ANALYSIS OF CONDUCTANCE SPECTRA AND TRANFERENCE NUMBER MEASUREMENTS ON POLYVINYL CHLORIDE – AMMONIUM THIO CYANATE POLYMER ELECTROLYTE ADDED WITH SrTiO3

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Abstract

Polymer electrolytes with polyvinyl chloride (PVC) as a host, ammonium thiocyanate (NH_4SCN) as salt and nano-sized strontium titanate ($SrTiO_3$) as filler were prepared using solution casting technique. The frequency dependence of conductivity of the system PVC-NH_4SCN and of $SrTiO_3$ added systems were studied by conductance spectra. In this study, the formation of the sites are found to be more for the system with 6wt% of $SrTiO_3$ which exhibited a maximum conductivity than the other systems studied. The transference numbers (t_{ion}) evaluated for PVC - NH_4SCN and PVC - NH_4SCN - $SrTiO_3$ systems using Wagner's polarization technique. The obtained ionic transference number varies in between 0.30 to 0.86. The finite values of t_{ion} indicted the presence of predominant ion transport in the systems.

Introduction

Solid State Ionics is an interdisciplinary science, fundamental and applied, which covers physics, chemistry, and materials science. The seed of technological achievement in this field has been sowed by Faraday. Since then development are done by various scientists on the electrolytes giving emphasis over the batteries to overcome basis drawbacks of liquid electrolyte such as corrosion, electrolyte leakage, and low operating temperature range.

The protonic transport in polymer electrolytes generally involves motion of the groups like H+ , NH4 + , H3O + , OHetc. Ammonium salts have been reported as good proton donors to the polymer matrix such as poly (vinyl alcohol) PVA **[1]** poly (ethylene oxide) PEO **[2]** poly (ethylene succinate) PESc **[3]** poly (vinyl acetate) PVAc **[4].** The ammonium salts with low lattice energy and larger anionic size like SCN- , I- , CF3SO3 - , ClO4 - , CH3COOetc., could be used as dopants to have new polymer electrolyte with high ionic conductivity and good mechanical strength.

SCN anion is known to be a linear anion and form complex with alkali metal ions (NH4 + , Li+ , Na+ , K+) through Sulfur or Nitrogen atom. Ammonium thiocyanate (NH4SCN) 2 is having lattice energy of 605 kJ mol-1 and can be easily dissociated into cation and anion when it is dissolved in the solvent (water). So, NH4SCN provides more ammonium ions to the polymer matrix. Literature survey reveals that studies on NH4SCN doped poly (vinyl chloride) are scarce

Solvent Casting Technique

The Solvent casting technique prepared polymer electrolytes. Appropriate quantities of PVC& NH4SCN were dissolved by adding in sequence to Tetrahydrafuran. After a complete dissolution of polymer and salt, the ceramic composites such as SrTiO3 was added and further stirred or 2- 3 hours. After stirring, a homogenous solution was obtained, and the resulting solution was poured on to a glass plate and the THF was allowed to evaporate in air at room temperature in dust free atmosphere. The films were dried for another one day to remove any trace of THF. In this technique, the concentration of SrTiO3 are varied and the films were prepared.

Characterization

Conductance Spectra

The electrical response of the material in the A.C frequency can be separated into three regions. At high frequencies electrical relaxations are associated with short range ion migration or hops between crystallographically defined sites. At intermediate frequencies, relaxations are associated with long range ion migration / conduction within the bulk of the electrolyte. The time dependence of these relaxations is affected by the presence of grain boundaries, 42 point defects and dopants within the material. At still lower frequencies, electrical relaxations may be attributed to space charge buildup, charge transfer and / or diffusion controlled reactions at the electrolyte surface **[5]**. The conductivity of ionic conductor is determined by both concentration of the mobile ions and the rate at which they are able to hop from one site to another site in the material **[6].** The a.c conductivity $\sigma(\omega)$ is found to vary with frequency as, $\sigma(\omega) = \sigma(0) + A(\omega) \alpha$ . . . . (3.6) Where $\sigma(0)$ is the d.c conductivity, A is the temperature dependent parameter and α is found to vary between 0 and 1. Jonscher has suggested that this power law is a universal property of materials that is related to the dynamics of hopping conduction.

