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Fabrication and electrical characterization of nano gel composite electrolyte

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Abstract— *In today's society, we stand before a change in energy paradigm. As our civilization grows, many countries in the developing world seek to have the standard of living that has been exclusive to a few nations, so their arises a need in the development of technology that is compatible enough with the resources provided by nature in order to have sustainable development to all class of the society. Climate change and continuous depletion of fossil fuels compels the society to move towards sustainable and renewable resources. As a result of which, researchers are looking forward to exploit a renewable energy production from natural resources like sun and wind. One of the most important sectors which influence the life of common people is transportation, which at present is strongly dependent on petroleum and natural gases. In order to overcome the prevailing challenges of huge energy crises in near future, there is an urgent need for the development of electrical vehicles or hybrid electrical vehicles with low CO_2 emissions using renewable energy sources. In view of the above, electrochemical capacitors can fulfill the requirements to some extent.*

Keywords— compatible, depletion, sustainable, renewable resources, electrochemical capacitors.

I. INTRODUCTION

Now a day's rechargeable batteries and supercapacitors having different types of solid state electrolytes are fabricated which are having different compositions, such as polymer blend electrolyte, polymer composite electrolyte, polymer gel electrolyte, ionic liquid-base polymer gel electrolyte etc., Almost all the electrolytes shows high conductivity almost equivalent to that of liquid electrolyte i.e. ~10^{-4}Scm^{-1} , but they deal with some serious problems which restrict their suitability for practical objectives. Poor dimensional stability, less thermal stability and low range of power window are some basic problems which has to be remove from these polymer electrolytes to make it efficient for its use in modern age highly sensitive technical inventions for eg. fuel cells, sensors, electrochromic tool etc. [1-4]. Preparation of nano composite polymer gel electrolyte is the best optional product to overcome these problems. Nano science is the new and emerging field which attracted the attentions of global scientist and research fraternity because it is clear till now that nano size of the materials can do the miracle in electrical as well as electronics field due to its exceptionally unique chemical, physical, and mechanical properties such as: high interfacial energy, exceptionally large aspect ratios, high degree of disorder, high ionic transport [5].

Although polymer gel electrolyte is having very good ionic conductivity of the range ~10^{-4}Scm^{-1}, fare flexibility, good electrode-electrolyte contact in fabrication of the device but due to its jelly or semisolid nature they have low geometrical safety, decline in ionic conductivity during long term use, less comfortable relation with electrode interface etc. One of the methods to solve these problems of polymer gel electrolyte is to add some inorganic filler in nano sizes, to convert polymer gel electrolyte in composite type of electrolyte having combined(features of constituent materials) as well as new characteristic features (other than reactants). When such fillers are added or dispersed to the polymer gel electrolyte, amorphous or porous nature of electrolyte increases (to many fold as compared to normal composite electrolytes) which enhances the liquid absorbing quality of polymer and helps in removing the drawbacks of polymer gel electrolytes such as leakage, poor mechanical and thermal stability etc. [6-7]Type of nano filler which is used to prepare the composite polymer gel electrolyte, contributes important part to modify structural configuration at microscopic level for the electrolytic system which further enhances the properties such as polarization, ionization and mobility of charge carriers, they have direct impact on ionic conduction and other phenomenon of good polymer gel electrolyte.

In this chapter dispersion of SiO_2 nano filler is done in the [PVdF (HFP)-PC-Mg $(ClO_4)_2$] arrangement for the synthesis of nano composite PGE [PVdF (HFP)-PC-MgClO$_4$- SiO_2]**.** Optimization and characterization of the NCPGE having SiO_2 was carried out by using various techniques.

II. EXPERIMENTAL DETAILS

As we know in any successful polymer electrolyte three major characteristic properties, which has to be seen are high ionic conductivity, mechanical stability as well as easy polarization of ions. All these conditions are satisfied by mixture of two polymeric materials Polyvinylidene fluoride and hexa fluoro propylene, therefore it is taken as host polymer in the present work, along with all these properties they have high dielectric constant of 8.4 (polarization of ions), PVdF contributes to the crystalline property which imparts mechanical stability and HFP contributes to the amorphous character which is responsible for ionic conductivity. [8-10].

