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Structural and Morphological Studies of Nano Composite Polymer Gel Electrolyte having SiO₂

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Abstract: *In today's society, we stand before a change in energy scarcity. As our civilization grows, many countries in thedeveloping world seek to have the standard of living that has been exclusive to a few nations, so their arises a need in thedevelopment of technology that is compatible enough with the resources provided by nature in order to have sustainabledevelopment to all class of the society. In order to overcomethe prevailing challenges of huge energy crises in near future, there is an urgent need for the development of electrical vehiclesor hybrid electrical vehicles with low CO_2 emissions using renewable energy sources. In view of the above, electrochemicalcapacitors can fulfil the requirements to some extent.Preparation of nano composite polymer gel electrolyte is the best optional product to overcome these problems. When fillers are added or dispersed to the polymer gel electrolyte, amorphous or porous nature of electrolyte increases 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. In this work dispersion of SiO_2 nano filler is done in the $[PVdF (HFP)-PC-Mg (ClO_4)_2]$ for the synthesis of nano composite PGE $[PVdF (HFP)-PC-MgClO_4- SiO_2]$. Optimization and characterization was carried out by using various techniques.*

Keywords -*Compatible, Electrochemical capacitor, Depletion, Renewable resources, sustainable*

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 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].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 theproperties 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 paper 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.

2. METHODOLOGY

2.1 Synthesis and optimization of nano PGE

NCPG electrolytic complex was synthesised by the chemical combination of poly vinylidene fluoride-co-hexa fluoro propylene as base polymer mixture, magnesium perchlorate Mg $(ClO_4)_2$ as salt, SiO_2 (<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 $(ClO_4)_2$ - SiO_2 has been developed by utilizing Standard "solution cast-techniques". When nano particle of SiO_2 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 liquified system and minimise the leakage problem of device. In the present work nano particle of SiO_2 is used as filler for optimized polymer gel electrolyte, [PVdF (HFP)-PC-Mg $(ClO_4)_2$] to prepare nano composite polymer gel electrolyte [PVdF (HFP)-PC-Mg $(ClO_4)_2$- SiO_2].[8-10] Hence the final optimized composition for nano composite polymer gel electrolyte is [PVdF (HFP)] (15 wt %)-[{ PC-Mg $(ClO_4)_2$} (0.3M)]-nano SiO_2 (12wt %). ionic conductivity at this composition was determined as ~$5.72 \times 10^{-3} Scm^{-1}$.

2.2 Instrumentation used in the present studies

XRD impression of the synthesized material was explained with Bruker D8 Advance diffractometer with Cu-K$_\alpha$ 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.

3. Results & Discussions

3.1 Structural and morphological properties

3.1.1 X- ray diffraction Studies

In the figure 1. plot (a) explains the XRD pattern of the Mg $(ClO_4)_2$ ionic salt which shows the predominant peaks at 2θ = 13.0, 17.5, 21.1, 22.7, 26.2, 28.0, 31.3, 34.4, 43.7, 51.3 and 56.9, which shows the pure crystalline nature of ionic salt. Figure 1(b). Signify the scattering pattern of polymer mixture peaks observed at 2θ = 18.4, 29.3, and 38.9 due to semi-crystalline nature having mixed characteristics of crystalline as well as amorphous regions. Figure 1(c). shows the stage when liquid electrolyte is adsorb by polymer electrolyte PVdF(HFP)- PC solution, we can clearly observed that some peaks of ~ 38.9 get disappeared, which was due to the increasing amorphous nature of [PVdF(HFP)(15wt%)-{PC-Mg$(ClO_4)_2$}(0.3M)] PGE. Figure1 (d) shows the peaks, when nano SiO_2 filler was mixed with optimized gel polymer electrolytes, some diffraction of PVdF (HFP) at peaks (~2θ = 29.3 and 38.9) are disappeared. This also confirms the complete interaction of filler and polymer gel electrolyte resulting into homogeneous mixture of nano polymer gel electrolyte. This makes the system more amorphous and flexible in nature, which is the cause of modification in ionic transportation. [11-12].

