

CHARACTERIZATION OF PROTON CONDUCTING PVDF-HFP/PEMA BLEND BASED SOLID ELECTROLYTES

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ABSTRACT

Proton conducting poly(vinylidene fluoride-cohexafluoropropylene)/polyethyl methacrylate (PVDF-HFP/PEMA) blend based electrolytes with different compositions of $\text{NH}_4\text{CF}_3\text{SO}_3$ salt have been prepared and characterized. XRD and SEM studies show that the addition of $\text{NH}_4\text{CF}_3\text{SO}_3$ helps to generate more amorphous region in the semicrystalline PVDF-HFP/PEMA system. The conductivity of the blend based electrolyte system increases with increasing content of $\text{NH}_4\text{CF}_3\text{SO}_3$. The system containing 40 wt % of salt exhibits the highest room temperature conductivity of $6.90 \times 10^{-4} \text{ S cm}^{-1}$. The temperature dependence of ionic conductivity of the system follows an Arrhenius behavior. The frequency dependence of conductivity of the system obeys the universal power law, $\sigma(\omega) \propto A\omega^n$. The pre-exponent, n is found to decrease with increasing temperature suggesting that the Correlated Barrier Hopping model can be used to explain the conduction mechanism in the system.

INTRODUCTION

Solid proton conducting polymer electrolytes have been studied because of the potential technological application in solid state ionic electrochemical devices such as batteries, fuel cell, super capacitor, etc. The interest in solid proton conducting electrolyte systems started with the development of perfluorinate sulfonic system in the 1960s [1]. A few groups of researchers have studied proton conducting electrolytes using strong inorganic acids such as H_3PO_4 , H_2SO_4 and HCl as the doping salts [1, 2]. However proton conducting polymer electrolytes containing inorganic acids suffer from chemical degradation and mechanical integrity and thus are unsuitable for practical applications [3]. Other than complexation with inorganic acids, proton conducting polymer electrolytes can also be prepared by complexation with ammonium salts which are considered as good proton donors to a polymer matrix. However, very little attention has been given to polymer electrolyte systems containing ammonium salts [3-5].

In this work PVDF-HFP/PEMA blend based proton conducting polymer electrolyte systems have been prepared using $\text{NH}_4\text{CF}_3\text{SO}_3$ as the doping salts. The structure, morphology and conductivity behavior of the system have been characterized using XRD, SEM and impedance spectroscopy.

EXPERIMENTAL

Sample preparation

In this work, proton conducting PVDF-HFP/PEMA blend based polymer electrolytes with various salt concentrations were prepared by solution casting technique. PVDF-HFP ($M_w \sim 400,000 \text{ g mol}^{-1}$), PEMA ($M_w \sim 515,000 \text{ g mol}^{-1}$) and $\text{NH}_4\text{CF}_3\text{SO}_3$ salt were obtained from Aldrich. PVDF-HFP and PEMA (weight ratio 85:15) were dissolved in DMF. Then, an appropriate amount of $\text{NH}_4\text{CF}_3\text{SO}_3$ salt was added into the polymer blend solution. The mixture was stirred at 40°C for 48 hours to obtain homogenous solution. The homogenous solution was then cast into Petri dishes and allowed to evaporate slowly at room temperature. PVDF-HFP/PEMA blend based polymer electrolytes in the form of films were obtained after about 2 weeks of drying time.

Sample characterization

The complex impedance of the samples prepared for this study were measured using HIOKI 3532-50 LCR HiTester in the frequency range from 42 Hz to 5 MHz. The conductivities of the samples were calculated using the equation,

$$\sigma = t/R_b A \quad (1)$$

where t is the thickness of the sample, R_b is the bulk resistance and A is the area of the blocking electrode. The impedance measurements were done at various temperatures in the range from 273 K to 333 K. The frequency dependent conductivity were calculated by

$$\sigma_{ac} = \varepsilon_o \varepsilon_i \omega \quad (2)$$

where ε_o and ε_i are vacuum space permittivity. D8 Advance X-Ray Diffractometer was used to investigate the structure of the samples. The morphology of the samples was studied by scanning electron microscopy LEICA S440.

