

Compositional Effect of ZrO₂ Nanofillers on a PVDF-*co*-HFP Based Polymer Electrolyte System for Solid State Zinc Batteries^{*}

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Abstract Composite polymer electrolytes (CPEs) comprising poly(vinylidene fluoride-hexafluoro propylene), PVDF-*co*-HFP and zinc triflate, Zn(CF₃SO₃)₂ with varying concentrations of ZrO₂ nanofillers were prepared by solution casting technique with *N,N*-dimethyl formamide (DMF) as the common solvent. The polymer electrolyte specimen with the particular composition 75 wt% PVDF-*co*-HFP: 25 wt% ZnTf + 7 wt% ZrO₂ showed the highest conductivity of 4.6×10^{-4} S/cm at 298 K as confirmed from impedance measurements and favored by the rich amorphous phase of the CPE revealed from room temperature X-ray diffraction analysis (XRD). The electrical conductivity relaxation time and its distribution within the materials have been evaluated from the electric modulus M'' and impedance Z'' data which showed the occurrence of non-Debye type of relaxation phenomenon. The changes in the surface morphology of the CPEs were examined using scanning electron microscopy (SEM). The electrochemical stability window of CPE is found to be 2.6 V with a thermal stability up to 300 °C. An electrochemical cell has been fabricated based on Zn/MnO₂ electrode couple under a constant load of 1 MΩ and its discharge characteristics have been evaluated.

Keywords: Nanocomposites; Dielectric properties; Thermal stability; Electrochemical stability; Batteries.

INTRODUCTION

Polymer solid electrolytes, based on solid-state coordination compounds have received considerable attention owing to their applications in several electrochemical devices such as high energy density batteries, super capacitors, fuel cells and sensors as promising electrolyte materials at ambient conditions^[1, 2]. The category of solid polymer electrolytes systems is often preferred in place of traditional liquid electrolytes by various researchers due to certain significant features like high ionic conductivity at room temperature, good mechanical properties, geometrical flexibility, ease of thin film formation, *etc.* The most common polymer host employed in the field of polymer electrolytes namely, poly(ethylene oxide) (PEO) suffers from a major drawback involving a very low value of conductivity at room temperature^[3–5]. As a result, numerous approaches including the addition of inorganic fillers have been employed in order to synthesize nano composite polymer electrolytes, and plasticized electrolytes possessing appreciably high conductivity values with improved electrochemical and physical properties^[4, 6–12]. Among various polymer host systems including poly(methyl methacrylate) (PMMA), poly(vinylidene fluoridehexafluoro-propylene) (PVDF-*co*-HFP), poly(acrylo nitrile) (PAN), poly(vinyl chloride) (PVC)^[13, 14], PVDF-*co*-HFP has now been considered as a polymer host during the present investigation due to its appreciably high dielectric constant. On the other hand, it is worthwhile to mention that as compared to salts based on lead, lithium, magnesium or cadmium, an appropriate salt based on zinc would play a vital role as an

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efficient dopant salt owing to the fact that zinc is basically a non-toxic, abundant and low-cost resource and hence may provide a good alternative for eco-friendly and safer batteries as well^[15]. With a view to further strengthen the mechanical stability of the chosen polymer host, inorganic nanofillers of ZrO₂ were also incorporated to obtain the configuration of PVDF-co-HFP-salt-nanofiller composite polymer electrolyte (CPE) matrix as the nanocomposite polymer electrolyte system. Now-a-days even though the primary interest of researchers is usually towards search for highly conducting materials, it is also essential to probe the prevailing conductivity mechanism and dielectric characteristics of such materials. Based on the literature reported earlier it is evident that frequency-dependent conductivity data are perceptible to the mobile charge species^[16, 17]. Therefore, detailed dielectric relaxation and frequency response analyses on the system under investigation by means of dielectric studies apart from structural characterization using X-ray (XRD), and thermal gravimetric analysis (TGA) have been undertaken. Furthermore, it is intended to perform electrical conductivity studies by means of impedance spectroscopy and evaluation of their surface morphology on the basis of scanning electron microscopic (SEM) results.

Interestingly, the present endeavor aims at synthesis of a series of CPEs consisting of PVDF-co-HFP and ZnTf with varying concentrations of ZrO₂ nanofillers and their characterization involving complex impedance spectroscopic analysis with a view to understand the effect of incorporation of ZrO₂ nanofillers into the polymer-salt matrix on various physico-chemical properties of the chosen polymer electrolyte system, PVDF-co-HFP: ZnTf + ZrO₂. Finally, it is desired to design a prototype solid state zinc battery configuration and evaluate its discharge features as well.

