

Effect of Frequency on AC Conductivity and Dielectric Constant on Composite Polymer Electrolyte

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Abstract: Polyvinyl alcohol (PVA), ammonium nitrate (NH_4NO_3) and nanofiller ZrO_2 composite proton conducting polymer electrolyte with different concentration have been prepared by solution cast technique. The FTIR analysis confirms the complex formation of polymer (PVA) with ammonium salt (NH_4NO_3). The ionic conductivity shows that 2 mole % dispersed nanofiller ZrO_2 in ($\text{PVA}:\text{NH}_4\text{NO}_3$) composite polymer electrolyte has been maximum. The frequency dependence of ac conductivity and dielectric constant have been analysed of composite polymer electrolyte. And frequency dependent ac conductivity follows universal Jonscher's Power law.

Keywords: Composite polymer electrolyte, FTIR, AC electrical conductivity, dielectric constant

1. Introduction

Composite which are made of polymer with nanofiller have been used in electrical and electronic industries. Nanofiller can improve mechanical thermal and electrical (conductivity and permittivity) properties [1]. The conductivity of proton conducting polymer increase due to addition of nanofiller [2]. Polyvinyl alcohol have been particular chemical and physical properties as well as industrial applications [3-4]. Its good film forming nature, high dielectric strength, good charge storage capacity, and dopant dependent electrical and optical properties. It has carbon chain backbone with hydroxyl group attach to methane carbon [5].

Ammonium salts are very good proton donor. Hema et al studied that the AC electrical conductivity of proton conducting solid polymer electrolyte based on PVA with ammonium salts (NH_4Cl , NH_4Br , NH_4I). It has been found that PVA doped with ammonium iodide have high ionic conductivity and its activation energy is low [6]. G. Hirankumar et al reported that the conductivity of pure PVA is of the order 10^{-10} S/cm at ambient temperature and its value increases 10^4 times when complex with 20% ammonium acetate [7]. So in the present work, to study, AC electrical conductivity of proton conducting composite polymer electrolyte PVA: NH_4NO_3 doped with nanofiller ZrO_2 of different molar ratio.

2. Materials and Experimental Technique

Polyvinyl alcohol with molecular weight 125,000 (AR grade Sd fine), ammonium nitrate (AR grade merck), nanofiller ZrO_2 and deionized distilled water as a solvent have been used to prepare composite polymer electrolyte by solution cast technique. In this method PVA and ammonium nitrate have been dissolved separately in deionized distilled water by mole percent. And this solution are mixed together. Then different mole percent of nanofiller ZrO_2 (0,0.5,1.0,1.5,2) in PVA: NH_4NO_3 (80:20) and the solution is stirred well using magnetic stirred, until homogeneous solution was formed.

These homogeneous solution was casted in petri dish and evaporated slowly at room temperature. The film have been formed with uniformed thickness. AC electrical conductivity have been measured at different temperatures (313K- 353K) at the different frequencies (20Hz to 1MHz) using 4284 LCR meter.

3. Result and Discussions

Fourier Transform Infrared spectroscopy (FTIR)

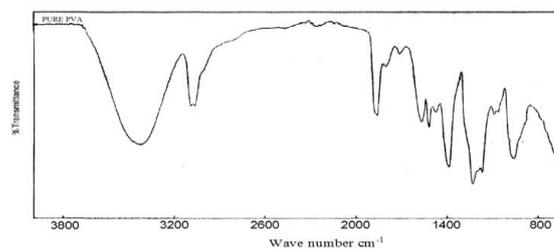


Figure 3.1 (a): FTIR of Pure PVA

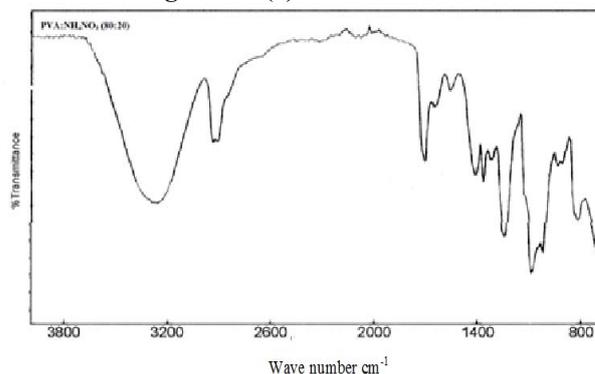


Figure 3.1 (b): FTIR of PVA: NH_4NO_3 (80:20)

