

Effect of Ionic Liquid Incorporation on Sodium-Ion Conducting Gel Polymer Electrolytes Based on PVDF-HFP and Sodium Triflate

M. D.M. Nayanakanthi

Uva Wellassa University

H. M.J.C. Pitawala

jagath@uwu.ac.lk

Uva Wellassa University

Research Article

Keywords: Energy storage, Sodium batteries, Gel polymer electrolyte, Ionic liquid, PVdF-HFP, NaTf

Posted Date: October 9th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11123578/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Effect of Ionic Liquid Incorporation on Sodium-Ion Conducting Gel Polymer Electrolytes Based on PVDF-HFP and Sodium Triflate

M. D.M. Nayanakanthi¹, H.M.J.C. Pitawala*¹

¹ Department of Science and Technology, Faculty of Applied Sciences, Uva Wellassa University, Badulla, Sri Lanka.

“Corresponding author: H.M.J.C. Pitawala (jagath@uwu.ac.lk)”

Abstract

In this work, sodium ion conducting gel polymer electrolytes (GPEs) based on 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTf) ionic liquid (IL) and poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) copolymer have been studied for their structure and physical properties. The salt, sodium triflate (NaTf) was used to facilitate the sodium ion conduction. All the samples are prepared using the well-known solvent casting method. The IL was added to the polymer-salt mixture in different concentrations to increase the Na⁺ ion conduction. The resulting membranes are free standing, flexible, non-volatile, and thermally stable up to 400 °C. Among the studied samples, the maximum room temperature ionic conductivity was 4.66 mS cm⁻¹ for the GPE having 67 wt.% IL. The x-ray diffraction (XRD) spectra showed a reduction in the degree of crystallinity and an increase in amorphous phase content of IL added GPEs. In addition, the decrease of melting temperature (T_m) and glass transition temperature (T_g) values with the incorporation of IL seen in the differential scanning calorimetry (DSC) thermograms points towards the improved segmental flexibility of the polymer chains. These findings demonstrated that the addition of IL has a clear influence on the structure and physical properties of the PVdF-HFP: NaTf mixture, resulting in increased mobility of conducting ions via structural changes, as further confirmed by FTIR vibrational spectroscopy.

Key Words

Energy storage, Sodium batteries, Gel polymer electrolyte, Ionic liquid, PVdF-HFP, NaTf

1. Introduction

The electrolyte is a key component of an energy storage device that facilitate the ion conduction between the anode and cathode. Due to their high ionic conductivities and improved electrode contacts, liquid electrolytes (LEs) are generally preferred. However, the hazards of leakage, the use of volatile and flammable organic solvents, electrode corrosion, and many more other factors make the use of LEs are subjected to various restrictions. On the other hand, solid polymer electrolytes (SPEs), which do not need liquid solvents, may thus provide a solution to these problems. However, SPEs often have very weak ionic conductivity at low temperatures and exhibit poor contact with electrode interfaces, leading to poor cell performance. Therefore, gel polymer electrolytes (GPEs) have shown more attention as a solution to above mentioned problems associated with LEs and SPEs because of their distinctive hybrid structure, which simultaneously provides cohesive qualities of solids and diffusive properties of liquids. They can function as separators in energy storage devices in addition to having electrolyte properties. For lithium batteries, there are several efforts have been taken to develop GPEs [1-5], whereas sodium battery applications have received less attention [2,6].

In high energy density rechargeable batteries, fuel cells, and electrochromic windows, gel polymer electrolytes (GPEs) are prospective candidates to be employed as electrolyte membranes. Numerous different polymer systems can be used to create GPEs. In comparison to other systems, poly(vinylidene fluoride-co-hexafluoropropylene) copolymer (PVDF-HFP) based membranes have drawn a lot of interest since they can trap a large amount of liquid electrolyte while being transparent, flexible, and dimensionally stable. Since ion conduction occurs in the liquid phase of the GPEs, the significant proportion of liquid phase ensures a high ionic conductivity. Among different polymer membranes, PVdF-HFP based membranes are also more chemically and thermally stable.

Due to their distinct characteristics, ionic liquid-based electrolytes for rechargeable batteries are currently receiving a lot of attention [1]. The term "ionic liquids" (ILs) refers to salts with exceptionally low melting points (less than 100 °C). They have substantially distinct physico-chemical characteristics from traditional organic solvents. Ionic liquid-based electrolytes show excellent thermal stability, low vapor pressure, and low flammability may boost safety by reducing pressure buildup and thermal runaway in rechargeable batteries [2,7-12]. Incorporating ionic liquid-based electrolytes onto a polymer membrane is a practical method of creating them for rechargeable batteries [13-15]. This resolves issues with mechanical instability and leakage that are related to liquid electrolytes. Additionally, a cell built solely of thin film electrodes and electrolytes can be used to create energy storage systems that are incredibly small, light, and reliable [16-17].

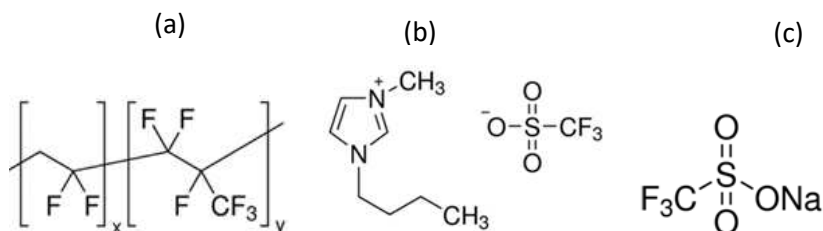


Fig.1. Chemical structures of (a) PVdF-HFP (b) BMIMTf and (c) NaTf

In the current study, we examined a novel sodium ion conducting gel polymer electrolyte based on PVdF-HFP copolymer with room temperature ionic liquid, 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTf), and its solutions with a Na-salt, sodium trifluoromethanesulfonate (NaTf). The chemical structures of PVdF-HFP (a), BMIMTf (b), and NaTf (c) are depicted in Fig. 1. Different experimental techniques, including AC impedance spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermo gravimetric analysis (TGA), and Fourier-transform infrared (FTIR) spectroscopy, have been used to investigate the various physico-chemical properties of synthesized GPEs. The aim of this study is to discuss how the membrane interacts with salt and IL, as well as correlate the thermal and transport properties with microscopic structure and interactions of the membrane and the ionic liquid electrolyte.

2. Experimental

2.1 Preparation of gel polymer electrolytes

Poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, average $M_w \sim 4 \times 10^5$), 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTf) and sodium triflate (NaTf) were purchased from Sigma Aldrich. Prior to use, PVdF-HFP and NaTf were vacuum dried at 60 °C for about 12 hrs. The common solvent casting technique was used to prepare the gel polymer electrolyte membranes, described as follows. The host polymer PVdF-HFP was first dissolved in tetrahydrofuran (THF) whereas the liquid electrolyte solution was prepared by dissolving NaTf in BMIMTf separately. Then, PVdF-HFP/THF mixture with different polymer content and different ratios of liquid electrolyte with different salt contents were mixed thoroughly at room temperature using a magnetic stirrer for 10 hrs (see Table 1). The mixtures were then poured in glass petri-dishes and allowed to evaporate the THF slowly. Finally, the dimensionally stable free standing transparent GPE thin films were obtained. However, the addition of BMIMTf content was not exceeded above 67 wt.% since it was difficult to obtain flexible free-standing transparent films above that composition. Prior to do all the characterizing, samples were vacuum dried.

