



ION TRANSPORT AND SPECTROSCOPIC STUDIES OF POLY ACRYLONITRILE COMPLEXED WITH AMMONIUM TRIFLUORO METHANE SULFONATE (NH₄CF₃SO₄) GEL POLYMER ELECTROLYTE SYSTEM

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ABSTRACT

Ion transport property of poly acrylonitrile (PAN) complexed with ammonium trifluoro methane sulfonate (NH₄CF₃SO₄) gel polymer electrolyte system is investigated with the aim of developing a high capacity solid state battery. The gel polymer electrolyte films have been prepared using dimethyl formamide (DMF) as solvent, ethylene carbonate (EC) as plasticizer, and ammonium trifluoro methane sulfonate (NH₄CF₃SO₄) as salt with host polymer PAN by using solution cast technique. These films have been characterized by FTIR, UV-Visible spectroscopy and SEM. The change of conductivity with different wt% of salt concentrations ranging from 10 to 40 wt% is studied. The FTIR spectroscopic studies have confirmed that the complex formation between PAN and NH₄CF₃SO₄. The absorption of pure and complexed electrolyte films have been studied in the visible and ultra-violet wavelength region and also observed that the new absorption peak was found at 290 and 375 nm, respectively. The surface morphology of different polymer electrolyte films has been explained by scanning electron microscopy (SEM). DC conductivity studies revealed that the increase in conductivity is due to increase of free ions. The conductivity - temperature studies of the gel polymer electrolyte films follow Arrhenius behavior with activation energy of ionic conduction are determined to be 0.09 eV to 0.26 eV. The maximum conductivity has been found to be 1.68 x 10⁻³ S cm⁻¹ at room temperature (303K) and 3.46 x 10⁻³ S cm⁻¹ at 378 K for 70:30 wt% films. The transport numbers both electronic (t_e) and ionic (t_i) are evaluated using Wagner's polarization technique. The ionic transport number of highest conducting film is found to be 0.992. It is revealed that the charge transport in these polymer electrolyte systems is predominantly due to ions.

Key words: Gel polymer electrolyte, Ionic conductivity, SEM, Ionic transport number.

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INTRODUCTION

Due to the rapid increase in the use of portable computers, mobile phones, video cameras, electric vehicles and unmanned vehicles in submarines, there is an increasing demand for larger capacity, smaller size, lighter weight and lower priced rechargeable batteries. Lithium-ion batteries have become the predominant battery technology for handheld electronic and novel engineering applications in the recent times due to their higher energy, high strength, high voltage, good life cycle and excellent storage characteristics. Lithium-ion cells have become a commercial reality after the initial announcement by Sony in the early 1990s because of an intense world-wide activity on lithium insertion compounds (electrode materials) during the past three decades. The tests that should be passed to get safe lithium ion batteries are with standing the conditions of low pressure (high altitude), thermal cycling, mechanical vibration, mechanical shock, short circuit, mechanical impact, over charging and forced discharge.

The gel polymeric electrolytes have a unique hybrid structure, which possesses cohesive properties of solids and diffusive properties of liquids simultaneously. The solvent or salt-solution is retained in solid polymeric electrolyte and helps in ionic conduction process, whereas the host polymer matrix provides applications as electrolytes/separators in rechargeable batteries, super capacitors, fuel cells and other electrochemical devices¹⁻⁴. Many research groups have reported various polymer electrolytes based on lithium, magnesium and zinc salts to realize respective battery systems. Particularly, the Li based batteries, which are mostly reported in literature, suffer from some safety limitations and many other problems^{5,6}. So, their alternatives in the form of magnesium, zinc and sodium batteries are reported, although these are not extensively studied⁷⁻⁹. The development of proton conducting rechargeable batteries would be an interesting study, with sodium as an alternative to lithium as a negative electrode (anode) due to its low cost, natural abundance, non-toxicity, low atomic mass (23.0) and high electrochemical reduction potential^{10,12}. It is therefore a need to develop high proton conducting non-aqueous electrolytes suitable for the fabrication of rechargeable batteries.

