

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

Investigation of the Structural, Electrical and Morphological properties of Mg²⁺ ion conducting Nanocomposite Solid Polymer Electrolytes based on PMMA

A. Arulsankar¹, K. Kulasekarapandian², S. Jeya³, S. Jayanthi⁴, B. Sundaresan⁵

Assistant Professor of Physics, Department of Physics, Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi – 626 124, Tamil Nadu, India¹

Assistant Professor of Physics, Department of Physics, Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi – 626 124, Tamil Nadu, India²

Assistant Professor of Physics, Department of Physics, Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi – 626 124, Tamil Nadu, India³

Research Scholar, Department of Physics, Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi – 626 124, Tamil Nadu, India⁴

Associate Professor of Physics, Department of Physics, Ayya Nadar Janaki Ammal College (Autonomous), Sivakasi – 626 124, Tamil Nadu, India⁵

Abstract: The structural, electrical and morphological properties of Poly (Methyl Methacrylate) (PMMA) complexed with magnesium perchlorate ($Mg(ClO_4)_2$) were investigated. The effect of addition of nanofiller, fumed silica (SiO_2) (1.29 nm) was also studied. The analysis of Fourier Transform Infrared Spectroscopy (FTIR) spectra of the samples revealed that there was complexation between PMMA and $Mg(ClO_4)_2$. It also revealed the plasticizing action of fillers in the electrolyte and hence the structural changes of systems studied. XRD Studies indicated the better dissolution of $Mg(ClO_4)_2$ in PMMA matrix. The amorphous nature of the polymer electrolyte has been enhanced by the incorporation of nano sized SiO_2 . Analysis by impedance studies showed that the two conductivity maxima have been observed for 2 and 10wt% of SiO_2 added system. The morphological changes have been observed through AFM studies.

Keywords: Poly (Methyl Methacrylate), Magnesium perchlorate, Silica, AC impedance studies, FTIR

I. INTRODUCTION

Solid polymer electrolytes (SPEs) have drawn much interest among researchers due to their high specific energy, good reliability, high ionic conductivity, solvent-free condition, light weight and wide electrochemical stability windows [1 – 4]. Among various SPEs, polyethylene oxide (PEO) – Lithium salt (LiX) complexes [5] were most studied, since they possess advantages like high energy density, better cycle ability and safety to be used as an electrolyte in solid – state batteries [6]. But PEO based SPEs exhibit low ionic conductivity at ambient temperature which limits their applications [7].

A number of researchers [8, 9] have demonstrated that, improved ionic conductivity is achieved by the inclusion of plasticizer into the polymer matrix. But they suffer several drawbacks like decomposition, volatilization, and also the deterioration of the mechanical properties.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

Another way to increase the ionic conductivity is done by the inclusion of nano fillers like SiO_2 , Al_2O_3 , TiO_2 , MgO , SnO_2 , ZnO , CuO , CdO and ZrO_2 [10]. In addition, the Lewis acid – base interactions between the polar surface groups of the nano fillers and the electrolyte ionic species yield a greater degree of salt dissociation through the formation of ionic – filler complex.

Poly (methyl methacrylate) (PMMA), has been chosen as a host polymer for the present study, due to its outstanding chemico-physical properties which represent a particularly suitable polymer component for the embedding of both microscopic and nanoscopic functional inorganic fillers. The wide use of such a matrix has to be traced back to the favourable combination of chemical and physical properties and easy processing. It has been well established that PMMA acts as a good host material for dielectric materials. PMMA-Ceramic composites exhibit remarkably low dielectric loss at high frequency, which makes them potential material for the capacitors in high frequency application. It is an amorphous polymer and it is a colorless, transparent, plastic with an excellent life period and good mechanical properties.

Fumed silica as a filler is of special interest because of its branched primary structure and the ability to tailor the surface functionalities. Composite Polymer Electrolytes based on fumed silica were shown to be highly transparent in the visible region and to have a wide electrochemically stable potential window [11].