Table 1. The compositions of polymer, salt and IL of prepared samples and their physical appearance at room temperature.

Sample Code	PVdF-HFP wt. %	NaTf wt. %	BMIMTf wt. %	Nature of casted film
M ₀	67	33	00	Free standing
M ₃₀	50	20	30	Free standing flexible
M ₅₀	33	16	50	Free standing flexible
M ₆₇	22	11	67	Free standing more like gel

2.2 Sample characterizations

The transport properties of samples i.e. ionic conductivities were measured using the computer interfaced impedance analyzer (Solartron SI 1260) over the frequency range 1Hz – 100 KHz. The conductivity measurements of gel electrolyte films were obtained using the film sandwiching between two stainless-steel (SS) electrodes. The temperature dependence of ionic conductivity values was obtained in a temperature range from 25 to 60 °C. Finally, the conductivity values were calculated using the equation, $\sigma = t/R_b A$, where t is the thickness of the electrolyte, A is the contact area of the electrolyte and R_b is the bulk resistance that was obtained from the plots of real and imaginary parts i.e. Z' and Z'' of the impedance plot. X-ray diffraction spectra were collected in order to determine the structure and crystallinity of the electrolyte samples and also raw materials. Here Rigaku Ultima IV X-ray diffractometer was used in an angle range (2θ) of 5 to 90°, at room temperature.

Thermal analysis of studied gel polymer electrolytes was performed using thermo-gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA was carried out from ambient temperature to 800 °C under dry nitrogen atmosphere at a heating rate of 10 °C/min using a TA Instrument- SDTQ600 Thermo Gravimetric Analyzer. The DSC was performed using a TA Instruments, Model: Q100 system, in where the samples were put in a sealed aluminum pan. DSC measurements were carried out from -90 to 400 °C at a heating rate of 10 °C/min in a static nitrogen atmosphere. In order to study the possible ion-ion and ion-polymer interactions of the synthesized materials, the FT-IR spectra were recorded between 500 and 4000 cm^{-1} in the absorbance mode using a Bruker Alpha Fourier-transform infrared (FT-IR) spectrophotometer.

3. Results and discussions

3.1 Impedance Spectroscopy

One of the most effective methods for examining the electrochemical characteristics of ion conducting materials, particularly ionic conductivity, is impedance spectroscopy [18]. Table 2 lists the measured ionic conductivity (σ) values of samples having various IL weight percentages at three distinct temperatures. Additionally, Fig. 2 displays the variation of ionic conductivity (σ) as a function of ionic liquid content in those GPEs at three different temperatures (room temperature, 45 °C, 60 °C).

Table 2. Ionic conductivities of GPEs with different amounts of IL at different temperatures.

Sample code/IL weight percentage	Temperature (°C)	Ionic conductivity σ (mS cm^{-1})
M ₃₀ 30%	29	0.06
	45	0.18
	60	0.38
M ₅₀ 50%	27	0.43
	45	1.04
	60	1.75
M ₆₇ 67%	29	4.66
	45	5.68
	60	8.80

The difference of conductivity values at all the temperatures with low IL content is slightly small, as shown in Fig. 2, and they have gradually increased. The difference is very significant for high IL content (67 wt. %). Since IL is also provide ions for the effective fraction of ions available to contribute to ion conduction process, high IL content will increase the total ionocity of the system resulting high ionic conductivity. In addition, at higher temperatures, ionic mobility will also increase. Both these effects will be contributed to the ionic conductivity behavior we see in Fig. 2. The maximum ionic conductivity was $8.8 \times 10^{-3} \text{ S cm}^{-1}$ at 60 °C for the sample M_{67} (see Table 2).

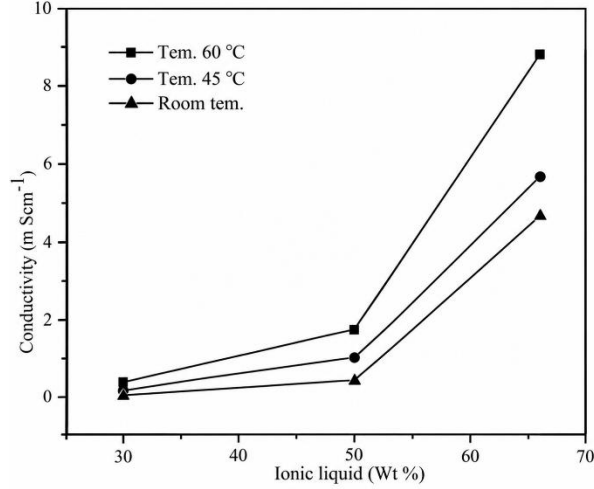


Fig. 2. Variation of ionic conductivity of PVdF-HFP:NaTf mixture as a function of IL.

Fig. 3 depicts the ionic conductivity as a function of the inverse temperature for the different IL contents. Over the examined temperature range, every curve in the plot closely correlates to the Arrhenius relation [19]. Similar behavior was reported for other PVdF-HFP based polymer electrolyte systems [14,20-21]. Ionic conductivity is seen to increase with temperature for all concentrations of IL, as seen in Fig. 3. This might be because the polymer chains enhanced segmental flexibility makes ion movement more rapid [1].

Further, our results show a clear ionic conductivity enhancement when the IL content increases. For example, the room temperature ionic conductivity of the sample having 30 wt. % is $0.06 \times 10^{-3} \text{ S cm}^{-1}$ and it has increased up to $4.66 \times 10^{-3} \text{ S cm}^{-1}$ for the sample having 67 wt. % IL (Fig. 2 & Table 2). This value is higher than the reported literature data ($0.21 \times 10^{-3} \text{ S cm}^{-1}$) in NaTFSI incorporated in PVdF-HFP/BMIMTFSI system [3]. It is an obvious that IL here acts as a plasticizer and make available a structural modification of PVdF-HFP:NaTf mixture. The improvement of the overall amorphous phase content, which we explain below in relation to our XRD and DSC data, is primarily responsible for this structural alteration. Fast ion conducting pathways are made available by the improvement of amorphous areas in polymer-salt mixtures. This increases fast ion mobility and contributes to improved ionic conductivity.

As mentioned above, a liner variation of $\ln \sigma$ vs $1/T$ plot suggests an Arrhenius type thermally activated process. Therefore, we can use bellow Eq.1 to describe the ionic conductivity-temperature behavior of the ionic liquid incorporated GPEs in more details [22].

$$\ln \sigma = -\frac{E_a}{RT} + \ln A \quad (1)$$

where σ is ionic conductivity, R is the molar gas constant, A is pre-exponential factor, E_a is the activation energy, and T is the absolute temperature. The activation energy (E_a) of above equation is also provide the additional information about ion

migration in GPE systems [20-21]. The calculated E_a values of our studied samples from ionic conductivities are shown in Table 3.