Results and Discussion

Conductance Spectra

The frequency dependence of conductivity of the system PVC-NH4SCN and of SrTiO3 added systems are shown in **Fig.1.1** The same plots for those systems for different temperatures are shown in **Figs 1.2 and 1.3.**

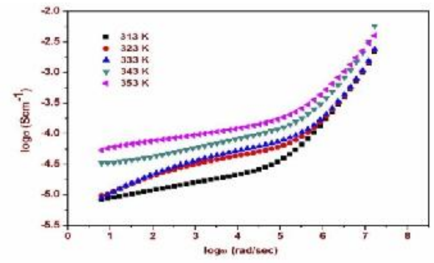


Fig.1.1. Frequency Dependent Conductivity of PVC - NH4SCN and Dependent Conductivity for PVC of SrTiO3

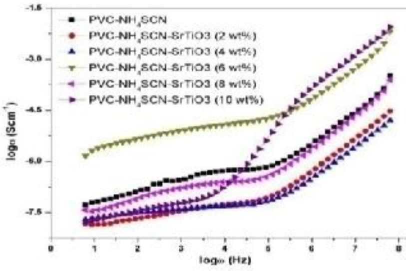


Fig. 1.2.Frequency PVC – NH4SCN at different Concentration NH4SCN at Different Temperature

All the plots given in **Figs from 1.1 to 1.3** show two distinct regions namely, low frequency plateau region and high frequency dispersion region. The low frequency plateau region, which describes the electrode- electrolyte interface phenomena, is attributed to the space charge polarization at the blocking electrode and is associated with dc conductivity (σ_{dc}). In the high frequency dispersion, the ionic conductivity increases with increasing frequency which is associated with the ac conductivity (σ_{ac}) of the NCPCPE's. The intercepts of these plots at zero frequency give the dc conductivity values of the samples and are given in **Table1.4**.The values are found to be in good agreement with the values calculated from Cole-Cole plots **[7].**

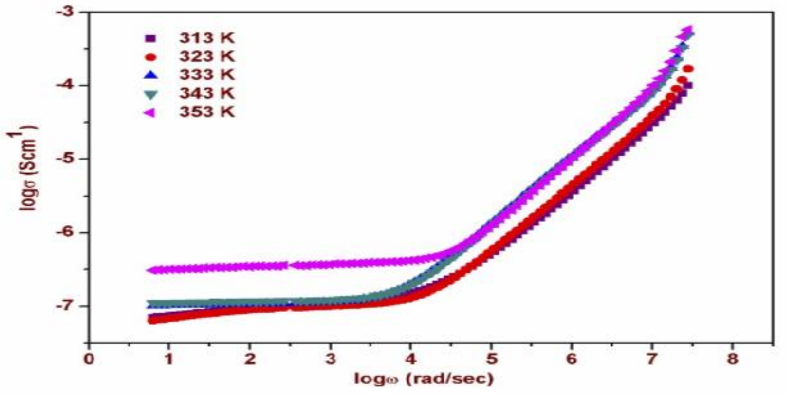


Fig. 1.3.Frequency Dependent Conductivity for PVC - NH_4SCN - $SrTiO_3$ at Different Temperatures

The conductivity spectra of the NCPCPE's are fitted to above equation and the evaluated parameters such as σ_0, A and n are shown in **Table.1.4** According to the Jump relaxation model **[8],** the power law exponent n relates the back hop rate to the site relaxation time. If n is less than one, the backward hopping is slower than the site relaxation. However, if the ratio exceeds one the backward hopping is faster than the site relaxation time. The value of 'n' given in the Table 1.4 are being less than one for all the systems except for the system with 10 wt% concentration of $SrTiO_3$ .This indicated the occurrence of backward hopping at a slower rate than the site relaxation. But it seems to be faster at 10 wt% $SrTiO_3$ added system for which the value of n exceeds one and it is 1.021.The value of n is lower as 0.904 for the systems with 6 wt% $SrTiO_3$ than the other. This shows that the backward hopping is very slower than the site relaxation for this system, when compared with other systems. This substantiates the observed maximum conductivity for that system.

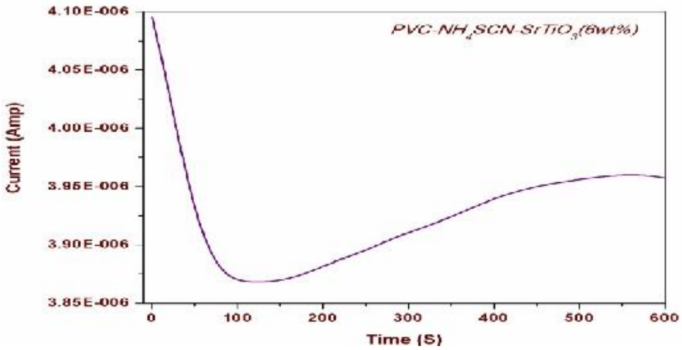
It has also been pointed out that, the lower values of n is due to the formation of free sites of NH_{4+} ion transport. In the present study, the formation of the sites is found to be more for the system with 6wt% $SrTiO_3$ which exhibited a maximum conductivity than the other systems studied.

