

Electrical Conductivity and Dielectric Behavior of Pure and Fe³⁺ doped poly (vinyl chloride) Solid Polymer Electrolyte Films

K. Bhagyasree, Y. Madhava Kumar, N.O. Gopal, Ch.Ramu*

Research Scholar, Department of Physics, Vikrama Simhapuri University PG centre, Kavali, India

Research Scholar, Department of Physics, Vikrama Simhapuri University PG centre, Kavali, India

Assistant Professor, Department of Physics, Vikrama Simhapuri University PG centre, Kavali, India

Associate Professor, Department of Physics, Vikrama Simhapuri University PG centre, Kavali, India.

ABSTRACT: Solid polymer electrolytes (SPEs) consisting of poly (vinyl chloride) complexed with FeSO₄ have been synthesized by solution casting method. The ionic conductivity, dielectric response of the SPE system is studied within the frequency range 100 Hz – 2 MHz. The electrical conductivity was evaluated from ac impedance spectroscopy studies in the temperature range 303-363 K and the conductivity was found to increase with increasing temperature. The maximum ionic conductivity value 4.78×10^{-4} S/cm has been observed for 5 mol% at 363 K using impedance spectroscopy technique. Dielectric relaxation studies of the polymer electrolyte have been undertaken and the results are discussed. It is observed that magnitude of dielectric permittivity is high in the lower frequency region due to electrode polarization (EP) effect.

KEYWORDS: PVC, Dielectric properties, Impedance Analysis

I. INTRODUCTION

Solid polymer electrolytes (SPEs) are playing a vital role in the fabrication of rechargeable batteries, electrochemical cells, supercapacitors, solar cells, and specific ion sensors [1-5]. Solid polymers have better mechanical strength than those of liquid and gel polymer electrolytes. SPE are synthesized using solution casting which facilitates fabrication in desired geometry. SPE also offers good contact between electrolyte and electrode [6-10]. The ion conducting polymer electrolytes are formed by the dissolution of alkali metal salts into the various polymer hosts. Dielectric or electrical insulating materials are understood as the materials in which electrostatic fields can persist for a long time. These materials offer a very high resistance to the passage of electric current under the action of the applied direct-current voltage and therefore sharply differ in their basic electrical properties of conductive materials. Layers of such substances are commonly inserted into capacitors to improve their performance, and the term dielectric refers specifically to this application.

The use of a dielectric in a capacitor presents several advantages. The simplest of these is that the conducting plates can be placed very close to one another without risk of contact. Also, if subjected to a very high electric field, any substance will ionize and become a conductor. Dielectrics are more resistant to ionization than air, so a capacitor containing a dielectric can be subjected to a higher voltage. Also, dielectrics increase the capacitance of the capacitor. An electric field polarizes the molecules of the dielectric producing concentrations of charge on its surfaces that create an electric field opposed (antiparallel) to that of the capacitor. Thus, a given amount of charge produces a weaker field between the plates than it would without the dielectric, which reduces the electric potential. Considered in reverse, this argument means that, with a dielectric, a given electric potential causes the capacitor to accumulate a larger charge.

Poly (vinyl chloride) (PVC) can act as a mechanical stiffener in the electrolyte due to its immiscibility with the plasticizer. Poly(vinyl chloride) (PVC) is one of the most important commercial polymers that have wide a range of applications. PVC is a linear, thermoplastic and substantially amorphous polymer, with a huge commercial interest due to the accessibility to basic raw materials and its properties. It is used as thermoplastic due to its many valuable

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 6, June 2017

properties like low price, good process ability, chemical resistance, good mechanical strength, thermal stability and low flammability [11]. Currently, PVC is one of the world's leading synthetic polymers with global consumption of above 40 million tonnes per annum [12]. The major aim of this study is to investigate a wide range of the electrical properties of PVC films by doping with different concentrations of Fe^{3+} and at different temperatures.

