1.   INTRODUCTION

Rechargeable lithium ion cells have been attracted in diverse scales for many applications in the modern technological society during the past decades. But, at present, there is a significant increase of concerns regarding the inherent drawbacks integrated with those cells. Some of the problems are related to employing liquid electrolytes, large volume change and dendrite formation[1]. As an alternative, a major research focus is now shed on cells based on non Li electrodes and gel polymer electrolytes (GPEs). Among the non Li materials, Zn, Mg, Al and Na are some of the materials that have offered the promise to replace Li. Replacing liquid electrolytes, GPEs have exhibited appealing performance in numerous applications encroaching the fields of medicine, transport, information technology, telecommunication and many more[2,3]. Their electrical and mechanical properties are compatible with liquid electrolytes and solid electrolytes respectively. GPEs are prepared using a polymer, a salt and a solvent/s mixture. Various types of polymers, salts and solvents have been used for preparing GPEs. As the salt/solvent mixture is assumed to be encapsulated inside the polymer host, the risk of leaking, spilling of the liquid is minimized with the GPEs. Polymer host is more responsible for providing the mechanical stability. With the global trend towards a cleaner future, the presence of toxic solvents are less desirable in the GPE based devices. It has been reported that volatility, flammability and toxicity of solvents may lead to interfacial stability in the electrodes, reduction of conductivity with time, poor dimensional stability and also low reliability[4].

In recent years, a surge of reports have been made in the arena of Ionic Liquids (ILs) as substitutes for organic solvents[5,6]. They are considered as room temperature molten salts consisting of bulky, asymmetric cations and inorganic anions. They bear some unique interesting properties including high conductivity, wide electrochemical window, non-toxicity and chemical stability. Due to those fascinating characteristics, there has been a resurgence in employing electrolytes based on ILs for a large number of applications[7,8]. Some have used ILs as liquid electrolytes while there are reports about GPEs having ILs as substitutes for organic solvents[9,10]. Many of the ILs do not require specific and controlled atmospheric conditions for the purpose of storage.

In this study, a GPE was prepared using the polymer, Poly-Vinylidene Fluoride co Hexa-Fluoro Propylene (PVdF-co-HFP) and the salt Zinc Tri-Fluoromethanesulfonate ($Zn(CF_3SO_3)_2$ – ZnTF). 1 Butyl 3 Methyl Immidazolium Tri-Fluoromethanesulfonate

(1B3MITF) was used as the IL. One of the novel steps in the present study is preparing a polymer electrolyte only with the polymer and the IL and then investigating the conductivity enhancement upon the addition of a salt. With the optimized composition, a cell was fabricated using Zn and graphite electrodes. To the best of our knowledge, there is no study carried out on a rechargeable cell with the configuration, Zn / GPE / graphite. Another innovative feature of the present study is using Sri Lankan graphite without any pretreatment for one of the electrodes which may assist to add value to this natural resource.

2.   METHODS AND MATERIALS

2.1   Preparation of GPE

Poly-Vinylidene Fluoride co HexaFluoroPropylene pellets (PVdF-co-HFP), Zinc Tri-Fluoromethanesulfonate ($Zn(CF_3SO_3)_2$ – ZnTF, 99%) and 1 Butyl 3 Methyl Immidazolium Tri-Fluoromethanesulfonate (1B3MITF) were used as received from Aldrich. Initially, the polymer and IL were weighed separately with the ratio of 1: 2. Polymer was dissolved in acetone (Aldrich) by magnetic stirring overnight. IL was added and again stirred well. The final homogeneous solution was poured in to a glass petry dish and allowed solvent evaporation. Then, for the same composition of the polymer/IL mixture, salt was introduced at different weight ratios. After stirring, the resultant solution was poured in to a petry dish. With the evaporation of the solvent, a thin film could be obtained.

2.2   AC conductivity measurements

A sample of circular shape was cut from the electrolyte film and it was assembled inside a spring loaded sample holder in between two Stainless Steel (SS) electrodes. Impedance of the films were measured from room temperature to 55 °C in the frequency range 37 kHz – 0.01 Hz using a Metrohm 101 frequency response analyzer. The procedure was repeated for all the samples.

2.3   DC polarization test

Circularly cut film of the electrolyte samples were used for DC polarization tests under blocking electrodes. Current variation with time was monitored applying a DC bias voltage of 1 V at room temperature.

