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A study of structural, electrical and electrochemical properties of PVdF-HFP gel polymer electrolyte films for magnesium ion battery applications

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Abstract: New magnesium ion conducting polymer electrolyte films are developed and their experimental investigations are reported. The polymer electrolyte films are composed of various poly(vinylidene fluoride-co-hexafluoropropylene):magnesium trifluoromethanesulfonate compositions (PVdF-HFP:Mg(Tf)₂ in weight ratio) with different quantities of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid (EMITf). X-ray diffraction reveals that the pristine PVdF-HFP polymer film possesses a semi-crystalline structure and its amorphicity increases with increasing Mg(Tf)₂ and EMITf concentrations. From thermal analysis, the melting temperature (T_m), relative crystallinity (χ_c) and thermal stability of the 90PVdF-HFP:10Mg(Tf)₂

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gel polymer electrolyte film doped with 40 wt.% EMITf are obtained as 112°C, 21.8% and 355°C, respectively. The room-temperature ionic conductivity of the gel polymer electrolyte film increases with increasing EMITf concentration and reaches a high value of approximately $4.63 \times 10^{-3} \text{ S cm}^{-1}$ at 40 wt.% EMITf due to its amorphicity increase and interconnected pore structure. For the 40 wt.% EMITf electrolyte film, the temperature dependence of ionic conductivity follows the Arrhenius relation with an activation energy of 0.35 eV. The electrochemical stability window of the 40 wt.% EMITf electrolyte film is determined as ~4.8 V. The findings from this study are promising and have great potential for practical ionic device applications, particularly in rechargeable magnesium ion batteries.

Keywords: Polymer electrolytes; Electrical properties; Ionic conductivity; Electrochemical properties; Magnesium ion batteries

1. Introduction

Gel polymer electrolytes (GPEs) have attracted great interest and attention worldwide as an excellent substitute for liquid electrolytes due to their specific properties. This makes them suitable for various technological applications such as rechargeable batteries, supercapacitors and fuel cells [1, 2]. GPE is a hybrid electrolyte material, which offers combined beneficial characteristics of both solid electrolyte and liquid electrolyte systems. The GPEs possess many distinct advantages over the liquid electrolytes such as improved safety, less reactivity, flexibility, leakage proof, good interface stability and better manufacturing integrity. These gel polymer electrolytes are prepared by dissolving the polymer host, inorganic salt and plasticizer/additive in a solvent and the resultant solution is cast as film after the evaporation of the solvent. Generally, low molecular weight plasticizers (polyethylene glycol (PEG), ethylene carbonate (EC), propylene carbonate (PC), etc.,) are used for preparation of gel polymer electrolytes, which produces highly conducting films but exhibits poor mechanical properties, thermal stabilities and electrochemical performances [3-5]. To overcome these problems, many researchers are currently focusing on the utilization of room temperature ionic liquids (RTILs) as an alternative group of plasticizers instead of traditional organic liquids in the GPE systems. The ionic liquid acts as a plasticizer as well as a supplier of extra charge carriers for conduction in the gel polymer electrolyte system. The room temperature ionic liquids typically consist of bulky asymmetric organic cations and inorganic anions, which possess specific properties such as wide liquid-phase, non-volatility, non-flammability,

negligible vapor pressure at room temperature, wide electrochemical stability window, excellent thermal and chemical stability, high ionic conductivity and ability to dissolve a variety of compounds [6, 7]. Therefore, majority of researchers are focusing on developing ionic liquid incorporated GPEs and investigating their structural, thermal and electrical properties for ionic device applications. The reported research is mainly involved in investigating different polymer host materials such as poly(vinylidene fluoride) (PVdF), poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) [8-12]. Among these systems, the PVdF-HFP-based gel polymer films have received much attention since they have both crystalline VdF and amorphous HFP units. The amorphous phase is capable of trapping large amount of electrolyte, facilitating ion migration, while the crystalline phase provides a structural integrity to support a free standing film formation. In addition, the PVdF-HFP-based gel polymer electrolyte films are mechanically stiff and strong, and thermally and chemically stable [13]. Hence, the PVdF-HFP was chosen as the polymer host for the preparation of gel polymer electrolytes in this study. The majority of reported investigations into the PVdF-HFP systems are lithium ion conducting gel polymer electrolytes with applications in lithium ion batteries [14-16]. However, lithium ion conducting gel polymer electrolytes have safety problems because they are highly reactive in nature. Apart from lithium batteries, certain magnesium, zinc and sodium batteries are reported [17-19]. The rechargeable magnesium battery system has attracted increasing attention due to its performance capabilities and better characteristics. As a

