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Impedance studies of polymer electrolyte based on PVA: PVdF: LiCF₃SO₃

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Abstract: Lithium ion conducting polymer electrolytes of PVA: PVdF complexed with Lithium triflate (LiCF₃SO₃) have been prepared by solution casting technique. Electrical characterization of all the prepared polymer electrolyte samples (composition of 90:10:2, 80:20:2 and 70:30:2) has been performed using AC impedance spectroscopy technique. From complex impedance plot, the maximum ionic conductivity has been found to be $3.9 \times 10^{-4} \text{ Scm}^{-1}$ in 80PVA:20PVdF: 2LiCF₃SO₃ polymer electrolyte system at 303 K. The ionic conductivity of the polymer electrolyte increases with the increase of temperature. Dielectric and modulus analysis have been studied for different temperature. Complex modulus suggests that negligible electrode polarization at low frequency region.

Keywords: ionic conductivity; dielectric; polymer electrolyte; AC impedance spectroscopy.

Introduction and Experimental

The development of ion conducting solid polymer electrolytes (SPE) has been the subject of research interest because of their potential applications such as batteries, sensors, fuel cells and other electrochemical devices [1]. The polymer electrolytes have greatly attracted for last two decades owing to their properties such as thin film formation, interfacial contacts, desirable sizes, easy mouldability, good electrode–electrolyte contact and light weight, etc [2]. It must satisfy several requirements, including high ionic conductivity, electrochemical stability, and superior mechanical properties when used in electric devices. In the present study, different composition of Poly vinyl alcohol (PVA) blend with poly(vinylidene fluoride) (PVdF) (90:10, 80:20, 70:30) doped with Lithium trifluoromethane sulphonate salt (LiCF₃SO₃) have been prepared by solution casting technique. AC impedance spectroscopic studies have been carried out and the results have been discussed.

Solid Polymer electrolytes have been prepared by solution casting technique. Material used for the preparation of the polymer electrolyte has been PVA, PVdF and LiCF₃SO₃ salt. Appropriate quantities of each constituent were dissolved in distilled N, N-dimethyl formamide solvent [DMF]. The dissolved polymers and the salt solutions were mixed together and stirred continuously for at 60°C until homogeneous solution was obtained. Thus, the obtained solution was casted onto petri dishes. The resulting films were visually examined and free standing nature. The thickness of prepared film sample has been 100-200 μm . The prepared polymer electrolyte film has been flexible, transparent and mechanically strong.

Impedance spectroscopy was studied using HIOKI make LCZ meter (model 3532) in the frequency window, 42Hz–1MHz at different temperatures from 303K to 343K using stainless steel blocking electrodes.

Result and Discussion

Cole-Cole plot analysis

The ionic conductivity of the polymer electrolytes mainly depends on the actual concentration of conducting species and their mobility. Figure 1 shows the cole-cole plot (Z' vs. Z'') for PVA: PVdF doped with LiCF_3SO_3 polymer electrolyte at different temperature. The disappearance of semicircular portion in the high frequency region of complex impedance plot indicates that the conduction is mainly due to the ions. The spike is observed at low frequency, due to the double layer capacitance at the blocking electrodes. The ionic conductivities were calculated using the relation, $\sigma = l/R_b A$. where l is the thickness, R_b is bulk resistance and A is the known area of the electrolyte film. As the temperature increases the ionic conductivity of the sample increases as shown in the figure 1.b. The increase of conductivity with temperature can be described on the basis of the ionic transport mechanism between coordinating sites, local structural relaxation and segmental motion of the polymer chain. This segmental motion either allows the ions to hop from one site to another site, or it provides a pathway for ions to move [3].

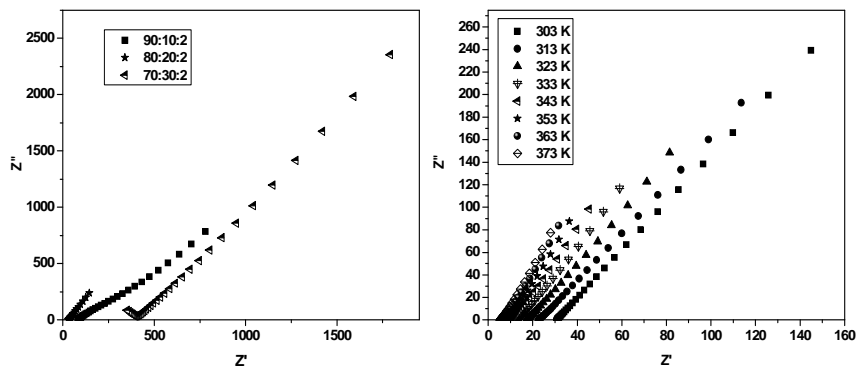


Fig 1: Cole-Cole plot for the PVA: PVdF: LiCF_3SO_3 polymer electrolyte for a) different composition (b) different temperature for highest conducting sample

Dielectric Plot analysis

The dielectric properties of solid polymer electrolyte may be characterized by frequency-dependent parameters that can be defined by the complex permittivity ϵ . complex dielectric constant of a system is defined by $\epsilon^* = \epsilon' - i\epsilon''$, where ϵ' is real part of dielectric constant and the ϵ'' is the imaginary part of dielectric constant of the material. Both ϵ' and ϵ'' sharply increases towards low frequencies due to the presence of space-charge effects [5], which is contributed by the accumulation of charge carriers near the electrodes, and the rise is displaced to higher frequencies at higher temperatures. When the frequency increases, the value of ϵ' has been found to decrease and then saturation reaches at higher frequencies. Even at higher temperature, the saturation of ϵ' has been notified. This is become, the jump frequency of the mobile ion is large and it resonates with the frequency of the applied electric field. The dominant relaxation peak appeared at higher temperature whose maximum shifts gradually to higher frequencies with increasing temperature. It may be due to the segmental motion of the polymer backbone [6].

