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)

OPTIMIZATION OF BLEND OF POLYMETHYL METHACRYLATE (PMMA) WITH POLY VINYLIDENE CHLORIDE-CO-ACRYLONITRILE (PVdC-co-AN) COMPOSITE ELECTROLYTES

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Abstract:*A novel polymer electrolyte membranes are prepared bycomprising of poly (vinylidene chloride -co-acrylonitrile) (PVdC-AN), poly (methylmethacrylate) (PMMA) with different ratio, with constant ratio of lithium per chlorate ($LiClO_4$), and Zirconia (ZrO_2) by solution cast technique. The formation of blend polymer electrolyte complex has been confirmed by XRD and FTIR spectroscopy analysis. The ac impedance studies are carried out to depict role of blendingof polymers on conductivity. The high ionic conductivity of 0.6 x 10^{-4} at 303K has been observed for the blend ratio 25:75 of PVdC-AN:PMMA. The temperature dependence of the blend polymer electrolyte is found to obey VTF relation. TG/DTA analysis has been performed in order to investigate the thermal stability of the blend polymer electrolyte. The three dimensional topographical image of the blend are investigated using AFM.*

Introduction

The ionic conductivity in alkali metal salt complexes of PEO was demonstrated by Wright in 1973[1]. Since,there has been large number of research work carried out to enhance the room temperature ionic conductivity of PEO. Several strategies were followed such as blendingof two polymers [2-4], adding low molecular weight organic liquid(plasticization)[5-7], doping with inert inorganic fillers in polymeric film [8,9], crosslinking two polymers[10]. Among them blending of low molecular weight polymer with high molecular weight polymer is preferablesince the physical and electrochemical properties can be modulated by changing the composition of the polymers.Therefore, the objective of our investigation is to identify blend polymerelectrolyte based on PVdC-AN with sufficiently high ionic conductivity to allow the operation of the solid state lithium batteries at ambient temperature. An attempt has been made to enhance the ionic conductivity of PVdC-AN based system blended with a compatible polymer PMMA. Several reports have been available as PMMA as a host polymer suchas (PVC–PMMA) blend [11], (PVA–PMMA) blend[12], (PVC–PVAc) blend [13]. Because of its compatible nature with otherpolymers, PMMA hasbeen chosen to blend with PVdC-AN.In thepresent work, solid polymer electrolytes were prepared withdifferent weight ratios of PVAc and PMMA for constant weight percentage (8wt.%) of lithium perchlorate($LiClO_4$), by solution-casting technique. $LiClO_4$has been chosensince it shows smaller dissociation energy [14].

Experimental

The blend polymer electrolytes of PVdC-AN/PMMA composition were prepared by solution casting technique with the blend ratios viz, 100:0, 25:75, 50:50, 25:75, 100 with salt content 8wt% and ZrO_2 filler 6wt%. P(VdC-AN) and PMMA were dried under vacuum at 80°C for 24h. Reagent grade anhydrous $LiClO_4$ was used after drying in vacuum at 80°C for 24 h. Appropriate quantity of the corresponding electrolyte constituents were dissolved separately in anhydrous Tetrahydrofuran (THF). The polymer and the salt solutions were mixed together and subjected to continuous stirring by magnetic stirrer to get homogenous solution. Thus obtained high viscous homogenous solution was stirred and evaporated at room temperature then cast into flat bottom petri plates. The cast films were allowed to evaporate in air at room temperature to allow slow evaporation of the solvent. The residual THF was removed by further drying under vacuum (1x10^{-3}Torr) for 24 h at 50°C.The peeled films were then kept in the desiccators;further drying has been adopted before the measurement and characterization studiesto be carried out. The electrolyte films were subjected for X-ray diffraction (XRD) using X'pert PRO PANalytical diffractometer in the scanning range 2θ=10–80° using CuKα (wavelength λ=1541Å) 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} in the transmittance mode. The AC impedance studies of the polymer complexeswere carried out in the temperature range 303–363K using Keithley LCZ 3330 M. Thermal analysis was performed by Perkin Elmer (Pyres diamond thermogravimetric/differential thermal analyzer (TG/DTA)) at a heating rate of 10°C/min from 40 to 800°C.

