Scientific Journal of Impact Factor (SJIF): 4.72
e-ISSN : 2348-4470
p-ISSN : 2348-6406

International Journal of Advance Engineering and Research Development

National Conference On Nanomaterials, (NCN-2017)

Volume 4, Special Issue 6, Dec.-2017 (UGC Approved)

EFFECT OF ZrO_2 NANOFILLER ON THE ELECTROCHEMICAL CHARACTERISTICS OF COMPOSITE POLYMER ELECTROLYTES BASED ON (PVDC-AN) COPOLYMER

M.Shanthi[a,b], R.Subadevi[a, *], M.Ramachandran[a,c], M.Sivakumar [a]

[a] #120, Energy Materials Lab, Department of Physics, Alagappa University, Karaikudi-630003. Tamil Nadu, India.
[b]Department of Physics, Kamaraj College of Engg. And Tech, Virudhunagar 626001, Tamil Nadu, India.
[c] Department of Physics, ArumugamPillaiSeethaiAmmal College, Tiruppathur-630 211, Tamil Nadu, India.

Abstract:-*A new composite polymer electrolyte (CPE) based on P(VdC-AN) copolymer, $LiClO_4$ as saltand ZrO_2 as nano filler has been prepared by solution casting technique. Impedance spectroscopic analysis of composite polymer electrolytes has been made to investigate the ionic conductivity by varying the composition of the nano filler ZrO_2. Room temperature ionic conductivity of the compositesincreases substantially from 7.2×10^{-4} $Scm^{-1}$and reaches the maximum value of 9.1×10^{-4} $Scm^{-1}$for P(VdC-AN) (92wt.%)/$LiClO_4$(8wt.%) and ZrO_2(6wt.%). The structural and the complex formation have been confirmed by X-ray diffraction spectroscopy and FTIR analyses. The surface morphology and surface roughness are studied by AFM.Thermal stability has been investigated from thermogravimetry/differential thermal analysis.Reductions in intensity of the emission peaks in the photoluminescence studies are good in agreement with ionic conductivity. The overall results indicate that the sample prepared with 6wt.%ofZrO_2shows maximum conductivity and exhibit good thermal behavior.*

Introduction

In recent years, the technological development of electronic products demands for high energy density rechargeable batteries.Ionically conducting polymer electrolytes with lithium salts are the promising candidatesinvestigatedworldwide for the application of rechargeable batteries and other electrochemical devices. During the inception of electrolyte research, dry polymer electrolytesbased on PEO exhibited ionic conductivity in the order of 10^{-8} cm^{-1}at room temperaturewasreported[1].Compared to liquid electrolyte, gel polymer electrolyte shows comparable ionic conductivity at room temperature. But, the high viscous nature of gel polymer electrolyte resulted in poor contact between the electrodes when assembled in batteries. In order to improve their mechanical property,incorporation of inorganic fillers has been suggested by several researchers. The nature and size of the inorganic filler plays significant role. The dispersion ofnano-sized filler particles has been found to be more effective in the improvement mechanical as well as the electrochemical properties of composite polymer electrolyte.It is well proved that the incorporation inorganic fillers such as Silica(SiO_2)[2],Alumina(Al_2O_3)[3], and Titania(TiO_2)[4] andZirconia (ZrO_2)[5]in the polymer electrolyte influences the mechanical property as well as the electrochemical property.

In this present work, an attempt has been made to investigate the preparation and characterization of PVdC-co-ANbased composite polymer via solution casting techniquecomposed of $LiClO_4$as salt and zirconium oxide nano filler. This study focuses on the impact of nano filler composition on the ionic conductivities of polymer electrolytes while adding ZrO_2 nanoparticles.

Experimental

The composite polymer electrolytes of Poly (vinylidene chloride-co-acrylonitrile) /$LiClO_4$/ZrO_2 were prepared by solution casting technique. PVdC-co-AN and $LiClO_4$ were dried under vacuum at 40°C for 24 h to remove any residual trace of impurity. The nano sized $ZrO_2$was used as ceramicfiller, which was synthesized by co precipitation method. All the electrolytes have been prepared with appropriate quantity of the polymer, salt were dissolved separately in anhydrous Tetrahydrofuran (THF). The polymer and the salt solutions were mixed together and subjected to continuous stirringby magnetic stirrer to get homogenous solution. In the resulting homogenous solution an appropriate quantity of $ZrO_2$was added. Finally the solution was cast onto the well cleaned flat bottom petri plateand allowed to evaporate inambienttemperature for several hours. The films were further dried at 50°C for 24 htoget rid of anyresidual solvent.

Characterization

X -ray diffraction (XRD) studies were carried out to investigate the crystalline structure, nature of crystallinity, complexformation and by X'pert PRO PANalyticaldiffractometer in the scanning range $2\theta = 10\text{-}80^o$ using Cu Kα (wavelength $\lambda = 1541$Å) radiation as source and operated at 40kV. Fourier transform infrared (FTIR) studies were carried with Perkin Elmer 577-IR spectrophotometer in the range of 4000-400 cm^{-1}. The AC impedance studies of the polymer complexeswerestudiedin the temperatures range 303 – 363K using 3330Keithley LCZ Meter with the signal amplitude of 5mV.Thermal analysis was performed by Perkin Elmer (Pyres diamond thermogravimetric analyzer (TGA)) at a heating rate of 10°C/min from 40 to 880°C. Finally, the sample exhibiting high conductivity was subjected to Atomic Force Microscope inorder to investigate the topography of the sample.