II. EXPERIMENTAL PART

Poly(vinyl chloride) (PVC) has a mean relative molecular mass of about 5,34,000 g/mol. PVC polymer films doped with $FeSO_4$ in various concentrations were prepared at room temperature by solution cast method. The desired concentration of $FeSO_4$ solutions (1, 2, 3, 4 and 5 mol%) were prepared by using distilled water. 1g/mol of PVC polymer is dissolved in tetrahydrofuran (THF) separately. Different amounts of $FeSO_4$ solution (1, 2, 3, 4 and 5 mol%) was added into the polymer solution. The mixture solution was magnetically stirred for 10-12 hours to get the homogeneous mixture and then cast onto poly propylene dishes. The film was slowly evaporated at room temperature to obtain free standing polymer film at the bottom of the dishes.

In order to investigate the nature of the polymer films, the electrical conductivity of polymer complexes was performed by using Hioki 3532-50 LCR Hi-Tester interfaced to a computer in the frequency range 100 Hz -2 MHz and temperature range 303-363.

III. DIELECTRIC STUDIES

The dielectric analysis is an important characteristic that can be used to fetch knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of storing electric charges by the material and capability of transferring the electric charge can be assessed. Dielectric properties are correlated with electro optic property of the crystals, particularly when they are non conducting materials.

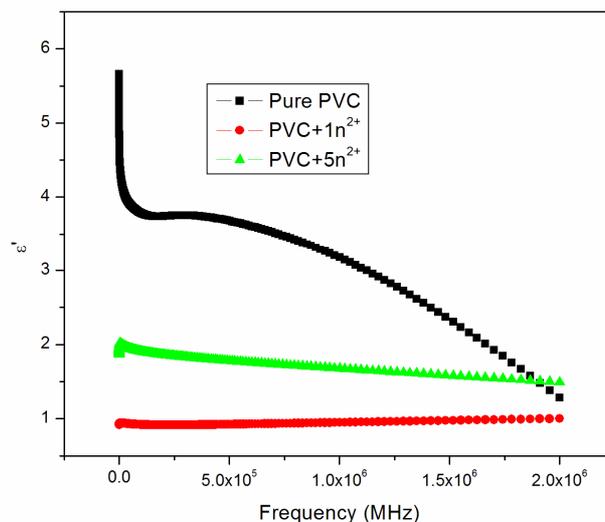


Fig 1. Variation of real part of dielectric constant with frequency of Fe^{3+} doped PVC electrolytes at 303K

From Fig 1, it is observed that with the increase in frequency, the value of dielectric constant decreases up to 100 kHz, thereafter it becomes almost constant for all the samples. The presence of all types of polarizations (dipolar, ionic, atomic and interface) may be primarily responsible for this type of trend at very low frequency for the samples. The value of ϵ' increases with increase in space charge polarization, which in turn may be due to a large concentration of

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 6, June 2017

defects [13]. But on increasing frequency, some of the polarizations slowly vanish except ionic and electronic polarization, which results in rapid decrease in dielectric constant. The value of dielectric constant also relies on some other features such as void, grain boundaries and dipolar interaction [14]. The frequency of hopping between ions could not follow the frequency of applied field and hence it lags behind, therefore the values of dielectric constant become reduced at higher frequency [15].

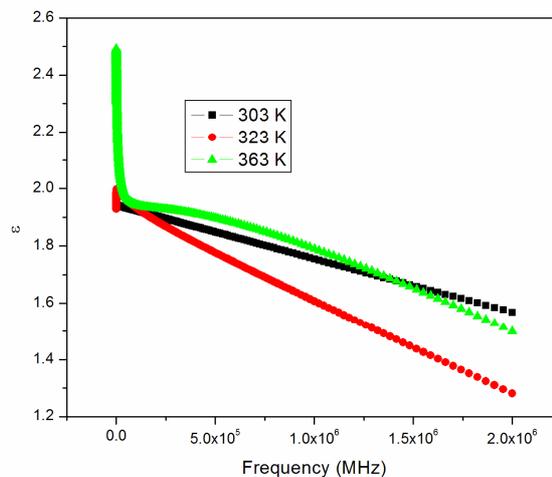


Fig 2. Dielectric constant vs. frequency plots of 5 mol% Fe³⁺ doped PVC electrolytes at different temperatures

Fig 2, show the variation of dielectric constant and dielectric loss with respect to frequency for temperatures (30°C, 50°C, and 90°C) for both pure and boron doped PVC films. It was found that the values of dielectric constant and dielectric loss increase with an increase in temperature and decrease with the increasing frequency. At low frequencies the dipoles can easily switch alignment with the changing field [16]. As the frequency increases the dipoles can rotate less and maintain phase with the field; thus they reduce their contribution to the polarization field, and hence the observed reduction in dielectric constant and dielectric loss. According to Miller rule, the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient [17, 18].

