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INVESTIGATION OF STRUCTURAL AND DIELECTRICAL PROPERTIES OF SOLID POLY (VINYLIDENE DIFLUORIDE-CO-HEXAFLUOROPROPYLENE) POLYMER FILM FOR ELECTRO CHROMIC DEVICE APPLICATIONS

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Abstract— An electrolyte for electro chromic device applications was prepared by simple solution cast method. The incorporation of functionalized Alkali metal (NaCl) into poly (vinylidene fluoride-co-hexafluoropropylene): Titanium dioxide (TiO₂) in the ratio of 80:5 provided an enhanced dielectrical and structural properties. The casting solution, effects of the solvent and non-solvent in addition of nano scale TiO₂ particles and Alkali metal (NaCl) complexes were investigated in this study. After annealing of the PVDF-co-HFP/ TiO₂ and AM samples at 160°C, the FTIR study showed many spectral changes including the spectral shift to high wavenumbers and the appearance of new peaks. These spectral changes indicate increasing of crystallinity, strong molecular bonds, and some crystal phase transitions. XRD results showed the change in the crystalline phase of PVdF-co-HFP electrolyte with the addition of surface modified TiO₂ and Alkali metal (NaCl). The effect of the TiO₂ nanoparticles and Alkali metal (NaCl) surface functionality on the degree of crystallinity of the polymer matrix was analyzed using TGA, scanning electron microscopy (SEM) results the surface morphology and porous nature of the fabricated membrane. The particular polymer electrolyte specimen having 15 wt% Alkali metal (NaCl) exhibited the large values of dielectric constant ϵ' in the low frequency region may be due to an enhanced level of storage of charge carriers at the electrolyte-electrode interface thereby resulting in an increase in the equivalent capacitance. Results show that tends to confirm that the best conducting sample with 15 wt% Alkali metal (NaCl) would possess the maximum number of charge carriers among the five different compositions of NCPE system considered during the present endeavor.

Keywords— PVDF-co-HFP, Dielectrical properties, XRD, TiO₂ nanoparticles, TGA, SEM, X-ray (EDX) analysis.

I. INTRODUCTION

Polymer electrolytes had played an important role in solid state Ionics because of their potential importance in the development of solid state polymer batteries, electrochemical sensors and electro chromic devices[1], Electro chromic devices (ECDs) are generally composed of an electrolyte, electro chromic layer, counter electrode and electrical conductors. Electrolytes and electro chromic materials are the most important and active components of an electro chromic device. These polymer electrolytes play a very essential role as the primary medium for ionic conduction in the ECD and it can be in the form of a liquid, gel or solid Among these types of polymer electrolyte systems, solid polymer electrolytes (SPEs) have many advantages such as high ionic conductivity, high-energy density, leak proof, solvent-free condition, wide electrochemical stability windows, easy process ability and lightweight. Many attempts have been made in recent years on the development of different solid polymer compositions of alkali metal salts based on their above superior attributes. The Alkali metal (AM) coordinated complexes in polymer hosts are used for numerous practical applications. Interactions between alkali metal ions and polymers have been displaying significance influence of the behavior of the polymers and their new properties. Nafion is the major proton conducting polymer electrolyte used to fuel cell applications because of its high proton conductivity, excellent mechanical and thermal stabilities. But Nafion membranes are high cost, hard to synthesize and it causes environmental problems, Nowadays there has been some effort to develop high proton conductivity in solid polymer electrolytes to replace Nafion, in order to deal with the afore said difficulties of proton



conducting polymer electrolytes various researches and commercialization activities have been activated with Nano composites polymer Electrolytes [NCPEs], specially PVDF-co-HFP polymer can be used as a proton exchange membrane due to its excellent mechanical strength, chemical resistance and thermal stability. And also it is known to be photo chemically stable even in the presence of TiO₂ and Pt, which confirms the suitability in NCPEs for long term stability outdoor applications,

The aim of this research is to evolve new polymer nan composites (Pvdf-co-Hfp) loaded with different content of TiO₂ Nanoparticles and alkali metals for used in various applications, To the better of our knowledge there has been no previous study of proton conducting polymer based on PVdF-co-HFP and Titania sulfuric acid with alkali metal. Hence, an attempt is made to study the influence of TiO₂ and AM on the dielectric properties of (TiO₂-PVdFco-HFP-AM) Nano composite polymer electrolyte films for Electro chromic device applications.

