

Structural and Ionic Mobility Study of Plasticized PVDF-HFP: LiCF₃SO₃ Nanocomposite System

Nidhi Asthana, Mrigank Mauli Dwivedi and Kamlesh Pandey*

National Centre of Experimental Mineralogy and Petrology, University of Allahabad, Allahabad

*Corresponding Author: Kamlesh Pandey, National Centre of Experimental Mineralogy and Petrology, University of Allahabad, Allahabad, India.

ABSTRACT

In order to develop the solid polymer electrolyte (SPE), PVdF-HFP with plasticizers and LiCF₃SO₃ phase inversion technique was adopted. The maximum AC conductivity of the SPE at room temperature was found as $1 \times 10^{-5} \text{ Scm}^{-1}$. The crystallinity and complexation behavior of SPEs were studied by spectroscopic experimental tools and electrical conductivity and mobility by impedance spectroscopy.

Keywords: Polymer salt interaction, PVdF-HFP, Polymer composite electrolyte, ionic conductivity.

INTRODUCTION

There has been growing recent interest in electrochemical capacitors (ECs) as high-power charge-storage devices that could possibly act as alternative or a complementary energy system to conventional secondary batteries. The application of semi-solid or gel electrolyte systems would be particularly become more popular due to their advantages over conventional systems having packing issues, corrosion, self-discharge or leakage current concerns.

For a gel polymer electrolyte to be effective, it needs to maintain high ionic conductivity over a wide temperature range and remain structurally stable [1-3]. Among various polymers, Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) has been extensively investigated because of its high mechanical strength and chemical stability with respect to non-aqueous electrolyte and electrode materials since it was first reported by Bellcore Corp. in 1994[4]. In PVdF-HFP, crystallite vinylidene fluoride (VdF) units facilitate excellent chemical stability and amorphous hexafluoropropylene (HFP) units increase its plasticity which associates with high ionic conductivity [5]. The approach of plasticization with low molecular weight plasticizer such as ethylene carbonate (EC), propylene carbonate (PC) is the conventional way to further reduce the crystallinity and increase the amorphous phase content of the polymer electrolyte [6-7]. Lithium triflate (LiCF₃SO₃) is used as doping salt, which

provides Li⁺ ions, have high thermal stability and is not susceptible to hydrolysis due to C-F bond. Plasticizer is to help in the dissociation of lithium salt, which allows greater numbers of free ions for conduction [8].

EXPERIMENTAL

Nanocomposite polymer electrolyte free standing films were prepared by well known phase inversion technique. PVdF-HFP (Aldrich sigma) with an average molecular weight of ($\sim 5.34 \times 10^5$), salt LiCF₃SO₃ (AR grade, Rankem, India), and plasticizers EC, PC (Sigma Aldrich) were used for synthesis of polymer electrolyte. Structural behavior of [PVdF-HFP: LiCF₃SO₃-(EC+PC)] systems were evaluated with the help of different experimental investigations. The XRD pattern was recorded between $2\theta=15-40^\circ$ at room temperature using Phillips X-pert diffractometer.

EPMA model JXA-8100 instrument was used to obtain SEM images of electrolytes with stub coated with graphite to a thickness $\sim 10-30$ nm under vacuum using JEOL high vacuum evaporator. The infrared spectrum was recorded on Bruker Alpha IR spectrophotometer in a range $4000-400\text{cm}^{-1}$. Micro Raman spectra were recorded using UniRAM confocal spectroscopy system with 785 nm laser beam. The electrical conductivity was evaluated from complex impedance plot obtained using computer controlled Hioki (JAPAN)-LCZ HI Tester (model 3520-01) in the frequency range of 40Hz to 100KHz. The impedance spectrum was used

to evaluate the bulk d.c. conductivity and mobility of the mobile ions.

