

An ionic liquid based gel polymer electrolyte to be employed in power generating applications

K.W. Prasadini, K.S. Perera* and K.P. Vidanapathirana

Department of Electronics, Wayamba University of Sri Lanka, Kuliyaipitiya, Sri Lanka

Correspondence: *kumudu31966@gmail.com;  <https://orcid.org/0000-0003-4491-662X>

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Abstract. Ionic liquid (IL) based gel polymer electrolytes (GPEs) are being investigated extensively at present as substitutes for conventional GPEs based on a polymer, a salt and solvents. The main reason behind this is the drawbacks in usage of solvents. IL based GPEs have been employed for energy storage devices such as batteries and super capacitors due to their interesting mechanical, physical and electrochemical properties. This study focused on synthesis preparation and characterization of an IL based GPE consisting of poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP), zinc trifluoro methanesulfonate ($Zn(CF_3SO_3)_2$ - ZnTF) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (1E3MITF). Thin film samples were prepared using solvent casting method. The optimized composition was found to be 1 PVdF-co-HFP: 1 1E3MITF: 3 ZnTF (by weight basis). This mechanically stable, thin film has the maximum room temperature conductivity of $7.42 \times 10^{-3} \text{ S cm}^{-1}$. Conductivity variation with temperature follows Vogel - Tamman - Fulcher (VTF) behavior confirming the relation of conductivity mechanism with the free volume theory. The IL based GPE is a purely an ionic conductor having a considerable anionic contribution. It shows stability up to 2.5 V which is very much convenient from a practical point of view. Oxidation and reduction of Zn takes place at the potentials of 0.5 V and -0.5 V, respectively. In addition, Zn plating and stripping occurs only on the Zn electrodes but not on the stainless steel (SS) electrodes. Impedance measurements taken for the GPE continuously for a long period of time exhibited a satisfactory stability with Zn electrodes.

Keywords. Solvent casting method, ionic conductor, VTF behavior, poly(vinylidene fluoride-co-hexafluoropropylene), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate.

1 Introduction

Over recent years, there has been a significant breakthrough in the field of solid polymer electrolytes due to their excellent features that are making them

suitable candidates in the arena of electrochemical devices. Even they possess attractive features, their low ambient temperature conductivities have set some limitations in applications (Wang *et al.* 2017). Various attempts have been made to improve the conductivity and the introduction of gel polymer electrolytes (GPEs) is one such outcome. GPEs are consisted of a polymer, a salt and solvents. They have been extensively employed in batteries, super capacitors, fuel cells etc due to the blended characteristics of high ionic conductivity and good mechanical properties (Hashmi *et al.* 2005, Kuo *et al.* 2002). Recently, ionic liquids (IL) based GPEs have motivated the attention of researchers owing to some inherent drawbacks of conventional GPEs such as reduction of conductivity with time, interfacial instability towards electrodes and some safety issues (Pandey *et al.* 2010). Many of those demerits have been identified as due to the presence of solvents. Therefore, the necessity to replace solvents by a suitable substitute has been well realized. ILs which are room temperature molten salts with bulky asymmetric organic cations and inorganic anions have been recognized as a suitable set of materials to be used in place of solvents (Shamsipur *et al.* 2010). They have attractive physiochemical properties including non-volatility, non-toxicity, wide electrochemical window, negligible vapor pressure, high conductivity and high thermal stability (Wang *et al.* 2017). When they are incorporated in a GPE with a polymer and a salt, conductivity enhancement has also been observed (Liu *et al.* 2014). Liew et al have reported that conductivity increase takes place in three ways, i.e., (i) softening polymer backbone, (ii) weakening transient coordination bonds, and (iii) demolishing crystalline structure (Liew *et al.* 2013). These IL based GPEs prepared using different polymer hosts like poly(etheleneoxide) (PEO), poly(acrylonitrile) (PAN), poly(vinylidene fluoride) (PVdF) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) have been employed for various applications [Singh *et al.* 2017, Chaurasia *et al.* 2011].