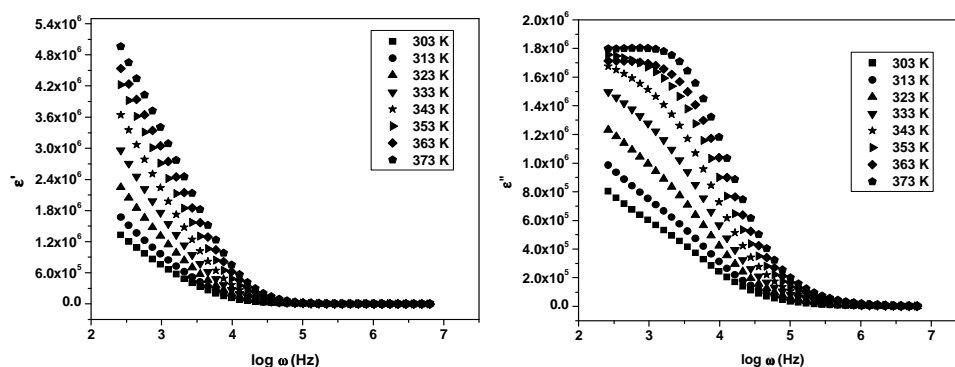


Fig 2: Dielectric plot of 80PVA:20PVdF: $2\text{LiCF}_3\text{SO}_3$ polymer electrolyte system at different temperature

Modulus analysis

The ion transport process in ionic conductors has been studied in terms of electrical modulus spectrum as shown in Fig.3. Modulus formalism shelters the low frequency dispersion due to electrode polarization effects.

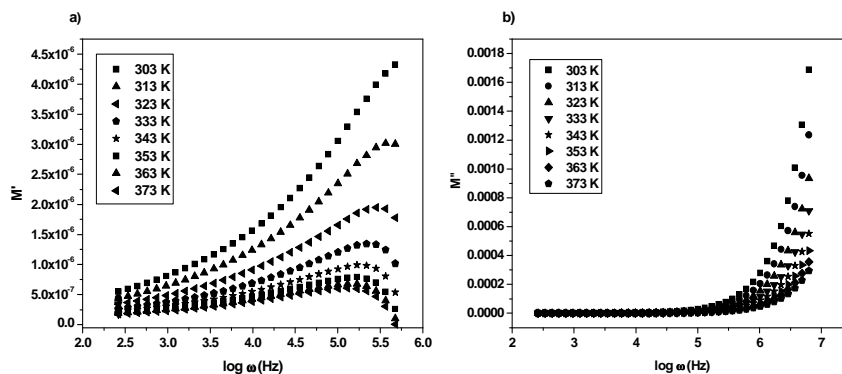


Fig 3: Modulus spectra of 80PVA:20PVdF: 2LiCF₃SO₃ polymer electrolyte system at different temperatures

The gradual variation of M' indicates that the relaxation processes are spread over a range of angular frequencies [4]. Long and flat tail occurs at low frequencies (Fig. 3.b) due to the large capacitance associated with the electrodes. As the temperature increase, the peak maximum shifts to the higher frequencies (Fig. 3.a). This reveals the relaxation is thermally activated and the charge carrier hopping takes place.

Conclusion

Different composition of PVA: PVdF: LiCF₃SO₃ solid polymer electrolyte has been prepared using solution casting technique. 80:20:2 composition of blend sample shows the maximum ionic conductivity of $3.9 \times 10^{-4} \text{ Scm}^{-1}$ at room temperature. Relaxation peak found in the dielectric plot describes the behavior of the polymer electrolytes. The modulus analysis reveals the non-Debye nature of the electrolytes. These high conductivity and dielectric properties will make the prepared polymer electrolytes has been well suitable for lithium ion batteries.

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References

1. Hema M., Selvasekarapandian S., Hirankumar G., Sakunthala A., Arunkumar D., Nithya H., Laser Raman and ac impedance spectroscopic studies of PVA: NH₄NO₃ polymer electrolyte, Spectrochim. Acta. A., 2010, 75, 474–478.
2. Gray F.M., Solid polymer electrolytes-fundamental and technological applications, New York: VCH, 1991.
3. Steele BCH, Weston SE., Thermal history—conductivity relationship in lithium salt-poly (ethylene oxide) complex polymer electrolytes, Solid State Ionics, 1981, 2, 347-354.
4. Ramesh S., Arof A.K., Ionic conductivity studies of plasticized poly(vinyl chloride) polymer electrolytes, Mater Sci. Eng. B., 2001, 85, 11–15.
5. Rachna Mishra, Rao K.J., Electrical conductivity studies of poly(ethyleneoxide)-poly(vinylalcohol) blends, Solid State Ionics, 1998, 106, 113-127.
6. Schmidt-Rohr K, Kulik AS, Beckham HW, Ohlemacher A, Pawelzik U, Boeffel C, Spiess HW., Molecular Nature of the .beta. Relaxation in Poly(methyl methacrylate) Investigated by Multidimensional NMR, Macromolecules, 1994, 27, 4733-4745.
