

Preparation and Characterization of Ammonium Ceric Nitrate Doped PVDF Polymer Electrolytes

K. Sundaramahalingam, M. Muthuvinayagam, D. Vanitha, M. Vahini

Abstract: Poly [vinylidene fluoride] (PVdF): Ammonium ceric nitrate ((NH₄)₂Ce(NO₃)₆) based Proton conducting solid polymer electrolytes (SPEs) are prepared by solution casting technique. Polymer electrolytes are characterized by several techniques. The Structural property of the electrolytes are confirmed by XRD. The functional groups present in polymer electrolytes are confirmed by FTIR. The conductivity of the polymer electrolytes are calculated by using AC impedance analysis. The Maximum ionic conductivity is obtained for 2wt% of ammonium ceric nitrate doped polymer electrolyte.

Keywords : XRD, FTIR, PVdF, ionic conductivity.

I. INTRODUCTION

In modern life, the development of portable devices like notebook computers, tablets, and mobile phones increase the demand of solid state high energy density batteries [1-3]. Proton conducting solid polymer electrolytes are more useful in fuel cells, batteries and electro chromic windows [4-7]. Recently, there are many researchers working on synthetic and natural polymers to prepare solid polymer electrolytes[8-13].

From the literature survey many authors report that PVdF based electrolytes have good conductivity and hydrophobicity because of porous surface structure [14]. PVdF has α and β crystalline forms [15-17]. It has semi crystalline nature and PVdF assist in higher ionization of salts provides higher concentration of charge carriers [18] and thus enhances to high conductivity. As well as PVdF is attractive polymer because of Piezo and Pyro electric effect, they are used in the development of electrochemical devices [19-22].

Ceric Ammonium nitrate (CAN) is a Water-soluble cerium salt and a specialized oxidizing agent in organic production. In organic synthesis, Ceric Ammonium Nitrate is suitable as an oxidant for many functional groups (alcohols and ethers) as well as C-H bonds, particularly those that are benzylic. In this work, various wt% of ammonium ceric

Revised Manuscript Received on December 16, 2019.

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nitrate is doped with PVdF and the ac conductivity values are measured.

II. EXPERIMENTAL PROCEDURE

Poly[vinylidene fluoride] of molecular weight, Mw=2,00,000g/mol, and Ammonium ceric nitrate were used as raw materials. Dimethyl formamide (DMF) was used throughout the experiment.

Polymer electrolytes are prepared with 0.5wt% - 2.5wt% of Ammonium ceric nitrate and stoichiometric quantities of PVdF. PVdF and Ammonium ceric nitrate were dissolved in DMF separately at 70°C and then stirred until it becomes viscous solution. These two solutions were mixed drop-wise to get high transparent liquid. This mixture solution was stirred. The final viscous liquid solution was poured in polypropylene dishes. And it kept in an oven at 70°C for 24 hours to removal of solvent. After drying, the smooth, transparent films had been obtained.

The XRD pattern of SPEs were recorded using Bruker X-Ray diffractometer having ($\lambda=1.540\text{\AA}$) in the scanning rate of 20° per minute in the range of 10°-80°. FTIR Transmittance spectra of SPEs were recorded using "SHIMADZU IR Tracer 100" Spectrometer. The spectra were obtained in the wave number of 400 to 4000 cm⁻¹. The impedance measurements were done by HIOKI 3532-50 Hi-tester in the frequency range of 42Hz- 1MHz.