With the new global insight towards the clean and efficient devices, much attention has been focussed on replacing Li which is a very harmful, toxic and expensive material by environmental friendly, non toxic and abundant materials such as Zn, Mg, Na and Cu [Agrawal *et al.* 2013, Kim *et al.* 2015, Perera *et al.* 2017]. In this regard, various GPEs with non Li salts have received a substantial attention from the scientific community. As far as IL based GPEs are concerned, there are very few reports based on non Li based systems. Therefore, by considering the above facts, this study is focused on the synthesis and characterization of an IL based GPE comprising 1-ethyl-3-methylimidazolium trifluoromethanesulfonate(1E3MITF) as the IL and zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$ - ZnTF) as the salt entrapped in PVdF-co-HFP. Here, PVdF-co-HFP co polymer was selected due to its promising characteristics like low glass transition temperature, low crystallinity and high dielectric constant (Tripathi *et al.* 2013, Liu *et al.* 2014). Moreover, it has been identified as a semicrystalline polymer with crystalline

VDF and amorphous HFP phases. Crystalline nature is sufficient to maintain mechanical stability while liquid electrolytes are retained well due to amorphous nature. Electrochemical impedance spectroscopy (EIS), DC polarization test, cyclic voltammetry (CV) and linear sweep voltammetry (LSV) have been used as characterization techniques.

2 Experimental Methods

2.1 Materials

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) with average molecular weight $400,000 \text{ g mol}^{-1}$, 1-ethyl-3-methylimidazolium trifluoromethane sulfonate (1E3MITF, 98%), zinc trifluoromethane sulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$ - ZnTF, 98%) and acetone (99.5%) were purchased from Sigma Aldrich and used without further purification.

2.2 Preparation of IL based GPE

GPE was prepared using solvent casting technique. PVdF-co-HFP was first dissolved in acetone by magnetically stirring at room temperature. Then appropriate amounts of 1E3MITF and ZnTF were added to the resulting mixture and it was again magnetically stirred overnight. Finally, the resulting homogeneous, viscous solution was poured in to a glass petri dish and allowed to evaporate acetone to obtain a free standing film. Different samples were prepared by varying the composition of ZnTF and PVdF-co-HFP.

2.3 Optimization of the GPE composition

A circular shaped sample obtained from one of the above samples was sandwiched between two stainless steel electrodes of a brass sample holder. Impedance data were collected using a Metrohm Autolab Impedance Analyzer M101 in the frequency range from 0.1 Hz to 400 kHz. By placing the sample holder inside a glass tube furnace, measurements were taken from room temperature to 55°C . The thickness of the electrolyte was measured using a micrometer screw gauge before starting the measurements. Above procedure was repeated for all the above samples prepared with different compositions. The sample that showed the highest conductivity was taken for further characterizations.

2.4 Transference number measurements

A circular shaped, thin film GPE sample obtained from the electrolyte which showed the highest conductivity at room temperature was sandwiched between two stainless steel (SS) electrodes in a brass sample holder. A DC potential of 1 V was applied between the two stainless steel electrodes and the variation of the current flowing through the circuit was monitored with the time at room temperature.

2.5 Linear sweep voltammetry (LSV) study

A circular shaped GPE sample was sandwiched between a Zn electrode and a SS electrode. LSV study was performed in the potential range from 0 V to 3 V at the scan rate of 10 mV s⁻¹ using a three electrode electrochemical cell. SS electrode was used as the working electrode whereas Zn electrode was used as reference and counter electrodes. A computer controlled Metrohm Autolab Potentiostat M101 was used to obtain the current variation with voltage.

2.6 Cyclic voltammetry (CV) study

Using the same setup as in section 2.5, CV study was carried out for the cells with configurations of Zn/ IL based GPE/ Zn and SS/ IL based GPE/ SS in the potential range from -1.5 V to 1.5 V at the scan rate of 10 mV s⁻¹.

