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Preparation and Characterization of Gel Polymer Electrolyte Based on PAN- $NH_4CF_3SO_4$ and Nano ZrO_2 Filler –Application as an Electrochemical cell

Hari Prasad Dara, Narasimha Rao Maragani, K.Vijayakumar, K.Sunil Babu

***Abstract:** In the present investigation, the Nano Composite Gel Polymer Electrolyte (NCGPEs) based on nano fillers ZrO_2, Polyacrylonitrile (PAN), and Ammonium Triflate ($NH_4CF_3SO_4$) doped at various wt% ratios prepared with the help of solution cast technique. The better amorphous nature observed for the 70PAN:30$NH_4CF_3SO_4$ composition with addition of 1-4 wt% of ZrO_2 nano fillers and structural, complexation studies of NCGPEs were confirmed by XRD technique. The micro structural studies and particle size can be revealed by SEM technique. DC Conductivity studies reveal the ionic conductivity performance on effect of temperature and composition wt% of nano powder. The ionic conductivity studies observed for 70PAN:30$NH_4CF_3SO_4$ with nano powder ZrO_2 concentration ranging from 1-4 wt%. The sample containing 3wt% of ZrO_2 exhibits the highest conductivity order of $4.20x10^{-4}$ S cm^{-1} at room temperature (303K) and $4.65x\ 10^{-3}$ S cm^{-1} at 373K. The cell parameters like Open Circuit Voltage, Short Circuit Current, energy density and power density were perfectly determined which were useful to explain electrochemical cell behaviour.*

***Keywords:** NCGPEs; Surface morphology, Discharge parameters; Electrochemical Cell Applications.*

I. INTRODUCTION

Now a day's a tremendous role play in technical applications of electrochemical energy storage devices therefore Most of the research is devoted to identify the materials which are suitable to computers, communication devices, industrial controls, electric vehicles, space chips etc [1]. Batteries are crucial components of such devices; they must meet certain standards of reliability, weight, size, shape. NCGPEs based batteries were improved to satisfy these requirements. This gel polymer electrolyte material in electrochemical cell system has two different functions such as an electrolyte and as a separator between anode and cathode. Nano composite Gel Polymer electrolytes exhibits better ionic conductivity and dimensional stability. To improve electro chemical performance and thermal stability of GPEs nano ceramic fillers can be added. This is the better way for getting good ionic conductivity and hence proved by experimental [2-5]. This study describes the preparation of a series of Gel polymer PAN based nano composite electrolytes that incorporate ZrO_2 nano powders and revealed changes of structural, electrical properties, discharge characteristics perfectly.

II. MATERIALS

PAN ($M_{w.}$150, 000) was received from Aldrich (USA), Ammonium Triflate ($NH_4CF_3SO_4$), Ethylene Carbonate (EC) and dimethyl formamide (DMF) were obtained from Merck chemicals Co.(Nottingham, United Kingdom).

A. *Preparation of gel PAN/ $NH_4CF_3SO_4$-ZrO_2 nano composite electrolytes:*

The molar ratio of polymer Polyacrylonitrile (PAN) doped with plasticizers like EC and DMF stirred continuously then after getting homogeneous solution. Now the dopant salt $NH_4CF_3SO_4$ added to that obtained solution. After that nano sized ceramic powder ZrO_2 with different ratios like (1, 2, 3, 4 wt %) added to the formed solution and stirred for several hours for getting transparent solutions by using solution cast method. The prepared gel solution taken into Petri dishes for drying and finally the transparent and flexible films of thickness ranging from 100-118 μm have been obtained.

III. CHARACTERIZATION

XRD diffractometer (Xpert Pro) was equipped with Cu target and Ni filter and operated at a scanning rate of 10 min analyzed prepared samples for determining the structural properties and determine the chemical composition. In the present investigation, the surface morphology of newly synthesized PAN based on NCGPEs measured with the help of SEM [model: JEOL-JXA 8100]. By applying dc potential directly on to sample using four probe process the ionic conductivity was measured in between 300-373K. The fraction of current is carried out by ions mobility hence to determine transport numbers Wagner's polarization technique can be used [6-7]. The GPEs film 70PAN:30NaF:3 wt% of ZrO_2 taken between the positive and negative electrodes. After that constant load 100kΩ applied to measure the parameters of cell like OCV, SCC and Discharge time.