RESULTS AND DISCUSSION

XRD analysis

Figure 1 shows the XRD patterns of $\text{NH}_4\text{CF}_3\text{SO}_3$, pure PEMA, pure PVDF-HFP, PVDF-HFP/PEMA blend and PVDF-HFP/PEMA- $\text{NH}_4\text{CF}_3\text{SO}_3$ electrolytes systems. The XRD pattern of pure PVDF-HFP system exhibits a peak at 2θ around 20° indicating semicrystalline nature of the system. The peak becomes broader with the addition of PEMA. Further broadening and reduction in the intensity of the peak are observed with the addition of $\text{NH}_4\text{CF}_3\text{SO}_3$ salt. This can be attributed to the increase in amorphous domain in the polymer electrolyte system. The absence of peaks corresponding to $\text{NH}_4\text{CF}_3\text{SO}_3$ in the XRD patterns (e) and (f) indicates complete dissolution of salt in the polymer matrices [6, 7]. The XRD pattern of PVDF-HFP/PEMA- $\text{NH}_4\text{CF}_3\text{SO}_3$ with

polymer:salt weight ratio of 55:45 reveals a very amorphous nature of the electrolyte system.

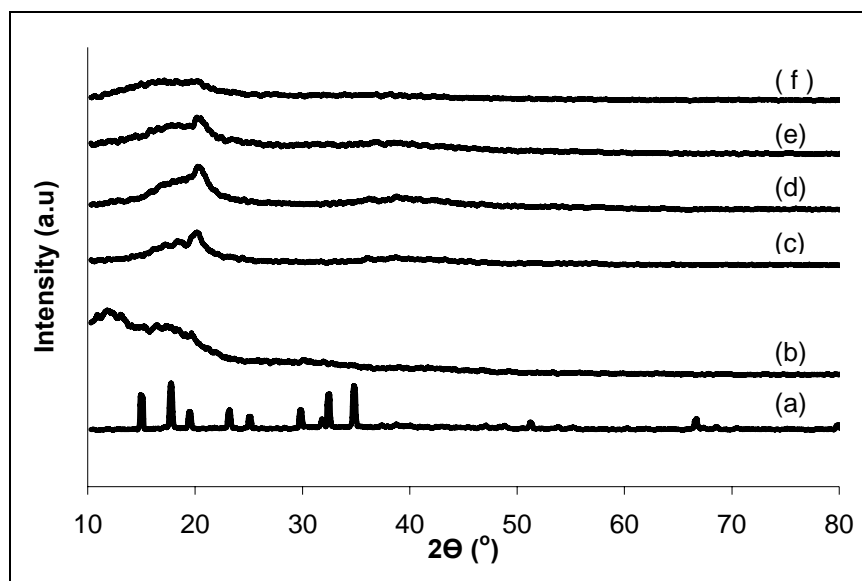


Figure 1: XRD patterns of (a) $\text{NH}_4\text{CF}_3\text{SO}_3$ (b) pure PEMA (c) pure PVDF-HFP (d) PVDF-HFP/PEMA blend (e) PVDF-HFP/PEMA containing 40 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$ (f) PVDF-HFP/PEMA containing 45 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$

SEM analysis

The surface morphology of the PVDF-HFP/PEMA blend, PVDF-HFP/PEMA containing 5 wt % 40 wt % and 45% of $\text{NH}_4\text{CF}_3\text{SO}_3$ are shown in Figures 2(a), (b), (c) and (d) respectively. The image of PVDF-HFP/PEMA blend shows large size of grains distributed quite homogeneously. The size of the grains greatly reduced after addition of 5 wt % of $\text{NH}_4\text{CF}_3\text{SO}_3$. Further increase of salt concentration resulted in further decrease in the size of granule in the polymer electrolytes. This shows the addition of $\text{NH}_4\text{CF}_3\text{SO}_3$ has further disrupted the morphology of the PVDF-HFP/PEMA blend and reduced the degree of crystallinity in the system. This observation is consistent with the results of the XRD study discussed in section 3.1.

Salt concentration and temperature dependence of d.c. conductivity

Figure 3 shows the plot of room temperature conductivity versus ammonium salt concentration for the PVDF-HFP/PEMA blend based electrolyte system. Conductivity of the system increases with increasing salt concentration from $\sim 10^{-9} \text{ S cm}^{-1}$ to $\sim 10^{-4} \text{ S cm}^{-1}$. PVDF-HFP/PEMA system containing 40 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$ shows the highest conductivity of $6.90 \times 10^{-4} \text{ S cm}^{-1}$. The increase in conductivity with increasing salt concentration can be associated to the increase in the number of mobile ion [8] and enhancement of amorphous region as shown by XRD and SEM studies. The conductivity decreases slightly upon the addition of 45 wt % of $\text{NH}_4\text{CF}_3\text{SO}_3$. The decrease in conductivity can be attributed to the aggregation of the dopant ions leading

to the formation of ion clusters and thus decreasing the number of mobile charge carriers [5].