XRD method is helpful in calculating various structural parameters such as crystal size, scherrer length (l), d-spacing, relative peak intensity of pure salt, pure polymers, PGE, NPGE. All these parameters are given in tabular form:
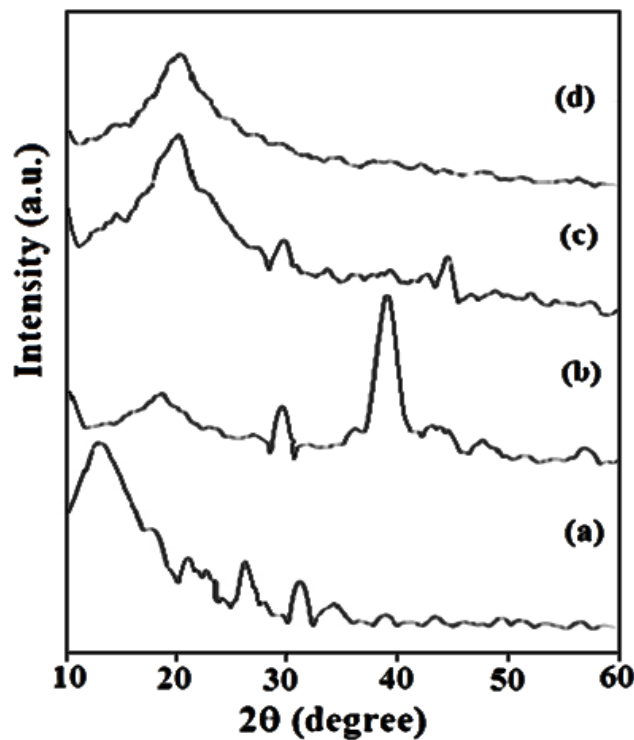
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Fig: 1. XRD impression of : (a) Mg(ClO$_4$)$_2$ (b) PVdF(HFP) film (c) [PVdF(HFP)](15wt%)-[PC-Mg(ClO$_4$)$_2$]{0.3M} polymeric system and its composite film with (d) 12wt% of SiO$_2$ nanoparticles.

Table 1(a): X-ray diffraction data of pure Mg (ClO$_4$)$_2$, pure PVdF (HFP) film, [PVdF (HFP)] (15wt %) - [PC-Mg (ClO$_4$)$_2$]{0.3M} polymer electrolytes and nano gel polymer electrolytes

Sample	2θ(deg)	Θ	D	l(A^o)	Intensity
Mg(ClO$_4$)$_2$	13.0	6.5	6.76	0.17	100
Pure PVdF(HFP)	38.9	19.4	2.30	0.63	100
PGE	20.3	10.1	4.36	0.09	100
PGE-SiO$_2$ (12wt%)	20.3	10.18	4.4	0.11	100
PGE-SiO$_2$ (16wt%)	20.2	10.15	4.4	0.10	100

Table 1(b): Detail studies of XRD technique:

Sample	2θ (deg.)	Θ	D	l((A^o)	Intensity
Mg(ClO$_4$)$_2$	13.0	6.5	6.76	0.17	100
	26.2	13.1	3.39	1.09	38.4
	31.3	15.6	2.85	1.02	28.2
	34.4	17.2	2.59	1.03	16.2
	43.7	21.8	2.06	0.78	9.8
Pure PVdF(HFP)	18.4	9.2	0.78	0.11	44.4
	38.9	19.4	2.30	0.63	100
	57.1	28.5	1.60	0.87	14.1
PGE	20.3	10.1	4.36	0.09	100
	29.7	14.8	3.00	0.64	51.2
	44.5	22.2	2.03	0.67	43.3

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PGE- SiO$_2$ (12wt%)	20.3	10.18	4.4	0.11	100
PGE-SiO$_2$ (16wt%)	20.2	10.15	4.4	0.10	100

