Conductivity and Electrochemical Studies on Polymer Electrolytes Based on Poly Vinyl (chloride) - Ammonium Triflate-Ionic Liquid for Proton Battery

S. K Deraman[1, *], *N.S. Mohamed*[2,] *and R.H.Y. Subban*[1,]

[1] Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia
[2] Centre for Foundation Studies in Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
[*]E-mail: sitikhatijah8585@yahoo.com

Solid polymer electrolyte films of poly (vinyl) chloride (PVC) with ammonium trifluoromethane sulfonate ($NH_4CF_3SO_3$) and ionic liquid, butyltrimethyl ammonium bis (trifluoromethyl sulfonyl) imide (BATS) as plasticizer have been prepared by solution-cast technique. The films were characterized electrically by Impedance Spectroscopy for its ionic conductivity. The highest ionic conductivity achieved at room temperature was for 85 wt. % (PVC -$NH_4CF_3SO_3$) + 15 wt. % BATS with ionic conductivity of 1.56×10^{-4} Scm^{-1}. Ionic transference number of the mobile ions estimated by dc polarization method and the H^+ ionic transference number was found to be ~ 0.82 which revealed that the conducting species are predominantly ions. Linear sweep voltammetry results revealed that the film is electrochemically stable up to 1.1 V. An electrochemical cell fabricated using configuration of: $Zn+ZnSO_4.7H_2O$ +PTFE (anode) | 85 wt. % (PVC -$NH_4CF_3SO_3$) + 15 wt. % BATS | MnO_2+PTFE (cathode) produced a maximum open circuit voltage of ~ 1.52 V while its discharge characteristics demonstrated a capacity of 6.0 mAh using 1.5 k Ω load resistance.

1. INTRODUCTION

Electrochemical cells are composed of three main components: anode, cathode and electrolyte. Electrolyte is the key component of the cell which contains free ions that behave as an electrically conductive medium. It generally consists of ion in solution. Electrolytes are also known as ionic solution but molten and solid electrolytes are also possible. To form an electrolyte, salt needs to be added into a solvent such as water and individual atomic component are separated by the force applied

upon the solute molecule, in a process called chemical dissociation in which the solution applies force to hold the ions apart [1].

In the last few decades, ion conducting polymers or polymer electrolytes have attracted increasing interests because of their potential application as electrolytes in solid-state electrochemical devices like fuel cells, batteries, super capacitors, sensors, electrochemical windows etc [2-4]. The main advantages of polymeric electrolytes are their good mechanical properties, ease of fabrication into thin film of desirable sizes and the ability to form good electrode/electrolyte contact [5-6]. Recent challenge is to find a low-cost membrane with good ionic conductivity, good dimensional and mechanical stability.

The inherent properties of polymer electrolytes like shape versatility, flexibility, light weight, processability etc make them more promising than other materials for device applications. However, low ionic conductivity of the polymer electrolytes act as a barrier for their applications. There have been various approaches, undertaken by many workers, to achieve higher conductivity, viz. formation of cross-linked networks [7-8], blending of polymers [9-11], addition of inorganic fillers [12-14] and plasticization [15-19]. Out of these, plasticization is one the most effective ways to get desirable enhancement in conductivity. In plasticization, commonly low molecular weight and high dielectric constant polymers like ethylene carbonate, propylene carbonate, diethylene carbonate etc, are added to the polymer electrolytes. These plasticizers help in maximizing ion dissociation and enhancement of amorphicity of polymer electrolyte [20].

Apart from that ionic liquids have been used as plasticizer in recent years [21]. Ionic liquids are molten liquid at room temperature with low melting point [22]. They are composed of bulky cations and anions and are considered as promising green electrolytes due to their unique and excellent characteristics such as negligible vapor pressure, non-flammability, non-corrosive with high thermal stability which makes them suitable for applications as electrolytes for energy conversion and storage devices [23]. These properties make them suitable as plasticizers as reported by Rupp and co-workers [24] who investigated a lithium ion conducting polymer electrolyte based on PEO which was crosslinked with LiTFSI and plasticised with butyltrimethyl ammonium bis (trifluoromethyl sulfonyl) imide. They obtained room temperature conductivity of about 10^{-4} S cm^{-1}. Similar findings have been reported by Chew and co-workers on a lithium conducting Ppy based composite electrolytes [25]. In another study, epoxidised natural rubber (ENR-50) doped with LiTFSI and plasticized with 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl)imide (EMITFSI) ionic liquid produced polymer electrolytes with ionic conductivity of 10^{-4} S cm^{-1} [21].

