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Conductivity studies of nano gel polymer Electrolytes for its application in EDLCs.

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Abstract *Electrochemical capacitors fabricated by sandwiching nano gel polymer electrolyte between two blocking electrodes are showing better ionic conductivity along with mechanical as well as dimensional stability. Therefore preparation of such nano gel polymer electrolyte is the main area of concern. In this paper synthesis of nano gel polymer electrolyte comprising of poly (vinylidene fluoride-co-hexafluoropropylene)-propylene carbonate-magnesium perchlorate-nano alumina has been done by using conventional solution cast technique. The resultant nano gel polymer electrolyte shows the good ionic conductivity, mechanical stability, dimensional stability and wide range of power window, which are compatible for its application in electrochemical capacitors. Finally the fabricated supercapacitor was characterized by a.c impedance technique, cyclic voltammetry and charge-discharge techniques.*

Keywords : *nano gel polymer electrolytes, potential window, ionic conductivity, dimensional stability, electrochemical capacitor.*

I. INTRODUCTION

In the recent years the 'scarcity of electricity' is the main area of concern, amongst the researchers and scientists of all the interdisciplinary fields. The electrochemical energy sources which are more commonly used now a day's are rechargeable batteries which have high energy density but low power density and conventional capacitors having liquid electrolytes, have their own drawbacks like bulky model, self- discharge, leakage, corrosion etc. Therefore the nano gel polymer electrolytes are the better alternative electrolyte which can be used as conducting medium. They have amorphous nature causing high ionic conductivity of ~10^{-4} to 10^{-3} Scm^{-1}, low glass transition temperature, easy fabrication, flexibility, mouldibility etc. all these characteristic properties make them compatible conducting medium for their use in various electrochemical devices such as rechargeable batteries, fuel cells, sensors, electrochromic devices etc.[1]. To improve the ionic conductivity, mechanical stability, thermal stability etc numbers of electrolytes are prepared with different compositions. All the polymer electrolytes which are in use nowadays are polymer blend electrolyte, polymer composite electrolyte, polymer gel electrolyte, and ionic liquid-base polymer electrolyte. They all have some problems, like low mechanical stability, low range of power window, and high reaction rate at electrode- electrolyte interface etc. Polymer gel electrolyte is having very good ionic conductivity of ~$10^{-3}Scm^{-1}$, flexibility, good electrode-electrolyte contact in fabrication of the device but due to its gelly or semisolid nature they have poor dimensional stability, reduction in ionic conductivity with time, less stability towards electrode interface etc. One of the methods to solve these problems of polymer gel electrolyte is to add some organic/ inorganic filler (in micro or nano sizes) to convert polymer gel electrolyte in composite type of electrolyte. When such fillers are added or dispersed to the polymer gel electrolyte, amorphous or porous nature of electrolyte increases, which enhances the liquid adsorbing quality of polymer and hence problems of leakage, poor mechanical and thermal stability can be sorted out [2-5]. It was observed that ionic conductivity increases, when nano particle of alumina was added as filler because, when (Al_2O_3) was added to the system they interact with paired ions and undissociated salts which enhances the concentration of free ions and further increases the ionic mobility and ionic conductivity.

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In this paper nano gel polymer electrolyte having alumina filler **[**PVdF (HFP)-PC-$Mg(ClO_4)_2$ - Al_2O_3]was successfully synthesized and characterized for its compatibility by a.c impedance spectroscopy technique, linear sweep cyclic voltammetry and Galvanostatic charge-discharge techniques.

For fabrication activated charcoal was taken as electrode material due to its easy availability, cheap cost, amorphous nature, large active surface area and environmental friendly nature. (PVdF-HFP) Polyvinylidene fluoride-co-hexa fluoro propylene is taken as host polymer because it has high dielectric constant of 8.4 as well as PVdF contributes to the crystalline property which imparts mechanical stability and HFP contributes to the amorphous character which is responsible for ionic conductivity [6-8], magnesium perchlorate $Mg(ClO_4)_2$ is taken as a salt because previously used Li salt is explosive in nature so it is dangerous to use.

II. Experimental methods

2.1 Synthesis of nano gel polymer electrolyte

The nano gel polymer electrolyte [PVdF (HFP)-PC-$Mg(ClO_4)_2$-Al_2O_3] has been prepared by using 'standard solution cast-technique'. To prepare nano gel polymer electrolyte, nano particles of Al_2O_3 in different weight ratios (from 0 to 20 wt % w.r.t the weight of polymer) were dispersed. Finally, the mixtures were poured in glass petri dish and allowed to evaporate volatile solvent THF to obtain solid-like free-standing nano composite gel films of thickness ~250 μm.