Results and discussion

XRD Analysis

XRD pattern (Fig.1) displaysthe influence of nano-sized filler content on the crystalline structure of the PVdC-co-AN based electrolytes.The sharp characteristic peaks of purePVdC-co-ANappeared at2Ө=40.25,46.76 and 67.94° in Fig.1, confirm the crystalline nature of the polymer. The XRD pattern of pure$LiClO_4$ shows intense peaks at angles 2θ =18.36, 23.2, 27.5, 32.99 and 36.58° reveals the crystalline nature of the ionic salt. On comparing d-values of $LiClO_4$ with JCPDS data [JCPDS: 30-0751] it exhibit hexagonal structure[6].The XRD pattern of pure ZrO_2displays diffraction peaks 2θ = 28.07, 31.46, 33.70, 35.30, 49.26 and 50.39°, which shows monoclinic structure of ZrO_2 [JCPDS:78-1807]. The diffraction pattern of the sample SF1,SF2and SF3 containno peaks pertaining to PVdC-co-ANand$LiClO_4$,whichshows the complete dissolution of salt in the polymer matrices. The sharp peaks pertaining to ZrO_2 disappeared in the samples containing ZrO_2upto6wt%. From the diffraction patterns, it is understood that the crystallinity of the bare electrolyte has been reduced upon adding the ZrO_2 content and the crystallinity of the prepared electrolyte membranes were greatly reduced by the addition of ZrO_2upto 6wt%.The nano sized ZrO_2dispersoid penetratesinto the space between the polymer chains and retards thecrystallization[7]. As a result, there is a decrease in the crystallinitythat softens the polymer backbone and significantly increases the ionic diffusivity which inturn increases the ionic conductivity.In the sample SF3, there is a small increase in the intensity of the peaks.The peak intensity is further increased when the filler content is 12wt%.The addition of filler beyond the optimum value (6 wt.%) increases the crystallinity of the complex which is reflected in the decrement of the conductivity values.

The sharp crystalline peaks at2θ=28.07 and 31.46°pertaining to ZrO_2that are appearedin polymer complex which contains filler 12wt.%(sample SF4). This indicates that the addition of nanofillerZrO_2 beyond the optimum value leads to increase in the crystallinity of the complex.

FTIR Studies

Fig.2shows the FTIR spectra of pure PVdC-AN,$LiClO_4$, ZrO_2 and their complexes with different ratio of ZrO_2. The $C{=}CH_2$ symmetric stretching of pure PVdC-co-AN at 2975cm^{-1} [8] is shifted to 2969, 2973 and 2973 cm^{-1} in the complexes. The peaks observed at 2245and 1642cm^{-1} of pure PVdC-co-ANare attributed to the strong stretching vibrations of nitrile groups such as C≡ N and C= N[8]. In Figure 2there is no change in the position ofthe transmittancepeak ofthe vibrational band of PVdC-co-AN at 2245$cm^{-1}$with the addition of nanofiller ZrO_2, but the intensity increased. This is due to the interaction of nitrile group in acrylonitrile with Li+ ions[8]. The C=O stretching at 1710 cm^{-1}[7] and CH_2 wagging at 1357 cm^{-1}[7,8]are shifted to 1754,1769,1769 and 1769 cm^{-1} and1421,1413and 1405 cm^{-1} in the complexes.The peak corresponding $LiClO_4$at940$cm^{-1}$is absent in all complexes. This shows the complete dissociation of the salt in the polymer matrix.

Conductivity studies

Conductivityis the vital property to be considered in the fabrication of polymer electrolyte.AC impedance spectroscopy has been used to study the ionic conductivity of the electrolytes. The ionic conductivity studies were carried out with the help of stainless steel blocking electrodes using Keithley 3330 LCZ meter. The impedance measurement was recorded in the frequency range 40Hz-100 KHz with signal amplitude of 10mV.The prepared polymer films were cut into circular shape that fit the size of the electrode and was kept between two stainless steelelectrodes of the cell and an AC voltage (5 mV) was applied. The complex impedance wasmeasured by varying the frequency 40Hz to 300Hz. The ionic conductivities of the polymer electrolytes are calculated from the relation

$$\sigma = t / R_b A,$$

where, t - thickness of the sample.
A - area of the electrolyte sample membrane.
R_b -is the bulk resistance obtained fromthe intercept on the real axis at the highfrequency end of the complex impedance plot [9].