Appetecchi *et al.*, studied the kinetics and stability of the lithium electrode in PMMA-based gel electrolytes [12]. Sekhon *et al.*, reported the transport properties of lithium electrolytes gelled with PMMA. [13]. When PMMA is combined with inorganic materials such as Silica (SiO_2), Titania (TiO_2) or zirconia (ZrO_2) at the nanometer level, the resulting hybrid materials have high strength and thermal stability [14]. Addition of filler grains also gives rise to the inhibition of polymer recrystallization and decreases the glass transition temperature (T_g) of the solid polymer electrolytes [15].

It has been reported that, gel polymer electrolyte, PMMA– $\text{Na}(\text{ClO}_4)$ –4wt% SiO_2 , showed a maximum conductivity of $3.4 \times 10^{-3} \text{ S cm}^{-1}$ [16].

Nevertheless, lithium-ion batteries are relatively expensive and suffer from some safety limitations. Magnesium-based rechargeable battery system has attracted attention due to its performance capabilities that are close to those of lithium-based alternatives [17–19]. Magnesium is an attractive anode material for batteries of high specific energy because it has a low electrochemical equivalence (12.15 g equiv.⁻¹) and a considerably negative electrode potential (−2.3V versus SHE). In addition, it is cost effective due to natural abundance and safer than lithium. The use of magnesium as a negative electrode in aqueous primary and rechargeable batteries has been reported [20] and hence $\text{Mg}(\text{ClO}_4)_2$ is chosen as the electrolyte for the present study.

Though lot of lithium salts have been studied to enhance the conductivity of PMMA based solid polymer electrolytes, here it is attempted to study the conductivity of the non lithium salt $\text{Mg}(\text{ClO}_4)_2$ and the effect of addition of 1.29 nanometre sized silica (SiO_2) particles.

II. EXPERIMENTAL

Materials and Methods

The polymer electrolyte complexes PMMA- $\text{Mg}(\text{ClO}_4)_2$ and PMMA- $\text{Mg}(\text{ClO}_4)_2$ - SiO_2 are prepared by solvent casting technique using tetrahydrofuran as solvent. The prepared samples are analyzed to understand the effect of addition of SiO_2 , to PMMA- $\text{Mg}(\text{ClO}_4)_2$ complexes, on the structural and electrical properties of the complexes. The samples are characterized using FTIR, XRD, AC impedance and AFM techniques.

The FTIR spectra are recorded by a SHIMADZU-8400S, FTIR Spectrometer, in the region of 400 – 4000 cm^{-1} , with a signal average of 20 scans at a resolution of 4 cm^{-1} . X-ray diffraction (XRD) measurements are carried out with XPERT-PRO System. Conductivity studies were carried out by AC Impedance Analyzer Model PSM 1735 (10 μ Hz-35MHz) supplied by Newtons 4th Ltd., UK. 3D AFM images were taken to show the morphological changes occurred at the surface of the samples at microscopic level.

III. RESULTS AND DISCUSSION

A. FTIR

Infrared spectroscopy is a powerful tool for characterizing the organic-inorganic composite materials. Figure 1 shows the infrared spectra of PMMA - $\text{Mg}(\text{ClO}_4)_2$ - SiO_2 system. The peak assignments of these spectra are given.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

The FTIR spectrum of PMMA is shown in figure 1a. The peaks at 2966, 1726, 1456, 1122 and 1192 cm⁻¹ are assigned to CH₃ asymmetric stretching, C=O symmetric stretching, CH₃ asymmetric deformation, C-O-C single bond symmetric stretching and O-CH₃ symmetric stretching modes respectively.

Figure 1b shows the FTIR spectrum of Mg(ClO₄)₂. It has a contact ion pair vibration at 627 cm⁻¹. The peaks at 1100 and 1632 cm⁻¹ are assigned to ClO₄⁻ asymmetric stretching and internal vibrational mode. Mg²⁺ ... O solvent coordinated vibration appeared at 941 cm⁻¹[21].

From the FTIR spectrum of PMMA-Mg(ClO₄)₂, as given in figure 1c, the addition of Mg(ClO₄)₂ to PMMA downshifts the C=O peak from 1672 to 1650 cm⁻¹. The downshift of this peak is due to the weak electrostatic attraction between the cation and the carbonyl group, which is the highly reactive group of PMMA [22].