Materials and Methods

The host polymer, namely poly(vinylidene fluoride-hexafluoro propylene), PVDF-co-HFP (M_w –400000, Sigma Aldrich) and dopant salt, ZnTf (M_w –363.53, Sigma Aldrich), nano powder ZrO₂ (< 100 nm, Sigma Aldrich) and *N,N*-dimethyl formamide, DMF (Sigma Aldrich) were used as procured. To start with, based on the observed room temperature electrical conductivity values and mechanical stability of freshly-prepared thin film specimens of PVDF-co-HFP/ZnTf complex the optimized molar ratio of salt and polymer host in the case of the chosen polymer electrolyte system, PVDF-co-HFP:ZnTf was kept fixed as 75:25 during the course of preparation of specimens by solution casting technique. The homogenous solution of 75 PVDF-co-HFP:25 ZnTf complex was thus maintained using DMF as the common solvent into which appropriate amounts of ZrO₂ nanoparticles were also subsequently dispersed. The resulting solution mixture was cast into glass petri dishes and dried in a vacuum oven at 60 °C for 12 h in order to remove any traces of DMF. All those thin film specimens belonging to the polymer electrolyte system, 75 wt% PVDF-co-HFP:25 wt% ZnTf + x wt% ZrO₂ (when x = 1, 3, 5, 7 and 10 respectively) derived after the complete removal of DMF were subsequently stored in a vacuum desiccator with a view to avoid any exposure to the moisture prior to their systematic characterization studies.

Analyses

AC impedance measurements were carried out on freshly prepared thin film samples of the polymer electrolyte system in the frequency range 1 MHz–20 Hz with an excitation signal of 50 mV using a computer-controlled Hewlett-Packard Model HP 4284A Precision LCR Meter at room temperature (298 K). The appropriate thin film specimens of CPEs were sandwiched between a pair of polished stainless steel (SS) disks so as to form symmetrical cells involving blocking electrodes having the configuration-[SS/CPE/SS] for an accurate measurement of their electrical conductivity values in the form of Nyquist plots.

The electrical conductivity (σ) was subsequently estimated using the equation:

$$\sigma = \frac{l}{AR_b} \quad (1)$$

where l is the thickness of the sample, R_b bulk resistance and A is the area of contact. Detailed X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance diffractometer equipped with a scintillation counter detector in conjunction with Cu K α radiation (λ = 0.154 nm) source involving a generator voltage of 40 kV and

current of 30 mA over the Bragg angle (2θ) range 10° – 80° at 25°C . The surface morphology of all these CPE samples was examined by means of a Hitachi S-3400 model scanning electron microscope and by appropriately coating them with gold by the process of vacuum sputtering carried out for 20 s before imaging in order to prevent the feasibility of electrostatic charging phenomenon. The CPE specimen was freeze-ruptured under liquid nitrogen so as to obtain the cross section for SEM analysis.

The evaluation of electrochemical stability in the case of the best conducting sample designated as Z7 was performed using a CHI instrument by constructing a three-electrode cell with zinc as counter and reference electrodes and a stainless steel (SS) as working electrode in the voltage range from 0 to 4 V at a sweep rate of 10 mV/s. Thermo-gravimetric analysis (TGA) of synthesized CPEs 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 containing 7 wt% ZrO_2 (Z7). To verify the reversibility of Zn plating/stripping of the composite polymer electrolyte, cyclic voltammetric analysis was performed at a scan rate of 10 mV/s using the Zn/polymer electrolyte/SS cell configuration over the domain -1.5 V to $+1.5\text{ V}$ at room temperature. To analyze the battery performance, prototype Zn| composite polymer electrolyte| MnO_2 cell was also fabricated based on the above mentioned polymer electrolyte and its discharge characteristics tested. For this purpose, the composite cathode, namely manganese dioxide was specially prepared by casting a mixture of battery grade $\gamma\text{-MnO}_2$ (electrolytic manganese dioxide, EMD) (80 wt%), graphite powder (10 wt%) and polymer electrolyte (10 wt%) as a binder and crushing the mixture along with a small amount of acetone and the slurry was subsequently applied onto a nickel grid. The nickel grid was exposed to degrease with NaOH solution followed by etching in dilute HCl, prior to use. The nickel grid along with the slurry was heated at 80°C for 5 min and also subjected to a pressure of 250 MPa. Freshly-synthesized CPE films were suitably sandwiched between MnO_2 cathode and zinc foil, and the open-circuit voltage of the cell was measured without any load whereas its short circuit current was measured under an infinite load (*i.e.*, short-circuited condition). As a result, the discharge characteristics of the cell were monitored under a constant load of 1 M Ω with the aid of a digital voltmeter and ammeter, connected in parallel and series to the load, respectively^[15].

RESULTS AND DISCUSSION

AC Impedance Analysis of CPEs

The electrical conductivity data in the case of all these prepared CPEs were determined by impedance spectroscopic analysis. Figure 1 shows the hypothetical equivalent circuit suggested on the basis of the impedance plot obtained in the case of the best conducting composite polymer electrolyte (CPE) thin film sample with 7 wt% loading of ZrO_2 nanofiller which has yielded the maximum conductivity (σ) value of $4.6 \times 10^{-4}\text{ S/cm}$ at room temperature (298 K). It is evident that two regions are observed in Fig. 1: (A) a high frequency semicircle and (B) a low frequency spike. The intercept of the semicircle seen on the real axis at the high frequency of the impedance plot represents the bulk electrolyte resistance (R_b) which is inversely proportional to the electrical conductivity (σ) of the sample.

