

## **Highly Ion Conductive PEO based Plasticized Nanocomposite Polymer Electrolytes**

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**ABSTRACT:** Nanocomposite polymer electrolytes were prepared by adding nano-sized fumed silica in optimized composition to polyethylene oxide (PEO) based polymer electrolytes containing ammonium salt. Increase in the ionic conductivity has been observed with the addition of fumed silica concentrations which suggests that the addition of nanoparticles induces the changes in ion transport properties of polymer electrolytes. Further, the addition of high dielectric constant plasticizer in the optimum composition of nanocomposite polymer electrolytes has increased the number of free ions due to dissociation of salt/ion aggregates and hence the ionic conductivity. Maximum conductivity value of the order of  $10^{-4}$  S/cm (at room temperature) has been obtained for optimized sample. Dielectric studies and temperature dependence of ionic conductivity of polymer electrolytes with the addition of fumed silica and PC has also been studied. The variation of  $^1\text{H}$  and  $^{19}\text{F}$  NMR line width with temperature for plasticized nanocomposite polymer electrolyte has studied and it has been observed that a line narrowing has been observed to take place at which diffusion motion of ions starts after glass transition temperature. This new approach of development of plasticized nanocomposite polymer electrolytes with high ion conductivity and improved mechanical properties (as observed visually) may lead to the development of a new generation of polymer nanocomposite electrolytes for technological applications.

**Keywords:** Conductivity; polyethylene oxide; plasticizer; nano-sized fumed silica

### **INTRODUCTION**

Potential applications of polymer electrolytes in polymer batteries, super capacitors, sensors and electrochromic devices have been grown remarkably [1-2]. Polymer electrolytes in film form exhibit a number of advantages over liquid electrolytes, which include chemically compatible with electrode materials, possessing good mechanical strength and flexibility as well as leak free [3]. The major advantages of polymer electrolytes are their good mechanical stability and flexibility, ease of fabrication of thin films of desirable sizes, improved electrode electrolyte contacts and hence enhanced electrical conductivity at ambient temperature [4]. Polyethylene oxide (PEO) has been extensively studied and best candidate to be used as electrolyte in view of ionic conductivity. However, PEO has low ionic conductivity at low room temperature which limits its use in device applications [5-6]. Due to of having its crystalline nature, it hinders ion transportation; therefore various methods have been used to increase ion transportation and its amorphous phase when used as electrolytes. Addition of micro and nano fillers ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$ ) in polymer matrix has become an attractive approach due to the improved mechanical stability and enhanced ionic conductivity of the polymer electrolytes [7-8]. Due to large surface area of nano sized filler, it results in flexibility of the polymer chains for ion migration and hence improves the ion transport properties. Also, plasticization (EC, DMA and PC) has

been observed to reduce the crystallinity and hence increases the amorphous phase of the polymer electrolytes which leads to high conductivity [9-10]. It has also been reported that adding plasticizer not only reduces the crystallinity but also enhances dielectric constant of the polymer, which leads to a higher dissociation of the ions at room temperature [11]. But its presence in excess use has also been observed to deteriorate the mechanical properties of polymer electrolytes [12].

In the present work, efforts have been made to improve the ionic conductivity, dielectric properties of PEO based polymer electrolytes significantly. PEO based polymer electrolytes containing  $\text{NH}_4\text{HF}_2$  have been synthesized and an attempt has been made to improve above properties of PEO-  $\text{NH}_4\text{HF}_2$  polymer electrolytes with the combined effect of fumed silica and PC.

### **MATERIAL AND METHODS**

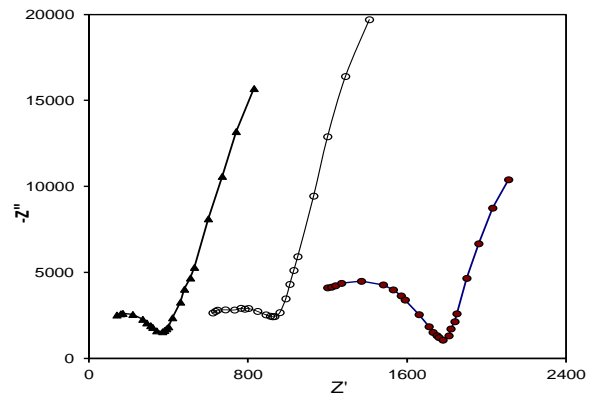
Polyethylene oxide (PEO) (Aldrich, av. mol. wt.= $5 \times 10^6$ ), ammonium bifluoride ( $\text{NH}_4\text{HF}_2$ ) (CDH), fumed silica (Aldrich) with average particle size 7 nm and propylene carbonate (PC) (Merck) have been used as the starting materials for the preparation of polymer electrolytes by solution casting method using methanol as solvent. The stirring of PEO solution was carried out at  $27^\circ\text{C}$  until solution gets well mixed. Desired amount of additives i.e. fumed silica and PC is added in the above samples having optimized proper-