The maximum room temperature ionic conductivity value of 9.1 x 10^{-4} Scm^{-1}has been observed for the system PVdC-co-AN/ $LiClO_4$/ZrO_2/(6wt%). Temperature dependent ionic conductivity values of the prepared samples with different composition of ZrO_2 are listed in Table1 over the temperature range of 303–353 K. From the Table 1, it is observed that the ionic conductivity of the composite polymer electrolyte increases with the increase of ZrO_2 content upto the optimum value of 6wt.%. The result reveals that the addition of nano size particle does not obstruct the mobility of the ions but decreases the degree of crystallinity of the polymer electrolyte and enhances the ionic conductivity. On the otherhand the addition of nano filler ZrO_2 creates new conformational pathways lead to high ionic conductivity. This is due to larger amount of oxygen vacancies on ZrO_2 surface which may acts as the active Lewis acidic site which interact with both PVdC-co-AN and ClO^{4-} ions[10] the composite electrolyte maintain amorphous nature up to a particular concentration of ZrO_2. After the optimum value is reached the ionic conductivity decreases due to high concentration of the filler. The excess of filler content beyond 6% built a crystalline phase, which hinders the segmental movement ofpolymer chain and hence the ionic conductivity.

Fig.3(a) shows the Cole-Coleplot of PVdC-co-AN/ $LiClO_4$/ZrO_2 composite polymer electrolyte at room temperature with 6wt. % of ZrO_2. The disappearance of semicircular portion in the high frequency region ofcomplex impedance plot indicates that the conduction is mainly due to the ions [11]. Itdepicts that the ionic conductivity increases with increase of temperature.An increase in the temperature of the polymer membrane increases the free volumehence the segmental mobility of the ion solvated polymer molecule increases. This accelerates the ion and polymer segmental mobility and enhances the ionic conductivity.The temperature dependent ionic conductivity plots indicate thatthe ionic conduction in the polymer electrolyte system obeys Arrhenius relation.

Atomic Force Microscopy

AFM is used to obtain the three dimensional and two dimensional topographic images of the samples in view of studying the surface morphology. The samplePVdC-co-AN (92wt.%)/$LiClO_4$ (8wt.%) and ZrO_2 (6wt.%) with high conductivity values was subjected to topographical analysis inorder to measure the pore size and the roughness factor of the sample. The root means square roughness of the sample is 271.3nm.This image clearly shows the dispersion of the inorganic fillers and the presence of pores within the scanned area of 50×50µm. It also shows the dispersion of the fillers and it contains small poreswhich assists for fast ionic motion.

Thermogravimetric Analysis

In order to investigate thermal stability of the prepared samplesthermogravimetric analysis was performed.Fig.5 shows the TGA thermogramsofPVdC-co-AN(92)- $LiClO_4$(8)- ZrO_2 (X) (where X= 3,6,9 and12wt%) composite systems. There is a very small initial weight loss of 8% for electrolytesis possibly due to the evaporation the residual solvent in the electrolyte membrane and moisture during loading the sample in the pan. From Fig.5,the sample starts melting around 182°Cand ends around 270°C with the weight loss of ~52%. From TGA, it is clear that all the prepared composite polymer membranes preserve their composition and stable up to180°C, which is higher than the required battery operating range.

Fluorescence studies

Fluorescence emission spectra of the composite polymer electrolyte with different filler content are shown in Fig.6. The ionic mobility in polymeric media is relatedto the local viscosity surrounding the charge carriers in the polymer electrolytes[12]. The viscous surroundings of the charge carriers play vital role in ionic mobility. High viscous medium hampers the movement of the ion. Fluorescence studies explore the local viscosity of the polymeric membrane. The intensity of the fluorescence emission spectra is directly proportional to the local viscosity of the polymeric media[13]. The photoluminescence emission intensity decreases, when the local viscosity of the polymeric membrane decreases which influences the ionic movement.

Conclusion

A new composite polymer electrolyte (CPE) based on P(VdC-AN) copolymer, $LiClO_4$ as salt and ZrO_2 as nano filler has been prepared by solution casting technique. The interaction between the nano filler and the polymer-salt complex has been confirmed by XRD and FTIR analyses. It is observed that the room temperature ionic conductivity of the parent electrolyte has been enhanced when adding dispersoid in to it. It increases upon adding ZrO_2 filler up to 6wt%, i.e., P(VdC-co-AN) (92wt.%)/$LiClO_4$(8wt.%) and ZrO_2(6wt%) system. Further addition of ZrO_2 causes ion aggregation in the path of the mobile charge carriers in the composite polymer electrolytes. For the application of polymer electrolytes in batteries not only the conductivity, but also the thermal stability are the key factors should be considered. From thermogravimetric analysis, all the prepared electrolyte complexes are stable up to 270°C. Photoluminescence studies reveal the electrolyte having maximum conductivity shows minimum emission intensity. The AFM image of the high ionic conducting sample depicts pores in the electrolyte, which supports ionic conductivity.All the above analysis validated the composite polymer electrolyte based on (PVdC-AN) copolymer comprising of ZrO_2nanofiller is a suitable candidate for the application of lithium ion secondary battery.

References

[1] D.E. Fenton, J.M. Parkar, P.V. Wright, Polymer 14 (1973)589.
[2] D.K. Pradhan, B.K. Samantaray, R.N.P. Choudhury, A.K. Thakur, J. PowerSources 139 (2005) 384–393.
[3] X. Qain, N. Gu, Z. Cheng, X. Yang, E. Wang, S. Dong, Electrochim. Acta 46 (2001) 1829–1836.

