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Structural and Conductivity Studies of PAN-based Al_2O_3 Nanocomposite Gel Polymer Electrolytes

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Abstract: *An attempt has been focused to develop a new aluminum ion conducting non aqueous polymer electrolyte for high power rechargeable batteries having applications in rapidly growing markets, such as laptops, handy tele communication equipments, electric vehicles, camcorders, etc. These features have given a thrust to develop a suitable nano composite GPE based on PAN as polymer host and sodium fluoride (NaF) as dopant salt and Al_2O_3 as nano filler in the form of thin films through solution casting technique, consuming N,N-dimethyl formamide (DMF) as a common solvent. Nano composite gel polymer electrolyte films have been prepared by solution casting technique. The XRD pattern of 70PAN-30NaF with addition of wt% Al_2O_3 ceramic filler indicated reducing degree of crystallinity. Using IR studies revealed that the complexation of the polymer poly (acrylonitrle) with NaF. The conductivity of the GPEs was studied with enhancement of nano fillers. The sample containing 3 wt% of Al_2O_3 exhibited the highest conductivity of $4.82x10^{-3}S\ cm^{-1}$ at room temperature (303K) and $5.96x10^{-3}S\ cm^{-1}$ at 378K. With the help of Wagner's polarization technique electronic (t_e) and ionic (t_i) values can be determined.To determine profiles of discharge characteristics (70PAN-30NaF-3wt% Al_2O_3) NCGPE solid-state electrochemical cell was fabricated and various cell profiles were evaluated.*

Keywords: *NCGPE, Solvent casting procedure, Discharge characteristics, Electrochemical cell applications.*

1. INTRODUCTION

The development of polymer systems with high ionic conductivity is one of the main objectives in polymer research. This is because of their potential applications as electrolytes in solid-state batteries, fuel cells, electrochemical display devices/smart windows, photo electrochemical cells etc. [1-3], due to their high conductivity, high energy density, wide electrochemical stability and easy process ability. The main advantages of polymer electrolytes are their mechanical properties, ease of fabrication of thin films of desirable sizes and their ability to form proper electrode/electrolyte contact in electrochemical devices. Generally, there are three types of polymer electrolytes: solid polymer electrolytes (SPEs), Gel polymer electrolytes (GPEs), and composite polymer electrolytes (CPEs) [4-12]. The present work Reports on a composite polymer electrolyte (PAN+NaF+ Al_2O_3) and it was concerned with solid-state electrochemical cells which are based on (PAN+NaF) electrolyte films. Several experimental techniques such as optical, electrical, XRD, FTIR, SEM and transport number measurements were performed to characterize these polymer electrolytes. Based on these electrolytes, electrochemical cells were fabricated with anode/polymer electrolyte/cathode configuration. The discharge characteristics of the cell were studied for a load of 100 kΩ.

2. EXPERIMENTAL TECHNIQUES

The nano composite gel polymer electrolyte films of pure and sodium fluoride salt doped- PAN were prepared by weight % ratio 70PAN: 30NaF, 70PAN: 30NaF: 1wt%Al_2O_3, 70PAN: 30NaF: 2wt%Al_2O_3, 70PAN: 30NaF: 3wt% Al_2O_3 and 70PAN: 30NaF: 4wt% Al_2O_3. Ethylene carbonate (EC) was used as plasticizer. The polymer PAN had M_w $1.5x10^5$ g/mol. All the solvents were obtained without any further purification. The polymer electrolytes were prepared by dissolving PAN and NaF salt in dimethyl formamide (DMF).The solution thus obtained was stirred in magnetic stirrer for about 2 hours until we got a homogeneous translucent gel after the plasticizer ethylene carbonate (EC) was added to this solution and stirred for about 2 hours. After that, the nano filler Al_2O_3 was added to this solution and stirred for 48 hours to get homogeneous mixture. Then, it was cast into polypropylene dishes and evaporates slowly at room temperature. The polymer electrolyte films were then transferred into desiccators for further drying before the test. The average thickness of prepared samples was 128μm.