Prepared polymeric electrolyte was then characterised for its conductivity and compatibility in EDLC by following techniques.

2.2 Conductivity studies

Figure 1 shows the ionic conduction spectra of nano gel polymer electrolyte [PVdF(HFP)(15%)-PC-$Mg(ClO_4)_2$(0.3M)-Al_2O_3 (8wt%)] system, as the function of frequency at different temperature. As we can see from the plot that almost all the plot are having two different regions. The lower region enhancement in ionic conductivity is due to electrode- electrolyte interfacial chemical reactions and the higher zone ionic conductivity is explained as dc conductivity. At low frequency zone the accumulation of ionic charge carrier ions at electrode- electrolyte interface is more dominant so the concentration of mobile ions decreases due to which the ionic conductivity decreases. While in high frequency zone the movement of charge carrier is very high so the ionic conductivity increases.[9]. At high temperature the viscosity of the system decreases hence the free volume around the polymeric chain increases which cause the easy mobility of ions through polymeric chain or segment. This phenomenon of dispersion in conductivity is expressed by Jonscher's law [10].expressed as $\sigma(\omega) = \sigma dc + A\omega n$. Where,'σdc' is the direct current (dc) conductivity of the sample, '*A'* is a constant for a particular temperature, $\omega = 2\pi f$ is the angular frequency and 'n' is the frequency exponent lying in between the range of 0 to 1. Extent of interaction between the mobile ions and the surrounding environment is represented by factor 'n'. (for ionic conductor material the value of 'n' is in between 0.5 to 1), which shows the long diffusion range of ions and this process can be explained by 'hopping models'[10]. According to this model when the value of 'n' is =0 then ionic motion is completely random and independent. In general the transportation mechanism in ionic conductor can be explained by the thermally activated hopping process between two different sites separated by energy barriers. Frequency dispersion behaviour of ionic conductors can be explained by the physical model known as 'jump relaxation model'.[11]. Which states that at very low frequency ions available at one site can jump to its neighbouring vacant sites very easily, enhancing the dc conductivity.

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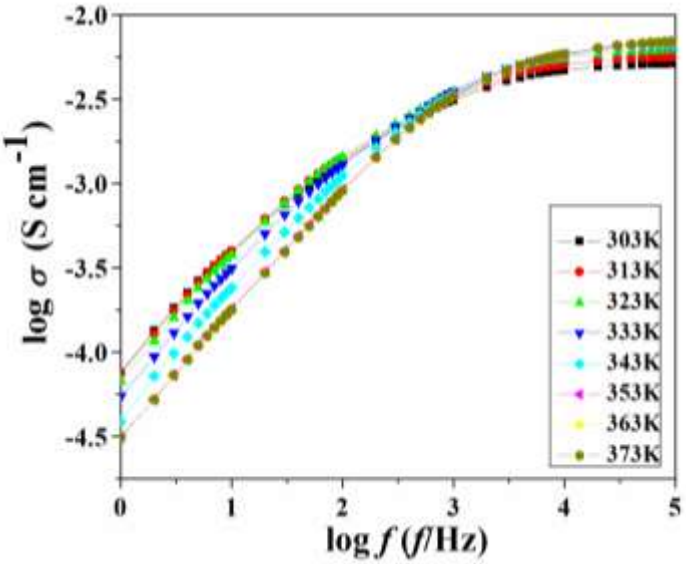

Figure 1: Variation of ionic conductivity as a function of frequency with temperature for nano gel polymer electrolytes system[PVdF (HFP)](15 wt%)-{PC-Mg $(ClO_4)_2$}(0.3M)]-nano Al_2O_3(8 wt%)].

At higher frequency, the excited ion can return back to its actual site due to very less periodic reversal time period of the electric field. This is the reason of high probability of forward- backward hopping in this region; along with this relaxation of the dynamic cage potential is the reason of high frequency dispersion in its conductivity.

