Chemical Science Review and Letters ISSN 2278-6783

Research Article

Thermal and Discharge Characteristics of PVP-CH_3COONa Based Polymer Electrolyte Films

M. Seshu Kumar[1,2] and M.C. Rao[2]*

[1]Department of Physics, Krishna University, Machilipatnam-521001, India
[2]Department of Physics, Andhra Loyola College, Vijayawada- 520008, India

Abstract

PVP based polymer electrolyte films are prepared by dissolving sodium acetate with different wt% compositions by using solution cast technique. Differential scanning calorimetry is used to identify the phase changes of the prepared samples. The lowest decrement in T_g occurs at 34.15 ^oC for (80:20) wt% compositional ratio due to lubricating effect. The maximum ionic conductivity has been obtained by increasing the wt% composition upto (80:20) wt%. Transport properties state that the charge contribution is due to ionic with lower contribution of electrons takes place in these polymer electrolyte systems. Finally a polymer battery has been fabricated from the prepared films and the discharge parameters are studied.

Keywords: Solid polymer electrolyte, Solution cast technique, DSC, Transport properties and Discharge studies

***Correspondence**
Author: M.C. Rao
Email: raomc72@gmail.com

Introduction

In the present scenario, an attractive attention has been made towards solid polymer electrolytes due to their vast advantages and low production cost. Solid polymer films have taken a revolutionary development in the fields of batteries, fuel cells and humidity sensors [1]. Solid polymer films are prepared by doping inorganic salt in the host polymer. Due to the advantages of solid polymer electrolytes, they have taken a new development role in the application field of energy storage devices. The physical and electrochemical studies of polymer electrolytes bring a new revolution in the fields of energy storage applications [2]. The work on these polymer electrolytes, has received great interest which leads a new way to the researches for the development of applications of new energy devices [3, 4].

Polyvinyl pyrrolidone (PVP) was chosen because of its wide properties, besides it possesses high performance in electrochemical stability [5, 6]. Most of the researchers have focused on PVP based solid polymer electrolytes because it shows good electrochemical performance of the cell such that it can be used in many potential applications [7]. It is also used as an electrochromic display material in microelectronics as well as in pharmaceuticals as a binary agent [8, 9]. Inorganic salt like potassium acetate is used as dopant material to the host polymer in order to enhance the ionic conductivity. Rao et al. presented their results in their earlier studies [10-36]. In the present investigation, solid polymer films were prepared with different wt% composition ratios of PVP-CH_3COONa in order to improve the ionic conductivity of the composite films.

Experimental

All the chemicals such as PVP polymer with an average molecular weight (M.W: 36,000), sodium acetate (CH_3COONa) 98% were used for the preparation of solid polymer films. All the chemicals used in the present investigation were purchased from Sigma Aldrich, India. Double distilled water was used as a common solvent in this process. All the chemicals were dried under vacuum oven at 40 ^oC for 1 hour. Later the precursor materials of PVP polymer and sodium acetate were weighed properly in different wt% concentrations PVP: x wt% CH_3COONa (where x = 5, 10, 15 and 20). This homogeneous mixture was added to 20 ml double distilled water and kept continuous stirring for 24 Hrs. Later it was poured into polypropylene dishes and allowed to evaporate the solution slowly in a hot air oven to remove the moisture and solvent solution. Finally the obtained samples were placed in vacuum desiccator.

Results and Discussion

Thermal analysis

Thermal analysis of the prepared films with different wt% percentage ratios were shown in **Figure 1**. Figure shows that the glass transition temperature (T_g) of pure PVP is found at 35.75 °C, which clearly indicates the phase transformation point.