In this work, PVC is used as the base polymer for studies on proton-conducting films with application in proton electrochemical cells. (PVC-NH$_4$CF$_3$SO$_3$)-BATS films were prepared and characterized electrically. Electrochemical cells with configuration of Zn+ZnSO$_4$.7H$_2$O +PTFE (anode) | 85 wt. % (PVC-NH$_4$CF$_3$SO$_3$)+ 15 wt. % BATS (electrolyte) | MnO$_2$ +PTFE (cathode) were fabricated and characterized.

2. EXPERIMENTAL

2.1. Sample preparation of solid polymer electrolyte.

The proton conducting polymer electrolytes were prepared by solution-cast technique. PVC (molecular weight 2.33×10^5 g mol^{-1}) and $NH_4CF_3SO_3$ from Aldrich were mixed with BATS from Fluka in various weight fractions. Solution cast films were obtained by pouring the solution of PVC, $NH_4CF_3SO_3$ and BATS in tetrahydrofuran (THF) from Aldrich into glass petri dishes which were subsequently dried at room temperature (300 K). The films formed were further dried in a vacuum oven at 313 K with a pressure of 10^{-3} torr for 24 hours. The polymer films thus obtained were stored in a desiccator. The highest conducting polymer electrolyte was used for fabrication of solid state electrochemical cells with configuration: Zn + $ZnSO_4.7H_2O$ + PTFE | 85 wt. % (PVC -$NH_4CF_3SO_3$) + 15 wt. % BATS | MnO_2 +PTFE. The cathode was prepared using a simple physical grinding method by mixing manganese dioxide (MnO_2) (TOSOH Corporation) and polytetrafluoroethylene (PTFE) (Aldrich, USA) as a binding agent and pressing the mixtures under a pressure of 1.4×10^3 kg m^{-2} to form pellets of thickness 0.451 mm. The same method was used to prepare the anode but for the anode a mixture of zinc powder (Zn) (SHOWA Chemical co.ltd, Japan) and zinc sulphate ($ZnSO_4.7H_2O$) (of mass ratio 4:1) (R & M chemical, U.K) were used.

2.2. Characterization of samples and electrochemical cell.

Complex impedance measurements were carried out on the polymer electrolytes using HIOKI 3532-50 LCR Hi Tester for frequencies ranging from 100 Hz until 1 M Hz. Transference number measurement was carried out using d.c polarization technique using Solartron Analytical 1260 Impedance/gain-phase Analyzer. The results were analyzed using CorrWare, ZPlot and MultiStat software packages for electrochemical measurement and analysis. In this technique, the d.c.current was monitored as a function of time on application of a fixed d.c. voltage across the sample with blocking electrodes. The electrochemical stability window of the polymer electrolyte was determined by means of linear sweep voltammetry using 0.1 mVs^{-1} scan rate. The open circuit voltage (OCV) and cell potential measurements were carried out with the help of True RMS Multimeter. The cell was discharged under load of 1.5 kΩ. The voltage and current were recorded as a function of time.

3. RESULTS AND DISCUSSION

3.1 Conductivity studies.

Fig. 1 shows a typical complex impedance plot for the highest conducting 85 wt. % (PVC -$NH_4CF_3SO_3$) + 15 wt. % BATS proton conducting polymer electrolytes film at room temperature (300 K). It consists of a high frequency semicircle and a low frequency spike. The semicircle corresponds to bulk resistance while the spike corresponds to interfacial impedance of the electrolyte. The semicircle can be represented by a parallel combination of a capacitor, which is due to the immobile polymer chain and a resistor which is due to the mobile ions inside the polymer matrix [26]. If the electrodes

and electrode/electrolyte interface were ideal, vertical spike at the low frequency end should have been obtained. In our work, the semicircle is significantly broadened while the electrode spike at the low frequency end of the spectrum is distinctly non-vertical indicating roughness of the electrode/electrolyte interface [27].
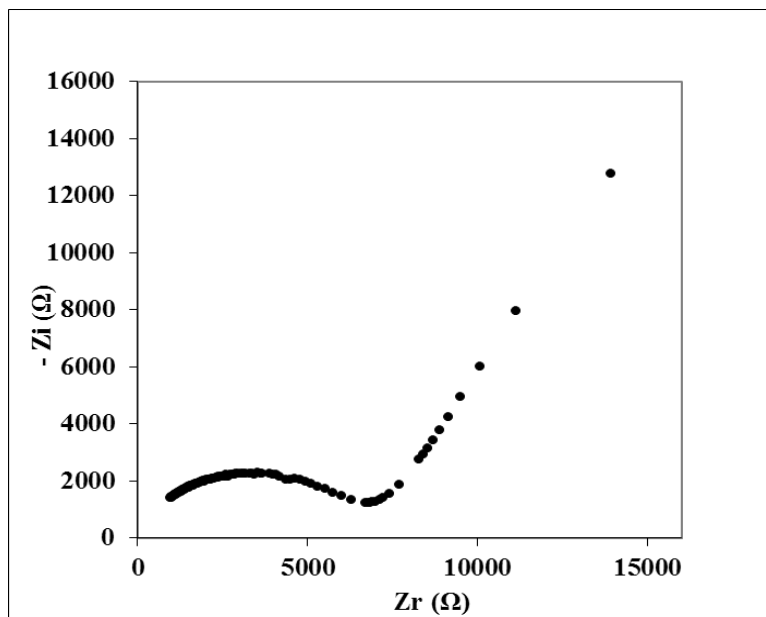

