iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 5 **Issue:** XII **Month of publication:** December 2017

DOI:

www.ijraset.com

Call: 08813907089 | E-mail ID: ijraset@gmail.com

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor :6.887
Volume 5 Issue XII December 2017- Available at www.ijraset.com

Electrical Characterisation of Polymer Blend Electrolyte System Doped with SiO_2

V. Balasubramanyam Achari[1]
[1]*Department of Physics, Govt. Degree & PG College, Puttur, Affiliated to S.V.University ,Tirupati,India-517501.*

Abstract: Composite polymer blend electrolyte system based on polyvinyl alcohol (PVA) and polyethylene glycol (PEG) complexed with $NaIO_4$ was prepared using solution cast technique. The effect ofnano sized silica (SiO_2) on the properties of Sodium ion conducting electrolyte was studied. The structural properties of these electrolyte films were examined by XRD studies. The XRD data revealed that the amorphous domains of polymer blend matrix increased with addition of nano particles. DC conductivity of the films was measured in the temperature range 303–398 K. The electrical conductivity increased with increasing dopant concentration, which is attributed to the formation of charge transfer complexes. The polymer complexes exhibited Arrhenius type dependence of conductivity with temperature. It was found that addition of SiO_2significantly improved the ionic conductivity. The total ionic transport number was evaluated by means of Wagner's polarization technique .Transport number for Sodium ion is ranged from 0.94 to 0.98 depending on the composition.
Keywords : Polymer blend electrolyte, DC conductivity, Transport number, Nano particle

I. INTRODUCTION

Solid polymer electrolytes have recently received considerable attention in view of their wide potential applications in various electrochemical devices such as solid state batteries, sensors, fuel cells, super- capacitors, electro chromic display devices etc. [1-3]. However, the low ionic conductivity of solid polymer electrolytes at ambient temperatures has limited their potential applications. The major efforts in this field have remained concentrated in developing new polymer electrolytes having high ionic conductivity and high mechanical, thermal and electrochemical stability [4-6].Various investigations have been performed by blending of polymers, cross linking, insertion of ceramic fillers and plasticization in order to enhance the ionic conductivity [7-8].The main advantages of the blend based polymer electrolytes are simplicity in preparation and easy control of physical properties by compositional change. Polymer blends often exhibit properties that are superior to the individual component polymers[9-10].

Most of the recent research efforts to improve the room temperature conductivity without the fall of mechanical and potential stability have been directed towards the addition of nanoscale ceramic fillers such as SiO_2,Al_2O_3,TiO2 and CeO_2 into polymer electrolytes[11-12].The nanosize fillers interact with the cations and anions and provide additional sites creating favourable high conducting pathways in the vicinity of filler grains for the migration of ions [13].The particle size of the filler is also expected to have a wide influence on the ionic conductivity of the composite polymer electrolytes. The conductivity increases with decrease in particle size i.e., increasing specific surface area of the ceramic fillers. In the present investigation, nano composite polymer electrolytes composing of PVA/PEG as host polymer ,$NaIO_4$ as a salt and SiO_2 as nano particle have been prepared .we report here the results of our investigation on the ionic conductivity, transport and electrochemical nature of polymer blend electrolyte films.

II. EXPERIMENTAL

Films (thickness ~100 µm) of pure blends of PVA+PEG and various compositions of complexed films of (PVA + PEG) with $NaIO_4$salt were prepared in the weight percent ratios (47.5:47.5:5), (45:45:10),(42.5:42.5:15) and (40:40:20) by solution cast technique using tetrahydrfuranas a solvent. $SiO_2$was used in small quantity (2 wt%) as a nano particle in these films.The solutions were stirred for 10-12 h to geta homogeneous mixture and were then, cast onto polypropylene dishes and evaporated slowly at ambient atmosphere. The final product was vacuum dried thoroughly

In order to investigate the nature of these polymer blend electrolyte films, X-ray diffraction studies were carried out usingHLG4/B-PC X-ray diffractometer with Cu Kα radiation and graphite monochromator at room temperature. The dc conductivity was measured by means of an in-house conductivity set-up [14] in the temperature range303-398K.The total ionic transport number was evaluated by means of Wagner's polarization technique [15].in this technique, freshly prepared polymer electrolyte films were polarized in the configuration Na/polymer electrolyte/C under a dc bias(step potential of 1.5V). The resulting current was monitored as a function of time.