2.7 Impedance measurements to investigate the stability

A circular shaped GPE was loaded inside a brass sample holder in between two Zn electrodes. Impedance measurements were gathered at different time intervals for the cell configuration Zn / IL based GPE / Zn for 450 min. using a Metrohm Autolab Impedance Analyzer M101 at room temperature. Bulk electrolyte resistance (R_b) variation was monitored with time.

3 Results and Discussion

3.1 Impedance data for determining conductivity

One of the resultant impedance (Nyquist) plots is shown in Figure 1(a). Generally, for a symmetric cell with the configuration, SS/ IL based GPE/ SS, impedance plot contains two semi circles at high and medium frequency ranges and a tilted spike at low frequency range. The first semi-circle at the high frequency region represents bulk electrolyte and the other semi-circle

corresponds to charge transfer phenomena at the electrode and the electrolyte interface while the tilted spike represents the diffusion process taken place.

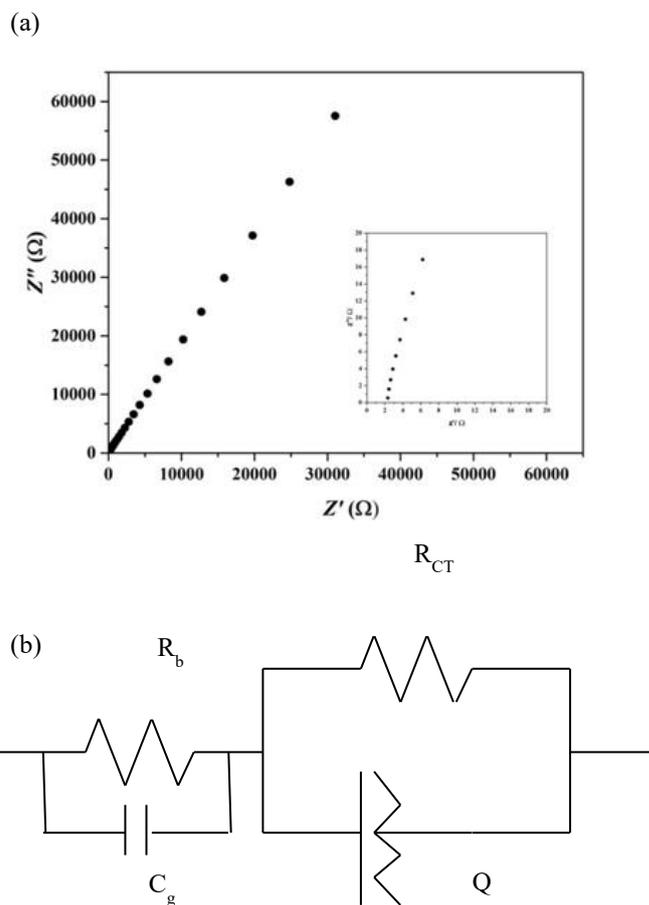


Fig.1 (a) AC-impedance plot for PVdF-co-HFP:ZnTF:1E3MITF polymer electrolyte (Inset – expansion of high frequency region), and (b) Equivalent circuit of SS/IL based GPE/SS cell

In Figure 1(a), the semi-circle at high frequency range is absent and it may be due to absence of required high frequency. The low frequency spike is also not visible due to the insufficient low frequency range. Only in the mid frequency region, a part of the corresponding semi-circle appears. This may be also due to the absence of required frequency range. The impedance plot can be described by the equivalent circuit shown in the Figure 1(b). In the figure, R_b and R_{CT} correspond to bulk resistance and charge transfer resistance respectively. C_g stands for geometric capacitance and Q represents the

constant phase element. In the present study, conductivity values were calculated using the values of R_b obtained at different temperatures for various salt and polymer concentrations using the following equation,

$$\sigma = (1/R_b)(l/A) \quad (1)$$

where σ is the ionic conductivity, l is the thickness of the IL based GPE film, A is the surface area of the electrolyte and R_b is the bulk resistance of the electrolyte.