Figure 1. Complex impedance plot for the highest conducting 85 wt. % (PVC -NH$_4$CF$_3$SO$_3$) + 15 wt. % BATS polymer electrolyte film at 300 K
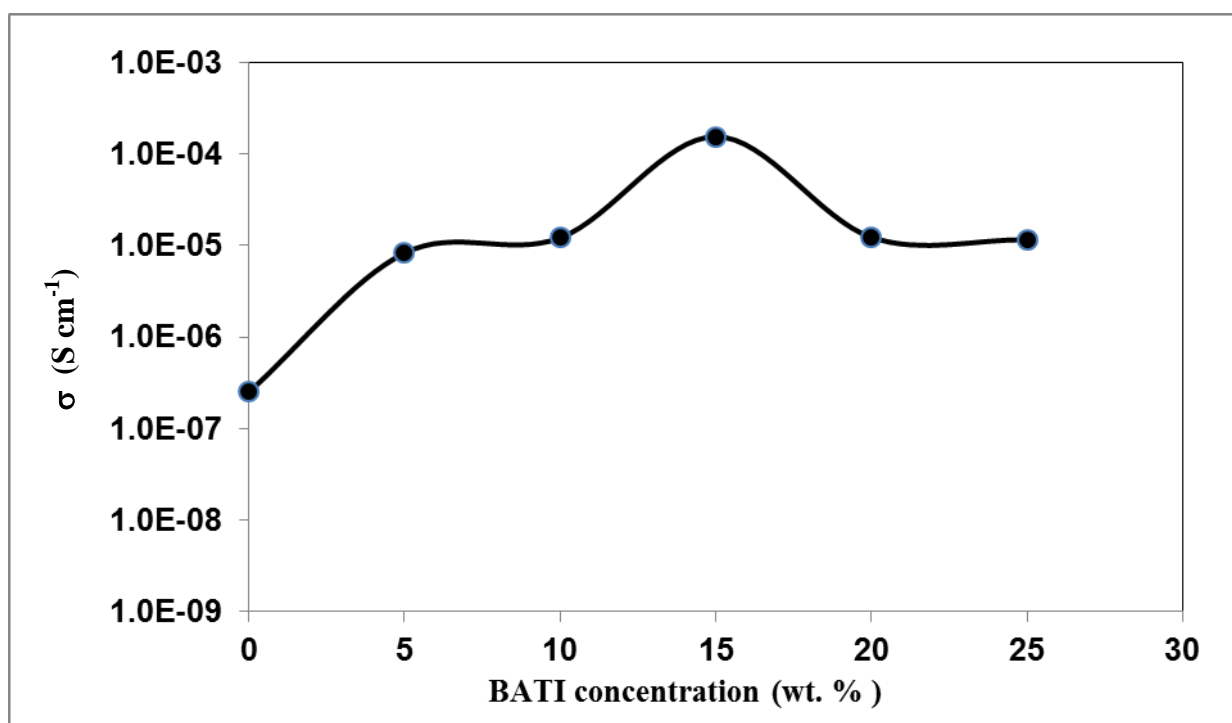

Figure 2. Ionic conductivity dependence on concentration of BATS in weight %.

The highest conductivity was obtained for the sample with 15 wt. % BATS as shown in Fig. 2 where dependence of conductivity on concentration of BATS is displayed. Presence of ionic liquid, BATS increased the conductivity to three times when compared to the ionic-liquid free sample. Addition of ionic liquid has increased the number of free ions due to dissociation of salt leading to an increase in the number of charge carriers. The incorporation of BATS into this polymer-salt system has also lowered the viscosity that led to increase in ionic mobility which consequently led to increase in conductivity [28].