©IJRASET (UGC Approved Journal): All Rights are Reserved

III. RESULTS AND DISCUSSION

A. *X-ray diffraction*

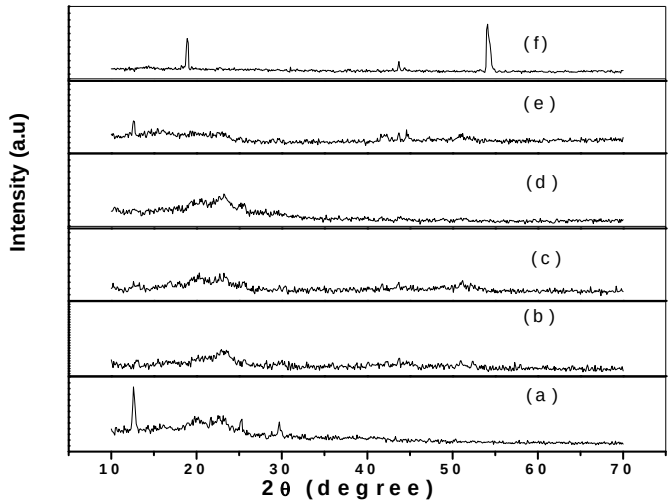


Fig 1. XRD patterns of(a) Pure PVA+PEG(b) PVA+PEG++$NaIO_4$ (47.5 :47.5 :5)(c) PVA+PEG+$NaIO_4$ +SiO_2 (47.5 :47.5 :5)(d) PVA+PEG+$NaIO_4$ (42.5 :42.5 : 15) (e) PVA+PEG+$NaIO_4$ +SiO_2 (42.5 :42.5 :15)(f) $NaIO_4$ salt.

Fig. 1 shows the XRD patterns of (PVA+PEG+$NaIO_4$),PVA+PEG+$NaIO_4$plasticizer and pure $NaIO_4$ films. Figure 1(a–f) shows peak intensity at $2\theta = 20^0$for pure blend film. The intensity of this peak decreases with increasing concentration of $NaIO_4$ which implies decrease of degree of crystallization and increase of amorphous nature. Hodge *et al* [16] established a correlation between intensity of the peak and degree of crystallinity. The peaks exhibit further decrease in intensity at higher concentrations of $NaIO_4$ salt in the polymer. This indicates a decrease in the crystalline phase with lowering of crystallite size of the polymer electrolyte. The crystalline peaks of 2θvalues at 15 and 62^0 corresponding to $NaIO_4$are absent in nanocomposite polymer bend complexed films. This amorphous nature results in greater ionic diffusivity and highionic conductivity, which can be observed in amorphous polymers having flexible back-bone [17-18]. This behaviour demonstrates that complexation between PVA,PEG,$NaIO_4$and nano particle occurs and takes place in the amorphous region