2. 1. Materials Characterization

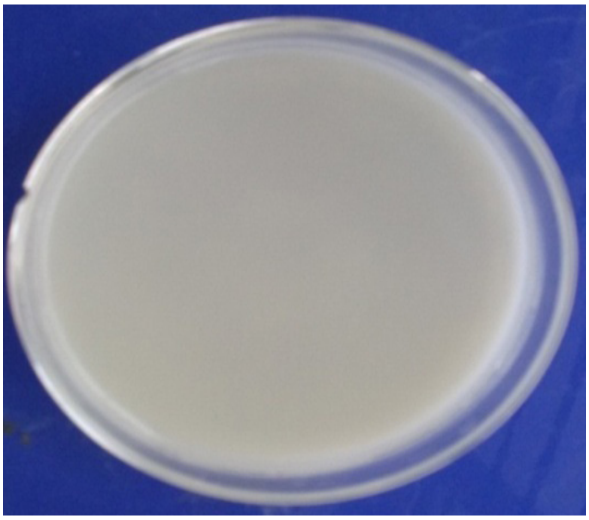


Fig. 1. Prepared Nano composite Gel polymer electrolyte film.

The prepared films characterized by using X-ray diffraction, PANalytical X'pert PRO (Philips, Netherlands). The FTIR Spectra were recorded with the help of Perkin Elmer FTIR Spectrophotometer in range 500 to 4000 cm-1 using KBr pellet method. The DC conductivity of gel polymer electrolyte thick films was measured by using Keithley 6514 electrometer connected to lab made conductivity set up [13]. The Scanning electron microscope (SEM) is one of the most versatile instruments used for the analysis of microstructure morphology[14]. The transport numbers were calculated by using Wagner's Polarization Technique [15]. The discharge characteristics like open circuit voltage (OCV),short circuit current(SCC),power density,etc were monitored a constant load of 100KΩ.

3. RESULTS AND DISCUSSION

3. 1. XRD Studies

In current investigation structural studies determined by PANalytical X'pert PRO (Philips, Netherlands) where 2θ angles were between 10° to 80°.The structural formation and complexation between the polymer and salt was analyzed by XRD technique [16-20].

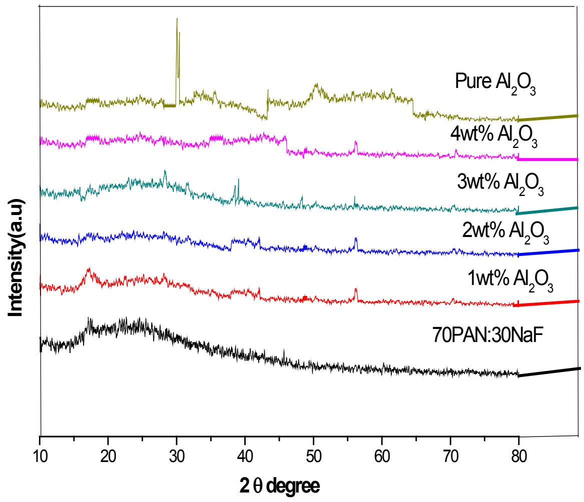


Fig.2. XRD spectra of (a) 70PAN:30 NaF (b) PAN+NaF+Al_2O_3 (70:30:1%) (c) PAN+NaF+Al_2O_3 (70:30:2%) (d) PAN+NaF+Al_2O_3 (70:30:3%) (e) PAN+NaF+Al_2O_3 (70:30:4%).

- According to Fig. 2, a diffraction peak is observed for Pure PAN and PAN complexed with stoichiometeric ratio of the inorganic salt with addition of nano particles NaF+Al_2O_3 polymer thin films between 2θ = 10- 80° and observed that a broadened peak was formed having less intensity.

- With enhancement of salt the peak was gradually decreased so full width half maxima (FWH) is increased.

- When the stoichiometeric ratio of salt (PAN+NaF+Al_2O_3) is increasing in the polymer the crystalline nature of film is gradually changes.

- By adding the nano particles a sharp peaks were observed at along the rotation of angles 2Θ.

- With raising of Al_2O_3 in the host polymer matrix the degree of peak intensity can be reduced which reveals the amorphous nature of the polymer. Also, the peaks were corresponding to filler-free 70PAN:30NaF have been found out to be absent in the other complexes up to 4 wt% of Al_2O_3.

