Studies on Nano Gel Polymer Electrolyte based Supercapacitors

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ABSTRACT

In the present work, nano gel composite polymer electrolyte comprising of poly(vinylidine fluoride-co-hexafluropropylene) PVdF(HFP) - propylene carbonate (PC) - magnesium perchlorate $Mg(ClO_4)_2$- aluminium oxide (Al_2O_3) as an inert nano filler has been synthesized which exhibits ionic conductivity of 5.9 x 10^{-3} S cm^{-1}, showing good mechanical and dimensional stability which is suitable for their application in electrochemical devices like supercapacitors. The synthesized electrolyte material has been successfully checked in supercapacitors using activated charcoal as an electrode material. The electrochemical evaluation of EDLCs has been carried out by using a.c impedance spectroscopy techniques. The maximum capacitance of 153 mF cm^{-2} which is equivalent to single electrode specific capacitance of 44.0 F g^{-1} achieved from the fabricated EDLCs.

Keywords

Nano Gel Polymer electrolyte, Nano filler, activated charcoal, impedance spectroscopy.

1. NTRODUCTION

Nano composite polymer electrolyte (NCPE) is a new and emerging class of materials that combines the properties of inorganic particles with the processibility and flexibility of an organic polymer matrix. The resulting synthesized composite materials offer the possibility of a new generation of nano-structured materials with various promising electrochemical applications such as batteries, supercapacitors, sensors etc. Since solid polymer electrolytes have some drawbacks such as low ionic conductivity at room temperature, poor interfacial stability between the electrodes, poor mechanical strength etc [1-3]. In order to overcome these drawbacks, several approaches were adopted by different researchers such as blending of polymers, addition of plasticizers and addition of inorganic ceramic fillers such as TiO_2, SiO_2, MgO, MnO_2, SnO_2, ZrO, ZnO, CuO, etc. have been used to prepare the plasticized blended polymer electrolytes [4-5], gel polymer electrolytes [6] and nano composite solid polymer electrolytes etc.

In nano composite polymer gel electrolytes, the matrix polymers are normally related to poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVdF) (or its copolymer). Amongst them, poly(vinylidene fluoride-co-hexa fluro propylene) (PVdF(HFP)) is widely used because of its excellent mechanical and chemical stability.

In the present work, the effect of nano-aluminium oxide (Al_2O_3) on the electrical and electrochemical properties of Mg^{2+} ion conducting polymer electrolyte systems PVdF(HFP)-$Mg(ClO_4)_2$ has been reported and its suitability in energy storage devices, especially supercapacitors using activated charcoal as electrode materials has been checked.

2. EXPERIMENTAL

2.1 Electrolyte Preparation

The nano composite gel polymer electrolyte comprising of PVdF(HFP)-PC-$Mg(ClO_4)_2$-Al_2O_3 has been prepared by using classical solution cast technique. Poly (vinylidene fluoride-hexafluoro propylene) PVdF(HFP) (M. Wt. ~ $4×10^5$ Aldrich) as polymer, tetra hydro furan (THF) (Merck), propylene carbonate (PC) (Loba Chemie) as solvent, magnesium perchlorate $Mg(ClO_4)_2$ (Aldrich) as salt, aluminium oxide as nano filler were used as received without further purification. Initially, a liquid electrolyte solution has been synthesized by dissolving the salt magnesium perchlorate in solvent PC and it was found to be optimized at a concentration of 0.3 M. This optimized solution was then added in different amount to an another solution containing PVdF(HFP)-THF, that was prepared separately by thorough stirring at ~60 °C using magnetic stirrer. Further nano-aluminium oxide in different weight ratios (from 0 wt% to 12 wt% with respect to the weight of PVdF(HFP)) were dispersed in the optimized composition having [PVdF(HFP) (15 wt%)-{PC-$Mg(ClO_4)_2$ (0.3M)} (85 wt%)] to obtain nano composite polymer gel electrolyte. Then the mixtures were poured into glass Petri dishes and kept at room temperature until the formation of thin solid free standing electrolyte film. The thickness of all polymer electrolyte films was ~250 μm.

2.2 Electrode Preparation

For the preparation of electrodes activated charcoal powder (Loba Chemie) and PVdF(HFP) were mixed in the ratio of 90:10 (w/w) in a common solvent acetone. Further, the prepared slurry was coated on carbon cloth (Ballard, USA) and dried in an oven at 70 °C for 10-12 h.