consequence, the development of magnesium ion-conducting electrolytes has become one of the important issues to realize rechargeable and solid-state magnesium batteries in which the gel polymer electrolyte is a vital constituent. This work focuses on the preparation of magnesium ion conducting gel polymer electrolyte films along with the investigation into their structural, electrical and electrochemical properties in an attempt to achieve optimized properties for magnesium rechargeable battery applications.

2. Experimental

2. 1. Materials

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) with an average molecular weight of 400,000 was obtained from Sigma Aldrich and dried in an oven at 50 °C for 4 h prior to use. Magnesium trifluoromethanesulfonate ($\text{Mg}(\text{Tf})_2$) salt and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ionic liquid (EMITf) were obtained from Sigma Aldrich and used as received. Tetrahydrofuran (THF) with a purity of 99 % was purchased from Sigma Aldrich and used as the common solvent for the preparation of polymer electrolyte films.

2. 2. Preparation of polymer electrolyte films

The polymer electrolyte films were prepared by a standard solution cast technique. In this process, the host polymer PVdF-HFP was first dissolved in THF by magnetically stirring at 50 °C. Then predetermined quantities of $\text{Mg}(\text{Tf})_2$ salt were dissolved in THF and added into the PVdF-HFP polymer solution under continuous stirring at 50 °C for 20 h to obtain a homogeneous solution. The stirred solution was

cast onto glass petri dishes and the solvent was allowed to evaporate slowly at 35 °C, followed by vacuum drying to obtain free-standing polymer films at the bottom of the dishes. The obtained polymer films were dried for 4 h at 40 °C in a furnace to remove any traces of residual solvent in the polymer films. From the X-ray diffraction analysis, the 90PVdF-HFP:10Mg(Tf)₂ system was identified as the optimum composition in weight ratio because this composition gives a stable film with a high amorphicity.

As far as the preparation of EMITf incorporated GPE films is concerned, the predetermined amount of 90PVdF-HFP:10Mg(Tf)₂ was dissolved in the THF by magnetic stirring at 50 °C for 5 h to obtain a homogeneous mixture. Then different quantities of EMITf were added into the homogeneous mixture and stirred continuously for 20 h to obtain a viscous solution. The different compositions of gel polymer electrolytes are denoted as 90PVdF-HFP:10Mg(Tf)₂ + x EMITf, where x = 10, 20, 30, 40, and 50 wt.%. Finally, the viscous solutions were poured into glass petri dishes and allowed to evaporate the intermediate solvent THF slowly at 35 °C to acquire free-standing polymer electrolyte films. The resulting gel polymer electrolyte films were semi-transparent and did not crack when repeatedly bended and stretched, indicating that they were flexible with a certain strength. Fig. 1 shows a photomicrograph of the 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film. The obtained gel polymer electrolyte films were stored within a vacuum desiccator for further characterization. The thickness of these films was determined to be approximately 120 μ m with an accuracy of $\pm$ 5 μ m by means of spiral micrometer

gauge.

2. 3. Characterization

X-ray diffraction (XRD) is a useful method to study the structural characteristics of polymer films. The XRD patterns of the polymer films were recorded using a D/max Rigaku X-ray diffractometer with Cu K_{α} radiation ($\lambda=1.5406 \text{ \AA}$) in the Bragg angle (2θ) range of 5 to 65° with a scan rate of 2° per minute. Surface morphological features of the polymer films were examined using scanning electron microscopy (Hitachi S-4700 SEM, Japan). In order to understand both the thermal history and stability of the polymer films, the thermal analysis of the samples was carried out by a thermal analyzer (STA 449F3 Jupiter, Germany) under a nitrogen atmosphere over the temperature range of 30 to 650°C at a heating rate of $10^{\circ}\text{C min}^{-1}$. The mechanical properties of the polymer films were measured at room temperature using a universal testing machine (CMT7504, China) with a crosshead speed of 25 mm/min. In this measurement, the rectangle sheet-shaped samples were used with dimensions 25 mm (length) $\times$ 15 mm (width) $\times$ 0.12 mm (thickness).