3. 2. FTIR Studies

FTIR spectra of 70PAN:30NaF: wt% Al_2O_3 in the range between 500 and 4000 cm^{-1} recorded in Fig.3.The complexation of NaF in PAN has also been observed in FTIR spectral studies. It is also observed that the peak level is shifted towards the higher wave number side(1492 to 3517 cm^{-1}).The C=O group symmetric stretch mode of EC appeared at 1740 Cm^{-1}.There is also appeared of new peaks along with changes in existing peaks or disappearance in infrared spectra directly indicates the complexation of PAN-NaF and Al_2O_3. Different functional groups and vibrational band is observed for the different concentration of the sample. A symmetrical starching and bending bands are formed which is depend on their functional groups of the material. The transmittance occurs at 1492, 1683, 1645, 2361 cm^{-1} were corresponding to C=O stretching, C=N bending and C=C rocking respectively. The spectra of PAN, NaF and Al_2O_3 films show variation in peaks at different wavelength. The increasing in the intensity at higher wave length is obtained due to the more interaction between polymer matrix which is assigned to Na-F-Al2 -O stretching and dopant, and it is found at 2938 cm^{-1}. Hence it is confirmed that stronger molecular interaction exists between polymers and dopant attributed to the charge of p- π conjugation associated with the amide group of PAN arising dopant. The peak intensity changes at 2242-3517 cm^{-1} because of the dissolution of nano fillers with salt and the host polymer. The appearance and disappearance of peaks in the FTIR-spectra directly indicates the complexation of PAN with NaF, Nano Particles.

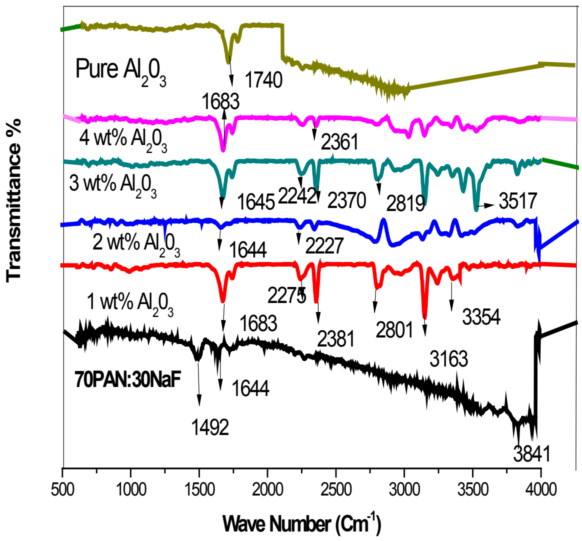
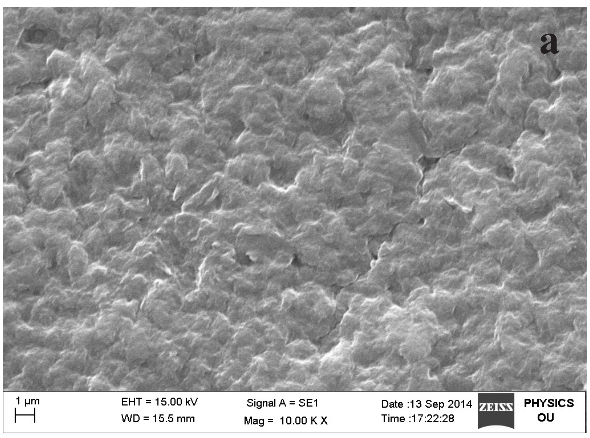
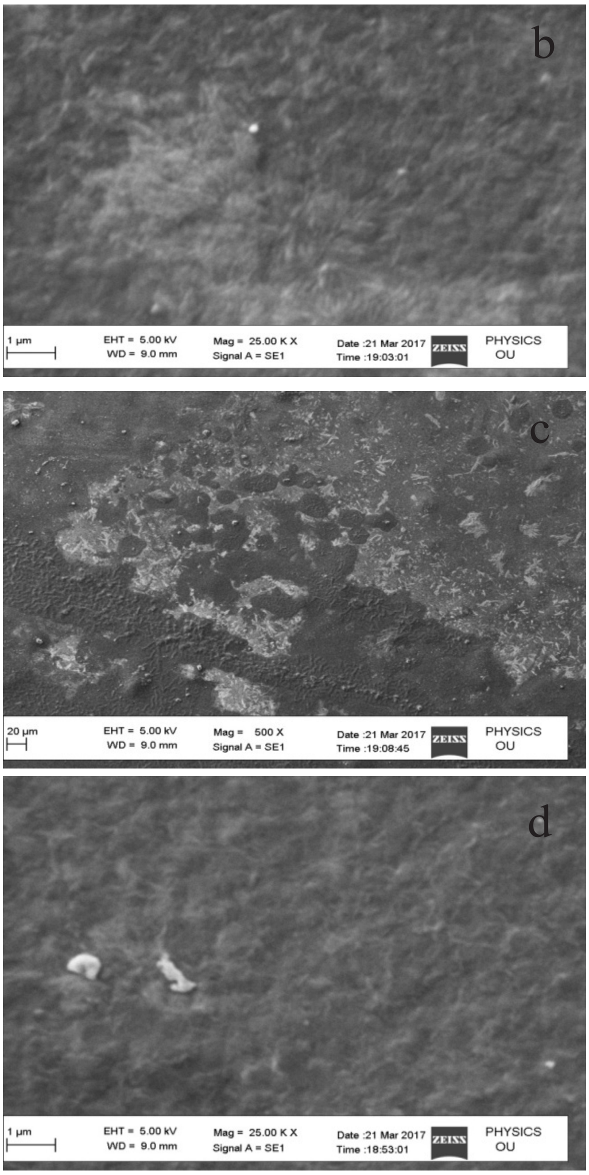