The peak due to CH₃ asymmetric deformation at 1456cm⁻¹ downshifts to 1439cm⁻¹ for the polymer electrolyte system. The peak at 1192cm⁻¹ due to O-CH₃ symmetric stretching of PMMA is upshifted to 1200 cm⁻¹ after the addition of Mg(ClO₄)₂ to PMMA which confirms the complex formation between PMMA and Mg(ClO₄)₂. The peak due to free ClO₄⁻ ion is shifted from 627 cm⁻¹ to 626 cm⁻¹ for the electrolyte added system. Further new peaks appearing at 2387, 2291, 2048 and 987 cm⁻¹ confirm the complex formation.

From the FTIR spectrum of pure Nanosized SiO₂, as given in figure 1d, the peak at 1122 cm⁻¹ is assigned to Si-O-Si asymmetric stretching. The peaks at 808 cm⁻¹ and 465 cm⁻¹ are attributed to Si-O₄ tetrahedron ring stretching and O-Si-O deformation of SiO₂ respectively [23].

Figure 1e, shows the FTIR spectrum of 10 wt% SiO₂ added PMMA-Mg(ClO₄)₂ system. The peak assignments for 10wt% of nano-silica is discussed in detail, because, it achieves the maximum ionic conductivity compared to other wt% of nano-silica added systems.

The peak at 1717 cm⁻¹ for the Mg(ClO₄)₂ added PMMA, due to the C=O symmetric stretching upshifts to 1726 cm⁻¹. This demonstrates that the polymer carbonyl (>C=O) groups are involved in the direct interaction with the nano-silica filler, which has also been observed for the polymer electrolyte samples by the earlier investigations [23]. The peak at 1439 cm⁻¹ assigned to CH₃ asymmetric deformation is positively shifted to 1442 cm⁻¹ for SiO₂ added system.

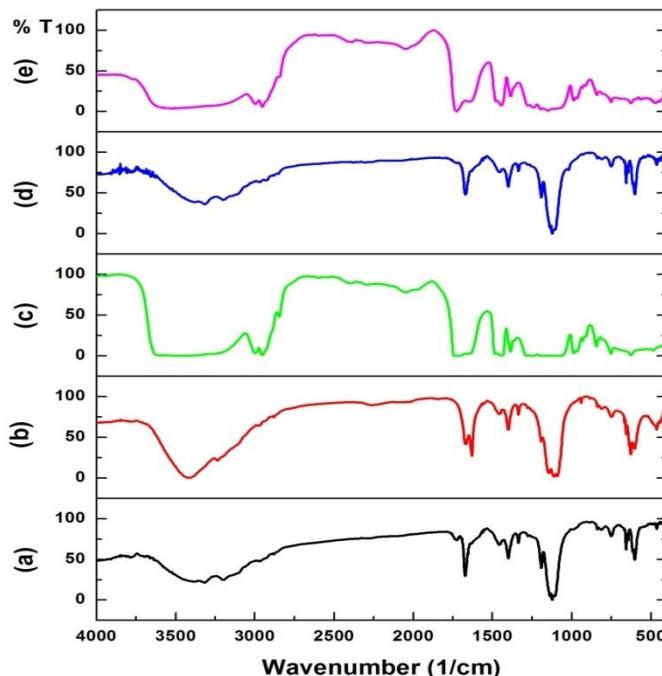


Fig. 1 FTIR spectra of (a) pure PMMA (b) pure Mg(ClO₄)₂ (c) PMMA - Mg(ClO₄)₂ complex (d) pure SiO₂ (e) PMMA - Mg(ClO₄)₂ - 10 wt% SiO₂

The peak due to ClO₄⁻ ion at 626 cm⁻¹ gets shifted to 622cm⁻¹. The peak due to O-CH₃ symmetric stretching at 1200 cm⁻¹ is shifted to 1150 cm⁻¹ for 10 wt% filler added system. Further the peak due to Si-O-Si asymmetric

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

stretching at 1122 cm^{-1} is shifted to 1150 cm^{-1} for 10 wt% SiO_2 added system. Hence the changes in the FTIR result provide convincing evidence for polymer-filler interaction [24].

B. XRD

Figure 2 shows the XRD patterns of the nanocomposite polymer electrolytes. The XRD pattern of pure PMMA in figure 2a shows a broad peak at $2\theta = 14^\circ$ and at $2\theta = 27^\circ$, which indicates the amorphous nature of PMMA. The peak at 14° was broad and intense whereas the other one was broad, but with lesser relative intensity.