Generally gel polymer electrolytes consist of polymer host, solvents and a salt. They show high ionic conductivities while having good mechanical stabilities¹³⁻¹⁵. The basic concept behind the gel polymer electrolytes is that they make the liquid electrolyte immobile in a polymer host. When compared to the liquid electrolyte, gel polymer electrolytes show reasonable conductivities and polymer host provides the mechanical stability. Compared to solid electrolytes and liquid electrolytes, Gel polymer electrolytes (GPEs) have several advantages, including no shape restrictions, faster charging/discharging and higher power

density¹⁶. Currently, there are four major polymer host materials for GPEs: polyethylene oxide (PEO), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), and polyvinylidene fluoride (PVdF). It is believed that polymers like polyacrylonitrile (PAN) tend to dissolve in different plasticizers, which are used to enhance the conductivities^{17,18}. Hence, in this study, it was attempted to investigate the role of PAN in a gel polymer electrolyte with different percentages of salt and plasticizer. The effect of plasticizer in the polymer electrolyte system is to decrease the glass transition temperature and making the polymer become more amorphous and then allowing the ionic carriers to travel freely inside the electrolyte consequently as to raise the ionic conductivity of the electrolyte¹⁹. PAN has unique properties involving low density, thermal stability, high strength and modulus of elasticity has made PAN as an essential polymer in high-tech and useful in many fields. When compared to liquid electrolytes gel electrolytes have emerged as potential elements for various applications because they have feasible ionic conductivities including mechanical stability. Compared with SPEs, GPEs are much closer to actual applications because they inherited the major properties from the bulk liquid electrolytes, including ion conduction, electrochemical stability on carbonaceous anode and various metal oxide cathode materials, safety, and tolerance against mechanical and electric abuses. The most popular GPE systems that were based on PEO, Poly acrylonitrile (PAN)²⁰, poly methyl methacrylate (PMMA)²¹, and poly vinylidene fluoride (PVdF)²², along with an excellent discussion of the fundamental aspects concerning the formation, morphological structure, and physical stability of GPE. A detailed literature survey indicates that the PAN complexes with ammonium salts have found less attention as proton conducting polymer electrolytes. Hence, this paper focuses on preparation, characterization and transport studies of high conducting gel polymer electrolytes for high conductivity in rechargeable cells.

In the present work, gel polymer electrolyte films have been prepared with $\text{NH}_4\text{CF}_3\text{SO}_4$ in PAN using EC and DMF as plasticizing solvents by adopting solution casting technique. These prepared films are characterized using spectroscopic techniques like FTIR, UV-Vis Spectroscopy, SEM, and DC conductivity. Finally the investigation is pertaining to transport number measurement by using Wagner's polarization technique.

EXPERIMENTAL

The composition and selected chemicals were PAN with average molecular weight 1, 50,000 g/mol and Ethylene carbonate (Aldrich,) DMF (Merck), Ammonium triflate $\text{NH}_4\text{CF}_3\text{SO}_4$ (Aldrich) were used in this research work. After taken the required quantities of PAN and $\text{NH}_4\text{CF}_3\text{SO}_4$ in plasticizing solvents (EC+DMF), the solution was continuously stirred magnetically for several hours at 60°C until a homogeneous solution has been obtained.

After complete dissolution, the solution was poured into Petri dish and left to dry under vacuum at 60°C for one week until the films were formed. The film was then kept in a desiccators for further drying. Then the sample was completely dried then a membrane like or thick film appears with thickness ranging from 100-160 μm . The prepared free-standing, transparent and stretchy thick films are as shown in Fig.1. The FTIR Spectra were recorded in the range 500-4000 cm^{-1} at room temperature using Perkin Elmer FTIR spectrometer. The SEM is one of the most versatile instruments used for the analysis of structural morphology. The absorption peaks were observed and optical energy band gap was determined by UV-Vis spectrum images. The SEM photographs of the prepared electrolyte systems were recorded using FE-SEM, Carl Zeiss, Ultra 55 model. The DC Conductivity of the films was measured using Keithley 6514 in the temperature range 303-373K²³. The transport numbers were calculated by using Wagner's polarization technique²⁴. In this technique, a new prepared polymer electrolyte film was polarized in the configuration Ag/polymer electrolyte /Ag under a DC bias of 1.5 V. The resulting current was observed as a function of time with a Keithley 6514 electrometer.