2.4   Preparation of the graphite electrode

The graphite sample received from Bogala Graphite Lanka Ltd was used without prior treatment. It was mixed with activated carbon, ZnTF and PVdF-co-HFP. The weight ratios were 80%, 5%, 5% and 10% respectively. All materials were weighed using an electronic balance. After addition of acetone, mixing was done using a magnetic stirrer. The resulting slurry was applied on a stainless steel substrate using doctor blade method. Drying was done for about 3 hrs.

2.5   Fabrication and characterization of Zn rechargeable cell

Circular shape film was cut from the electrolyte sample that showed the highest conductivity and it was assembled between a Zn electrode and a graphite electrode in the configuration Zn / GPE / graphite electrode in a sample holder. Both the electrodes were circular in shape with the diameter similar to the GPE sample.

Discharge characteristics were monitored under constant loads of 1 kΩ, 10 kΩ and 100 kΩ.

3.   RESULTS AND DISCUSSION

Impedance data analysis was done using the corresponding equivalent circuits. The conductivity was calculated using the equation,

$$\sigma = (1/R_b)(t/A) \tag{1}$$

where R_b is the bulk electrolyte resistance, t and A are thickness and area of the electrolyte film respectively.

Figure 1 shows the variation of conductivity with temperature. It is seen that there is an enhancement of conductivity with addition of salt initially. At higher salt concentrations, the conductivity decreases but it is still higher than the conductivity of the GPE with only the polymer and the IL. It is a general fact that, conductivity is governed by several factors. Mainly, the concentration and the mobility of charge carriers are known to be responsible for the conductivity. When the salt is added to the polymer/IL combination, the charge carrier

concentration may increase resulting a higher conductivity. When the salt concentration is increased further, there may be more charge carriers. But, the viscosity of the system which increases with the salt concentration may disturb the charge carrier motion so that, conductivity decreases.
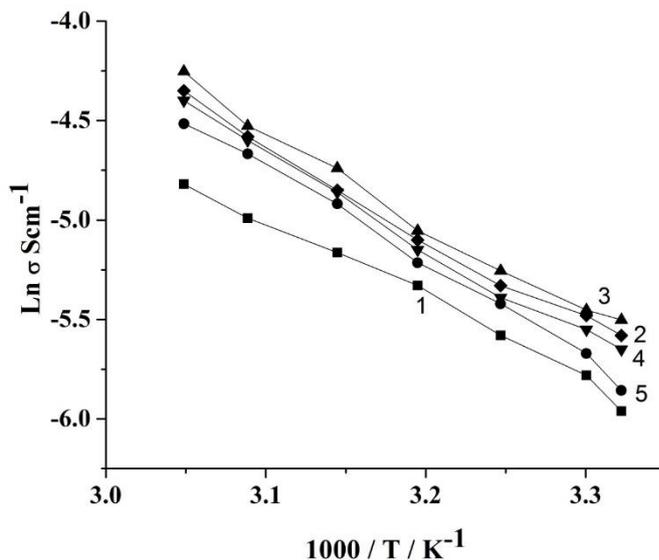

Figure 1 : Temperature dependence of conductivity of PVdF / 1B3MITF / ZnTF GPE with the salt concentration (**1**- IL : Polymer = 2 : 1, **2** - IL : Polymer : salt = 2 : 1 : 2, **3** - IL : Polymer : salt = 2 : 1 : 2.5, **4** - IL : Polymer : salt = 2 : 1 : 3, **5** - IL : Polymer : salt = 2 : 1 : 5)

From Figure 1, it is seen that conductivity of each sample increases with the temperature. An expansion of polymer network can be expected at elevated temperatures and then, mobile charge carriers find more pathways between near by sites. Due to this reason, ionic mobility increases giving rise to higher conductivities[11]. On the other hand, when the temperature goes up, molecules are energized and their amplitudes of oscillations become larger. This in turn favors the polymer segmental motion which assists to increase the conductivity[11]. Conductivity – temperature relationship of all three samples shows a linear pattern. This implies that typical Arrhenius behavior is obeyed by all five samples. Arrhenius behavior is given by the equation,

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \qquad (2)$$

Here, σ_0 is the pre exponential factor, E_a is the activation energy, k_B is the Boltzmann constant and T is the absolute temperature[12].

All linear relationships have regression values close to unity. This suggests that ion migration takes place via hopping mechanism where ions jump into neighboring vacant sites with well defined pathways[13]. As the temperature increases, polymers undergo expansion effect giving rise to more local vacant spaces and as a result, more free volumes are available for segmental motion. This weakens the interactions between the polymer and mobile charges. With the promotion of decoupling process of charge carriers from the segmental motion, ion migration is facilitated. And also, when vibration modes of polymer segments increase, sufficient energy is gained to diminish the pressure formed by the atoms. This assists the formation of voids and free charges are permitted to hop from one site to the next.

