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Carbon Nanofibers Reinforced P(VdF-HFP) Based Gel Polymer Electrolyte for Lithium-Ion Battery Application

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***Abstract*—**The effect of carbon nanofibers (CNFs) on the electrical properties of Poly(vinylidene fluoride-hexafluoropropylene) (P(VdF-HFP)) based gel polymer electrolytes has been investigated in the present work. The length and diameter ranges of CNFs used in the present work are 5-50 μm and 200-600 nm respectively. The nanocomposite gel polymer electrolytes have been synthesized by solution casting technique with varying CNFs content in terms of weight percentage. Electrochemical impedance analysis demonstrates that the reinforcement of carbon nanofibers significantly enhances the ionic conductivity of the polymer electrolyte. The decrease of crystallinity of P(VdF-HFP) due the addition of CNFs has been confirmed by X-ray diffraction (XRD). The interaction of CNFs with various constituents of nanocomposite gel polymer electrolytes has been assessed by Fourier Transform Infrared (FTIR) spectroscopy. Moreover CNFs added gel polymer electrolytes offer superior thermal stability as compared to that of CNFs free electrolytes as confirmed by Thermogravimetric analysis (TGA).

***Keywords*—**Polymer electrolytes, CNFs, Ionic conductivity, TGA.

I. Introduction

MUCH attention have so far been given to polymer electrolytes due to their possible application in electrochemical devices such as fuel cells, sensors, etc. which operates at sub-ambient to moderately high temperatures. Lithium batteries normally use liquid electrolytes with organic solvents, which are flammable and there is a possibility of getting ignited on exposure to high temperature. To solve this safety problem, there is a strong desire to move to non-flammable electrolytes [1]. As a result, polymer electrolyte is a promising candidate, as these have several advantages over their liquid counterparts. The advantages of these electrolytes include no internal shorting, no leakage of electrolytes as compared to the liquid electrolytes [2]-[4]. Gel polymer electrolytes (GPEs) can exhibit good electrochemical stability and high ionic conductivity. In order to increase the ionic conductivity of the polymer electrolyte some additives such as plasticizers and/or fillers are used [5]. For nanofillers, it was found that ionic conductivity is strongly dependent on the filler size and concentration. It was found that small filler sized and small quantities increase the ionic conductivity of the samples. Nanofillers have a high surface area to volume ratio so they have more than 50% of its atoms on the surface and are thus very reactive [6]. Among different inorganic fillers, carbon nanofibers (CNFs), owing to have properties like extremely high strength, high stiffness and high aspect ratio, are looked upon as ideal nanofillers in the preparation of gel polymer electrolyte. The researchers have reported that CNFs may be combined with polymers to produce functional composite materials with superior properties [7]. Because of the high aspect ratio and the low density, nanometer scale elements such as carbon nanofibers (CNFs), may be used as reinforcing elements in polymer matrices. Also CNFs are highly flexible which may improve the interaction and cross-linking with polymer molecules that further enhances the ionic conductivity of nanocomposite electrolytes [8]. This leads to the development of high performance nanocomposite material for the next generation lithium-ion battery.

In the present work, an attempt has been made on the preparation of Poly(vinylidene fluoride-hexafluoropropylene) (P(VdF-HFP)) based nanocomposite gel polymer electrolytes (NCGPEs) reinforced with CNFs. The selection of the copolymer P(VdF-HFP) is due to its more appealing properties such as high dielectric constant (ε =8.4) and low crystallinity. Further, the co-polymer possesses excellent combination of chemical stability due to VdF unit and plasticity due to HFP unit [9].

II. Experimental

A. Materials

The host copolymer P(VdF-HFP) was received from Alfa Aesar. The plasticizers used were propylene carbonate (PC) and diethyl carbonate (DEC) (both Aldrich, USA, purity > 99%). $LiClO_4$ (purity > 99%, Aldrich) used was dried initially at 70 ˚C and kept under vacuum for 24 hours before use. CNFs (TNM3, Chengdu Organic Chemicals Co. Ltd. Chinese Academy of Sciences, China) used have outer diameter of 200-600 nm and length of 5-50 μm respectively. Tetrahydrofuran (THF) (Hi Media, purity>99%) was used as solvent without further purification.