The XRD pattern of $\text{Mg}(\text{ClO}_4)_2$ in figure 2b shows sharp peaks at 22° , 23° , 32° and 47° along with many small Bragg's peaks. The peaks at 22° , 23° and 32° are shifted to 24° , 28° and 34° in PMMA - $\text{Mg}(\text{ClO}_4)_2$ complex as shown in figure 2c. The addition of $\text{Mg}(\text{ClO}_4)_2$ to PMMA has led to the disappearance of the peak at 14° corresponding to PMMA. Further, some of the Bragg's peaks due to $\text{Mg}(\text{ClO}_4)_2$ disappeared in the electrolyte added system. This indicated the better dissolution of $\text{Mg}(\text{ClO}_4)_2$ in PMMA and hence the complex formation between PMMA and $\text{Mg}(\text{ClO}_4)_2$.

Figure 2d shows the XRD pattern of SiO_2 which shows a single peak at 22° . The XRD pattern of 10 wt% SiO_2 added system is shown in figure 2e. When 10wt% of nano-sized SiO_2 was added to PMMA- $\text{Mg}(\text{ClO}_4)_2$, the Bragg's peak observed for PMMA at 27° was further broadened which indicates the increase in degree of amorphicity of PMMA - $\text{Mg}(\text{ClO}_4)_2$ - SiO_2 system [25].

The increased amorphous nature of the nano-composite polymer electrolyte has led to the enhancement of ionic conductivity. It can also be pointed out through XRD studies that the added SiO_2 has acted as "solid plasticizer" to PMMA- $\text{Mg}(\text{ClO}_4)_2$ polymer electrolyte system.

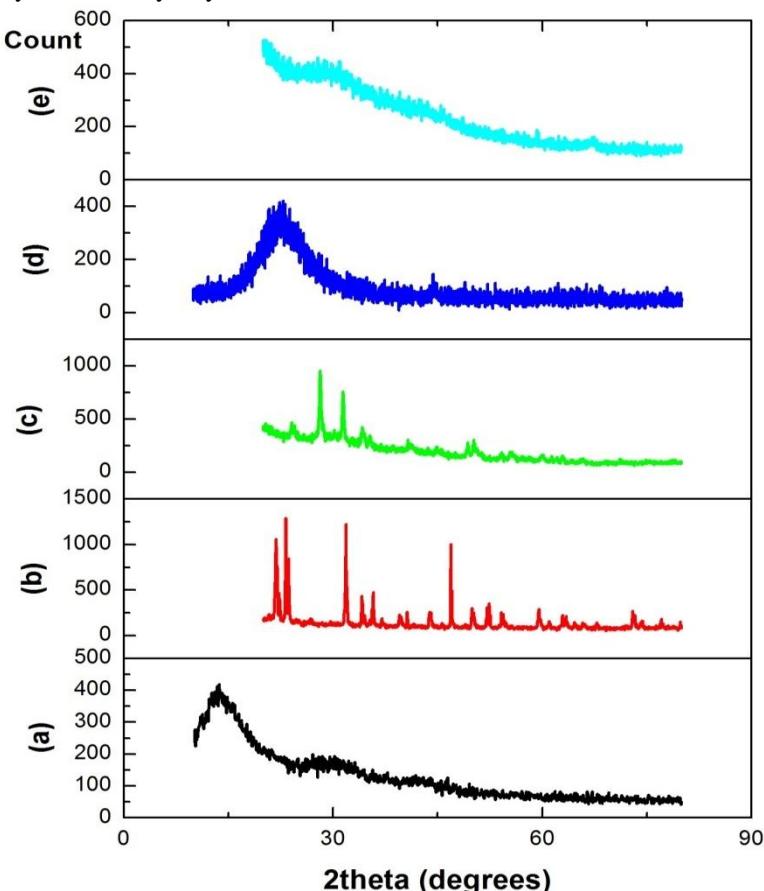


Fig. 2 XRD pattern of (a) pure PMMA (b) pure $\text{Mg}(\text{ClO}_4)_2$ (c) PMMA - $\text{Mg}(\text{ClO}_4)_2$ complex (d) pure SiO_2 (e) PMMA - $\text{Mg}(\text{ClO}_4)_2$ - 10 wt% SiO_2