RESULTS AND DISCUSSION

FTIR Analysis

Fig. 2 shows the FTIR spectra of pure PAN and $\text{NH}_4\text{CF}_3\text{SO}_4$ salt doped PAN complexes of various weight % ratios in the range between 450 and 4000 cm^{-1} . From the spectra, the absorption band observed at 2244 cm^{-1} , can be assigned to the most characteristic band of nitrile group $\text{C}\equiv\text{N}$ stretching of PAN. The absorption band doublet frequencies observed at 1782 cm^{-1} and 1793 cm^{-1} can be assigned to $\text{C}=\text{O}$ stretching of EC and DMF²⁵. The position of these $\text{C}\equiv\text{N}$ and $\text{C}=\text{O}$ peaks are not changed with the addition of salt. It indicates that only a weak physical electrostatic interaction exists between the ammonium ion and $\text{C}=\text{O}$ / $\text{C}\equiv\text{N}$.



Fig. 1: Polymer electrolyte films of PAN : $\text{NH}_4\text{CF}_3\text{SO}_4$

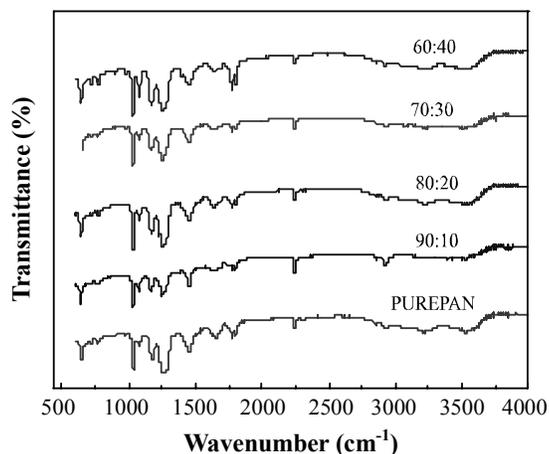
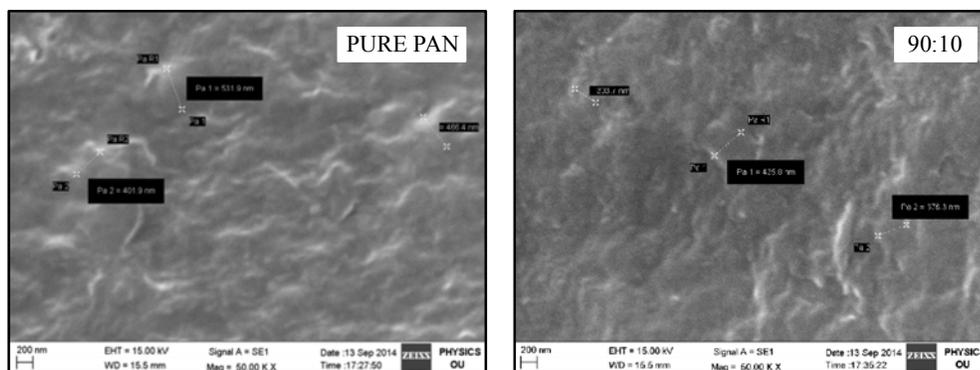


Fig. 2: FTIR spectra of pure PAN and PAN-complexed films for different wt % of $\text{NH}_4\text{CF}_3\text{SO}_4$

SEM Analysis

The morphology of pure PAN and $\text{NH}_4\text{CF}_3\text{SO}_4$ complexed PAN polymer electrolyte systems are studied using Scanning electron microscopy (SEM) technique. The typical SEM images of pure PAN and PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ (90:10, 80:20, 70:30 and 60:40) have been shown in Fig. 3. It is evident from the figure that the surface of the film is somewhat rough and uneven. For PAN, the surface structure is in the form of cylindrical shaped entities, which represents the crystalline domains. For PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ (90:10, 80:20, 70:30 and 60:40) films the surface shows that the cylindrical shaped entities are too closure and still maintained cylindrical shapes with improved smoothness²⁶. This may be due to better interaction of PAN molecules with ammonium ion²⁷ leading to polymer molecules closure around ammonium ion.