3.2 Variation of isothermal conductivity at different salt concentrations

Figure 2 illustrates the variation of conductivities of all samples with the salt concentrations at different temperatures.

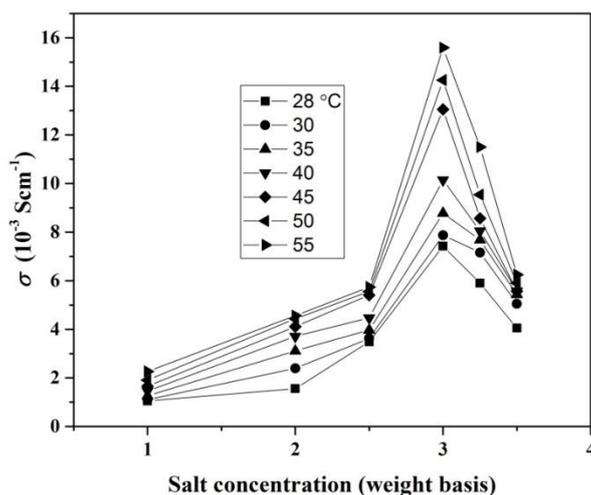


Fig. 2. Conductivity isotherm curves for IL based GPE with different salt concentrations

Conductivity has initially increased up to the salt concentration ratio of 3 showing the maximum conductivity and then started to decrease. This feature is seen repeatedly at each temperature. It is a well-known fact that conductivity is depending on both charge carrier concentration and mobility of the charge carriers. Then the initial enhancement of the conductivity can be due to the increment of mobile charge ions with increment of salt concentration (Jayathilake *et al.* 2014). But with the further increment of the salt concentration, viscosity increases disturbing the mobility of the charge

carriers in the medium which lowers conductivity greatly. On the other hand, at the higher concentrations of charge carriers, aggregation and the formation of ion pairs which are in neutral state are also taking place (Ramesh *et al.* 2012, Jayathilake *et al.* 2015). Both phenomena may be responsible for the reduction of ionic conductivity with further increment of salt concentration.

3.3 Variation of isothermal conductivity at different polymer concentrations

The ionic conductivity variation with the polymer concentration is shown in Figure 3.

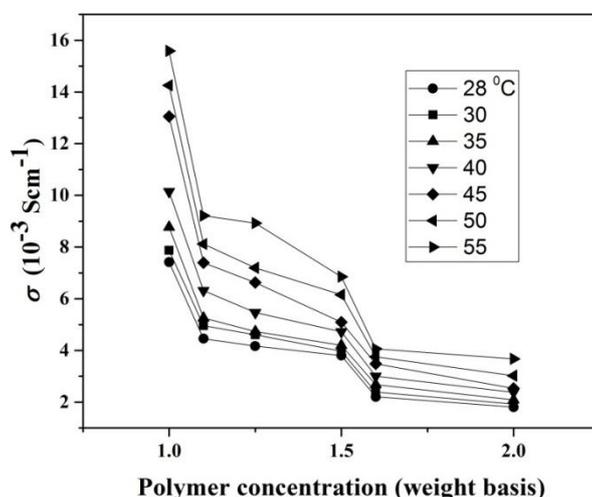


Fig. 3. Conductivity isotherm curves for IL based GPE with different polymer concentrations

At lower concentrations of PVdF-co-HFP (less than 1 g), it was not possible to fabricate a free standing GPE. Thus in this study, polymer concentration was increased from 1 (by weight ratio). According to the present study, the maximum conductivity has been reported at the polymer ratio of 1. When increasing the PVdF-co-HFP concentration, paths for ion conduction may become tortuous and thereby it limits the mobility of the charge carriers leading to decrease the ionic conductivity (Rajendran *et al.* 2002). Some have reported that molecular level blending of polymer with salt/IL takes place with increasing polymer concentration and that will lead the conductivity to reduce very much (Xu *et al.* 2005).