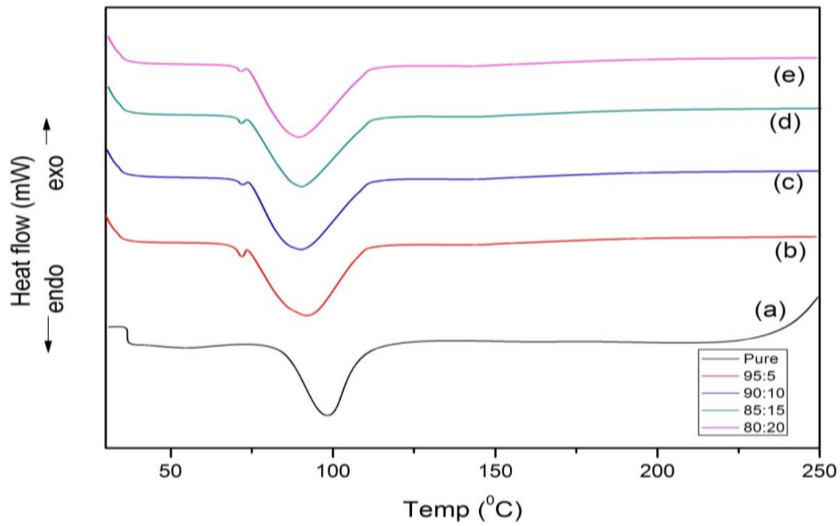

Figure 1 DSC thermograms of PVP-CH_3COONa polymer electrolyte films for different wt% ratios

As increasing the wt% of CH_3COONa salt to the PVP polymer, the position of the T_g is shifted towards lower value. The shift in the glass transition temperature is found to be 35.64, 35.33, 35.14 and 34.15 ^{o}C. It is observed from the figure that that the DSC curves exhibit only single T_g value. It may be due to the complete soluble of the salt in the host polymer matrix which leads to increase the amorphous nature as increasing the wt% of salt in the polymer. This decrement in T_g is due to the interaction of CH_3COONa salt with the host polymer. The decrease in T_g helps to soften the polymer backbone due to plasticization effect and increase its ions. While increasing the temperature through the material, pin holes are formed through the matrix where the ions are exhausted freely through the holes [37, 38]. When compared with the wt% compositional ratios, (80:20) wt% ratio has observed the lowest T_g value at 34.15 ^{o}C. At the lowest T_g point the crystalline nature turns in to amorphous phase [39, 40].

Wt% composition studies

The logarithmic value of dc conductivity with different wt% ratios, with respect to concentration of CH_3COONa in PVP at different temperatures is shown in **Figure 2**.

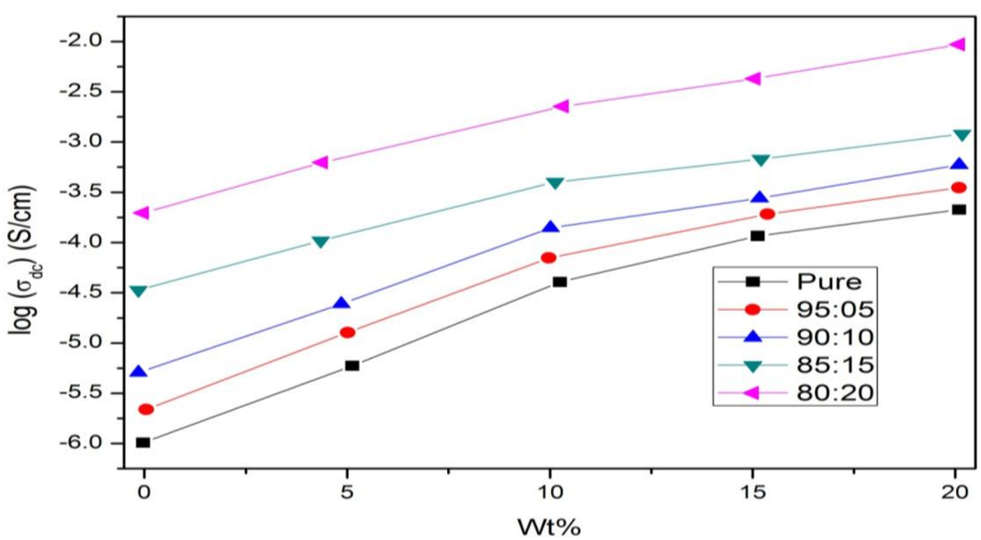

Figure 2 Wt% Composition plots of PVP-CH_3COONa polymer electrolyte films for different wt% ratios

From the conductivity values of PVP-CH_3COONa, it is noticed that the ionic conductivity for pure PVP is found at the order of ~10^{-9} $S.cm^{-1}$ at room temperature. By increasing the salt concentration, the values sharply increases to ~10^{-5} $S.cm^{-1}$ for (80:20) wt% composition sample. This variation is due to the state of change from semicrystalline to amorphous phase such that the ionic conductivity increases abruptly as increasing the wt% composition in the polymer.