III. RESULTS AND DISCUSSION

A. XRD Analysis

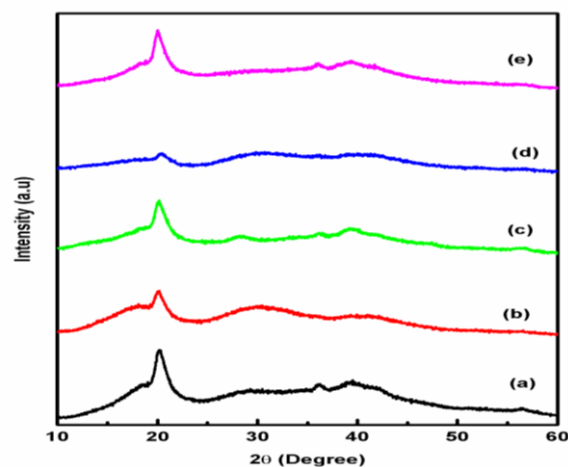


Fig. 1. XRD Pattern of PVdF:Ammonium ceric nitrate polymer electrolytes. a) 0.5wt% ammonium ceric nitrate b) 1 wt% ammonium ceric nitrate c) 1.5 wt% ammonium ceric nitrate d) 2.0 wt% ammonium ceric nitrate e) 2.5 wt%

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ammonium ceric nitrate

Fig. 1. Shows the XRD pattern for various wt% (0.5wt% - 2.5) % of ammonium ceric nitrate doped PVdF polymer electrolytes. At 0.5% sample (a) shows peak at $2\theta = 20^\circ$ and one hump at 36° due to the presence of PVdF. When increasing the Ammonium ceric nitrate concentration along with the PVDF, the Peak intensity and hump are decreasing. 2wt% of ceric nitrate doped system (d) shows maximum amorphous nature. Further increasing the salt, the peak intensity increases.

B. FTIR Analysis

Various wt.% of ammonium ceric nitrate doped PVdF polymer electrolytes depicted in fig. 2. The peak at 875cm^{-1} is due to the Beta-Phase (out of phase combination), the peak at 1232cm^{-1} is appeared due to Alpha-Phase of PVDF. The peak at 1400cm^{-1} is due to Beta-Phase of PVdF because of bending or scissoring. Peaks at 2922cm^{-1} and 3020cm^{-1} are due to CH_2 Symmetric Stretching in PVDF.

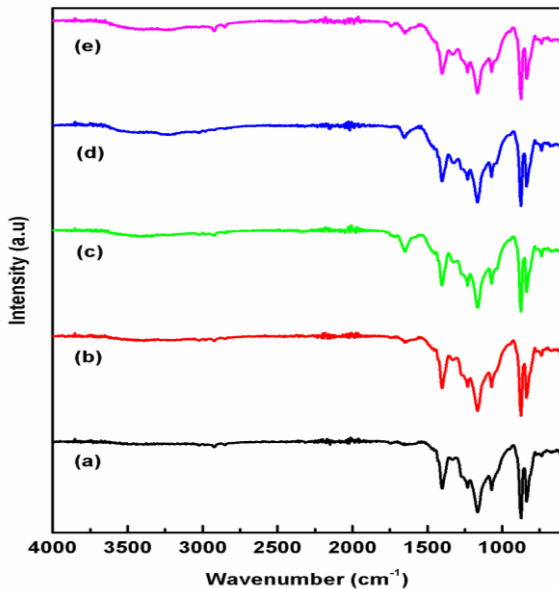


Fig. 2. FTIR Spectrum of Ammonium ceric nitrate doped PVDF Polymer electrolytes a) 0.5% salt doped b) 1% salt doped c) 1.5% salt doped d) 2.0% salt doped e) 2.5% salt doped system

C. AC impedance analysis

Cole-Cole plot

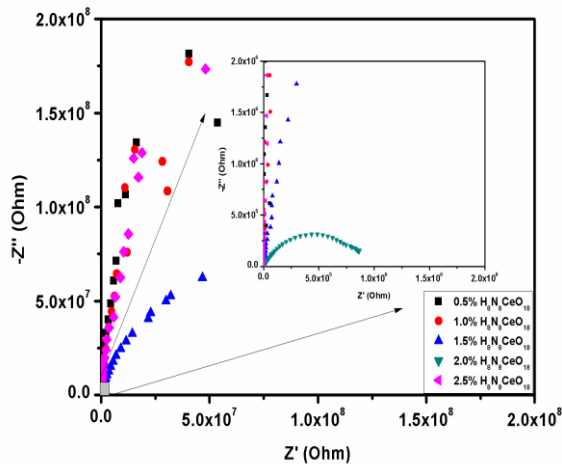


Fig. 3. Cole-Cole plot for ammonium ceric nitrate mixed PVdF polymer electrolytes