2.3 Electrochemical measurements

To study the conductivity behaviour of the polymer electrolytes, impedance spectroscopy was performed using LCR Hi TESTER (3522-50, Hioki, Japan). The samples were cut into proper size and sandwiched between two stainless steel electrodes. The conductivity (σ) was calculated using the equation $\sigma_0 t / R_b A$ where, t is thickness of the electrolyte, A is electrolyte contact area, and R_b is the bulk resistance obtained from the plots of real impedance Z_r against imaginary impedance Z_i.

Electrochemical measurements of capacitor cell were carried out by impedance spectroscopic technique using a computer-controlled CHI 608C, CH Instrument, USA in the frequency range from 1 mHz to 100 kHz.

3. RESULTS AND DISCUSSION

3.1 Electrical Conductivity

The method of synthesis, optimization and electrical characterization of PVdF(HFP)-PC-$Mg(ClO_4)_2$ were mentioned elsewhere [7]. The gel polymer electrolytes having composition [PVdF(HFP) (15 wt%)-PC-$Mg(ClO_4)_2$ (0.3M) (85 wt%)] has been chosen to prepare nano composite gel polymer electrolyte, since it exhibits maximum ionic conductivity of 5.0 x 10^{-3} S cm^{-1} at room temperature amongst all other prepared compositions. Fig. 1 shows room temperature electrical conductivity pattern of nano composite gel polymer electrolytes with different concentration of aluminium oxide nano-particles. The addition of nano Al_2O_3 increases the concentration of charge carriers by interaction with either or both the anion and cation thereby reducing ion pairing and this phenomenon supports the enhancement in ionic conductivity. Further the migration of magnesium ion on the surface of nano Al_2O_3 occurs due to the structural modification of polymer chain, that results from the interaction of Al_2O_3 nano-particles with host polymer PVdF(HFP) and ClO_4^- anions.

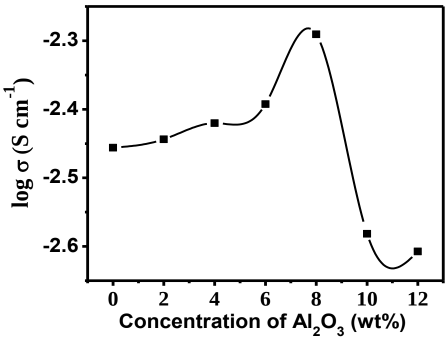

Figure 1: Variation of ionic conductivity of nano-composite gel polymer electrolyte as a function of different weight percent of Al_2O_3 concentration

The addition of nano Al_2O_3 after 8 wt% results in drop in conductivity as can be seen from Fig. 1. This may be possible due to the aggregation of nano Al_2O_3 that can strongly interact with the polymer chains and immobilizing the polymer chains in the process.

3.2 Temperature Dependent Studies

Fig. 2 shows the temperature dependence ionic conductivity behavior of composite gel films. As can be seen from the plot there exist two temperature range above room temperature for which the variation of σ is different from one another. These are the characteristics of semi-crystalline to amorphous phase transition in the conductive polymeric films. The presence of these two distinct and well defined regions in the plots also suggests that the transport properties of Mg^{2+} are fundamentally controlled by two different mechanisms. The temperature dependence of the conductivity follows Vogel-Tammann-Fulcher (VTF) model, which describes the transport properties in a viscous matrix. The activation energy for the system is found to be 0.046 eV which decreases as conductivity of sample increases which shows that the ions in highly conducting sample require less energy for migration. This is possibly due to the smaller size of nano filler and plasticizer molecule as compared to host polymer molecules [8]. This in all may reduce the cohesive forces operating between the polymer chains, thereby resulting to an increase in chain segmental motion. Here the role played by filler needs a special consideration. The addition of filler to the polymer complex can contribute to the lowering of T_g by increasing the volume fraction of amorphous phase caused by the modification of the host of polymer structure. A dominant contribution to the conductivity enhancement due to the filler at temperature below T_m should possibly due to this effect. According to Vogel-Tammann-Fulcher (VTF) model [9], the migration of ions is mainly due to the segmental motion of polymer chain in the amorphous region and the temperature of the conductivity of the nano gel polymer electrolyte films is given as:

$$\sigma = AT^{-1/2}\exp(-B / T - T_0)$$

where, the parameter B has the dimension of energy and is related to the critical free volume for ion transport, A is the pre-exponential factor, i.e. the conductivity at infinitely higher temperature and T_0 is equilibrium glass transition temperature close to the T_g values. The parameters have been evaluated by non-linear least square fitting of the data.