Transference number

The transport properties of PVP-CH_3COONa electrolyte system are calculated by using Wagner's D.C. Polarization technique. When a constant of DC voltage (1.5 V) is applied around the SPE of a configuration of Na(A)/polymer electrolyte/C of a polymer battery, then the obtained DC current is screened and noted with respect to time. Similar procedure is applied and calculated for other samples. The transport properties of ionic and electronic currents with respect to time are calculated by following equitation's [41],

$$t_{ion} = \frac{i_{ion}}{\sigma_T} = \frac{i_T - i_{ele}}{i_T}\ ; \quad t_{ele} = \frac{\sigma_{ele}}{\sigma_T} = \frac{i_{ele}}{i_T} \qquad (1)$$

Where, "i_T" is the initial current and "i_{ele}" is the final residual current.

The current vs time plot of PVP-CH_3COONa polymer electrolyte films for different wt% ratios is shown in **Figure 3**. From the plot, it is observed that the current is suddenly decreased as the time increases and after steady state, long time of polarization takes place in the samples. This decrement may be due to the flow of current across the electrode interfaces [42, 43]. From the calculated data, it confirms that among all the stichiometric ratios of polymer films for (80:20) wt% have the high ionic charge and minute number of transfer of electrons takes place. The transport properties of all ratios of PVP-CH_3COONa solid polymer electrolytes and their data are presented in **Table 1**.

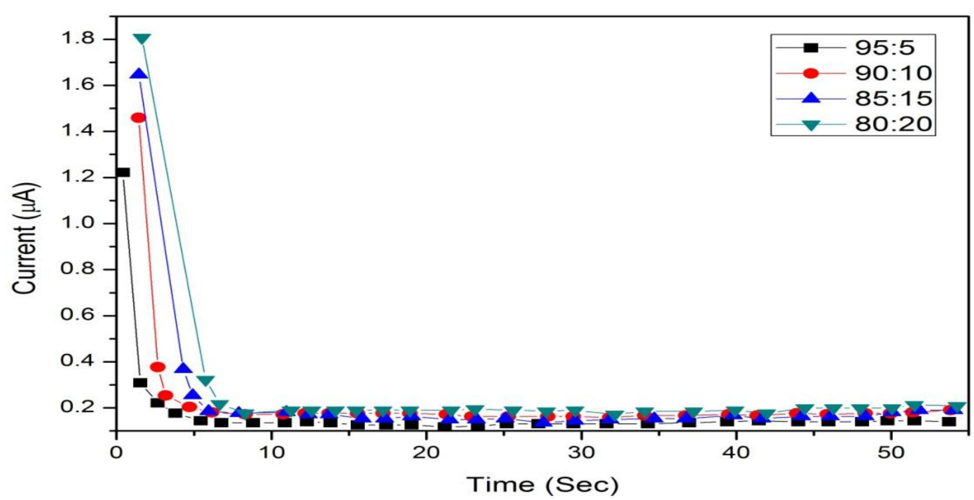

Figure 3 Transport properties of PVP-CH_3COONa polymer electrolyte films for different wt% ratios

Table 1 Transference number of PVP-CH_3COONa solid polymer films

Solid polymer films	t_{ion}	t_{ele}
PVP-CH_3COONa (95:5)	0.94	0.06
PVP-CH_3COONa (90:10)	0.96	0.04
PVP-CH_3COONa (85:15)	0.97	0.03
PVP-CH_3COONa (80:20)	0.98	0.02

Discharge studies

Discharge studies were measured by fabricating solid state electrochemical cells using the prepared electrolyte films of different compositions (95:5), (90:10), (85:15) and (80:20) as shown in **Figure 4**. The measurements were done with the configuration of Na(anode)/[PVP CH_3COONa]electrolyte/(I_2+C+electrolyte) for a constant load of 100 kΩ [44, 45]. Initially a sharp decrease in the voltage is observed, it might be due to the polarization or the formation of a thin layer of sodium metal at the electrode-electrolyte interface [46, 47]. When compared with the other compositional ratios of the cells, PVP-CH_3COONa (80:20) wt% ratio of the cell exhibits long durability with better performance upto 120 Hrs. Different cell parameters of the fabricated cell have been calculated and the obtained data is presented in **Table 2**.