[4] C.W. Lin,C.L. Hung,M. Venkateshwarlu,B.J. Hwang, J. Power Sources146 (2005) 397–401.
[5] M.Ramachandran ,R.Subadevi , Fu-Ming Wang , Wei-Ren Liu , M.Sivakumar, International J. Chem. Tech Research Vol.6, No.3, (2014) 1687-1689.
[6] S. Rajendran, M. Sivakumar, R. Subadevi, Solid State Ionics 167 (2004) 335–339
[7] W. Wieczorek, J.R. Steven, and Z. Florjanczyk, Solid State Ionics, 85, 67 (1996).
[8] Shanthi M, Mathew CM, Ulaganathan M, RajendranSSpectrochimActaA 109(2013)105–109.
[9] M.L. Oshea, C. Morterra, M.J.D. Low, Mater. Chem. Phys. 27 (1991) 155–179.
[10] A. Subramania, N.T. Kalyanasundaram, A.R.SathyaPriya, G.Vijaya Kumar, J.Membrane Science 294(2007)8-15.
[11] M.Watanabe, K. Sanui, N. Ogata, T. Kobayashi, Z. Ohbaki,.*J.Appl.phys*. 57(1) (1985) 123.
[12] U.S. Park, Y.J. Hong, S.M. Oh, Electrochem. Acta 41 (1993) 849.
[13] D.A. Waldow, M.D. Ediger, T. Tamaguchi, T. Matsushita, E. Noda, Macromolecules 24 (1991) 3147.

FIGURE CAPTIONS

Figure 1.XRD pattern of pure and the prepared samples.

Figure 2. FTIR spectra of pure and the prepared samples

Figure 3 a) Cole-Cole plot ofPVdC-co-AN(92wt.%) – LiClO$_4$ (8wt.%) – ZrO$_2$ (X wt.%) where(X= 3,6,9,12) composites

Figure 3 b) Arrhenius plotofPVdC-co-AN(92wt.%) – LiClO$_4$ (8wt.%) – ZrO$_2$ (X wt.%) where(X= 3,6,9,12) composites

Figure 4 Topographical image of sample with high conductivity
a) Three Dimensional image b) Three Dimensional image

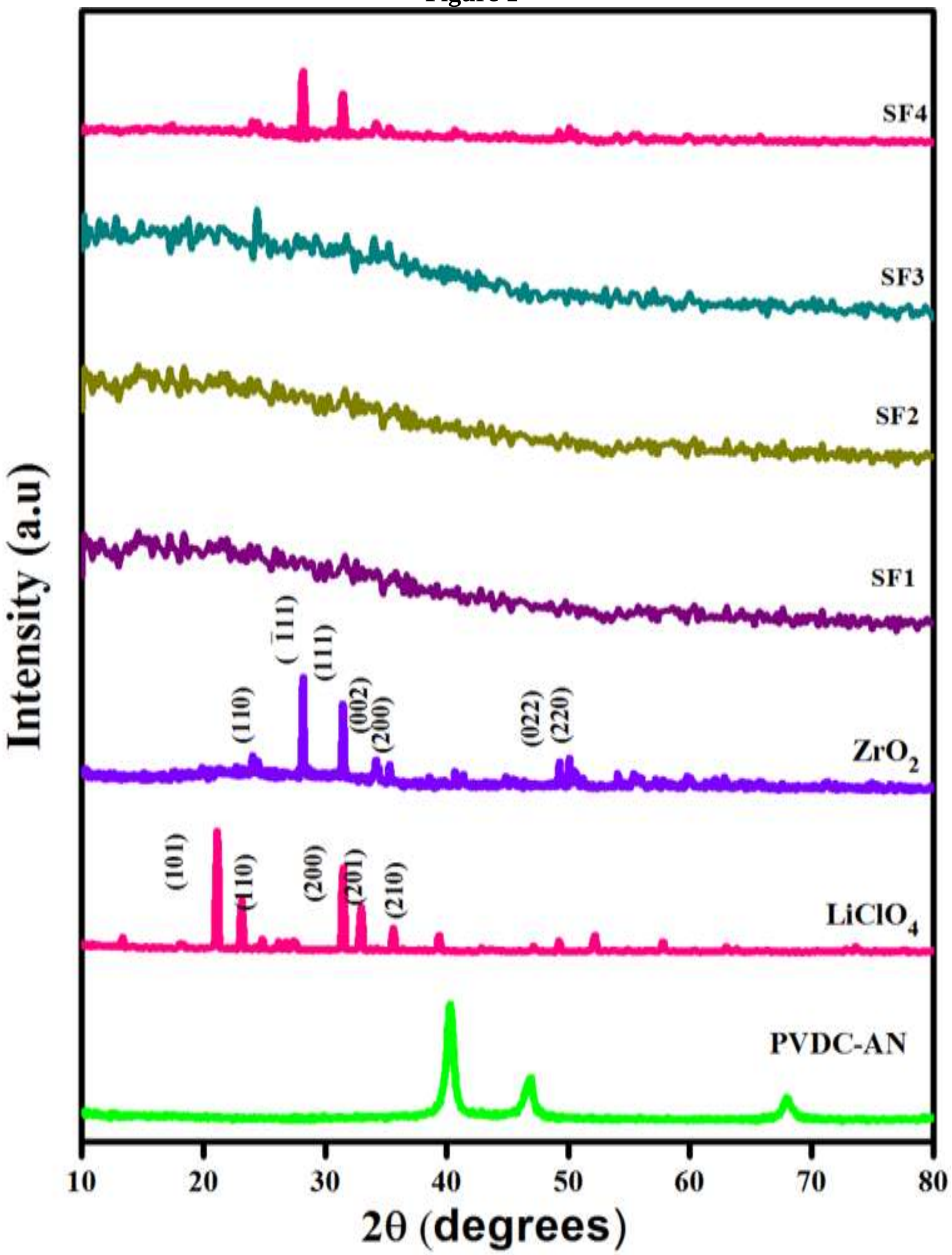
Figure 5 TG curve of the polymer electrolyte P(VdC-co- AN) (92wt.%)/LiClO$_4$(8wt.%) and ZrO$_2$(X wt.%) (X= 3,6,9,12) composites.