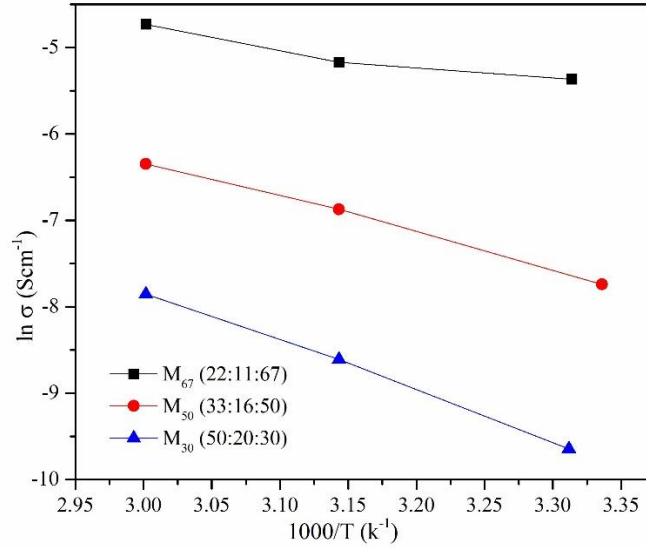


Fig. 3. Ionic conductivity as a function of inverse temperature for GPEs with different amounts of IL.

It is clear that with an increase in IL concentration, activation energy values steadily drop. The increase in amorphous nature, which promotes rapid segmental motion of the polymer chains and mobility of ions, could be the cause of the decreased E_a for ion transport. These effects lead to increase the ionic conductivity [1] .

Table 3. Parameters obtained from the ionic conductivity data fitted with the Vogel–Tammann–Fulcher equation

Sample	Activation energy (E_a) (KJ mol ⁻¹)	Pre-exponential factor ln(A)
M ₃₀	49.6	10.076
M ₅₀	35.1	6.3435
M ₆₇	16.7	1.2321

3.2 X-ray Diffraction

In previous studies XRD spectra were recorded to investigate the microstructure and degree of crystallinity of pure polymer matrix and various polymer salt mixtures [23-24]. To understand the ion transport characteristics of polymer-based electrolytes, it is crucial to understand the XRD spectra and their peak positions and shapes as they reveal significant information about the structure of GPEs. Fig.4 shows the x-ray diffraction patterns of pure PVdF-HFP film, pure NaTf, and complexes of PVdF-HFP/NaTf (70:30) and PVdF-HFP/NaTf/BMIMTf (22:11:67) of this study. The XRD spectrum of pure PVdF-HFP film exhibits semi-crystalline characteristics [25]. This semi-crystallinity should be caused by crystalline regions, where polymer chains are ordered and packed in amorphous polymer regions. However, the shape of the spectrum can be varied according to the recast method, solvent use and molecular weight of PVdF-HFP. The similar type of spectrum we found in our results can be seen from other reported data [24]. The major peaks recorded in pure PVdF-HFP film (Fig. 4) are observed at 2θ values of 17.6°, 19.7°, 26.5° and 38.9° along with broad hump between 15° and 45° indicating the semi-crystalline nature of the PVdF-HFP as mentioned [13,26-27].

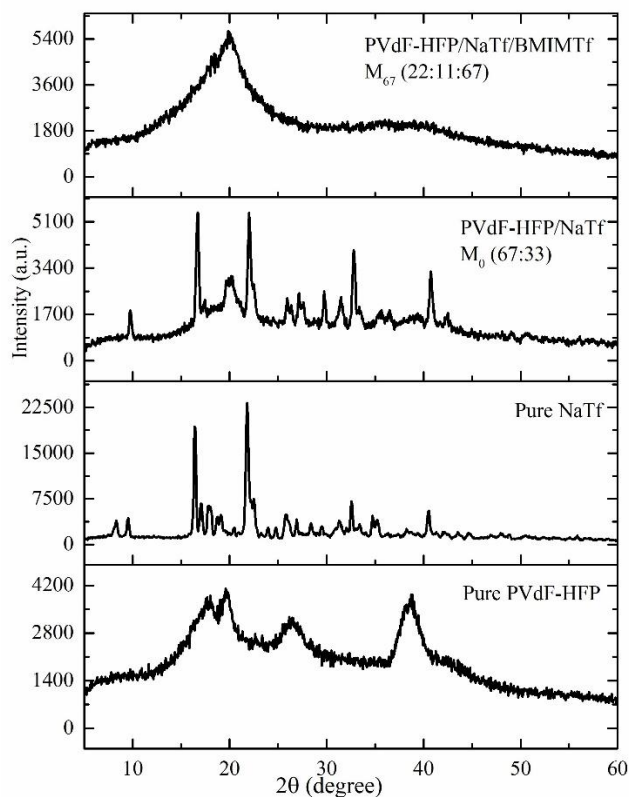


Fig. 4. XRD patterns of PVdF-HFP, NaTf, PVdF-HFP/NaTf and PVdF-HFP/NaTf/BMIMTf

As we already know, when we have salts with small symmetric anions (e.g. Cl), they of course show very high crystalline nature. Although, we used a salt having large and asymmetric anion i.e. Tf (see Fig. 1), still the very sharp and very high intense diffraction peaks shown in Fig. 4 support the high crystalline nature of pure NaTf. The highest intense two peaks can be detected at the 2θ values of 16.2° and 22.7° . Other crystalline peaks of pure NaTf can be found as minor peaks emerged in the noisy background at 2θ values of 8.4° , 9.5° , 18° , 25° , 32.5° , 35° and 40° . The recorded values in our study is very well matched with the published results [7].

The addition NaTf into PVdF-HFP has changed the XRD spectra of pure NaTf and also PVdF-HFP matrix. Even though, some sharp peaks are still found in the PVdF-HFP/NaTf mixture, it indicates considerable drop in intensity of salt peaks. This may be a result of salt has well dissolved into the polymer matrix. The broad peaks are observed for pure PVdF-HFP at 2θ values of 26.5° and 38.9° [28] has disappeared whereas 2θ values of 17.6° and 19.7° has overlapped with the salt peaks found in the range of 15° and 25° . This indicates that possible ion dissociation and complexation process has occurred in atomic level between polymer and salt. However, the crystallinity cannot be completely eliminated as seen in Fig. 4 and also discussed in DSC results for the sample (M_0) having this salt composition [(70:30)-(Polymer:salt)] due to high salt concentration and high crystallinity of the salt. Similar behavior has been reported for PVdF-HFP based polymer electrolyte systems [29-30].

Among studied samples, the addition of IL/NaTf mixture into PVdF-HFP has shown a clear enhancement of amorphous phase content in PVdF-HFP/NaTf/BMIMTf GPE system. The sharp peaks are found in PVdF-HFP/NaTf mixture has completely disappeared and only a broad hump centered on 2θ value of 20° can be observed due to the availability of some crystalline phases. This shows that IL serves as a plasticizer in this instance to make the GPEs more amorphous and to facilitate ion mobility by making the polymer backbone more flexible and enhanced ionic conductivity.

3.3 Thermal measurements

As previously mentioned, thermal properties of pure PVdF-HFP, PVdF-HFP/NaTf mixture and IL incorporated membranes were examined using DSC and TGA measurements. DSC data have usually been used to study the thermal transitions such as glass transition, melting and crystallization temperatures of GPEs and these phase transitions will provide the additional information on amorphous nature. In addition, the thermal stability of GPEs can be observed from TGA data.