Impedance spectroscopy has been widely employed to study the ionic conductivities of the polymer electrolyte films. The ionic conductivity measurements were carried out by an impedance analyzer (PSM 1735, Newton 4th Ltd, UK) over the frequency range of 1 kHz to 5 MHz. In this technique, the prepared polymer films were cut into circular pieces and sandwiched between two stainless steel foil electrodes, and the measurements were conducted in every 10°C interval from 303 K to 353 K. The electrochemical stability window of the gel polymer electrolyte film

was evaluated using cyclic voltammetry (CV) with the help of an electrochemical analyzer (CHI 760D, CH Instruments, China). The sample was scanned from -3 V to 3 V at a rate of 20 mV s^{-1} using symmetrical stainless steel electrodes (electrode cross-section area = 0.785 cm^2).

3. Results and discussion

3. 1. Structural analysis

The crystal structure and crystallinity of the polymer films were determined by XRD. Fig. 2 depicts the XRD patterns of pristine PVdF-HFP and PVdF-HFP: $\text{Mg}(\text{Tf})_2$ complexed polymer electrolytes with different $\text{Mg}(\text{Tf})_2$ concentrations. The XRD pattern of pristine PVdF-HFP film shows four prominent peaks at the diffraction angles (2θ) of 18.2° , 20° , 26.6° and 39° as well as a broad amorphous halo centered at $2\theta = 18.6^\circ$, indicating the coexistence of mixed crystalline and amorphous regions. The crystalline peaks can be associated with the reflections (100)+(020), (110), (021) and (002)/(211) orientation planes, respectively [20,21]. The sharp peaks are attributed to the crystalline phase of PVdF-HFP units (VdF), which originates from the ordering of polymer side chains due to the intermolecular interaction between chains, and the broad halo comes from the amorphous phase of PVdF-HFP units (HFP). Several small crystalline peaks are also visible due to different phases of PVdF-HFP. With the addition of $\text{Mg}(\text{Tf})_2$ salt up to 10 wt.%, the intensities of the crystalline peaks at $2\theta = 18.2^\circ$ and 39° decrease and the widths of the peaks (broadness) increase, indicating a decrease in the degree of crystallinity of PVdF-HFP or an increase of amorphicity. This should be associated with interactions between the host

polymer matrix and dopant salt, leading to a decrease in the intermolecular interaction between the polymer chains. This would reduce the degree of crystallinity of the host polymer. No peaks for the salt are present in the PVdF-HFP:Mg(Tf)₂ complexed system, indicating a complete dissociation of salt in the polymer matrix. Furthermore, the peak at $2\theta = 26.6^\circ$ is almost invisible and the peak height at $2\theta = 20^\circ$ increases with increasing Mg(Tf)₂ salt concentration. It indicates the formation of PVdF-HFP:Mg(Tf) complexed system. In addition, all crystalline peak intensities of the 85PVdF-HFP:15Mg(Tf)₂ complexed polymer electrolyte are relatively higher than those for the 90PVdF-HFP:10Mg(Tf)₂ complexed system, suggesting a higher amorphicity in the 90PVdF-HFP:10Mg(Tf)₂ electrolyte film. This implies that the 90PVdF-HFP:10Mg(Tf)₂ is a optimal system.

Fig. 3 shows the XRD patterns of 90PVdF-HFP:10Mg(Tf)₂+EMITf gel polymer electrolyte films with different EMITf concentrations. As can be seen, all crystalline peaks are broadened and their relative intensities decrease with an increase of EMITf concentration from 10 wt.% to 40 wt.%, suggesting an increase in the amorphicity of the host polymer. When the EMITf is incorporated into the 90PVdF-HFP:10Mg(Tf)₂ system, the interaction between PVdF-HFP and Mg(Tf)₂ decreases and its crystalline structure is interrupted, thereby increasing its amorphous nature. Moreover, the peaks at $2\theta = 26.6^\circ$ and 39° are no longer visible and no other peaks are observed, suggesting that no other crystalline complex is formed. The evidence of decreasing crystallinity or increasing amorphicity of polymer electrolyte will be further verified by DSC analysis in the next section.