ties. The obtained mixture was again stirred at room temperature until its homogenous mixing. Finally the solution was poured into a Teflon Petri dish and allowed the sample to evaporate slowly at ambient temperature and then dried in an oven at 40°C for 2 days to ensure the removal of the solvent traces. The dried films were then peeled off from the Petri-dish and were stored in desiccator till their further use. The ionic conductivity using Cole-Cole plot and dielectric properties of polymer electrolytes were measured by complex impedance spectroscopy using computer interfaced Hioki 3532-50 LCR meter. The conductivity of different polymer electrolytes at different temperatures in the 30-100°C temperature range was measured by keeping the sample holder containing polymer electrolyte in a temperature controlled furnace. <sup>1</sup>H and <sup>19</sup>F NMR measurements at different temperatures were carried out by a home-made pulsed spectrometer at 6.4 T with a corresponding Larmor frequency of 270.10 MHz and 254.12 MHz respectively.

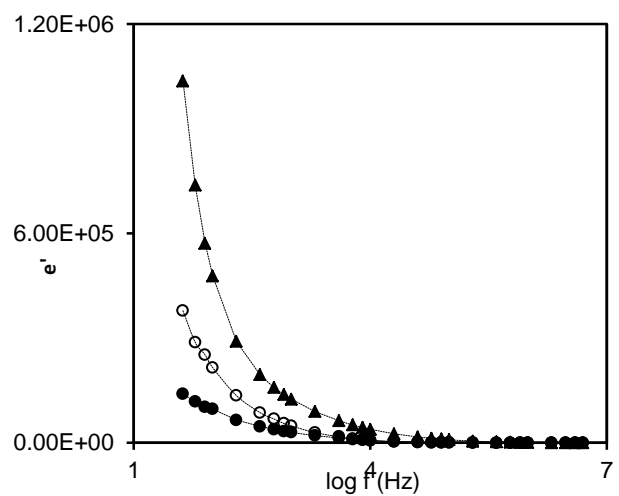
**RESULTS AND DISCUSSION**

Fig. 1 shows Cole-Cole plot of Re. Z vs. Im. Z for PEO-10 wt% NH<sub>4</sub>HF<sub>2</sub>, PEO-10 wt% NH<sub>4</sub>HF<sub>2</sub> containing 3 wt% fumed silica and 3 wt% fumed silica-0.3 ml PC polymer electrolytes. Semicircle observed in the high frequency region is due to the bulk effect of the electrolytes and linear region in the low frequency range is attributed to the effect of the blocking electrodes. The ionic conductivity of polymer electrolytes has been obtained by using the relation  $\sigma=L/R_bA$ , where L is the thickness, R<sub>b</sub> is bulk resistance, and A is the cross-sectional area of polymer electrolyte film. The maximum conductivity achieved was 1.55 × 10<sup>-4</sup> S/cm in case of plasticized nanocomposite polymer electrolytes containing 3 wt% fumed silica and 0.3 ml PC.

It is observed that at low frequency, the dielectric constant is relatively high and decreases with increase in frequency. The low frequency region is attributed to the high contribution of charge accumulation at the electrode-electrolyte interface and high frequency region is observed to have almost constant value of dielectric constant. Also, incorporation of fumed silica and PC in polymer electrolyte has been observed to increase the values of dielectric constant at room temperature. The increase in the values of dielectric constant with the addition of fumed silica and PC can be attributed to the creation of more conducting pathways resulting in an increase in chain flexibility and increase in charge carrier density which results in an increase in ionic conductivity.

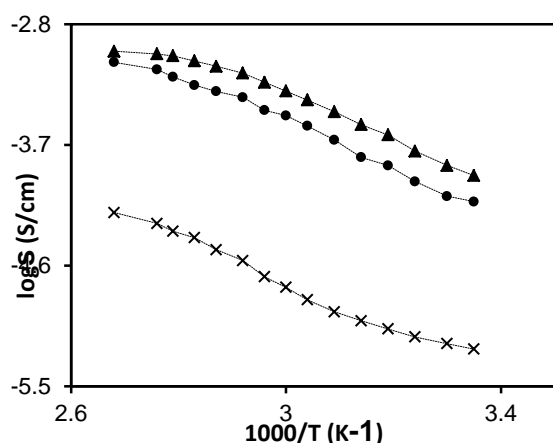


**Figure.1. Cole-Cole plots for PEO-10 wt% NH<sub>4</sub>HF<sub>2</sub> (●) containing 3 wt% fumed silica (○) and 3 wt% fumed silica-0.3 ml PC (▲) polymer electrolytes.**



**Figure2. Variation of dielectric constant (ε') as a function of log of frequency for PEO-10 wt% NH<sub>4</sub>HF<sub>2</sub> (●), PEO-10 wt% NH<sub>4</sub>HF<sub>2</sub>-3 wt% fumed silica (○) and PEO-10 wt% NH<sub>4</sub>HF<sub>2</sub>-3 wt% fumed silica-0.3 ml PC (▲) polymer electrolytes**

The variation in the ionic conductivity with reciprocal temperature in the temperature range 25-100°C of polymer electrolytes containing 3 wt% fumed silica and PEO-10 wt% NH<sub>4</sub>HF<sub>2</sub>-3 wt% fumed silica-0.3 ml PC has been studied and results are compared with the conductivity results of unplasticized polymer electrolyte as shown in Fig. 3 and Table I. As temperature increases, the ionic conductivity of different polymer electrolytes also increases which is due the expansion of polymer producing free volume and hence leads to enhanced ionic mobility and polymer segmental motion.