3.1.2 Scanning electron microscopy studies

Fig.2.express the morphological arrangement of polymer electrolyte and nano polymer gel electrolyte at microscopic level. For this purpose (SEM) scanning electron microscope is used which can show the high resolution images that can give us the idea about atomic and molecular distribution throughout the system. Figure 2(a) indicates the uniform distribution of small pores of polymer gel electrolyte which is attributed to the random and irregular nature of the gel polymer electrolyte while figure 2 (b)& 2(c) indicate complete interaction between polymer gel electrolyte and fillers, which are visible in the form of homogenous and uniform distribution of small pores connected to the polymeric chain (at different magnifying levels) , due to which the polymer gel electrolyte can able to adsorb more amount of liquid electrolyte which will result into two advantages first due to this mechanism ionic conductivity increases and second the leakage tendency decreases.
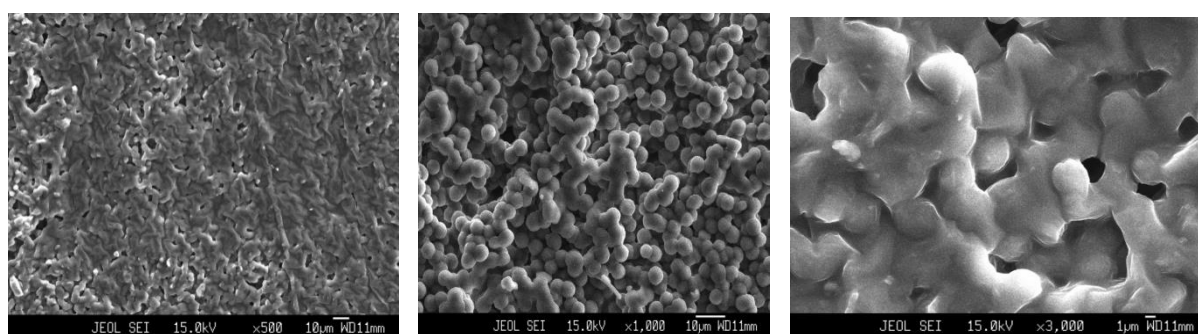
(a)   (b)   (c)

Fig:2. SEM images of [PVdF (HFP)](15wt%)-[PC-Mg(ClO$_4$)$_2$]{0.3M}-SiO$_2$(12wt%) polymer gel electrolytes system with different magnification.

3.1.3 Fourier transform infrared spectroscopy studies

The internal microscopic and molecular structure of amorphous region, organic molecules and their interactions with the functional groups in polymeric system, can be detected with the help of vibrational peaks of electrolytic system, appearing in FTIR spectra. Figure 3 (a-e) shows the FTIR spectra for polymer (PVdF (HFP), [(PVdF-HFP)-PC-Mg (ClO$_4$)$_2$ and optimized NCPG electrolytes with different wt. % of SiO$_2$ as fillers.

Various absorption peaks are observed in the FTIR spectra which can be explained and assigned to different characteristics vibration bands, functional groups and interactions of salt, plasticizer or solvent, polymer and nano filler in the nano gel polymer electrolytes etc.

Figure (a) shows the plot of pure polymer (PVdF(HFP) in which many peaks can be seen at the wavenumber 3024 and 2984 /cm is on account of asymmetric and symmetric stretching vibration, indicates the crystalline as well as amorphous nature of polymer, assigned by CH$_2$. Fig: (b) The appearance of peak at wave number 1787, 874, 840, 758 and 490 cm^{-1} , corresponds to the presence of vinylidene group and appears due to the presence of -CF=-CF$_2$- group, assigned to the CH$_2$ rocking of the vinylidene band, -CF$_2$ shows asymmetric stretching, CH$_2$ wagging vibration and CF$_2$ scissoring vibration of the vinyl group, respectively , which explains that the crystalline phase is present in the polymer. [13].

Fig:(c) Further, when liquid electrolytes was added to the polymer materials some new vibration peak are observed at wave numbers 1631, 1553, 1484, 1389, 776, 711 and 627 cm^{-1}. The wavenumber 1631 and 1553/cm was attributed to the C=O stretching vibration of plasticizer (PC). The wavenumber 1484 and 1389/ cmwas assigned to bending vibration of -CH$_3$ of plasticizer. The vibration peaks at wave number 776 and 711 cm^{-1} represents the C-Cl stretching vibration. The peak at wave number 627cm^{-1} is assigned to the vibration of ClO$^-_4$ ions. The interaction vibration of ionic pairs between Mg and ClO$^-_4$ is observed at the peak of wave number 1119 to 1078 cm^{-1}.

