Int. J. Chem. Sci.: 14(1), 2016, 409-414
ISSN 0972-768X
www.sadgurupublications.com

EFFECT OF BLENDING ON ELECTRICAL AND ELECTRO-CHEMICAL STUDIES OF SOLID PROTON CONDUCTING POLYMER ELECTROLYTES BASED ON PVP AND PMMA

C. AMBIKA and G. HIRAN KUMAR*

Centre for Scientific and Applied Research, PSN College of Engineering and Technology,
MELATHEDIYOOR – 627152 (T.N.) INDIA

ABSTRACT

Solid proton conducting polymer electrolytes of PVP_{K30} (poly vinyl pyrrolidone) –MSA (Methanesulfonic acid), PMMA (poly methyl methacrylate)-MSA and PMMA-PVP_{K30}-MSA in various compositions are prepared by conventional solution casting technique. The conductivity values for all the prepared polymer electrolytes are calculated from cole-cole plot. The conductivity value is enhanced due to blending. The maximum conducting sample is identified in each set of polymer matrices and it is utilized for the construction of proton battery as solid electrolyte. The configuration of the primary proton battery is Zn + $ZnSO_4.7H_2O$ + AC| solid polymer electrolytes |MnO_2 + AC. Discharge profile of the proton battery is monitored at a constant current of 0.01 mA. Electrochemical impedance value of the constructed proton battery is calculated for both before and after discharge. Electrochemical impedance value is found decreased for the proton battery constructed with blend solid polymer electrolyte. The proton battery constructed with PMMA-MSA matrices shows poor discharge performance because of the high electrochemical impedance value.

Key words: Solid proton conducting polymer electrolytes, proton battery, discharge profile, electrochemical impedance.

INTRODUCTION

Solid polymer electrolytes have become increasingly attractive because of their technological applications in the development of solid state electrochemical devices. Among various types of solid polymer electrolytes, H^+ conducting polymer electrolytes have attracted the attention of scientists worldwide due to their potential application as solid electrolyte in electrochemical devices such as proton batteries, fuel cells, supercapacitors, electrochromic devices etc. To construct an electrochemical device, one of the necessary things required is an electrolyte with high ionic conductivity, good electrochemical, thermal and mechanical

---

*Author for correspondence; E-mail: hiran.gp@gmail.com stability. Several approaches are reported[1] in the literature to enhance the ionic conductivity of the solid polymer electrolyte. Among them, blending is one of the methods and it is carried out in the present work. Polymer-acid complexes and blend polymer matrices are prepared based on PMMA (poly methyl methacrylate) and PVP (poly vinyl pyrrolidone) as host polymer and MSA (methanesulfonic acid) acts as proton provider. In the present work, the effect on electrical and electrochemical properties upon blending the host polymers (PMMA and PVP) of proton conducting solid polymer electrolytes is investigated.

EXPERIMENTAL

PMMA (HIMEDIA) ($M_w = 15,000$) and PVP ($M_w = 40,000$) (HIMEDIA) and MSA (Sd-fine chem.) were the raw materials used in the preparation of solid polymer electrolytes. DMF (N, N-Dimethyl formamide) (Merck) was used as solvent. Preparation of polymer-acid complexes and blend polymer electrolytes and also the preparation of cathode and anode for the construction of proton battery were already discussed in ref[2,3], respectively.

AC impedance spectroscopy study was performed on IM6 Zahner elektrik workstation, in the frequency range of 100 mHz to 1 MHz at room temperature. The sample was cut into 1 × 1.4 cm and sandwiched between two stainless steel blocking electrodes. The constant current discharge and electrochemical impedance spectra were also recorded by Biologic-SP300 electrochemical workstation.