II. EXPERIMENTAL PROCEDURE–

A. Materials used

The host polymer, namely PVDF-co-HFP (weight-average molecular weight (M_w) 400,000, Sigma Aldrich, and ionic dopant, namely, NaCl(AM) (M_w 363.53 g mol⁻¹, Sigma Aldrich), Nano filler TiO₂ (>100 nm, Sigma Aldrich), and N,N-dimethyl formamide (DMF; Sigma Aldrich) were used as starting material for the Nano composite polymer electrolytes (NCPEs) preparation, All the materials described above were used directly without any further modification or treatment.

B. Nano composite polymer electrolyte preparation

The PVdF-co-HFP+NaCl+TiO₂-based Nano-composite polymer electrolyte films (NCPEs) were made by a simple solvent casting technique, PVDF-co-HFP: TiO₂ was kept fixed as 80: 5 during the course of preparation of specimens by in this solution casting technique. The homogenous solution of 80 PVDF-co-HFP: 5 TiO₂ complexes was thus maintained using DMF as the common solvent into which appropriate amounts of NaCl salts were also subsequently dispersed. The resulting solution mixture was cast into clean glass petri dishes and dried in a vacuum oven at 50 °C for 12 h in order to remove any traces of DMF. All those specimens belonging to the polymer electrolyte system, 80 wt% PVDF-co-HFP: 5 wt% TiO₂ + x wt% NaCl (when x = 0, 5, 10, and 15 respectively) derived after the complete removal of DMF, This procedure yielded mechanically stable, freestanding, and flexible films, this films were subsequently stored in a vacuum desiccator for 24 h prior to their systematic characterization studies.

C. Characterization

Dielectric parameters were measured using PC-based Precision Impedance Analyzer (Model 6500B) with PID temperature controlled having a frequency range of 40 Hz to 1 MHz and temperature range of 303 to 323 K. The films were examined under scanning electron microscope (SEM) (ZEISS EVO18) for their morphological properties. X-ray diffraction (XRD) patterns of NCPE films were recorded at room temperature in an X-ray diffractometer (Bruker AXS, model D8 advance) using Cu-K α radiation (λ = 0.154 nm) with a scan rate of 0.3° /s and a step size of 0.02° over the 2 θ range of 10° -70°. The FTIR spectra were recorded using IRPrestige-21 (Shimadzu) spectrophotometer over the wavenumber range of 4000–400 cm⁻¹. Thermo-gravimetric analysis (TGA) of synthesized NCPEs was also performed using a NETZSCH STA 409 PL analyzer, in the temperature range from 25 °C to 500 °C at constant heating rate of 10 K/min under a dynamic dry nitrogen atmosphere with a view to determine the extent of thermal stability of the typical sample.

III. RESULTS AND DISCUSSION

A. FTIR analysis

FTIR spectroscopy is a powerful tool for identification of functional groups present in the organic compounds. The FTIR spectra of TiO₂ Nano ceramic filler, PVdF-co-HFP:NaCl (80:20) and different concentrations of nano ceramic fillers dispersed Nano composite polymer electrolyte films are shown in Fig 4.2. The vibrational bands observed at 1453 cm⁻¹, 1321 cm⁻¹, 1121 cm⁻¹ are ascribed C-H bending of CH₂, C-H wagging, C-C stretching vibrations, these bands shifted to addition of TiO₂ nano particles. Some new bands at 2890 cm⁻¹, 1239 cm⁻¹ are observed and 425 cm⁻¹ band is disappeared with the addition of TiO₂ nanoparticles. IR studies confirm

Interactions involving filler added i.e. polymer–salt interactions are weekend upon the addition of inorganic fillers. The filler Salt polymer interactions seem to occur when the Nano ceramic filler TiO₂ is used as an additive. From the figure it was found that the intensity of some bands in PVdF-co-HFP:NaCl complex decreases with increase of TiO₂ Nano ceramic particles in polymer matrix. This result suggests that the competition between nano filler TiO₂ and anions with respect to Na⁺ ions. Especially at high salt concentrations the addition of filler results in the breaking of the cross links formed between polymeric chains, most probably due to the interaction of filler molecules with iodide ion.