3. 2. Thermal analysis

The glass transition temperature, melting temperature, crystallinity and thermal stability are important properties of a polymer electrolyte as they affect the overall properties of the polymer electrolyte in the battery. Hence, thermal behavior and stability of the present polymer films are investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

DSC thermograms of the pristine PVdF-HFP, 90PVdF-HFP:10Mg(Tf)₂ and 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer films are shown in Fig. 4. It is obvious that the PVdF-HFP film exhibits a strong endothermic peak at around 137 °C, corresponding to the crystalline melting of PVdF-HFP. The melting temperature is taken at the apex of melting endotherm. When 10 wt.% Mg(Tf)₂ salt and 40 wt.% EMITf ionic liquid are added, the melting temperature of the PVdF-HFP is shifted to lower temperatures [22], which should be associated with the suppression of crystallinity or the promotion of amorphicity in the polymer matrix. As a result of additional flexible amorphous surroundings getting trapped, the crystalline portion of PVdF-HFP complex would melt probably at lower temperatures. In addition, the intensity of endothermic melting event decreases and broadens with the addition of Mg(Tf)₂ salt and EMITf ionic liquid, suggesting a decrease in the crystallinity of the host polymer.

The relative crystallinity of a polymer electrolyte (χ_c) may be calculated from its DSC curve based on the following equation with the assumption that the pristine PVdF-HFP polymer is 100% crystalline [23,24]

$$\chi_c = (\Delta H_m / \Delta H_m^0) \times 100 \quad (1)$$

where ΔH_m^0 is the enthalpy of fusion of the pristine PVdF-HFP and ΔH_m is the enthalpy of fusion of the polymer electrolyte. The endothermic peak area gives the melting enthalpy of polymer films, which can be easily determined by a computer software package “STARe”.

The measured values of melting temperature (T_m), enthalpy of fusion (ΔH_m) and relative crystallinity (χ_c) are listed in Table 1. It is seen that the 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer film exhibits a small ΔH_m (21.3 J/g) and χ_c (21.8%) due to its high amorphicity. This is in good agreement with the results obtained from XRD analysis. The polymer chain in amorphous phase is more flexible compared with the chain in crystalline phase, which results in an enhancement of segmental motion in the polymer, thereby increasing the ionic conductivity. Therefore, it can be expected that the 40 wt.% EMITf gel polymer electrolyte would exhibit a higher ionic conductivity due to its high amorphicity. The detailed electrical conductivity studies of the prepared polymer films will be presented in the later section.

TGA curves of pristine PVdF-HFP, 90PVdF-HFP:10Mg(Tf)₂ complex, and 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer films are shown in Fig. 5. Clearly, there is no weight loss for the host PVdF-HFP film up to ~430 °C, indicating its high thermal stability. Beyond ~430 °C the PVdF-HFP film shows a sharp weight loss due to its thermal decomposition. The initial weight loss (~5 to ~7 wt.%) has occurred until 140 °C for both the 90PVdF-HFP:10Mg(Tf)₂ complex and

90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer films, which may be due to the moisture absorption of the films. With the addition of 10 wt.% Mg(Tf)₂ salt in the PVdF-HFP matrix, the thermal stability is significantly deteriorated and the onset of degradation temperature is ~390 °C. The decrease in the thermal stability of the 90PVdF-HFP:10Mg(Tf)₂ complexed polymer electrolyte is due to the relatively poor thermal stability of Mg(Tf)₂ salt. The addition of 40 wt.% EMITf into the 90PVdF-HFP:10Mg(Tf)₂ system leads to further deterioration of the thermal stability and its onset temperature is found to be 355 °C. Nevertheless, the observed thermal stability (~355 °C) of the 40 wt.% EMITf gel polymer electrolyte is still high enough for potential applications as electrolyte/separator in magnesium rechargeable batteries.