The heating cycles of DSC thermograms of pure PVdF-HFP, PVdF-HFP/NaTf and two GPEs of PVdF-HFP/NaTf/BMIMTf mixtures are shown in Fig. 5. Fig. 6 shows the cooling cycles of same samples. The extracted values of melting (T_m) and crystallization (T_c) temperatures of different crystalline phases of pure polymer, polymer:salt and polymer:salt:IL mixtures are presented in Table 3.

It was found that the PVdF-HFP matrix exists different polymorphs (α -phase, β -phase and γ -phase) depending on the molecular chain conformation and preparation conditions [31-32]. Therefore, the melting behavior can also be varied. In our study, the pure PVdF-HFP film shows main three phase transitions in studied temperature range. Among them, very broad endothermic peak is observed at 142 °C corresponding to the melting of the highly ordered major crystalline phases of the pure PVdF-HFP matrix [9,13,33]. The weak melting signatures with less melting enthalpy are found at 82 °C and 52 °C should be attributed to other minor crystalline phases of matrix.

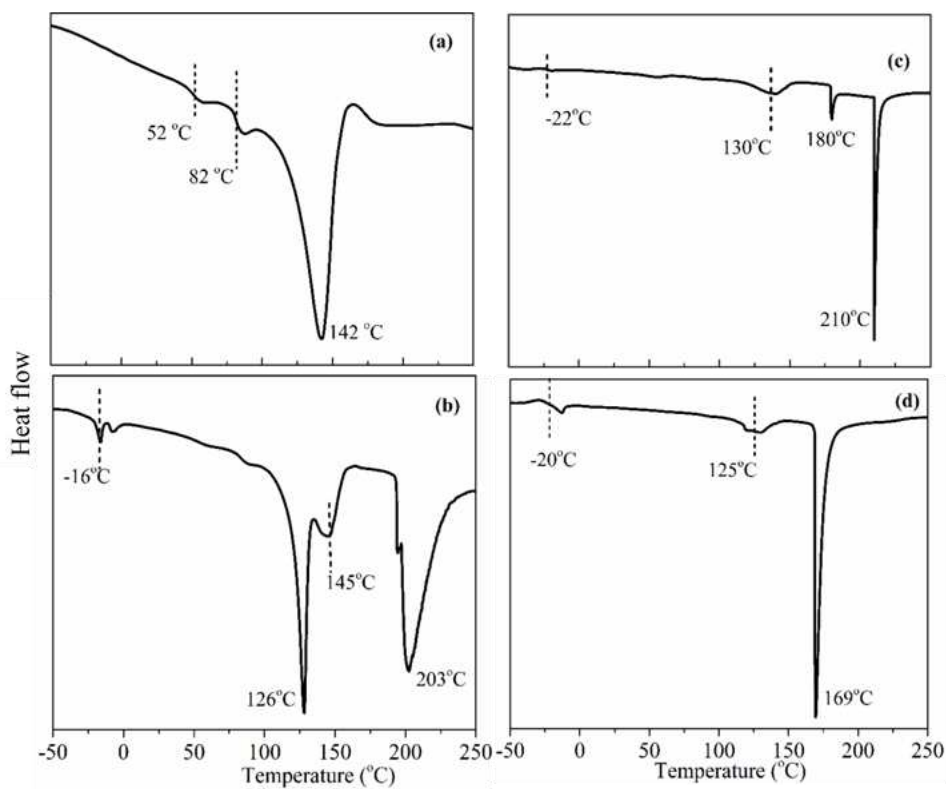


Fig. 5. Heating cycle of DSC thermograms of (a) pure PVdF-HFP film, (b) PVdF-HFP/NaTf mixture, (c) PVdF-HFP /NaTf /BMIMTf (60:10:30) GPE and (d) PVdF-HFP/NaTf /BMIMTf (22:11:67) GPE.

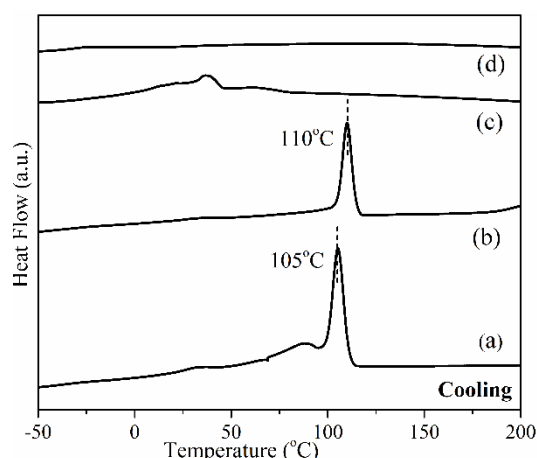


Fig. 6. Cooling cycle of DSC thermograms of (a) pure PVdF-HFP film, (b) PVdF-HFP/NaTf mixture, (c) PVdF-HFP /NaTf /BMIMTf (60:10:30) GPE and (d) PVdF-HFP/NaTf /BMIMTf (22:11:67) GPE.

Table 4. T_m , and T_c values of PVdF-HFP, PVdF-HFP/NaTf and IL incorporated GPEs with two IL concentrations.

Sample	T_m^1 (°C)	T_m^2 (°C)	T_c (°C)
(PVdF-HFP film)	142	-	105
M_0 - (PVdF-HFP/NaTf) (70:30)	126	203	110
M_{30} - (PVdF-HFP/NaTf/BMIMTf) (60:10:30)	130	210	25
M_{67} - (PVdF-HFP/NaTf/BMIMTf) (22:11:67)	125	169	-

T_m^1 , T_m^2 and T_c are representing the melting and crystallization temperatures of different crystalline phases of pure polymer, polymer:salt and polymer:salt:IL mixtures.

It is interesting to discuss the behavior of thermal transitions of PVdF-HFP/NaTf parent electrolyte [Fig. 5 (b)]. The reported value of melting temperature of pure NaTf is 253 °C (not shown here) [23,26] . After incorporation of NaTf into PVdF-HFP, a new broad endothermic peak is appeared at high temperature regime (peak value, 203 °C) but less than its original melting temperature. This indicates that the NaTf has dissociated in electrolyte preparation and form new very stable crystalline phases due to strong ion-dipole interactions in the polymer i.e between Na^+ ion and F atoms of PVdF-HFP and it can be further confirmed by our FTIR results [34]. Due to this ion dissociation will make more free-cations and helps to upraise the conductivity. Our XRD results also further confirmed this enhanced and reduction of crystalline nature of pure PVdF-HFP and NaTf respectively in PVdF-HFP/salt mixture. The melting signature of pure PVdF-HFP matrix (142 °C) has also changed due to the addition of salt. It has dropped to 126 °C but having a broad peak with a shoulder around 145 °C. The melting enthalpy of crystalline phases of the pure PVdF-HFP matrix has also lowered with NaTf addition. All these results strongly point out that the macroscopic behavioral changes occur due to their different structural modifications in microscopic level.