3.2 Ionic transference number

The ionic transference number for the highest conducting (PVC-NH$_4$CF$_3$SO$_3$) +BATS polymer electrolyte was determined by D.C polarization technique. In this technique, the dc current is monitored as a function of time on the application of a fixed 0.5 V dc bias voltage across the sample using copper electrodes at 303 K. The value of t_{ion} was calculated from the normalized polarization current versus time plot using the equation:

$$t_{ion} = (i_T - i_e) / i_T \qquad\qquad (2)$$

where i_T and i_e are the total and residual current respectively. Figure 3 depicts the plot of the normalized polarization current versus time for the highest proton conducting electrolyte film. The ionic transference number of the electrolyte system studied was found to be ~ 0.82.
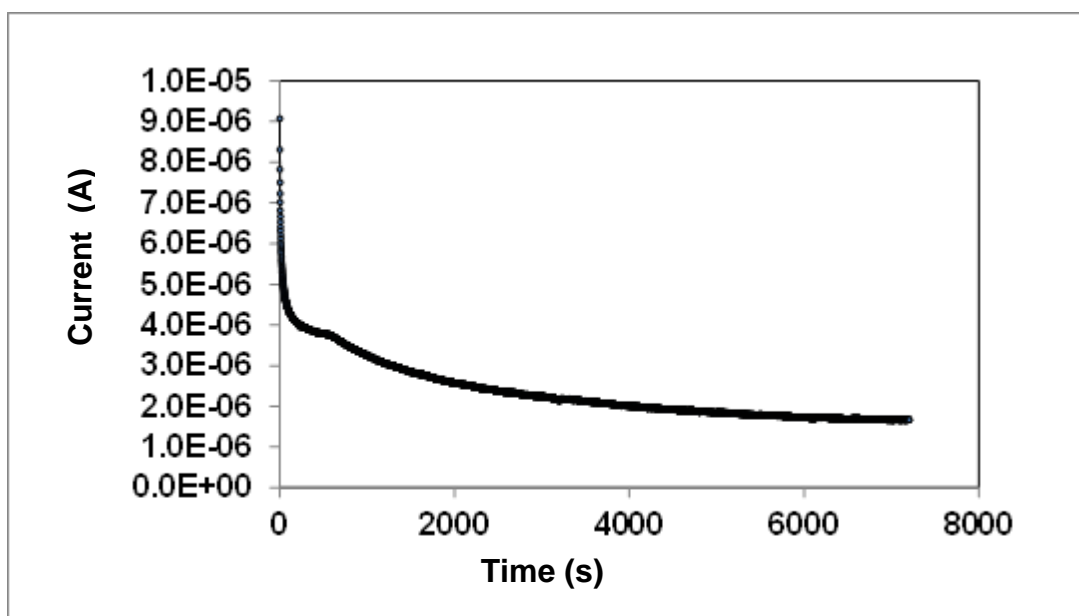

Figure 3. Polarization current versus time for highest conducting 85 wt. % (PVC-NH4CF3SO3)+15 wt. % BATS polymer electrolyte film.

This suggests that the ionic conductivity of (PVC-NH$_4$CF$_3$SO$_3$) +BATS polymer electrolyte was predominantly due to ions and only negligible contribution came from electron [29]. This result is found to be in agreement with that reported by Hashmi et al. (1990) who obtained ionic transference number of ~ 0.85 for polymer electrolyte PEO-NH$_4$ClO$_4$ by Wagner's polarization technique [30].