3. 3. Analysis of mechanical properties

Mechanical properties of polymer electrolytes such as Young's modulus, yield strength and breaking elongation are important for their applications. The mechanical properties based on tensile tests have been widely recognized as valid parameters to study the structural stabilities of polymer electrolytes [25]. Typical stress versus strain curves of pristine PVdF-HFP and 90PVdF-HFP:10Mg(Tf)₂ + *x* EMITf polymer electrolytes with different EMITf compositions (*x* = 0, 20 and 40 wt.%) are showed in Fig. 6 with an inset for the enlarged early stage of deformation. Young's moduli of the polymer films are calculated from the slopes of curves in the linear portion. As can be seen, the pristine PVdF-HFP polymer film exhibits higher Young's modulus (208 MPa), yield strength (9.7 MPa) and breaking stain (715%) compared to the other polymer films. With the addition of 10 wt.% Mg(Tf)₂ and 20 wt.% EMITf, all the

mechanical properties are decreased due to interactions between the ions and host polymer. It is also observed that with increasing EMITf concentration from 20 wt.% to 40 wt.%, the Young's modulus, yield strength and breaking strain are further decreased. These mechanical data, as listed in Table 2, show that the 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film exhibits the lowest mechanical properties in all systems under study. This is in good agreement with the results obtained from the XRD and DSC analyses. Nevertheless, it is worth mentioning that the mechanical properties of the 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film are still high enough for practical ionic device applications.

3. 4. Ionic conductivity analysis

Ionic conductivity of a polymer electrolyte is one of the most important parameters because the polymer electrolyte is used as separator between anode and cathode in the ionic device applications. It works as a medium to transport ions from anode to cathode and produce the electric power in the circuit/device. The impedance measurements were performed to evaluate the ionic conductivities of polymer electrolyte films.

Typical Nyquist impedance plots of the 90PVdF-HFP:10Mg(Tf)₂ + EMITf gel polymer electrolyte films with different EMITf concentrations at room temperature are shown in Fig 7. As can be seen, all the plots have two well-defined regions, namely, a depressed semicircle in the high frequency range and an inclined spike in the low frequency range, which are typical in ionic conducting solids with blocking

electrodes [26]. The high frequency semicircle represents the bulk effect of the polymer electrolyte. This is equivalent to a parallel combination of bulk resistance and capacitance. The low frequency spike represents the formation of double-layer capacitance at the electrode-electrolyte interface, which is produced by the migration of ions at interface. The magnitude of blocking double-layer capacitance (C_{dl}) can be determined from any position on the spike using the equation: $Z_W = 1/(2\pi f C_{dl})$, where f is the frequency, C_{dl} is the capacitance and Z_W is the impedance corresponding to the frequency f . Furthermore, the inclination of the spike at an angle less than 90° to the real axis is associated with the inhomogeneity of the electrode-electrolyte interface or irregularities at the interface. The bulk resistance (R_b) of the polymer electrolyte is obtained by the intercept of the low frequency end of semicircle arc on the real axis. Obviously, the magnitude of bulk resistance decreases with increasing EMITf concentration up to 40 wt.% and then increases with further increasing EMITf concentration. The ionic conductivities of gel polymer electrolyte films are calculated by

$$\sigma = l/R_b A \quad (2)$$

where R_b is the bulk resistance, l is the film thickness, and A is the electrode area.

At room temperature, the ionic conductivities of the 90PVdF-HFP:10Mg(Tf)₂ and 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer electrolytes are $\sim 1.07 \times 10^{-5} \text{ S cm}^{-1}$ and $\sim 4.63 \times 10^{-3} \text{ S cm}^{-1}$, respectively. Obviously, the ionic conductivity of the 40 wt.% EMITf gel polymer electrolyte is two orders of magnitude higher than that of the 90PVdF-HFP:10Mg(Tf)₂ complexed one. These values are acceptable and

comparable with the literature reports [27,28].