2.3 Analysis of electrochemical potential window of polymer gel electrolytes

In the present work the Potential window of the nano polymer gel electrolyte is detected by sandwiching the polymer gel electrolyte [PVdF(HFP)(15%)-PC-$Mg(ClO_4)_2$(0.3M)-Al_2O_3 (8wt%)] in between two stainless steel, as blocking electrodes. Figure 8 shows the linear sweep cyclic voltammograms of nano polymer gel electrolyte at the scan rate of 5 mVs^{-1}. This analysis gives the idea about the working voltage range of the electrolyte to know its compatibility for the device fabrication. In the present work the nano polymer gel electrolyte [PVdF(HFP)(15%)-PC-$Mg(ClO_4)_2$-Al_2O_3 (8wt%)] shows the working potential window of ~2.5 V, which is the indication of its safe use in any electrochemical device.

2.4 Ionic transport number measurement

Ionic transport number was determined by using d.c.polarization method [12].

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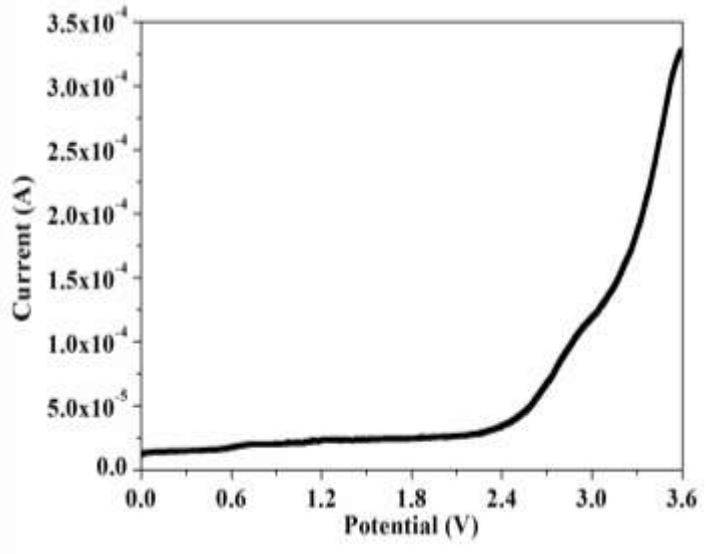

Figure 2: Linear sweep curves of nano gel polymer electrolytes Cell SS| NGPE|SS recorded at room temperature at a scan rate 5 mVs^{-1}.].

When d.c. voltage was applied to the electrolyte material below its decomposition potential then the resultant current was observed with respect to time. Figure 2 shows the plot of polarization current as the function of time for nano gel polymer electrolyte [PVdF(HFP)(15%)-PC-$Mg(ClO_4)_2$(0.3M)-Al_2O_3 (8wt%)] . the voltage applied to the system was 1.0 V(within the potential window range).

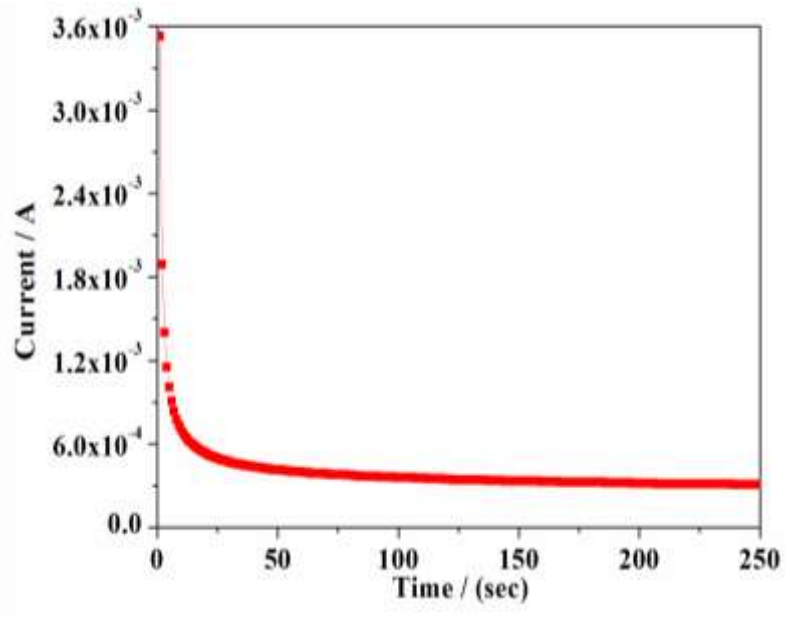

Figure 3: dc polarization curve as a function of time for nano gel polymer electrolyte[PVdF (HFP)](15 wt%)-{PC-Mg $(ClO_4)_2$}(0.3M)]-nano Al_2O_3(8 wt%)].