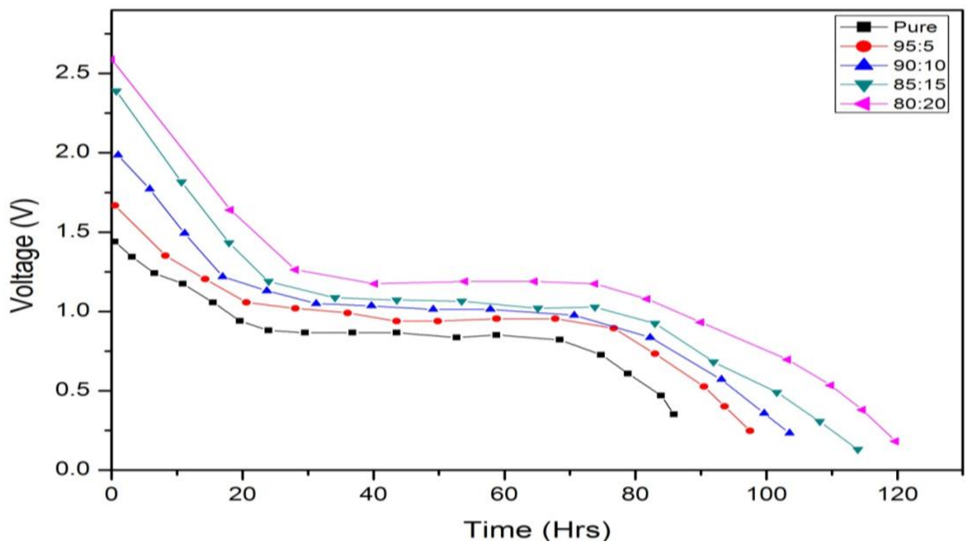

Figure 4 Discharge studies of PVP-CH_3COONa polymer electrolyte films for different wt% ratios

Table 2 Cell parameters of PVP-CH_3COONa solid polymer films

Cell parameters	**PVP-CH_3COONa (80:20)**
Cell weight (g)	1.86
Area of the cell (cm^2)	1.41
Open circuit voltage (OCV)	2.60
Discharge time (Hrs)	120
Current density (μA/cm^2)	210.45
Discharge cell (μA/h)	1.50
Power density (W/Kg)	0.31
Energy density (Wh/Kg)	67.51

Conclusion

Solid polymer films have been prepared with different wt% ratios of PVP-CH_3COONa by solution cast technique. The lowest decrement in T_g occurs at 34.15 ^oC for (80:20 %) wt% compositional ratio due to lubricating effect. Transport properties state that current is decreased as the time increases and after steady state, long time of polarization takes place in the samples. The majority charge of ions is found to be 0.98 for the compositional ratio of 80PVP:20CH_3COONa. Finally a solid polymer battery has been fabricated from the prepared films and the discharge characteristics were studied for a constant load of 100 kΩ.

References

[1] Wright PV, Br Polym J 1975, 7, 319.
[2] Fenton DE, Parker JM, Wright PV, Polym 1973, 14, 589-592.
[3] Armand MB, Ann Rev Mater Sci 1986, 16, 245-261.
[4] Wang X, Zhi L, Muellen K, Nano Lett 2008, 8, 323-327.
[5] Guo S, Dong S, Wang E, ACS Nano 2010, 4, 547-555.
[6] Zhang L, Shi GJ, Phys Chem C 2011, 115,17206-17212.
[7] Li N, Cheng W, Ren K, Luo F, Wang K, Fu Q, Chin, J Poly Sci 2013, 31, 98-109.
[8] Lin L, Deng H, Gao X, Zhang S, Bilotti E, Peijs T, Fu Q, Poly Int 2013, 62, 134-140.
[9] Gao X, Zhang S, Mai F, Lin L, Deng Y, Deng H, Fu Q J Mater Chem 2011, 21, 6401-6408.
[10] Rao M C, Hussain O M, J Alloys Compd 2010, 491(1), 503- 506.
[11] Rao M C, J Crys Growth 2010, 312(19), 2799- 2803.
[12] Rao M C, Optoelect Adv Mater (Rapid Commu) 2011, 5, 85-88.