C. Ionic Conductivity

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

Figure 3 shows the complex impedance plot for PMMA-Mg(ClO₄)₂ and PMMA-Mg(ClO₄)₂ with different compositions of SiO₂ (2wt% - 10wt%) at room temperature (302 K). Depressed semicircle, as given in figure 3, at high frequency side, and an inclined spike at lower frequency side, together are characteristic behaviour of ionically conducting polymer electrolyte with blocking electrodes [26].

The semicircle is due to the parallel combination of bulk resistance (due to the migration of ions) and bulk capacitance (due to the immobile polymer chains). The presence of the depressed semicircle reveals the non-Debye nature of the sample [6] due to the potential well for each site, through which the ion transport take place, not being equal. The inclined spike represents the formation of double layer capacitance at the electrode-electrolyte interface due to the migration of ions at low frequency [27]. Furthermore, the inclination of the spike at an angle less than 90° to the real axis is due to the roughness of the electrode-electrolyte interface [28].

The ionic conductivity of the NCSPEs has been calculated by the following relation,

$$\sigma = \frac{L}{R_b A} \quad \dots(1)$$

where L = Thickness of the sample, A=Area of the electrode, R_b=Bulk resistance.

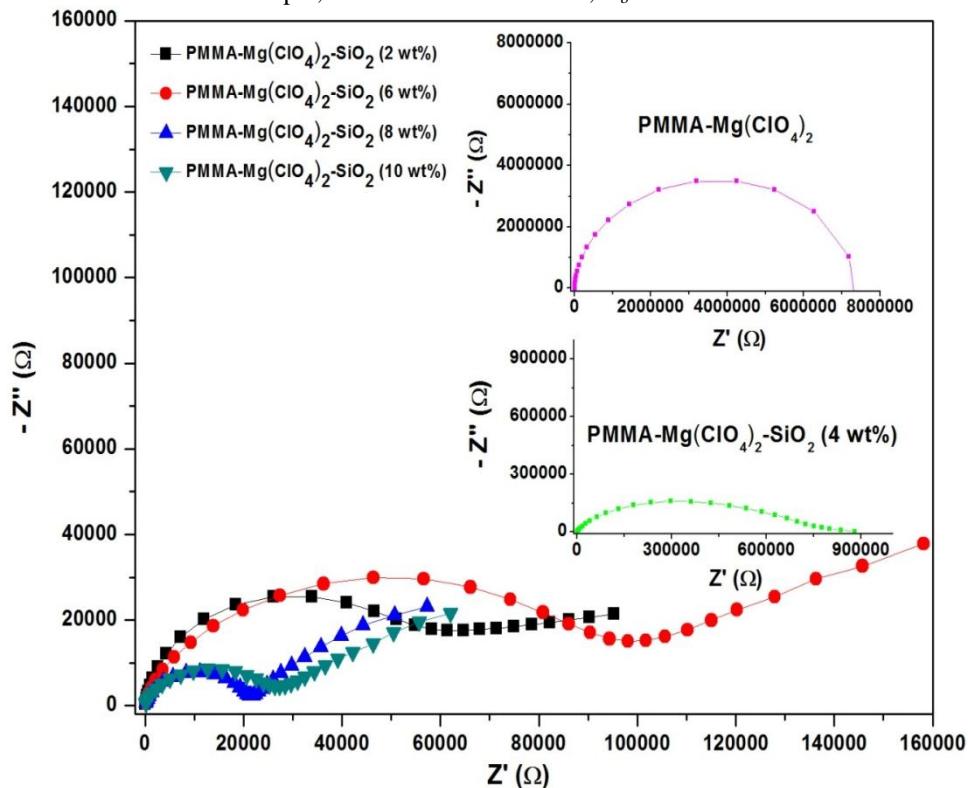


Fig. 3 Complex Impedance Plot of PMMA - Mg(ClO₄)₂ - SiO₂ NCSPEs

The bulk resistance (R_b) was calculated from the intercept of the spike at the low frequency side of the plot, with the real axis. The ionic conductivity values for PMMA-Mg(ClO₄)₂-SiO₂ NCSPEs are given in Table I. From the Table I, it is observed that the ionic conductivity for PMMA-Mg(ClO₄)₂ without filler is 4.303x10⁻¹⁰ Scm⁻¹. An increase of ionic conductivity is observed for 2wt% of SiO₂ as 2.34x10⁻⁸ Scm⁻¹ at room temperature.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