X-Ray Diffraction Analysis

Fig.1(a–h) shows the X-ray diffraction patterns of PVdC-AN, PMMA, $LiClO_4$, ZrO_2 and their complexes. The diffractogram of pure PVdC-AN in Fig.1(a) shows sharp peak at 2ϴ=40.25,46.76 and 67.94° confirms the crystalline nature of the polymer. Fig.1(b) shows the diffraction peaks of PMMA at 2θ =17.20and 30.82°. The XRD pattern of $LiClO_4$ in Fig.1(c) shows intense peaks at angles 2θ=18.36, 23.2,27.5, 32.99 and 36.58° reveal the crystalline nature of the ionic salt. Fig.1(d) shows the diffraction peaks of ZrO_2 at 2θ = 28.07, 31.46, 33.70, 35.30, 49.26, 50.39˚ . In Fig.1(e-h) all the complexes contain no sharp peaks and the intensity of peaks decreases.. No peaks corresponding to $LiClO_4$ are found in the polymer complexes show the complete dissolution of salt in the polymer matrices. Diffraction pattern of the complexes confirms the amorphous nature, which isresponsible for higher conductivity.

FTIR Analysis

In order to examine the complex formation and interactions between the electrolyteconstituents in the polymer membrane,FTIR spectroscopy have been carried out [15].Fig.2(a–h) shows the FTIR patterns of PVdC-AN, PMMA, $LiClO_4$, ZrO_2 and their complexes. In Fig.2(e), the peak corresponding to C=O symmetric stretch of PMMA has been appeared at 1735cm^{-1}as broadened peak. The $–O–CH_3$stretching vibration of PMMA has been appeared at 1450cm^{-1}. The transmittance peak intensity of $–CH_3$symmetrical bending of PMMA at 1383cm^{-1}gets decreased, which is depicted in the Fig.2(g-h). In PVdC-AN, the vibrationalband at 2245 cm^{-1}corresponds to the stretching vibration of nitrile band(C≡N) is shifted towards the higher frequency side in all the complexes.This is due to the inductive effect created by the interaction between thenitrogen atoms in C≡N with Li^+ion [16]. Thus the above observations confirmthe complex formation among the constituents of electrolytes.

Conductivity measurements

The ionic conductivity of the blend polymer electrolytes were evaluated by the complex impedance plot which was established using the Stainless Steel (SS) / PE / SS cell couple andKeithleyLCZ 3330 Meter. The blend polymer membranes were sandwichedbetween stainless steel blocking electrodes with the radius of 1×10^{-2} m and placed inside a cylindrical glass container.The impedance measurements were recorded in the frequencyrange 40 Hz–100 kHz with a signal amplitude of 10 mV.The ionic conductivity of the synthesized electrolytes

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

wheret - thickness of the sample.
A - area of the electrolyte sample
R_b -is the bulk resistance of the polymer electrolyte membrane obtained fromcomplex impedance plot .

Figure 3 shows the Cole-Cole plot of all prepared electrolyte membrane at room temperature.

Among all the compositions studied themaximum room temperature ionic conductivity value 0.6 x 10^{-4}S/cm is obtained for the blend ratio From figure, it is observed that when the PMMA ratio increases from 25% to 75% in the polymer complexes,the bulk resistance values are decreasing. Hence, the ionic conductivity value increases with the increase of PMMA content.

Thermogravimetric Analysis

Thermogravimetric Analysis provides the quantitative measurement of any weight change associated with transition. Fig.4 shows the TG/DTA curves of maximum conducting sample and depicts the weight loss with temperature. The initial weight loss about 5% may be due to the residual solvent or moisture content at the time of loading the sample. The major weight loss~70% takes place in the temperature range 170-270°C, which is attributed to its melting along with the corresponding exothermic peaks in DTA curves. Hence, from the thermogram, one can confirm that the electrolyte films are thermally stable more than the operating temperature, 70°C.

Atomic Force Microscopic analysis

The prepared sample having maximum ionic conductivity is subjectedto atomic force microscopicanalysis to study the two andthreedimensional topographical imagea maximum ionic conductivity. Fig.5 clearly depicts the pores present in the scanned area. These pores increase the segmental motion of the polymer chain which results in high ionic conductivity.