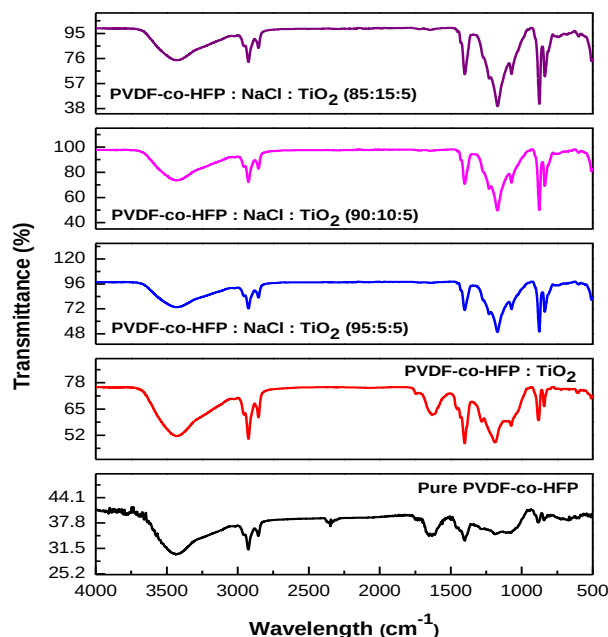


Fig 1. FTIR spectra of (A) PVDF-co-HFP copolymer and (B) Electrolyte filled PVDF-co-HFP solid membrane

B.SEM analysis of PVDF-co-HFP-NaCl-TiO₂ membranes:

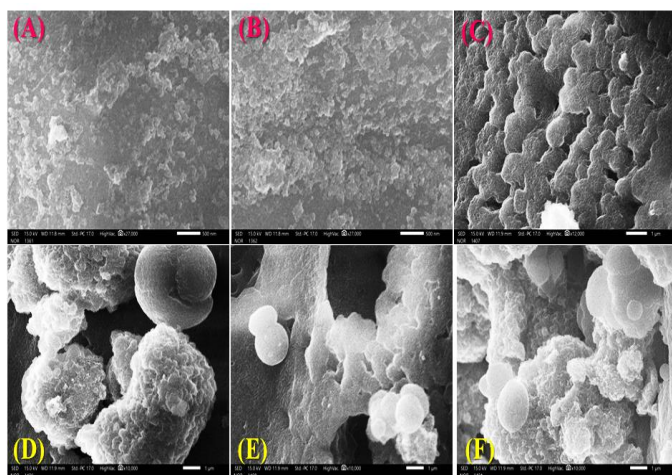


Fig 2. SEM images of PVDF-co-HFP membranes before filling with (A, B & C); after filling with NaCl and TiO₂ (D, E & F) with different magnifications.

The appropriate microstructural and morphological characteristics of pure PVDF-co-HFP and the best conducting NCPEs, having X (0, 2, 4, 6) wt% TiO₂ have been carefully