RESULTS AND DISCUSSION

AC impedance analysis

The typical impedance plot (Z' Vs Z'') for the prepared polymer electrolyte membranes of PVP_{K30}-MSA, PMMA-MSA and PMMA-PVP_{K30}-MSA are shown in Fig. 1, 2 and 3, respectively. The complex impedance diagram of the samples showed two regions: a depressed semi-circle in the high frequency region, which corresponds to bulk property of the membrane and the linear region in the low frequency region, attributes to the effect of double layer capacitance at the blocking electrodes. The bulk electrical resistance value (R_B) is calculated from the intercept on the real part of the impedance (Z') axis and the conductivity value can be calculated from the relation $\sigma = L/R_BA$ where L and A are the thickness and area of the sample, respectively. The calculated conductivity values at 303 K for PVP_{K30}-MSA matrices of S1, S2, S3, S4, S5, S6, S7 and S8 are 1.09×10^{-7}, 2.48×10^{-7}, 9.72×10^{-6}, 1.43×10^{-6}, 4.62×10^{-6}, 5.55×10^{-6}, 6.74×10^{-6} and 6.37×10^{-7}, respectively. Similarly for PMMA-MSA complexes of M1, M2, M3, M4 and M5 are 2.13×10^{-8}, 2.43×10^{-8}, 2.86×10^{-7}, 1.49×10^{-6} and 1.96×10^{-10}, respectively and also for blend matrices of BS1, BS2, BS3, BS4 and BS5 are 7.17×10^{-9}, 6.04×10^{-6}, 2.51×10^{-5}, 1.08×10^{-5} and 6.14×10^{-7}, respectively. The maximum conductivity value is obtained for S3, M4 and BS3 membranes.

It is also observed that the conductivity value increases with the addition of MSA and it reaches a maximum value. The enhancement of conductivity with increase in acid concentration may be due to the increase in concentration of mobile ions. After that, the conductivity drops even with the raise in MSA concentration. This may be due to the formation of ion pairs ($CH_3SO_3^- H^+$) or ion aggregates.

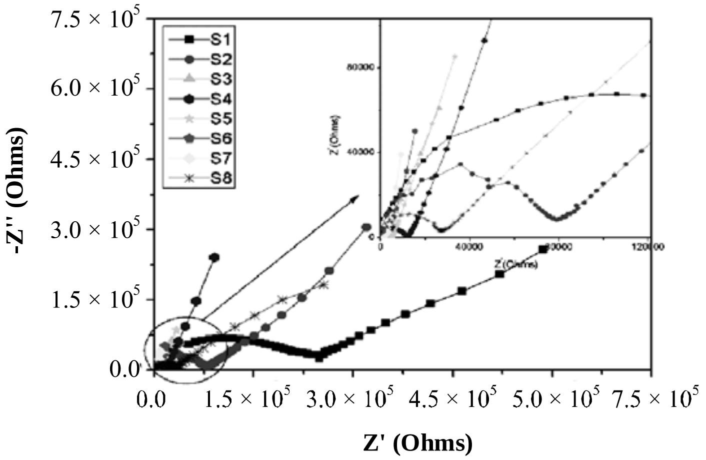


Fig. 1: Cole-Cole plot for PVP_{K30}-MSA complexes of S1: 95.75-4.25, S2: 91.56-8.44, S3: 83.23-16.77, S4: 79.18-20.82, S5: 75.19-24.81, S6: 69.21-30.79, S7: 65.35-34.65, S8: 59.50- 40.50

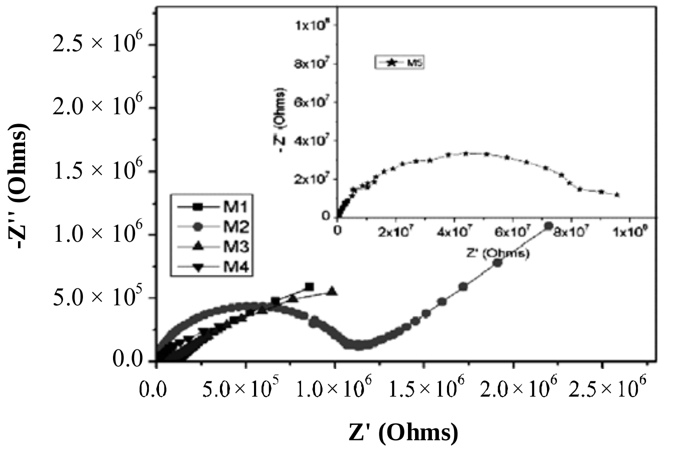


Fig. 2: Cole-Cole plot for PMMA-MSA complexes of M1: 90.40-9.60, M2: 84.67-15.33, M3: 82.78-17.22, M4: 80.88-19.12, M5: 75.20-24.80