The special attention should be paid with the incorporation of BMIMTf/NaTf mixture into PVdF-HFP membrane [Fig. 5 (c and d)]. Our results showed that the high temperature melting transition we found in PVdF-HFP/NaTf sample has clearly changed after introducing IL. It shows very narrow and high intense melting peak at 210 °C. However, the melting enthalpy of this new crystalline phase is reduced considerably. It reveals that composition of ordered structure formed by salt and

polymer has reduced by IL, lowering the salt-polymer interactions. Additionally, it is proven that the degree of crystallinity of PVdF-HFP matrix has declined even since a minor melting signature is first revealed about 130 °C [31]. The influence of IL addition can be further investigated after increasing the IL concentration [Fig. 5 (d)]. The sample having high IL concentration has shown further decrease in melting transition of new crystalline phase discussed above. The peak value of this transition can be found around 169 °C. In addition, melting signature of crystalline phases of PVdF-HFP matrix is further suppressed when IL concentration increases. All these results evidently have shown the role played by IL for the improvement of the amorphous phase content and increase the number of free ions. This combined effect of IL has resulted high ion transport in studied GPEs.

Thermal properties of pure polymer, polymer:salt mixture and GPEs can be further studied using cooling cycles of DSC thermograms (Fig. 6). Pure PVdF-HFP matrix exhibits a distinct exothermic peak upon cooling at 105 °C as a result of the crystallization of polymer melt [35]. The crystallization temperature of salt doped sample has slightly increased compared to pure polymer matrix due to salt can interact easily with the melted polymer and decrease the polymer chain flexibility. Our XRD results and DSC heating scans have evidenced these additional ion-polymer interactions. However, this behavior has reversed after addition of IL since we see a very weak crystalline signature at low temperature for the sample having low IL concentration. For the sample with a high IL content, it is easy to see how the addition of IL increased the volume fraction of the amorphous phase. It does not crystallize over the temperature range studied. Again, these structural modifications are very well matched with XRD and DSC results discussed above.

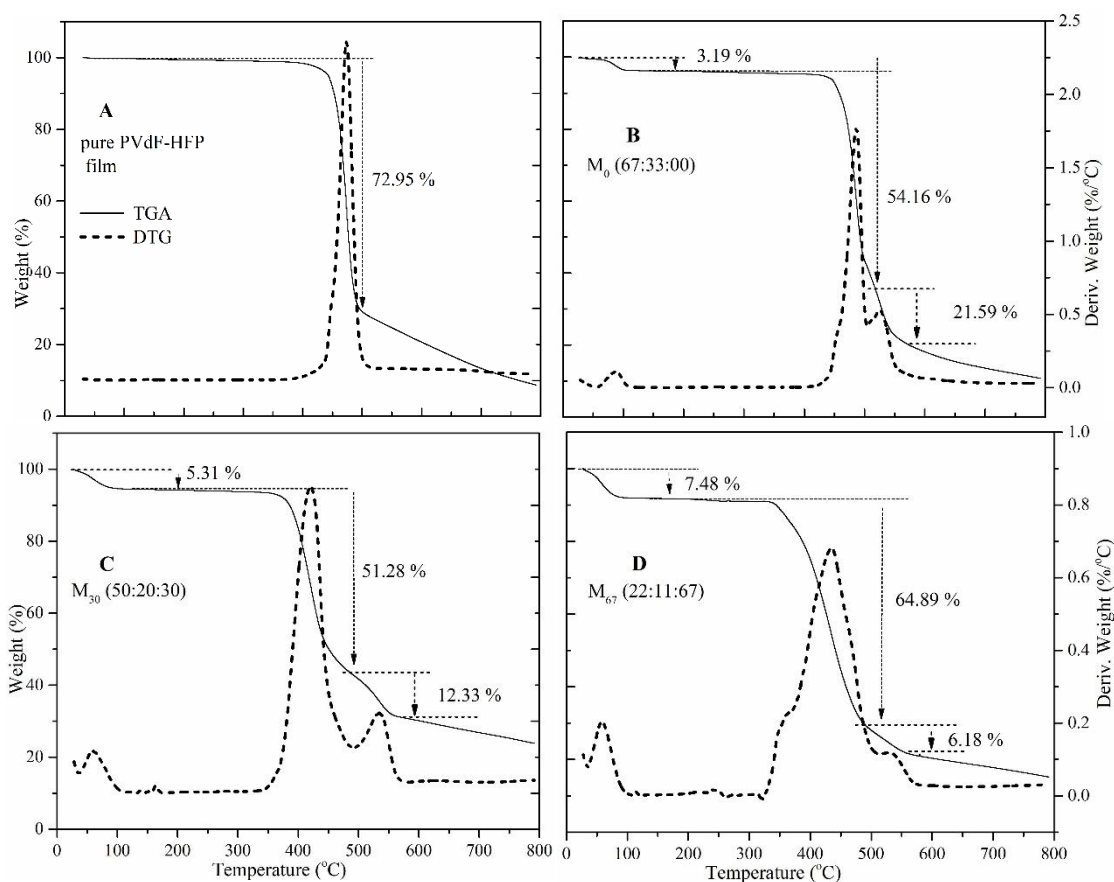


Fig. 7. TGA-DTG plots of (A) pure PVdF-HFP matrix, (B) PVdF-HFP/NaTf mixture, (C) PVdF-HFP /NaTf /BMIMTf (60:10:30) GPE and (D) PVdF-HFP/NaTf /BMIMTf (22:11:67) GPE.

Thermal stability of GPEs is directly related with the safety of the electrochemical devices. To measure weight loss as a function of temperature and time, TGA measurement on GPEs is frequently used [6]. Fig. 7 shows TGA and DTG plots of pure PVdF-HFP matrix, PVdF-HFP/NaTf mixture and two different GPEs with different wt% of IL. The DTG curve, which is the first derivative of the TGA curve, calculates the rate of decomposition. The extracted DTG peak values of different decompositions are shown in Table 4. It is indicated that there is no considerable weight loss for pure PVdF-HFP membrane (Fig. 7-A) over a wide temperature range (30 to 400 °C) and only a single weight loss is found with the DTG-peak value of 473 °C for the decomposition of PVdF-HFP [23,25,36-37]. All other samples show minor weight loss at low temperature in the region 50-100 °C. This should be related to the volatilization of excess solvent (THF) that was used in sample preparation since boiling point of THF is 66 °C. The salt doped PVdF-HFP displays (Fig. 7-B) different thermal decomposition behavior having high intense DTG peak and less intense peak appearing as a shoulder. In this sample, PVdF-HFP has first decomposed slightly higher temperature (486 °C, Table 4) due to salt interactions with polymer chains and making a more rigid structure. The second DTG peak (524 °C, Table 4) should be related to the decomposition of Tf anion in NaTf salt [26].

After addition of NaTf/ BMIMTf mixture into PVdF-HFP, the decomposition temperature of PVdF-HFP in GPE has considerably lowered and appears at 418 °C in DTG plot. The similar behavior was observed when NaTf/ EMIMTf liquid electrolyte is entrapped in PVdF-HFP [25]. However high IL loading improves thermal stability of PVdF-HFP further, and decomposition is detected at 434 °C. The decomposition of pure and salt-doped PVdF-HFP matrix is higher, nevertheless, this suggests that IL has reduced PVdF-HFP polymer crystallinity, as shown by the XRD and DSC data. In addition, the decomposition temperature of Tf anion has increased and appears as a distinguish peak at 534 °C in GPE. This indicates that the solvation structure of Tf anion has influenced by the IL and it further increases having high IL concentration (537 °C). The shoulder is appeared in the left hand side of the main peak of DTG plot (Fig. 7-D) should be related to the decomposition of organic BMIM cation [27]. Even though BMIMTf is also a salt, it should show low thermal stability compared to NaTf since asymmetrical configuration of BMIM cation must reduce the electrostatic interaction with Tf anion.