RESULTS AND DISCUSSION

The XRD patterns of different polymer electrolytes are recorded at room temperature (Figure 1). In XRD pattern of PVdF-HFP film presence of different crystalline peak (main peak at $2\theta = 20.5^\circ$) confirm the semicrystalline nature of the co- polymer electrolyte. The broad base on lower intensity peaks represents the amorphous phase. The effect of (EC+PC) on PVdF-HFP clearly reduces the crystalline peak and enhances the amorphous content in the polymer matrix. The increase in broadness of both characteristic peaks at $2\theta=20.4^\circ$ after plasticization / interaction of polymer/ salt in $[0.3PVdF-HFP + 0.7(EC+PC)]_{0.9} : (LiCF_3SO_3)_{0.1}$ system. No distinct diffraction peak of salt LiCF₃SO₃ is observed, in the composite system, this proves that the salts are completely dissolved and form the nanocomposite polymeric system. The addition of salt gives some new small peaks, which is an indication of no traces of plasticizer is present in the electrolyte which confirms complete dissolution. The average crystallite size of Li⁺ ion was evaluated by Scherrers formula [9] and was found to be 47.0 nm.

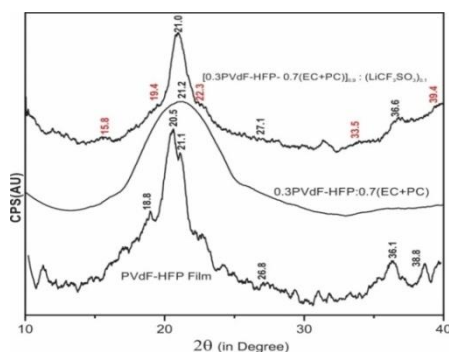


Figure1. XRD curve of different polymeric systems.

To examine the surface morphology and microstructure of the polymer composite electrolyte system, scanning electron microscopic (SEM) image was recorded and shown in Figure 2. Typical texture along with dark boundaries can be seen in $[0.3PVdF-HFP + 0.7(EC+PC)]_{0.9} : (LiCF_3SO_3)_{0.1}$ demonstrating its partial crystalline nature. Significant surface morphology changes are observed after addition of salt (LiCF₃SO₃) in polymer matrix. The micrograph shows the beautiful uniformly distributed grains, with dark region (i.e. pores) which is responsible for the high conductivity in the electrolyte system. This high conductivity is due to liquid

in the pores of the polymer. The high magnified images also confirm the polymer-salt-interaction and formation of composite electrolyte.

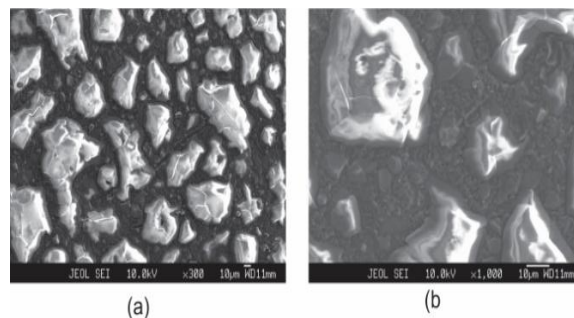


Figure2. SEM image of the polymer composite system at (a) 300X and (b) 1000X magnification.

The laser Raman spectra of $[0.3PVdF-HFP + 0.7(EC+PC)]_{0.9} : (LiCF_3SO_3)_{0.1}$ electrolyte system is shown in Figure 3. From the figure it is clear that the prominent characteristic peaks of electrolyte system after the film formation by the solution cast technique (marked in the figure) are present. It has been reported that pure PVdF-HFP contains three different crystalline phases noted as form-I (β -phase), form-II (α -phase) and form-III (γ -phase).The characteristics Raman frequency $836cm^{-1}$ is due to the $-CH_2$ rocking mode for the crystalline form I.

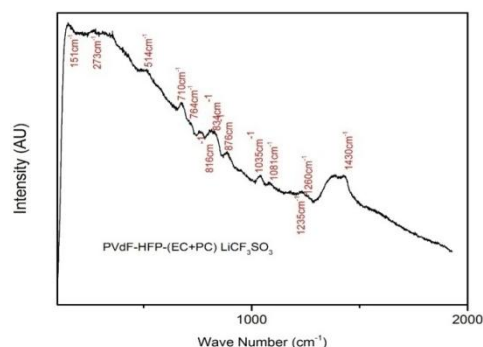


Figure3. Laser-Raman spectra of $[0.3PVdF-HFP + 0.7(EC+PC)]_{0.9} : (LiCF_3SO_3)_{0.1}$ system.