Lithium ion based electrochemical devices are widely used, but they have some major drawbacks such as: they are expensive, highly sensitive with humidity, explosive in nature and other related problems [11-17]. In order to overcome these problems, other metal ion based polymer electrolyte provides a better alternative for lithium ion such as: sodium, magnesium and zinc etc. [18-27, 12]. Out of all these ions, magnesium ion is better alternative for lithium due to their high specific energy and low electrochemical equivalence (12.15 g equiv.-1), effective cost, comparable ionic size, negative electrode potential of -2.63 V versus SHE, ecofriendly nature etc. [12-14]. Mg2+ ion based gel polymer electrolytes are generally used in systems having aprotic organic flexibility enhancer (plasticizers) such as propylene carbonate (PC), ethylene carbonate (EC) etc. [12, 14, 15, 28]. Therefore magnesium perchlorate Mg (ClO4)2 is taken as a salt for the present work. In this Mg (ClO4)2 salt, (ClO4)-2anion is bulkier in nature so the mobility of Mg ion is larger.

PC is taken as plasticizer to dissolve the salt and enhance the flexibility of the polymer, which is required for the easy conduction of ions through the polymeric chain.

(THF) tetrahydrofuran is taken as intermediate solvent which is volatile in nature and used to dissolve the polymer (PVdF-HFP), after the final preparation of the nano composite polymer gel electrolytes they get evaporated at room temperature by its own.

And nano size SiO2 is taken as filler to improve the amorphicity hence ionic transportation capacity of the polymeric arrangement.

Combining all the above said properties, NGPE [PVdF (HFP)-PC-Mg (ClO4)2-SiO2] based on nano SiO2 filler is synthesized by solution cast technique.

2.1 Synthesis of nano PGE

NCPG electrolytic complex was synthesized by the chemical combination of poly vinylidene fluoride-co-hexa fluoro propylene as base polymer mixture, magnesium perchlorate Mg (ClO4)2 as salt, SiO2 (<50 nm) as nano filler (all obtained from Sigma-Aldrich), Propylene carbonate (PC) as solvent and tetrahydrofuran (THF) as volatile intermediate solvent. The nano composite polymer gel electrolyte PVdF (HFP)-PC-Mg (ClO4)2 - SiO2 has been developed by utilizing Standard “solution cast-techniques”.

2.2 Instrumentation used in the present studies

Various structural, electrical, thermal and electrochemical techniques are formulated for the optimization and specification of nano composite polymer gel electrolytes PVdF (HFP)-PC-Mg (ClO4)2 - SiO2 having silica nano filler.

The electrical conduction of the electrolytic complex were measured by means of an a.c impedance spectroscopic techniques with the help of LCR Hi-Tester (HIOKI-3522-50, Japan) in freq.100 kHz to 1 Hz with a signal strength of 10 mV.

XRD impression of the synthesized material was explained with Bruker D8 Advance diffractometer with Cu-Kα radiation over the Bragg angle (2θ) range of 10-60°. The scan rate was fixed at 5°/ min.

The superficial texture analysis was demonstrated by applying SEM technique (JEOL JXA - 8100 EPMA).

Fourier transform infrared (FTIR) spectral examinations of the polymeric systems were performed by Bruker vertex 70 spectrophotometer.

The trend temperature dependency of the polymer gel systems were practiced by differential scanning calorimetry (Mettler Toledo DSC 822E) from -70 -175 °C heating at 10 °C/ min in inert atmospheric condition of N2.

Compiling of electrolytic complex product was done by inserting the suitable length material in the middle of two blocking terminals made up of stainless steel and then capitalized for conduction measurements. For eg. Ionic transference number and electrical power window of the electrolytes by CHI 608C, CH Instruments, USA.