Table 4. Thermal decomposition values of PVdF-HFP and NaTf crystalline phases in different electrolyte systems.

Sample	PVdF-HFP (°C)	NaTf (°C)
Pure PVdF-HFP	473 (72.95 wt%)	-
M ₀	486 (54.16 wt%)	524 (21.59 wt%)
M ₃₀	418 (51.28 wt%)	534 (12.33 wt%)
M ₆₇	434 (64.89 wt%)	537 (6.18 wt%)

3.4 FTIR analysis

FTIR spectroscopy is an important tool to investigate the interactions between the polymer, salt and ionic liquid also can study the changes in the vibrational modes of particular bonds of molecules in the electrolyte systems. Spectral changes in the electrolyte system due to the addition of ionic liquid can be identified by comparing spectra of PVdF-HFP/NaTf mixture and PVdF-HFP/NaTf/BMIMTf GPEs. Fig. 8 shows the FTIR spectra of pure PVdF-HFP, PVdF-HFP/NaTf mixture and PVdF-HFP/NaTf/BMIMTf GPE, in the range of 500-2000 cm⁻¹ where the region significant changes noticed for vibrational modes. Important vibrational assignments of pure samples and significant changes due to addition of NaTf and IL have illustrated in the Table 5.

When NaTf incorporate in to the PVdF-HFP, new vibrational peak at 627 cm⁻¹ has indicated in the spectrum which represent SO₃ vibrations of triflate anion (section 2, Table 5). Upon incorporation of IL in the PVdF-HFP/NaTf mixture, the intensity of this peak increases and clearly make a new peak at left hand side of the peak. This can be expected because since IL also consists SO₃ groups in their anions and can make new coordination structure from both anions from salt and IL and make new

ion pairs. This again indicates that the complete dissociation of salt and dissolution of IL. Also, it is revealed that decrease of the crystallinity in the PVdF-HFP/NaTf system after addition of IL as discussed above in XRD results.

It is clear that, the peak positions at 836 cm^{-1} and 876 cm^{-1} belongs to the amorphous phase of PVdF-HFP (β -phase) remain unchanged after addition of NaTf, however, it is very clear that the peak intensity has dropped significantly since dipole moment of vibrational mode is directly related to the intensity of an IR absorption band. Vibrational modes at 836 cm^{-1} and 876 cm^{-1} representing mixed mode of vibrations of CH_2 rocking, combined CF_2 and CC symmetric stretching of PVdF-HFP [2,38], and those vibrational bands have dropped their bonding strengths after addition of NaTf. This indicates the improvement of flexibility of the polymer back bone. These changes clearly evidenced the coordination between polymer back bone and triflate anion. Even with addition of IL, these vibrational bands have not changed their vibrational bands. This shows that addition of NaTf and BMIMTf increases the amorphous nature of the polymer matrix, giving a conclusion which was also drawn from XRD results discussed earlier.

NaTf has high ion dissociation compared to general Na salts due to the strong electron-withdrawing ability of large SO_2CF_3 groups and also has a low tendency to form ion-pairs [2,39]. Moreover, the high dielectric constant of PVdF-HFP helps dissociating the salt, hence, fostering high free ion concentration in the gel. Combined effect of those together with incorporation of IL, should produce a strong dissociation of the NaTf, resulting in a great amount of free Tf anions. The wavenumber range $1000\text{--}1080\text{ cm}^{-1}$ has further analyzed to confirm Tf anions are in the form of free or forming ion pairs in the GPE. Bands associated with free triflate anions indicate values around at 1034 cm^{-1} [2,38]. As we can see in Fig. 8, an intense band is appeared at $\sim 1031\text{ cm}^{-1}$, indicating that free triflate anions are present for PVdF-HFP/NaTf (section 2, Table 5) system and IL-based GPEs (section 3, Table 5). Moreover, the stability of this peak confirms that a similar triflate interaction or less impact of IL for the vibrations of triflate anion.

The asymmetric vibrational mode of CF_3 of PVdF-HFP (1168 cm^{-1}) (section 1, Table 5), does not change in the PVdF-HFP/NaTf complex, however, this vibrational mode has downshifted when IL incorporated to GPE and it is found at 1157 cm^{-1} (section 3, Table 5). Downshift of the peaks confirms the complex formation between PVdF-HFP, NaTf and IL. The symmetrical stretching mode of CF_3 of NaTf at 1192 cm^{-1} , shows the upshift in the PVdF-HFP/NaTf complex and found at 1230 cm^{-1} (section 2, Table 5), indicating uplifting in CF_3 vibrations in the system with addition of NaTf. Pure NaTf spectra represent symmetric and asymmetric SO_3 vibrations as a peak range at $1231\text{--}1301\text{ cm}^{-1}$ [22,38], these have converged in to one peak at 1255 cm^{-1} in PVdF-HFP/NaTf complex (section 2, Table 5). These changes clearly indicate the coordination between polymer back bone and triflate anion as discussed in low wave numbers. Bands found at 1230 and 1255 cm^{-1} are representing SO_3 vibrations (section 2, Table 5) and both appear in the IL added electrolyte system with slight change of peak positions. Therefore, these changes in IR spectra provided additional evidence for the complexation of host polymer matrix with salt and IL.

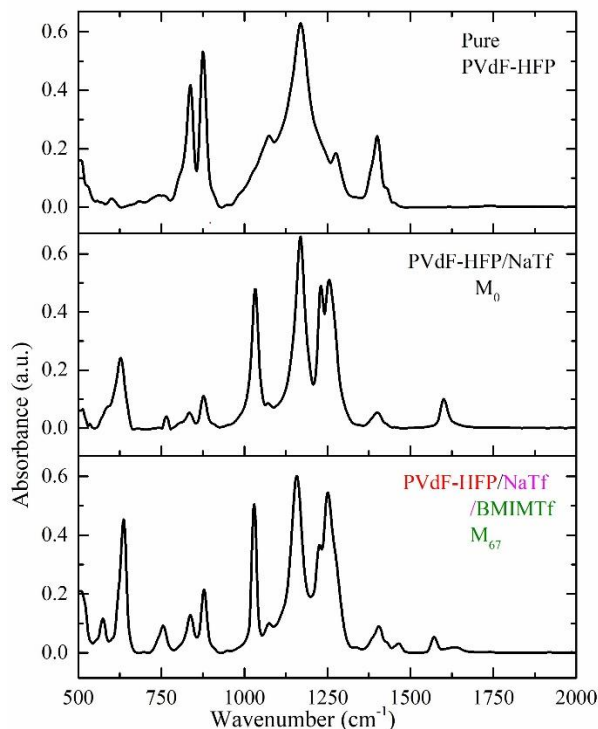


Fig. 8. FTIR spectra of pure PVdF-HFP, PVdF-HFP/NaTf mixture and PVdF-HFP/NaTf/BMIMTf GPEs.