Fig. 3. FTIR Spectra of 70PAN:30NaF & complexed films for different wt% of Al_2O_3

3. 3. SEM Studies

The morphology surface for PAN- NaF complexed with Al_2O_3 NCGPE systems were analyzed by using SEM technique. These images of PAN, PAN+NaF+ Al_2O_3 having different ratios (70:30:1%, 70:30:2%, 70:30:3% and 70:30:4%) are shown in Fig 4. The SEM morphology of Pure PAN, PAN+NaF (70:30:1%, 70:30:2%, 70:30:3% and 70:30:4%) and the surfaces of the films are uniform such that the polymer and salt are completely dissolved and no phase separation has occured as shown in Figure 4. This analysis agrees well with the XRD analysis [21]





3. 4. DC Conductivity Studies:

The conduction mechanism helps to study conductivity properties for prepared GPEs. Ionic conductivity of resulted composites in temperature interval of 303 - versus the amounts of used nano filler (Al_2O_3) is represents in Fig. 5.The conductivity readings are also represented in Table 2.From this, we conclude that the conductivity enhanced with addition of Al_2O_3 upto 3 wt%. The amorphous nature of polymer substances should be responsible for this conductivity [22].

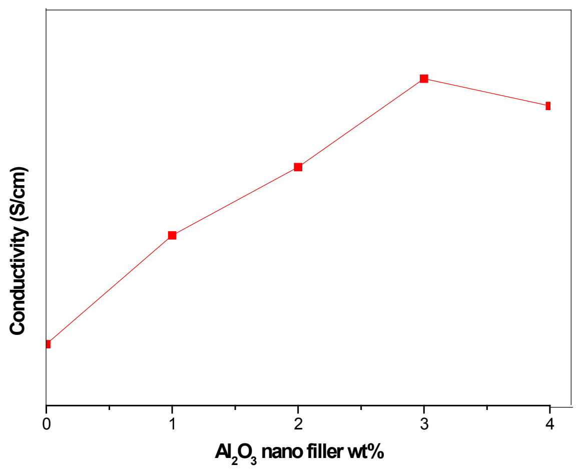


Fig. 5. Composition dependence of conductivity in

70PAN +30 NaF+wt% Al_2O_3 System

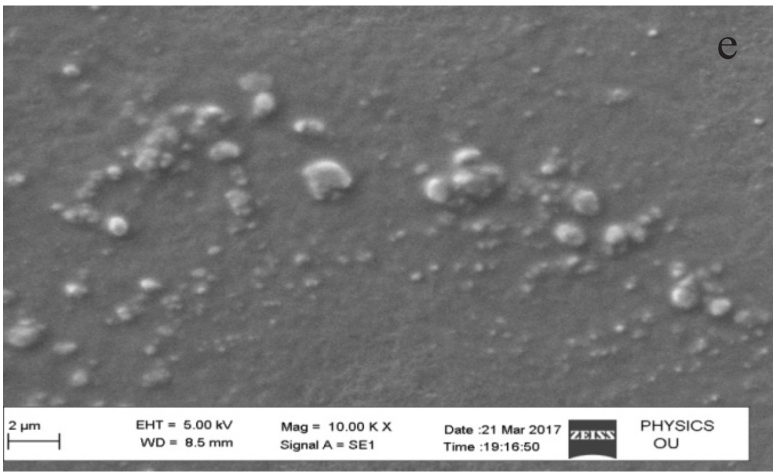


Fig. 4. Morphological surface SEM of (a) 70PAN:30 NaF (b) PAN+NaF+Al_2O_3 (70:30:1%) (c) PAN+NaF+Al_2O_3 (70:30:2%) (d) PAN+NaF+Al_2O_3 (70:30:3%) (e) PAN+NaF+Al_2O_3 (70:30:4%).