Figure 6 Photoluminescence spectra P(VdC-co- AN) (92wt.%)/LiClO$_4$(8wt.%) and ZrO$_2$(X wt.%) (X= 3,6,9,12) composites.

Name of the Autho: M.Shanthi[a,b], R.Subadevi[a, *], M.Ramachandran[a,c], M.Sivakumar [a]

Title of the manuscript: EFFECT OF ZrO_2 NANOFILLER ON THE ELECTROCHEMICAL CHARACTERISTICS OF COMPOSITE POLYMER ELECTROLYTES BASED ON (PVDC-AN) COPOLYMER

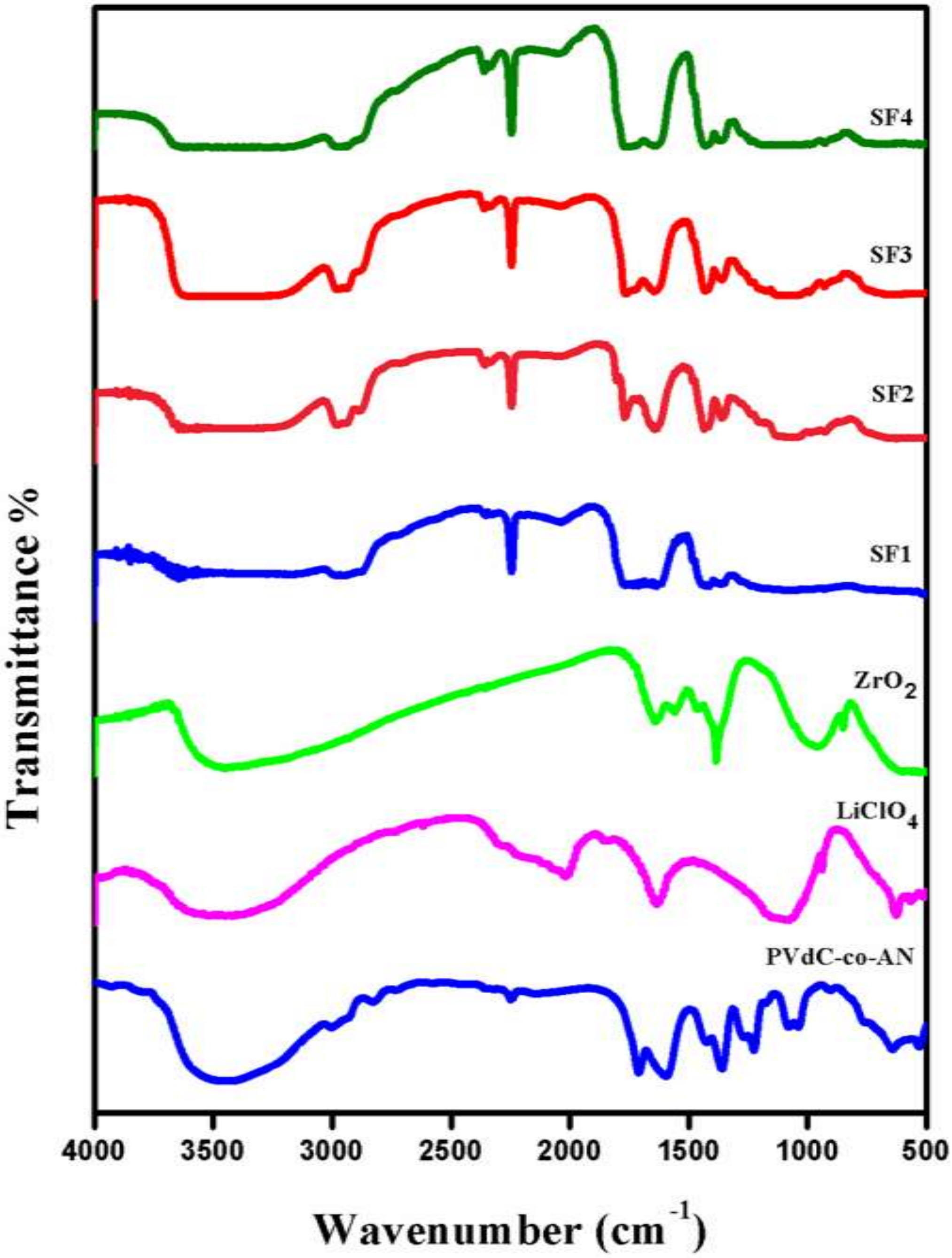
Figure 1



Name of the Autho: M.Shanthi[a,b], R.Subadevi[a, *], M.Ramachandran[a,c], M.Sivakumar [a]

