Research Paper

Volume : 2 | Issue : 10 | October 2013 • ISSN No 2277 - 8179

Structural and AC Impedance Analysis of Blend Polymer Electrolyte Based on PVA and PAN

Physics

KEYWORDS : Polyvinylalcohol, Polyacrylonitrile, Proton conductor, AC Impedance spectroscopy, Relaxation

S. Siva devi	Research and Development Centre, Bharathiar University, Coimbatore-641046, Tamilnadu, India
S.Selvasekarapandian	Materials research Centre, Coimbatore- 641045, Tamilnadu, India.
S.Karthikeyan	Department of Physics, Ramco Institute of Technology, Rajapalayam- 626 117 , Tamilnadu, India
N.Vijaya	Department of Physics, The S.F.R. College for Women, Sivakasi- 626123, Tamilnadu, India.
F. Kingslin Mary Genova	Department of Physics, The S.F.R. College for Women, Sivakasi- 626123, Tamilnadu, India.
C.Sanjeeviraja	Department of Physics, Alagappa Chettiar College of Engineering and Technology, Karaikudi, Tamilnadu

ABSTRACT - Synthesis and characterization of new polymer electrolytes for electrochemical applications is one of the topics of current research. In this work, polymer electrolytes are prepared by blending two polymers Polyvinylalcohol (PVA) and Polyacrylonitrile (PAN) of different compositions by solution casting method using DMF as solvent. The prepared polymer films are characterized by X Ray Diffration and AC impedance spectroscopic techniques. XRD analysis shows the amorphous nature of the electrolytes. AC impedance analysis gives conductivities of the electrolytes. The highest conductivity at room temperature (305K) has been found to be 1.2x10-7 S cm-1 for 92.5PVA-7.5PAN system. The activation energy calculated for blend polymer electrolytes have been found to vary from 0.1 to 0. 21eV. The loss tangent curves for the samples reveal the presence of low frequency relaxation peaks which shift towards high frequency at high temperature.

Introduction

Solid polymer electrolytes have attracted the attention of scientists in the recent years, because of their impressive properties such as high ionic conductivity, flexibility and long life, which find applications in electrochemical devices. Over the last decades the miscibility of blends of polymers has been intensively investigated. Many blend polymer electrolyte systems have been studied and reported in the literature [1-5]. It has been observed from the literature that a little attempt has been made to prepare polymer blend using Polyvinyl alcohol (PVA) and Polyacrylonitrile (PAN)[6]. PVA has excellent film forming nature, high tensile strength and flexibility. PAN is a resinous, fibrous, or rubbery organic polymer which possess good mechanical strength. For fuel cell applications polymer electrolyte should have good mechanical strength and high conductivity. To achieve this, blend polymer electrolytes with PVA:PAN ratio equal to 90:10, 92.5:7.5, 95:5, 97.5:2.5, 100:0 are prepared. Then this blend polymer electrolytes are characterized by XRD and AC impedance spectroscopy. The highest conducting blend composition (PVA: PAN=92.5:7.5) is found by AC impedance analysis.

Experimental Technique

PVA (MW 1,25,000), PAN (MW 1,50,000) and Ammonium Nitrate have been used to prepare blend polymer electrolyte of various compositions using Di Methyl Formamide (DMF) as solvent by solution casting technique. 92.5% by weight of PVA is stirred in DMF at 60oC for about 3 hours and after its complete dissociation, 7.5% by weight of PAN is added and stirred for 2 hours till it becomes homogeneous. Then it is poured in the Petri dish and evaporated at 60oC in vacuum oven. Free standing film is obtained after 48 hours. XRD patterns are recorded with XPERT-PRO Diffractometer system using Cu Kα radiation in the range of 2θ=100 to 800. The impedance studies are made using a computer controlled HIOKI 3532 LCR meter over a frequency range of 42 Hz to 5 MHz with a cell having aluminium electrodes.

Results and discussions

X-Ray Diffraction (XRD) Analysis

Figure 1 represents the XRD pattern of pure PVA, pure PAN, and blend polymer system of different compositions. Peaks around 19.6° and 40.80 [7, 8], which are ascribed to the pure PVA, have been found to be slightly shifted in the complex system. In addition, decrease of intensity of this peak and increase of full-width half maximum of this peak has also been observed. This increase in broadness of the peak reveals the amorphous nature of the blend system. Peak corresponding to pure PAN at 17.80 is shifted in the blend polymer system, which reveals complex formation in the blend. These results can be interpreted in terms of the Hodge et al. [9] criterion, which has established a correlation between the height of the peak and the degree of crystallinity.