B. *Temperature dependent DC conductivity*

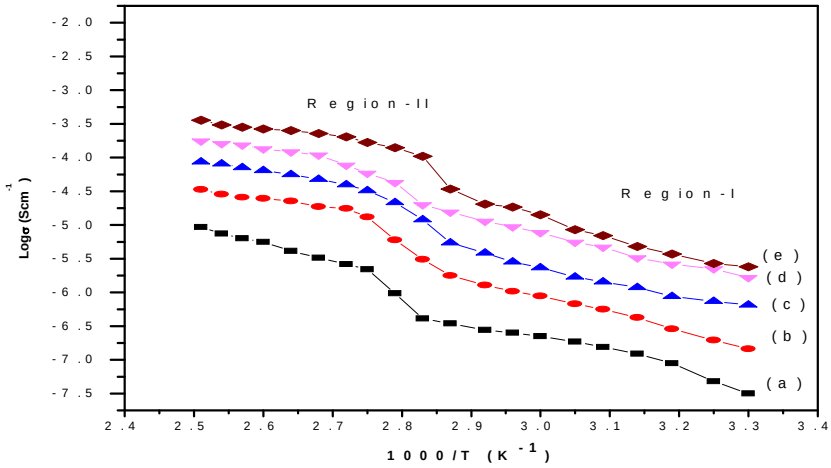


Fig 2. Temperature dependent conductivity of(a) (PVA+PEG)(50:50)(b) PVA+PEG++$NaIO_4$ (47.5 :47.5 :5)(c) PVA+PEG+$NaIO_4$ +SiO_2 (47.5 :47.5 :5)(d) PVA+PEG+$NaIO_4$(42.5 :42.5 : 15)(e) PVA+PEG+$NaIO_4$ + SiO_2 (42.5 :42.5 :15)

©IJRASET (UGC Approved Journal): All Rights are Reserved

Fig. 2 shows the variation of dc conductivity as a function of inverse temperature for different composition of (PVA+PEG+$NaIO_4$), (PVA+PEG+$NaIO_4$+SiO_2) polymer electrolyte in the temperature range of 303-398 K. From the plots it is clear that the conductivity is found to increase with increase of temperature in polymer blend as well as in all the compositions of (PEA+PEG+$NaIO_4$) polymer electrolyte. With the addition of nanoparticles ,the conductivity was found to increase when compared to $NaIO_4$ doped films. Nanoparticles penetrates the polymer matrix and establish attractive forces with the chain segments, these attractive forces reduce the cohesive force between the polymer chains and increases the segmental mobility ,which enhance the conductivity and the discharge time. The increase in degree of ionic segmental mobility and interaction between Na ions and the polymer chains induced the higher ionic conductivity in polymer electrolyte system. The particle size of SiO_2also influences the kinetics of polymers chain. This promotes localized amorphous regions and thus enhance the Na ions transport in the amorphous polymer electrolytes[19].The temperature –dependent conductivity plots follow an Arrhenius behaviour throughout with two regions having different activation energies. Similar behaviour has been observed in a number of other polymer blend electrolyte films [11, 20].
The conductivity σ may be expressed as

$$\sigma=\sigma_o \exp(-E_a/kT) \qquad \text{..... (1)}$$

where σ_0 is the pre-exponential factor, E_a, the activation energy, k, the Boltzmann constant and T is the absolute temperature.
The increase in the conductivity with temperature plots may be attributed to the transition from crystalline/semi-crystalline phase to amorphous phase. The increase in conductivity with temperature is interpreted in terms of a hopping mechanism between coordination sites, local structural relaxation and segmental motion of polymer [21]. As the amorphous region increases, however, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favours the hopping inter-chain and intra-chain movements, and the conductivity of the polymer thus becomes high [22]. The activation energies evaluated from the slopes of log σ versus 1000/T plots, for both the regions are given in the Table 1. From the table it is clear that the activation energies in both the regions decrease with the increase of salt concentration in all the samples. Increase in the electrical conductivity and decrease in the activation energy values of polymer electrolytes can be explained on the basis that the polymer films are known to be a mixture of amorphous and crystalline region and the conductivity behaviour of such films may be dominated by the properties of the amorphous regions.

Table 1.DC conductivity and Activation energies of (PVA+PEG+$NaIO_4$) polymer electrolyte system at different temperatures

Polymer Electrolyte system (wt %)	Conductivity(Scm^{-1})	Activation Energy(E_a)	
	303 K	Region I (eV)	Region II (eV)
PVA+PEG (50:50)	3.05×10^{-8}	0.67	0.53
PVA+PEG+$NaIO_4$ (47.5 :47.5 :5)	1.48×10^{-7}	0.60	0.40
PVA+PEG+$NaIO_4$ + SiO_2(47.5 :47.5 :5)	6.47×10^{-7}	0.49	0.28
PVA+PEG+$NaIO_4$ (42.5 :42.5 :15)	1.68×10^{-6}	0.37	0.23
PVA+PEG+$NaIO_4$+SiO_2 (42.5 :42.5 :15)	2.51×10^{-6}	0.34	0.23