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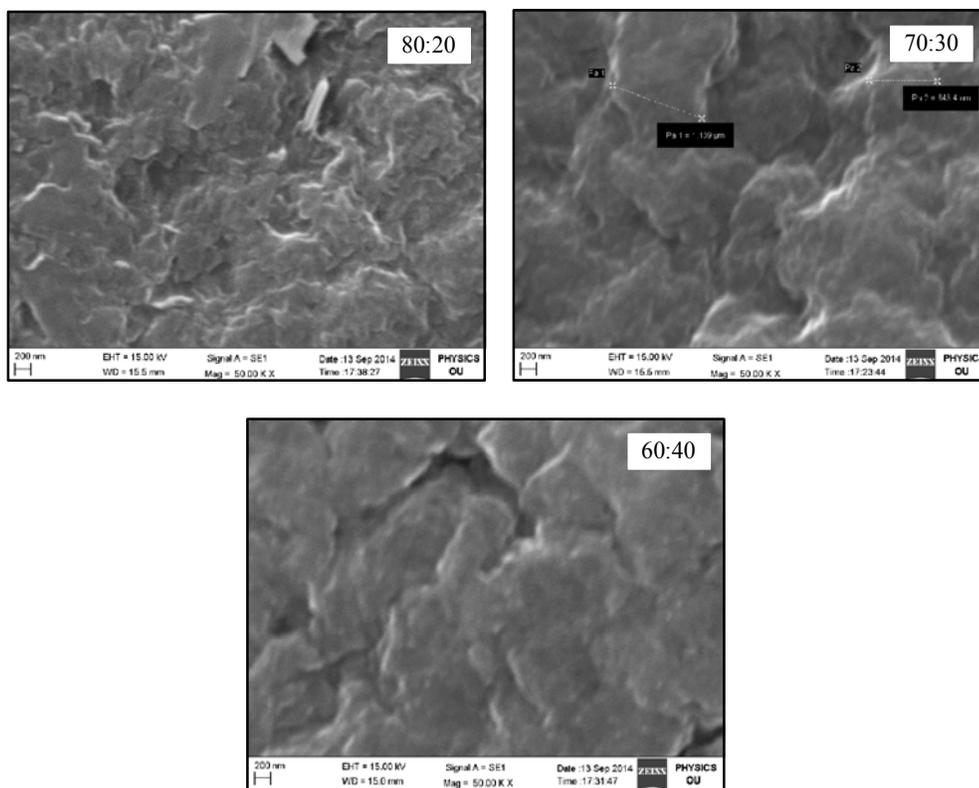


Fig. 3: SEM images of pure PAN and PAN-complexed films for different wt % of $\text{NH}_4\text{CF}_3\text{SO}_4$

DC conductivity

The conductivity versus salt concentration for different wt% of PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ at different temperatures was given in Fig 4. It is clear that with the increasing of salt content, conductivity also increasing up to 30 wt% of salt. This is due to the high amorphousness of the polymer electrolyte films which provides free mobile ammonium ions thus giving rise to higher conductivity. Generally the conductivity of ion conducting polymer electrolytes is directly proportional to the mobility and number of charge carriers. Generally, the increase in the conductivity with increasing salt concentration can be related to the increase in the number of mobile charge carriers in the polymer electrolytes.

The enhancement in conductivity is not only due to the increment of salt, but also due to EC. EC allows greater dissolution of the electrolyte salt resulting in increased number of charge carriers hence conductivity²⁸. The conductivity data at room temperature and at

373 K is presented in Table 1. The DC conductivity versus reciprocal temperature plots obey the Arrhenius type thermally activated process given by the relation is –

$$\sigma = \sigma_0 \exp (-E_a/KT) \quad \dots(i)$$

Where σ_0 is the pre exponential factor, E_a is the activation energy, K is the Boltzmann constant and T is the absolute temperature. Maximum value of conductivity obtained from this system at room temperature is $1.68 \times 10^{-3} \text{ S cm}^{-1}$ for 70PAN:30 $\text{NH}_4\text{CF}_3\text{SO}_4$ film. This conductivity value is 10 orders greater than that of pure PAN ($<10^{-14} \text{ Scm}^{-1}$) as reported²⁹. However, when more than 30 wt% of $\text{NH}_4\text{CF}_3\text{SO}_4$ has been added, the conductivity decreases and this might be due to ion pair or ion aggregates formation³⁰. Higher amount of salt incorporated in the polymer electrolytes leads to increase the viscosity of the polymer electrolyte films. As a result, free space for ammonium ion transportation is reduced and then impedes the mobility of charge carriers. Hence, the ion conductivity is decreased.