**TABLE I
IONIC CONDUCTIVITY OF PMMA-Mg(ClO₄)₂-xSiO₂**

Conc. of SiO₂ (x) in wt%	σ S cm⁻¹
0	4.303×10^{-10}
2	2.34×10^{-8}
4	1.82×10^{-9}
6	3.26×10^{-9}
8	3.72×10^{-8}
10	6.59×10^{-8}

There is an initial sudden increase of ionic conductivity by almost two orders of magnitude when 2 wt% of SiO₂ is dispersed in the polymer electrolyte system, followed by another maxima at 10 wt% of SiO₂. The conductivity decreases on further addition of silica nanoparticles. Two such maxima feature in the conductivity variation with respect to filler content for solid polymer electrolytes have been reported. A maximum conductivity of 2.34×10^{-8} S cm⁻¹ is observed for the nanocomposite solid polymer electrolyte dispersed with 2 wt% SiO₂ nano filler. Such higher values of conductivity are attributed to the higher amorphicity of the materials and space charge defects generated around SiO₂ nanoparticles in the polymer matrix. The first conductivity maximum, which is observed at a lower content (2 wt%) of SiO₂ nanoparticles, is associated with the generation of free ions followed by their pairing/re-association. The second conductivity maximum is related to the composite effect and is explained on the basis of the formation of a high conducting interfacial layer between the SiO₂ nanoparticles and polymer electrolyte due to the instantaneous presence of SiO₂:ClO₄⁻ species [29–32]. As discussed above, such charged layers (which induce a local electric field) are responsible for the generation of free ions for conduction and their mobility, and hence enhance the overall electrical conductivity.

D. AFM

The surface morphology of PMMA, PMMA-Mg(ClO₄)₂ and nanofiller SiO₂ dispersed PMMA-Mg(ClO₄)₂ materials are examined by Atomic Force Microscope and are given in figure 4.

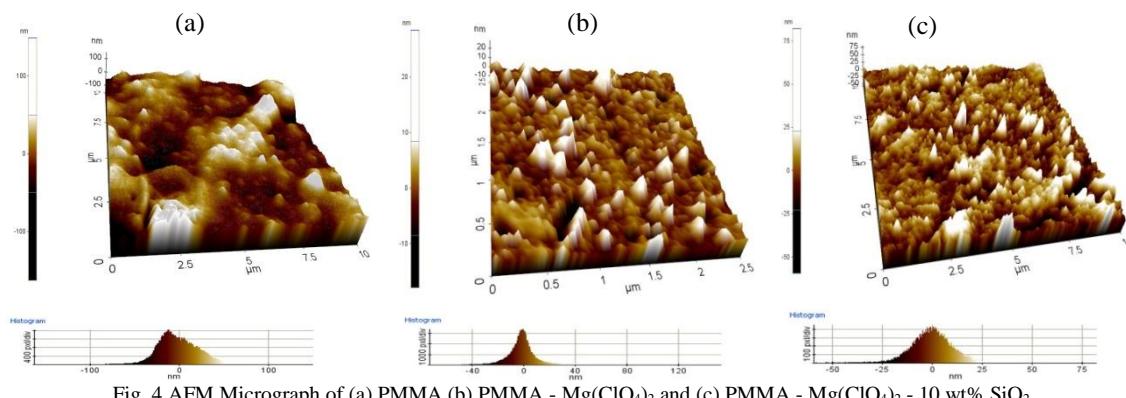


Fig. 4 AFM Micrograph of (a) PMMA (b) PMMA - Mg(ClO₄)₂ and (c) PMMA - Mg(ClO₄)₂ - 10 wt% SiO₂