B. Preparation of the Electrolytes

The electrolytes were prepared by the solution casting technique. The solutions were prepared by dissolving separately appropriate amounts of polymer, plasticizer and salt in anhydrous tetrahydrofuran (THF) solvent. The solutions were then mixed in a Teflon moulder and the solvent was

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allowed to evaporate at room temperature. Mechanically stable free standing films were obtained after the evaporation of solvent. The films were then further dried in a temperature controlled vacuum oven at 50 ˚C for 24 hours to remove trace amount of THF, if any. The following codes P0, P1, P2, P3 and P4 were assigned to the NCGPE samples containing 0, 0.5, 1.0, 1.5 and 2.0 wt% CNFs respectively. The composition of polymer base prepared in which the CNFs were reinforced, is0.60P(VdF-HFP)-0.30(PC+DEC)-0.10$LiClO_4$. Mechanically stable free standing polymer electrolyte films were obtained after the solvent evaporation of the as cast films. The samples were in the form of film whose thickness was 0.34 mm. The samples were then dried at 50 ˚C for 24 hours in a temperature controlled vacuum oven.

C. Characterization Techniques

The ionic conductivity of the samples was determined by impedance spectroscopy technique over the frequency range of 42 Hz - 1MHz using LCR Hi Tester (HIOKI 3532-50). X-ray diffraction patterns of the samples were obtained by X-ray diffractometer (XRD) (Bruker D8 advance), using Cu Kα radiation (λ= 1.541 Å). Fourier Transform Infrared (FTIR) (Nicolet NEXUS Aligent 1100 series) analysis of the samples was carried out. The thermal analysis of the samples was carried out in nitrogen atmosphere over the temperature range of 30 ºC - 1000 ºC at a heating rate of 10 ºC min^{-1} by Perkin Elmer (Pyris Diamond) thermal analyzer.

III. Results and Discussion

A. Conductivity Analysis:

Fig. 1 shows the plots between real (Z′) and imaginary (Z″) parts of impedance measurements of the samples P0, P1, P2, P3 and P4 at room temperature. Each impedance spectrum consists of a depressed semicircular arc in the high frequency region followed by a spike in the lower frequency region. The high frequency semicircle is due to the bulk effect and the low frequency spike is due to the electrolyte and electrode interfacial resistance effect. Therefore, the bulk resistance (R_b) is calculated from the intercept of the arc at the higher frequency side on the Z′ axis. The ionic conductivity (σ) is calculated following the equation:

$$\sigma = l/(R_b A)$$

where l is the thickness of the polymer electrolyte sample film and A the surface area of the film. The conductivities are presented in Table I.

TABLE I
Estimated Conductivities at Room Temperature for All of the Samples

Sample	AC Conductivity (Scm^{-1})
P0	5.43×10^{-4}
P1	1.73×10^{-3}
P2	2.52×10^{-3}
P3	3.19×10^{-3}
P4	2.94×10^{-3}

It is observed that the ionic conductivity increases with increase in CNFs content used in the study. Maximum conductivity found is 3.19×10^{-3} Scm^{-1} for P3 sample at room temperature and the conductivity increases to 8.72×10^{-3} Scm^{-1} at 70 ˚C. The conductivity enhancement is perhaps due to the fact that the dispersion of CNFs in the polymer matrix prevents chain reorganization because of the high aspect ratio of the CNFs and therefore results in the reduction in crystallinity of the polymer and this in- turn gives rise to an increase in ionic conductivity.

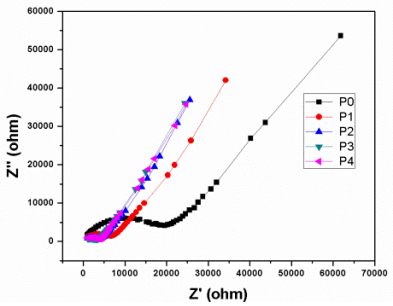


Fig. 1 Nyquist plots of samples P0; P1, P2, P3 and P4

The variation in conductivity as a function of CNFs content in NCGPEs at room temperatures is given in Fig. 2. It is observed that conductivity increases with the increase in CNFs content. However, beyond 1.5 wt% CNFs the value of conductivity decreases. However, the nanocomposite electrolyte materials become brittle and fragile with higher CNFs content i.e. when the content is more than 1.5 wt%.