IV. IMPEDANCE ANALYSIS

Impedance spectroscopy is employed to establish the conduction mechanism, observing the participation of the polymer chain, mobility and carrier generation processes. The conductivities of the polymer complexes were calculated from the bulk resistance obtained by the intercepts of the typical impedance curves for various temperatures. The impedance curves of Fe³⁺ doped PVC films are shown in Fig 3 and 4, for the temperature range 302 – 363 K. The disappearance of the semicircular portion in the impedance curve leads to a conclusion that the current carriers are ions and this leads one to further conclude that the total conductivity is mainly the result of ion conduction [19]. The ionic conductivity were calculated using the relation

$$\sigma = \frac{l}{R_b A} \dots\dots\dots(1)$$

Where l is the thickness, R_b is bulk resistance and A is the known area of the electrolyte film.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 6, June 2017

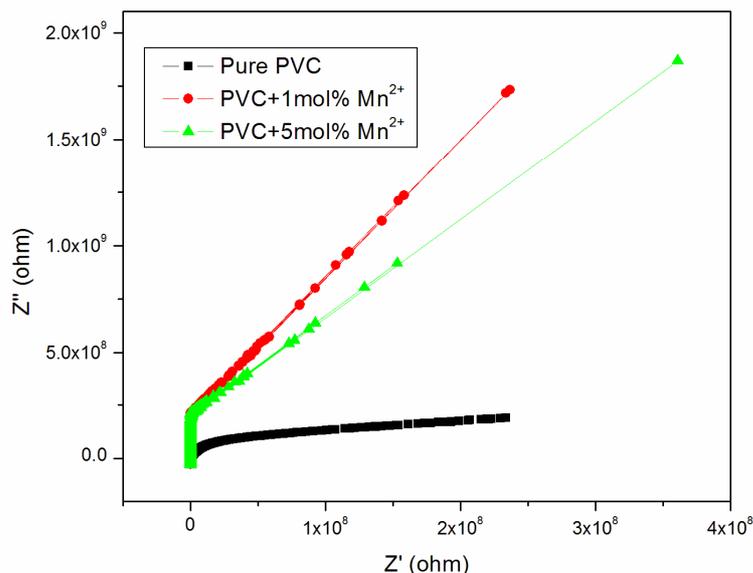


Fig 3. Nyquist plots of Fe^{3+} doped PVC polymer electrolyte at different compositions at 303 K

Table 1 shows the conductivity values of the temperature increases, the conductivity also increases for all complexes and this behavior is in agreement with the theory established by Armand et al. [20]. This can be rationalized by recognizing the free volume model [21].

Table 1: Ionic conductivity values of PVC complexed with FeSO_4

Composition	Ionic conductivity values of PVC doped Fe^{3+} ($*10^{-4}$ S/cm)		
	303	323	363
Pure	1.65	1.66	1.04
1 mol	2.00	2.06	3.88
5 mol	2.70	3.51	4.78