Comparing figure 4a and figure 4b, a definite morphological change has been observed after the introduction of Mg(ClO₄)₂ salt to PMMA, which confirms the complex formation between polymer and salt as observed through FTIR studies. The height histogram of surface morphology of PMMA has a distorted Gaussian like distribution reflecting the important roughness information of the surface feature. The surface roughness of PMMA was 22.5 nm. After the introduction of Mg(ClO₄)₂ into the PMMA matrix, the complex has the surface roughness of 6.386 nm. This confirms the morphological change in the complex. The side view of the AFM of nano sized SiO₂ added PMMA - Mg(ClO₄)₂ system (Figure 4c) exhibited a mountain valley pattern with wider distribution observed from the height histogram, when compared with that of filler free system (Figure 4b). For this system, the height histogram of surface morphology showed a distorted Gaussian distribution and the roughness is found to have increased to 7.816 nm. This reveals that the amorphicity of SiO₂ added system has increased over SiO₂ free system which would support the

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

transport of Mg^{2+} ions through the PMMA matrix. This substantiates the observed maximum ionic conductivity of the SiO_2 added system [33]. This assures the occurrence of intermolecular interaction among the species involved and hence the structural modification which facilitates the fast Mg^{2+} ion transport as mentioned in the ionic conductivity studies. The presence of small voids in the micrographs of filler added system is attributed to the rapid solvent evaporation from the cast film during the sample preparation [34].

IV. CONCLUSION

The analysis of FTIR spectra of the samples revealed that there was complexation between PMMA and $Mg(ClO_4)_2$. It also revealed the plasticizing action of nanofiller, fumed silica, in the electrolytes and hence accounted for the structural changes in the systems studied. XRD patterns of the samples complemented the results obtained by FTIR analysis.

AC impedance spectroscopic studies threw light on the ionic conductivity of the samples studied. The DC ionic conductivity was determined from complex impedance plot. Two ionic conductivity maximum were obtained. The first conductivity maximum is associated with the generation of free ions followed by their pairing/re-association. The second conductivity maximum is related to the formation of a high conducting interfacial layer between the SiO_2 nanoparticles and polymer electrolyte due to the instantaneous presence of $SiO_2:ClO_4^-$ species. The increase in ionic conductivity with the addition of filler was attributed to the enhancement of amorphicity in polymer electrolyte matrix, thereby resulting in the promotion of more channels for Mg^{2+} ion transport. AFM pictures assured the occurrence of intermolecular interaction involved and hence resulting in the structural modification so as to facilitate the fast Mg^{2+} ion transport. The height histogram of surface morphology and roughness values of AFM micrographs confirmed the conclusions drawn through FTIR, XRD and AC impedance studies.

ACKNOWLEDGMENT

The author wishes to thank Mr. K. Kulasekarapandian, Mrs. S. Jeya and Ms. S. Jayanthi for their moral support and immense help in analysing the results. The author wishes to thank the Management, Ayya Nadar Janaki Ammal College for providing necessary infrastructure, instrumental and computational facilities to carry out this work.