3.3 Linear sweep voltammetry

Electrochemical stability window is an important parameter to evaluate the stability of the polymer electrolyte. The electrochemical stability window of the highest conducting (PVC-NH$_4$CF$_3$SO$_3$) +BATS polymer electrolyte was performed to observe the ability of the polymer electrolyte to endure operating voltage of a battery system. This was obtained by linear sweep voltammetry experiment. Figure 4 shows the linear sweep voltammogram of the highest conducting (PVC-NH$_4$CF$_3$SO$_3$) +BATS polymer electrolyte as a function of voltage. There is no obvious current through the working electrode from open circuit potential to 1.0 V, and then the current that is related to the decomposition of the polymer electrolyte increased gradually when the electrode potential is higher than 1.0 V. The results revealed that the electrochemical stability window for (PVC-NH$_4$CF$_3$SO$_3$) +BATS system is up to 1.1 V. Hence, this polymer electrolyte is compatible for application in proton battery, which has a working voltage of ~1.1 V [31]. This result is lower than that reported by Ng and Mohamad [32] who reported electrochemical stability window of 1.80 V for polymer electrolyte film chitosan-NH$_4$NO$_3$-EC at room temperature with conductivity of ~ 10^{-3} S cm^{-1}.
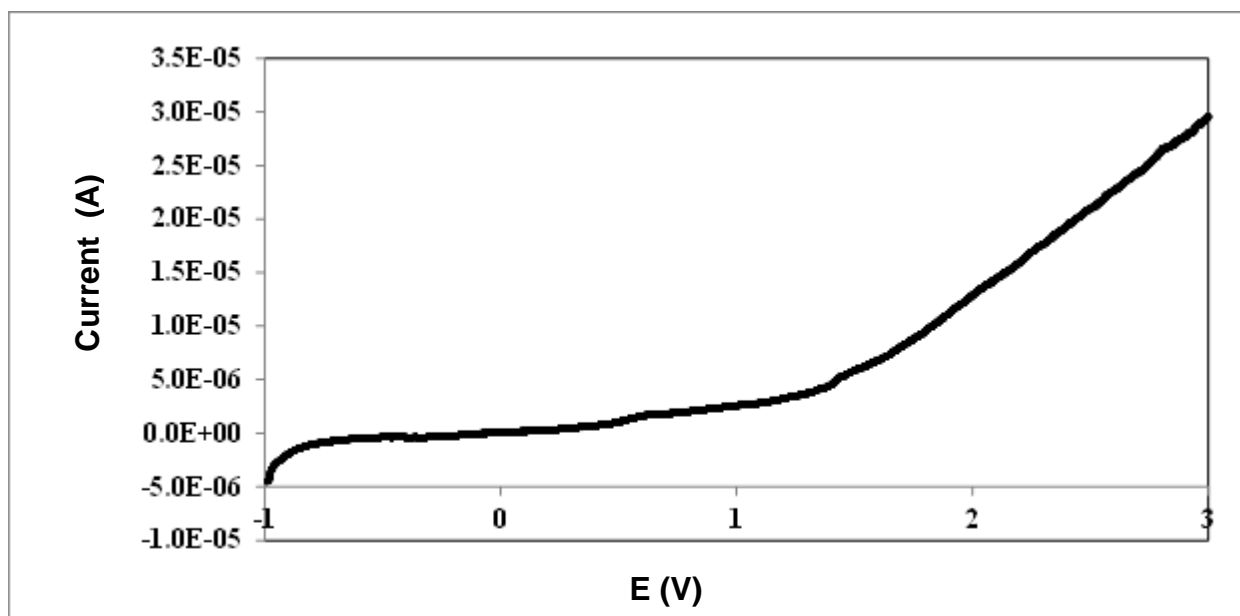

Figure 4. Linear sweep voltammogram for the highest conducting polymer electrolyte film of 85 wt. % (PVC-NH$_4$CF$_3$SO$_3$) +15 wt. % BATS

3.4 Battery characterization

The OCV characteristics of the proton battery at room temperature is shown in Fig. 5. There seems to be a voltage delay at the time of assembly when the voltage was observed higher in the first 2 hours and later stabilized at ~ 1.30 V. The OCV remained constant at ~1.30 V until after 24 hours of storage.
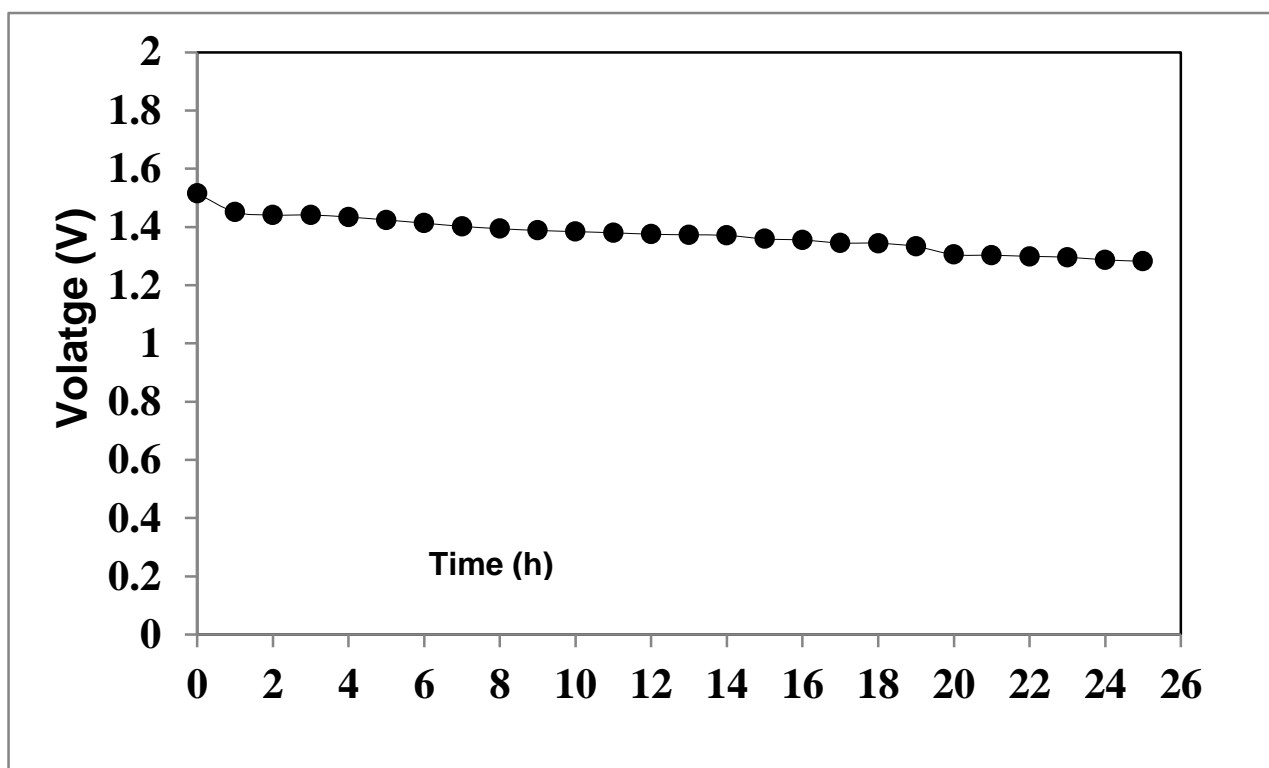