examined by scanning electron microscopy. Accordingly, Figs. 8(a), 8(b) and 8(c) show the SEM micrographs of pure PVDF-co-HFP sample and its cross sectional view respectively. In the case of 80[PVDF-co-HFP]:20 [NaCl]:X(0,2,4,6) wt% TiO₂ system the inter-granular structure of grains is found to be more tightly-packed than in the case of pure PVDF-co-HFP film. It is well known that PVDF-co-HFP which is essentially a semi-crystalline polymer in nature and forms a freestanding translucent film, its morphology shows the presence of many spherical grains [24]. From Fig. 8(b) it is evident that loading of TiO₂ Nano filler would have resulted in an improved morphology since the filler particles may occupy existing pores and hence such a pore distribution over the surface layer of the polymer electrolyte would become denser with an increase in the filler content. The observed tightly-packed structure of grains also indicates the presence of Nano sized TiO₂ particles within the polymer network as a separate phase. Moreover, it is interesting to note from Fig. 8 that the modified morphology and texture of the Nano composite polymer electrolyte system may be responsible for the occurrence of reduction in both crystallite- and pore- size [23]. The changes witnessed as a result of loading of X wt% TiO₂ material also indicate the existence of compatibility between the chosen filler and polymer matrix.

C. X-ray diffraction analysis:

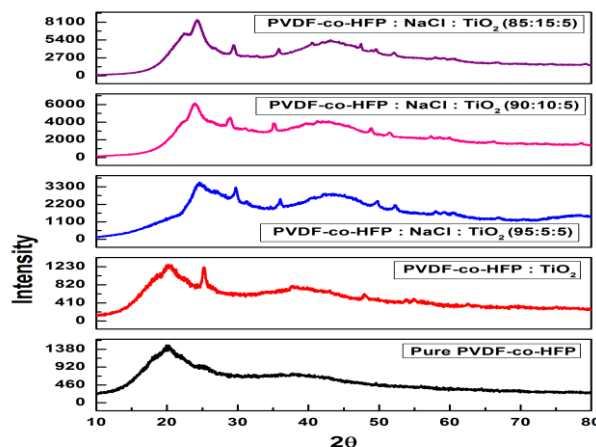


Fig. 3. XRD spectra of (A) PVDF-co-HFP- membrane before filling and (B) after filling with TiO₂ Nano powder.

The X-ray diffraction patterns of PVDF-co-HFP: NaCl, Nano ceramic powder TiO₂ and different concentrations of Nano filler dispersed Nano composite polymer films are shown in fig 3. A comparative study of XRD patterns of PVDF-co-HFP: NaCl, nano ceramic powders and Nano composite polymer electrolyte films reveals the following. From fig. 3, it is clear



that a peak around 23.68° is found in the XRD pattern of PVDF-co-HFP: NaCl (85:15). When Nano ceramic filler is added to PVDF-co-HFP: NaCl complex, the intensity of this peak decreases. As the wt% of Nano filler increases the intensity of PVDF-co-HFP diffraction peak weakens, suggesting that the interaction between PVDF-co-HFP chains and Nano filler particles which lead to the decrease of intermolecular interaction of PVDF-co-HFP chain there by resulting the increase in the amorphocity of PVDF-co-HFP. This facilitates significant motion of Polymer chain in the amorphous phase or some defects and free volumes existing at interface of polymer phase. The XRD patterns of nano ceramic powder shows intensive sharp peaks, which indicates its crystalline nature. The observed peaks are well matched with the JCPDS card no: 43-1481, which confirms TiO_2 is rhombohedra system. The average particle size of Nano ceramic filler in different compositions of composite electrolytes has been calculated by the Scherrer formula [21], and it was found to be 17 nm. As the Nano filler concentration increases the peaks corresponding to the nano filler become prominent as observed in fig 3. Some of the crystalline peaks pertaining to TiO_2 are found to disappear and some peaks are shifted in the composites indicates the involvement of Nano ceramic filler particles in disrupting the structure (or) interaction between constituents of the polymer complex. Persistence of crystalline peaks of Nano ceramic fillers in the Nano composite polymer films suggesting the presence of undisclosed Nano filler particles in the polymer matrix. Similar type of behavior was observed by many researchers [22, 23].