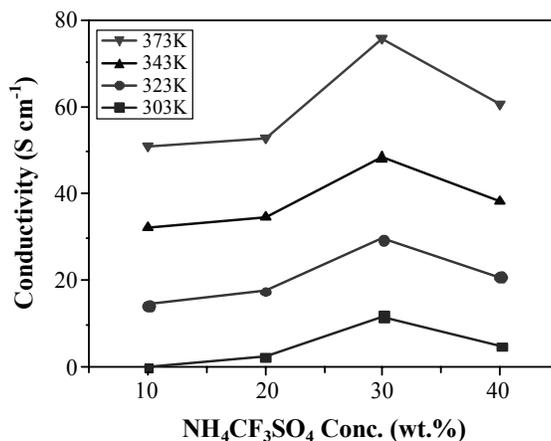


Fig. 4: Ion conductivity (σ) of polymer electrolyte films as a function of $\text{NH}_4\text{CF}_3\text{SO}_4$ concentration

The logarithmic of ionic conductivity versus $10^3/T$ for polymer complex PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ system with varying weight percentage of salt in the temperature range 303-373 K is shown in Fig 5. It is also cleared that the conductivity of PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ films was found to be increasing with increasing temperature. Activation energies of PAN complexed films were calculated from Arrhenius plots drawn between the temperature versus conductivity ($1000/T$ vs $\log \sigma$) and the values have been presented in Table 3. From Table 1, we conclude that the complexed PAN (with 30 % of $\text{NH}_4\text{CF}_3\text{SO}_4$) conductivity was increased from $1.68 \times 10^{-3} \text{ S/cm}$ at 303 K to $3.46 \times 10^{-3} \text{ S/cm}$ at 373 K.

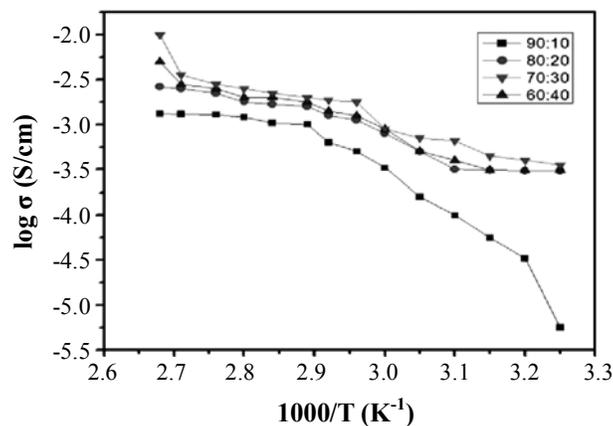


Fig. 5: Plots of $\log \sigma$ versus $1000/T$ of PAN-complexed films for different wt.% of $\text{NH}_4\text{CF}_3\text{SO}_4$

Transference number measurements

Further, the ionic transference numbers of PAN complexed films have been measured using Wagner's polarization method³¹. The variation of time versus polarization current has been given clearly in Fig 6.

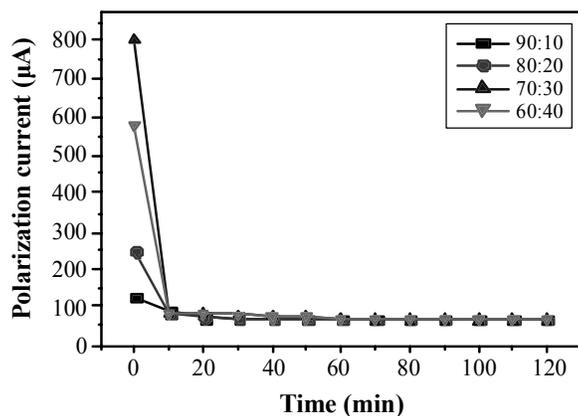


Fig. 6: Transference number measurements of PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ polymer electrolyte films in different weight proportions at room temperature

In this method, the D.C. current was altered as a function of the time on application of a constant dc voltage 1.5 V across the cell: Ag/polymer electrolyte/Ag. Graphs were plotted between the polarization current and time using equation:

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

$$t_{\text{ele}} = I_f/I_i$$

where I_i is the initial current and I_f is the final residual current as shown in Fig 5.