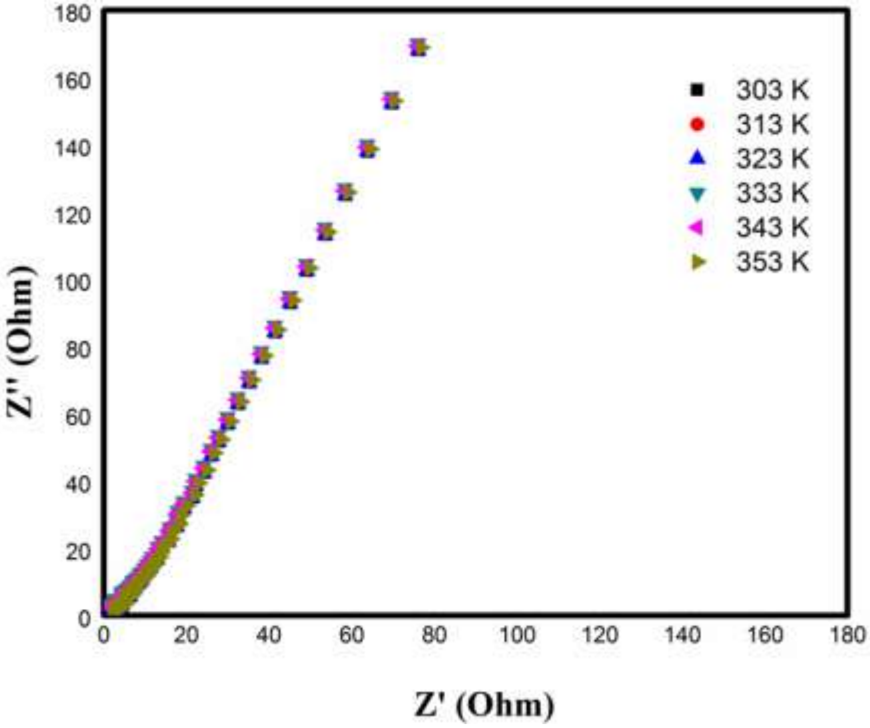
Title of the manuscript: EFFECT OF ZrO_2 NANOFILLER ON THE ELECTROCHEMICAL CHARACTERISTICS OF COMPOSITE POLYMER ELECTROLYTES BASED ON (PVDC-AN) COPOLYMER

Figure 2



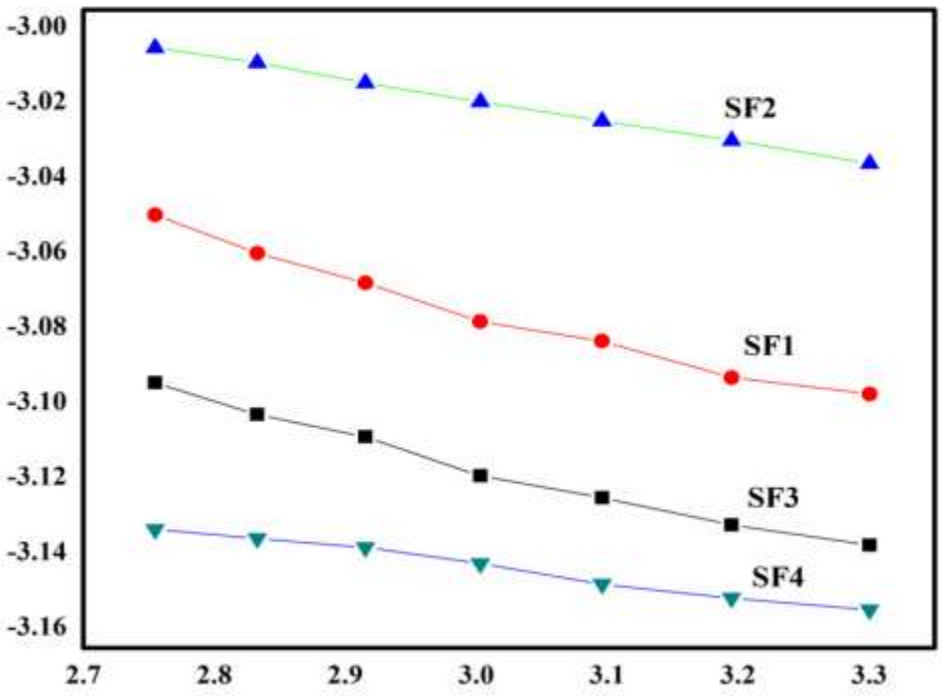
Name of the Autho: M.Shanthi[a,b], R.Subadevi[a, *], M.Ramachandran[a,c], M.Sivakumar [a]
Title of the manuscript: EFFECT OF ZrO_2 NANOFILLER ON THE ELECTROCHEMICAL CHARACTERISTICS OF COMPOSITE POLYMER ELECTROLYTES BASED ON (PVDC-AN) COPOLYMER