The electrical conductivity value is found to increase from $5.5 \times 10^{-5}\text{ S/cm}$ for ZrO_2 -free polymer-salt complex to a maximum of $4.6 \times 10^{-4}\text{ S/cm}$ at 298 K for 7 wt% loading of ZrO_2 nanofiller material. The observed electrical conductivity (σ) values obtained at 298 K for all the CPEs are presented in Table 1 for a comparative analysis.

Figure 1 tends to reveal that the experimental conductivity data could be compared satisfactorily with those evaluated from the best fitting equivalent circuit. In this circuit, sample resistance denoted by R_s is in series with the first parallel combination of constant phase element and charge transfer resistance, R_1 . Here, the constant phase element is presumed to act as an imperfect capacitor Q_1 and its n value would range from 0 to 1. An ideal capacitor may be ascribed as having $n = 1$ whereas $n = 0$ would denote a pure resistor^[18], however in the present case, the n value of an imperfect capacitor is 0.8. The roughness of the electrode, its porosity and inhomogeneity

may be represented by the constant phase element which is used in the place of a capacitor^[19]. Therefore, in the present system the formation of a constant phase element appears to suggest the non-Debye behavior of the sample under test. The second parallel combination of Q_2 and R_2 represents the actual resistance obtained from the intercept of the diminished semicircle on the real axis at the low frequency region. Finally, the third parallel combination (CR_3) implies the most probable capacitance effect prevalent at the electrode-electrolyte interface.

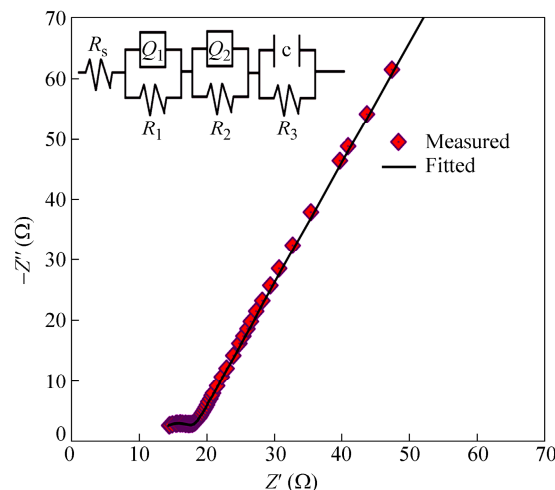


Fig. 1 The tentative equivalent circuit and room temperature impedance plot corresponding to the best conducting composite polymer electrolyte thin film sample having 7 wt% loading of ZrO_2 nanofiller

Table 1. Electrical conductivity data for all the CPEs with different wt% of nanofiller at room temperature (25 °C)

ZrO_2 x (wt%)	Sample designation	σ at 298 K (S/cm)
1	Z1	2.8×10^{-4}
3	Z3	4×10^{-4}
5	Z5	4.4×10^{-4}
7	Z7	4.6×10^{-4}
10	Z10	1.2×10^{-4}

Dielectric Behavior

It is well known that electrical conductivity (σ) depends on both the number of charge carriers and their mobility as,

$$\sigma = \sum ne\mu \quad (2)$$

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 CPE samples as a function of frequency. The value of dielectric constant ϵ' increases when the content of ZrO_2 nanofiller is raised from 1 wt% to 7 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 CPEs in terms of the dielectric components the relevant expression is given as,

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (3)$$

where ϵ' represents dielectric constant and ϵ'' denotes dielectric loss. It is noted that the value of dielectric constant decreases with increasing frequency.

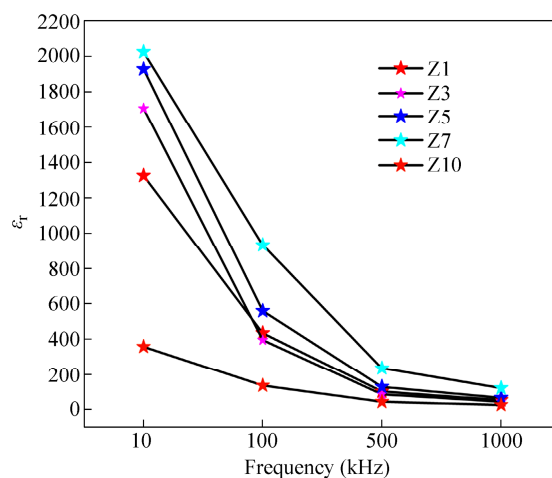


Fig. 2 Variation of dielectric constant as a function of frequency obtained for CPEs containing five different amounts of ZrO_2 (wt%) filler at room temperature (298 K)

The occurrence of large values of ϵ' for the typical sample having 7 wt% ZrO_2 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 CPEs having five different amounts of ZrO_2 nanofillers viz., 1 wt%, 3 wt%, 5 wt%, 7 wt% and 10 wt% at room temperature (298 K) as shown in Fig. 2 reaches the maximum tends to confirm that the best conducting sample with 7 wt% ZrO_2 nanofiller would possess the maximum number of charge carriers among the five different compositions of CPE system considered during the present endeavor^[20].