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 6, June 2017

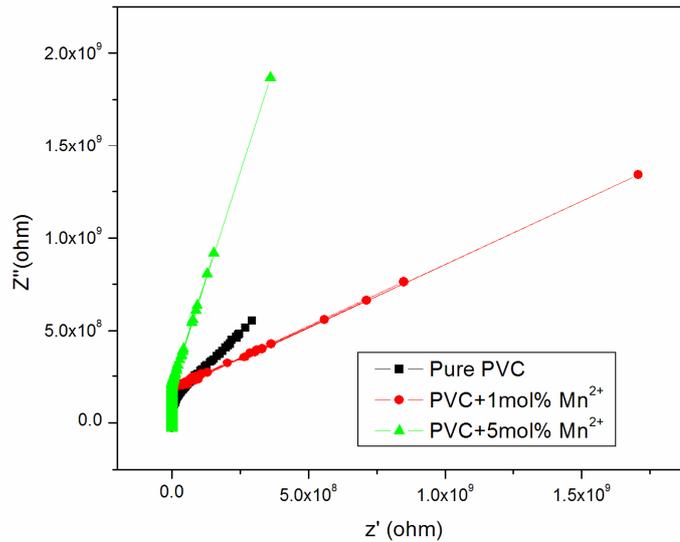


Fig 4. Nyquist plots of Fe^{3+} doped PVC polymer electrolyte at different compositions at 363 K

When temperature is increased, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighbouring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur [22].

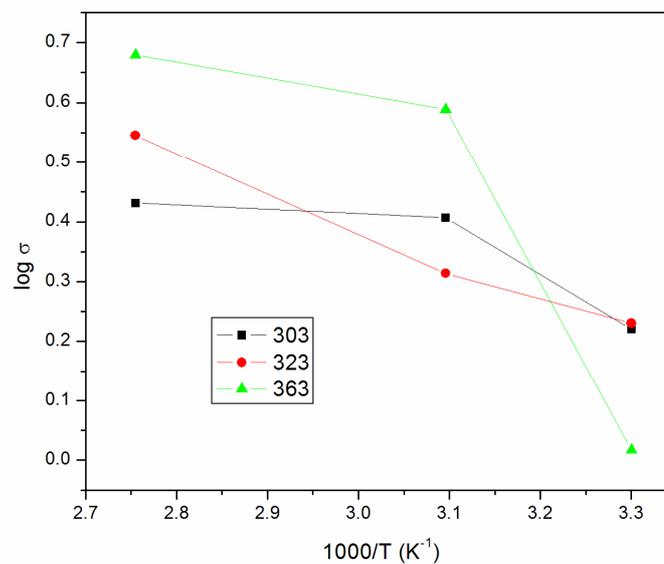


Fig 5. Variation of ac conductivity with temperature of $FeSO_4$ doped PVC films at different temperatures

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Website: www.ijirset.com

Vol. 6, Issue 6, June 2017

Fig 5, Shows that the ionic conduction in all polymer electrolyte system obeys the VTF (Vogel – Tamam – Fulcher) relation, Which describes the transport properties in a viscous matrix [23]. It supports the idea that the move through the plasticizer rich phase, which is the conductivity medium and involves.

V. CONCLUSIONS

PVC based polymer electrolytes were prepared by solvent cast technique. All electrolytes show appreciable conductivity even at room temperature. Maximum conductivity (4.78×10^{-4} S/cm) at 363 K temperature with good mechanical stability has been observed for PVC doped 5mol% Fe^{3+} . The maximum conductivity (2.70×10^{-4} S/cm) at room temperature with good mechanical stability has been observed for 5mol%, Fe^{3+} system among the various compositions studied. The dielectric relaxation of the samples was also discussed. Large magnitudes of values are observed in the low frequency region is due to EP effect. A substantial increase in the thermal stability (323 K) is observed for Fe^{3+} complex as compared to pure PVC.