Table1.4. Fitting Parameter from Jonscher's Power Law

Samples name	**σ (Scm^{-1})Cole-Cole plot**	**σ_0 (Scm^{-1})**	**A**	**n**
PVC-NH_4SCN	5.233×10^{-8}	5.157×10^{-8}	9.022×10^{-12}	0.928
-NH_4SCN - $SrTiO_3$(2wt%)	1.447×10^{-8}	1.474×10^{-8}	8.060×10^{-13}	0.966

PVC-NH$_4$SCN SrTiO$_3$(4wt%)	1.902 x10^{-8}	1.928x 10^{-8}	7.291x10^{-13}	0.937
PVC-NH$_4$SCN-SrTiO$_3$(6wt%)	1.457 x10^{-6}	1.451x 10^{-6}	2.669x10^{-10}	0.904
PVC-NH$_4$SCN-SrTiO$_3$(8wt%)	3.705 x10^{-8}	3.717x 10^{-8}	2.798x10^{-12}	0.986
PVC-NH$_4$SCN-SrTiO$_3$(10wt%)	1.605 x10^{-8}	1.618x10^{-8}	9.774x10^{-11}	1.021

Fig.2.1. Transference Number Measurement for PVC-NH$_4$SCN-SrTiO$_3$ (6 wt %)



It is seen from the **Table 1.4**. that the value of n is less than one for the filler free system and it oscillates with increasing SrTiO$_3$ contents.

Transference Number Measurements

The transference numbers (t_{ion}) have been evaluated for PVC - NH$_4$SCN and PVC - NH$_4$SCN -SrTiO$_3$ systems using Wagner's polarization technique [106]. In this technique, the DC current is monitored as a function of time on application of fixed DC voltage across the samples with blocking electrodes. The results of DC polarization measurements for all the samples were taken with SS blocking electrode by applying 0.5 V DC bias voltage,

Fig.2.1 shows the DC polarization current as a function of time for PVC-NH$_4$SCN-SrTiO$_3$ (6wt%)sample. The ionic transference numbers is calculated using the following equation

$$t_{ion} = (I_i-I_f)/I_i \quad \text{- - - - - - - - - - - - -} \ (1)$$

Where I_i is the initial current and I_f is the final residual current. The ionic transference numbers are calculated by setting the values I_i and I_f from the Wagner's polarization method and are given in **Table 2.1**

Table2.1.Ionic Transference Number (t_{ion}) of PVC-NH_4SCN and PVC-NH_4SCN System with Different Concentrations of $SrTiO_3$

Samples Name	t_{ion}
PVC-NH_4SCN	0.74
PVC-NH_4SCN-$SrTiO_3$ (2 wt%)	0.30
PVC-NH_4SCN-$SrTiO_3$ (4 wt%)	0.65
PVC-NH_4SCN-$SrTiO_3$ (6 wt%)	0.86
PVC-NH_4SCN-$SrTiO_3$ (8 wt%)	0.60
PVC-NH_4SCN-$SrTiO_3$ (10 wt%)	0.48

The obtained ionic transference number varies in between 0.30 to 0.86. The finite values of t_{ion} indicates the presence of predominant ion transport in the systems and it varies as a function of $SrTiO_3$concentration. Initially t_{ion} is 0.74 for $SrTiO_3$ free system and it decreases for 2 wt% $SrTiO_3$ content. Increase of $SrTiO_3$ content to 6 wt% has led to an increased value of 0.86 and further increase led to a fall in t_{ion} value. On comparing the values of t_{ion} of the systems, it is higher as 0.86 for 6 wt% $SrTiO_3$ added system than any other system. This may be associated with the effect of ion-ion and polymer-ion interaction on the macroscopic transport parameters **[4].**

Conclusion

With reference to the temperature depence of loss spectra, the charge carriers are found to be thermally activated. The transference number (t_{ion}) of the optimized system has been determined as 0.86 which revealed that the charge transport in the system is predominantly due to ions.

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