Furthermore, Fig. 3 shows the dependence of dielectric loss (ϵ'') observed as a function of frequency for the above nanocomposite polymer electrolyte samples having five different ZrO_2 filler concentrations of 1 wt%, 3 wt%, 5 wt%, 7 wt% and 10 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 a

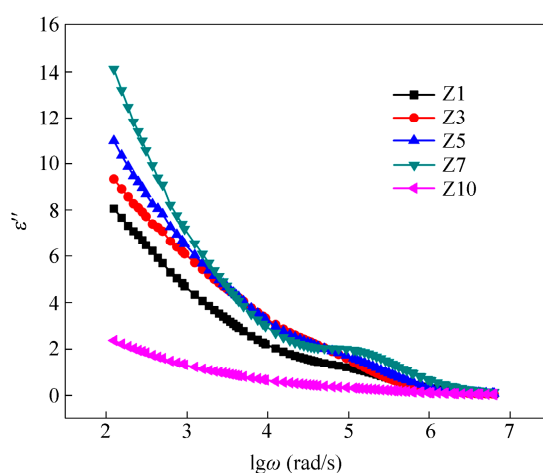


Fig. 3 Variation of dielectric loss ϵ'' with frequency observed for CPEs having five different amounts of ZrO_2 (wt%) filler at room temperature (298 K)

measure of energy dissipated, the observed variation of ε'' in the case of five different CPEs 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^[21]. 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 CPEs.

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^[18].

Electric Modulus

Figure 4 shows the observed frequency dependence of the imaginary part (M'') of electric modulus M^* for the CPE samples having five different ZrO_2 nano filler concentrations of 1 wt%, 3 wt%, 5 wt%, 7 wt% and 10 wt% respectively at room temperature (298 K).

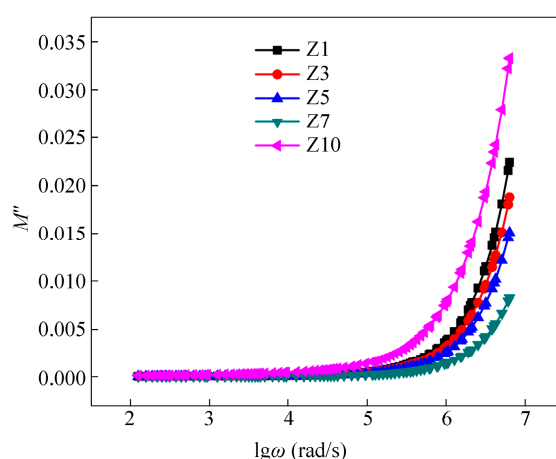


Fig. 4 Variation of M'' with frequency for CPEs having five different amounts of ZrO_2 (wt%) filler at room temperature (298 K)

It is clear from Fig. 4 that the imaginary part of electric modulus (M'') increases with an increase in frequency thereby suggesting and demonstrating the fact that for the best conducting sample loaded with 7 wt% ZrO_2 , the maximum value of M'' would shift towards a higher frequency as compared to remaining compositions. It is also seen that the observed dispersive M'' peaks noticed at high frequency region may be correlated to the behavior of relevant conductivity relaxation time as well^[16]. As a result of incorporation of ZrO_2 nanofiller material up to 7 wt%, the appropriate conductivity relaxation time is found to appreciably decrease and such a trend may be associated with an increase in the electrical conductivity owing to the fact that beyond 7 wt% loading (e.g. 10 wt% ZrO_2) the observed trend becomes reversed. Moreover, it is also obvious from these results that M'' peaks represent the non-Debye type of relaxation thus implying that the available mobile ions may exhibit more than one relaxation time. The decreasing trend of the observed modulus data which tends to approach the value of zero at low frequencies may be attributed to the negligible polarization effects occurring at electrodes^[22].

Plots of room temperature normalized impedance and electric modulus spectra obtained for the chosen CPEs as a function of frequency are presented in Figs. 5 and 6, respectively and it is apparent that they are superimposable with each other in the case of all the CPE specimens. It is seen that both impedance and electric modulus spectra show similar trends wherein a dispersion associated with no relaxation peak is found to occur probably due to wide range of conductivity data^[18]. This feature indicates that the relevant dynamic process of ions would remain the same throughout the range of compositions considered during the present work.

Furthermore, the fact that the maxima of the above spectra occur at different frequencies also confirms the existence of non-Debye type of relaxation in all these CPEs^[15, 16].