Fig. 8 shows the variation of room-temperature ionic conductivity with EMITf concentration. The ionic conductivity increases with increasing EMITf concentration up to 40 wt.% due to the generation/increase of mobile charge species and the enhancement of polymer chain flexibility. When the EMITf concentration exceeds 40 wt.%, the decrease in ionic conductivity is observed, which may be attributed to the ion association effect of component ions. The 40 wt.% EMITf gel polymer electrolyte exhibits the highest ionic conductivity of $\sim 4.63 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature due to the fact that the gel polymer electrolyte is more amorphous. It is in good agreement with the results obtained by XRD and DSC in aforementioned sections.

In general, ionic conductivity of a polymer electrolyte depends on charge carrier concentration (n_i), charge of mobile carrier (q_i) and carrier mobility (μ_i), which is governed by

$$\sigma = \sum n_i q_i \mu_i \quad (3)$$

According to Equation (3), the increase of ionic conductivity can be achieved by increasing n_i and μ_i . When the EMITf is added into the 90PVdF-HFP:10Mg(Tf)₂ system, it will introduce two new types of charge carrier and therefore the overall charge carrier concentration is increased, resulting in an increase in ionic conductivity. The number of charge carriers plays a key role in the ionic conduction at a lower EMITf concentration while the mobility of ions is predominantly important in the ionic conduction at a higher EMITf concentration.

The microstructure of a polymer electrolyte plays an important role in the

transport of ions through a porous matrix. The SEM images of 90PVdF-HFP:10Mg(Tf)₂ + EMITf gel polymer electrolyte films with different EMITf concentrations are shown in Fig. 9. The 90PVdF-HFP:10Mg(Tf)₂ polymer film possesses a normal porous structure with uniformly distributed small-sized pores at a microscopic level (Fig. 9a). Similar morphology was also observed by Ramesh et.al in the PVdF-HFP:LiTf complexed system [29]. With the addition of 20 wt.% EMITf in the 90PVdF-HFP:10Mg(Tf)₂ system, the size of pores is increased and the pores are interconnected. The interconnections between pores are favorable for ionic transportation or ionic conduction because the mobile ions or polymer chain segments can migrate more easily along the internal free surfaces as compared with their bulk migration [30]. Furthermore, when the EMITf concentration is increased from 20 to 40 wt.%, the pore size and pore-pore interconnection are significantly increased, leading to a higher ionic conductivity for the 40 wt.% EMITf ionic liquid gel polymer electrolyte. In general, higher ionic conductivity in polymer electrolytes may be achieved through continuous pathways to absorb liquid electrolyte within interconnected pores of films [31]. The interconnected pores in the polymer structure have the capability of retaining ionic liquid or liquid electrolyte to obtain higher connectivity through the polymer. As a consequence, the 40 wt.% EMITf gel polymer exhibits a high ionic conductivity.

The Nyquist impedance plots of the 90PVDF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film at different temperatures are represented in Fig. 10. As can be seen, the bulk resistance decreases with increasing temperature. In addition, the

depressed semicircle diameter shrinks with rising temperature. The variation of ionic conductivity with reciprocal temperature is shown in the inset of Fig. 10. It is evident that $\ln(\text{conductivity})$ increases linearly with increasing reciprocal temperature in the considered temperature range. The increase of ionic conductivity with temperature could be associated with the reduced viscosity and enhanced mobility of polymer chains. These results can be explained on the basis of the free volume and the hopping of charge carriers between localized sites. The mobility of polymer chains increases with increasing temperature, thereby producing more free volume and making polymer chain segments more active. The segmental motion either stimulates ions to hop from one site to another or offers a pathway for ions to move, leading to an enhancement in ionic conductivity. As can be also seen, the ionic conductivity does not show any abrupt jump in the considered temperature range, indicating its high amorphous nature. The 90PVDF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte possesses an ionic conductivity of $\sim 4.63 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. This value rises with increasing temperature and reaches a high value of $\sim 3.18 \times 10^{-2} \text{ S cm}^{-1}$ at 80 °C. Therefore, this polymer electrolyte is promising for magnesium rechargeable battery applications in a wide temperature range.