IV. RESULTS AND DISCUSSIONS

B. *XRD Studies:*

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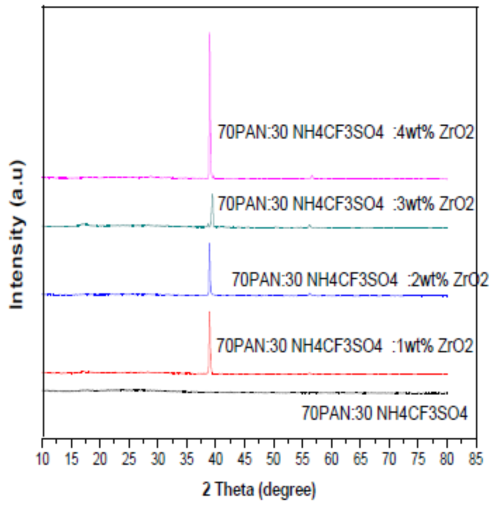
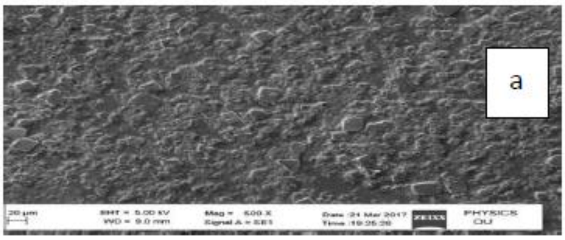
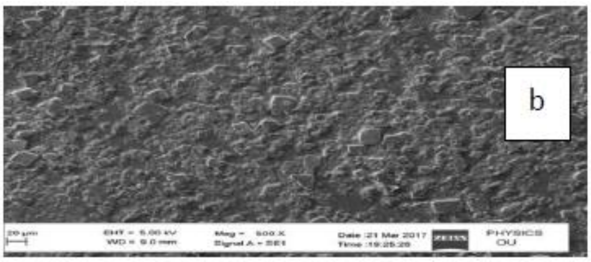


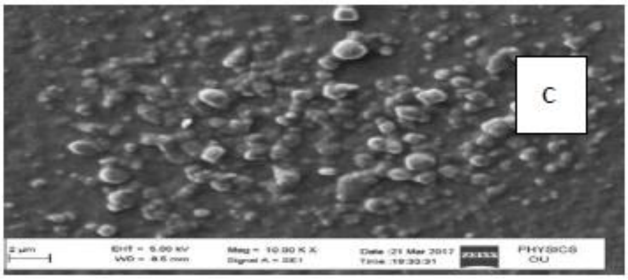
Fig. 1: XRD of 70:30 (PAN: $NH_4CF_3SO_4$) complexed films with wt % of ZrO_2.

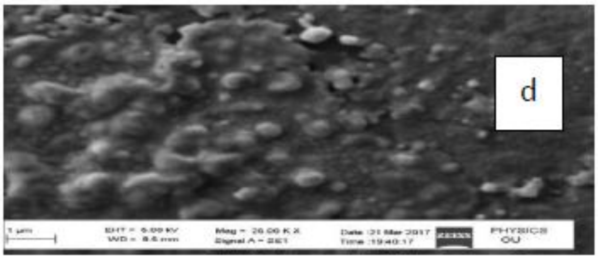
The plots of XRD for 70PAN:30 $NH_4CF_3SO_4$, 70PAN:30 $NH_4CF_3SO_4$:1wt% ZrO_2 , 70PAN:30 $NH_4CF_3SO_4$:2wt% ZrO_2 , 70PAN:30 $NH_4CF_3SO_4$:3wt% ZrO_2 , and 70PAN:30 $NH_4CF_3SO_4$:4 wt% ZrO_2 systems are shown in Fig.1.From these spectra a sharp peak identified at 2 θ =37^0 which corresponds to orthorhombic PAN (110) reflection [8-10]. The sharp peak at 2θ values around 37º is less intense in complexed PAN films compared to those in 70PAN:30 $NH_4CF_3SO_4$ film. Degree of crystallinity of the 70PAN:30 $NH_4CF_3SO_4$ complexes decreased with addition of ZrO_2 nano ceramic fillers. The broad peak shifted to a lower or higher value by addition of ZrO_2 nano powder .Therefore, it may be due to internal adjustment in the amorphous nature, indicates that high ionic conductivity [11]. The relative intensity of 70PAN:30 $NH_4CF_3SO_4$ decreased with the increasing in ZrO_2 nano powder concentration. XRD pattern indicates that enhancement of the amorphous nature of the gel polymer electrolyte and confirms the complexation of nano powder with polymer-salt matrix.