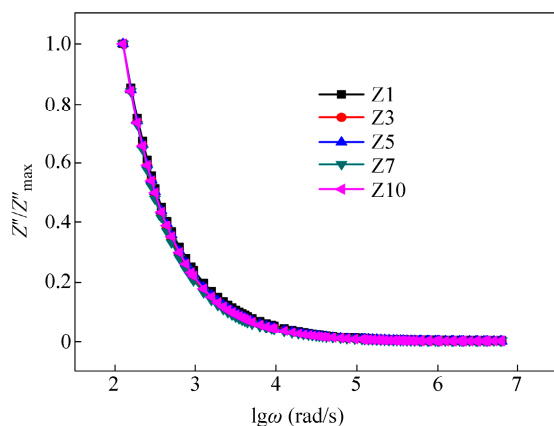


Fig. 5 Plots of room temperature normalized impedance spectra of five different CPEs as a function of frequency

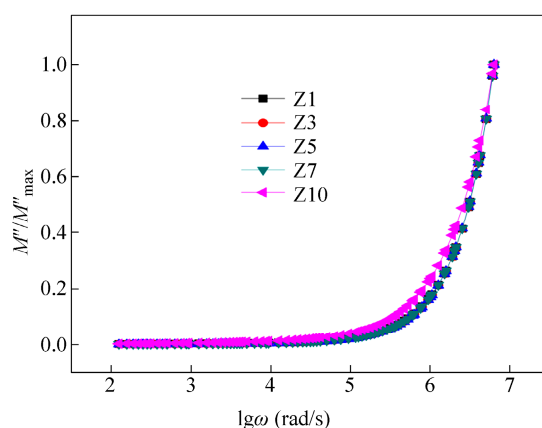


Fig. 6 Plots of room temperature normalized modulus spectra of five different CPEs as a function of frequency

X-ray Diffraction (XRD) Analysis

Figure 7 displays the series of X-ray diffraction (XRD) patterns recorded at room temperature (298 K) for thin film specimens of pure PVDF-*co*-HFP (a), 75[PVDF-*co*-HFP]:25[Zn(CF₃SO₃)₂] (b) and five different CPEs designated as Z1 (c), Z3 (d), Z5 (e), Z7 (f) and Z10 (g) respectively. The characteristic peaks of ZrO₂ nanoparticles are distinctly observed at $2\theta = 28^\circ, 32^\circ, 36^\circ, 47^\circ, 56^\circ, 59^\circ, 68^\circ, 76^\circ$ and 79° in the case of various composite polymer electrolytes wherein ZrO₂ filler particles are dispersed (c–g in Fig. 7) and found to remain as a separate phase within the present polymer-salt system. The typical X-ray diffraction pattern as shown in Fig. 7(a) tends to reveal that the semi crystalline PVDF-*co*-HFP film would exhibit three predominant diffraction peaks at $2\theta = 18^\circ, 19.8^\circ$ and 37.8° respectively^[15, 23, 24]. With the addition of zinc triflate into the PVDF-*co*-HFP matrix it is seen that those crystalline peaks corresponding to the host polymer disappear substantially showing

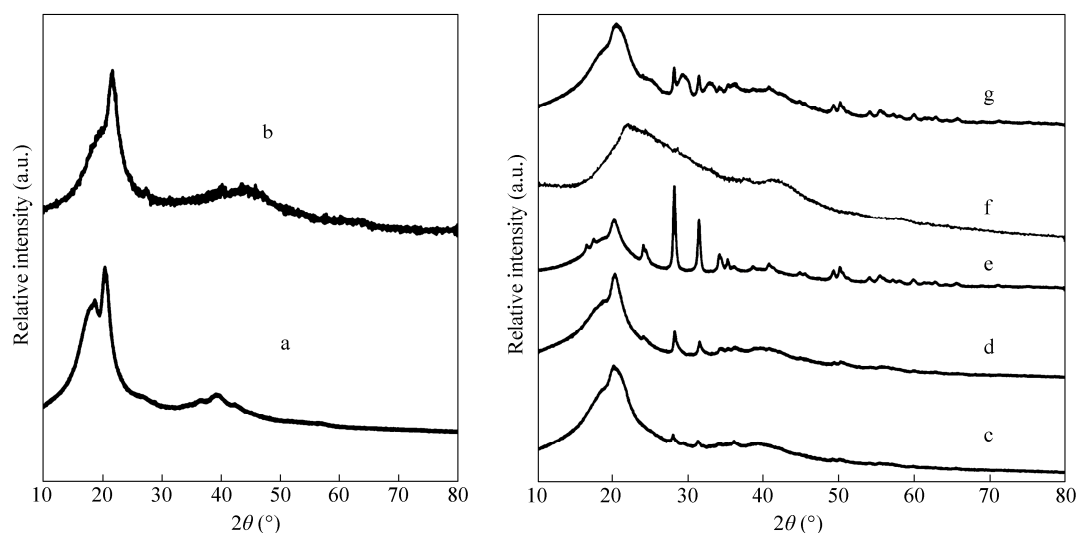


Fig. 7 XRD patterns of pure PVDF-*co*-HFP film (a), 75[PVDF-*co*-HFP]:25[Zn(CF₃SO₃)₂] polymer electrolyte (b), and nanocomposites dispersed with ZrO₂ particles of 1 wt% (c) 3 wt% (d) 5 wt% (e) 7 wt% (f) and 10 wt% (g) respectively