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The ionic transport number was calculated by using the given equation: $t_{ion} = I_t - I_e/I_t$. where Ie and I_t are electronic and total current respectively. The ionic transport number was found to be 9.6 which shows that nano gel polymer electrolyte [PVdF(HFP)(15%)-PC-$Mg(ClO_4)_2$-Al_2O_3 (8wt%)] using magnesium ion salt is dominantly ionic in nature.

Characterization of fabricated supercapacitor device

To check the compatibility of optimized nano gel polymer electrolyte for its use in energy storage devices, symmetrical supercapacitor having following configuration was fabricated: AC | [PVdF(HFP)(15%)-PC-$Mg(ClO_4)_2$(0.3M)-Al_2O_3 (8wt%)] |AC. Where AC is electrode made up of activated charcoal.

Impedance spectroscopy analysis

Electrical properties such as bulk properties of electrolytes, charge transfer, ion accumulation in electrode-electrolyte interfacial region and low frequency capacitance values etc. can be evaluated by this method [13]. In the present paper a.c impedance measurement was done in the frequency range of 1mHz to 100 mHz. Figure 10 shows the complex impedance plot for above mentioned cell. In the plot two regions were seen, first high frequency semicircle region which is related to bulk resistance (R_b) and charge transfer resistance (R_{ct}) and second low frequency straight line due to Warburg impedance which is associated with the charge accumulation in electrode- electrolyte interfacial region that results into the formation of electrical double layer [14]. The semicircle region indicates the parallel combination of resistance and capacitance while straight rising line indicates the capacitive behaviour of the fabricated cell. The values of (R_b) and (R_{ct}) have been calculated by expanded plot in higher frequency region, and overall capacitance was calculated by the equation: C =- 1/ωZ" where, ω is angular frequency (2лf) and Z"is imaginary part of impedance. Various electrical parameters (R_b), (R_{ct}), total resistance (R) and capacitance (C) at frequency range of 1mHz to 10 mHz.are given in table number 1

Table 1: Electrical parameters of fabricated EDLC cell from impedance analysis

R_{ct} (Ω cm^2)	R_b (Ω cm^2)	10 mHz			1 mHz		
		R	C		R	C	
		(Ω cm^2)	(mF cm^{-2})[a]	(F g^{-1})[b]	(Ω cm^2)	(mF cm^{-2})[a]	(F g^{-1})[b]
14.4	5.0	68	95	27	556	153	44

[a] Overall capacitance of the cells. [b] Single electrodes specific capacitance of the cells.

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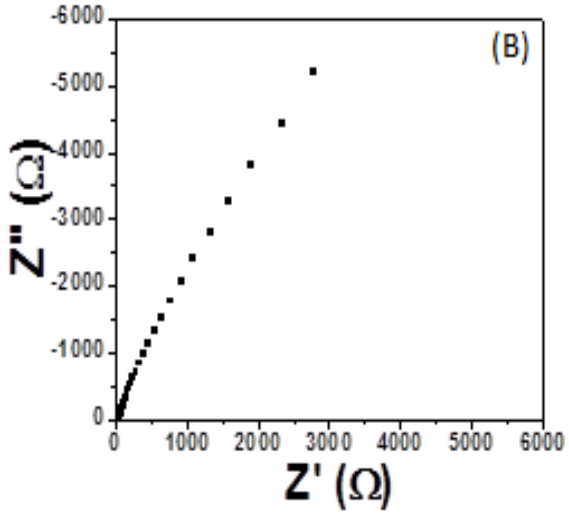

Figure 4: impedance plot of cell: AC| [PVdF(HFP)(15%)-PC-Mg$(ClO_4)_2$(0.3M)-Al_2O_3 (8wt%)] |AC.

Cyclic voltammetry analysis

Figure 5 shows the specific capacitance of the fabricated cell at different scan rates. From the figure it was seen that the cell retains its ideal rectangular geometry even at higher scan rate. This behaviour ensures its application at higher scan rate also. Some initial deviation from the ideal behaviour can be seen which may be due to fast ion behaviour change at electrode-electrolyte interfacial region. There were no redox peaks present which confirms the non-faradic process and hence confirms the EDLCs behaviour [15]. The capacitance value can be calculated by the equation: C = i/s. where, I is constant current and s scan rate. The calculated capacitance value was found to be almost in the range of capacitance calculated by a.c impedance and charge- discharge method.