Conclusion

The blend ratio of PVdC-AN and PMMA based electrolytes has been optimized using solution casting technique. The complexation of the electrolytes has been elucidated through XRD and FT-IR analyses. Also, all the peaks pertaining to lithium salt was disappeared in the complexes, which reveals the complete dissociation of salt in the polymer matrices. The maximum room temperature ionic conductivity was obtained for the blend ratio 25:75 (PVDC-AN:PMMA–$LiClO_4$ (8wt.%) – ZrO_2 (6wt%). The ionic conductivities calculated using ac impedance. The two and three-dimensional topographic images of the sample having a maximum ionic conductivity show the presence pores that are responsible for ionic conduction.

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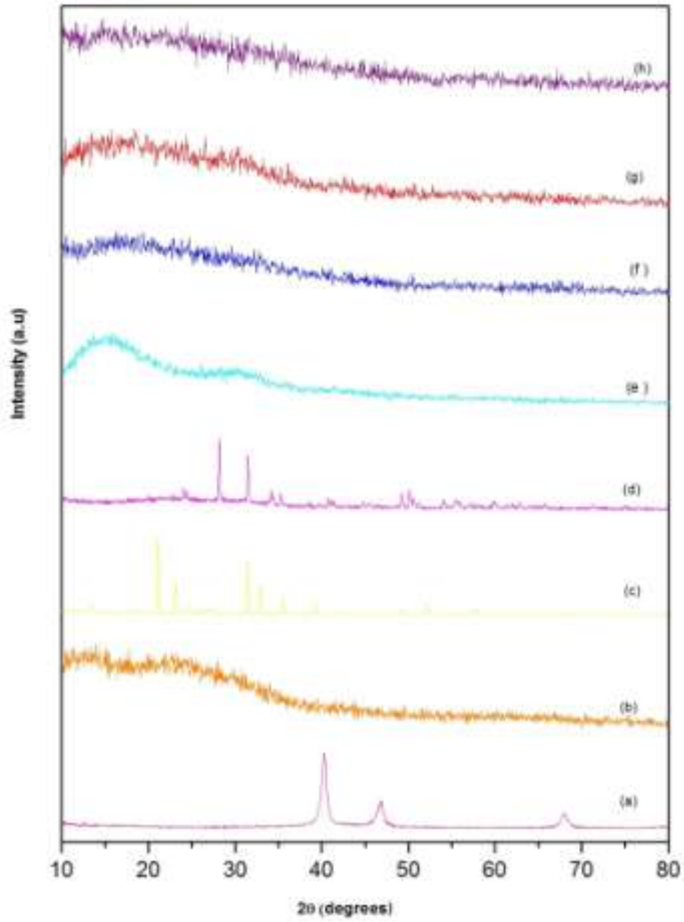

Figure 1. XRD pattern of
(a) Pure PVDC-AN, (b) PMMA (c) $LiClO_4$ (d) ZrO_2

(e) PVdC-AN(0) – PMMA(100) –$LiClO_4$ (8wt.%) – ZrO_2 (6wt%)
(f) PVdC-AN(75) – PMMA(25) – $LiClO_4$ (8wt.%) – ZrO_2 (6wt%)
(g)PVdC-AN(25) – PMMA(75) – $LiClO_4$ (8wt.%) – ZrO_2 (6wt%)
(h)PVdC-AN(100) – PMMA(0) – $LiClO_4$ (8wt.%) – ZrO_2 (6wt%)