The optimum composition that results the highest conductivity is related to the weight ratios of the polymer, IL and salt as 1:2:2.5. The corresponding room temperature conductivity is 3.88×10^{-4} Scm^{-1}. This value is quite suitable for employing this GPE for applications.

The variation of the ionic transference number (t_i) with the salt concentration is shown in the Table. 1. t_i was calculated using the following equation.

$$t_i = (I_t - I_s) / I_t \tag{3}$$

where , I_t is the total current, I_s is the saturated current.

Table 1: The variation of the ionic transference number (t_i) with the salt concentration

Salt concentration	t_i
0	0.91
2.0	0.95
2.5	0.98
3.0	0.97
5.0	0.96

It is seen that without the salt, the transference number is lower but it increases upon the addition of the salt. The highest transference number is available with the composition having the highest conductivity. This well proves the fact that high ion contribution exists in that composition. The lowest t_i value in the sample with only the polymer and the IL can be

attributed to the fact that sufficient ion contribution arises from the salt. Due to the large size of the cation of the IL, it may not be mobile. The lower transference number might be due to the triflate anion.

Open circuit voltage of the cell fabricated using the optimized GPE was about 1.0 V. This value is quite suitable for low power applications.

Figure 2 shows the discharge characteristics of the cell. Under 1 kΩ, the decrease of current is very sharp and quick. The discharge characteristics obtained under 10 and 100 kΩ are shown in inset in Figure 2. With 100 kΩ, it was observed a more or less constant current in the cell. But, with 10 kΩ, there is a slight decrease of current initially. This may be due to the polarization effect build up. With 1 kΩ, the current drop is very fast. These observations reveal the fact that the cell under consideration is very much suitable for low current drains. The specific discharge capacity (C_d) was calculated for the cells under 100 kΩ and 10 kΩ using the equation,

$$C_d = \int I dt \tag{3}$$
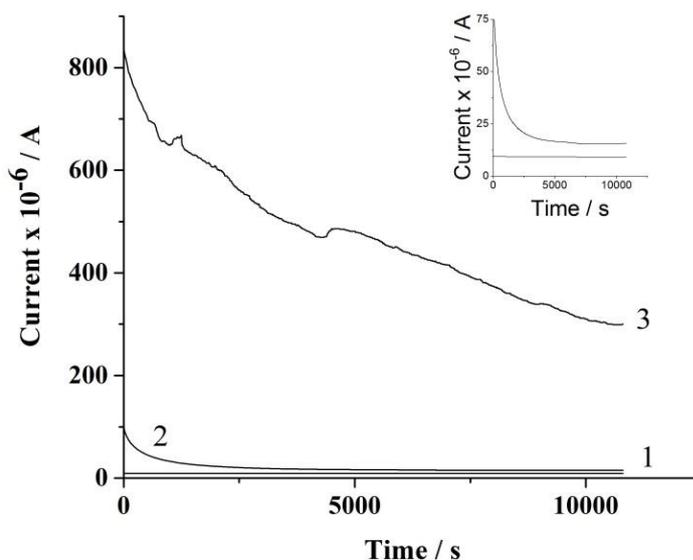
Here, I is the current and dt is the time duration[14].

Figure 2 : Discharge characteristics of the cell, Zn / GPE / graphite electrode under different constant loads (1 - 100 kΩ, 2 – 10 kΩ, 3 – 1 kΩ)

The average discharge capacity was calculated as 6.85 mAhg^{-1}, which is satisfactory for low power requirements. The specific power and energy densities are 2.14 mWg^{-1} and 6.35 mWhg^{-1} respectively. These values are higher than the values reported for a Mg cell based on polyethylene oxide[1].

4.   CONCLUSION

The GPE based on PVdF-co-HFP, ZnTf and 1B3MITF of the composition 1 : 2.5 : 2 showed the highest room temperature conductivity of 3.88×10^{-4} Scm^{-1} which is quite suitable for ambient temperature applications. In the absence of the salt, the conductivity is low only with the polymer and the IL. Upon introducing the salt, conductivity increases but further increment of the salt reduces the conductivity. The sample with the highest conductivity was free from pin holes, very thin and flexible. Conductivity depends on charge carrier concentration as well as their mobility. Use of IL paves the path to avoid toxic solvents and fabricate environmental friendly GPEs. The constant load discharge characteristics of the cell in the configuration, Zn / GPE / graphite, has shown satisfactory performance to be used for low power requirements. Investigations are being carried out to analyze and improve the properties of the GPE further to be used for advanced power requirements.

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