Figure 3 (a)



Name of the Autho: M.Shanthi[a,b], R.Subadevi[a, *], M.Ramachandran[a,c], M.Sivakumar [a]
Title of the manuscript: EFFECT OF ZrO_2 NANOFILLER ON THE ELECTROCHEMICAL CHARACTERISTICS OF COMPOSITE POLYMER ELECTROLYTES BASED ON (PVDC-AN) COPOLYMER

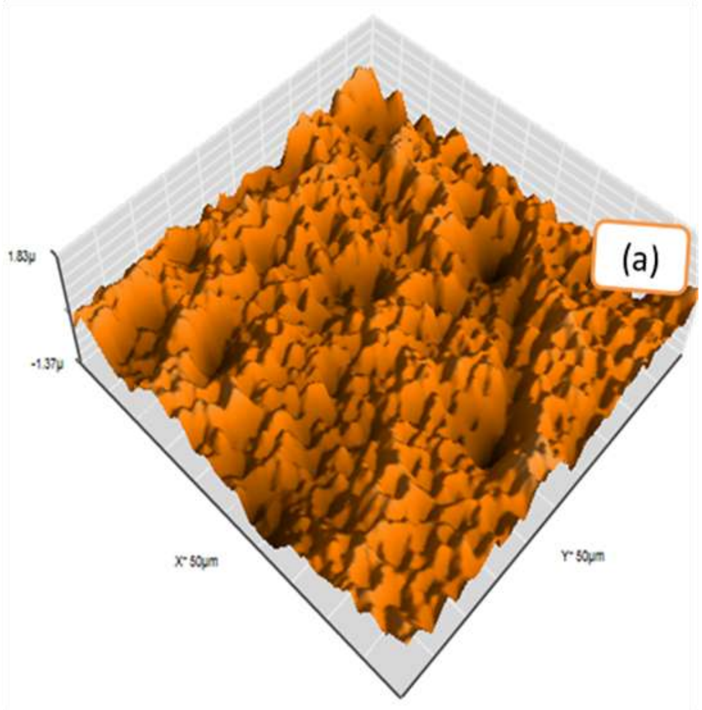
Figure 3 (b)



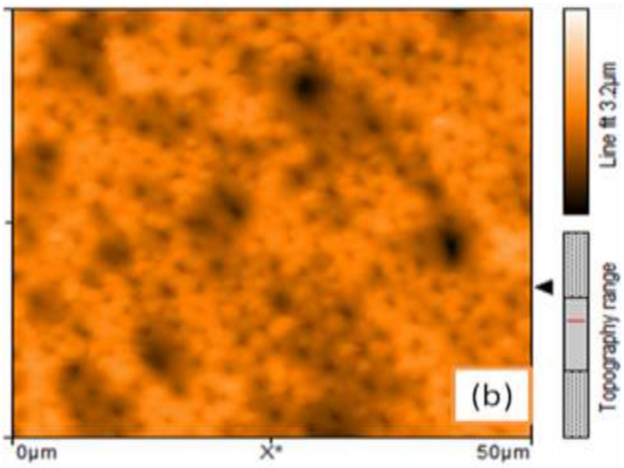
Name of the Autho: M.Shanthi[a,b], R.Subadevi[a, *], M.Ramachandran[a,c], M.Sivakumar [a]

Title of the manuscript: EFFECT OF ZrO_2 NANOFILLER ON THE ELECTROCHEMICAL CHARACTERISTICS OF COMPOSITE POLYMER ELECTROLYTES BASED ON (PVDC-AN) COPOLYMER