Figure 5. OCV of electrochemical cell based on 85 wt. % (PVC-NH$_4$CF$_3$SO$_3$) +15 wt. % BATS polymer electrolyte film

In order to study its discharge performance, the cell was discharged at a load of 1.5 k Ω. Fig. 6 shows the discharge characteristic of this cell. From Fig. 6, it can be observed that the discharge voltage of the cell exhibited a rapid decrease. The voltage dropped from an initial voltage of ~ 1.20 V to ~ 0.50 V within one (1) hour and decreased to 0.2 V in 9 hours. The initial drop is attributed to cell polarization [33]. The voltage subsequently remains nearly constant at this value for up to 9 hours after which it dropped further. The same trend is seen for the current drawn from the cell, Fig. 7. Table 1 lists some important electrochemical cell parameters evaluated from the discharge profile of the cell. The discharge capacity of the cell was calculated to be 6.0 mA h. This is lower than those reported by Kadir et al. [9] but similar to those reported by Bansod et al [33]. The low discharge capacity value could be due to high internal resistance of the cell [34].

Table 1. Some important electrochemical cell parameters evaluated from discharge profile of the cell.

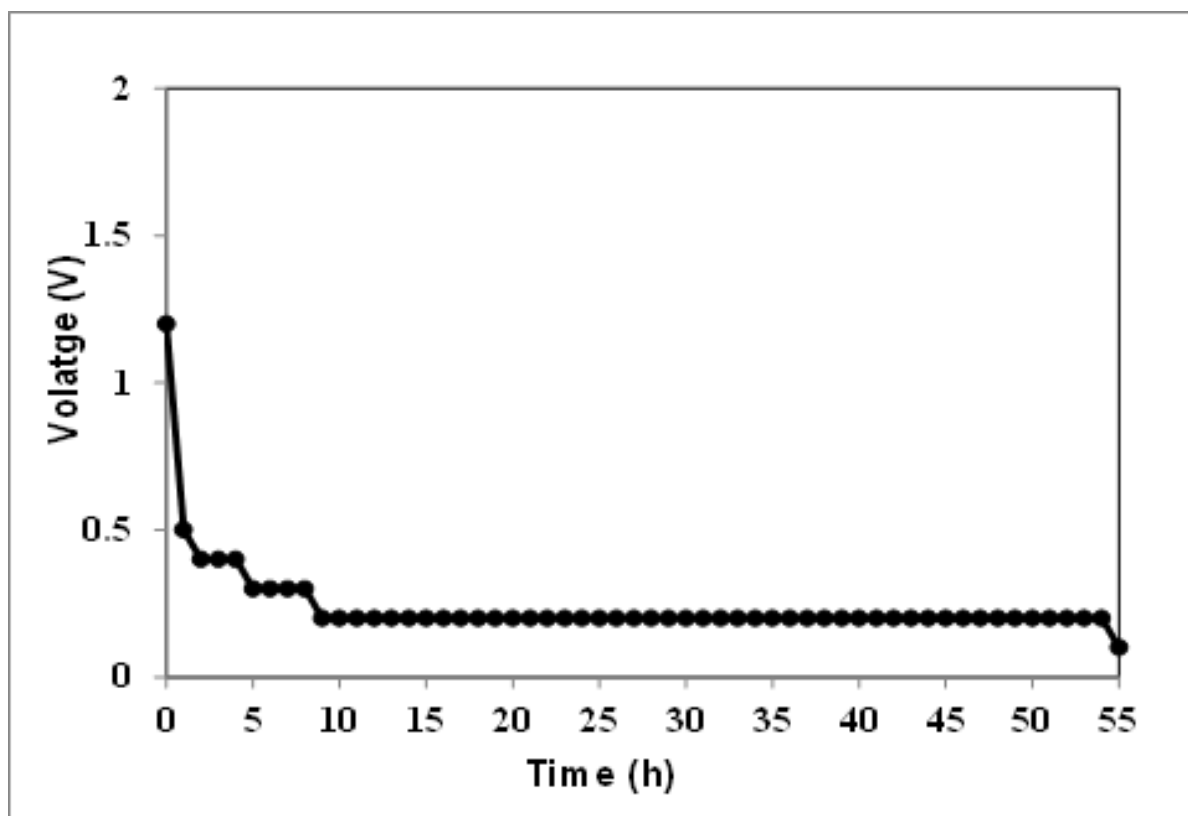| Parameters	Cell
Cell weight (±0.0001 g)	0.9271
Cell thickness (± 0.001 mm)	1.333
Cell area (± 0.1 cm^2)	3.0
Open circuit voltage (± 0.01 V)	1.52
Load (k Ω)	1.5
Plateau time (Hour)	45
Plateau voltage (± 0.01 V)	0.2
Discharge capacity (mA h) (calculated for plateau region)	6.0