**Figure 3: Variation of log conductivity with reciprocal temperature for PEO-10 wt% NH<sub>4</sub>HF<sub>2</sub> (x) containing 3 wt% fumed silica (•) and PEO-10 wt% NH<sub>4</sub>HF<sub>2</sub>-3 wt% fumed silica-0.3 ml PC (▲) polymer electrolytes**

**Table 1 Conductivity of different polymer electrolytes**

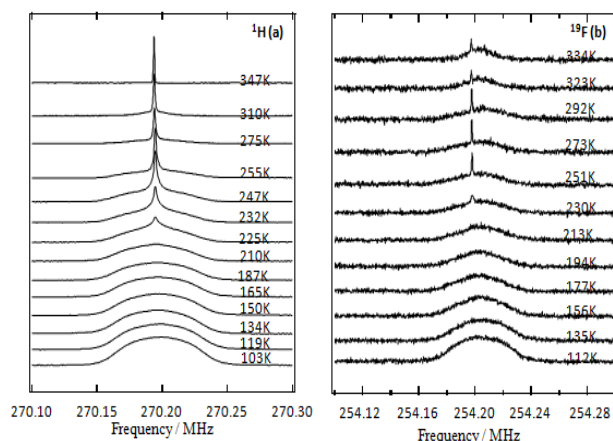
Polymer Electrolyte	Conductivity (S/cm)			
	27°C (RT)	50°C	65°C	80°C
PEO-10 wt% NH <sub>4</sub> HF <sub>2</sub>	5.96x 10 <sup>-6</sup>	1.13 x 10 <sup>-5</sup>	2.07 x 10 <sup>-5</sup>	4.05 x 10 <sup>-5</sup>
PEO-10 wt% NH <sub>4</sub> HF <sub>2</sub> -3 wt% fumed silica	1.19x 10 <sup>-5</sup>	2.43 x 10 <sup>-5</sup>	3.83 x 10 <sup>-5</sup>	5.05 x 10 <sup>-5</sup>
PEO-10 wt% NH <sub>4</sub> HF <sub>2</sub> -3 wt% fumed silica-0.3 ml PC	1.55x 10 <sup>-4</sup>	3.78 x 10 <sup>-4</sup>	5.22 x 10 <sup>-4</sup>	7.19 x 10 <sup>-4</sup>

lytes

The conductivity of unplasticized polymer electrolyte increases non-linearly at the melting temperature (65°C), which is due to transition from the semicrystalline to elastomer phase. Reduction in the above transition in polymer electrolytes containing fumed silica and PC is believed to have predominant phase in amorphous rich polymer electrolytes. A small change in conductivity with temperature variation along with the curved nature of the graph for plasticized polymer electrolytes containing fumed silica and PC suggests VTF behavior of these electrolytes.

The variation of <sup>1</sup>H and <sup>19</sup>F NMR linewidth with temperature for plasticized nanocomposite polymer electrolyte has been shown in Fig. 4. At low temperatures, broadened line width of <sup>1</sup>H and <sup>19</sup>F NMR line along with a line narrowing at higher temperatures has been observed. The line narrowing is generally occurring after the glass transition temperature (T<sub>g</sub>) of polymer

electrolytes at which diffusion motion of ions starts. Line narrowing has also been observed by different authors previously for <sup>7</sup>Li and <sup>1</sup>H spectra in other polymer electrolytes [13-14]. This study is very helpful in determining the nature of mobile species whether both cations and anions are mobile in these polymer electrolytes.



**Figure 4 <sup>1</sup>H (a) and <sup>19</sup>F (b) NMR spectra with temperature for PEO-NH<sub>4</sub>HF<sub>2</sub>-fumed silica-PC polymer electrolyte.**

### CONCLUSIONS

Ion transport properties (conductivity and dielectric) of PEO-NH<sub>4</sub>HF<sub>2</sub> polymer electrolytes with the addition of nano sized fumed silica and high dielectric constant plasticizer (PC) have been studied. It was observed that ionic conductivity of polymer electrolytes containing both the above additives is more as compared to others which is due to increase in both the amorphous phase and dielectric constant of PEO. Maximum ionic conductivity of 1.55x10<sup>-4</sup> S/cm at room temperature has observed in case of polymer electrolytes containing optimum concentration of fumed silica and PC. The variation of log conductivity with reciprocal temperature revealed curved nature of graph in case of plasticized nanocomposite polymer electrolytes which suggests VTF behavior. Line narrowing associated with the increase in temperature has been observed in case of polymer electrolytes using <sup>1</sup>H and <sup>19</sup>F NMR.

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