the presence of a broader hump between 10° and 30° as suggested by Fig. 7(b). Meanwhile, it is quite obvious that as the area under the peak noticed at $2\theta = 19.8^\circ$ has appreciably increased with a substantial increase in the amount of loading of ZrO_2 nanofiller, the apparent crystal morphology around the peak would have become amorphous in nature^[24]. On the other hand, these characteristic peaks observed at $2\theta = 28^\circ, 32^\circ, 36^\circ, 47^\circ, 56^\circ, 59^\circ, 68^\circ, 76^\circ$ and 79° tend to confirm the dispersion of ZrO_2 nanofiller which may remain as a separate phase within the CPE matrix. Therefore the present XRD results are found to be in good agreement with the room temperature electrical conductivity data.

Scanning Electron Microscopy (SEM)

The appropriate microstructural and morphological characteristics of pure PVDF-co-HFP and the best conducting CPE, having 7 wt% ZrO_2 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, Z7 sample and its cross sectional view respectively. In the case of 75 [PVDF-co-HFP]:25 [$\text{Zn}(\text{CF}_3\text{SO}_3)_2$]:7 wt% ZrO_2 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 free-standing translucent film, its morphology shows the presence of many spherical grains^[24]. From Fig. 8(b) it is evident that loading of ZrO_2 nanofiller 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 nanosized ZrO_2 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 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 7 wt% ZrO_2 material also indicate the existence of compatibility between the chosen filler and polymer matrix. Such interpretations pertaining to these micrographs are found to be congruent with these results obtained from X-ray diffraction analysis and presented in the previous section.

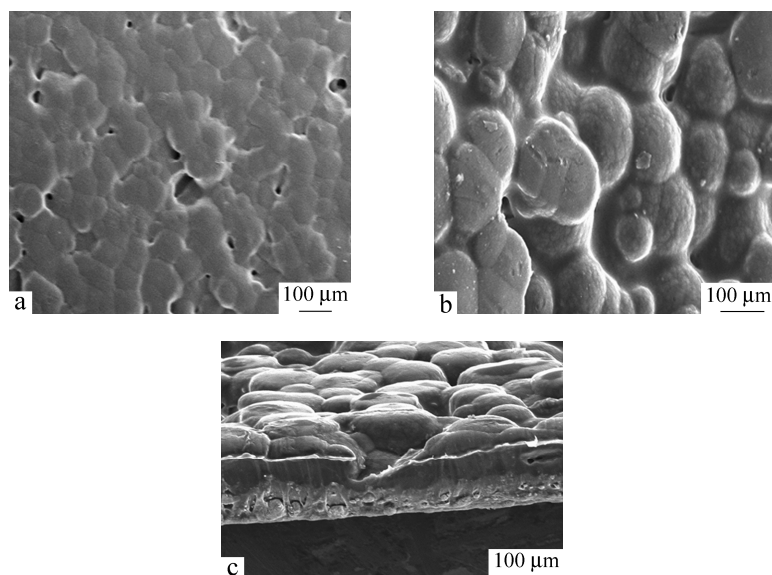


Fig. 8 SEM micrographs of PVDF-co-HFP film (a), 7 wt% ZrO_2 loaded polymer electrolyte (b) and its cross section (c)

Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry is widely used to determine electrochemical stability and decomposition potential in the case of polymer electrolytes (oxidation potential)^[25].

In case of practical applications an electrolyte is expected to be electrochemically stable when placed in contact with an appropriate electrode material. Figure 9 shows the current-voltage responses obtained for samples of pure PVDF-*co*-HFP/Zn(CF₃SO₃)₂ polymeric complex (CPE) as well as 7 wt% ZrO₂-loaded polymer electrolyte system. The upper limit of stability of the polymer electrolyte was considered to be the point of intersection resulting from suitable extrapolation of the plot of linear current as a function of voltage in the higher voltage region with the voltage axis.