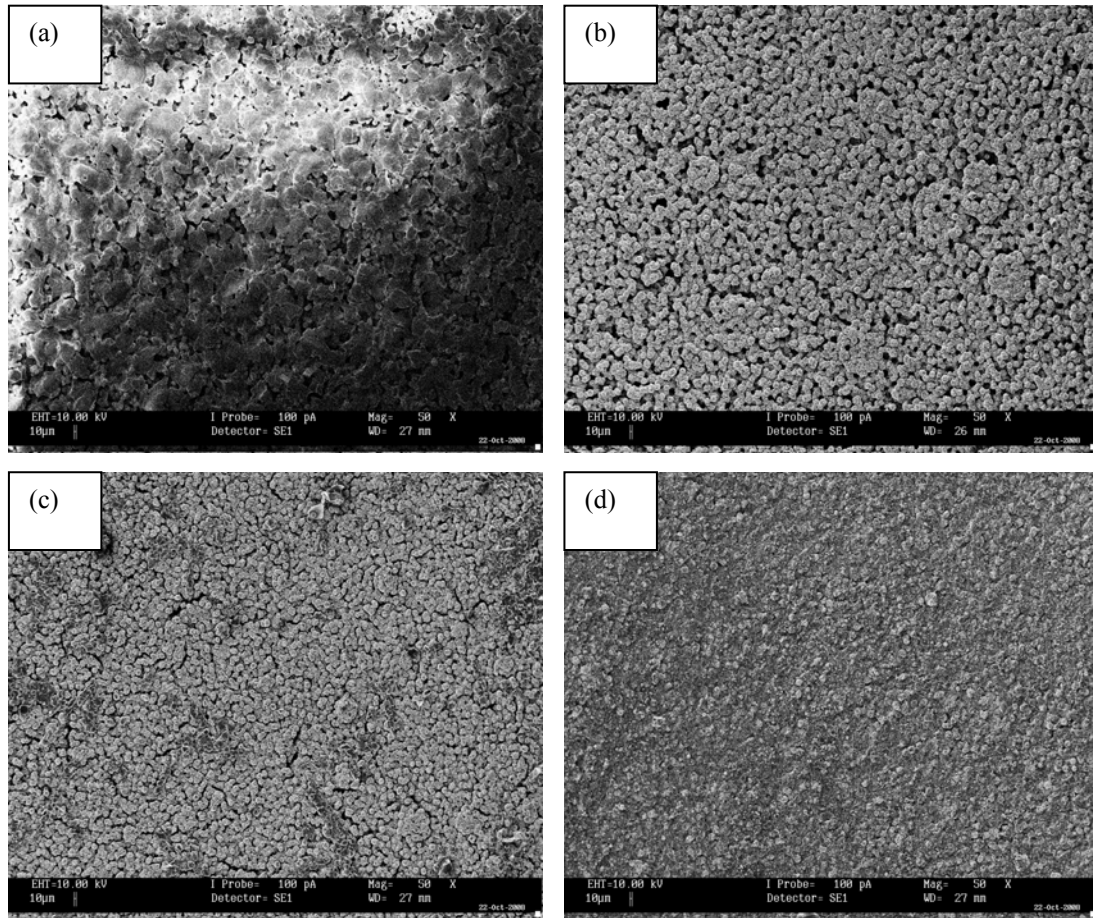


Figure 2: SEM morphology of (a) PVDF-HFP/PEMA blend (b) PVDF-HFP/PEMA containing 5 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$ (c) PVDF-HFP/PEMA containing 40 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$ (d) PVDF-HFP/PEMA containing 45 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$

Figure 4 shows the Arrhenius plot of the PVDF-HFP/PEMA with 40 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$. The conductivity is observed to increase with increasing temperature and obeys the Arrhenius law,

$$\sigma = \sigma_o \exp (-E_a/kT) \quad (3)$$

where σ_o is the pre-exponential factor, E_a is the activation energy of the system and k is the Boltzman's constant. As temperature increases, the polymer expands easily and produces free volume. Ions, solvated molecules or polymer segments can move into the free volume. The increase in free volume leads to the increase in ionic mobility and segmental mobility. This assists ion transport and hence increases the conductivity of the system [3, 9]. The activation energy (a combination of the energy defect formation

and the energy for migration ion) of the system, determined from the slope of the $\log \sigma$ versus $1000/T$ plot, is 0.11 eV.