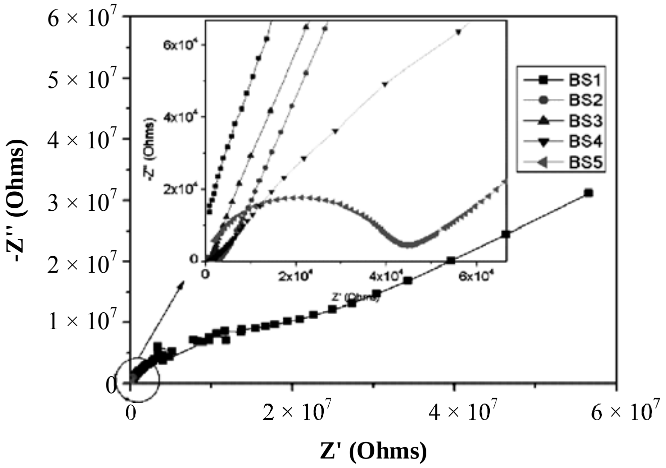


Fig. 3: Cole-Cole plot for PMMAPVP$_{K30}$-MSA complexes of BS1: 47.98-47.98-4.05, BS2: 44.96-44.96-10.08, B3: 42.98-42.98-14.04, BS4: 40.02-40.02-19.97, BS5: 37.08-37.08-25.84

Discharge characteristics

The discharge profile of the proton batteries constructed with S3 and BS3 polymer electrolyte membranes at a constant current of 0.01 mA are shown in Fig. 4. From Fig. 4, it is observed that the open circuit voltage is 1.4 V for both cells but the load voltage varies and is found to be 1.1 V and 1.2 V for the cell with S3 and BS3 membrane, respectively.

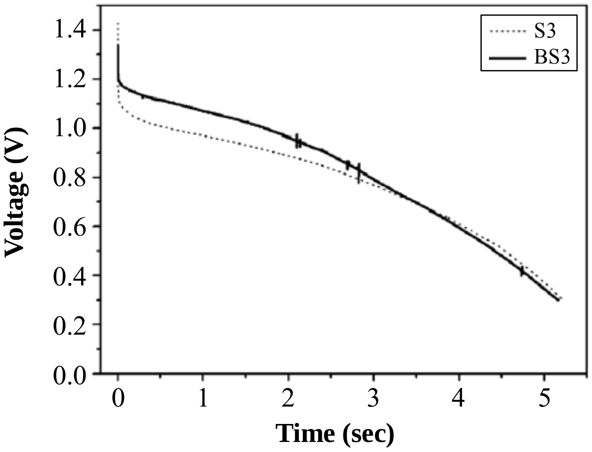


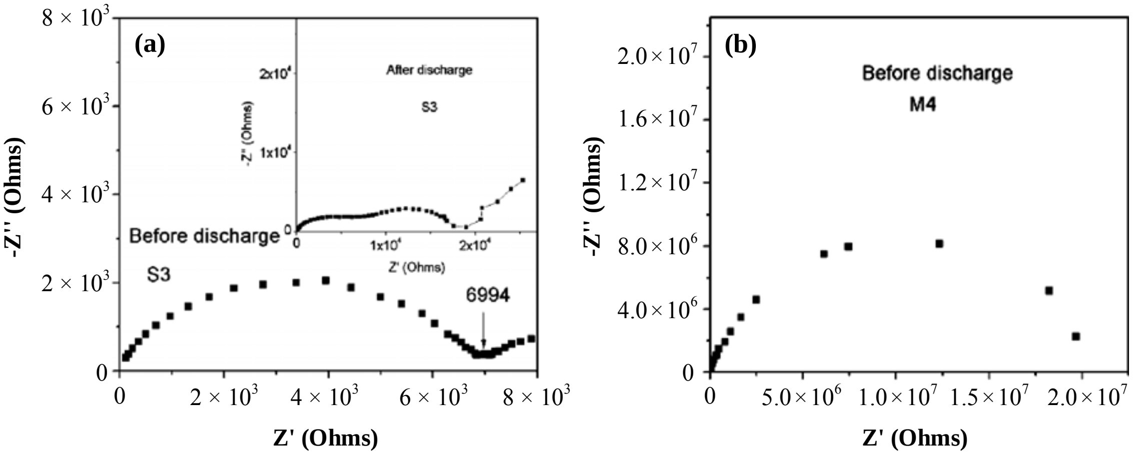
Fig. 4: Discharge pattern at the constant current drain of 0.01 mA for the proton battery constructed with S3 and BS3 proton conducting solid polymer electrolyte