III. RESULTS & DISCUSSIONS

3.1 Electrical characterization

3.1.1 Synthesis and optimization of liquid electrolytes

Synthesis and optimisation of liquid electrolyte was done by "standard solution cast technique". The optimised concentration value of salt in the liquid electrolyte {PC-Mg (ClO4)2} was found to be 0.3M, and R.T σ of this electrolyte was detected as ~ σ = 3.63 x 10-3S cm-1.

3.1.2 Production and standardisation of polymer gel electrolytes

PGE, [PVdF (HFP)-PC-Mg (ClO4)2] was prepared by taking different weight percent of polymer, poly vinylidine fluoride-hexa fluoro propylene [PVdF (HFP)] between (0- 50%) in optimized liquid electrolyte of (0.3) M system and then it was characterized. The optimized value of polymer was found to be 15 wt% in [PVdF (HFP)-PC-Mg (ClO4)2] polymer gel electrolyte. The R.T conduction of polymer gel electrolyte was found to be ~ σ = 5.0 x10-3 S cm-1.

3.1.3 Synthesis and optimization of nano PGE

Electrolytic material prepared is having high ionic conductivity and flexibility but due to semisolid gel like texture they experiences poor mechanical stability, dimensional stability, thermal stability, less interfacial stability towards electrode and reduction in ionic conductivity with time etc., to solve these problems certain fillers are added to enhance the various stabilities, self-life, less passivation towards electrode- electrolyte interface etc., when nano particle of SiO2 filler was added in polymer gel electrolyte, it enhances the porous and amorphous nature of the system which in turn, increases the captivation capacity of liquefied system , and minimize the leakage problem of device. In the present work nano particle of SiO2 is used as filler for optimized polymer gel electrolyte, [PVdF (HFP)-PC-Mg (ClO4)2] to prepare nano composite polymer gel electrolyte [PVdF (HFP)-PC-Mg (ClO4)2- SiO2]. Figure 3.1 shows the change of electrical transport capacity of polymeric electrolyte with respect to varying wt% of nano- SiO2 filler concentration.

As we can see from the plot, that initial addition of nano SiO2 filler in PGE, enhances the ionic conductivity of the system this may happen due to the various interactions of the nano particles either with cations or anions or with paired ions, these interactions results in to the enlarge quantity of mobile ion concentration and ultimately ionic conductivity increases.

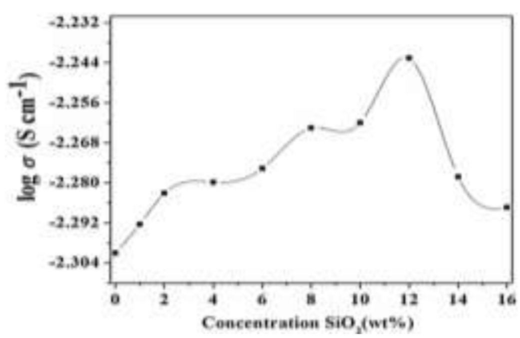

Fig. 3.1: Alteration of electrical conductivity of electrolytic material w.r.t SiO_2 filler wt%.

Fillers can also modify the structural arrangement of ions in polymeric segment by interacting with polymeric chain (PVdF-HFP) as well as salt anions (ClO4)2- and facilitate the easy and suitable path for magnesium ion conduction on the nano SiO2

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fabricated surface. This increase in ionic conductivity can be seen till 12 wt% of SiO2 nano fillers; ionic conductivity at this composition was determined as ~5.72x10-3Scm-1. Further addition of SiO2 nano particle shows the gradual decrease in ionic conductivity; due to increase in viscosity and ionic pairing (aggregation) of the system the ionic mobility becomes difficult, resulting into reduced ionic conductivity. Hence the optimized value of nano SiO2 filler is taken as 12 % by weight of polymer electrolyte for the assembling of nano composite polymer gel electrolytes.