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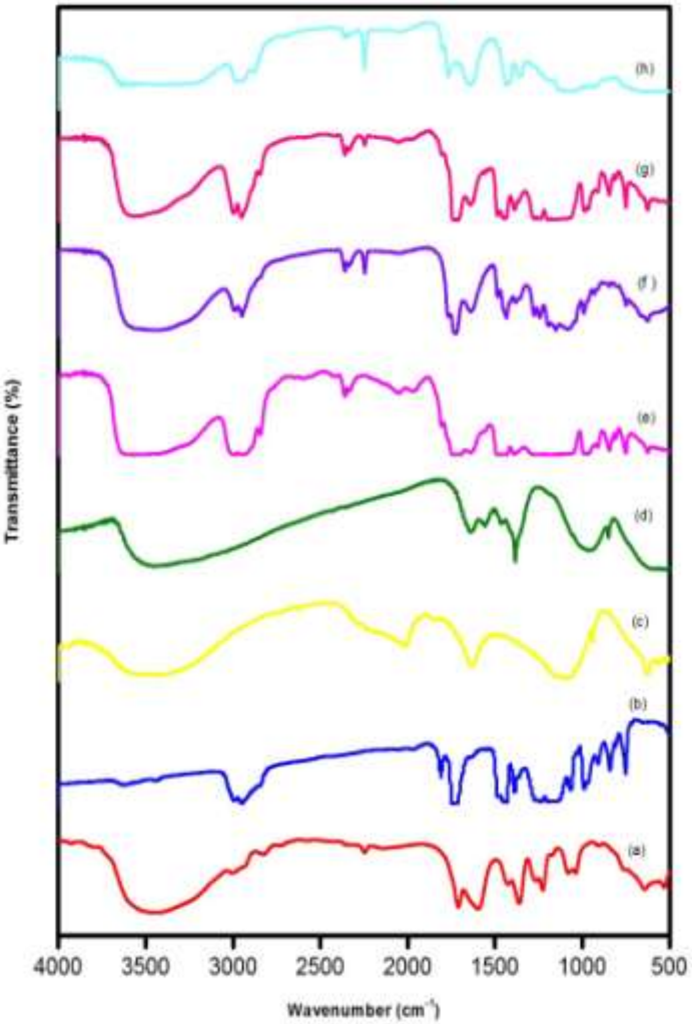

Figure 2.FTIR Spectra of
(a)Pure PVDC-AN, (b) PMMA (c) $LiClO_4$ (d) ZrO_2
(e) PVDC-AN(0) – PMMA(100) –$LiClO_4$ (8wt.%) – ZrO_2 (6wt%)
(f) PVDC-AN(75) – PMMA(25) – $LiClO_4$ (8wt.%) – ZrO2 (6wt%)
(g)PVDC-AN(25) – PMMA(75) – $LiClO_4$ (8wt.%) – ZrO2 (6wt%)
(h)PVDC-AN(100) – PMMA(0) – $LiClO_4$ (8wt.%) – ZrO2 (6wt%)

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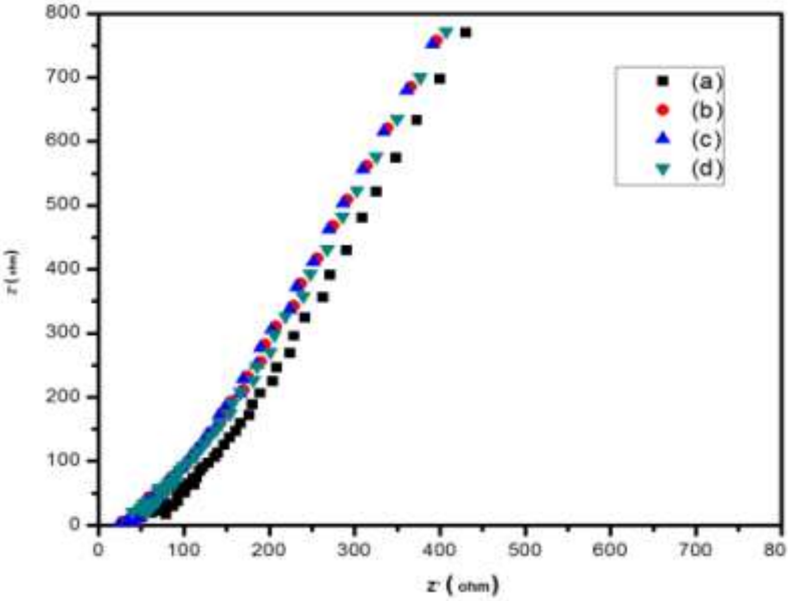

Figure 3.AC Impedence spectra at room temperature
(a) PVdC-AN(0) – PMMA(100) – $LiClO_4$ (8wt.%) – ZrO_2 (6wt%)
(b) PVdC-AN(75) – PMMA(25) – $LiClO_4$ (8wt.%) – ZrO_2 (6wt%)
(c) PVdC-AN(25) – PMMA(75) – $LiClO_4$ (8wt.%) – ZrO_2 (6wt%)
(d)PVdC-AN(100) – PMMA(0) – $LiClO_4$ (8wt.%) – ZrO_2 (6wt%)