C. Transference numbers

The conductivity measurements are inadequate if performed without the information on the possible type of charge carriers. The transference numbers corresponding to ionic (t_{ion}) and electronic (t_{ele}) transport were evaluated using the Wagner's polarization

©IJRASET (UGC Approved Journal): All Rights are Reserved

technique [14]. In this technique, the current is monitored as a function of time on the application of a fixed DC potentialof 1.5 V across the cell. The transference numbers were calculated using the following equation

$$t_{ele} = i_s/i_t \qquad \text{..... (2)}$$

$$t_{ion} = 1 - \frac{i_s}{i_T} \qquad \text{..... (3)}$$

where I_i is the initial current and I_f is the final residual current.

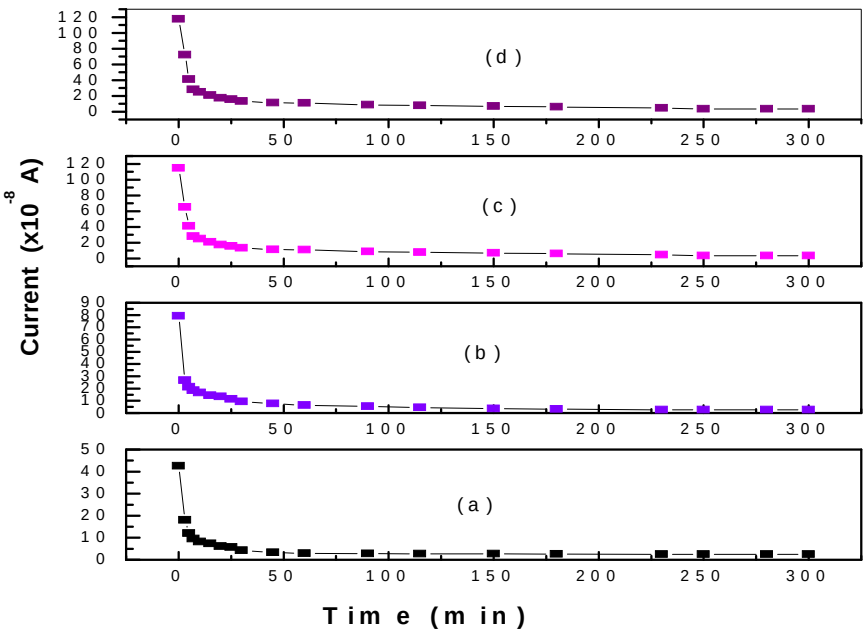


Fig.3 Current vs time plots of(a) PVA+PEG+$NaIO_4$ (47.5:47.5:5) (b) PVA+PEG+$NaIO_4$+SiO_2 (47.5:47.5:5)(c) PVA+PEG+$NaIO_4$ (42.5:42.5:15) (d) PVA+PEG+$NaIO_4$+SiO_2(42.5:42.5:15)

Figure 3 shows the variation of current as a function of time upon the application of a DC voltage of 1.5 V across the (Na/electrolyte/C) cell. The transference numbers evaluated from the plots are given in Table 2. The ionic transference number was found to be in the range 0.94–0.98 in these polymer electrolyte systems. This suggests that the charge transport in these polymer electrolytes is predominantly due to ions, with negligible contribution from the electrons.

Table 2: Transference numbers of $NaIO_4$ doped (PVA + PEG) polymer blend films.

Polyblend electrolyte	Transference numbers	
	t_{ion}	t_{ele}
PVA+PEG+$NaIO_4$ (47.5 :47.5 :5)	0.94	0.06
PVA+PEG+$NaIO_4$+ SiO_2 (47.5 :47.5 :5)	0.95	0.05
PVA+PEG+$NaIO_4$ (42.5 :42.5 : 15)	0.97	0.03
PVA+PEG+$NaIO_4$+SiO_2(42.5 :42.5 :15)	0.98	0.02

Nanocomposite polymer electrolytes thus offer an interesting alternative to other reported electrolyte system for room temperature solid –state batteries [23-25].