Sample with the composition of 1 PVdF-co-HFP:1 1E3MITF : 3 ZnTF was found to be showing the maximum room temperature conductivity of $7.42 \times$

10^{-3} Scm^{-1} and hence it was selected for further studies. Apart from the optimum conductivity, it exhibited good mechanical integrity blended with translucent, flexible properties.

3.4 Temperature dependence of conductivity

Figure 4 shows the conductivity-temperature correlation of the IL based GPE having the optimized composition. As it shows a curvature, the conductivity and temperature correlation can be explained by Vogel – Tamman – Fulcher (VTF) behavior (Juan *et al.* 2015),

$$\sigma = AT^{-1/2} \exp(-E_a/k_B(T-T_0)) \quad (2)$$

where A is the pre-exponential factor, E_a the activation energy, k_B the Boltzmann constant, T the temperature and T_0 the equilibrium glass transition temperature.

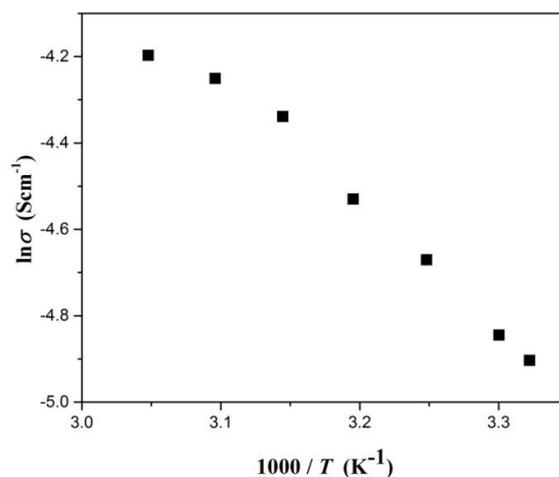


Fig. 4. Variation of the natural logarithm of conductivity with 1000 / T for the optimized IL based GPE composition

This proves that conductivity mechanism takes place in association with the free volume theory. According to that, the mobility of charge carriers is governed by polymer segmental motion by providing sufficient free spaces. When the polymer network expands, more free space is created between adjacent interstitial sites allowing migration from one site to another (Wang *et al.* 2017). This polymer network expansion may be supported by increasing temperature of the system. Therefore, this might be one of the reasons for observing a noticeable conductivity increase with increasing temperature. In

addition, when temperature increases, mobile charges may become energetically rich. Thus, they speed up the motion in the medium and as a result, conductivity increases. Also, the viscosity reduction that is possible with increasing temperature may assist ion mobility favorably for conductivity.

3.5. Transference number measurements

Figure 5 shows the current variation with time for the electrolyte with the electrode configuration of SS/ IL based GPE/ SS.

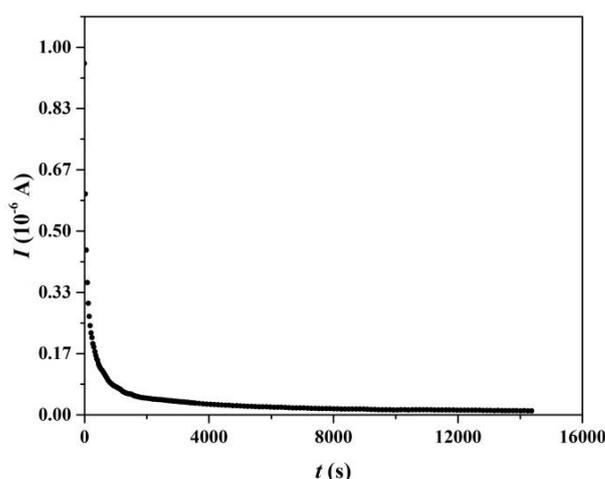


Fig. 5. Current variation with time for the electrolyte with electrode configuration SS/ IL based GPE/ SS under 1 V DC potential

As can be seen from the figure, the initial current has dropped quickly and reached to a stable state. The presence of initial current is due to ions. Since the SS electrodes were of ion blocking nature, the resulting current drops very fast. Thereafter, a constant current flows through the cell due to electrons. Ionic transference number (t_i) was calculated by the following equation

$$t_i = (I_t - I_e) / I_t \quad (3)$$

Here I_t is the total current due to ions and electrons and I_e is the current due to electrons. According to the equation, calculated value was 0.98 and it suggests that IL based GPE is predominantly an ionic conductor (Deraman *et al.*, 2013).