The variation of ionic conductivity with temperature follows the Arrhenius equation as follows

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (4)$$

where E_a is the activation energy for ionic conduction, σ_0 is the pre-exponential constant, k is the Boltzmann constant, and T is the absolute temperature. Linear fitting

of data points can obtain the values of E_a and σ_0 as 0.35 eV and $3.32 \times 10^3 \text{ S cm}^{-1}$, respectively. The activation energy is the sum of mobile charge-carrier creation and migration energies. In general, it is desirable for a polymer electrolyte to have a low activation energy, thereby leading to a high ionic conductivity for practical applications.

3. 5. Electrochemical stability analysis

The electrochemical stability window, i.e., the working voltage range of a polymer electrolyte is another important parameter for its potential application in electrochemical devices such as batteries and supercapacitors. The CV pattern of the 90PVDF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film is shown in Fig. 11. As can be seen, the current remains in a steady value in the voltage range of approximately -2.4 V to 2.4 V. This means that the potential window is in the range of -2.4 V to 2.4 V (~4.8 V), which is a sufficient working voltage for ionic device applications, especially as an electrolyte in magnesium rechargeable battery systems.

4. Conclusions

Based upon investigation of various compositions of PVdF-HFP:Mg(Tf)₂ in combination with different quantities of EMITf ionic liquid, novel magnesium ion conducting complexed and gel polymer electrolyte films are developed and characterized with different techniques. The prepared polymer electrolyte film is semi-transparent and has acceptable mechanical properties. The pristine PVdF-HFP possesses a semicrystalline characteristic and its amorphicity increases with an addition of Mg(Tf)₂ salt and EMITf ionic liquid. At room temperature, the ionic

conductivity of the 90PVdF-HFP:10Mg(Tf)₂ system is $\sim 1.07 \times 10^{-5} \text{ S cm}^{-1}$. It increases with increasing EMITf concentration and reaches a high value of $\sim 4.63 \times 10^{-3} \text{ S cm}^{-1}$ at the 40 wt.% EMITf composition. The temperature dependence of ionic conductivity of the 40 wt.% EMITf gel polymer electrolyte film follows the Arrhenius relation with an activation energy of 0.35 eV. The electrochemical stability window of the gel polymer electrolyte film is $\sim 4.8 \text{ V}$. All these results demonstrate that the 40 wt.% EMITf gel polymer electrolyte is a promising electrolyte material for magnesium ion device applications.

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FIGURE CAPTIONS

Fig. 1. Photomacrograph of 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film.

Fig. 2. XRD patterns of pristine PVdF-HFP and PVdF-HFP:Mg(Tf)₂ complexed polymer electrolyte films.

Fig. 3. XRD patterns of 90PVdF-HFP:10Mg(Tf)₂ + *x* EMITf gel polymer electrolyte films (*x* = 0, 20, 40 and 50 wt.%).

Fig. 4. DSC curves of (a) pristine PVdF-HFP, (b) 90PVdF-HFP:10Mg(Tf)₂ and (c) 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer electrolyte films.

Fig. 5. TGA curves of (a) pristine PVdF-HFP, (b) 90PVdF-HFP:10Mg(Tf)₂ and (c) 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer electrolyte films.

Fig. 6. Stress-strain curves of (a) pristine PVdF-HFP, (b) 90PVdF-HFP:10Mg(Tf)₂, (c) 90PVdF-HFP:10Mg(Tf)₂+20EMITf and (d) 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer electrolyte films. The inset shows the early stage of deformation.

Fig. 7. Nyquist impedance plots of the 90PVdF-HFP:10Mg(Tf)₂ + *x* EMITf gel polymer electrolyte films where *x* = 20, 30, 40, and 50 wt.% at room temperature. The inset shows the plots for *x* = 0 and 10 wt.%.

Fig. 8. EMITf concentration dependence of room-temperature ionic conductivity of 90PVdF-HFP:10Mg(Tf)₂+EMITf gel polymer electrolyte films.

Fig. 9. SEM images of (a) 90PVdF-HFP:10Mg(Tf)₂, (b) 90PVdF-HFP:10Mg(Tf)₂+20EMITf, and (c) 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer electrolyte films.

Fig. 10. Nyquist impedance plots of 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film at different temperatures. The inset shows ln(conductivity) of the film (lnσ) as a function of reciprocal temperature (1/*T*).