©IJRASET (UGC Approved Journal): All Rights are Reserved

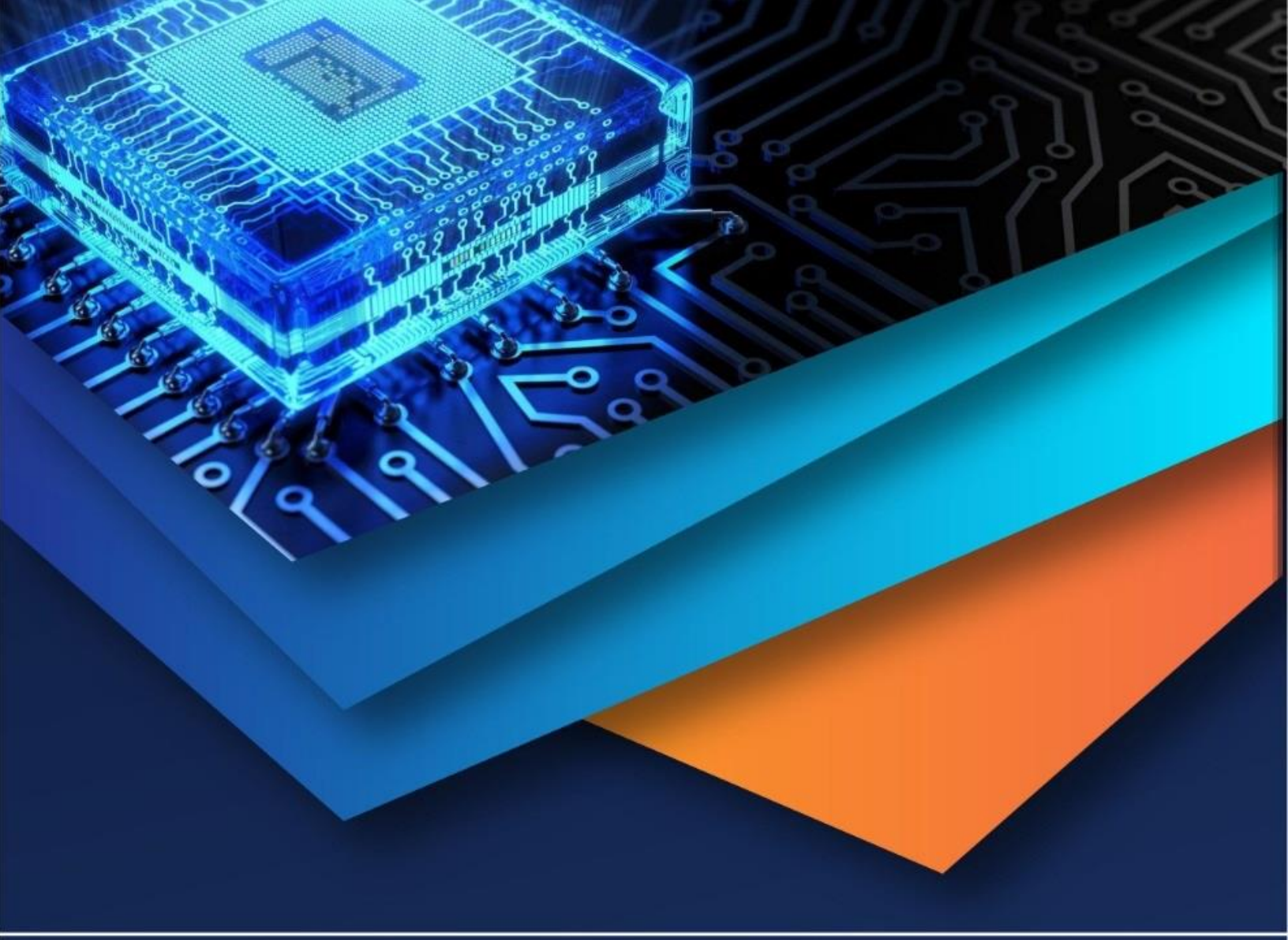
IV. CONCLUSIONS

The introduction of salts and nanoparticles has proved to be a convenient method to increase the ionic conductivity at ambient temperatures. The value of activation energy decreases with increasing do pant concentration and nanoparticles. The nanocomposite electrolyte films exhibit better performance, which indicates that such electrolytes are more suitable for fabricating sold-state batteries. The XRD study reveals the amorphous nature of the polymer electrolytes. The charge transport in these polymer electrolytes is predominantly due to ions, with negligible contribution from the electrons.

REFERENCES

[1] M.B. Armond, Ann. Rev. Mater. Sci. 16 (1986) 245.
[2] J.R. MacCullum, C.A. Vincent, in: J.R. MacCullum, C.A. Vincent (Eds.), Polymer Electrolytes Reviews 1 & 2, Elsevier Applied Science, London, , 1987 and 1989.
[3] M.A. Ratner, D.F. Shriver, Chem. Rev. 88 (1988) 109.
[4] C.A. Vincent, Prog. Solid State Chem. 88 (1989) 109.
[5] F.M. Gray, Solid Polymer Electrolytes, Fundamentals and Technological Applications, VCH, New York, 1991.
[6] B. Scrosati (Ed.), Applications of Electroactive Polymers, Chapman and Hall, London, ,1993.
[7] S.Rajendran,M.Sivakumar,R.Subadevi Mater.Lett.58(2004)641.
[8] S.Ramesh,A.K.Arof,J.Mater.Sci.44(2009) 6404
[9] E.M.Abdelrazek, H.M. Ragab, M. Abdelaziz. Plastic and Polymer Technology 2(2013)1