In the prepared gel polymer electrolyte system conductivity due to ions majorly depends upon mobility of ion species and the polymer which is determined by the free volume made by filler and plasticizer around the polymer chain. The present results explain the improvement of conductivity due to doping of salt NaF and nano filler Al_2O_3 content. The gel polymer electrolytes followed Arrhenius type of conduction. The polymer electrolyte containing 3 wt% nano filler showed an ionic conductivity of 4.82 ×10-3 Scm^{-1}.

$$\sigma = t / AR_b \tag{1}$$

where t and A expressed thickness and the area of the electrolyte specimen respectively [23]. R_b is the bulk resistance of the electrolyte obtained from the complex impedance measurement. Plots of log σ vs 1000/T of 70PAN-30NaF complexed films for different wt % of Al_2O_3 given in Fig.6.

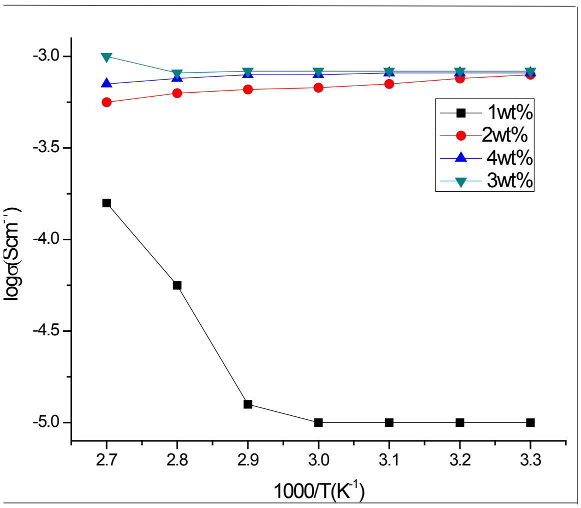


Fig.6. Plots of log σ versus 1000/T of 70PAN-30NaF complexed films for different wt % of Al_2O_3.

3. 5. Measurement of Ionic Transference Numbers

The ionic transference numbers of PAN complexed with nano filler Al_2O_3 was measured using polarization method of Wagner. Here the D.C current was altered as a combination of the time on application of a constant dc voltage (1.5V) across the cell: Ag/PAN: NaF/Ag + nano filler cell. After polarization of the cell with 1.5 DC, the polarization current versus time plot at room temperature is obtained, which is given in Fig. 7.The ionic transference numbers were measured by

$$t_{ion}=1-I_{f/}I_{i,}\ t_{ele}=I_f/I_i \tag{2}$$

Where I_i is the initial current and I_f is the final current. The measured transference numbers values are given in Table 1.The current decreases with time show that the total conductivity of the sample is predominantly due to ions. Hence, it proved that NaF salt and nano filler have provided protons as mobile species in the systems. The values of ionic transference numbers are in the range of 0.965-0.989.

The solid type electrochemical cell was made with the combination of anode Na/70PAN:30NaF/Cathode (I_2+C+Electrolyte+ 3wt% Al_2O_3). 1mm thickness provided by two electrodes. The system 70PAN+ 30NaF+ 3wt% Al_2O_3 having surface area and thickness of 1.28cm^2 and 128 µm, respectively. The discharge characteristics of the prepared cell for a constant load of 100KΩ were evaluated at room temperature which their results are observed in Fig. 8. Due to polarization and formation of a layer of sodium salt at the

Table 1. Conductivity, activation energies and ionic transference numbers for different NCGPEs.

GPEs	Conductivity at		Activation Energy(e)	Transference Number	
	303K	373K		t_{ion}	t_{ele}
70PAN:30NaF:1 wt%	$5.46x10^{-6}$	$2.85x10^{-5}$	0.35	0.965	0.05
70PAN:30NaF:2 wt%	$1.62x10^{-5}$	$2.42x10^{-5}$	0.30	0.972	0.04
70PAN:30NaF:3 wt%	$4.82x10^{-3}$	$5.96x10^{-3}$	0.21	0.989	0.03
70PAN:30NaF:4 wt%	$3.46x10^{-3}$	4.50x10-3	0.25	0.969	0.01