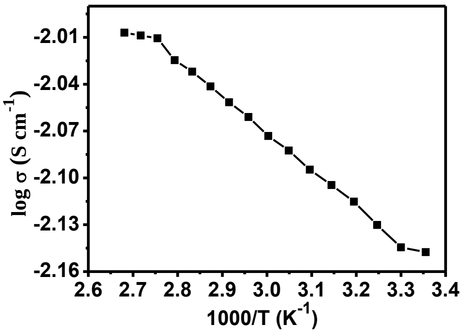

Figure 2: Variation of ionic conductivity as a function of temperature for [PVdF(HFP)(15 wt%)-{PC-$Mg(ClO_4)_2$(0.3M)}(85 wt%)] - nano Al_2O_3 (8 wt% of the polymer) based electrolyte system

It may be noted that the optimized magnesium ion based composite gel polymer electrolyte exhibits ionic conductivity of the order of ~10^{-3} S cm^{-1} at 25 °C and ~10^{-2} S cm^{-1} at 80 °C.

3.3 Dielectric spectra analysis

The dielectric relaxation behaviour of the polymer electrolyte brings about important insights into ionic transport phenomenon [10]. The measured impedance data were used to calculate the real and imaginary parts of the complex permittivity using the relation:

$$\varepsilon^* = \varepsilon'(\omega) - \varepsilon''(\omega) = 1 / j\omega C_0 Z^*$$

where real ε' (ω) and imaginary ε" (ω) components are the storage and loss of energy in each cycle of the applied electric field [11]. Frequency dependence plot of ε' (ω) for 8 wt% nano Al_2O_3 dispersed in PVdF(HFP) at eight different temperatures are shown in Fig 3. From the figure it is clear that the values of ε' (ω) are very high at low frequency region. Such high values of dielectric permittivity at low frequencies have been explained by the presence of space charge effects, which is contributed by the accumulation of charge carriers near the electrodes [12-13]. At higher frequencies, ε' (ω) has been found to be relatively constant with frequency. This may be due to the periodic reversal of the field that takes place so rapidly that the charge carriers will hardly be able to orient themselves in the field direction resulting in decrease of dielectric constant [14].

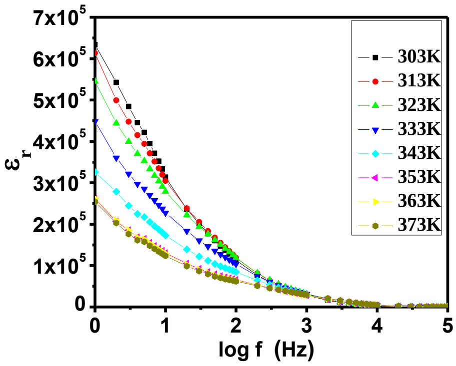

Figure 3: Variation of dielectric constant of [PVdF(HFP)(15 wt%)-{PC-Mg(ClO_4)$_2$(0.3M)}(85 wt%)] - nano Al_2O_3 (8 wt% of the polymer) of polymer electrolyte system as a function of frequencies at various temperature

At higher temperature, there is an increase in the value of dielectric constant and is attributed to the higher charge carrier density. As temperature increases, the degree of salt dissociation and re-dissociation of ion aggregates increases, resulting in the increase in number of free ions or charge carrier density.

3.4 Modulus Spectra

In order to understand the bulk properties of the material, analysis of modulus spectroscopy has been carried out; it is also complementary to impedance spectroscopy which basically explains the electrode and grain boundary effect. The complex electric modulus can be evaluated from the following relations:

$M^*(\omega).\varepsilon^*(\omega) = 1$

Where,

$M^*(\omega) = M_r(\omega) + iM_i(\omega)$

$M_r(\omega) = \varepsilon'(\omega) / \varepsilon'^2(\omega) + \varepsilon''^2(\omega)$

$M_i(\omega) = \varepsilon''(\omega) / \varepsilon'^2(\omega) + \varepsilon''^2(\omega)$

Fig. 4 shows the real part (M_r) of electrical modulus as a function of frequency at various temperatures for nano composite gel polymer electrolyte. The modulus spectrum for filler free electrolyte has been shown somewhere else [7]. It has been observed that the values of M_r tends to increase in the higher frequency region and are giving long tail at lower frequency region. At high frequencies the formation of peak shows that the polymer electrolyte films are predominantly ionic conductors [15]. At higher frequencies peak curve is may be due to bulk effect.