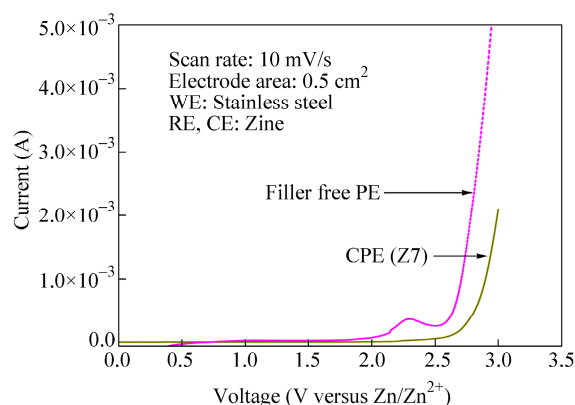


Fig. 9 Linear sweep voltammograms obtained for SS|CPE|Zn and SS|CPE with 7 wt% of ZrO₂|Zn cells at room temperature (298 K)

As seen from Fig. 9, it is evident that incorporation of ZrO₂ filler would increase the effective electrochemical stability of the polymer complex upto 2.7 V above which anodic current begins to flow. The observed current response was found to be negligible below 2.7 V versus Zn/Zn²⁺ in the case of the typical CPE loaded with 7 wt% ZrO₂ nanofiller. This feature implies that there is no decomposition of any components below 2.5 V for the filler-free polymeric complex whereas the value becomes 2.7 V for the 7 wt% ZrO₂-loaded polymer electrolyte system. Therefore, it is inferred that the particular CPE film specimen having 7 wt% ZrO₂ may be effectively employed in order to construct zinc-based battery systems for ambient conditions.

Thermo-gravimetric Analysis (TGA)

The typical TGA curve obtained for the best conducting sample of the composite polymer electrolyte (CPE) system, namely Z7 is shown in Fig. 10. The thermal stability of the above specimen having 7 wt% ZrO₂ was found to remain up to an elevated temperature of 300 °C characterized with two distinct stages of thermal degradation process. Such a behavior clearly shows the occurrence of a marginal weight loss of less than ~7% around 100 °C which may be attributed to the removal of surface-adsorbed moisture content^[23]. The fact that no weight loss is noticed from 100 °C to 300 °C confirms the absence of volatile components^[26]. The substantial decomposition noticed above 300 °C may be due to the possible degradation of polymer chain and oxidation of triflate ions resulting in a weight loss of 37.6 % as revealed from Fig.10. The better thermal stability of the above nanocomposite polymer electrolyte sample may be due to the significant barrier occurring as an influencing effect of the nanofiller which would have slowed down the process of product volatilization at higher temperatures^[27]. Hence the non-volatile nature of the typical sample containing 7 wt% ZrO₂ up to 300 °C indicates the existence of an appreciably good thermal stability thus implying the feasibility of its safety performance in practical applications.

Cyclic Voltammetric (CV) Studies

Figures 11(a) and 11(b) show the respective cyclic voltammograms obtained for the cell configurations of Zn/CPE/SS and Zn/CPE with 7 wt% ZrO₂/SS involving nanofiller-free optimized composition of PVDF-*co*-HFP-ZnTf system *i.e.*, CPE sample and CPE with 7 wt% ZrO₂ at a constant scan rate of 10 mV/s. The present

cyclic voltammetric (CV) analysis has been carried out with a view to examine the evidence for the occurrence of zinc plating/stripping processes.

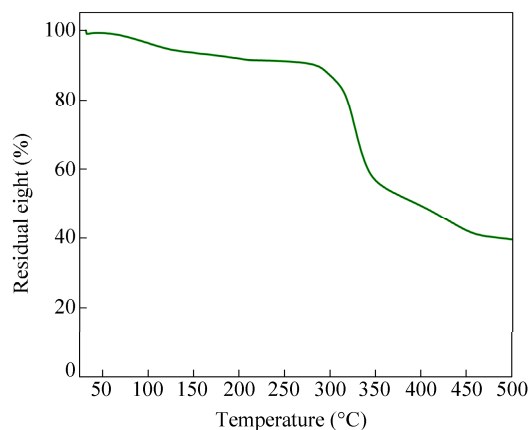


Fig. 10 TGA thermogram of CPE designated as Z7 under nitrogen atmosphere

It is interesting to note from Figs. 11(a) and 11(b) that two peaks are observed in each voltammogram thereby suggesting the occurrence of cathodic deposition (plating) and anodic oxidation (stripping) processes of zinc occurring at the Zn/electrolyte interfaces during the reverse scans^[23, 25]. Incidentally, nanofiller-free complex (Fig. 11a) is found to exhibit two peaks corresponding to the process of zinc deposition upon stainless steel electrode at -1.5 V and stripping of zinc at 0.76 V occurring during the reverse scan. Furthermore, the relevant CV analysis performed on the CPE sample with 7 wt% loading of nanofiller (Fig. 11b) has indicated the presence of a cathodic peak at -1 V corresponding to the plating of zinc and an anodic peak at 0.7 V corresponding to the stripping of zinc.