C. SEM Studies:









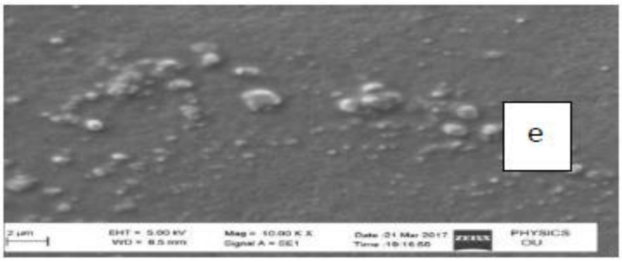


Fig.2. SEM Photographs of (a) 70 PAN: 30 $NH_4CF_3SO_4$ (b) 70PAN+30 $NH_4CF_3SO_4$+ 1wt% ZrO_2 (c) 70PAN+30 $NH_4CF_3SO_4$+ 2wt% ZrO_2 (d) 70PAN+30 $NH_4CF_3SO_4$+ 3 wt%ZrO_2 (e) 70PAN+30 $NH_4CF_3SO_4$+ 4wt%ZrO_2

SEM Studies of 70PAN:30 $NH_4CF_3SO_4$, 70PAN:30 $NH_4CF_3SO_4$:1wt% ZrO_2 , 70PAN:30 $NH_4CF_3SO_4$:2wt% ZrO_2 , 70PAN:30 $NH_4CF_3SO_4$:3wt% ZrO_2 , and 70PAN:30 $NH_4CF_3SO_4$:4 wt% ZrO_2 systems are shown in Fig.2.From these spectra particle grain size and perception of phase separations revealed. These results affects on structural properties and conductivity properties i.e phase segregation of prepared samples. With the addition of nano powder ZrO_2 to the polymer-salt matrix the particle grain size varied and it can be represented in SEM photographs. The surface morphology also explained by SEM photographs.

D. Ionic conductivity based on Temperature:

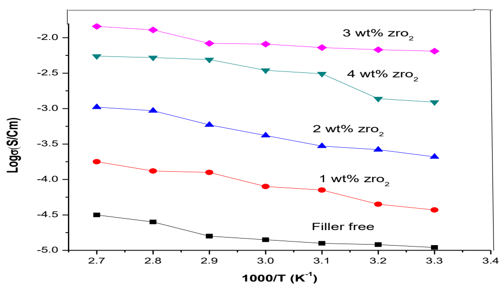


Fig.3. Temperature dependence of proton conductivity for 70PAN:30 $NH_4CF_3SO_4$ GPEs with different wt% of nanofiller ZrO_2.

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70PAN:30NH$_4$CF$_3$SO$_4$: (1-4) wt% ZrO$_2$ structured films conductivity with respect of temperature represented in Fig.3. The obtained graph follows the Arrhenius relation. The activation energy values measured from this relation for all compositions. In addition of nanofiller ZrO$_2$ the ionic conductivity enhanced up to 3 wt% which indicates that ionic conductivity depends upon no of charge carriers in polymeric electrolyte substances [12]. The ionic conductivity and E$_a$ values for prepared nanocomposite membranes were taken from Arrhenius plots drawn between the ionic conductivity versus Temperature and illustrated in Table 1. ZrO$_2$ nano filler doped Gel Polymer membranes exhibit higher ionic conductivity when compared to filler-free electrolytes due to the mobility of charge carriers getting more velocity and exhibiting greater conductivity.