[10] Anji Reddy Polu, RanveerKumar,KVijaya Kumar Adv. Mat. Lett.,3(5)(2012), 406
[11] Yuan A & Zhao J,Electrochemica Acta,51 (2006)2454
[12] Wang X L,MeiA,LiM,Lin Y H & Nan C W,J Appl Phys,102(2007) 054907.
[13] WieczorekW,Florjanczyk Z & Stevens J R Electrochem Acta,40(1995)2251
[14] J.B. Wagner, C. Wagner, J. Chem. Phys. 26 (1957) 1597.
[15] NadimicherlaReddeppa , A.K. Sharma, V.V.R. NarasimhaRao, Wen Chen. Ionics(2014)
[16] R.M. Hodge, G.H. Edward, G.P. Simon, Polymer 37(1996) 1371–1376.
[17] R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura, T.Hattori, J. Phys. Chem. Solids 68 (2007) 407.
[18] G.K. Prajapati, P.N.Gupta, Physica B 406 (2011) 3108
[19] D.R.Macfarlane,J.Sun,P.Meakin and M.Forsyth,Electrochemica Acta,40(1995)2131
[20] Wang, Y.-J., Pan, Y., and Kim, D. J.PowerSourc., 159 (1)(2006): 692.
[21] Devendrappa, H., SubbaRao, U.V., and Ambika Prasad, M.V.N. J. Power Sourc., 155 (2)(2006)368.
[22] NarasimhaRao, V.V.R., Mahendar, T., and SubbaRao, B. J. Non-cryst. Solid.,104 (1)(1988) 224
[23] NadimicherlaReddeppa, A.K. Sharma, V.V.R. NarasimhaRao, Wen ChenMeasurement 47 (2014) 33–41
[24] Anji Reddy Polu&Ranveer Kumar&Hee-Woo Rhee Ionics 20,6(2014)809
[25] M. Ravi, K. Kiran Kumar, V. Madhu Mohan, V.V.R. NarasimhaRao. Polymer testing 33(2014)152

©IJRASET (UGC Approved Journal): All Rights are Reserved



10.22214/IJRASET

45.98

IMPACT FACTOR: 7.129

IMPACT FACTOR: 7.429

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Call : 08813907089 (24*7 Support on Whatsapp)