REFERENCES

- [1] D. Teeters, G.N. Robert, D.T. Brain, *Solid State Ionics*, Vol.85, pp.239, 1996.
- [2] A.M. Sukeshini, A.R. Kulkarni, A. Sharma, *Solid State Ionics*, Vol.179, pp.113, 1998.
- [3] H.M.J.C. Pitawala, M.A.K.L. Dissanayake, V.A. Seneviratne, *Solid State Ionics*, Vol.178, pp.885, 2007.
- [4] J.Y. Kim, S.H. Kim, *Solid State Ionics*, Vol.124, pp.913, 1999.
- [5] Z. Stoeva, I. Martin-Litas, E. Staunton, Y.G. Andreev, P.G. Bruce, *J. Am. Chem. Soc.*, Vol.125, pp.4619, 2003.
- [6] J.M. Tarascon, M. Armand, *Nature*, Vol.414, pp.359, 2001.
- [7] G. MacGlashan, Y.G. Andreev, P.G. Bruce, *Nature*, Vol.398, pp.792, 1999.
- [8] R. Frech, S. Chintapalli, *Solid State Ionics*, Vol.85, pp.61, 1996.
- [9] Y.T. Kim, E.S. Smotkin, *Solid State Ionics*, Vol.149, pp.29, 2002.
- [10] S.L. Agrawal, M. Singh, M. Tripathi, M.M. Dwivedi, K. Pandey, *J. Mater. Sci.*, Vol.44, pp.6060, 2009.
- [11] S.A. Agnihotry, S. Ahmad, D. Gupta, S. Ahmad, *Electrochim. Acta*, Vol.49, pp.2343–2349, 2004.
- [12] Appetecchi G B, Croce F and Scrosati B, *Electrochim. Acta*, Vol.40, pp.991, 1995.
- [13] Sekhon S S, Pradeep and Agnihotry S A, *Solid State Ionics Science and Technology* (eds) B V R Chowdari *et al* (Singapore: World Scientific), pp.217, 1998.
- [14] Takeshi Otsuka and Yoshiaki Chujo, *Polymer Journal*, Vol.42, pp.58-65, 2010.
- [15] C. G. Tan, W. O. Siew, W. L. Pang, Z. Osman, K. W. Chew, *Ionics*, Vol.13, pp.361-364, 2007.
- [16] Deepak Kumar, S.A. Hashmi, *Journal of Power Sources*, Vol.195, pp.5101-5108, 2010.
- [17] J.-M. Tarascon, M. Armand, *Nature*, Vol.414, pp.359–367, 2001.
- [18] P. Novak, W. Scheifele, O. Hass, *J. Power Sources*, Vol.54, pp.479–482, 1995.
- [19] D. Aurbach, Y. Gofer, Z. Lu, A. Schechter, O. Chusid, H. Gizbar, Y. Cohen, V. Ashkenazi, M. Moshkovich, R. Turgeman, E. Levi, *J. Power Sources*, Vol.97–98, pp.28-32, 2001.
- [20] J.L. Robinson, in: N.C. Coohoon, G.W. Heise (Eds.), *The Primary Battery*, vol. II, Wiley, New York, p.149, 1976.
- [21] R.Nimma Elizabeth, S. Kalyana sundram, Yuria satrio and A.Manuel Stephan, *Polimeros :Cienciae Tecnologia.*, Vol.15, pp.46, 2005.
- [22] Kamira Aouachria , Naima Belhaneche Bensera, *Polym .Test.*, Vol.25, pp.1101, 2006.
- [23] Lucas P. Johnson and JanisG. Matisons, *J.Mater.Sci.*, Vol.44, pp.2805, 2009.
- [24] N. Belhaneche- Bensemra and A.Bedda, *Macromol. Symp.*, Vol.151, pp.202, 2003.
- [25] A.Ahamd, M.Y.A. Rahman and M.S.Su'ait, *Physica B*, Vol.403, pp.4128, 2008.
- [26] I.Nicoteria, I.Coppola, C.Oliviero and G.A Ranieri, *Solid State Ionics*, Vol.11, pp.1101, 2005.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 2, Issue 9, September 2013

- [27] G.N Kumaraswamy and C.Ranganathaiah, *Polym. Eng. Sci.*, Vol.46, pp.1231, 2006.
- [28] S.Ramesh and A.K.Arof, *J.Mater.Sci.*, Vol.44, pp.6404, 2009.
- [29] B.K. Choi, K. Shin, *Solid State Ionics*, Vol.86–88, pp.303–306, 1996.
- [30] S.A. Hashmi, H.M. Upadhyaya, A.K. Thakur, in: B.V.R. Chowdari, W. Wang (Eds.), *Solid State Ionics: Materials and Devices*, World Scientific, Singapore, p. 461, 2000.
- [31] G.P. Pandey, S.A. Hashmi, R.C. Agrawal, *Solid State Ionics*, Vol.179, pp.543–549, 2008.
- [32] Deepak Kumar, S.A. Hashmi, *Journal of Power Sources*, Vol.195, pp.5101–5108, 2010.
- [33] Guijie Liang, Jie Xu, Weilin Xu, Xiaolin Shen, Hui Zhang, Mu Yao, *Polymer Composites*, Vol.32, pp.511–518, 2011.
- [34] D. Zhang, D.H. Gracias, R. Ward, M. Gauckler, Y. Tian, Y.R. Shen, G.A. Somorjai, *J. Phys. Chem. B.*, Vol.102, pp.6225, 1998.