Fig. 3 shows the Cole cole plot for (0.5wt% to 2.5wt%) ammonium nitrate doped PVdF polymer electrolytes. In this figure 2wt% of ammonium ceric nitrate doped PVdF polymer electrolyte shows a depressed semicircle at higher frequency region and 0.5wt%, 1.0wt%, 1.5wt%, 2.5% wt% salt doped samples show enlarged semi-circles. This semi-circle is due to parallel combination of resistor (polymer matrix mobile ions migrates in free voids of) and capacitor (static polymer chains polarization) present in the polymer electrolytes. Upto 2wt% of ammonium ceric nitrate, the bulk resistance decreases and again increases for higher salt concentration. Using the formula, the conductivity of the SPE is calculated,

$$\sigma = l / R_b A \text{ S/cm} \quad (1)$$

Where, σ = Conductivity, l = Polymer electrolyte thickness, R_b = Resistance of the sample, A = Polymer electrolyte area.

Table I. The conductivity of various wt% of ammonium ceric nitrate doped PVdF Polymer electrolytes

Compositions	Conductivity (S/cm)
PVdF/ 0.5wt% $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	2.85×10^{-10}
PVdF/ 1.0wt% $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	3.35×10^{-10}
PVdF/ 1.5wt% $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	4.07×10^{-10}
PVdF/ 2.0wt% $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	2.68×10^{-08}
PVdF/ 2.5wt% $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	5.44×10^{-10}

Conductance spectra

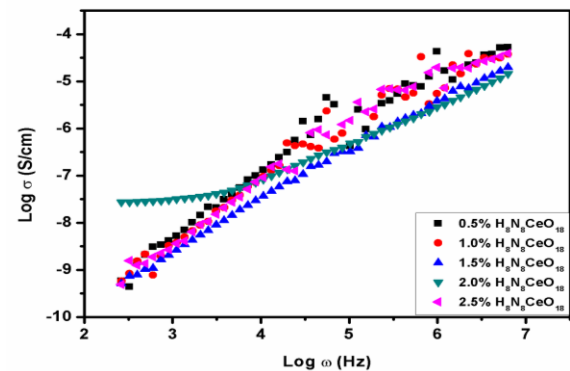


Fig. 4. Conductance spectra for various wt% of ammonium ceric nitrate doped PVdF polymer electrolytes

Frequency dependent conductivity is one of the properties for amorphous polymers. The Conductance spectra analysis deals with the variation of conductivity with frequency. In the Conductance spectra, there are two regions namely low-frequency region as the frequency independent plateau region. In lower frequencies, frequency independent nature is occurred due to presence of activated hopping of ion that produces the dc conductivity. In high-frequency region is called frequency dependent dispersion region. In higher frequency region, frequency dependent nature is occurred due to ion motion with Jonchler's power law. The overall conductivity in terms of frequencies is explained by Jonchler's power law.

$$\sigma(\omega) = \sigma_{ac}(\omega) + A \omega^{\alpha} \quad (2)$$

In the above equation, σ_{dc} and A are the temperature dependent terms which

represents the conductivity is thermally activated process.

