows a general trend of $\tau_E > \tau_Y > \tau_{tan} > \tau_Z > \tau_M$ [41]. In the figure 8(b), the spectra of loss tangent clearly shows two relaxation peaks corresponding to electrode polarization and segmental relaxation in the PE film. On addition of the PIL, the low frequency relaxation peak corresponding to the electrode polarization shifted to higher frequency suggestive of faster charge carrier dynamics. However, the segmental relaxation peak didn’t show any shift to high frequency side as the PIL increases from 0 to 20 wt%. At higher concentration of PIL, both the relaxation peaks merged and broadened to indicate a strong coupling of conductivity with structural relaxation in the PEM samples [42].

4. Conclusion

Non-aqueous proton conducting polymer electrolyte were prepared using both phosphoric acid and [dema] [TfO] as active proton conductive media hosted in PVDF-HFP matrix. Effect of concentration of PIL i.e. [dema] [TfO] in the primary electrolyte (PE) system containing only phosphoric acid (H₃PO₄ in PVDF-HFP) were investigated in terms of changes in structural, microstructural, thermal and electrical properties. The crystallinity fraction of the host polymer decreases with the introduction of PIL into the membrane as evident from XRD and DSC analyses. Scanning electron micrographs suggest that at higher PIL loading (≥ 80 wt%), white elongated structures observed on the membrane surface due to the leaching of phosphoric acid and PIL. Micro-pores were also seen on surface of membranes containing PIL. Vibrational spectroscopy analysis using FTIR shows that the host polymer in the PEM preferably crystallizes into polar $\beta$ and $\gamma$ phases whereas that in the PE film is predominantly in non-polar $\alpha$ phase. Thermo-gravimetric study indicates that the presence of PIL in polymer electrolytes also acts as deterrence for the condensation dehydration reaction of phosphoric acid in the temperature range of 100 °C–200 °C. The maximum ionic conductivity at room temperature (RT) is observed to be $6.3 \times 10^{-4}$ S cm⁻¹ for PEM containing 40 wt% of [dema][TfO]. This is almost two orders higher than that of the primary electrolyte (PE) containing only phosphoric acid. The dielectric analysis of the PEM shows that the charge carrier dynamics becomes faster due to the presence of [dema][TfO]. A strong coupling of ionic conductivity with structural relaxation of the host polymer is also observed in the PEM films. Hence, a wholesome study of electrical and dielectric properties by varying both temperature and frequency can reveal more on the charge carrier dynamics in these electrolytes. Nevertheless, looking at good ionic conductivity at RT and thermal stability over a wide range of temperature, these polymer electrolytes seems to be promising for intermediate temperature PEMFC applications.

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