The determined transference values are given in Table 1. The values of ionic transference numbers t_{ion} are given in the range between 0.950-0.992. The decrease of current with time shows that the total conductivity of the polymer electrolytes is predominantly due to ions. Hence, it is proved that $\text{NH}_4\text{CF}_3\text{SO}_4$ salt has provided ammonium ions as mobile species in the polymer electrolyte systems.

Table 1: Conductivity, activation energies and transference numbers of PAN based polymer electrolytes.

Polymer electrolyte	Conductivity at 303 K	373 K	Activation energy (eV)	Transference number	
				t_{ion}	t_{ele}
PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ (90:10)	4.64×10^{-6}	3.68×10^{-5}	0.35	0.950	0.05
PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ (80:20)	3.67×10^{-5}	6.64×10^{-5}	0.27	0.985	0.015
PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ (70:30)	1.68×10^{-3}	3.46×10^{-3}	0.15	0.992	0.008
PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ (60:40)	5.76×10^{-6}	1.62×10^{-5}	0.12	0.974	0.026

UV – Vis Spectroscopy characteristics

The structural effect of salt on the conductivity was also confirmed by UV/Vis spectroscopy. The Fig. 7 shows that the UV/Vis spectra of PAN with different wt. % ratios of $\text{NH}_4\text{CF}_3\text{SO}_4$ salt at room temperature. The UV-Vis spectrum was recorded by a Hewlett-Packard HP8452A diode array spectrometer. The optical absorption particularly studying the shape and shift of absorption edge is very useful technique for understanding the basic mechanism of optically induced transitions in crystalline and non crystalline materials³². The absorption rate is slightly changed by increasing the salt ratio of solvents³³. The optical band gap of the polymer electrolytes was determined using UV-Visible spectra. It can be determined by using formula –

$$E = hc/\lambda \quad (\text{iii})$$

where h is the Plancks constant, it's value is 6.626×10^{-34} joules sec. C is the light velocity its value is 3×10^8 meter/sec. λ is the cut off wavelength. From the spectra of UV-Vis the wavelength values are given in Table 2. It is cleared that the optical energy band

gap is minimum for 70:30 samples and cleared that the conductivity is more when compared to remaining samples due to low optical band gap.