The Raman peaks at $795cm^{-1}$, $873cm^{-1}$ and $1426cm^{-1}$ are a combined CH_2 rocking and CF_2 stretching modes, a combination of CC symmetric stretching and CCC skeleton bending modes and a combination of CH_2 scissoring and CH_2 wagging mode respectively for the crystallite form. This also confirms the salt-polymer interaction and composite formation.

The FTIR spectra is an important experimental tool for studying the polymer-salt interactions and complexation in polymer electrolytes. The interaction between polymer and salt influence vibrational modes of atoms or molecules which in turn generates change in chemical and

physical properties of the polymer. The FTIR plasticized polymer electrolyte films of PVDF – HFP, LiCF₃SO₃ salt and their complexes are shown in the Figure 4.

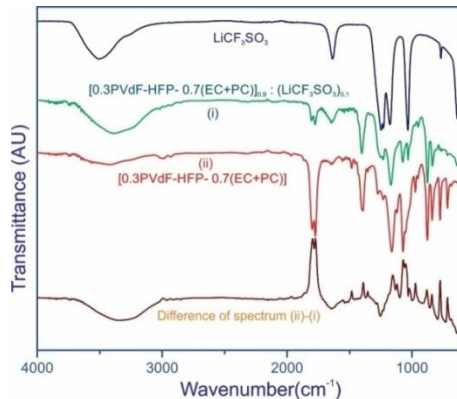


Figure 4. FTIR spectra of Salt, Pristine and Composite system with difference spectra of composite and pristine electrolyte.

The vibrational bands at 765 cm⁻¹, 876cm⁻¹, 973 cm⁻¹ (corresponds to α - phase) and 950 cm⁻¹, 1072 cm⁻¹, 1167cm⁻¹ (corresponds to β -phase) reflects the crystalline nature of PVDF – HFP which has been shifted to low frequencies at 759cm⁻¹, 848cm⁻¹, 970cm⁻¹ and 948cm⁻¹, 1071cm⁻¹, 1163 cm⁻¹ with slightly changed intensity due to incorporation of Lithium triflate salt; which show the decrease of crystalline nature of the pure PVDF – HFP polymer, which is favorable for the ionic conductivity[10,11].

The vibrational band at 872cm⁻¹ in pure PVDF – HFP has been shifted to higher frequency with increasing intensity transmittance at 877cm⁻¹, due to inclusion of LiCF₃SO₃ salt which confirms presence and complexation of salt with host polymer matrix.

The band at 1208 cm⁻¹ corresponds to symmetrical stretching mode of which is shifted to higher frequencies at 1226 cm⁻¹, and formation of new peak at 1646 cm⁻¹ (corresponds to characteristic peak of triflate ion) due to inclusion of salt concentration which confirms the complexation of the polymer electrolyte, shows an indicator for the dissociation of lithium triflate salt.

This indicates only certain amount of salt is able to dissolve which limits the number of Lithium ions generated which affects the ionic conductivity. The absorption band at 2919 cm⁻¹ and 3007 cm⁻¹ corresponds to ν (CH) is new peak recorded after complexation of polymer – salt plasticizer [12-13]. The peak at 1032 cm⁻¹,

1450 cm⁻¹, 1771cm⁻¹ and 1804 cm⁻¹ belongs to plasticizers peak. The absorption peaks at 1641 cm⁻¹ to 1644 cm⁻¹ corresponds to –CH=CF skeletal breathing of PVDF – HFP polymer. The vibration band at 1275 cm⁻¹ corresponds to CF stretching vibration which has been shifted to 1245 cm⁻¹ but found to be missing in some peaks of absorption bands. The broad peak around the 3400 cm⁻¹ belongs to –OH and –OOH bond of the polymer composite. This occurs due to highly hygroscopic nature of LiCF₃SO₃ salt and Tetra hydrofuran solvent that absorbs moisture from the atmosphere. The difference spectra also confirms the formation of new peaks and interaction of polymer and salt during the complex formation.

Generally, contribution from plasticizer towards the enhancement of conductivity is twofold: a higher percentage of plasticizer would (i) open up the narrow rivulets of plasticizer-rich phase for greater ionic transport, and (ii) provide large free volume of relatively superior conducting phase. The higher conductivity in [0.3PVdF-HFP + 0.7(EC+PC)]_{0.9} : (LiCF₃SO₃)_{0.1} electrolyte system is because of the salt. In LiCF₃SO₃, all the anions are counter ions of strong acids and the difference in conductivity is presumably due to the difference in lattice energies. LiCF₃SO₃ has the lowest lattice energy and therefore easier solvation of Li⁺ ion by the polymer matrix, which facilitates for higher ionic conductivity.