Figure 6. Discharge voltage of $Zn+ZnSO_4.7H_2O$ +PTFE | 85 wt. % (PVC-$NH_4CF_3SO_3$) +15 wt. % BATS | MnO_2 +PTFE electrochemical cell.
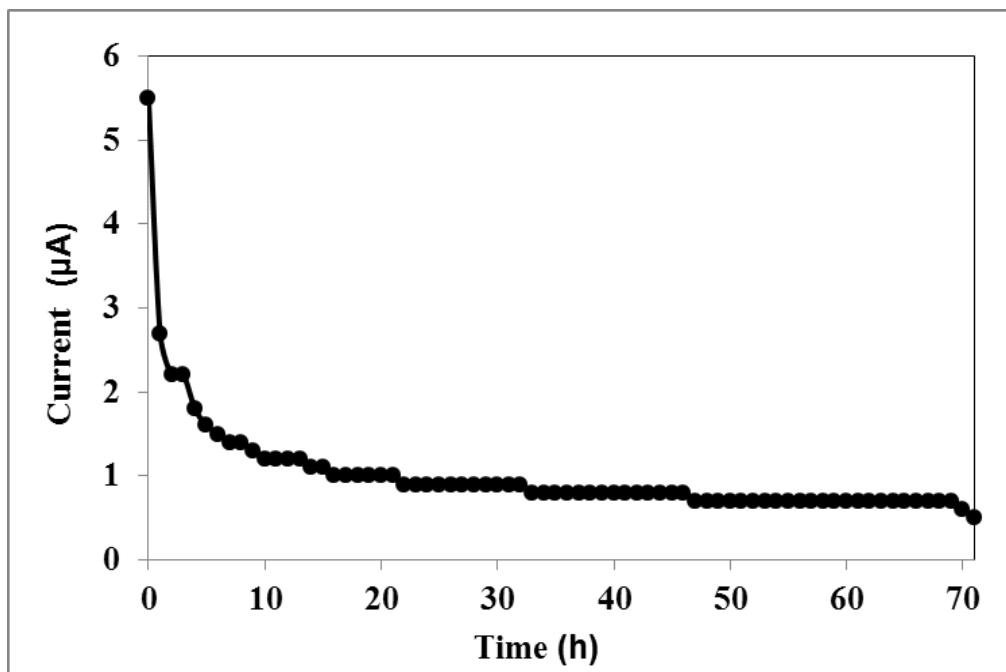
Figure 7. Discharge current of Zn+ZnSO$_4$.7H$_2$O +PTFE | 85 wt. % (PVC-NH$_4$CF$_3$SO$_3$) +15 wt. % BATS | MnO$_2$ +PTFE electrochemical cell.

4. CONCLUSION

(PVC-NH$_4$CF$_3$SO$_3$)+BATS proton conducting polymer electrolytes have been prepared by solution cast technique. Highest ionic conductivity was obtained for the electrolyte (PVC-NH$_4$CF$_3$SO$_3$) +BATS with weight ratio of 85:15 with a value of 1.56 x 10^{-4} S cm^{-1}.The transference number of the electrolyte was found to be 0.82 while its window stability was 1.1 V. The OCV of a cell based on the highest conducting electrolyte with configuration: Zn+ZnSO$_4$.7H$_2$O+PTFE | 85 wt. % (PVC-NH$_4$CF$_3$SO$_3$) +15 wt. % BATS | MnO$_2$+PTFE was ~ 1.52 V while its discharge capacity was 6.0 mA h.