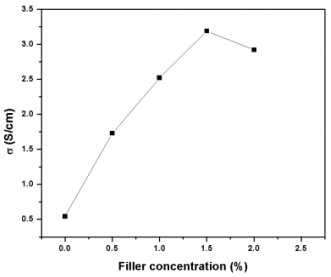


Fig. 2 Conductivity versus filler concentration (wt%) of NCGPE samples

Polymer electrolytes are widely disorganized heterogeneous systems and hence the temperature dependence of conductivity σ(T) does not follow strictly the Arrhenius equation:

$$\sigma(T) = \sigma_o \exp(-E_a/kT)$$

where σ_o, E_a, k and T respectively are the pre exponential factor, activation energy of ionic mobility, Boltzmann constant and temperature in K at which the R_B has been determined. But σ(T) obeys the VTF relationship:

$$\sigma = B \exp(-Ea/k(T-T_o))$$

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where B is a constant and T_o is the idealized glass transition temperature typically 20-50 K below the glass transition temperature (Tg) of the polymer. The VTF describes the ionic transport properties in a viscous polymer matrix [8]. The addition of liquid plasticizer to the gel polymer reduces its Tg and consequently T_o becomes significantly lower than the temperature region of measurements.

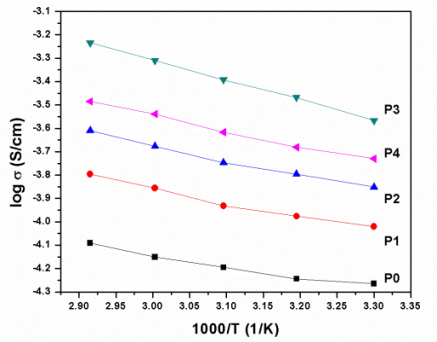


Fig. 3 Temperature dependent ionic conductivity plots of the samples P0, P1, P2, P3 and P4

B. XRD Analysis

Fig. 4 shows the XRD peaks of P(VdF-HFP), $LiClO_4$ and CNFs and NCGPE samples i.e. P0, P1, P2, P3 and P4 respectively. The peaks at 2θ = 18.8°, 20.4°, 26.6° and 39.9° correspond well with the (100), (020), (110) and (021) reflections of PVdF which confirms semi-crystalline morphology for P(VdF-HFP). The sharp peaks of the salt $LiClO_4$ in the XRD pattern indicate the salt is crystalline. The XRD pattern of CNFs has diffraction peaks (002) and (101) at about 2θ = 26° and 44° respectively. The degree of crystallinity (K) of polymer electrolyte is measured by the relation:

$$K = (S/S0) \times 100$$

where S is the sum of areas of all the peaks due to crystallinity and S0 is the sum of areas of profile of crystalline peaks and amorphous hump (i.e., total area under the diffraction profile). Area has been estimated by dividing the area under X-ray diffraction pattern profile into smaller square grids of size 0.5 mm × 0.5 mm. Therefore, for the profile of P(VdF-HFP) i.e. P0, K = 157 units / 540 units × 100 = 29%. For the sample P3, K = 9 units / 50 units × 100 = 18%

The crystallinity of NCGPEs is greatly lower than that of P(VdF-HFP). The XRD peaks due to $LiClO_4$ are not observed for the all samples since $LiClO_4$ is dissolved in the polymer matrix and is longer exists as a separate phase. Increased amorphicity gives rise to higher ionic conductivity which is consistent with the conductivity results.

C. FTIR Analysis

FTIR spectra of P(VdF-HFP), $LiClO_4$, CNFs and NCGPE samples P0, P1, P2, P3 and P4 are shown in Fig. 5. Absorption peaks at wave number 2955 cm^{-1} is assigned to C-H stretching vibration. Peak at 1786 cm^{-1} is assigned to $–CF=CF_2$. Wave number 1401 cm^{-1} is assigned to C-F stretching vibration of P(VdF-HFP) and 1290-1060 cm^{-1} are assigned to –C-F- and CF_2- stretching vibration. Peak at 881cm^{-1} is assigned to vinylidene group of polymer. Some of the vibrational peaks at 1717, 1355, 1210, 1094, 905 and 542 cm^{-1} of NCGPEs appear at the same wavenumber after adding CNFs in them, indicating the coordination to the fibers did not occur.