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The vibration peaks of 3024, 2984, 1787, 874, 840 and 490 cm^{-1} are shifted to 2993, 2926, 1792, 877, 838 and 476 /cm in the nano composite polymer gel electrolytes. The shuffling of peaks in the IR spectra of PVdF (HFP)-PC-Mg(ClO$_4$)$_2$- SiO$_2$, nano composite polymer gel electrolytes is due to the homogeneous mixing and interaction of constituents in the complex system. Figure 3(d&e) shows the identical pattern.
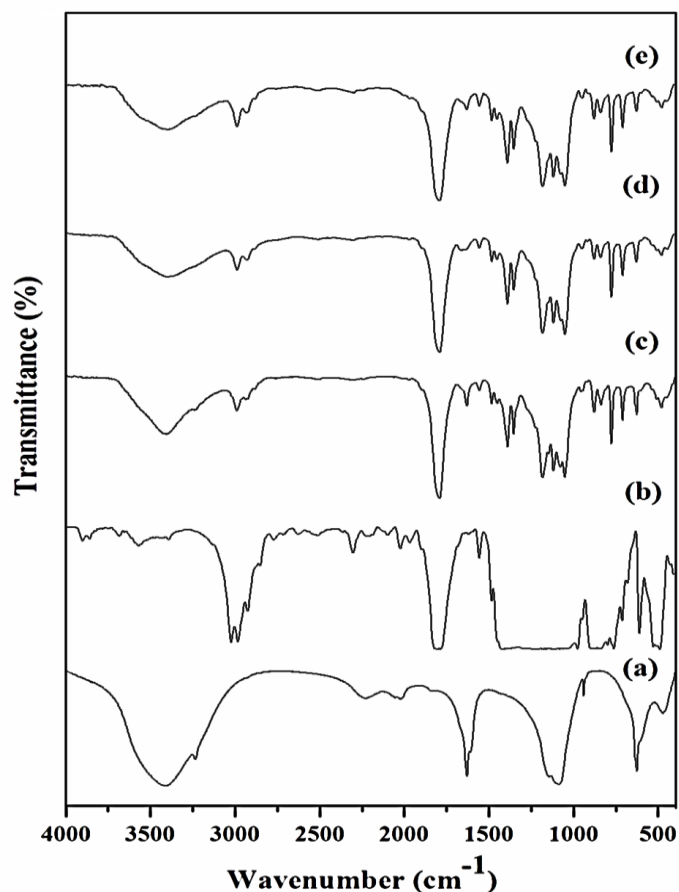

Fig:3. FTIR Spectral impression of: (a) Pure Mg(ClO$_4$)$_2$ (b) pure PVdF-HFP film (c) [PVdF(HFP)](15wt%)-[PC-Mg(ClO$_4$)$_2$]{0.3M} polymer films containing SiO$_2$ nanoparticles (d) 8wt% (e) 12wt%.

Table 2: Designation of specific FTIR zones of pure PVdF (HFP), gel polymer electrolytes with different concentration filler in nano gel polymer electrolytes

Band Assignment (Cm-1)	PVdF(HFP) film	[PVdF(HFP)-PC-Mg(ClO$_4$)$_2$	4wt% SiO$_2$	12wt% SiO$_2$
	-	3406	3404	3396
CH$_2$ Asym. Stret.	3024	2989	2993	2986
CH$_2$ Sym. Stret.	2984	2926	2926	2926
-CF=-CF$_2$-	1787	1792	1787	1789
C=O stret. Vib.	-	1631	1649	1631

of plasticizer		-	1553	1553
-CH$_3$ bending vib.	-	1484	1486	1486
		-	1456	1456
CH$_2$ group	-	1389	1394	1384
		1354	1360	1354
-CF$_2$ Sym. Stret.	-	1184	1179	1179
		1119	1119	1119
		1078	-	-
		1052	1046	1052
		-	-	950
CH2 Rocking αPhase	874	878	877	877
CH2 Asym. Stret & CF2 Asym. Stret. β Phase	840	839	838	838
C-Cl Stret.	-	776	781	780
CH2 wagging vib.	758	-	-	-
C-Cl Stret.	-	711	715	712
ClO$^-_4$	-	627	626	627
CF$_2$ scissoring vib α Phase	490	481	476	480

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 (ClO$_4$)$_2$(0.3M)-SiO$_2$ (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 demonstrated data the summarised points can be written as:

- ✓ The "standard solution cast "procedure was capitalised for the preparation of electrolytic complex system.
- ✓ The maximum value for ionic conduction of optimized nano composite polymer gel electrolyte was calculated as 5.72 x10^{-3}Scm^{-1} at room temperature.
- ✓ The surface morphology and topography image has been obtained from scanning electron microscopy, which shows the porous texture and hence supports the electrical conductivity throughout the polymeric network.
- ✓ The FTIR method clearly gives the idea about complete homogeneous mixing of all the constituents' electrolyte, polymer, and nano materials which results into the synthesis of nano composite polymer gel electrolyte having very good flexibility as well as good mechanical stability.

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