D. Thermo gravimetric analysis (TGA):

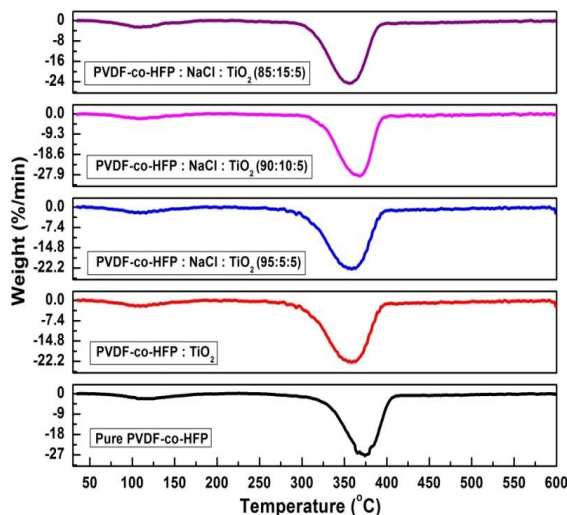


Fig.4. TGA curves of PVDF-co-HFP solid polymer membrane, NaCl and TiO_2 Nano powder filled film.

Subsequently, TGA analysis was used in an investigation of the decomposition pattern and the thermal stability of TiO_2 nanoparticles, and the results are listed in Fig 4. In these curves, the first stage of weight loss is noticed nearly at 100°C , which could be attributed to the evaporation of physically-trapped and chemically-bonded water. The pristine PVDF-co-HFP shown in Fig. 4(a) displays a slight weight loss of about 3% between 300°C and 400°C due to the loss of hydroxyl groups in TiO_2 . However, the PVDF-co-HFP: NaCl in Fig. 4(b) exhibits a weight loss of about 13.7% at the same condition. Comparing Fig. 4(b) with 4(c), the decomposition temperature of PVDF-co-HFP: NaCl/ TiO_2 was consistent with that of PVDF-co-HFP: NaCl, which further confirmed the successful grafting of PVDF-co-HFP: NaCl on the surface of TiO_2 nanoparticles and the weight loss was mainly due to the thermal decomposition of the grafted PVDF-co-HFP: NaCl. The results also suggested that the grafting ratio of PVDF-co-HFP: NaCl was approximately 10.7%.

E. Dielectric Behavior:

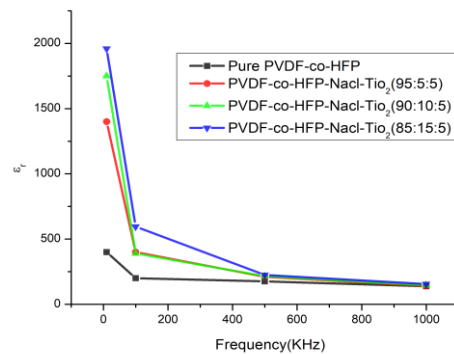


Fig. 5 Variation of dielectric constant as a function of frequency obtained for NCPEs containing four different amounts of NaCl (wt%) alkali metal at room temperature (298 K)

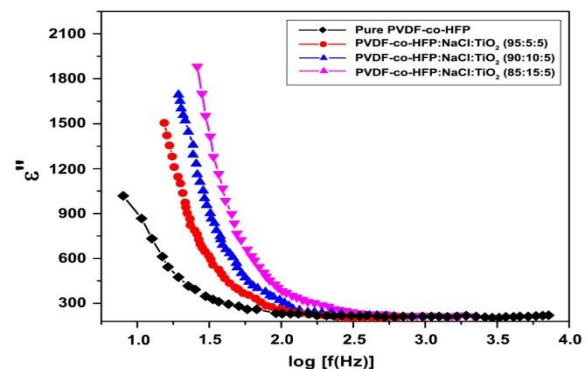




Fig. 6 Variation of dielectric loss ϵ'' with frequency observed for NCPEs having four different amounts of NaCl (wt %) alkali metal at room temperature (298 K).