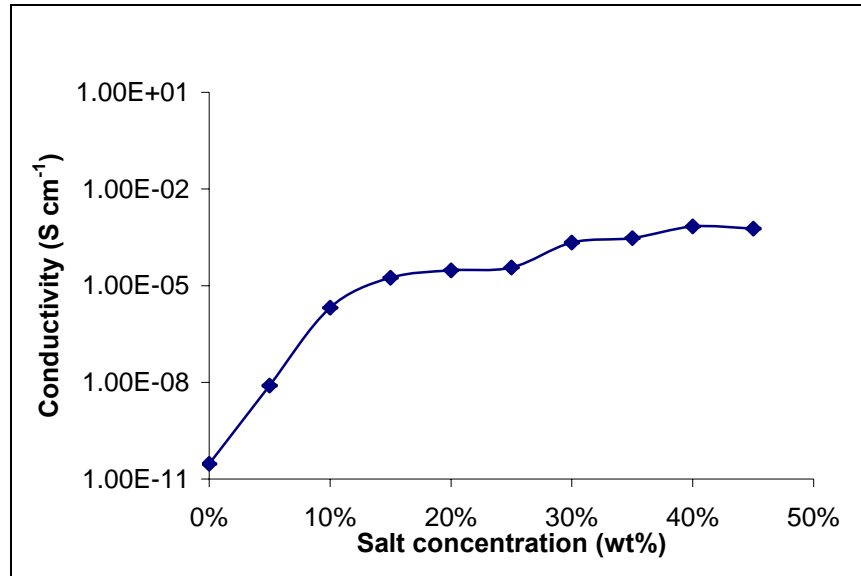


Figure 3: Plot of conductivity versus $\text{NH}_4\text{CF}_3\text{SO}_3$ concentration

Frequency and temperature dependence of a.c. conductivity

The a.c. conductivity for majority of materials increases with frequency and obeys a power law given by

$$\sigma_{ac}(\omega) = A\omega^n \quad (4)$$

where A is a temperature dependent constant and n is a pre-exponent factor with value in the range $0 < n < 1$. The specific transport mechanism for a material can be determined by studying the temperature dependence of n . According to the quantum mechanical tunneling (QMT) model [10, 11], the exponent n is almost equal to 0.8 and increases slightly with increasing temperature or independent of temperature. In the overlapping polaron tunneling (OLPT) model [12, 13], n is both temperature and frequency dependent. n decreases with temperature to a minimum value at a certain temperature then increases with further increase in temperature. The small polaron (SP) model [14] predicts n to increase with temperature whereas in the correlated barrier hopping (CBH) model [15, 16], n is expected to decrease with temperature.

Figure 5 depicts the frequency dependence of a.c. conductivity for the system of PVDF-HFP/PEMA containing 40 wt % of $\text{NH}_4\text{CF}_3\text{SO}_3$ system for different isotherms. The figure clearly shows that the a.c. conductivity increases linearly with frequency and follows the power law given by Eq. (4). The temperature dependent of n shown in Figure 6 shows that the pre-exponent n is between 0.6 to 0.7 and decreases with

temperature. Therefore, it can be concluded that the CBH mechanism is the most probable conduction mechanism for the electrolyte system of PVDF-HFP/PEMA doped with 40 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$. The same conduction mechanism has been identified for the polymer system of PANI-HCL blended with PVA reported by Dutta and coworkers [17].

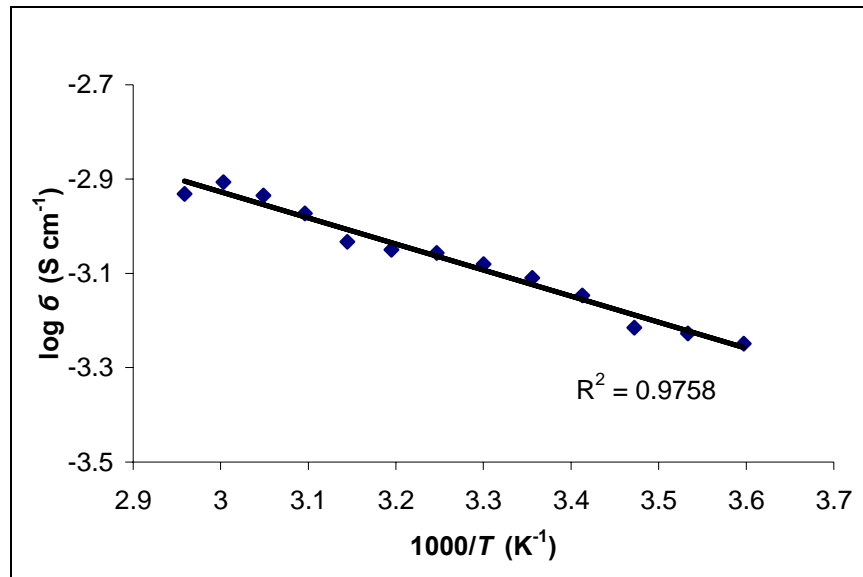


Figure 4: Arrhenius plot for PVDF-HFP/PEMA containing 40 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$.