Temperature dependent conductivity of plasticized polymer electrolyte is shown in Figure 5. Initially the conductivity slightly decreases due to removal of adsorbed water at low temperature. Then increase in conductivity is due to higher number of charge carriers generated by the salts. The decrease in conductivity after 180°C is possibly due to the dissociation of the system.

The frequency dependent a. c. conductivity at different temperatures is shown in Figure 5. From figure we observe that the variation of conductivity with frequency is very small. The conductivity follows the Universal Power Law [14]. Two major dips were recorded at 60°C and 180°C. The first is possibly due to removal of water and second is due to dissociation. The 3D conductivity pattern shows a frequency independent nature which is also an indication of electrode polarization.

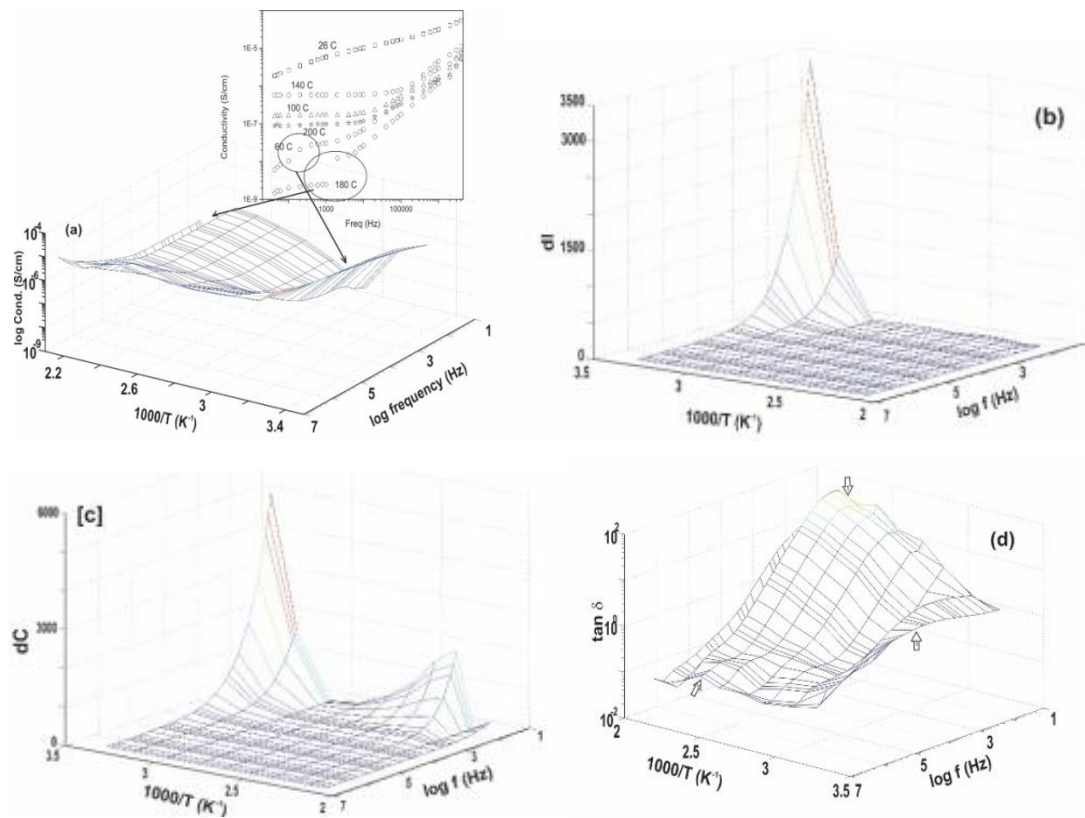


Figure 5. Variation of (a) electrical conductivity, (b) Dielectric Loss, (c) Dielectric Loss and (d) $\tan \delta$ with frequency and temperature.