Dielectric constant and Dielectric loss

The charges accumulated in material represent the dielectric constant and when the polarity of the electric field is reversely applied, energy losses are generated due to movement of ions, this is called the dielectric loss of material. The dielectric constant and losses are calculated using the following equation,

$$\epsilon' = \frac{Z''}{\omega C_0 (Z'^2 + Z''^2)} \quad - (3)$$

$$\epsilon'' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)} \quad - (4)$$

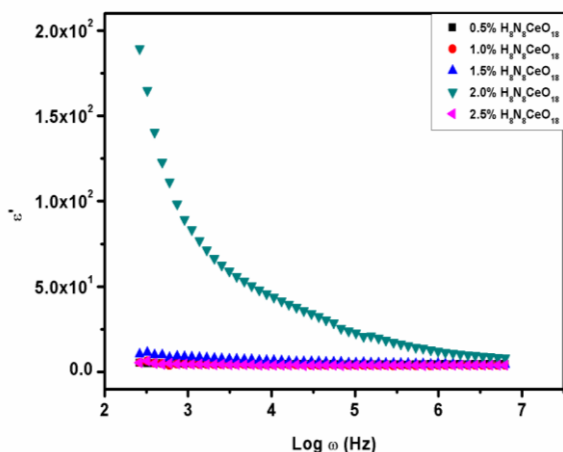


Fig. 5a. Dielectric constant for various wt% of ammonium ceric nitrate doped PVdF polymer electrolytes.

In this fig. 5a, there is some distinction in ϵ' with the frequency, this may be due to the space charge polarization at electrolyte and electrode interface [23]. In lower frequency region, dielectric constant is maximum due to accumulation of more number of charge carriers at near electrodes [24, 25]. When the applied frequencies are increased, the dielectric constant is decreased due to the orientation of the charge carrier themselves at high periodic reversal applied field [26]. In the figure, 2wt% of ammonium ceric nitrate doped PVdF system shows maximum dielectric constant compared than other prepared samples.

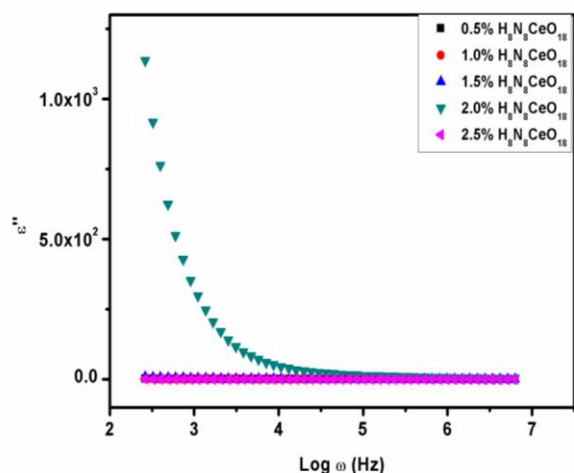


Fig. 5b. Dielectric Loss for Various wt% of Ammonium ceric nitrate doped PVdF polymer electrolytes.

Dielectric loss can be expressed in terms of conductivity,

$$\epsilon'' = \frac{\sigma}{\omega \epsilon_0} \quad - (5)$$

The figure shows the dielectric loss of prepared polymer films at different concentration of ammonium ceric nitrate doped PVdF matrix. It is clearly concluded that the higher conducting polymer electrolyte shows higher dielectric loss.

IV. CONCLUSION

Different wt% of ammonium ceric nitrate $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ doped PVdF based polymer electrolytes are prepared by simple solution casting technique. The structural analysis is confirmed by XRD. From XRD, the peak intensity of pure PVdF is reduced while increasing the concentration of ammonium ceric nitrate. 2wt% of ammonium ceric nitrate doped PVdF SPE shows more amorphous nature. Functional groups present in the SPEs are confirmed by FTIR. Ac impedance analyses are carried out for the prepared polymer electrolytes. The maximum ionic conductivity is 2.68×10^{-8} S/cm for 2.0wt% of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ doped PVdF polymer electrolyte.

ACKNOWLEDGMENT

The authors acknowledge the management of Kalasalingam Academy of Research and Education, Krishnankoil-626126, for providing research facilities with research fellowship.

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