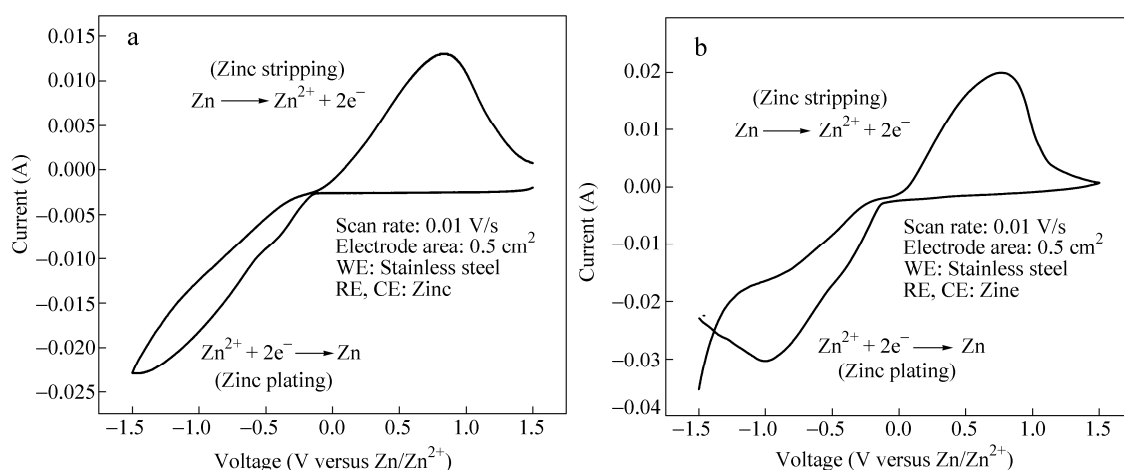


Fig. 11 Cyclic voltammetric response of SS|CPE|Zn (a) and SS|CPE with 7 wt% ZrO_2 |Zn (b) cells obtained at a scan rate of 0.01 V/s

Battery Performance (Discharging)

The room temperature (298 K) discharge curve observed in the case of a freshly fabricated electrochemical cell, viz., Zn/Z7/ MnO_2 involving the typical CPE with 7 wt% ZrO_2 (Z7) at a constant load of $1 \text{ M}\Omega$ is shown in Fig. 12. The above test cell has exhibited an open circuit voltage (OCV) of 1.7 V and short circuit current (SCC) of 0.82 mA. The initial drop in voltage noticed in Fig. 12 may be due to the polarization effect and/or the

formation of a thin layer of zinc salt at the electrode-electrolyte interface. In the present investigation, zinc has been used as an effective anode in conjunction with γ - MnO_2 as cathode material for the evaluation of cell parameters. Incidentally, γ - MnO_2 has been chosen as the cathode element since it is known to reversibly intercalate/deintercalate zinc ions^[15, 28]. The fact that the working voltage of a freshly prepared cell is 1.7 V shows the mechanical stability and electrochemical compatibility of the chosen nanocomposite polymer electrolyte system namely 75 PVDF-HFP: 25 ZnTf :7 wt% ZrO_2 as a promising polymer electrolyte and tends to demonstrate its performance in such type of solid-state batteries. This feature is found to be in conformity with a plateau noticed at ~ 1.33 V over a discharge time of 160 h, thereby suggesting its practical application in the future.

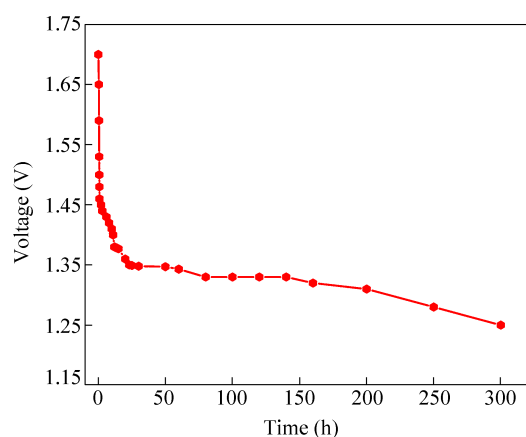


Fig. 12 Discharge curve observed for the Zn| CPE with 7 wt% ZrO_2 | MnO_2 cell at a constant load of 1 M Ω at room temperature (298 K)

CONCLUSIONS

A series of new composite polymer electrolytes (CPEs) obtained by immobilizing a solution of zinc triflate in combination with ZrO_2 nanofiller within the host polymer matrix PVDF-co-HFP were characterized in terms of their electrical, structural, morphological and electrochemical features. The impact of dispersion of ZrO_2 nanofillers on the electrical conductivity relaxation and dielectric behavior of these CPE systems has also been investigated. The present impedance and electric modulus analyses have revealed the distribution of relaxation processes occurring within these CPEs thereby confirming the non-Debye nature of relaxation. The incorporation of 7 wt% ZrO_2 nanofiller has resulted in an enhanced room temperature electrical conductivity of the polymer electrolyte system by an order of magnitude, thus offering an excellent thermal stability up to 300 °C. The feasibility of attaining a reduction in crystallinity has been confirmed from XRD analysis whereas the highly conducting composition has exhibited an appreciably good electrochemical stability window of 2.7 V. An electrochemical cell based on the Zn/ MnO_2 electrode couple has exhibited many interesting and stable discharge characteristics at room temperature.

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