In pure polymer spectrum vibrational mode at 1401 cm^{-1} represents C-F stretching vibration [38]. This peak has dropped its intensity considerably after addition of NaTf and BMIMTf. In this case after addition of IL vibrational peak has shifted to 1404 cm^{-1} (section 3, Table 5). According to those results, it can be predicted that C-F bonds attached to polymer backbone have weakened their bond strength and have made new interactions with IL. Furthermore, the PVdF-HFP/NaTf/BMIMTf has featured a new absorption peak at 1468 cm^{-1} (section 3, Table 5), which is assigned to the symmetrical in-plane bending of imidazole ring. Vibrational mode at 1570 cm^{-1} (section 3, Table 5) represents either characteristic peak of Tf anion or C-C/C-N bending mode of BMIM⁺. These changes count evidence for incorporation of IL in to the PVdF-HFP/NaTf system.

Table 5. Possible assignments of some significant peaks in FTIR spectra of PVdF-HFP, PVdF-HFP/NaTf mixture and PVdF-HFP/NaTf/BMIMTf GPE.

Sample	Wavenumber (cm^{-1})	Assignments
PVdF-HFP <i>Section 1</i>	836	α -phase of PVDF (very weak) (mixed mode of CH_2 rocking)
	876	Strong amorphous phase of PVDF-HFP (combined CF_2 and CC symmetric stretching)
	1072	Crystal phase of (PVDF-HFP)
	1168	Symmetrical stretching mode of CF_3
	1280	Symmetrical stretching vibrations of CF_2
	1401	C-F stretching
PVdF-HFP/NaTf <i>Section 2</i>	627	Symmetric/asymmetric vibrations of SO_3
	764	Symmetrical bending of $-\text{CF}_3$
	836	α -phase of PVDF

	878	Strong amorphous phase of PVDF-HFP
	1031	SO ₃ symmetric stretching
	1168	Asymmetrical stretching mode of CF ₃
	1230	Symmetrical stretching mode of CF ₃
	1255	Symmetric/asymmetric vibrations of SO ₃
	1401	C-F stretching
	1600	Characteristic peak of Tf ⁻
PVdF-HFP/NaTf/	634	Symmetric/asymmetric vibrations of SO ₃
BMIMTf	757	Symmetrical bending of -CF ₃
Section 3	839	α -phase of PVDF
	878	Strong amorphous phase of PVDF-HFP
	1031	SO ₃ symmetric stretching
	1157	Symmetrical stretching mode of CF ₃
	1225	Asymmetrical vibrations of CF ₃
	1251	Symmetric/asymmetric vibrations of SO ₃
	1404	C-F stretching
	1468	Symmetrical in-plane bending of imidazole ring
	1570	Characteristic peak of Tf ⁻ / C-C/C-N bending

According to the Fig.8, the intensity of some of the peaks from PVdF-HFP/NaTf mixture have slightly decreased after addition of IL. The lower the peak intensity of crystalline phases, the greater the amount of amorphous material of a sample can be found. That could be because of BMIM⁺ competes with Na⁺ to form a neutral ion-pair with Tf anion and gradually lowers the crystallinity at low viscous medium after addition of IL. These results lead to a better ion conduction process after addition of IL.

4. Conclusions

Gel polymer electrolytes (GPEs) with poly (vinylidene fluoride-hexafluoropropylene) [PVdF-HFP] copolymer doped with sodium trifluoromethanesulfonate (NaTf) salt and different concentrations of 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIMTf) IL were synthesized using a common solvent casting method. The Na⁺ ion conduction in the PVdF-HFP/NaTf electrolyte system was increased due to the addition of IL at an optimum weight percentage of 67 wt% and it shows the maximum ionic conductivity of 4.66 mS cm⁻¹ at room temperature. It is clearly evidenced from our XRD analysis, the crystallinity of the polymer:salt mixture decreases upon the addition of IL. This implies that IL disrupts the crystalline region and increases the amorphous region of the PVdF-HFP/NaTf membrane. The increasing amorphous domain in the GPEs is evident from the broadening of the crystalline reflections at 2 θ value 20°. FTIR results also showed that IL has interacted with the PVdF-HFP/NaTf electrolyte system, leading to the formation of new interactions between the PVdF-HFP/NaTf mixture. The thermal stability of GPEs has increased when the IL entrapped in PVdF-HFP/NaTf mixture. It is evidently shown by the high temperature of the third degradation stage in IL added GPEs. Even though the thermal stability has slightly reduced when IL wt% increase in GPEs, thermal stability has slightly reduced, it indicates enough properties for battery applications.

5. Acknowledgements

Authors are acknowledged the financial supports received from Uva Wellassa University for the research grant no. UWU/RG/2020/010 to the research assistantship.