Variation of current with time for the cell with configuration Zn/ IL based GPE/ Zn is shown in Figure 6. As in the previous case, current drops initially as the Zn electrodes block the anion movement. The following near constant

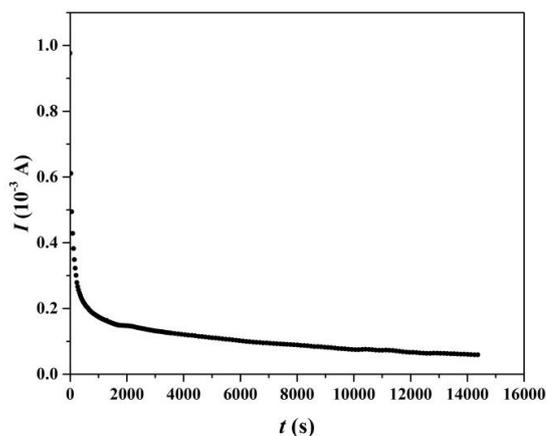


Fig. 6. Current variation with time for the electrolyte with electrode configuration Zn/ IL based GPE/ Zn under 1 V DC potential

current is due to cations. Calculated cationic transference number (t_{cation}) was 0.08 according to the equation

$$t_{\text{cation}} = I_{\text{cation}} / I_{\text{t}} \quad (4)$$

where I_{cation} is constant current and I_{t} is total current due to anions and cations. Accordingly, anionic transference number was 0.92. This is an indication for the anionic nature of the conductivity of the sample. Dominant anionic nature may be due to the bulky cationic group in the IL which is less mobile and a large amount of similar anions in the salt and the IL (Kumar *et al.* 2009).

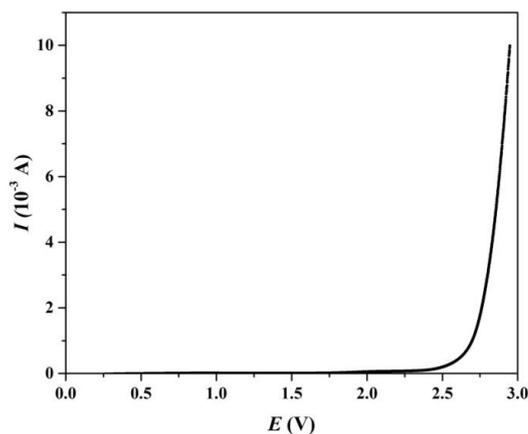


Fig. 7. Linear sweep voltammogram of Zn/ IL based GPE/ SS cell at a scan rate 10 mV s^{-1}

3.6 Determination of the electrochemical stability window

The electrochemical stability window is defined as the potential range in which a significant faradic current is absent. A better GPE should possess a wide electrochemical stability. The resulted liner sweep voltammogram is shown in Figure 7. The GPE membrane is stable up to a wide range (2.5 V). This value is very suitable for energy generating devices from a practical point of view.

3.7 Plating / stripping effect of Zn ions

Figure 8 shows cyclic voltammograms (CVs) obtained between the potential window of -1.5 V to 1.5 V for the cell configurations, SS/ IL based GPE/ SS and Zn/ IL based GPE/ Zn at a scan rate 10 mV s^{-1} . Here, the SS and Zn electrodes are serving as blocking and non-blocking electrodes respectively.