FTIR absorption spectra of pure PVA and PVA: NH_4NO_3 (80:20) as shown in fig 3.1a and 3.1b. The absorption band 3411cm^{-1} is the vibrational frequency due to OH bond alcohol and phenols in pure PVA. This (OH) band shifts to 3277cm^{-1} in 80PVA:20 NH_4NO_3 . The hydroxyl group shifts towards lower wave number due to addition of ammonium

salts is characteristic to an interaction in polymer matrix. The FTIR spectra in pure PVA is clearly seen that the absorption band 2961cm^{-1} is the vibrational frequency due to asymmetry C-H stretching in fig 3.1a. This C-H band shifts to lower frequency in 80PVA:20 NH_4NO_3 is observed in fig 3.1b respectively. An absorption peak C-O stretching have been shifted to the lower wave number when the addition of ammonium salt in PVA [8]. The absorption band C-H rocking vibration of PVA appears near 840cm^{-1} [9-10]. The intensity of other peaks reduce due to addition of ammonium nitrate content in pure PVA. This result shows that the complexation have been occurred between PVA and ammonium nitrate.

3.2 AC electrical conductivity

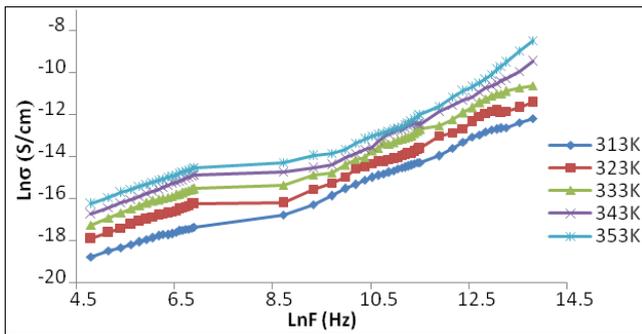


Figure 3.2 (a): Variation of conductivity (σ_{ac}) with Frequency at different temperatures for Pure PVA

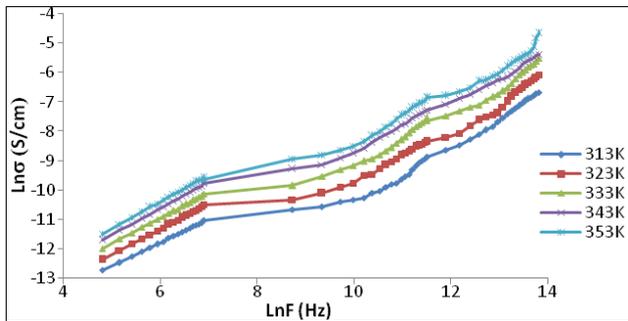


Figure 3.2 (b): Variation of conductivity (σ_{ac}) with Frequency at different Temperatures for PVA: NH_4NO_3 (80:20) with different mole %.

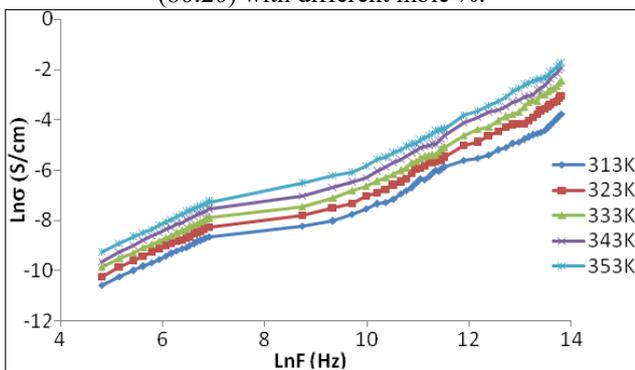


Figure 3.2 (c): Variation of conductivity (σ_{ac}) with Frequency at different Temperatures for PVA: NH_4NO_3 (80:20) : ZrO_2 with 2 mole %

Fig 3.2a, Fig 3.2b, and fig 3.2c shows that the relation between ac conductivity with frequency at Different constant temperatures 313K, 323K, 333K, 343K and 353K. It is seen that the conductivity increases with an increase of

frequency in all composition due to more number of free ions. This will increase mobile of charge carrier. In Fig 3.2a,3.2b, 3.2c shows that two region i.e. low and high frequency region. In low frequency region more and more charge accumulation occurs at electrode- electrolyte interface and to decrease number of mobile ions and conductivity also decreases. Therefore electrode polarization effect is occur [11]. The platue region is representing the DC conductivity. In high frequency region, the AC conductivity increases due to high mobility of charge carrier [12], and it is related to the variation of bulk conductivity. It is found that AC conductivity variation with frequency follows the universal Jonscher's power law [13].