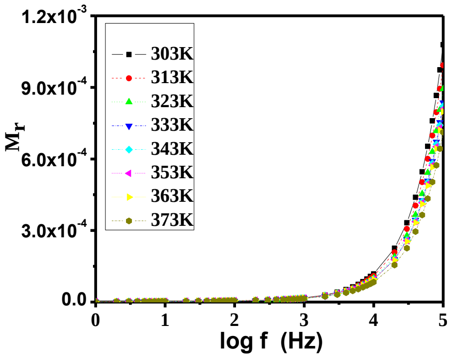

Figure 4: Variation of real part of electrical modulus of [PVdF(HFP)(15 wt%)-{PC-Mg(ClO_4)$_2$(0.3M)}(85 wt%)] - nano Al_2O_3 (8 wt% of the polymer) of polymer electrolyte system as a function of frequencies at various temperature

3.5 Impedance Spectra of Super capacitor Cell

In order to check the suitability of the nano gel polymer electrolyte for its application in energy storage devices, supercapacitor cell has been fabricated using activated charcoal as electrode material by sandwiching nano gel polymer electrolyte in between two carbon electrodes. Impedance spectroscopy technique has been used to characterize the supercapacitor performance. The configuration of the supercapacitor cell is as follows:

AC | PVdF(HFP)-PC-Mg(ClO_4)$_2$-Al_2O_3 | AC

The impedance plot of the fabricated capacitor cell is shown in Fig. 5. Impedance spectra technique is one of the reliable techniques which are being used to characterize supercapacitor cell. It gives an idea about the various electrical parameters that are associated with the bulk properties of electrolyte, equivalent internal resistance, electrode-electrolyte interface of the overall cell. Ideally, the impedance response of a capacitor is a straight line parallel to the imaginary axis of the complex impedance plots. But in the real capacitor, the steep rising capacitive impedance response is observed in low-frequency region accompanied with high-frequency semicircular features owing to the bulk and interfacial properties. The impedance response of a capacitor cell shows a small semicircular spur in the higher frequency region followed by a straight line in a lower frequency region. The obtained impedance pattern resembles the real capacitor characteristics. The steep rising behaviour

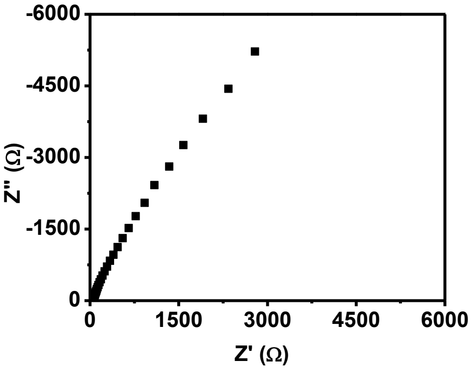

Figure 5: Impedance Spectra of Supercapacitor Cell

indicates the capacitive behaviour in lower frequency region and depressed semicircular spur shows the bulk properties of the electrolytes and the interfacial charge transfer processes. The capacitance values (C), charge transfer resistance (R_{ct}), bulk resistance (R_b) and overall resistance (R) at 1 mHz for the fabricated cell is found to be 153 mF cm^{-2} (which is equivalent to single electrode specific capacitance of 44 F g^{-1}), 4.0 Ω cm^2, 8.0 Ω cm^2 and 555 Ω cm^2 respectively. The lower values of internal resistance and higher specific capacitance obtained for the combination of activated charcoal and alumina based nano-composite polymer electrolyte suggests the suitability of materials used in the present investigation for its application in energy storage devices, especially in supercapacitor application.

4. CONCLUSION

Nano composite polymer electrolyte has been successfully synthesized by using solution cast technique which exhibits a maximum room temperature conductivity of 5.0×10^{-3} S cm^{-1}. The polymer gel electrolyte film is flexible and free standing with good mechanical strength. The temperature variation of the conductivity plot shows the VTF behavior of the electrolyte system. The activation energy of the electrolyte system is found to be of the order of 0.046 eV. Preliminary studies on supercapacitor have been carried out by using activated charcoal as an electrode material. The overall capacitance has been found to be of the order of 153 mF cm^{-2} which is equivalent to single electrode specific capacitance of 44 F g^{-1}. In conclusion, synthesized electrolyte material shows promising results and it can be successfully used in energy storage devices.

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