Fig. 11. Cyclic voltammogram of 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film using SS|electrolyte|SS cell (SS: stainless steel electrode) recorded at room temperature at a scan rate of 20 mV s⁻¹ (electrode cross-section area = 0.785 cm²).

Fig. 2. XRD patterns of pristine PVdF-HFP and PVdF-HFP:Mg(Tf)₂ complexed polymer electrolyte films.

Fig. 3. XRD patterns of 90PVdF-HFP:10Mg(Tf)₂ + x EMITf gel polymer electrolyte films ($x = 0, 20, 40$, and 50 wt.%)

Fig. 4. DSC curves of (a) pristine PVdF-HFP, (b) 90PVdF-HFP:10Mg(Tf)₂ and (c) 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer electrolyte films.

Fig. 5. TGA curves of (a) pristine PVdF-HFP, (b) 90PVdF-HFP:10Mg(Tf)₂ and (c) 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer electrolyte films.

Fig. 6. Stress-strain curves of (a) pristine PVdF-HFP, (b) 90PVdF-HFP:10Mg(Tf)₂, (c) 90PVdF-HFP:10Mg(Tf)₂+20EMITf and (d) 90PVdF-HFP:10Mg(Tf)₂+40EMITf polymer electrolyte films. The inset shows the early stage of deformation.

Fig. 7. Nyquist impedance plots of the 90PVdF-HFP:10Mg(Tf)₂ + x EMITf gel polymer electrolyte films where $x = 20, 30, 40$, and 50 wt.% at room temperature. The inset shows the plots for $x = 0$ and 10 wt.%.

Fig. 8. EMITf concentration dependence of room-temperature ionic conductivity of 90PVdF-HFP:10Mg(Tf)₂+EMITf gel polymer electrolyte films.

Fig. 9. SEM images of (a) 90PVdF-HFP:10Mg(Tf)₂, (b) 90PVdF-HFP:10Mg(Tf)₂ + 20EMITf, and (c) 90PVdF-HFP:10Mg(Tf)₂ + 40EMITf polymer electrolyte films.

Fig. 10. Nyquist impedance plots of 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film at different temperatures. The inset shows $\ln(\text{conductivity})$ of the film ($\ln\sigma$) as a function of reciprocal temperature ($1/T$).

Fig. 11. Cyclic voltammogram of 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film using SS|electrolyte|SS cell (SS: stainless steel electrode) recorded at room temperature at a scan rate of 20 mV s⁻¹ (electrode cross-section area = 0.785 cm²).

Fig. 1. Photomicrograph of 90PVdF-HFP:10Mg(Tf)₂+40EMITf gel polymer electrolyte film.

HIGHLIGHTS

- 1) The prepared electrolyte have sound mechanical flexibility and thermal stability.
- 2) The 40 wt.% EMITf gel polymer electrolyte exhibits a high amorphicity.
- 3) The room-temperature ionic conductivity reaches $\sim 4.63 \times 10^{-3} \text{ S cm}^{-1}$ at EMITf = 40 wt.%.
- 4) The electrochemical stability window is $\sim 4.8 \text{ V}$ for the 40 wt.% EMITf electrolyte.

Table 1. Melting temperature (T_m), enthalpy of fusion (ΔH_m) and relative crystallinity (χ_c) of the polymer electrolyte films

Sample	T_m (°C)	ΔH_m (J/g)	χ_c (%)
Pure PVdF-HFP	137	97.5	100
90PVdF-HFP:10Mg(Tf) ₂	126	42.8	43.9
90PVdF-HFP:10Mg(Tf) ₂ +40EMITf	112	21.3	21.8

Table 2. Mechanical properties of the polymer electrolyte films

Samples	Young's modulus (MPa)	Yield strength (MPa)	Breaking strain (%)
Pure PVdF-HFP	208	9.7	715
90PVdF-HFP:10Mg(Tf) ₂	167	6.4	686
90PVdF-HFP:10Mg(Tf) ₂ +20EMITf	68	5.0	645
90PVdF-HFP:10Mg(Tf) ₂ +40EMITf	66	3.4	633