3.3. Dielectric constant

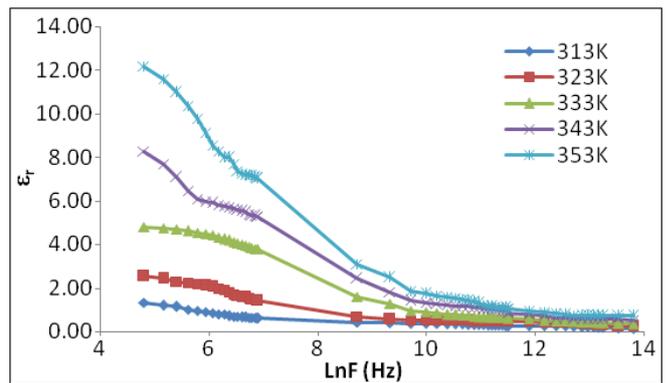


Figure 3.3 (a): Variation of Dielectric constant (ϵ_r) with Frequency at different temperatures for Pure PVA

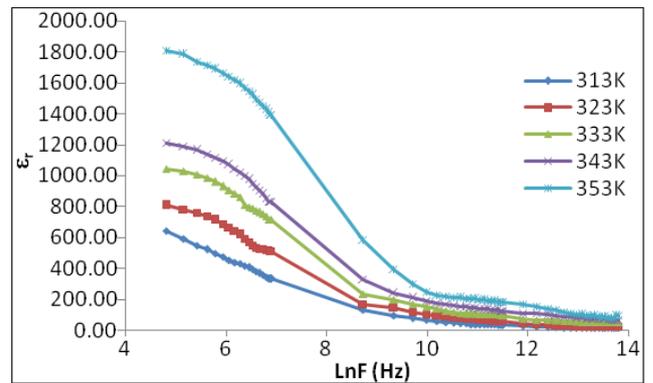


Figure 3.3 (b): Variation of Dielectric constant (ϵ_r) with Frequency at different Temperatures for PVA: NH_4NO_3 (80:20) with different mole %.

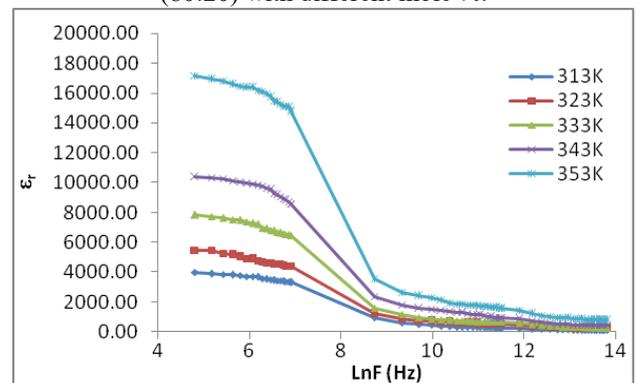


Figure 3.3 (c): Variation of Dielectric constant (ϵ_r) with Frequency at different Temperatures for PVA: NH_4NO_3 (80:20) : ZrO_2 with 2mole %

The frequency dependent dielectric constant of pure PVA, PVA:NH₄NO₃ (80:20) and PVA:NH₄NO₃ (80:20) : ZrO₂ 2 mole % as shown in fig 3.3a, 3.3b and 3.3c. It is observed that dielectric constant is high at low frequency. Due to contribution of charge (collection) accumulation at electrode-electrolyte interface. But in high frequency dielectric constant decreases and nearly constant value with increases in frequency. This is due to the dipole not being able to follow apposite of electric field variation at higher frequency [14-15].

4. Conclusion

AC electrical conductivity and dielectric constant have been measured with frequency at different temperature, it is found that ac electrical conductivity of film increases with increase in frequency and dielectric constant decreases with increase in frequency. The polymer PVA and ammonium salt NH₄NO₃ complex formation have been confirm from FTIR spectra studies.

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