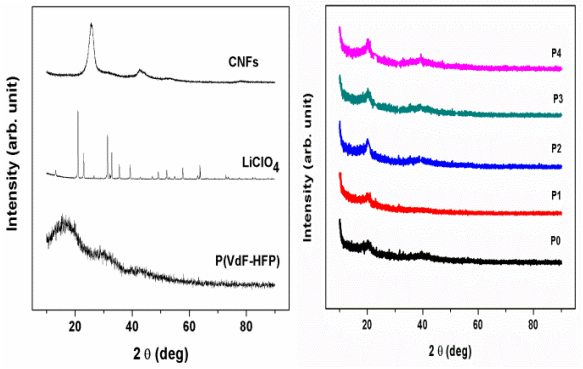


Fig. 4 XRD of samples (a) P(VdF-HFP), $LiClO_4$ and CNFs; (b) P0, P1, P2, P3 and P4 samples

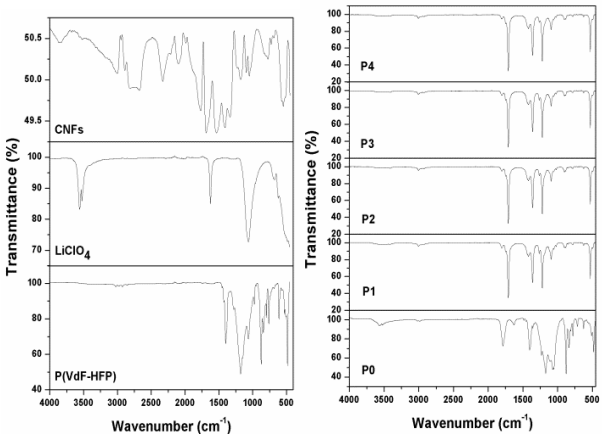


Fig. 5 FTIR of samples (a) P(VdF-HFP), $LiClO_4$ and CNFs; (b) P0, P1, P2, P3 and P4 samples

D. Thermal Analysis

Thermal stability of the NCGPE samples were determined and presented in Fig. 6. It can be seen from the Fig. 6 that P0 shows weight loss over the temperature range of 250-500˚C. Only 12% residue was found at 800 ˚C for the sample P0. Incorporation of CNFs increases the thermal stability of P(VdF-HFP) polymer electrolyte in sample P3 and this is evident from the existence of higher (>22 %) residual masses. Also, a slight increase in the initial decomposition temperature of P(VdF-HFP) was observed for NCGPE samples in Fig. 6. Therefore, the molecular level interaction between the fluorine atoms in the P(VdF-HFP) and the groups in the CNFs takes place [9].

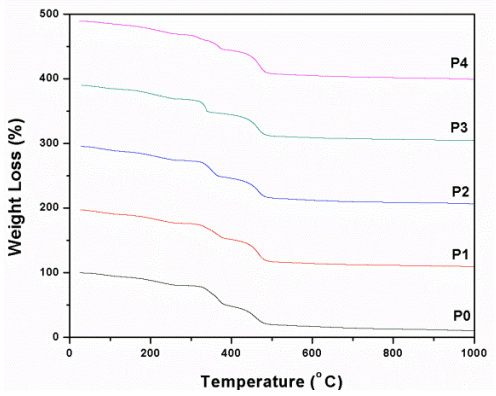


Fig. 6 TG profiles of P0, P1, P2, P3 and P4 samples.

IV. Summary

NCGPEs reinforced with CNFs have been synthesized by solution casting technique. The ionic conductivity of the P3 sample containing 1.5wt% of CNFs increases to 3.19×10^{-3} Scm^{-1}, which is higher than 5.43×10^{-4} Scm^{-1} of the P0 sample. The degree of crystallinity is reduced from 29% for pure P(VdF-HFP) to 18% which shows there is increase in amorphicity in P3 sample. Also P3 sample dispersed with 1.5wt% CNFs has decomposition temperature of 485 ºC which is significantly higher as compared to the sample P0.

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