Dielectric Behavior It is well known that electrical conductivity (σ) depends on both the number of charge carriers and their mobility as, $\sigma = \Sigma ne\mu$ where n denotes the number of charge carriers, e the electronic charge and μ is the mobility of charge carriers. Figure 2 shows the variation of dielectric constant ϵ' of NCPE samples as a function of frequency. The value of dielectric constant ϵ' increases when the content of TiO₂ Nano filler is raised from 0 wt% to 6 wt% at ambient temperature (298 K) as revealed from Fig. 2. This aspect may be explained on the basis of the fact that the value of dielectric constant is directly related to the number density of charge carriers. In order to understand the dielectric behavior of NCPEs in terms of the dielectric components the relevant expression is given as, $\epsilon^* = \epsilon' - j\epsilon''$ where ϵ' represents dielectric constant and ϵ'' denotes dielectric loss. It is noted that the value of dielectric constant decreases with increasing frequency. The occurrence of large values of ϵ' for the typical sample having 4 wt% TiO₂ in the low frequency region may be due to an enhanced level of storage of charge carriers at the electrolyte-electrode interface thereby resulting in an increase in the equivalent capacitance. At the high frequency region, owing to the fast periodic reversal of the applied electric field there may not be any feasibility of having excess ions available to diffuse along the direction of the electric field and therefore the effective contribution towards the observed dielectric constant may decrease accordingly. At a particular frequency of 10 kHz, the fact that the value of dielectric constant observed for NCPEs having five different amounts of TiO₂ Nano fillers viz., 0 wt%, 2 wt%, 4 wt% and 6 wt% at room temperature (298 K) as shown in Fig. 2 reaches the maximum tends to confirm that the best conducting sample with 6 wt% TiO₂ Nano filler would possess the maximum number of charge carriers among the four different compositions of NCPEs system considered during the present endeavor. Furthermore, Fig. 3 shows the dependence of dielectric loss (ϵ'') observed as a function of frequency for the above Nano composite polymer electrolyte samples having four different TiO₂ filler concentrations of 0 wt%, 2 wt%, 4 wt%, and 6 wt at room temperature. Both dielectric constant (ϵ') and dielectric loss (ϵ'') are found to decrease with increasing frequency as evidenced from Figs. 2 and 3. Since dielectric loss ϵ'' is usually measure of energy dissipated, the observed variation of ϵ'' in the case of four different NCPEs with frequency as presented in Fig. 3 may be explained as follows. During the course of AC impedance measurements, as the polarity reverses, the diffusion of ions and orientation of dipoles may be reversed by the successive processes of deceleration and acceleration. Such polarized ions would be expected to overcome the reverse process thus resulting in an energy loss in the form of heat by the internal friction. At the

low frequency region, the dielectric loss becomes very large in view of the fact that the applied alternating field makes these charges to oscillate freely within the NCPEs. At the high frequency region, these ions may not be able to realign themselves in the direction of the applied electric field and hence the electrode polarization would decrease.

IV. CONCLUSION

In nutshell, we have prepared a new system of Nano composite polymer electrolyte having Sodium ion as conducting species with highest conductivity for ECD of NCPE i.e. 80PVDF-co-HFP: 15NaCl:5 TiO₂ is 1.41×10^{-4} S/cm at 33 °C with lowest activation energy(0.40), have been prepared by solution casting method. The XRD study reveals the encapsulation of salt by polymer and some degree of crystallinity. The complex formation in PVdF-co-HFP- TiO₂-NaCl has been confirmed from the FTIR studies. The amorphous phase is responsible for the conduction of ions which take place through the matrix of PVdF-co-HFP, which is revealed by TGA analysis. The Nano-in-polymer electrolytes prepared from the PVdF-co-HFP matrix shows a strong enhancement of both dielectric constant (ϵ') and dielectric loss (ϵ'') are found to decrease with increasing frequency by the addition of NaCl alkali metals. The ionic conductivity of the resulting polymer electrolyte with Nano filler and alkali metal is better than the polymer electrolyte. The polymer composite electrolyte containing TiO₂ Nano filler retains the low crystallinity, amorphous phase regions, less dielectric constant and stable interfacial properties, indicating a possible application in Electro chromic devices

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