REFERENCES

1. M. A. Ratner, D. F. Shriver, "Ion transport in solvent-free polymer", Chemicals Reviews, 88(1), 109-124, 1988.
2. E. Ruiz-Hitzky, P. Aranda, "Polymer-salt intercalation complexes in layer silicates", Advanced Materials, 11, 545-547, 1990.
3. F. Croce, G. B. Appetecchi, L. Parisi, B. Scrosati, "Noncomposite polymer electrolytes for lithium batteries", Letters to Natures, 394, 456-458, 1998.
4. K. Murata. "An overview of research and development of solid polymer electrolyte batteries", Electrochimica Acta, 40, 2177-2184.
5. M. Jaipal Reddy, P. P. Chu, T. Sreekanth, U. V. Subba Rao, "PEO: KIO₃ polymer electrolyte system – Its applications to solid state electrochemical cell", Journal of Materials Science: Materials in Electronics, 12, 153-156, 2001.
6. Y. L. Lee, B. Crist, "Phase behaviour and conductivity in poly (ethylene oxide)-sodium thiocyanate system", Journal of Applied Physics, 60, 2683-2689 1986.
7. S. Sreepathi Rao, M. Jaipal Reddy, E. Laxmi Narsaiah, U.V. Subb A Rao, "Development of electrochemical cells based on (PEO+ NaYF₄) and (PEO+KYF₄) polymer electrolytes", Materials Science and Engineering B, 33, 173-177, 1995.
8. T. Sreekanth, M. Jaipal Reddy, S. Ramalingaiah, U. V. Subba Rao, "Ion-conducting polymer electrolyte based on poly (ethylene oxide) complexed with NaNO₃ salt-application as an electrochemical cell", Journal of Power Sources, 79, 105-110, 1999.
9. Bac, M. Ciosek, M. Bukat, M. Marczewski, H. Marczewska, W. Wiczorek, "The effect of type of the inorganic filler and dopant salt concentration on the PEO–LiClO₄ based composite electrolyte–lithium electrode interfacial resistivity", Journal of Power Sources, 159, 405-411, 2006.
10. J. Siva Kumar, A. R. Subrahmanyam, M. Jaipal Reddy, U. V. Subba Rao, "Preparation and study of properties of polymer electrolyte system (PEO+NaClO₃)", Materials Letters, 60, 3346-3349, 2006.
11. Mediha KOK, Demirelli K, Aydogdu Y, "Thermo physical Properties of Blend of Poly (Vinyl Chloride) with Poly (Isobornyl Acrylate)", International Journal of Science & Technology, 3(1), 37-42, 2008.
12. Warren H, "Global vinyls outlook: Building on change", In Proceedings of 30 Annual World Petrochemical Conference; Houston, Texas, USA. p. 479-503 2015 Mar 24-27.
13. S. Pattanayak, R.N.P. Choudhary, P. R. Das, J. Mater. Sci.: Mater. Electron., 24, 2767, 2013.
14. B.K. Barick, K.K. Mishra, A.K. Arora, R.N.P. Choudhary, Dillip K. Pradhan, J. Phys. D: Appl. Phys., 44 (2011) 355402.
15. G.B. Kumar, S. Buddhudu, "Optical, thermal and dielectric properties of Bi₄(TiO₄) ceramic powders" Ceram. Int. 36, pp. 1857-1861, 2010.
16. S. Suresh, A. Ramanand, D. Jayaraman and P. Mani, "Growth, Photoconductivity and Dielectric Properties of Triglycine Sulfate (TGS) Single Crystals," Optoelectronics and Advanced Materials, Vol. 4, No. 11, pp. 1763-1765, 2010.
17. C. Balarew and R. Duhlew, "Application of the Hard and Soft Acids and Bases Concept to Explain to Ligand Co-ordination in Double Salt Structures," Journal of Solid State Chemistry, Vol. 55, No. 1, pp. 1-6. doi:10.1016/0022-4596(84)90240-8, 1984.
18. M. Meena and C.K. Mahadevan, "Growth and Electrical Characterization of L-Arginine Added KDP and ADP Single Crystals," Crystal Research and Technology, Vol. 43, No. 2, pp. 166-172, 2008.
19. M.M.E. Jacob, S.R.S. Prabaharan, S. Radhakrishns, Solid State Ionics 104, 267, 1997.
20. M.B. Armand, J.M. Chabagno, M.J. Duclot, P. Vashishta, L.N. Mundy, G. Shenoy, Fast-Ion Transport in Solids, North-Hol-Land, Amsterdam, 131, 1979.
21. T. Miyaamoto, K. Shabayama, J. Appl. Phys. 44, 537, 1973.
22. J.A. MacCallum, C.A. Vincent, Polymer Electrolyte Reviews-1, Elsevier, London, 1987.
23. S. Rajendran, T. Uma, T. Mahalingam, European Polymer Journal, 36, 2617, 2000.