References

- 1 Abreha M, Subrahmanyam A, Kumar JS (2016) Ionic conductivity and transport properties of poly (vinylidene fluoride-co-hexafluoropropylene)-based solid polymer electrolytes. *Chem Phys Lett* 658:240-247.
- 2 Adelhelm P, Hartmann P, Bender CL, Busche M, Eufinger C, Janek J (2015) From lithium to sodium: cell chemistry of room temperature sodium–air and sodium–sulfur batteries. *Beilstein J Nanotechnol* 6:1016-1055.
- 3 Balducci A (2017) Ionic liquids in lithium-ion batteries. *Ionic Liquids II*:1-27.
- 4 Lane GH, Bayley PM, Clare BR, Best AS, MacFarlane DR, Forsyth M, Hollenkamp AF (2010) Ionic liquid electrolyte for lithium metal batteries: physical, electrochemical, and interfacial studies of N-methyl-N-butylmorpholinium bis(fluorosulfonyl) imide. *J Phys Chem C* 114:21775-21785.
- 5 Noor SAM, Yoon H, Forsyth M, MacFarlane DR (2015) Gelled ionic liquid sodium ion conductors for sodium batteries. *Electrochim Acta* 169:376-381.
- 6 Hashmi S, Bhat MY, Singh MK, Sundaram N, Raghupathy BP, Tanaka H (2016) Ionic liquid-based sodium ion-conducting composite gel polymer electrolytes: effect of active and passive fillers. *J Solid State Electrochem* 20:2817-2826.
- 7 Aziz SB, Abidin ZHZ (2013) Electrical conduction mechanism in solid polymer electrolytes: new concepts to Arrhenius equation. *J Soft Matter* 323868- 323876.
- 8 Castillo J, Santiago A, Judez X, Garbayo I, Coca Clemente JA, Morant-Miñana MC, Armand M (2021) Safe, flexible, and high-performing gel-polymer electrolyte for rechargeable lithium metal batteries. *Chem Mater* 33 (22):8812-8821.
- 9 Chaurasia S, Singh R, Chandra S (2013) Thermal stability, complexing behavior, and ionic transport of polymeric gel membranes based on polymer PVdF-HFP and ionic liquid [BMIM][BF₄]. *J Phys Chem B* 117:897-906.
- 10 Chojnacka J, Acosta J, Morales E (2001) New gel electrolytes for batteries and supercapacitor applications. *J Power Sources* 97:819-821.
- 11 Priya WLM, Suthanthiraraj SA (2013) Electrochemical and FTIR studies of PVDF-HFP/(CF₃SO₃)₂Zn/Fe₂O₃ composite polymer electrolytes. *International Journal of Innovative Research in Science and Engineering* 5–8.
- 12 Wu F, Zhu N, Bai Y, Liu L, Zhou H, Wu C (2016) Highly safe ionic liquid electrolytes for sodium-ion battery: wide electrochemical window and good thermal stability. *ACS Appl Mater Interfaces* 8:21381-21386.
- 13 Singh VK, Singh RK (2015) Development of ion conducting polymer gel electrolyte membranes based on polymer PVdF-HFP, BMIMTFSI ionic liquid and the Li-salt with improved electrical, thermal and structural properties. *J Mater Chem C* 3:7305-7318.
- 14 Pandey G, Hashmi S (2009) Experimental investigations of an ionic-liquid-based, magnesium ion conducting, polymer gel electrolyte. *J Power Sources* 187:627-634.
- 15 Tripathi AK (2021) Ionic liquid–based solid electrolytes (ionogels) for application in rechargeable lithium battery. *Mater Today Energy* 20:100643.
- 16 Pitawala J, Navarra MA, Scrosati B, Jacobsson P, Matic A (2014) Structure and properties of Li-ion conducting polymer gel electrolytes based on ionic liquids of the pyrrolidinium cation and the bis(trifluoromethanesulfonyl) imide anion. *J Power Sources* 245:830-835.
- 17 Yuan C, Su L, Yang K, Li Z, Cheng X, Wang Y, Li L (2015) Effect of pressure on the structure and properties of polymeric gel based on polymer PVdF-HFP and ionic liquid [BMIM][BF₄]. *Colloid Polym Sci* 293:925-932.
- 18 Ariyoshi K, Siroma Z, Mineshige A, Takeno M, Fukutsuka T, Abe T, Uchida S (2022) Electrochemical impedance spectroscopy part 1: Fundamentals. *Electrochemistry* 90 (10): 102007.
- 19 Yeon S-H, Kim K-S, Choi S, Cha J-H, Lee H (2005) Characterization of PVdF(HFP) gel electrolytes based on 1-(2-hydroxyethyl)-3-methyl imidazolium ionic liquids. *J Phys Chem B* 109:17928-17935.
- 20 Luo K, Shao D, Yang L, Liu L, Chen X, Zou C, Wang X (2021) Semi-interpenetrating gel polymer electrolyte based on PVDF-HFP for lithium ion batteries. *J Appl Polym Sci* 138:49993.
- 21 Kumar KK, Ravi M, Pavani Y, Bhavani S, Sharma A, Rao VN (2011) Investigations on the effect of complexation of NaF salt with polymer blend (PEO/PVP) electrolytes on ionic conductivity and optical energy band gaps. *Physica B Condens Matter* 406:1706-1712.

- 22 Aziz SB, Woo TJ, Kadir M, Ahmed HM (2018) A conceptual review on polymer electrolytes and ion transport models. *J Sci Adv Mater Devices* 3:1-17.
- 23 Kumar D, Hashmi S (2010) Ionic liquid based sodium ion conducting gel polymer electrolytes. *Solid State Ionics* 181:416-423.
- 24 Kumar A, Sharma R, Suresh M, Das MK, Kar KK (2017) Structural and ion transport properties of lithium triflate/poly(vinylidene fluoride-co-hexafluoropropylene)-based polymer electrolytes: effect of lithium salt concentration. *J Elastomers Plast* 49:513-526.
- 25 Pandey G, Agrawal R, Hashmi S (2009) Magnesium ion-conducting gel polymer electrolytes dispersed with nanosized magnesium oxide. *J Power Sources* 190:563-572.
- 26 Ranjana PAB (2019) Enhancement of Na⁺ ion conduction in polymer blend electrolyte P(VdF-HFP)–PMMA–NaTf by the inclusion of EC. *J Polym Res* 26:1-13.
- 27 Ramesh S, Lu S-C, Vankelecom I (2013) BMIMTf ionic liquid-assisted ionic dissociation of MgTf in P(VdF-HFP)-based solid polymer electrolytes. *J Phys Chem Solids* 74:1380-1386.
- 28 Mishra K, Rai D (2021) Studies on ionic liquid-based nanocomposite gel polymer electrolyte and its application in sodium battery. *Mater Sci Eng B* 267:115098.
- 29 Xie M, Li S, Huang Y, Wang Z, Jiang Y, Wang M, Chen R (2019) An ionic liquid/poly(vinylidene fluoride-co-hexafluoropropylene) gel-polymer electrolyte with a compatible interface for sodium-based batteries. *Chem Electro Chem* 6:2423-2429.
- 30 Mahendrakar S, Anna M, Reddy J (2015) Structural, morphological and FTIR of PVDF-HFP and lithium tetrafluoroborate salt as polymer electrolyte membrane in lithium ion batteries. *Int J Chem Technol Res* 8:319-328.
- 31 Noor M, Buraidah M, Careem M, Majid S, Arof A (2014) An optimized poly(vinylidene fluoride-hexafluoropropylene)–NaI gel polymer electrolyte and its application in natural dye sensitized solar cells. *Electrochim Acta* 121:159-167.
- 32 Cai X, Lei T, Sun D, Lin L (2017) A critical analysis of the α , β and γ phases in poly(vinylidene fluoride) using FTIR. *RSC Adv* 7:15382-15389.
- 33 Kumar D, Suleman M, Hashmi S (2011) Studies on poly(vinylidene fluoride-co-hexafluoropropylene)-based gel electrolyte nanocomposite for sodium–sulfur batteries. *Solid State Ionics* 202:45-53.
- 34 Jeya S, Arulsankar A, Abarna S, Sundaresan B (2019) Effect of ionic liquids on the electrical, structural and morphological properties of P(VdF-HFP)–NaTF electrolytes. *Ionics* 25:5963-5977.
- 35 Parveen S, Sehrawat P, Hashmi S (2022) Triglyme-based solvate ionic liquid gelled in a polymer: a novel electrolyte composition for sodium ion battery. *Mater Today Commun* 31:103392.
- 36 Vo DT, Do HN, Nguyen TT, Nguyen TTH, Okada S, Le MLP (2019) Sodium ion conducting gel polymer electrolyte using poly(vinylidene fluoride hexafluoropropylene). *Mater Sci Eng B* 241:27-35.
- 37 Tang X, Muchakayala R, Song S, Zhang Z, Polu AR (2016) A study of structural, electrical and electrochemical properties of PVdF-HFP gel polymer electrolyte films for magnesium ion battery applications. *J Ind Eng Chem* 37:67-74.
- 38 Choi J, Shim E-G, Scrosati B, Kim D-W (2010) Mixed electrolytes of organic solvents and ionic liquid for rechargeable lithium-ion batteries. *Bull Korean Chem Soc* 31:3190-3194.
- 39 Moreno JS, Maresca G, Panero S, Scrosati B, Appetecchi GB (2014) Sodium-conducting ionic liquid-based electrolytes. *Electrochem Commun* 43:1-4.