electrode-electrolyte interface, an initial sharp decreased in the voltage is seen for these cells. Cell parameters like open circuit voltage (OCV), short circuit current (SCC), current density, power density, energy density and discharge capacity, have been evaluated to the highest conducting gel polymer electrolyte system 70PAN: 30NaF + 3wt% Al_2O_3 and the obtaining data are given in Table 2.The current density is calculated using SCC value and area of the cell. Power density value is obtained by taking OCV and weight of the cell into consideration. Energy density value is calculated by evaluating the time taken for the plateau region .From Table 2 , it is obvious that the cell with the composition 70PAN: 30NaF 3wt% Al_2O_3 exhibits better performance and stability than PEO:$NaYF_4$ and PEO:NaI complexed polymer electrolyte systems[24-26] . Hence, in this work offers interesting alternatives for the cell developing at different temperatures of solid state batteries.

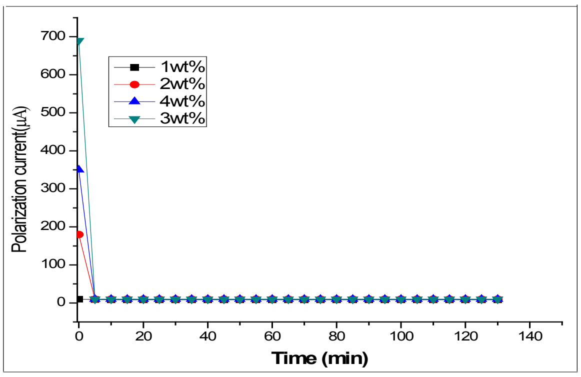


Fig. 7. Ionic transference number measurements of 70PAN-30NaF complexed films for different wt % of Al_2O_3 at room temperature.

3. 6. Discharge Characteristics:

The discharge characteristics profile observed by Fig. 7. Cell parameters of 70PAN: 30NaF+ 3wt% Al_2O_3/(I_2+C+Electrolyte) polymer electrolyte battery were given in Table 2. It was confirmed that gel state cell parameters are better than the earlier reported sodium based polymer electrolyte cell system [27-32].

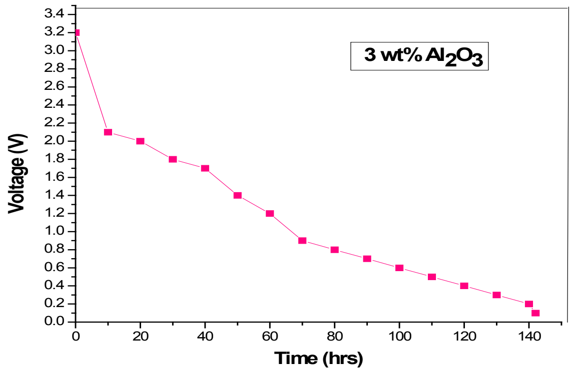


Fig. 8. Discharge profiles of 70PAN:30 NaF complexed with 3 wt% of Al_2O_3 electro chemical cell (load =100KΩ).

4. CONCLUSION

The proton conducting gel polymer electrolytes consisting of sodium fluoride salt dissolved in a plasticizing solvent, EC and DMF, immobilized in a host polymer 70PAN +30NaF+wt% Al_2O_3 (nano filler) have been synthesized and characterized. The complexation of the salt and nano filler with the polymer was confirmed by XRD and FTIR studies. Inter planar spacing was also verified theoretically and experimentally. It was Found

Table 2. Cell parameters of 70PAN: 30NaF+ 3wt% Al_2O_3 /(I_2+C+Electrolyte)polymer electrolyte battery.

Parameters of NCGPEs cell	70PAN: 30NaF:3 wt%Al_2O_3
Area of the electrolyte (cm^2)	1.20
Weight of cell (g)	1.64
Open circuit voltage (V)	3.20
Short Circuit Current (mA)	1.6
Discharged time for plateau region (h)	142
Density of power(W /Kg)	2.94
Density of Energy (Wh/ Kg)	324.7
Density of current (Mw/ Kg)	2.35
Capacity of Discharge (µA h^{-1})	168.2

that with increasing of salt and nano filler concentration the surface roughness of the films was decreased and phase segregation was revealed with cylindrical shape. Decrease in the degree of crystallinity and increase in the amorphous nature observed, while increase in conductivity with increasing concentration of nano filler and temperature. The transference number data indicated that the conduction in these polymer electrolytes was predominantly due to ions rather than electrons. Using PAN: NaF (70:30), gel polymer electrolyte solid–state battery (Na/PAN: NaF (70:30) +EC+DMF/(I_2+C+Electrolyte)) was fabricated.

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