References

1. S.R Majid , A.K Arof, *Physica B* , 355 (2005) 78-82.
2. J. R. Mac Callum and C. A. Vincent, *"Polymer Electrolyte Review-I"*, Elsevier   (Eds.), London, (1987)
3. F.M. Gray, *"Solid Polymer Electrolytes",* CVH, New York, (1991)
4. J. C. Lasseques, in: P. Colomban (Ed.), *"Proton Conductors: Solid Membranes and gel –Materials and Devices"*, Cambridge University Press, Cambridge, (1992).
5. S. Rajendran, O. Mahendran, T. Mahalingam, *Euro. Polym. J.* 38 (2002) 49.
6. N. Binesh, S.V. Bhat, *J. Poly. Sci. (B)* 36 (1998) 1201.

7. Y. Kang, J. Lee, J. Lee and C. Lee, *J. Power Sources*, 165 (2007) 92-96.
8. Y. Kang, W. Lee, D. H. Suh and C. Lee, *J. Power Sources*, 119-121, (2003) 448-453.
9. M.F.Z. Kadir, S.R. Majid and A.K. Arof, *Electrochemica Acta*, 55, (2010) 1475-1482.
10. T. Hamaya, S.Inoue, J. Qiao and T.Okada, *J. Power Sources*, 156, (2006) 311-314.
11. I. Nicotera, L.Coppola, C. Oliviero, M. Castriota and E. Cazzanelli, *Solid State Ionics,* 177 (2006) 581-588.
12. F. Croce, G. B. Appetecchi, L. Persi and B. Scrosati, *Nature*, 394 (1999) 456-458.
13. G.P. Pandey, S.A. Hashmi and R.C. Agrawal, *Solid State Ionics*, 179 (2008) 543-549.
14. G.P. Pandey, S.A. Hashmi and R.C. Agrawal, *J. Phys. D: Apply. Phys.,* 41 (2008)055409.
15. M.S. Michael, M.M.E. Jacob, S.R.S. Prabhaharan and S. Radhakrishna, *Solid State Ionics*, 98 (1997) 167-174.
16. D. K. Pradhan, R.N.P. Choudhary and B.K. Samantaray, *Materials Chemistry and Physics*, 115 (2009) 557-561.
17. X. Qian, N. Gu, Z. Cheng, X. Yang, E. Wang and S. Dong, *Materials Chemistry and Physics*, 74 (2002) 98-103.
18. L.S. Ng and A.A. Mohamad, *Journal of Membrane Science*, 325 (2008) 653-657.
19. Y. Li, J. Wang, J. Tang, Y. Liu and Y. He, *J. Power Sources,* 187 (2009) 305-311.
20. M. Kumar and S.S. Sekhon, *European Polymer Journal*, 38 (2002) 1297-1304.
21. N. Zainal, R. Idris and N. S. Mohamed, *Advanced Materials Research*, 287-290 (2011) 424- 427
22. J.H. Shin, W.A. Henderson, and S. Passerini: *Electrochem. Commun*. 5 (2003) 1016
23. D.R.Macfarlane, M. Forsyth, P.C. Howlett, J.M Pringle, J. Sun, G. Annat, W. Neil, andE.I. Izgorodina: *Acc. Chem. Res*. 40 (2007) 1165
24. B. Rupp, M. Schmuck, A. Balducci, M. Winter, W. Kern, *European Polymer Journal* 44 (2008) 2986–2990
25. S.Y.Chew, J.Sun, J.Wang, H. Liu, M. Forsyth, D. R. MacFarlane, *Electrochemica Acta*53 (2008) 6460–6463
26. S. Ramesh , A.K Arof. *Mater Sci Eng B* (2001) 85:11.
27. M. Venkateswarlu, K.N Reddy, B. Rambabu, N. Satyanarayana, *Solid State Ionics*, 127(2000) 177–184.
28. R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura & T. Hattori, *Solid StateIonics* 177 (2006) 2679–2682.
29. R. Baskaran, S. Selvasekarapandian, G. Hirankumar, & M.S Bhuvaneswari, *J. Power Sources* 134 (2004) 235- 240.
30. S.A Hashmi, A. Kumar, K.K. Maurya, S. Chandra, *J. Phys. D: Appl. Phys*.23 (1990) 1307- 1314.
31. R. Pratap, B.Singh, S.Chandra, *J. Power Sources*, 161 (2006) 702-706.
32. L.S. Ng, A.A. Mohamad, *Journal of Membrane Science* 325 (2008) 653-657.
33. S. M. Bansod & S. S. Bhoga & K. Singh & R. U. Tiwari, *Ionic* (2007) 13:329–332
34. G. Ning, B. Haran, B. N. Popov, *J. Power Sources* 117 (2003) 160–169