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Figure 4

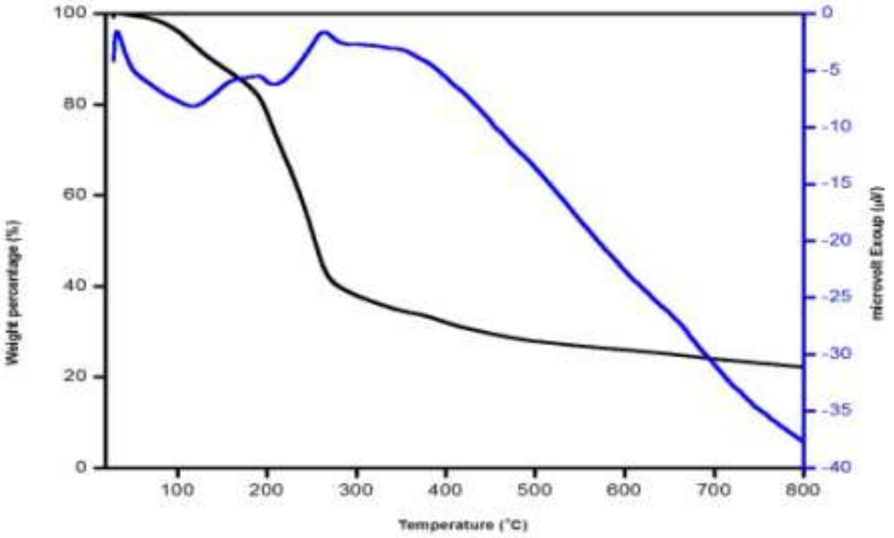

Figure 4.Tg/DTA curve the polymer electrolyte with blend ratio 25:75 (PVdC-AN:PMMA–$LiClO_4$ (8wt.%) – ZrO_2 (6wt%).

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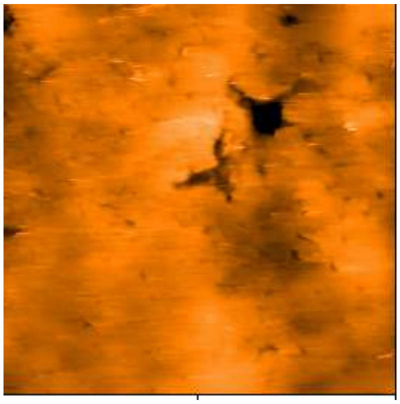
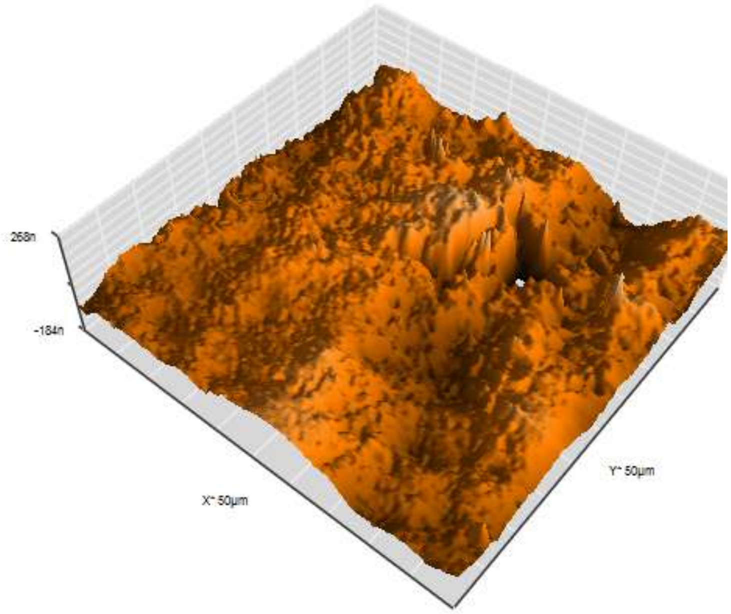
Figure 5



(a) Two dimensional image



b) Three dimensional image

Figure 5.The topographical image of maximum conducting sample PVdC-AN(25) – PMMA(75) – $LiClO_4$ (8wt.%) – ZrO_2 (6wt%)