Hence with the reference of above studies it is clear that the final optimized composition for nano composite polymer gel electrolyte is [PVdF (HFP)] (15 wt %)-[{ PC-Mg (ClO4)2} (0.3M)]-nano SiO2 (12wt %).

3.1.4 Temperature dependent conductivity

Almost all the inventions emphasizing on chemical reaction for the production of electricity such as capacitors and cells etc. follow the mechanism of ionic conductivity for their energy generation as well as storage. Generally they have very wide range of working temperature (negative to positive temperature range). Fig: 3.2 depict the influence of changing temperature on the trend of ionic conductivity given by nano composite polymer gel electrolyte [PVdF (HFP) (15 wt %)-{ PC-Mg (ClO4)2} (0.3M)]-nano SiO2 (12wt %).

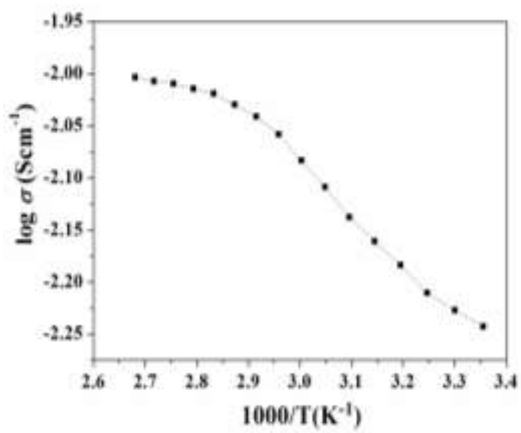

Fig. 3.2: Alteration of ionic conductivity of optimized nano gel polymer electrolyte with varying temp.

The above graph shows the ionic conduction of the nano composite polymer gel electrolyte system having nano SiO2 as filler in 12wt%. As we can see from the above plot that ionic conduction capability follow the direct relationship with the fluctuating temperature; it continues till ~1000C, and follow the Arrhenius pattern, ionic conductivity at this stage was found to be 9.92x10-3Scm-1. The increasing trend of ionic conductivity with increasing temperature can be explained as, when the temperature of the system increases the viscosity decreases resulting into increase in segmental mobility of the ion and hence flexibility of polymeric chain also increases resulting into higher conduction [29]. This feature at any temperature is calculated by Arrhenius equation as explained in previous chapters.

$$\sigma = \sigma 0 \exp(-Ea / kT) \quad (1)$$

Ionic conductivity of 12 wt% SiO2 compositions is calculated from above equation, which was found to be ~ 9.92x103Scm-1. The activation Energy of the system is calculated as 0.041 eV and was simplified by fitting the curve in the temperature range of 1000C.

IV. CONCLUSION

From the detail studies of various characterization technique, it was clear that the nano composite polymer gel electrolyte [PVdF (HFP) (15%)-PC-Mg (ClO4)2(0.3M)-SiO2 (12wt %)] which was synthesised in present chapter was efficient and compatible to the other electrolyte that are already in use for the fabrication of electrochemical devices such as supercapacitors.

Illustrating all the above studies the following conclusions can be drawn:

- The nano gel polymer electrolyte [PVdF (HFP) (15%)-PC-Mg (ClO4)2(0.3M) - SiO2 (12wt %)] has been prepared by "standard solution cast" technique.
- The optimized concentration of Mg (ClO4)2 salts was found to be 0.3M for the preparation of liquid electrolytes having conductivity in the range of ~3.63 x 10-3 S cm-1 which was used for the preparation of polymer gel electrolytes.
- 15wt% of polymer PVdF (HFP) is sufficient for the synthesis of polymer gel electrolytes having electrical conductivity of ~5.0 x10-3S cm-1 at room temperature with acceptable mechanical strength.
- For the preparation of desired nano composite polymer gel electrolyte, the optimized value of SiO2 nano filler was found to be 12wt %.
- The maximum ionic conductivity of optimized nano composite polymer gel electrolyte was found to be 5.72 x10-3Scm-1 at room temperature.

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