The dielectric constant (ϵ') and loss (ϵ'') plasticized electrolytes are shown in Figure 5. These curves give a peculiar nature of the polymeric substance means the low frequency dispersion. The high value at low frequency regime is indication of electrode polarization. It can be deduced that plasticizers with high dielectric constant allows greater dissolution of the electrolyte salt resulting in increased number of charge carriers. The apparent role of plasticizer in a host polymer is to change the viscosity of electrolyte and assist in the dissociation of the salt thereby increasing the number of charge carriers. The value of real and imaginary part of dielectric relaxation shows a regular increase in the plasticized sample. This increase in ϵ' and ϵ'' value is directly based on production of more charge carriers / dipoles in the matrix. The temperature dependent tangent loss variation, clearly gives two peaks. The new peak appears at the lower temperature side near 10K frequency and become relatively intense in (EC+PC) systems. The tangent loss peak shifted to higher frequency with higher ionic conductivity. The peak at the higher frequency region is due to β relaxation peak of the host polymer as well as second peak may infer that plasticizer EC or EC/PC have dissociated more salt and generated more ions.

It was evidenced that good combination of EC/PC and lithiumtriflate increased the amorphusity of the materials with optimum amount of free ionic charge carrier.

The ionic conductivity is represented by

$$\sigma = \sum n_i Z_i e \mu_i \quad (1)$$

where n_i , Z_i , e , and μ_i are the charge carrier density, electronic charge and ionic mobility of the i^{th} ion respectively. Ignoring the sign of the charge number Z_i ,

we can write $\sigma = e (n^+ \mu^+ + n^- \mu^-)$. From this equation and considering the transport number measured for these GPEs, we can obtain the anionic, σ^- , and cationic σ^+ , conductivities. In general, an increase of ionic conductivity of the complex system is due to an increase of number of mobile charge carriers introduced/produced in the material with a change of constituent concentration.

The mobility of mobile charge carrier was estimated by the Rice and Roth model [15]. The mobility of the different electrolyte groups are calculated by the impedance and dielectric parameters. The variation of charge carriers and mobility for the different electrolyte systems are shown in Figure 6. To confirm the role of ionic

mobility and charge carriers, we also present the temperature dependence of conductivity evaluated by cole-cole plot. On the basis of figure, we can conclude that the change in mobility is a significant parameter for the conductivity measurement. The value of mobility is also dependent on the ionic size of the charge carrier. This supports the result obtained in conductivity measurement.

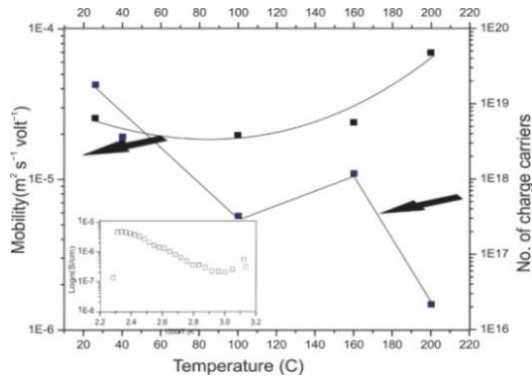


Figure6. Variation of ionic mobility and Number of Charge carriers with temperature in nano composite polymer electrolyte system. Temperature dependence conductivity is shown in inset of figure.

To analyze the dielectric response of the material, study of electrical modulus is an important approach [16,17]. Electrical modulus is defined in terms of the reciprocal of the complex relative permittivity, $\epsilon^*(\omega)$ as

$$M^*(\omega) = \frac{1}{\epsilon^*(\omega)} = M'(\omega) + iM''(\omega) \quad (2)$$

where $M'(\omega)$ and $M''(\omega)$ are the real and imaginary part of the electrical modulus which can be represented by using the complex dielectric constant with the following relation

$$M'(\omega) = \frac{\epsilon'(\omega)}{\epsilon'^2(\omega) + \epsilon''^2(\omega)} \quad (3)$$

$$M''(\omega) = \frac{\epsilon''(\omega)}{\epsilon'^2(\omega) + \epsilon''^2(\omega)} \quad (4)$$

where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ real and imaginary part of the complex dielectric property.

Variation of electrical modulus with frequency and temperature is shown in Figure7. A well defined asymmetric loss peak formed in the studied temperature range. It is important to note that the two peak formation in given frequency range after 40°C. At room temperature we observe only dielectric relation peak but the second peak due ionic conduction[18]. The formation of well-defined peak is an indication of strong coupling of ionic conduction with polymer segmental motion in the polymer electrolyte system.