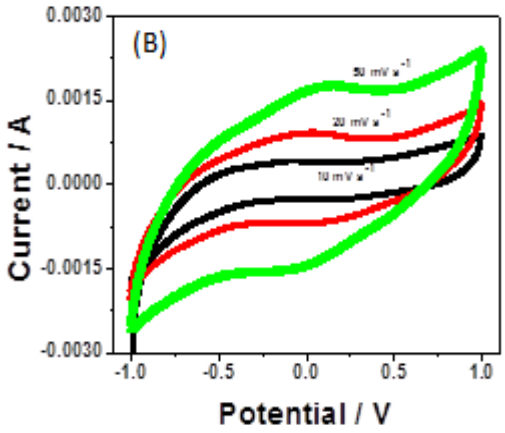

Figure 5: Cyclic voltammograms of cell: AC| [PVdF(HFP)(15%)-PC-Mg$(ClO_4)_2$(0.3M)-Al_2O_3 (8wt%)] |AC. at different scan rates.

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Charge- discharge analysis

Figure 6 shows the charge- discharge plot for the fabricated cell at a constant current of 2mAcm-1 between the potential range of 0-1 V. from the figure it was clear that the plot follows the ideal linear triangular profile, this linear profile confirms the capacitive behaviour of fabricated cell and it also confirms that the energy storage process is based on the charge accumulation in electrode- electrolyte interfacial region. Initial voltage drop was also observed due to internal resistance of the capacitor cell. The internal resistance has been calculated by this drop and was found to be 60Ω cm-1. The specific capacitance was calculated by linear part of discharge curve by the equation: $C_d = i\Delta t/\Delta V$. Where, 'i' is constant current, 'Δt' is time interval for the voltage change ΔV. From this specific capacitance the corresponding energy density and power density can be calculated by the following equations: Energy density = ½ CV2 and power density = (½ CV2)/Δt. Different electrical parameters such as specific conductance, energy density, power density has been calculated and reported in table number 2.

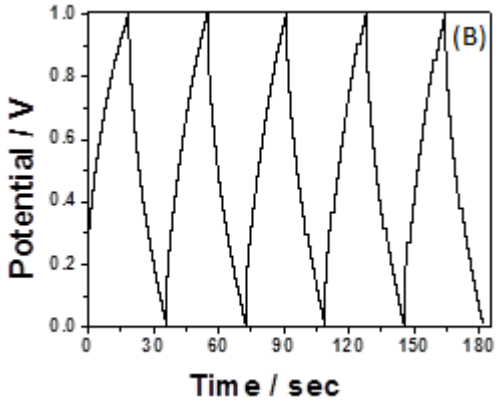

Figure 6 Charge- discharge curve of cell: AC| [PVdF(HFP)(15%)-PC-$Mg(ClO_4)_2$(0.3M)-Al_2O_3 (8wt%)] |AC.at current density of 2.0mA cm^{-2}

Table 2: Typical charge-discharge characteristics of fabricated EDLC cell at current density of 2.0m Acm^{-2}

R_i (Ω cm^2)	Discharge capacitance, C_d		Working voltage (V)	Energy density (Wh kg^{-1})	Power density (kW kg^{-1})
	(mF cm^{-2})[a]	(F g^{-1})[b]			
64	94	27	1.0 V	3.8	0.9

[a] Overall capacitance of the cells.

[b] Single electrodes specific capacitance of the cells.

Conclusion

From all the above experimental analysis, we can conclude the following important conclusions:

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- ✓ The nano gel polymer electrolyte [PVdF(HFP)(15%)-PC-$Mg(ClO_4)_2$(0.3M)-Al_2O_3 (8wt%)] has been prepared by conventional "solution cast" method and then optimized. The maximum ionic conductivity was found to be $7.0x10^{-3}Scm^{-1}$ at room temperature.
- ✓ The compatibility of synthesized nano gel polymer electrolyte has been checked by using it for the successful fabrication of supercapacitor having activated charcoal as electrode materials.
- ✓ The fabricated capacitor shows non-faradic behaviour which confirms its EDLCs nature.
- ✓ The maximum capacitance value for above cell was found to be 94 mF cm^{-2}, which is equivalent to a single electrode specific capacitance of 27 Fg^{-1}. The energy density was 3.8 Wh kg^{-1} and power density was 0.9 $kWkg^{-1}$.

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