[13] Muntaz Begum Sk, Rao M C, Ravikumar R VS S N, Spectrochim Acta Part A Mol Biomol Spec, 2012, 98, 100-104.
[14] Rao M C, J Optoelect Adv Mater 2011, 13, 428-431.
[15] Rao M C, Hussain O M, Eur Phys J Appl Phys, 2009, 48(2), 20503.
[16] Muntaz Begum Sk, Rao M C, Ravikumar R VS S N, J Inorg Organometa Poly Mater 2013, 23(2), 350-356.
[17] Rao M C, J Optoelect Adv Mater 2010, 12, 2433-2436.
[18] Rao M C, Optoelect Adv Mater (Rapid Commu) 2011, 5(5-6), 651-654.
[19] Rao M C, J Optoelect Adv Mater 2011, 13(1-2), 72-75.
[20] Rao M C, Optoelect Adv Mater (Rapid Commu), 2012, 6, 511-515.
[21] Prasad P V, Ramachandra Rao K, Rao M C, J Mol Struc 2015, 1085, 115-120.
[22] Rao M C, J Optoelect Adv Mater 2011, 13, 78-81.
[23] Rao M C, Muntaz Begum Sk, Optoelect Adv Mater (Rapid Commu) 2012, 6, 508-510.
[24] Rao M C, Int J ChemTech Res, 2014, 6(3), 1904-1906.
[25] Rao M C, Optoelect Adv Mater (Rapid Commu) 2010, 4, 2088-2091.
[26] Muntaz Begum Sk, Ravindranadh K, Rao M C, Ravikumar R V S S N, AIP Conf Proc 2013, 1536, 27-28.
[27] Rao M C, AIP Conf Proc 2016, 1728(1), 020077.
[28] Ravindranadh K, Rao M C, AIP Conf Proc 2016, 1728(1), 020079.
[29] Ravindranadh K, Rao M C, AIP Conf Proc 2016, 1536(1), 219-220.
[30] Rao M C, AIP Conf Proc 2016, 1536(1), 215-216.
[31] Rao M C, Optoelect Adv Mater (Rapid Commu) 2012, 6, 245-248.
[32] Rao M C, Optoelect Adv Mater (Rapid Commu) 2016, 10, 889-892.
[33] Rao M C, Muntaz Begum Sk, AIP Conf Proc 2012, 1447, 613-614.
[34] Ravindranadh K, Rao M C, Int J ChemTech Res 2016, 9(4), 598-603.
[35] Rao M C, AIP Conf Proc 2012, 1447, 613-614.
[36] Rao M C, AIP Conf Proc 2013, 1536, 27-28.
[37] Di CA, Wei DC, Yu G, Liu YQ, Guo YL, Zhu DB, Adv Mater 2008, 20, 3289-3293.
[38] Owens BB, Smyrl WH, Xu JJ, J Power Sources 1999, 150, 81-82.
[39] Pandey GP, Agrawal RC, Hashmi SA, J Solid State Electrochem 2012, 15, 2253-2264.
[40] Yang XF, Wang GC, Wang RY, Li XW, Electrochem Acta 2010, 55, 5414-5419.
[41] Gregory TD, Hoffmann RJ, Winterton RC, J Electrochem Soc 1990, 137, 775-780.
[42] Liew CW, Ramesh S, J Mater Res 2012, 27, 2996-3004.
[43] Stoller MD, Park S, Zhu Y, An J, Ruoff RS, Nano Lett 2008, 8, 3498-3502.
[44] Yuxi X, Wenjing H, Hua B, Chun L, Gaoquan S, Carbon 2009, 47, 3538-3543.
[45] Stankovich S, Dikin DA, Piner RD, Kohlhaas KM, Kleinhammes A, Jia Y, Wu Y, Nguyen ST, Ruoff RS, Carbon 2007, 45, 1558-1565.
[46] Shahenoor Basha SK, Ranjit Kumar B, Veera Bhadra Reddy K, Rao M.C, Chem Sci Rev Lett 2017, 6(22), 832-837.
[47] Kojima Y, Usuki A, Kawasumi M, Okada A, Fukushima Y, Karauchi T, Kamigaito OJ Poly Sci 1993, 31, 1775-1778.

Publication History
Received 12th May 2018
Revised 04th June 2018
Accepted 08th June 2018
Online 30th June 2018