From Fig. 4, battery constructed with S3 and BS3 membrane shows the same trend of discharge, which implies that there no effect is observed in the discharge characteristics due to blending of PMMA and PVP and it reaches the cut-off potential of 0.3 V in 5 hrs. A cell with PMMA-MSA matrices shows sudden discharge, which may be due to high internal resistance (not shown in Fig.).

Electrochemical impedance spectroscopy

Primary proton batteries are constructed by using S3, M4, BS3 and AS2 (high conducting samples) and are undergone electrochemical impedance (EIS) analysis before it get discharged to a constant current of 0.01 mA. The electrochemical impedance before discharge is shown in Fig. 5(a), (b) and (c) for the proton batteries constructed with S3, M4 and BS3 solid polymer electrolytes respectively. It is worthy to note that the constructed proton batteries are made of same type of anode and cathode but the electrolyte is different. So, it is expected that the discharge/electrochemical impedance of the cell purely depends on the effect of polymer electrolytes that is used in the cell. Before discharge, the electrochemical impedance for the proton batteries constructed with S3, M4 and BS3 are observed as 6994 ohms, 2×10^7 ohms and 860 ohms respectively. The EIS value is found maximum for proton battery constructed with M4 membrane, which may be due to the poor interfacial contact between the electrode and electrolyte. Due to blending, the EIS value is found decreased and it may be due to improved interfacial contact.

From the inset of Fig. 5, the increase in internal resistance of the proton battery is observed after it is subjected to constant current discharge of 0.01 mA when compared to before discharge.



Cont…

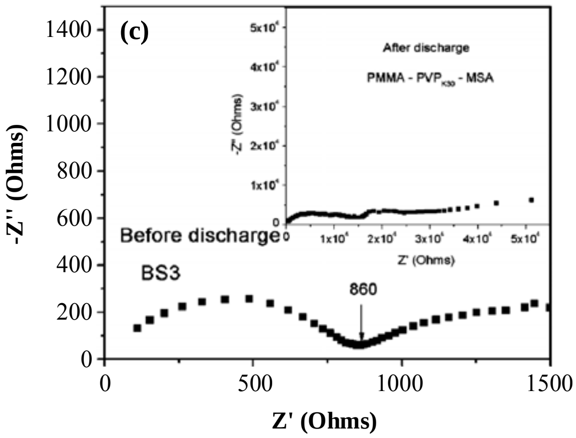


Fig. 5: Electrochemical impedance of the proton battery constructed with (a) S3 (b) M4 (c) BS3 proton conducting solid polymer electrolytes before it under gone discharge (Inset fig.: After it is subjected to discharge)

CONCLUSION

The host polymers of PMMA and PVP based proton conducting solid polymer electrolytes such as polymer-MSA complexes and blend – MSA matrices are prepared by solution casting technique. The conductivities of all prepared membranes are calculated and is found maximum for PMMA-PVP$_{K30}$-MSA matrices and is 2.51×10^{-5} S/cm. Ionic conductivity is enhanced due to blending of PMMA and PVP$_{K30}$ when compared to polymer-acid complexes. EIS value is found less for the constructed cell with BS3 membrane than the cell with S3 membrane but the same trend of discharge pattern is observed for both the cells. Blending results in improved electrical and similar electrochemical performance when compared to PVP$_{K30}$-MSA complexes.

REFERENCES

1. S. Ramesh and C.-W. Liew, Iran Polym. J., **21**, 273 (2012).
2. C. Ambika, G. Hirankumar, S. Karthickprabu and R. S. Daries Bella, Int. J. Chem. Tech. Res., **6**, 1690 (2014).
3. C. Ambika and G. Hirankumar, Appl. Phys. A (2016) (Accepted).

Accepted : 16.03.2016