Table I. D.C Conductivity, E$_a$, various compositions of 70PAN + 30 NH$_4$CF$_3$SO$_4$+ wt% ZrO$_2$ GPEs systems

NCGPEs	Conductivity 303K	373K	Activation energy(eV)
70PAN:30 NH$_4$CF$_3$SO$_4$:1 wt% ZrO$_2$	2.92x10^{-5}	3.10x10^{-5}	0.26
70PAN:30 NH$_4$CF$_3$SO$_4$:2 wt% ZrO$_2$	3.42x10^{-5}	4.62x10^{-5}	0.29
70PAN:30 NH$_4$CF$_3$SO$_4$:3 wt% ZrO$_2$	4.20x10^{-4}	4.65x10^{-3}	0.21
70PAN:30 NH$_4$CF$_3$SO$_4$:4 wt% ZrO$_2$	4.10x10^{-4}	4.92x10^{-4}	0.27

E. Ionic conductivity based on nano filler Composition:

Fig.4 explores that the modifications of ionic conductivity with adding of nano ceramic filler ZrO$_2$ composition It was cleared that the ionic conductivity increased from 1-3 wt% ZrO$_2$ and for 4 wt% decreased..These results explain that with an addition of nanofillers up to 3 wt% the no of free charge carriers increased i.e. the better ionic conductivity obtained for 3 wt% of ZrO$_2$ .The ionic conductivity values noted in Table 1. The highest ionic conductivity obtained for 3 wt% of ZrO$_2$ was 4.65 × 10^{-3} S/cm at 373K.

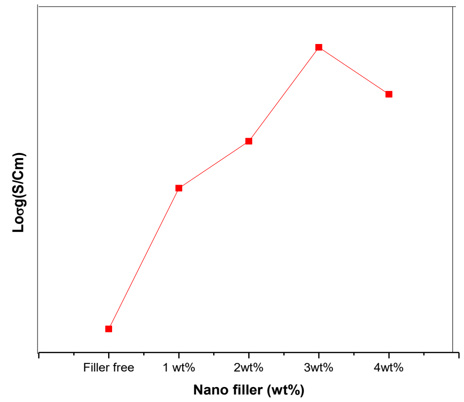

Fig.4. Composition dependence of conductivity in 70PAN +30 NaF+wt% ZrO$_2$ System

F. Transference number measurement:

70PAN:30 NH$_4$CF$_3$SO$_4$ based ZrO$_2$ nanofiller doped Transference number measured by using ion transport phenomena. Fig.5 illustrates that change of polarization current vs time .From these graph the polarization current can be reduced while increasing time. The presence of predominantly ions the polarization current decreased [13-18]. The transference numbers for 1- 4 wt% of ZrO$_2$ 0.910, 0.915, 0.936 and 0.921.were given in Table 2

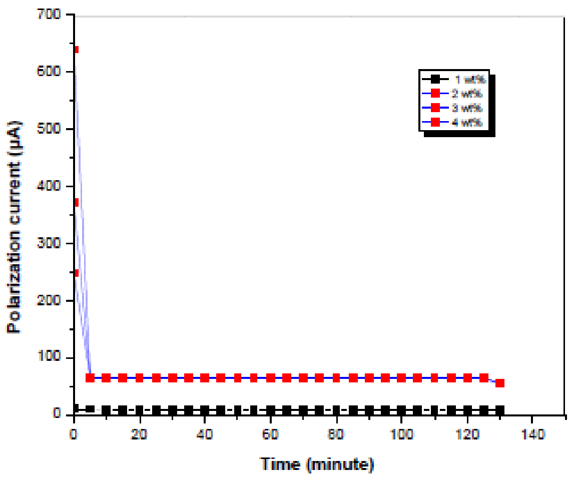

Fig.5: Polarization current vs time plot for 70PAN:30 NH$_4$CF$_3$SO$_4$: wt% ZrO$_2$ polymer composite at 303 K