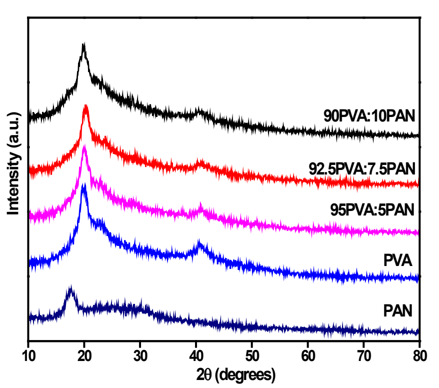
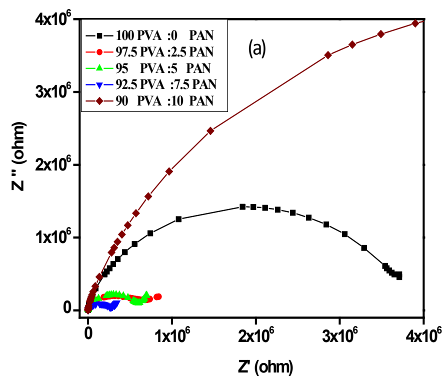


Figure 1. XRD pattern of polymer electrolytes for various PVA- PAN ratios

Impedance analysis

Figure 2(a) shows the Cole-Cole plot of PVA-PAN blend for different concentrations at 303K. The impedance can be calculated from the intercept of spike or semicircle on the Z' axis. The impedance (Cole-Cole) plot shows that the ionic conductivity is maximum for blend composition PVA:PAN equal to 92.5:7.5. The ionic conductivity values are calculated by using the equation σ=l/RbA, where l and A are thickness and area of the electrolyte film respectively and Rb is the bulk resistance of the electrolyte film. The highest conductivity at room temperature has been found to be 1.13 x 10-7 Scm-1 for concentration ratio 92.5:7.5 of the blend polymer. For other concentrations, the conductivity is found to decrease. From Figure 2(b), it can be seen that as the temperature is increased, the bulk resistance decreases, the mobility of polymer chain increases, which enhances the ionic conductivity. This is favorable to a high conductivity at higher temperatures [3].



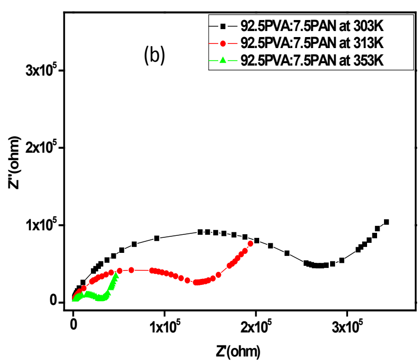


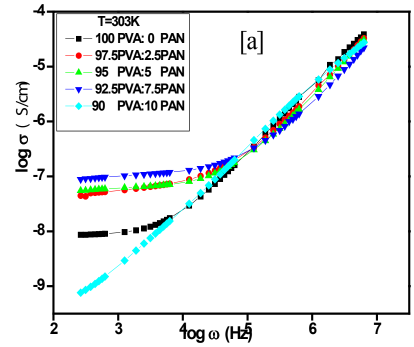
Figure 2. Cole-Cole plot of Blend polymer electrolytes showing (a) concentration dependence (b) temperature dependence of impedance

Conductance Spectra

The conductance spectra describe the frequency dependence of the conductivity. The spectrum of log frequency versus log conductivity of pure PVA and different molar ratios of PVA-PAN are shown in Figure 3. The frequency independent low frequency dispersion region is due to space charge polarization at the blocking electrodes and the high frequency region corresponds to bulk relaxation mechanism. In high frequency region, conductivity increases as frequency increases. The ionic conductivity is maximum for 92.5PVA:7.5PAN system. Figure 3(b) shows the increase in conductivity with temperature which indicates the increase in chain flexibility. The variation of conductivity with temperature can be elucidated with the help of the Arrhenius equation, given by

$$\sigma = \sigma_0 \exp(-E_a/kT)$$

where σ0 is pre-exponential factor and Ea is the activation energy of the polymer electrolytes. The experimental data indicates that the ionic conductivity is enhanced with increasing temperature.



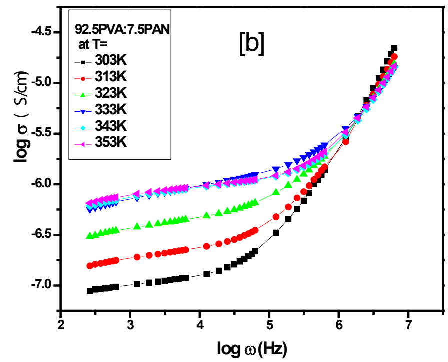


Figure 3: Conductance spectra for blend polymer electrolytes for different [a] compositions [b]different temperatures of 92.5PVA:7.5PAN blend polymer electrolytes

When the temperature is increased, the mobility of the polymer chain is enhanced, and the fraction of free volume in the polymer electrolyte system increases accordingly, which facilitates the transitional motion of ions [4]. In high frequency region, the conductivity is observed to be less temperature dependent and the conductivity spectra obeys Joncher's power law[10] $\sigma_{ac}(\omega)=\sigma_{dc}+A\omega^{\alpha}$, where α is the power law exponent. Both σdc and A are thermally activated quantities. Table 1 gives the conductivities for different compositions of the blend and shows that the activation energy decreases with increase in amorphous nature of the polymer electrolytes. Here the low activation energy means high ionic conductivity [11].