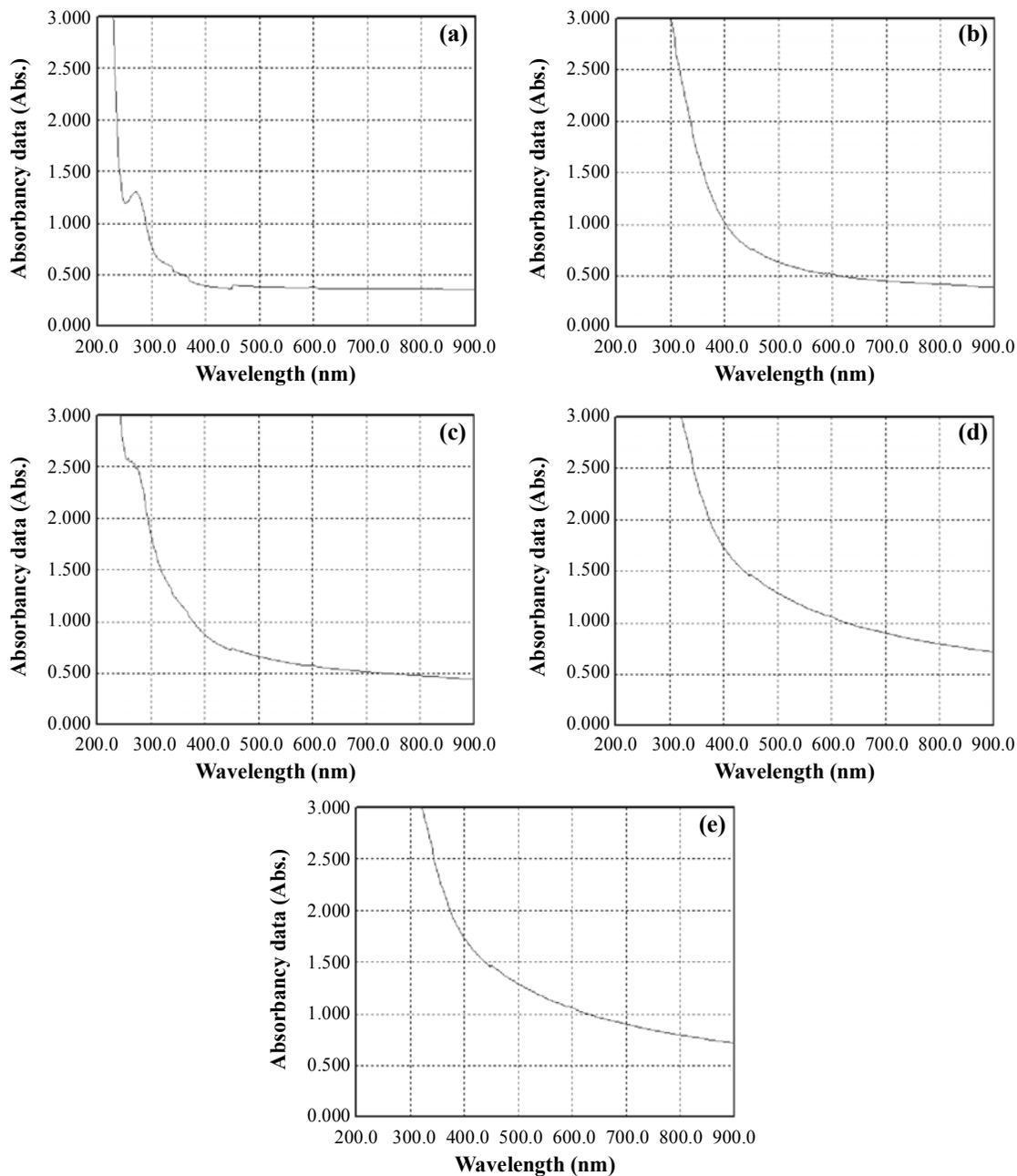


Fig. 7 (a-e): UV-VIS Spectroscopic images of PAN: $\text{NH}_4\text{CF}_3\text{SO}_4$ polymer electrolyte films in different wt. % ratios at room temperature

Table 2: Optical energy band gap for PAN based polymer electrolytes

Polymer electrolyte	Plancks constant (h)	Light velocity (C)	Wavelength (Å)	Optical energy band gap in (ev)
Pure PAN	6.626×10^{-34} joules sec	3×10^8 meter/sec	350.12	3.54842
90:10	6.626×10^{-34} joules sec	3×10^8 meter/sec	500.20	2.48475
80:20	6.626×10^{-34} joules sec	3×10^8 meter/sec	450	2.7608
70:30	6.626×10^{-34} joules sec	3×10^8 meter/sec	610	2.0366
60:40	6.626×10^{-34} joules sec	3×10^8 meter/sec	590	2.1057

CONCLUSION

The ionic conducting gel polymer electrolytes having ammonium triflate salt dissolved in a plasticizing solvent, EC and DMF, immobilized in a host polymer PAN have been prepared and characterized. The complexation of the salt with the polymer is confirmed by XRD and FTIR studies. Inter planar spacing is also verified theoretically and experimentally. It is clear that with increasing of salt concentration the surface of the films roughness has been decreased and phase segregation is revealed with cylindrical shape. Decrease in the degree of crystallinity and increase in the amorphous nature observed while increase in conductivity with increasing concentration of $\text{NH}_4\text{CF}_3\text{SO}_4$ and temperature. The transference number data indicate that the conduction in these polymer electrolytes is predominantly due to ions rather than electrons. UV-Vis light absorption reveals that the chemical structure of the polymer is identical to that of the polymer formed electrochemically. The various absorption rates given for different wavelengths and optical energy band gaps was determined.

ACKNOWLEDGEMENT

We wish to offer our sincere thanks to Prof. S. V. Suryanarayana for his utmost assistance. The authors thank Mr. Koneru Satyanarayana, President, Koneru Raja Harin, Vice President, Dr. L. S. S. Reddy-Vice chancellor, K. L. University, Dr. A. Anand Kumar, Principal and Dr. K. L. Narayana Dean R&D, Dr. B. Raghu Kumar Director, FED for their

constant support and encouragement. I specially thank Padmaja Kakkera who gave financial support in doing the research work.

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Revised : 28.02.2016

Accepted : 02.03.2016