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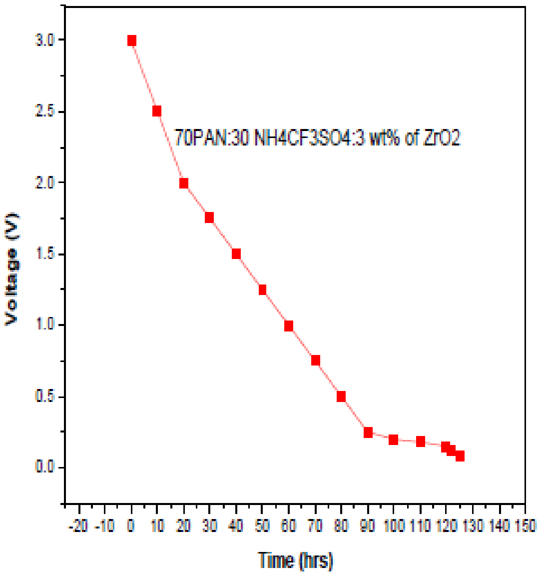
Table II: E_a, Ionic Transference numbers various compositions of 70PAN: 30 $NH_4CF_3SO_4$ films at different wt % ZrO_2.

NCGPEs	AE (ev)	Transference Number	
		t_{ion}	t_{ele}
1 wt% ZrO_2	0.28	0.910	0.03
2 wt% ZrO_2	0.31	0.915	0.02
3 wt% ZrO_2	0.27	0.936	0.05
4 wt% ZrO_2	0.23	0.921	0.04

Fig.6. Discharged curve of solid-state cell configuration of Na/70PAN: 30 $NH_4CF_3SO_4$:3wt% ZrO_2 /(I_2+C+Electrolyte) at load 100kΩ.



G. *Discharge Characteristics:*

In previous studies 70PAN:30 $NH_4CF_3SO_4$ based GPEs exhibiting maximum conductivity. For getting more conductivity the ceramic filler ZrO_2 doped with host polymer matrix. From Fig.6 the 3 wt%ZrO_2 having maximum conductivity when compared to other compositions. The sharpness of initially decreased in terms voltage of the cell due to polarization effect [19-22]. Hence proton type battery using this composition films constructed to study the discharge characteristics. The cell configuration such as anode material taken as Na and mixture of iodine, graphite and a small piece with the ratio of 5:5:1 considered as a cathode material. The GPEs film 70PAN:30 $NH_4CF_3SO_4$:3 wt% of ZrO_2 taken between the positive electrode and negative electrode. After that constant load 100kΩ applied to measure the parameters of cell like OCV, SCC and Discharge time. The cell parameters of these nanocomposite gel polymer electrolyte film illustrated in Table 3. The OCV of cell was 3.02V.

Cell parameters	70PAN: 30 $NH_4CF_3SO_4$:3 wt% ZrO_2
Electrolyte area (cm^2)	1.18
Cell Weight (gm)	1.42
OCV (V)	3.02
SCC (μA)	1.7
Discharging time for plateau region (h)	125
Density of power(Mw/ Kg)	2.72
Density of Energy (mWh /Kg)	296.2
Density of current	2.23
Capacity of Discharge (μA h^{-1})	156.4

V. CONCLUSIONS

Blending of different concentration of $NH_4CF_3SO_4$ with pure PAN with doping of nano powder ZrO_2 using solution casting procedure nano composite GPEs were fabricated. The characterization techniques like XRD, SEM and DC Conductivity studies were studied. The polymeric blends exhibit Semi crystalline nature. Further, the doping of nano powder to polymer salt complexed film has been performed better ionic conductivity. With the help of 70 PAN: 30$NH_4CF_3SO_4$ Gel polymer electrolyte system hybrid solid –state battery configuration with (Na/PAN: $NH_4CF_3SO_4$ (70:30) +3 wt% ZrO_2 +EC+DMF/ (I_2+C+Electrolyte)) has been fabricated and their discharge characteristics are studied and these results are found to be comparable with existing results.

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