Figure 4



a) Three Dimensional

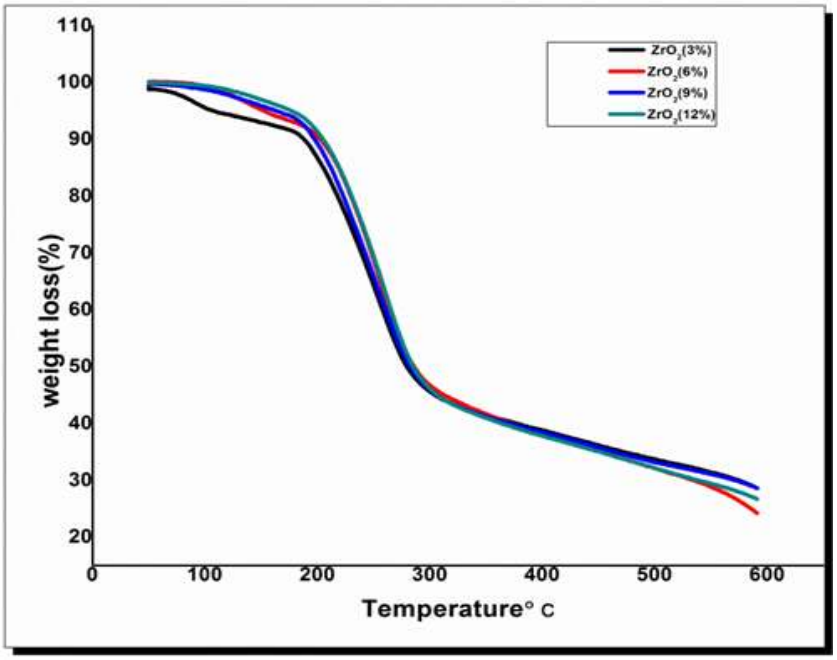


image

b) Three Dimensional image

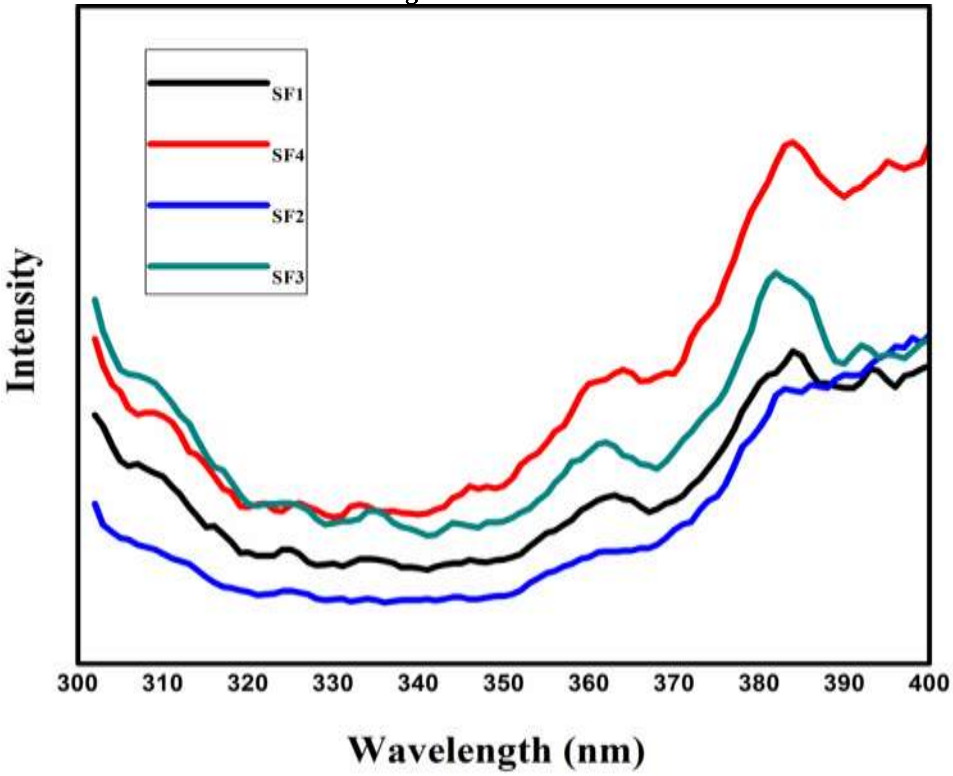
Name of the Autho: M.Shanthi[a,b], R.Subadevi[a, *], M.Ramachandran[a,c], M.Sivakumar [a]
Title of the manuscript: EFFECT OF ZrO_2 NANOFILLER ON THE ELECTROCHEMICAL CHARACTERISTICS OF COMPOSITE POLYMER ELECTROLYTES BASED ON (PVDC-AN) COPOLYMER

Figure 5



Name of the Autho: M.Shanthi[a,b], R.Subadevi[a, *], M.Ramachandran[a,c], M.Sivakumar [a]
Title of the manuscript: EFFECT OF ZrO_2 NANOFILLER ON THE ELECTROCHEMICAL CHARACTERISTICS OF COMPOSITE POLYMER ELECTROLYTES BASED ON (PVDC-AN) COPOLYMER

Figure 6



Name of the Autho: M.Shanthi[a,b], R.Subadevi[a, *], M.Ramachandran[a,c], M.Sivakumar [a]
Title of the manuscript: EFFECT OF ZrO_2 NANOFILLER ON THE ELECTROCHEMICAL CHARACTERISTICS OF COMPOSITE POLYMER ELECTROLYTES BASED ON (PVDC-AN) COPOLYMER
Table 1:
Ionic conductivity values for PVdC-co-AN(92wt.%) – $LiClO_4$ (8wt.%) – ZrO_2 (X wt.%)

Sample	ZrO_2 ratio	Ionic conductivity x 10^{-4} S cm^{-1}					
		303K	313K	323K	333K	343K	353K
SF1	3	7.93	7.98	8.07	8.16	8.23	8.34
SF2	6	9.10	9.23	9.34	9.45	9.56	9.68
SF3	9	7.24	7.29	7.34	7.41	7.47	7.52
SF4	12	6.92	6.97	7.03	7.12	7.19	7.23