At room temperature the low value of electrical modulus is due to larger value of capacitance associated with the electrode polarization effect [19]. The region before the peak determine the range in which charge carriers are mobile over long distance, while region to the right side (i.e. higher frequency region) are confined to potential well being mobile over short distance[20]. This type of nature suggests the hopping mechanism of electrical conduction in composite electrolyte. The shift of relaxation peak with temperature in lower frequency region tells the ionic conduction relaxation is thermally activated with the hopping charge carriers [21]. At higher temperature peaks move toward the lower frequency region, due to reduction of mobile (Li^+) ion in the polymer composite. It also reduced the relaxation time due to increase in mobility of ionic carriers. The regression value $R^2=0.9$ shows the linear nature ionic conduction in limited temperature range.

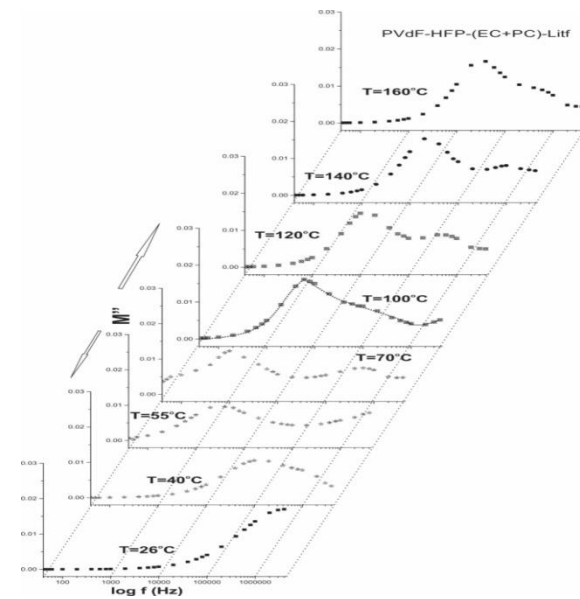


Figure7. Variation of electrical modulus (imaginary) with frequency at different temperatures.

CONCLUSION

A group of plasticized polymer nanocomposite electrolytes having heterogeneous combination (Polymer – Salt- filler- Plasticizer) were prepared and characterized. Result shows the effect of plasticization on electrical conductivity and other physical property. XRD curve emphasizes the increase of amorphous content after plasticization. The uses of combination of plasticizers provide the better solubility and higher electrical conductivity. The maximum conductivity was obtained at room temperature and it is almost stable in the low temperature range which is better for device application. The observations confirms that the number of charge

carriers and their mobility is very much responsible for the enhancement of conduction at different temperatures.

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AUTHOR'S BIOGRAPHY



Nidhi Asthana, was born in Jaunpur (U.P.) in 1979. She has completed M.Sc. In Environmental Sciences (2004) from Purvanchal University Jaunpur (U.P.), India. She did her Ph. D. in 2017 from MGCGV, Chitrakoot, India. She has 7 years Research Experience. She has 19 International Publication in different prominent Journals. Dr. Asthana is presently working as Research Assistant in NCEMP University of Allahabad, Allahabad. She has also got Women Scientist Project from DST, Government of India, New Delhi.



Dr. Mrigank Mauli Dwivedi, was born in India (1970). He completed his B. Tech. (Electronics and Communication (1991), M. Tech. (Electronics) (1993) from University of Allahabad, Allahabad, India. He did his Ph. D. in experimental mineralogy and petrology from department of Earth and Planetary sciences, University of Allahabad in 2003. His major fields of study include petrology, polymer electrolytes, and nanocomposite. He is working as Engineer/ Scientist in National Centre of Experimental Mineralogy and Petrology, University of Allahabad. He has more than 50 research publications in reputed national and international journals. He has edited two books. He is life member of IETE, India.



Dr. Kamlesh Pandey, was born in 1967. He has graduated and post graduated from Gorakhpur University, Gorakhpur, India. He has completed his Ph. D. degree in solid state ionics from Banaras Hindu University, Varanasi in 1995. He has 27 years research experience in polycrystalline, polymeric materials and high pressure and high temperature physics. He has published more than 55 Research Paper in reputed national and international journals and edited two books. He is the life member of Indian solid state ionic society.

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