Table.1 Conductivity for the blend polymer films for different composition

PVA:PAN composition (mol%)	σ (conductivity) S/cm			Activation Energy (eV) (for T = 303 K)
	T = 303 K	T = 323 K	T = 343 K	
100:0	1.5×10^{-8}	7.4×10^{-8}	2.5×10^{-7}	0.18
97.5:2.5	5.1×10^{-8}	1.9×10^{-7}	5.9×10^{-7}	0.13
95:5	6.4×10^{-8}	2.3×10^{-7}	1.7×10^{-6}	0.12
92.5:7.5	1.2×10^{-7}	4.3×10^{-7}	6.8×10^{-7}	0.10
90:10	6.7×10^{-10}	3.8×10^{-9}	2.7×10^{-8}	0.21

3.5 Loss tangent Spectral analysis:

Figure 4 (a) shows the variation of tan δ as a function of frequency for different mol% of blend polymer electr.

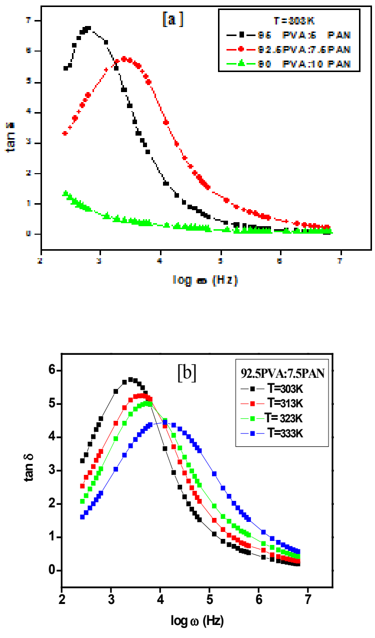


Figure.4 Loss tangent spectra for different concentrations (b) temperatures of highest conducting sample

The dielectric loss tangent (tanδ) can be defined by the equation tan δ= ε"/ ε'. Figure 4(b) shows the variation of tanδ as a function of frequency for 92.5PVA:7.5PAN polymer electrolyte for different temperatures. As the temperature increases the relaxation peak shifts to higher frequencies indicating that the charge carrier is thermally activated [12].

Conclusion

Polymer electrolyte films of pure polyvinyl alcohol and polyacrylonitrile with different compositions are prepared by solution cast technique. It has been observed that the system comprising 92.5PVA:7.5PAN has the highest conductivity $1.2x10^{-7}$ S cm^{-1}. The activation energy of the dc conductivity is low for this system which is 0.1eV. From the loss tangent spectra, it may be concluded that the charge carrier responsible for both conductivity and relaxation are the same.

REFERENCE

[1] G.Hirankumar, S.Selvasekarapandian, N.Kuwata, J.Kawamura, T.Hattori (2005), 'Thermal, electrical and optical studies on the poly (vinyl alcohol) based polymer electrolytes', Journal of Power sources, 144, 262. | [2] N.Rajeswari, S.Selvasekarapandian, S.Karthikeyan,H.Nithya&C. Sanjeeviraja (2012), 'Lithium Ion Conducting Polymer Electrolyte Based onPoly (Vinyl Alcohol) – Poly (Vinyl Pyrrolidone) Blend with LiClO4', International Journal of Polymeric Materials, 61:14, 1164-1175 | [3] J.M.G.Cowie, in: Polymer Electrollytes Reviews (J.R.MacCallum, C.A.Vincent, eds.) (1987), Vol.1, Elsevier Applied Science, London, p.92 | [4] S. Ramesh, A.K. Arof (2001), 'Ionic conductivity studies of plasticized poly(vinyl chloride) polymer electrolytes', Materials Science and Engineering, B, 85, 11-15 | [5] M.Siekierski, W.Wieczorek, J.Przyluski (1998), 'Ac Conductivity Studies of Composite Polymeric Electrolyte', Electrochim Acta 43:1339 | [6] A.Subramanian, N.T.Kalyana Sundaram, G.Vijaya Kumar, T.Vasudevan (2006), 'Effect of salt concentration in (PVA-PAN) based plasticized polymer blend electrolyte for Li-ion battery application', Ionics 12: 175-178, | [7] James R MacCallum, Anthony S. Tomlin, Colin A Vincent (1986), 'An investigation of the conducting species in polymer electrolytes', European Polymer Journal, 22 787. | [8] G.G. Cameron, M.D. Ingram, G.A. Sorrie (1986), 'Ionic conductivity in liquid polymeric electrolytes', Journal of Electro analytical Chemistry, 198 205. | [9] R.M. Hodge, G.H. Edward, G.P. Simon (1996), 'Water absorption and states of water in semicrystalline poly(vinyl alcohol) films', Polymer 37;1371-1376 | [10] A.K.Joncher (1977), 'Universal Dielectric Response', Nature, 267: 673. | [11] M.Hema, S.Selvasekara Pandian (2007), ' Vibrational and impedance spectroscopic analysis of poly(vinyl alcohol)-based solid polymer electrolytes', Ionics 13, 483-487 | [12] R.Mishra (1998), 'Lithium ion conduction in extreme polymer in salt regime', Solid State Ionic 112 261-273. |