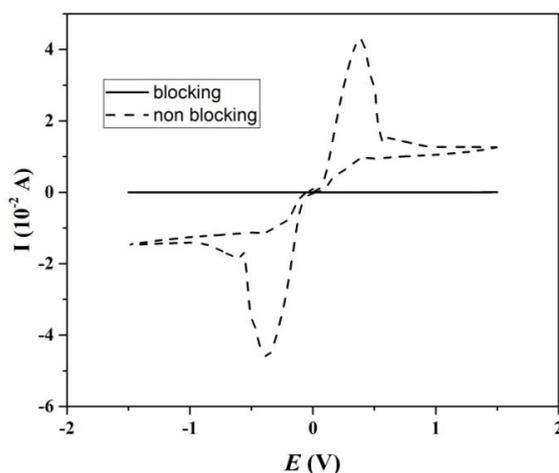


Fig. 8 Cyclic voltammogram for cells Zn/ IL based GPE/ Zn and SS/ IL based GPE/ SS at a scan rate 10 mV s^{-1}

There are no peaks in the respective cyclic voltammogram when blocking electrodes are used. But, with non-blocking electrodes, oxidation and reduction peaks can be seen. This elucidates the fact that Zn plating and stripping is possible only on Zn electrodes. According to the CV, oxidation and reduction take place at 0.5 V and -0.5 V respectively as reported by Xu *et al.* (2005). The result suggests the highly reversible Zn plating/ stripping which confirms satisfactory Zn ion conductivity (Kumar *et al.* 2010).

3.8 Investigation of the stability of the GPE

Figure 9 shows the variation of the bulk electrolyte resistance (R_b) with time.

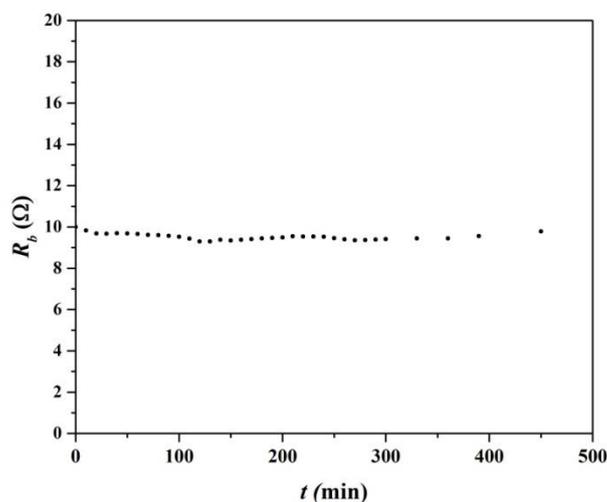


Fig. 9. Variation of bulk electrolyte resistance (R_b) with time

According to that, R_b does not change very much with time showing that it is quite stable with Zn electrodes. This feature makes the IL based electrolyte investigated in the present study more suitable for practical applications. If it varies with time, there can be distortions for the proper and efficient operation of any device due to the deterioration of the electrolyte. In addition, this result well confirms the fact that presence of IL assists the electrolyte to retain its properties unlike solvents.

4 Conclusions

By varying the salt and polymer concentrations, it was found out that an electrolyte comprised with 1E3MITF ionic liquid exhibiting the highest room temperature of $7.42 \times 10^{-3} \text{ S cm}^{-1}$ can be obtained by using the chemical composition of 1 PVdF-co-HFP : 1 1E3MITF : 3 ZnTF by weight basis.

A free standing, bubble free, mechanically stable thin film could be obtained by this composition. The conduction mechanism is associated with the free volume theory. Transference number studies reveal that the IL based GPE is a purely ionic conductor having a major anionic contribution. The sample is stable up to 2.5 V. CV studies describes that the oxidation and the reduction of Zn ions take place at 0.5 V and -0.5 V respectively on Zn electrodes. Moreover, this proves plating and stripping of Zn is possible only

on Zn electrodes but not on SS electrodes. Also, the sample is very stable with Zn electrodes. Based on these findings, it can be concluded that the electrolyte with the above optimized chemical composition can be employed in energy generating devices such as batteries and super capacitors. Further studies are being done to employ this IL based GPE in different types of batteries and super capacitors.

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