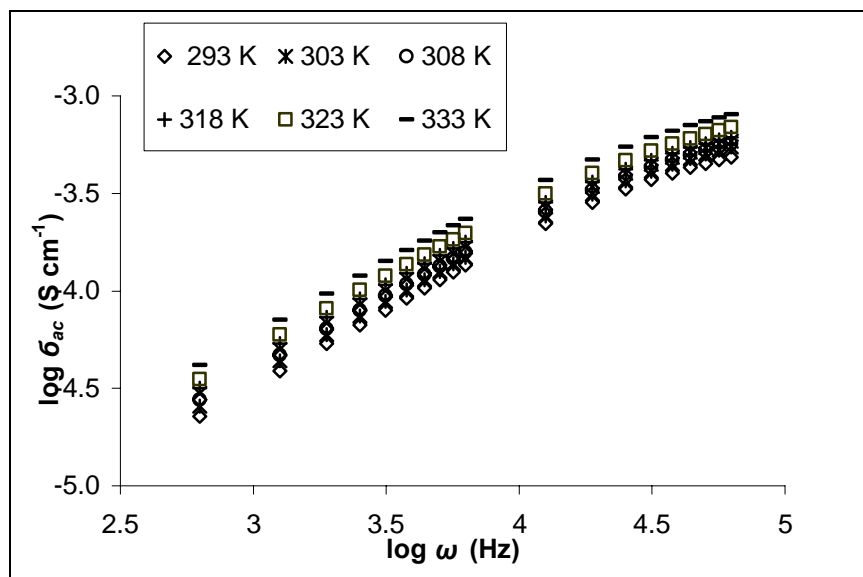


Figure 5: Plots of $\log \sigma_{ac}$ versus $\log \omega$ at various temperatures for PVDF-HFP/PEMA containing 40 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$.

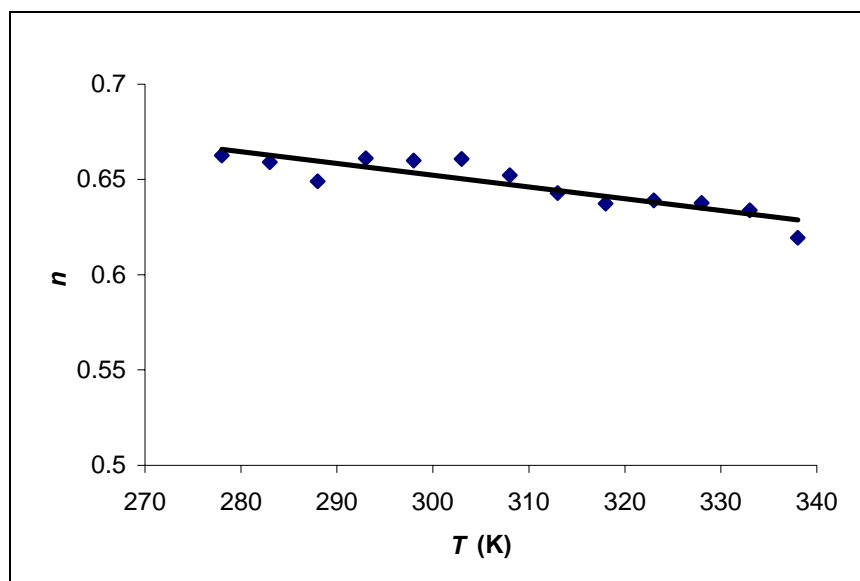


Figure 6: Plots of pre-exponential factor versus temperature for PVDF-HFP/PEMA containing 40 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$.

CONCLUSION

The conductivity of the PVDF-HFP/PEMA/ $\text{NH}_4\text{CF}_3\text{SO}_3$ solid electrolyte system increases with the increase in salt concentration. This is attributable to the increase in the number of ions in the system. The increase in conductivity can also attributed to the increase in the amorphosity as shown by the XRD and SEM studies. The film of PVDF-HFP/PEMA containing 40 wt % $\text{NH}_4\text{CF}_3\text{SO}_3$ exhibits the highest room temperature conductivity. The frequency dependence of a.c. conductivity of this system obeys the $A\omega^n$ power law with n decreases with increasing temperature. The behavior of n indicates that the a.c. conductivity can be interpreted by the CBH model.

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